ICCE 2023
VENICE

18TH INTERNATIONAL CONFERENCE ON CHEMISTRY AND THE ENVIRONMENT

www.icce2023.com

11 – 15 JUNE 2023 VENICE, ITALY

Venue:

SCIENTIFIC CAMPUS

CA'FOSCARI UNIVERSITY OF VENICE (ITALY)

Book of Abstracts

Società Chimica Italiana

Ca' Foscari University of Venice

EuChemS
European Chemical Society

Dear colleagues,

On behalf of the Executive Board of the European Chemical Society, I wish you a warm welcome to this 18th International Conference on Chemistry and the Environment. The European Chemical Society – in short EuChemS – is an overarching society at the European level with over 50 national member societies as members. In this way, EuChemS represents approximately 130,000 chemists from all over Europe. Did you ever realize that by being a member of your national society, you are a member of EuChemS too?

The slogan of this conference is 'Towards a pollution free society', which is well aligned with activities from EuChemS. The European Commission recently set up the Zero Pollution Stakeholder Platform and EuChemS was invited to join. The platform will effectively mainstream the zero pollution agenda by bringing together stakeholders and experts of different policy areas, including health, agriculture, research and innovation, transport, digitalization and the environment. EuChemS will emphasize to address the Zero Pollution challenges from the chemistry perspective in a science-based approach.

I am here in the Netherlands, but you are in the beautiful city of Venice, that I am sure will inspire you to have fruitful and constructive discussions on how to get to zero pollution and how to address many other challenges to create a sustainable environment. I wish you a very enjoyable conference!

Floris Rutjes

President of the European Chemical Society (EuChemS)

ICCE 2023 SPONSORS

Gold Sponsors

Waters™

Silver Sponsors

Agilent
Trusted Answers

BRUKER

toxics
an Open Access Journal by MDPI

Springer

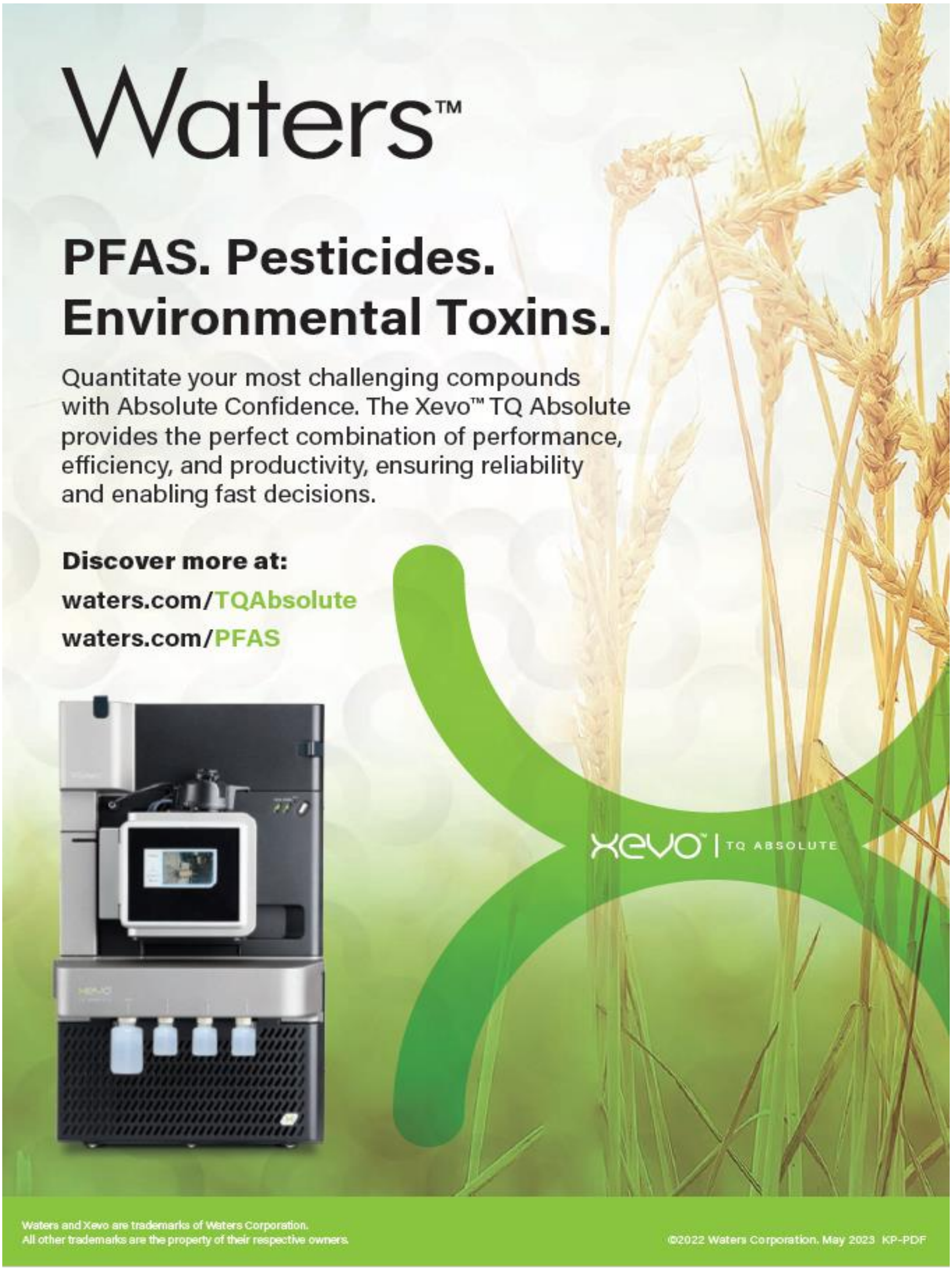
fkv
PASSIONEIDEESOLUZIONI

Sponsors

EuChemS
European Chemical Society

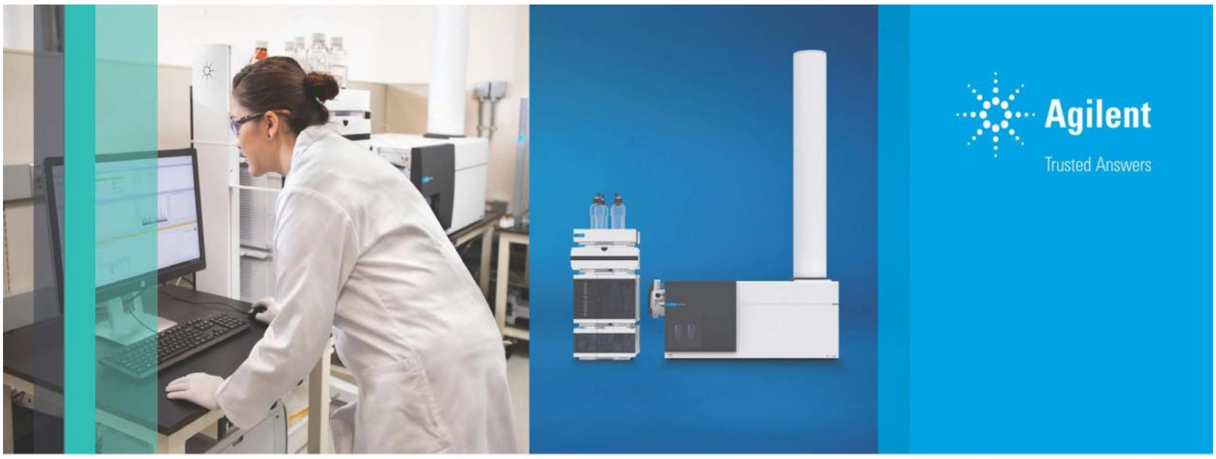
Ca' Foscari University of Venice

ROVALTAIN FOUNDATION
RESEARCH IN ECO-TOXICOLOGY
For a world without pollution

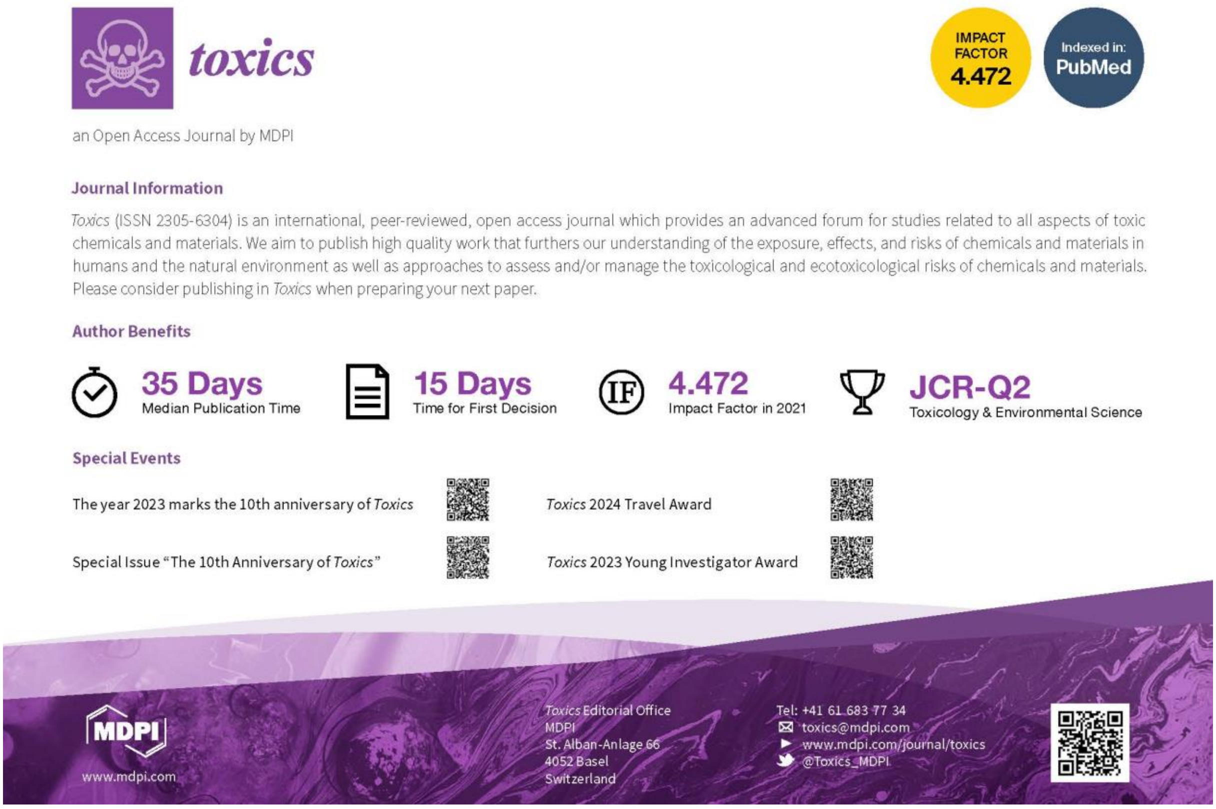


xevo™ | TQ ABSOLUTE


fkv
PASSIONE IDEE SOLUZIONI
IL TUO PARTNER DAL 1974
per la strumentazione di laboratorio
PlasmaQuant MS Elite
Vendita e supporto Tecnico/Applicativo per la strumentazione da laboratorio.
FKV.IT


Agilent
Trusted Answers

impact II VIP



Plenary Lectures

Chemistry and the Environment – Where do we Stand in 2023?

M. Scheringer

ETH Zürich, Dep. of Environmental Systems Science, Rämistrasse 101, 8092 Zurich, Switzerland

scheringer@chem.ethz.ch

Over the last decades, substantial progress has been made in the scientific understanding of the uses, emissions, environmental fate and adverse impacts of a large number of chemicals. In addition to many specific new insights, this has also led to a more comprehensive picture of the overall "chemical footprint" of the modern society and globalized economy, as it is, for example, presented in UNEP's Global Chemicals Outlook II. Chemical pollution is now seen as one of the three main global crises in addition to climate change and biodiversity loss. A global science-policy panel on chemicals, waste and pollution prevention, similar to the Intergovernmental Panel on Climate Change (IPCC) and Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem Services (IPBES) will be established in 2024 or 2025. What are the implications of these developments for scientific research in the area of environmental chemistry, for regulatory risk assessment, and for science communication about chemicals, health and the environment? In this lecture, possible answers to these questions will be offered for discussion and upcoming tasks for the environmental chemistry community will be outlined.

PFAS: Allrounders or Problem Generators? - Environmental and Analytical Perspectives

C. Zwiener[1]

[1]Environmental Analytical Chemistry, Department of Geosciences, Universität Tübingen, Schnarrenbergstr. 94-96, 72076 Tübingen, Germany

christian.zwiener@uni-tuebingen.de

Poly- and perfluoroalkyl substances (PFAS) form a large group of anthropogenic compounds with about 4700 highly fluorinated members and just as many substances with at least one fully fluorinated methyl or methylene group. The chemical and thermal stability combined with hydrophobic and lipophobic properties make PFAS very attractive for a broad range of industrial and household applications, e.g. as aqueous film-forming foams, surfactants in electroplating and other industrial processes, in nonstick cookware, stain-resistant materials or food contact papers. In Europe an estimated amount of 140,000 to 310,000 t of PFAS was introduced to the market in 2020. Since many PFAS and the degradation products of so-called precursors can be highly persistent, bioaccumulative and (eco)toxic, concerns arise from PFAS emissions during manufacture, use and disposal.

Environmental monitoring showed the ubiquitous occurrence of PFAS in air, water, and soil, but also in plants and wildlife, even in remote regions (e.g. the Arctic). Also, human biomonitoring studies revealed the prevalent exposure and showed the widespread occurrence of PFAS in blood samples. This led to restrictions and phase-out of long-chain PFAS in the EU, like perfluorooctanesulfonic acid (PFOS in 2006) and perfluorooctanoic acid (PFOA in 2020) and other C9 to C14 perfluoroalkyl acids (PFAA in 2023). This led, however, to a shift in production to short-chain PFAS with different chemistries, such as per- and polyfluoroalkyl ether carboxylic acids. Again, environmental persistence, mobility and effects on human health raised concerns on the replacement chemicals. Therefore, more than ever, knowledge is required about identities, production volumes and use areas of PFAS to support research on their environmental input and fate, as well as their effects on ecosystems and human health. New analytical methods, parameters and screening approaches may help in this context with a focus on nontarget screening based on chromatography-high-resolution mass spectrometry.

Using two large-scale contaminated sites as examples, I will discuss methods and approaches for determining the causes, their mitigation, and long-term consequences, emphasizing the role of analytical screening approaches.

Using two large-scale contaminated sites as examples, I will discuss methods and approaches for determining the causes, their mitigation, and long-term consequences, emphasizing the role of analytical screening approaches. In southwest Germany, more than 14 Mio m2 of agricultural soils were contaminated with PFAS used for paper products. LC-HRMS analysis revealed 65 PFAS from 13 compound classes, e.g. perfluoroalkylphosphate diesters (diPAPs) (Bugsel et al. 2022). LC-HRMS analysis and a nontarget workflow (FindPFΔS; Zweigle et al. 2022) revealed 73 PFAS from 10 PFAS classes in soil contaminations from waste disposal in northwest Germany. These examples demonstrate the important role of advanced analytical screening techniques and the problematic nature of persistent contaminants in material recycling.

References

Bugsel, B. et al. (2022) LC-HRMS screening of per- and polyfluorinated alkyl substances (PFAS) in impregnated paper samples and contaminated soils. Analytical and Bioanalytical Chemistry 414, 1217-25. DOI: 10.1007/s00216-021-03463-9.

Zweigle, J. et al. (2022) FindPFAS: Non-Target Screening for PFAS─Comprehensive Data Mining for MS2 Fragment Mass Differences. Analytical Chemistry 94, 10788-96. DOI: 10.1021/acs.analchem.2c01521.

Human Exposure to Emerging Contaminants: Advances and Challenges

A. Covaci[1]

[1]University of Antwerp, Toxicological Centre, 2610 Wilrijk, Belgium

adrian.covaci@uantwerpen.be

Human biomonitoring methods are well established for the exposure assessment of many chemicals, including the chemicals of emerging concern. Such methods have resulted in establishing measures for regulations, following time trends of concentrations in human populations and in establishing reference values and ranges for a selected group of 250–300 known chemicals.

Yet, as more and more chemicals are added to the market, there is an increasing need to estimate the human exposure to these emerging contaminants. Recent efforts and advances in high-resolution mass spectrometry (HRMS) have seen the unprecedent rise of screening techiques with the aim to identify emerging contaminants and/or their metabolites present in consumer products, environmental matrices relevant for human xposure (dust, food, air, water) and in human biological matrices. Such analytical approaches are 1) target screening; 2) suspect screening and 3) non-target (or untargeted) screening eventually complemented by ion mobility MS. Using such advanced tools, we can capitalize even more on the identification of life style-specific exposure profiles, i.e. compounds that may differ in relation to specific behavioural patterns.

Furthermore, the use of HRMS screening techniques allows the coupling of human biomonitoring with the exposome approach. An exposomic approach (exposomics) theoretically includes all exposures of potential health significance, whether they are derived from exogenous sources (e.g., pollutants, diet, drugs) or endogenous sources (e.g., hormones, human and microbial metabolites). Since levels of chemicals in biological samples reflect a wide range of exposures (biomarkers of exposure), but also consequences of exposures (biomarkers of effect), an efficient approach is needed for the characterization of the overall individual exposure profiles. The incorporation of the exposome paradigm into traditional human biomonitoring approaches may improve exposure assessment in many ways.

With only a few hundred chemicals routinely measurable through targeted methods and with limitations for short-lived compounds, exposomic approaches are critical to understanding the daily exposure to thousands of chemicals and the consequences of exposure in exposome-wide association studies.

The processing of rich sets of data from untargeted analyses offers a path for discovering health-impairing exposures that have thus far escaped scrutiny, a largely unrecognized benefit of exposomics. This should give guidance towards more accurate prevention measures that protect against exposure to (emerging) environmental contaminants and their substitutes in new materials and products.

Unraveling Environmental Issues in the Soil-Plant System with X-Rays: Opportunities and Challenges

R. Terzano[1]*

[1]University of Bari "Aldo Moro", Department of Soil, Plant and Food Sciences, Via Amendola 165/A, 70126, Bari, Italy

roberto.terzano@uniba.it

Soil is a very complex environmental compartment where minerals, organic matter, (micro)organisms, plants, water and air are intimately connected at the micro/nano-scale. The fate of environmental pollutants (organic and inorganic) in soil is strongly influenced by many processes, both biotic and abiotic, taking place in this matrix. In particular, potentially toxic elements (PTE) tend to accumulate in soil and can be transferred from the solid phases to water, air and biota, especially plants, and then along the food chain, up to humans.

To study the processes occurring in soil and affecting the fate of PTE, analytical methods able to disentangle soil complexity at the micro/nano scale are needed. In this context, X-rays are electromagnetic radiations with a wavelength in the order of magnitude of atoms size (between 10^{-11} and 10^{-8} m) and therefore can provide many useful information about the composition and structure of matter. In addition, their high penetration capacity allows to investigate different type of materials almost without sample treatment, thus reducing the risks of artifacts and errors. Different types of X-rays-based analytical techniques are nowadays available to support environmental scientists dealing with PTE pollution in soil and plants. Beside both qualitative and quantitative bulk analytical capabilities, 2D and 3D chemical and structural imaging implementations make X-ray methods extremely appealing analytical tools in all fields of research, including environmental sciences (Terzano et al., 2019).

In this lecture, the most recent innovations in X-ray analysis will be reviewed and applications to the fate of PTE in the soil-plant system will be presented. X-ray-based methods available both at synchrotron radiation facilities and in the laboratory will be considered, as well as portable instruments to be used directly in the field. The advantages and limitations of these techniques will be discussed with a special focus on the combination of these methods. Challenges in instrument development and sample preparation will be also highlighted.

References

Terzano, R. et al. (2019) 'Recent advances in analysis of trace elements in environmental samples by X-ray based techniques (IUPAC Technical Report)', Pure & Applied Chemistry, 91, p.1029-1063. doi:10.1515/pac-2018-0605.

Degradation of Contaminants of Emerging Concern on Reactive Surfaces: Kinetics, Mechanisms and Transformation Products

D. Dionysiou[1]

[1]Environmental Engineering and Science Program, Department of Chemical and Environmental Engineering, University of Cincinnati, Cincinnati, Ohio, USA

dionysios.d.dionysiou@uc.edu

A variety of new catalysts, electrocatalysts, reactive surfaces, and other types of functional materials are being explored as alternative or complementary options to existing processes for the degradation of legacy pollutants and contaminants of emerging concern is water. Relevant technologies of application for the removal of such pollutants include catalytic, electrocatalytic, photocatalytic, piezocatalytic, as well as several other types of heterogeneous advanced oxidation technologies (AOTs) and advanced reduction technologies (ARTs). In this presentation, Prof. Dionysiou will provide an overview of latest developments of kinetics, mechanisms, and transformation products during the degradation of pollutants of concern (i.e., pharmaceuticals, pesticides, plasticizers, cyanotoxins, per- and polyfluoroalkyl substances (PFAS)) on various types of advanced functional materials (i.e., carbonaceous materials, Z-scheme photocatalysts, composites such as graphdiyne/γ-graphyne-quantum dots, single atom catalysts supported on various materials). Discussion will also be provided on selectivity of reactive surfaces, formation of primary reactive species, and reaction pathways such as radical vs. non-radical induced reactions. The role of select water quality parameters will be discussed in certain cases. Selective promising applications of such processes will be highlighted and comparison with homogeneous type processes will be provided for few examples. Current challenges, critical gaps, and potential future research topics will be discussed.

Keynote Lectures

Advanced Air Quality Parametres in Europe

X. Quero[1]

[1]Institute of Environmental Assessment and Water Research (IDAEA-CSIC), C/ Jordi Girona 18-26, 08034 Barcelona, Spain

xavier.querol@idaea.csic.es

Air quality (AQ) in Europe has markedly improved in the last decades due to the abatement of ambient concentrations of a number of pollutants (EEA, 2023). However, ambient concentrations for the key ones are still far from their respective WHO AQ Guidelines, and also, for a few of them, no decreasing trends are recorded. In this context the EC has started a revision of the current EU's AQ Directive, which will set up limit and target values closer to the WHO AQ Guidelines. Furthermore, again following WHO recommendations, it is proposed to implement harmonized measurements for advanced AQ parameters to obtain data to evaluate their implementation in AQ monitoring based on their potential health effects.

For a cost-effective continue abatement of the air pollutants, such as some of the secondary (formed into the atmosphere from precursors) ones, mainly most of the mass of fine atmospheric particulate matter (PM2.5) and tropospheric ozone (O3), scientific assessment is needed, given the complexity of processes and pollutants involved.

The major scientific challenges to abate PM2.5, O3 and to properly measure advanced air quality parameters, such as ultrafine particles (UFP), black carbon (BC), PM components, oxidative potential (OP), ammonia (NH3), volatile organic compounds (VOCs), and their source apportionment for an integrated scientific assessment, are summarized based on the experience gain in the EC H2020 Green Deal project RI-URBANS (Research Infrastructures Services Reinforcing Air Quality Monitoring Capacities in European Urban & Industrial AreaS, contract 101036245).

First, PM2.5 in the European urban background is made of around 70% secondary components, and >50% of organic aerosols (OA). Furthermore, the marked decrease of SO2 and NOx emissions, reduced the PM2.5 loads of ammonium sulphate and ammonium nitrate (both accounting for most of the secondary inorganic aerosols, SIA), with most secondary PM being of an organic origin. Furthermore, because O3 concentrations are increasing in urban areas, the oxidizing capacity of the urban atmospheres to from more secondary OA (SOA) from VOCs is also increasing; and because the NH3 emissions decreases only very slightly continuing abating SIA is highly challenging. In this context, there is a need for measuring speciated VOCs, analyzing the source apportionment of SOA and carrying out modelling studies for cost effective policy assessments.

Assessing on how to reduce ambient concentrations of O3 is also a scientific challenge, because the lack of adequate VOCs speciated measurements, and the complexity of the reactions and atmospheric processes governing its formation.

For UFP and BC, the main sources in urban Europe is road traffic, although nucleation of newly formed UFP might account for a relevant proportion. Abating UFP is requiring also a deep scientific assessment due to the complex emission controls needed and the secondary formation.

Oxidative potential of PM2.5 has been shown to be driven by different species to those driving the PM mass concentration. Furthermore, harmonized OP measurements are needed to obtain generalizable results across urban Europe.

References

EA, (2023). Air Quality in Europe 2023. https://www.eea.europa.eu//publications/europes-air-quality-status-2023.

Monitoring of Pesticides in Outdoor Air: The French Case Study

F. Botta[1]

[1]French Agency for Food, Environmental and Occupational Health & Safety

fabrizio.botta@anses.fr

Pesticides were firstly measured in air at the end of the 60s in the United States and first monitoring programmes are reported in the 70s. In France, the topic become of interested at the end of the 80s, and first regional monitoring were realised in 2001. Since then, a great improvement in data collection and knowledge is observed. In particular, Anses initiated in 2014 a collaborative work to establish common rules to set up an harmonized national monitoring (substance prioritisation scheme, site selection criteria, etc.). In particular, the list of substances to be measured was established on the basis of pesticide characteristics with regard to hazards, emission and persistence in the air, and criteria for their level of use in France. Following this work, a one year national exploratory pesticide campaign (CNEP) was launched in June 2018 by ANSES, INERIS and the regional associations involved in air quality monitoring (AASQA). It provided a snapshot of substances found in French ambient air (metropolitan and overseas) and their concentration levels in background areas (at a minimum of 100 or 200 meters from the nearest agricultural field). During this national campaign, 75 substances were monitored over 12 months according to this newly harmonised protocol leading to1.300 analyses for each of these substances. France is one of the few countries in Europe, besides Belgium, to have undertaken this kind of campaign for measuring pesticides in ambient air on a national scale. On the basis of the CNEP results, ANSES carried out a first interpretation work to assess the health impacts of the 70 substances found in ambient air and identified substances requiring further consideration for possible inclusion in ongoing national monitoring system for pesticides in air. Indeed, since 2021, a routine monitoring is ongoing in France at national level. It will permit to have a large number of data to supply pesticidovigilance.

However, most of data concerning pesticides in air are collected in background sites and few are currently available in France on the actual exposure of people living near crops, and near vineyards in particular (few meters to 100 meters). But, French population and public authorities are concerned about the health effects of pesticides under these exposure situations. The PestiRiv study currently ongoing (carried out jointly by both national agencies ANSES and SpF, with other partners for technical working packages) is therefore the first study undertaken throughout metropolitan France to explore exposure to pesticides in wine-growing and non-wine-growing areas. It is an original study in that it will investigate the population's actual level of exposure, assessed through biological sampling, to all possible exposure sources: air, food (including water), occupational activities including agriculture, and domestic uses. The primary objective is to find out whether exposure to pesticides differs between people living near grapevines and those living far from any crops. PestiRiv will seek to identify the sources that most contribute to pesticide exposure and determine how living distance from grapevines, the season, and the habits and behaviours of individuals may impact this exposure. Better understanding the origin of this exposure will help identify ways of limiting it and therefore avoid the potential health effects of these products.

In conclusion and after this overview of the history of pesticide monitoring in France, the main perspective and priorities concerning pesticide air monitoring will be presented, in particular regarding analytical methods, sampling tools and risk assessment needs.

Microplastic, Trace Contaminant, Antimicrobial Resistance and Nutrient Dynamics in a Conventional Municipal Wastewater Treatment Process Coupled to a Polishing Constructed Wetland

J. Wenk[1]*, F. Bydalek[1], E. Robertson[1], V. Hussey[2], G. Gordon[3], D. Ifayemi[1], A.J. Weightman[3], P. Johnes[2], R. Evershed[3], D. Goddy[4], R. Barden[5], B. K-Hordern[1]

[1]University of Bath, Department of Chemical Engineering/Chemistry, Claverton Down, BA2 7AY, Bath, UK
[2]University of Bristol, School of Geographical Sciences, University Road, BS8 1SS, Bristol, UK
[3]Cardiff University, School of Biosciences, CF10 3AX, Cardiff, UK
[4]British Geological Survey, Oxfordshire OX10 8BB | UK
[5]Wessex Water, Bath BA2 7WW, UK

j.h.wenk@bath.ac.uk

This presentation will provide an initial overview on a 4-year ongoing research project studying the fate and dynamics of several classes of wastewater pollutants in a conventional full-scale wastewater treatment process coupled to a newly established surface flow polishing constructed wetland.

The study site is a municipal wastewater treatment plant located at Cromhall, South-West Gloucestershire, UK. The site treats a daily volume of 1.4 ML from a combined sewerage of a rural catchment with a pollution load of 2100 population equivalent (PE). The treatment plant provides secondary treatment via an oxidation ditch and has been expanded in 2020 with an 8000m^2 constructed wetland acting as a polishing step for enhanced phosphorus removal. Here a selection of monitoring and experimental results for the first three years of operation for the combined treatment process will be presented. Specifically, the results include data on nitrogen and phosphorous dynamics, micropollutant concentrations in the water phase, sediments and biomass along the treatment process, linked to microbial community and antimicrobial resistance analysis. Employed methods consist of standard methods for monitoring of wastewater combined with more sophisticated tools such as high-resolution mass-spectrometry, isotope-fractionation, and biomolecular/bioinformatics approaches.

Beyond a general overview on the breadth of the available data of this multidisciplinary project, to date not fully analyzed and published, an in-depth look will be taken on the fate of microplastics in the treatment wetland and the microplastic biofilm, associated pathogen and antimicrobial resistance dynamics. Microplastic concentrations along the constructed wetland were measured for different types of microplastic i.e. fibres, fragments and films, and in three different size categories ranging from 25 micrometer to above 1000 micrometer. Results are discussed regarding physical processes within differently designed treatment cells of the constructed wetland and compared to suspended solids concentration and turbidity (Bydalek F. et. al. 2023)

In a follow-up experimental study (Bydalek F. et. al. 2023), sterilized microplastics mixtures were deployed at different treatment stages and inoculated for 4 days and 20 days at each stage, respectively. Microplastics were subsequently transferred to the next treatment stage to simulate microplastics transport through the treatment scheme. The microbial community grown on microplastics was analyzed via qPCR targeting selected antimicrobial resistance genes and 16S rRNA metagenomic sequencing and compared to the planktonic community along the treatment process.

Results show that surface flow constructed wetlands are capable of effective microplastic retention despite exhibiting no pronounced filtering capacity. When coupled together, conventional wastewater treatment and constructed wetland treatment can significantly reduce the pathogenic and antimicrobial resistance load carried by microplastics. However, ecological and public health risks may persist, in case of insufficient microplastics retention time in the treatment system.

References

Bydalek, F. et. al. (2023) ‘Microplastic dynamics in a free water surface constructed wetland’ Science of the Total Environment, 858, 160113, https://doi.org/10.1016/j.scitotenv.2022.160113.

Bydalek, F. et. al. (2023) ‘Microplastic biofilm, associated pathogen and antimicrobial resistance dynamics through a wastewater treatment process incorporating a constructed wetland’, accepted manuscript.

Plant Protection Product Residues in the Environment – Still Analytical and Environmental Challenges to Overcome!

J. Hollender*[1,2], K. Kiefer[1,2], B. Lauper[1,2], J. Raths[1,2], A. Rösch[1], J. Schorr[1,2], H. Singer[1]

[1]Swiss Federal Institute of Aquatic Science and Technology, Eawag, 8600 Dübendorf, Switzerland
[2]Institute for Biogeochemistry and Pollutant Dynamics, ETH Zürich, 8092 Zürich, Switzerland

juliane.hollender@eawag.ch

Pesticides are a major driver of environmental risk towards organisms such as macroinvertebrates where the risk has increased since the nineties. Furthermore, pesticides are responsible for biodiversity loss, and human exposure to contaminated drinking water and food is of high relevance and public interest. Therefore, reducing the risk caused by pesticides is an important goal in Europe and is being addressed by the EU Directive 2009/128/EC on the sustainable use of pesticides. A better understanding of the emission pathways, the concentration dynamics and fate in freshwater, as well as the uptake into organisms and the ecotoxicological and ecological effects in aquatic systems is important to design more appropriate mitigation measures and regulatory processes. A range of analytical methods is needed to cover the diverse physico-chemical properties of pesticides, reach the sensitivity needed for highly toxic pesticides and enable identification of transformation products where no reference standards are available.

LC coupled with electrospray ionisation to high-resolution tandem mass spectrometry (HRMS/MS) has enabled a broad suspect screening of a large part of all registered pesticides and the transformation products listed in the European registration dossiers.[1] This enabled a more comprehensive risk assessment of mixture toxicity and the identification of novel transformation products such as the transformation products of chlorothalonil that are difficult to abate with current drinking water treatment technologies.[1] Very mobile anionic pesticide transformation products that do not retard on LC columns such as novel dimethenamid transformation products have been separated and detected with ion chromatography coupled to HRMS. Non-polar pesticides such as pyrethroids have been sensitively quantified after enrichment using GC coupled with atmospheric pressure chemical ionisation to MS/MS and concentrations above the environmental quality standards in the pg/L range were frequently found.[2]

Temporally highly resolved in-situ measurements with LC-HRMS/MS (every 20 min) enabled to catch the exposure dynamic in surface water and karst groundwater and showed exceedance of quality standards especially after rain events during the pesticide application period. Several pesticides were detected in macroinvertebrates (gammarids) after pesticide exposure peaks showing their uptake and potential toxic effects.[3] For neonicotinoids (thiacloprid) irreversible binding to the nicotinic acetylcholin receptor was shown, leading to reduced elimination and indicating chronic effects also when no pesticides are anymore in the water phase.

All the studies with new analytical methods show that the national action plans to reduce the environmental risk caused by pesticides have only partly been successful so far and further changes in registration and pesticide management are necessary.

References

Kiefer, K. et al. (2019) New Relevant Pesticide Transformation Products in Groundwater Detected Using Target and Suspect Screening for Agricultural and Urban Micropollutants with LC-HRMS. Wat Res 165, 114972. doi.org/10.1016/j.watres.2019.114972.

Rösch, A. et al. (2019) Picogram per Liter Quantification of Pyrethroid and Organophosphate Insecticides in Surface Waters: A Result of Large Enrichment with Liquid–Liquid Extraction and GC Coupled to MS Using Atmospheric Pressure Chemical Ionization. ABC 14, 3151. doi.org/10.1007/s00216-019-01787-1

Lauper, B. et al (2021) Systematic Underestimation of Pesticide Burden for Invertebrates under Field Conditions: Comparing the Influence of Dietary Uptake and Aquatic Exposure Dynamics. ACS Env Au 2, 166. doi.org/10.1021/acsenvironau.1c00023.

Environmental Enantioselectivity of Chiral Pharmaceuticals

A. R. L. Ribeiro[1*]

[1]LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2]ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

ritalado@fe.up.pt

Many pharmaceutical active compounds are chiral, i.e., asymmetric 3D molecules with stereoisomers that can display a differing behaviour in chiral medium, as occurs in the interaction with natural macromolecules (e.g., enzymes, receptors, other binding-molecules). Hence, enantiomers can present different pharmacokinetic and/or pharmacodynamic properties and different attachment to binding sites and different dissociation from the same sites (Ribeiro et al. 2022). Depending on the pharmaceuticals, they are administered as enantiopure or enantiomeric mixtures. The potency, mode of action, and toxicity can differ for a pair of enantiomers. For instance, the antibiotic ofloxacin is sold either as racemate or S-(-)-ofloxacin (levofloxacin), levofloxacin having a lower minimal inhibitory concentration and less incidence of adverse effects. Therefore, in the environment, enantioselectivity can also occur in all biological processes and different responses in terms of ecotoxicity are expected. Although chirality is rarely considered in environmental studies, the knowledge on stereoselectivity in the environmental fate, distribution, (bio)transformation, (bio)degradation, ecotoxicity, and bioaccumulation is essential to provide a more realistic environmental risk assessment of chiral pharmaceuticals. Moreover, in the case of antibiotics, another environmental concern is the possible role of enantioselectivity on the development of antibiotic resistance in the environmental settings.

References

Ribeiro, A.R.L. et al. (2022). Chiral Analysis with Mass Spectrometry Detection in Food and Environmental Chemistry. In: Picó, Y., Campo, J. (eds) Mass Spectrometry in Food and Environmental Chemistry. The Handbook of Environmental Chemistry, vol 119. Springer, Cham. doi: 10.1007/698_2022_889

Acknowledgement: Funded by the European Union (ERC, ERA-ARE, project number 101039270). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Research Council Executive Agency. Neither the European Union nor the granting authority can be held responsible for them.

PFASs on Molecular and on Planetary Levels: Sequential Removal of CF2 Groups from Certain PFASs and Expansion of PFAS Name to all Substances with CF_2 Group

V. Nikiforov[1]

[1]The Climate and Environmental Research Institute NILU, Framsenteret, Hjalmar Johansens gate 14, 9007 Tromsø, Norway

van@nilu.no

1. PFASs on molecular level.

Substances with perfluroalkyl structural elements undergo oxidation in persulfate solution, so that perfluorinated part remains largely intact while other parts get removed. The stable end-products are perfluorinated carboxylic acids(PFCA) with the same or 1-3 CF2-groups shorter chain length than in the substrate. TOP assay is based on such oxidation (Houtz, E. et al., 2012, Cioni L., et al. 2022).

We demonstrated that derivatization of a PFCA, followed by oxidation can also lead to shortening of a perfluorinated chain. The approach can serve three purposes: (i) synthesis of yet unknown shorter PFCAs from known longer ones, (ii) structure elucidation of unkown longer PFASs based on the structure of known shorter ones, (iii) conversion to derivatives giving a molecular ion for confident identification or more sensitive detection.

A sequence was as follows: X-CF2-COOH – X-CF2-COOCH3 – X-CF2-CONHR – X-COOH, where X – perfluorinated part, R – Bu, Ph, -CH2CH2NH2. The sequence can be repeated with the product of the previous one. All reactions employed in this proof-of-concept study can be carried out on micro- or nanoscale with the standard equipment in a trace analysis lab.

2. PFASs on planetary level.

The recent restriction proposal, based on OECD definition of PFASs extended the name "PFASs" (Per- and polyfluroalkyl substances) to all derivatives of difluoromethane, CH2F2, with few exceptions (Proposal for a restriction. Per- and polyfluoroalkyl substances (PFASs). ECHA. 2023). It appears, the proposal aims at control of all those fluorinated substances that are or can transform in the environment to the so called "Forever Chemicals" – regardless their known or suspected harmful effect. Thus, extreme persistency on a planetary scale is declared a threat in itself. Truly innovative approach to protection of the planet, and some of emerging scientific questions are, in our opinion, as follows:

- How long is "forever"? (What are the minimal half-life time or maximal transformation/degradation rate?)
- What are compartment-specific and planetary half-life times for the best known PFASs like TFA, PFOS or PFOA?
- Are the "OECD PFASs" on average more persistent than common organic chemicals? Are they more toxic?
- What are the background level, LOD, LOQ in "kg/planet" for known PFASs, for total PFASs?
- What are the exact amount, distribution and origin of reported > 200 million tons of TFA(TP of PFASs with single CF3).
- What do we know of Difluoromalonic Acid - suspected end-product of chemicals with single CF2 group?
- What is the correct metric for regulation: grams? Moles? F-chain equvalents, CF2-equivalents, F-equivalents?
- What is the relation between the available planetary stock of fluorine (200-500 MT of Fluorite), projected emission of PFASs (4.5 MT), and PFASs in the deep ocean(200-280 MT of TFA)?
- Are there other equally persistent (non-organofluorine) man-made or natural chemicals?
- Shall or shal not truly persistent "Forever Chemicals" be treated the same way as degradable derivatives or precursors?

References

Houtz, E. et al., (2012) Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. Environ. Sci. Tech., 17, p. 9342. doi: 10.1021/es302274g.

Cioni, L., et al. (2022) Total Oxidizable Precursors Assay for PFAS in Human Serum. Environment International, 170, 107656. doi:10.1016/j.envint.2022.107656

Proposal for a restriction. Per- and polyfluoroalkyl substances (PFASs). ECHA. 2023. https://echa.europa.eu/sv/registry-of-restriction-intentions/-/dislist/details/0b0236e18663449b.

Sensor Systems in Water Analytics

G. Proll[1], G. Gauglitz[1]*

[1]Eberhard Karl University, Institute for Physical and Theoretical Chemistry, Analytical Chemistry,Auf der Morgenstelle 18, D-72076 Tübingen, Germany

gg@ipc.uni-tuebingen.de

To date, great progress has been made in the field of water protection and the protection of our drinking water resources, which are based in particular on purification measures, urban development measures and consistent analytical monitoring. The systematic analytical monitoring by means of various online and offline working methods of water analysis has achieved high standards. Despite all positive developments in classical analytical techniques, there are still further challenges that need to be addressed. For example, contamination with trace substances such as pharmaceutical residues and pesticides continues to pose a particular problem. Accordingly, there are special requirements for process control during the operation of wastewater treatment plants and new challenges arise in connection with climate change. Biosensors could be a key technology in coping with these tasks, as this group of analytical tools has already shown how powerful it can be in quantifying trace substances. More recently, these trace substances have played an increasing role in wastewater and the environment. Therefore, in many countries, wastewater treatment plants are being expanded to a 4th treatment stage to reduce the output of trance substances. There, actual concentrations of these pollutants must be constantly monitored so that the cleaning performance of the adsorption material and / or the effect of ozonation can be optimally adjusted.

Biosensors are analytical instruments that convert a signal from a biological recognition structure into a measurable response. The applicability of these devices is rapidly increasing, and their manufacture for continuous and real-time detection is gaining increasing attention. Some of the main advantages of these instruments today are that they can easily be designed as automated analysis systems, up to portable and easy-to-use instruments that can be further miniaturized, characterized by short response times and sometimes very good analytical performance. In addition, paper-based test strips comparable to lateral flow tests start to reach the necessary low limits of detection and even quantification. Detection arrays on one chip or combination of single use devices with advanced methods of artificial intelligence allow the establishment of intelligent sensor networks equipped with multiparametric sensor systems suitable for complex monitoring and even data acquisition in citizen science projects for control and trend analysis.

Principles, methods, and applications will be discussed.

Trace Analytics of Pharmaceutical Substances in the Environment - Opportunities and Challenges

P. Stepnowski[1]*

[1]University of Gdansk, Faculty of Chemistry, Wita Stwosza 63, Gdańsk 80-308, Poland

piotr.stepnowski@ug.edu.pl

The presence of trace residues of pharmaceutical substances in the environment is increasingly confirmed in water bodies and soils in almost all parts of the world. The most commonly detected drugs include psychotropic or antiparasitic agents, over-the-counter nonsteroidal anti-inflammatory and analgesic drugs, estrogenic hormones, antibiotics or beta-blockers. Methods that enable the determination of such a broad and chemically diverse group of analytes in complex environmental matrices require a special, individual methodological approach both at the level of analyte isolation and concentration, as well as final determinations. The presentation will overview the most important achievements of our team in the development of environmental sample preparation techniques (ASE, MAE, SPE, SPME, UAE) as well as quantitative analysis methods (GC-MS, LC-MS/MS). Also presented will be proprietary solutions for selective enrichment of analytes and alternative extraction techniques using carbon nanotubes or ionic liquids as receiving phases.

Complementary Techniques for GC-MS Environmental Analysis

A.T. Lebedev[1]*, V. B.Artaev[1]

[1]M.V. Lomonosov Moscow State University, Organic Chemistry Department, Moscow, Russia
[2]LECO Corporation, 3000 Lakeview Avenue, St. Joseph, MI, USA

a.lebedev@org.chem.msu.ru

It is becoming very daunting task to comprehensively monitor all environmentally significant compounds. Moreover, almost every day more and more new anthropogenic compounds or their transformation products appear in the environment. The most reasonable analytical approach involves preliminary non-target screening at certain site to discover the most relevant xenobiotics for future target monitoring. However, ordinary GC-MS usually is not capable to identify the unknowns. Here we demonstrate various spectacular examples when combination of high-resolution mass spectrometry, GCxGC, EI, PCI and ECNI was comprehensively applied to analyze the complex environmental samples of rainwater from France, Russia, and Chile, snow from Moscow and Russian Arctic islands, cloud water from France and soil from Montenegro. Samples we collected in 2017-2022 and their preparation in all the cases was in accordance with the EPA Method 8270. The high-resolution time-of-flight mass spectrometer coupled to GCxGC was used for analysis. NIST, WILEY and accurate mass users' libraries along with manual spectra interpretation with assistance from the software tools were used for analytes assignment. Retention indices along the first and the second chromatographic columns were used as well. The instrument was equipped with the ion source capable of producing EI, positive CI and ECNI spectra and GCxGC methods, which was significant for expanded coverage of analytes.

Environmental samples usually contain thousands of analytes. The most environmentally relevant compounds often present at trace levels and thus their identification is a challenge due to coelution with higher concentration compounds. The GCxGC is a very efficient method to eliminate this problem. The number of separated peaks in GCxGC results is usually 5-10 times higher than in one-dimensional GC. Several examples will demonstrate transformation of an unassignable mass spectrum in GC mode into 2-5 quality spectra easily assignable by using library. Retention indices along the secondary polar column allow identification and correctly assign constituents of the same nature.

Accurate mass measurements allowed correct compounds assignment even when the library similarity match score was low. It is also very helpful in the presented challenging cases when manual structural elucidation and reconstruction of mass chromatograms is necessary.

Chemical ionization as a soft method provides a chance to identify correctly certain compounds which do not show molecular ions in EI spectra. Dialkylphthalates are a good example. These priority pollutants are always environmentally relevant while their molecular ions are usually absent in EI spectra. CI spectra contain protonated molecule peaks, while fragmentation information enables assigning both alkyl moieties. Important complementary information is also obtainable with ECNI data. Examples demonstrate improved detection of the halogenated compounds. ECNI sensitivity may be thousands of times better than in EI mode for these compounds. Thus, PCBs with 7-8 Cl atoms, which often remain undetectable in EI mode, are easily found using ECNI mode. Nitro-containing compounds are another example of several orders improved sensitivity, when using ECNI. Another interesting example demonstrate detection of all isomers of dinitrotoluenes and dinitrobenzenes in GCxGC-ECNI-HRMS experiments.

Including Particle Characteristics in Modeling Environmental Exposure of Nanomaterials

Bernd Nowack[1*]

[1]Empa, Swiss Federal Laboratories for Materials Science and Technology, St. Gallen, Switzerland

nowack@empa.ch

The use of modeling to predict environmental release and exposure of engineered nanomaterials has matured a lot since first approaches have been published 15 years ago. The models are now in a state that they can predict current and future emissions of nanomaterials, incorporating changes in production and product use. An example are graphene-related materials which are at the beginning of a huge anticipated growth in production and use. However, most models still just consider a generic nanomaterial, e.g. "nano-TiO_2" although they are produced and used in many different forms and sizes. While we have a lot of data on specific materials synthesized in the lab or obtained from commercial sources, this information is difficult to directly use in exposure assessment. The missing link is information on actual production amounts and uses of the various nanoforms. This presentation will give an overview on the advancement made in the last years in adding such information to exposure models. In particular it will be shown how we can include size distributions of particles in release models together with a characterization of the crystal form with the example of pigment-TiO_2 and nano-TiO_2. This modeling allowed to determine the contribution of conventional TiO_2 pigments to the total amount of nano-scale TiO_2 released into the environment. The results show that even before engineered nano-TiO_2 had been produced, a nanoscale fraction from conventional pigment-TiO_2 was released and still contributes today about 50% to the nanosized fraction of TiO_2. This model allows us to determine the full size distribution up to the µm range of released particles. Such data are needed as input values for environmental fate models which address processes like agglomeration that are highly size-dependent.

Results from form-specific release assessments provide the basis to move the environmental risk assessment of nanomaterials to the next level by specifically targeting different forms of the materials with different hazards. Using some examples, it will be shown how this procedure can change the risk assessment of nanomaterials compared to a generic assessment.

References

Hong, H.; Part, F.; Nowack, B.; (2022) Prospective dynamic and probabilistic material flow analysis of graphene-based materials in Europe from 2004 to 2030. Environ. Sci. Technol. 56: 13798−13809.

Zheng, Y.; Nowack, B. (2021) Size-specific probabilistic material flow analysis of titanium dioxide releases to the environment. Environ. Sci. Technol. 55: 2392−2402.

Hong, H.; Adam, V.; Nowack, B. (2021) Form-specific probabilistic risk assessment of three engineered nanomaterials (nano-Ag, nano-TiO2, and nano-ZnO) for European freshwaters. Environ. Toxicol. Chem. 40: 2629–2639.

Bioavailability Reductions through Nature-Based Remediation of Soils and Sediments: Potential Regulatory Aspects

J.J. Ortega-Calvo[1]*

[1]Instituto de Recursos Naturales y Agrobiologia de Sevilla, Consejo Superior de Investigaciones Científicas, Avda. Reina Mercedes, 10, 41012-Sevilla, Spain

jjortega@irnase.csic.es

The strategic value of soil and water under a regime of global change, the extensive costs associated with the remediation of many polluted sites throughout Europe, and the need for a sustainable financial recovery from the COVID pandemic and Ukraine war demand for new solutions of site remediation. These new solutions must adhere to the European Green Deal (EUGD), where the European Commission proposes a comprehensive set of actions to address the restoration of contaminated sites. Nature-based solutions to environmental pollution are inspired and supported by nature, which are cost-effective, simultaneously provide environmental, social, and economic benefits and help build resilience. Three approaches are currently available to remediate soils and sediments polluted by organic chemicals through NBS: bioremediation, phytoremediation and amendment. Emphasis on their success was often placed on total pollutant removals, which is nowadays unpredictable and often not achieving the remediation goals set by legislation. The classification of a soil as polluted is, indeed, based on environmental standards relying on total concentrations, which do not consider the bioavailability of contaminants. This approach has been demonstrated to be unrealistic and inefficient in the management of polluted sites because it in general overestimates risks (Ortega-Calvo et al, 2015). With a focus on organic pollutants and bioremediation, this overview presentation will examine existing bioavailability concepts and methods, options for their application and standardization, as well as nature-based engineering components for addressing bioavailability reductions instead of only total pollutant removals as a paradigm shift.

Over the last 30 years, numerous publications have discussed the concepts of bioavailability of organic chemicals. Still with a general consensus at the scientific community on the relevant bioavailability processes, the main schools of thought considered bioavailability, bioaccessibility, and chemical activity. These concepts are the basis for different methodologies, ready to be used in regulation (desorption extraction, passive sampling, and biological tests) and mechanistic studies that consider the different processes that are involved (contaminant soil/sediment interactions, transport and passage across cell membrane, and biological processing towards toxic effects or biodegradation). Our group has proposed ways to operate at different levels on these processes for a better bioremediation performance in risk reduction. The approach is relevant because in some circumstances bioremediation may even increase risk of the pollutants. The prospected risk-minimizing strategies include targeting slow-desorption pollutant fractions with (bio)surfactants (Posada-Baquero et al, 2020) and the modulated deposition and motility of microbial degraders (Castilla-Alcantara et al, 2023).

We will finally examine how solving these bioavailability issues may impact the EU initiatives stemming from the Green Deal, such as the soil health and food mission, the action plan for zero pollution, and the chemicals strategy for sustainability.

References

Castilla-Alcantara J.C. et al (2023) Risk reductions during pyrene biotransformation and mobilization in a model plant-bacteria-biochar system, Science of the Total Environment, 868, 161600. DOI: 10.1016/j.scitotenv.2023.161600.

Ortega-Calvo, J.-J. et al (2015) From Bioavailability Science to Regulation of Organic Chemicals, Environmental Science and Technology 49, 10255-10264. DOI: 10.1021/acs.est.5b02412.

Posada-Baquero R. et al (2020) Rhizosphere-enhanced biosurfactanct action on slowly desorbing PAHs in contaminated soil, Science of the Total Environment, 720, 137608. DOI: 10.1016/j.scitotenv.2020.137608.

P/POS XX

Recent in Silico Model for Hazard Assessment and Early Warning

E. Benfenati[1*]

Mario Negri Institute, Department of Environmental Health Sciences, Via Mario Negri, 2, 20156, Milan, Italy

benfenati@marionegri.it

Computational models are improving more and more rapidly. There are multiple models based on different technological approaches and built up for different purposes. Furthermore, the results given by the advanced models provide detailed information and not simply the prediction. Overall, the modern models are much closer to the user needs.

We will describe some of the most recent tools present in the free, open-source systems. Hundreds of quantitative structure-activity relationships (QSAR) models are available, for environmental, ecotoxicological, toxicological, physico-chemical and kinetic properties. In particular, for environmental properties, the models cover acute and chronic toxicity for the three aquatic trophic levels (algae, daphnia and fish), plus other models for terrestrial toxicity (earthworm, insects, other invertebrates, mammals) are available. Wrapping about 50 QSAR models, the are tools to prioritize substances, also considering their environmental degradation products.

Tools for read-across are available too, exploiting the experimental data present in the internal database. Here we will also introduce the new software called SWAN, which, integrating read-across and QSAR models, provides a single assessment.

The results of the modern models typically offer three lines of evidence: the prediction, the read-across (and thus the experimental value) and the theoretical information about the mechanism in the form of structural alert or other rules. Specific tools for safer substances are also present, exploiting the read-across perspective or the presence of structural alerts associated to adverse effects.

Linking in silico platforms, it is possible to cover exposure and risk assessment.

Beyond the Limits of Environmental Analysis for Climate Research

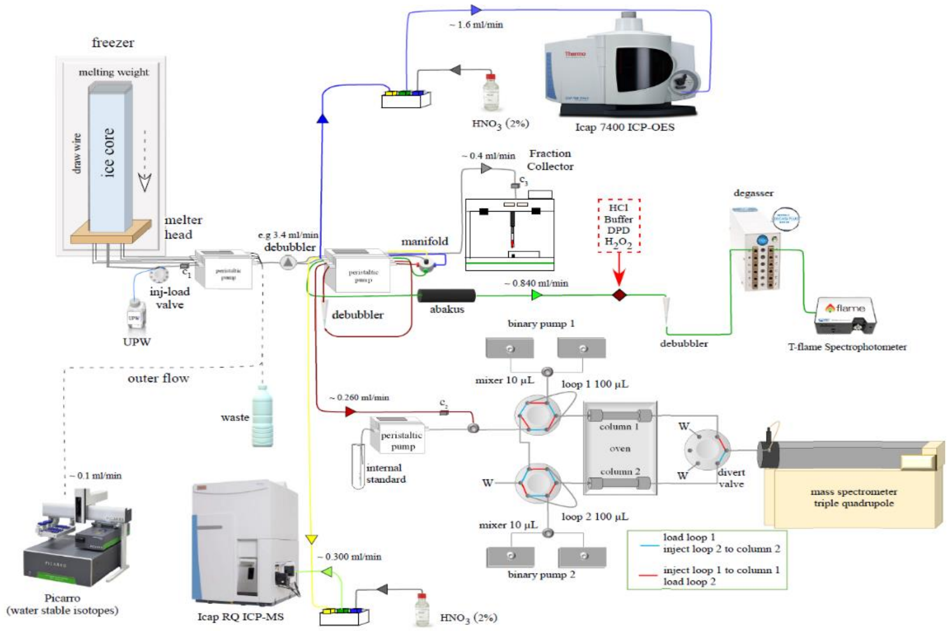
Carlo Barbante[1*]

Ca‘ Foscari University of Venice, Department of Environmental Sciences, Institute of Polar Sciences, CNR, Venice, Italy, Informatics and Statistics, Venice, Italy

**barbante@unive.it*

Advanced chemical analysis techniques are essential in modern chemical processes, as well as in the study and characterization of materials, the environment, and food. These techniques allow for precise and accurate determination and quantification of substances present at extremely low concentrations. Moreover, microscopic investigation methods have significantly enhanced our understanding of natural phenomena and processes occurring at the microscopic level by enabling the visualization and identification of specific atoms and molecules.

An exemplary case demonstrating the benefits of these techniques is the analysis of snow and ice. By continuously examining the layers of snow accumulated over centuries and millennia, it becomes possible to reconstruct the chemical composition of Earth's atmosphere. Numerous chemical species become trapped in either gaseous or particulate form within the snow and ice, and sophisticated analytical techniques enable us to measure their fluxes into the Earth's surface. This presentation emphasizes the substantial potential of inorganic and organic compounds to serve as indicators for both anthropogenic activities and natural processes. It will also delve into future research trends and opportunities in the field of ultra-trace analysis.



Treated Wastewater Reuse: Uptake of Chemicals of Emerging Concern and Risks

E. Heath[1,2]*, E. Andreasidou[1,2], A. Brus[1], A. Vehar[1,2], D. Potočnik[1],M. Jagodic Hudobivnik[1], D. Heath[1], M. Pintar[3], N. Kacjan Maršič[3],N. Ogrinc[1,2], U. Blaznik[4], A. Kovačič[1,2]

[1]Department of Environmental Science, Jožef Stefan Institute, Jamova cesta 39, Ljubljana 1000, Slovenia
[2]International Postgraduate School Jožef Stefan, Jamova cesta 39, Ljubljana 1000, Slovenia
[3]Department of Agronomy, Biotechnical Faculty, University of Ljubljana, Jamnikarjeva 101, Ljubljana 1000, Slovenia
[4]Environmental Health Centre, National Institute of Public Health, Trubarjeva 2, Ljubljana

ester.heath@ijs.si

Water scarcity is a major environmental issue facing many regions and people globally. A cost-effective and sustainable solution to water shortages in agriculture is irrigation with treated wastewater. However, the extent of the consequences on plant development, crop quality attributes, and uptake of chemicals of emerging concern (CEC), which can pose health risks, remains unclear. In this study, the uptake of 14 CEC and 27 potentially toxic elements (PTE) was studied in tomatoes grown in soil-less (hydroponically) and soil-media (lysimeters) irrigated with potable and treated wastewater using GC-MS/MS, LC-MS/MS and ICP-MS. The quality of tomato fruits was evaluated by analysing their amino acid and volatile organic compound profiles using optimised and validated methods based on GC-MS and HS-SPME GC-MS. It was shown that assessed quality parameters affected flavour, texture, structure, mouthfeel, colour, and content of bioactive compounds. In addition, specific elements that promote good health were also assessed and the stable isotopic composition of light elements ($\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$) was performed to study the influence of different treatments on the final product.

Our results showed that bisphenol S (BPS), 2,4 bisphenol F, and naproxen were present in fruits irrigated with spiked potable water and wastewater under both conditions, with BPS having the highest concentration (0.034–0.134 µg kg−1 f. w.). The levels of all three compounds were statistically more significant in tomatoes grown hydroponically (<LOQ - 0.137 µg kg−1 f. w.) than in soil (<LOQ - 0.083 µg kg−1 f. w.), while elemental composition showed differences between tomatoes grown hydroponically or in soil and tomatoes irrigated with wastewater and potable water. Importantly, we showed that the elemental composition in tomatoes was affected by the addition of CEC (Kovačič et al, 2023). Based on CEC uptake and elemental composition, no health risk from consuming tomatoes grown hydroponically or in soil was detected, while the aroma profile differentiates only between hydroponically or soil-grown tomatoes. These two groups also had significantly different stable isotopic compositions of $\delta^{13}C$ and $\delta^{15}N$.

Our data revealed how different irrigation regimes affect chemical uptake and tomato quality attributes. The results of this study add to the argument that, if properly monitored, reusing treated wastewater for irrigation can be a safe approach in agriculture and can support the decisions of policymakers and stakeholders in creating future legislative frameworks related to sustainable water resource management in agriculture. Nevertheless, more studies need to be performed for a definite answer on the safety of wastewater reuse for irrigation, providing more information about CECs, including the formation of metabolites and transformation products, possible synergistic effects and different agricultural practices.

References

Kovačič, A. et al. (2022) Contaminant Uptake in Wastewater Irrigated Tomatoes, Journal of Hazardous Materials, 448, 130964. https://doi.org/10.1016/j.jhazmat.2023.130964.

Analysing Microplastics in the Environment – Challenges and Pitfalls

N. Zumbülte[1]*

TZW: DVGW-Technologiezentrum Wasser (German Water Centre), Karlsruher Straße 84, 76139 Karlsruhe, Germany

nicole.zumbuelte@tzw.de

Due to the ubiquitous presence of microplastics, performing a robust and valid microplastic analysis of environmental matrices such as water, sediment, soil and air is a major challenge. In particular, the contamination of samples with microplastics, e.g. from one's own clothing, laboratory air or from chemicals and plastics used, must be reduced to a minimum and simultaneously recorded to a maximum. This includes, for instance, the avoidance of plastic materials in the laboratory and working under a laminar flow box as well as the consistent recording of a process blank value. Ideally, this process blank value represents the entire workflow from sampling to sample preparation and analysis.

It is important to match the sampling setup and subsequent sample handling to the analytical method that will be used to qualify and quantify the microplastic. For example, the use of a filtration unit with filter sieves on which the microplastics are accumulated during sampling is widely used in water sampling and provides the possibility to adjust the filter sieve mesh size accordingly to the investigated particle size and enables a high sampling volume. Subsequently, the particles and fibres are extracted from these filter sieves, e.g. by ultrasonification. The extract is then processed further depending on the composition of the sample and the analytics to be used. For most samples, sample treatment involves the separation of inorganic contaminants by means of density separation. Organic contaminants are reduced as far as possible, e.g. by using the Fenton reagent or enzymatic degradation. All treatment steps, involve a risk of sample contamination as well as sample losses. Microplastic losses can be determined by recovery experiments, which should ideally also be performed over the entire workflow and for polymer types of different densities, shapes and sizes.

Spectroscopic methods coupled to a microscope (micro-Raman spectroscopy, micro-fourier transform infrared spectroscopy, Laser Direct Infrared) and thermoanalytical methods coupled to a gas chromatograph (GC) with following mass spectrometer (MS) (Pyrolysis-GC/MS and Thermal Extraction and Desorption-GC/MS) have become established for analysing samples for microplastics. However, faults can also occur during analysis as well as evaluation. For example, stearates from disposable gloves can lead to false positive polyethylene results, both using spectroscopic methods as well as thermoanalytical methods.

The points listed above are only a small selection of facts that show that great attention must be paid to quality assurance and quality control when analysing environmental samples for microplastics.

References

Schymanski, D. et al. (2021) Analysis of microplastics in drinking water and other clean water samples with micro-Raman and micro-infrared spectroscopy: minimum requirements and best practice guidelines, Analytical and Bioanalytical Chemistry 413, 5969-5994. doi: 10.1007/s00216-021-03498-y.

Witzig, S. W. et al. (2020) When Good Intentions Go Bad – False Positive Microplastic Detection Caused by Disposable Gloves, Environmental Science & Technology 54(19), 12164-12172. doi: 10.1021/acs.est.0c03742.

How to measure sustainability in international chemicals management?

C. Blum*, H. Friege, E. Heidbuechel, H. C. Stolzenberg, B. Zeschmar-Lahl

christopher.blum@uba.de

The Strategic Approach to International Chemicals Management (SAICM) is a UN framework aiming at sound management of chemicals and waste (SMCW). SAICM complements the Chemical Conventions (e.g. Stockholm, Minamata etc.) by a multi-sector, multi-stakeholder approach. For the new mandate on SMCW (expected to be adopted in 2023), objectives and targets are under discussion that are partially linked to specific Sustainable Development Goals (SDG) of the Agenda 2030. The Concept of Sustainable Chemistry is a powerful tool to support the 2030 Agenda for Sustainable Development and especially the SAICM framework, as has been suggested by the UN Environment Assembly. The new mandate on SMCW affords appropriate indicators to measure progress of sustainable chemistry at the international level. In order to develop proposals for meaningful indicators, criteria need to be defined to frame the selection of SMCW indicators. In the first part of this presentation, the deduction of such appropriate criteria will be explained. In view of the experiences with reporting at UN Conventions, criteria for the selection and development of meaningful indicators have to be, among others, measurable, reliable, and should measure progress over time. For the development of criteria for SMCW indicators, special criteria for sustainable chemistry were aligned in a first step with UNEPs “Green and Sustainable Chemistry Framework Manual” and the “10 Key Characteristics of Sustainable Chemistry” of the International Sustainable Chemistry Collaboration Centre, ISC3. With experts from all UN regions, the criteria were discussed in interviews and revised several times in workshops with application tests to assess indicators. In the second part of this presentation, the final set of proposals for indicators will be analysed in relation to their general performance and linkage to Sustainable Chemistry as well as sustainable development. Many identified indicators address interfaces with global issues like health, climate, biodiversity, energy, and potential conflicts, like the extraction of chemicals from renewable raw materials.

Needs for Researchers in the Science-Policy Interface on Chemicals, Waste and Pollution Prevention and Ways of Effective Participation

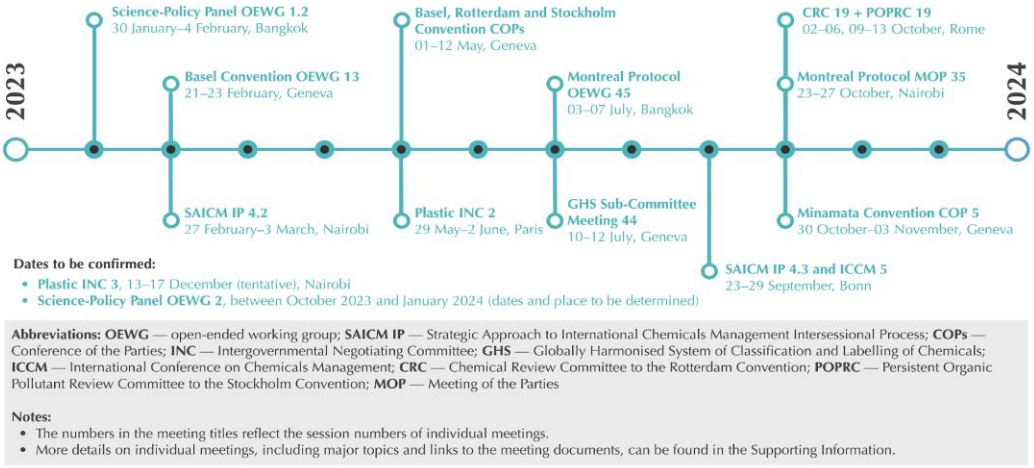
Z. Wang[1*]

Swiss Federal Laboratories for Materials Science and Technology (EMPA), Environmental Risk Assessment and Management (ERAM), Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland

zhanyun.wang@empa.ch

As the world confronts the detrimental impacts caused by anthropogenic chemicals and waste, it is becoming increasingly evident that concerted, science-based international action is imperative. Previous experiences have highlighted the need for widespread participation from researchers to guarantee the success of international policy-making and the long-term effectiveness of their outcomes (Wang et al., 2021). Researchers possess a crucial role in ensuring that policies are well-informed by the most current scientific knowledge available, which is frequently dispersed across the public domain or hidden behind high paywalls. Their involvement is also essential in facilitating the rapid integration of policy requirements into new research, which can produce the necessary scientific knowledge in a timely manner.

This presentation offers a comprehensive overview of the major topics to be discussed at crucial international policy-making meetings on chemicals and waste in 2023, based on an examination of the meeting agendas and previous meeting outcomes. Furthermore, this presentation outlines the general steps that can assist researchers in participating effectively in these meetings. By doing so, it can help ensure that the voices of researchers are heard, and their contributions are integrated into policy decisions that are well-informed by the latest scientific research, leading to better outcomes for all (Wang et al., 2021, 2023).



Dates to be confirmed:

- **Plastic INC 3**, 13–17 December (tentative), Nairobi
- **Science-Policy Panel OEWG 2**, between October 2023 and January 2024 (dates and place to be determined)

Abbreviations: OEWG — open-ended working group; **SAICM IP** — Strategic Approach to International Chemicals Management Intersessional Process; **COPs** — Conference of the Parties; **INC** — Intergovernmental Negotiating Committee; **GHS** — Globally Harmonised System of Classification and Labelling of Chemicals; **ICCM** — International Conference on Chemicals Management; **CRC** — Chemical Review Committee to the Rotterdam Convention; **POPRC** — Persistent Organic Pollutant Review Committee to the Stockholm Convention; **MOP** — Meeting of the Parties

Notes:

- The numbers in the meeting titles reflect the session numbers of individual meetings.
- More details on individual meetings, including major topics and links to the meeting documents, can be found in the Supporting Information.

Figure 1: Timeline of major international negotiations on chemicals and waste management in 2023. (repoduced from (2))

References

Wang, Z. et al. 2021. We Need a Global Science-Policy Body on Chemicals and Waste. Science 371 (6531), 774.

Wang, M. et al. 2023. Major International Negotiations on Chemicals and Waste for Researchers from All Disciplines to Watch for in 2023. ES&T Letters [in Press].

Wang, Z. et al. 2021. Enhancing Scientific Support for the Stockholm Convention's Implementation: An Analysis of Policy Needs for Scientific Evidence. ES&T 56(5), 2936.

Environment and Health: What Did We Learned After Five Years of Running of Comprehensive Interdisciplinary Bachelor and Master Study Programs in Brno, Czech Republic?

P. Šebej[1]*

[1]RECETOX, Faculty of Science, Masaryk University, Kamenice 5, 625 00, Brno, Czech republic

sebej@recetox.muni.cz

Change is the only constant in life. To keep the pace with the changes, we are adjusting all sectors of the society, including education. Education plays a prominent role in adaptation because it is paramount for the quality of future professionals.

Tertiary education often has to balance between providing students with general overview and focus on specific topics. This dichotomy is even more pronounced in more "recently" established fields, such as environmental sciences. The "interdisciplinarity" is a key concept here, but sometimes only plays a role of a keyword without an impact. Still not an easy task, e.g. Lammel et al. showed, that an “environmental chemistry” bachelor and master study programs (SP) at a European university could contain a share of unavoidable credit points given for chemistry courses anywhere between 0 and 60% for bachelor SP, and 0-100% for master SP (Lammel, 2014).

In the RECETOX Centre, Masaryk University, Brno we introduced new study programs focusing on Environment and health at all levels of tertiary education (bachelor to doctoral) in 2019 with a rather naïve desire to answer the societal demand and job market needs in this area. The programs were designed to integrate previously existing SP focused on environmental chemistry and ecotoxicology and bring new topics, such as exposome(Price, 2022) and offer students broader interdisciplinary overview.

During the five years we faced various issues and identified possible options for their change and improvement. The suggestions came from teachers and students and we have implemented them stepwise. The changes also included a division of SPs into particular specializations, courses and their curricula.

Today‘s graduates will be in the jobmarket until late 21st century and they will face accelerating changes in environment and society. To be successful the students will need evidence-based knowledge and approach, chemical and biological understanding of environmental issues, their origins and impacts, relationships to human health and society and holistic overview, but also transferrable skills for their careers. Life-long learning is a key concept required for us, both alumni and teachers to adopt to changes, in jobs and teaching/mentoring, respectively.

Our study programs are still unique within the Czech republic, and we are happy to see that similar initiatives are also appearing at various places around the world. Just like connections of topics and fields is a cornerstone of our SPs, the connections between different courses, and between theory and practice are critical for a good curriculum. Our experiences from first five years of running these study programs, as well as the curricula, feedback loop, changes in SPs and potential future outlook will be discussed.

We are also aware of need of adapting the curricula to challenges, but this text was (still) prepared without assistance of AI tools.

Acknowledgement: RECETOX RI (No. LM2018121), CETOCOEN EXCELLENCE (No. CZ.02.1.01/0.0/0.0/17_043/0009632) both by MEYS, and EU’s Horizon 2020 Research and Innovation Programme (No. 857560).

References

Lammel, G., Comas, EJ., Ivancev-Tumbas, I. (2014) Higher education in environmental sciences with chemistry emphasis: bachelor and master programmes in Europe. Environ Sci Pollut Res 21:7211. doi: 10.1007/s11356-014-2737-7.

Price, E.J. et al. (2022) Merging the exposome into an integrated framework for "omics" sciences. iScience, 25(3):103976. doi: 10.1016/j.isci.2022.103976.

How Far Have We Advanced in The Analytical Determination of Persistent and Mobile (Organic) Chemicals?

J.B. Quintana[1]*, R. Montes[1], S. Méndez[1], M. Lage-Díaz[1], R. Rodil[1]

[1]Universidade de Santiago de Compostela, Department of Analytical Chemistry, Institute of Research on Chemical and Biological Analysis (IAQBUS), 15782 Santiago de Compostela, Galicia, Spain.

jb.quintana@usc.es

Persistent and mobile (organic) chemicals, known as PMOCs (if organic), have gained an increasing attention in the latest 10 years due to the fact that their high polarity combined with persistency render them as a type of chemicals which can easily spread across the water cycle. Thus, they can become a potential threat to aquatic organisms and lately to human health, if they can also break through drinking water production barriers (Reemtsma, 2016). As an analogy to the known PBT/vPvB criteria under REACH, they have more generically been called PMT/vPvM (persistent mobile and toxic / very persistent, very mobile) chemicals, as proposed by the German Environmental Agency. So far, this initiative has also put pressure on EU regulation so that PMT/vPvM chemicals are considered to pose an equivalent level of concern to PBT/vPvB chemicals, which very recently led to them being added to the EU CLP legislation as one new hazard class (EU, 2023).

Such road could only be walked by the support of newly developed analytical methods capable of (partially) filling the analytical gap for these very polar chemicals, and their further application to water monitoring by both screening and target methods. In fact, a major problem 10 years ago was that there was little information on their environmental occurrence and fate because most analytical methods relied on generic solid-phase extraction (SPE) methods combined with reversed-phase liquid chromatography (RPLC) coupled to (high resolution-)mass spectrometry ((HR)MS). Those methods were not efficient enough in both preconcentrating and measuring them, particularly in the case of the most polar ones. Although methods for some particular families of polar analytes existed, e.g. by ion-pair LC, they posed important drawbacks and were unable to target/screen for a wide array of PMT/vPvM chemicals.

Therefore, this presentation will show the advances made in their chromatographic separation by introducing novel chromatographic modes into the game, such as hydrophilic interaction LC (HILIC), mixed-mode LC (MMLC) and supercritical fluid chromatography (SFC). It will also present which are the possibilities so far to (efficiently) enrich these very hydrophilic substances from aqueous matrices, including SPE and evaporative/freeze-drying based approaches, among others, as well as some selected existing applications to pinpoint some relevant PMT/vPvM chemicals occurring in water, such as e.g. some very short-chain per-/poly-fluoroalkylated substances (PFAS), melamine and several sulphonates (Zahn, 2020). As a final outcome, the presentation will critically discuss how far the analytical gap has been narrowed and where it still exist and, consequently, what occurrence data is still missing. Some examples are methods capable of determining PMT/vPvM chemicals at ultratrace level in the marine environment, or the lack of knowledge on human exposure to such compounds.

Acknowledgements: Xunta de Galicia (ED431C 2021/06) and the Spanish Agencia Estatal de Investigación – MCIN/AEI/10.13039/501100011033 (ref. PID2020-117686RB-C32, TED2021-129200B-C41 through NextGeneration/PRTR funds) for funding.

References

Reemtsma, T. et al. (2016). Mind the gap: Persistent and mobile organic compounds – water contaminants that slip through. Environmental Science & Technology, 50, p. 10308. doi: 10.1021/acs.est.6b03338.

EU (2023). COMMISSION DELEGATED REGULATION (EU) 2023/707 of 19 December 2022 amending Regulation (EC) No 1272/2008 as regards hazard classes and criteria for the classification, labelling and packaging of substances and mixtures. Official Journal of the European Union, L 93/7 (31.03.2023).

Zahn, D. et al. (2020). Analysis of mobile chemicals in the aquatic environment—current capabilities, limitations and future perspectives. Analytical and Bioanalytical Chemistry, 412, p. 4763. doi: 10.1007/s00216-020-02520-z.

The Unique Role of Natural Nonliving Soil Organic Matter (SOM) and Soil Humic Substances (HS). Environmental And Agricultural Issues with Focus on European and Mediterranean Regions.

N. Senesi[1*]

[1]University of Bari "Aldo Moro", Department of Soil, Pland Food Sciences, Via Amendola 165/A, 70126, Bari, Italy

nicola.senesi@uniba.it

A review will be presented on the multiple roles exerted by SOM in soil. SOM comprises a wide variety of components grouped in classes of different chemical composition and reactivity or in pools of different biological stability and activity. These include: (a) biomolecules of known chemical composition that are typical constituents of plant and animal debris or are produced by microorganisns; (b) a wide variety of partially degraded products originated during the decay processes of biomolecules; and (c) a composite mixture of chemically recalcitrant and biologically refractory compounds named "humic substances" (HS) that represent the most chemically complex and reactive fractions of SOM. The amount and quality of SOM and its fractions depend on delicate equilibria that are a function of several ecopedological, climatic, anthropic and intrinsic soil factors. In particular, the natural input of plant, animal and microbial residues, appropriate crop management practices (e.g., reduced tillage, cover crops, prescribed grazing and adequate biomass rotations), and organic amendment contribute to the conservation and increase of SOM content. In contrast, changes in land use (e.g., deforestation), inappropriate crop cultivation and harvesting, erosion, leaching of dissolved organic carbon and natural and/or anthropic degradation processes determine SOM loss. Globally, processes leading to SOM mineralization significantly increase atmospheric CO2 levels thus contributing markedly to climate changes. In recent years, serious environmental and agricultural concerns have raised in most European and Mediterranean regions on the decrease of soil quality due to various issues such as erosion, compactiom, acidification, desertification, nutrient depletion, chemical contamination and reduction of biodiversity and biological activity. Among the several factors affecting soil quality, the impact of SOM and especially soil HS deserve special attention due to the unique role they play in almost all soil chemical, physical and biological properties, functions, equilibria and processes. As it regards chemical properties, SOM and HS contribute markedly to soil acid-base buffering capacity, represents an important sink and source of macro- and micro-nutrients for plants and soil microorganisms, and are able to interact with organic and inorganic xenobiotics introduced into soil. In particular, SOM and especially HS play an important role in the environmental fate of trace metal ions and pesticide and other chemical residues in soil by controlling their physico-chemical behavior and performance, transport, mobilization/immobilization processes, chemical and biological availabilty and degradation, and photochemical decomposition. In the context of physical properties, SOM and HS are very active in binding mineral particles together thus promoting a good soil structure, improving soil aeration and moisture retention, reducing compaction and water and wind erosion and limiting the risk of drought and floods. As well, soil biodiversity and bioactivity are markedly affected by SOM and HS as they are the main source of food for soil organisms.

References

Senesi, N., Huang, P.M., Xing, B. (2009). Biophysico-Chemical Processes Involving Natural Nonlinving Organic Matter in Environmental Systems. Wiley-IUPAC Series on Biophysical-Chemical Processes in Environmental Systems. Vol.2, pp. 876. Wiley-Interscience, Hoboken, NJ, USA. ISBN: 978-0-470-53963-7.

Senesi, N. Plaza, C. (2008). Organic matter actions in protecting soil from physical, chemical and biological degradation. In: Geoecology 39 "Th Soils of Tomorrow-Soils Changing in a Changing World" (C. Dazzi and E. Costantini, Eds). pp. 285-297. Catena Verlag. ISBN: 978-3-923381-56-2.

Senesi, N., Loffredo, E. (1999). The chemistry of soil organic matter. In: Soil Physical Chemistry, 2nd Edit. (D.L. Sparks, Ed), Chapter 6, pp.239-270. CRC Press, Boca Raton, USA.

Identifying and Quantifying Atmospheric Sources of Organic Contaminants to the Habitat of the Saint Lawrence Estuary Belugas

F. Wania[1]*, F. Zhan,[1] Y. Li,[1] J. Oh,[1] C. Shunthirasingham,[2] Y. D. Lei,[1] Z. Lu,[3] K. Breivik,[4] A. B. Chaaben,[3] A. D. Castilloux,[3] N. Alexandrou,[2] C. Weng,[1] and H. Hung[2]

[1]Department of Physical and Environmental Sciences, University of Toronto Scarborough, 1265 Military Trail, Toronto, Ontario, Canada M1C 1A4
[2]Air Quality Processes Research Section, Environment and Climate Change Canada, Toronto, ON M3H 5T4, Canada
[3]Institut des Sciences de la Mer de Rimouski, Université du Québec à Rimouski, Rimouski, Québec G5L 3A1, Canada
[4]NILU Norwegian Institute for Air Research, Kjeller, Norway

frank.wania@utoronto.ca

Persistent organic contaminants, such as the polychlorinated biphenyls (PCBs), have been shown to bioaccumulate in the beluga whales residing in the St. Lawrence Estuary (SLE) and may be impacting their health (Béland et al. 1993). Atmospheric deposition is often the dominant source of organic contaminants to coastal aquatic ecosystems (e.g., Totten et al. 2006) and is likely also important in delivering PCBs to the SLE.

We quantified concentrations of organic contaminants of potential concern for the whales in air, water and atmospheric deposition using networks of passive air and water samplers across Southern Quebec, coupled with active air and deposition samplers on the north shore of the SLE. The passive air sampling network encompassed the St. Lawrence River valley between Montreal and Quebec City as well as the north and south shore of the SLE. Locally elevated air concentrations identified major PCB sources to the regional atmosphere, such as a waste incinerator in Quebec City and a location in Montreal where PCB-containing equipment had been stored. Conversely, the passive air sampling network could exclude several electrical transformer stations as significant sources of PCBs to the atmosphere. The analysis of a large number of PCB congeners and samples allows us to employ multivariate statistical approaches to distinguish between PCB sources related to the use of technical PCB mixtures and those resulting from unintentionally produced PCBs.

We further used the Nested Exposure Model (NEM) to simulate the atmospheric delivery of seven highly abundant congeners (PCB-28, 52, 101, 118, 138, 153, 180) to the SLE from 1930 to 2023. NEM is able to simulate the SLE region with high spatial resolution, while accounting for the influence of global and continental emissions (Breivik et al. 2021). NEM's ability to capture the spatial air concentration variability was evaluated by comparing results with measurements from the passive air sampler network. NEM predicted air concentrations in the SLE region generally agree within a factor of three with the measurements, with even better performance for the lighter congeners, i.e., PCB-28 and 52. The excellent agreement with observations allows us to use NEM to derive information that is inaccessible by measurements. For example, NEM suggests that Canadian emissions are on average responsible for half of the PCB-153 in the atmosphere of the SLE. This proportion is higher in cities such as Montreal and Quebec City where local sources are dominant. Emissions in the US and elsewhere in the world contribute almost equally to the other half. Domestic and international efforts are required to further reduce the input of PCBs to the SLE.

Combining measurements with atmospheric dispersion and deposition calculations, driven by historical emission estimates, facilitates the estimation of the time-varying atmospheric input of organic contaminants to the coastal habitat of endangered marine mammals.

References

Béland, P. et al. (1993) 'Toxic Compounds and Health and Reproductive Effects in St. Lawrence Beluga Whales', J. Great Lakes Res. 19, p. 766–775

Breivik, K., et al. (2021) 'Introducing a nested multimedia fate and transport model for organic contaminants (NEM)', Environ. Sci.: Processes Impacts, 23, p. 1146-1157

Totten, L. A. et al. (2006) 'Direct and Indirect Atmospheric Deposition of PCBs to the Delaware River Watershed', Environ. Sci. Technol. 40, p. 2171-2176

Oral presentations

Environmentally Persistent Free Radicals - Activation, Chemistry and Impact on Exposure Systems

S. Lomnicki[1]*, P Dangal[1], F. Hasan[1]

[1]Louisiana State University, Department of Environmental Sciences, and LSU Superfund Research Center, 93 South Quad Dr, Baton Rouge, LA 70803, USA

slomni1@lsu.edu

Environmentally Persistent Free Radicals (EPFRs) are a new type of pollutant, associated mainly (but not only) with ambient air particulate matter. Though discovered and described fairly recently (early 2000s) they are gaining more and more interest from environmental chemists, biochemists and human health experts. Since their discovery a lot has been revealed on their nature and potential human and ecological impact, however, still there are more questions then answers. It is well understood that the major source of EPFRs are various emissions from thermal sources such as combustion, thermal reactions etc., although it has been shown that they can also be formed at mild conditions driven by a long-time equilibrium system. An example of such processes is formation of EPFRs in the soils contaminated with organic pollutants, particularly substituted aromatic compounds. A significant implication of the EPFRs emission is their observed toxic human effect through generation of hydroxyl radicals followed by oxidative stress (T.E. Sussan, et al. 2015, j. Saravia, et al. 2014, A. Kelley et al. (+2013). The most intriguing question remains open - what is the mode of EPFRs activation in the redox cycling?

Methods: For kinetic studies of EPFRs activation and EPFR reactivity, EPFR samples were synthesized in the lab using well described techniques (adsorption of organic precursors on metal oxide/silica system) (E. Vejerano, et al. 2012). Reactivity with PAHs was studied in situ using 1-methyl naphtale as a PAH model chemical. Both EPFR and 1-MN were co-deposited on PM and suspended in PBS buffer for 30min, followed by extraction and GC-MS/MS analysis of the produced particulate matter. Low temperature emission of EPFR was studied from 3D printing by collecting PM at the outlet of the extrusion head of the 3D printer followed by EPR analysis.

Results: Our study has shown that it is a change of environmental pH that determines the onset of EPFRs activation. Kinetic expression describing the dependence of EPFR activation with pH has been developed. Additionally, it was shown that coexistence of EPFR on PM with other pollutants, such as PAHs, trigger oxidation of the latter, changing the exposure speciation and shifting the exposure burden to oxyPAHs. 3D printing process has been shown to be an example of the low temperature EPFR emission, as during this process a partial depolymerization and decomposition of filaments occurs thus resulting on emissions of EPFRs during printing. This shows a potentially hazardous condition for both operators and other persons present in the close vicinity.

References

T.E. Sussan, et al. (2015) 'Exposure to Electronic Cigarettes Impairs Pulmonary Anti-Bacterial and Anti-Viral Defenses in a Mouse Model', PLoS ONE, Vol. 10 No. 2, pp. e0116861.

j. Saravia, et al. (2014) 'Early-life exposure to combustion-derived particulate matter causes pulmonary immunosuppression', Mucosal Immunology, Vol. 7 No. 3, pp. 694-703.

A. Kelley, et al. (2013) 'Model Combustion-Generated Particulate Matter Containing Persistent Free Radicals Redox Cycle to Produce Reactive Oxygen Species', Chemical Research in Toxicology, Vol. 26 No. 12, pp. 1862-1871c.

E. Vejerano, et al. (2012) 'Lifetime of combustion-generated environmentally persistent free radicals on Zn(II)O and other transition metal oxides', Journal of Environmental Monitoring, Vol. 14 No. 10, pp. 2803-2806.

Ambient Air $PM_{2.5}$ and Associated PAHs Assessment at Urban Background Sites in Bulgaria

S. Naydenova[1], A. Veli[2], Z. Mustafa[2], E. Hristova[3], L. Gonsalvesh[4]*

[1]Prof. Dr Assen Zlatarov University, Department of Ecology and Environmental Protection, Burgas 8000, Bulgaria
[2]Prof. Dr Assen Zlatarov University, Central Scientific Research Laboratory, Burgas 8000, Bulgaria
[3]National Institute of Meteorology and Hydrology, Department of Meteorology, Sofia 1784, Bulgaria
[4]Prof. Dr Assen Zlatarov University, Chemistry department, Burgas 8000, Bulgaria

lenia_gonsalvesh@abv.bg

The cleanliness of the environment is a mandatory condition for ecological balance and normal people existence, which against the background of industrial and urbanization growth necessitates a critical and detailed approach for pollutants assessment, and, accordingly, more ambitious requirements and effective policies for pollution control. However, in large urban agglomerations, poor air quality still causes negative consequences on ecosystems, with one of the main burdens being the high levels of particulate matter (PM), especially those with a diameter bellow 2.5 µm ($PM_{2.5}$). Inasmuch as PM negative impact is hinging on their composition, researches on the topic are of a significant interest. For Bulgaria, studies on PM composition are particularly relevant, as the existing data are rather episodic and incomplete. Thus, the project CARBOAEROSOL (funded by BNS Fund, contract № КП-06-Н 34/9 -19.12.2019) has been developed to attain a knowledge about the concentrations and spatial-temporal variations of ecologically significant species in $PM_{2.5}$.

The aim of the study, part of CARBOAEROSOL, is to assess the concentrations of $PM_{2.5}$ and associated PAHs, as well as to distinguish PAHs pattern of distribution, their sources and health risk in two Bulgarian cities. The parallel $PM_{2.5}$ samplings were performed at sites classified as “urban background”, i.e. the Central Meteorological Observatory, Sofia (42.655 N, 23.384 E, at 586 m a.s.l.) and University "Prof. Dr Assen Zlatarov", Burgas (42.3141N, 27.2647E, at 30 m a.s.l.), in the periods 14th Jan – 13th Mar and 17th Oct – 20th Nov of 2022. A total number of 181 $PM_{2.5}$ samples were collected on PTFE and quartz-fibre filters, respectively for $PM_{2.5}$ and PAHs analyses. The analysis of 16 US EPA priority PAHs plus coronene, perylene and benzo[e]pyrene was performed by the use of GC–MS/MS and IS calibration technique as described in [1].

The results reveal that the average $PM_{2.5}$ concentrations in Sofia for the entire sampling period are higher than those in Burgas, but still within the average annual norm of 25 $\mu g\ m^{-3}$, correspondingly 18.43 (SD=9.50) $\mu g\ m^{-3}$ vs. 15.65 (SD=7.63) $\mu g\ m^{-3}$. The registered $PM_{2.5}$ bounded ΣPAHs concentrations vary in the range of 0.33 – 28.95 $ng\ m^{-3}$ with an average values of 6,88 (SD=6.05) $ng\ m^{-3}$ for Sofia and 2.19 (SD=1.16) $ng\ m^{-3}$ for Burgas. The seasonal peculiarities are as follows: Sofia – 7.51 (SD=4.65) $ng\ m^{-3}$ for winter and 6.33 (SD=7.17) $ng\ m^{-3}$ for autumn; Burgas – 2.95 (SD=1.31) $ng\ m^{-3}$ for winter and 1.62 (SD=0.60) $ng\ m^{-3}$ for autumn. The 4- and 5-rings PAHs are prevailing followed by 6-rings ones. This is associated with the pollution sources specificity and PAHs gas/particle partition. Source apportionment by diagnostic ratio approach demonstrates that the main PAHs portion in both cities can be certainly related to pyrogenic sources, i.e. traffic emission with dominant influences of diesel vehicles and fossil fuel/biomass combustion. A contribution from road dust and roadway soil is also suspected. The levels of ΣPAHs toxic BaP equivalency are 1.05 $ng\ m^{-3}$ for Sofia and 0.32 $ng\ m^{-3}$ for Burgas at an average yearly norm of 1 $ng\ m^{-3}$.

References

Naydenova S. et al. (2022) ‘Atmospheric levels, distribution, sources, correlation with meteorological parameters and other pollutants and health risk of PAHs bound in PM2.5 and PM10 in Burgas, Bulgaria – a case study’ Journal of Environmental Science and Health, Part A, 57(4) p. 306, doi: 10.1080/10934529.2022.2060669.

200 Years of NH3 Inventory in Europe Inferred From 15N Of NH4+ in Mont-Blanc Ice Core with Unexpected Recent Combustion-Related Emissions

A. Lamothe[1*], P. Akers[2], P. Ginot[1], S. Albertin[3,1], N. Caillon[1], A. Eichler[4,5], A. Gilbert[1], J. Savarino[1]

[1]Univ. Grenoble Alpes, CNRS, IRD, INRAE, Grenoble INP, IGE, 38000 Grenoble, France
[2]Trinity College Dublin, Department of Geography, Dublin, Ireland
[3]LATMOS/IPSL, Sorbonne Université, UVSQ, CNRS, 75005 Paris, France
[4]Paul Scherrer Institute, Laboratory of Environmental Chemistry, 5232 Villigen PSI, Switzerland
[5]University of Bern, Oeschger Centre for Climate Change Research, 3012 Bern, Switzerland

alexis.lamothe@univ-grenoble-alpes.fr

Ammonia (NH3) abatement is a priority to limit its impact on ecosystems, biodiversity, radiative forcing, and air pollution (Gu et al., 2021). So far, the abatement policies have had limited results on the amount of NH3 emitted.

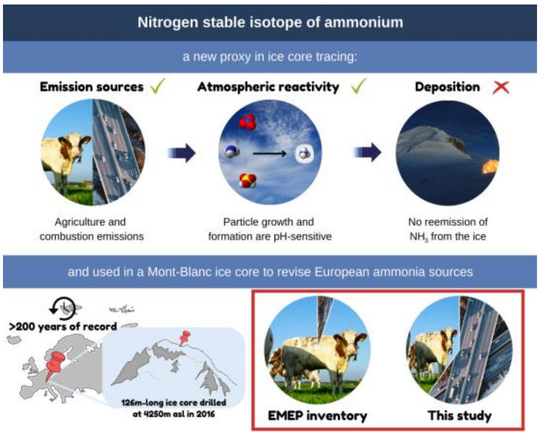
According to current European NH3 inventories, agriculture-related emissions account for 95% of NH3 sources (European Environment Agency, 2021). However, some studies are beginning to question the assumed source proportions in NH3 inventories (e.g., Chen et al., 2022).

Ice cores allow us to study past atmospheric composition. The drilling of the Col Du Dôme (Mont Blanc) in 2016 as part of the Ice Memory program made it possible to extract 126 m of ice and thus retrace more than 200 years of European atmosphere. Here, we present a method for analysing the 15N isotopes of ammonium in ice cores (δ15N(NH4+)), the deposited form of NH3, and 200 years of NH3 sources in Western Europe.

Today, only 38% of NH3 emissions come from agriculture, compared to 95% according to the inventories.

Our findings demonstrate that the agriculture emission abatement policies have had substantial results in diminishing its NH3 emissions while, the Euro5 and Euro6 policies unintendedly conducted to NH3 production.

In a desire to control air quality, our measurements show that public policies must now support a reduction in NH3 emissions from vehicular, industrial, and biomass combustion.



Graphical abstract to explain the new proxy δ15N(NH4+) in ice cores and the application to a Mont-Blanc ice core

References

Chen, Z.-L., et. al. (2022) 'Significant contributions of combustion-related sources to ammonia emissions', Nat Commun, 13, 7710. 10.1038/s41467-022-35381-4.

European Environment Agency, 2021. European Union emission inventory report 1990-2019 under the UNECE Convention on Long-range Transboundary Air Pollution (Air Convention) (Publication).

Gu, B., et. al. (2021), 'Abating ammonia is more cost-effective than nitrogen oxides for mitigating PM2.5 air pollution', Science, 374, 758–762, 10.1126/scie

Multi Source Analysis of VOCs in Rural, Semi-Urban and Urban Areas and their Role on Ozone and SOA Formation

I. Díez-Palet[1]*, C. Jaén[1], E. Marco[1], B. L. van Drooge[1], P. Fernández[1], J. O. Grimalt[1]

[1]Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Environmental Chemistry,
Jordi Girona 18-26, 08034, Barcelona, Spain

isabel.diez@idaea.csic.es

Volatile Organic Compounds (VOCs) are known to play a key role in atmospheric chemistry as they act as precursors of tropospheric ozone and secondary organic aerosols (SOA) by means of photochemical reactions and gas to particle conversion. Some of these compounds exhibit toxic and carcinogenic effects and thus suppose a risk for ecosystems and human health. Yet many source-apportionment studies focus on urban sites, scarce knowledge is available on the distribution of VOCs in rural and semi-urban areas and their sources. The present study is aimed to determine the main VOCs sources in three different locations, comprising rural (Mollerussa), semi-urban (Vic) and urban sites (Santa Perpetua de Mogoda), and to assess their role in O_3 and SOA formation. For this purpose, air (10 L) was sampled during seven campaigns (2021 and 2022) by low-flow pumping at 1.2 m above ground level (n = 82) through two types of stainless-steel sorbent cartridges: a) multi-bed tube composed of three graphitized carbon-based sorbents and b) TENAX TA. Both cartridges were coupled in parallel with sampling rates of 50 ml/min for 3 hours. Thermal desorption-gas chromatography mass spectrometry (TD-GC-MS) in full scan mode allowed the identification of 42 compounds by retention times and mass spectral interpretation. Quantification was performed by the external standard method. Multivariate Curve Resolution – Alternatives Least Squares (MCR-ALS) analysis (Tauler, 1995) of the obtained database was used for source apportionment of the VOC compositions in these rural, semi-urban, and urban sites. By this approach, a series of 5 main VOC sources were identified: 1) Diurnal biogenic, 2) Gasoil-related emissions, 3) Traffic emissions, 4) Nocturnal accumulation and 5) Industrial activity. Ground-level summer ozone formation was observed to be strongly associated to summer biogenic emissions of isoprene what was consistent with Ozone Formation Potential estimations (Carter, 2009). However, in winter and spring, tropospheric ozone formation was dominated mainly by VOCs emitted from vehicle exhausts and industrial activities. Nocturnal accumulation of VOCs was influenced by winter temperature inversions and stagnant tropospheric conditions. Calculations of Secondary Organic Aerosol Potential (SOAP) (Derwent et al., 2010) identified toluene, benzene and m-xylene as the main drivers of SOA formation in all studied locations.

References

Tauler, R. (1995) “Multivariate curve resolution applied to second order data.”, Chemometrics and intelligent laboratory systems, 30(1), pp. 133–146.

Carter, W.P. (2009) “Updated maximum incremental reactivity scale and hydrocarbon bin reactivities for regulatory applications.”, California Air Resources Board Contract, 339.

Derwent, R.G., Jenkin, M. E., Utembe, S. R., Shallcross, D. E., Murrells, T. P., & Passant, N. R. (2010).“Secondary organic aerosol formation from a large number of reactive man-made organic compounds.”, Science of The Total Environment, 408(16), pp. 3374–3381.

Chemical Composition of $PM_{2.5}$ Collected in São Paulo During the Covid-19 Pandemic

P.C. Vasconcellos[1]*, C. N. Farias[1], J. V. Martins[1], P. E. Artaxo-Netto[1]

[1]University of São Paulo (IQ-USP); Institute of Chemistry, Institute of Geosciences, University of São Paulo (IGc-USP); Institute of physics, University of São Paulo (IF-USP)

perola@iq.usp.br

In December 2019, the first cases of covid-19, a respiratory syndrome caused by the novel coronavirus (SARS-CoV-2), were reported. Due to the rapid transmission of SARS-CoV-2, the World Health Organization declared the pandemic of covid-19 in March 2020 (World Health Organization. 2020). Efforts to contain the spread of SARS-CoV-2 and avoid the collapse of health systems resulted in the reduction in vehicular traffic and air pollution in various urban centers. To evaluate the effects of social restriction measures in the atmosphere of São Paulo (Brazil) in 2020, chemical composition of PM2.5, including water soluble ions (WSI), elements, organic and elemental carbon (OC and EC), polycyclic aromatic hydrocarbons (PAHs) and its derivatives (oxy and nitro-PAHs), were determined.

PM2.5 (n=50 samples) were collected from march to august 2020 (autumn and winter) using quartz fiber filters and high-volume sampler. WSI were extracted by ultrasound and determined by ionic chromatography. Elements were extracted after microwave acid extraction and determined by ICP-MS. OC and EC were quantified by thermal optical analysis. PAHs and its derivatives were extracted by ultrasound, fractioned by silica-gel column, and quantified by GC-MS.

Lower concentrations of PM2.5, WSI, elements, PAHs, oxy and nitro-PAHs were observed compared to previous studies carried out in this site in the same period (Pereira G. M. et al. 2017). PM2.5 concentrations ranged from 5 to 35 µg m-3 (av. 17 µg m-3). Total WSI ranged from 1.3 to 9.5 µg m-3 (av. 4.0 µg m-3), and elements from 52 to 1,333 ng m-3 (av. 300 ng m-3), accounting for 23 % and 1.3 % of PM2.5, respectively. The results showed ionic species (SO42-, NO3-, Cl-, NH4+, Ca2+ and K+) and elements associated with oil and fossil fuel combustion (Pb and Zn), non-exhaust traffic emissions (Pb, Cu, Ba and Sb) and dust resuspension (Fe, Mn, Zn and Ti). Total PAHs ranged from 0.2 to 14.6 ng m-3 (av. 4.5 ng m-3), oxy-PAHs, from to 0.04 ng m-3 to 3.1ng m-3 (av. 0.5 ng m-3) and nitro-PAH from 0.02 to 0.63 ng m-3 (av. 0.27 ng m-3). The predominance of high-molecular-weight PAHs related to vehicular emissions suggested that the traffic was the main source. Benzo(a)pyrene equivalent index (0.01 to 1.9 ng m-3) indicated cancer risk in few samples (n=4). OC ranged from 0.47 to 17 µg m-3 (av. 4 µg m-3) and EC from 0.06 to 3.6 µg m-3 (av. 0.9 µg m-3), accounting for 22% and 5% of PM2.5, respectively. OC/EC ratios (av. 6.0) in this period indicated higher contribution of secondary process (Pereira G. M. et al. 2017). Overall, the results showed that during covid-19 outbreak in São Paulo, the reduction in vehicular traffic led to a decrease in the pollutants except OC, that presented comparable values with previous years. Concerning the PAHs derivatives, 3-NFlt (av.0.24 ng m-3) and 1-NPyr (av. 0.16 ng m-3) presented the highest concentrations among the nitro-PAHs and 9,10-AQ (av. 0.23 ng m-3) and 7,12-BaAQ (av. 0.30 ng m-3) were the most abundant oxy-PAHs. Despite the low concentrations, these compounds represents a major concern to human health risk due to its direct mutagenic effect (Galvão M. F. de O. 2018).

References

World Health Organization. (2020) "WHO Director-General’s opening remarks at the media briefing on COVID-19-11 March 2020."

Pereira, G. M. et al. (2017) ‘Particulate pollutants in the Brazilian city of Saõ Paulo: 1-year investigation for the chemical composition and source apportionment’, Atmospheric Chemistry and Physics, 17(19), pp. 11943–11969. doi: 10.5194/acp-17-11943-2017.

Galvão, M. F. de O. (2018) ‘Biomass burning particles in the Brazilian Amazon region: Mutagenic effects of nitro and oxy-PAHs and assessment of health risks’, Environmental Pollution, 233, pp. 960–970. doi: https://doi.org/10.1016/j.envpol.2017.09.068.

Contribution of Atmospheric Nitroaromatic Compounds to Light Absorption of Water-Soluble Brown Carbon and its Potential Aqueous-Phase Formation

I. Grgić[1]*, K. Vidović[1] and S. Frka[2]

[1]National Institute of Chemistry, Department of Analytical Chemistry, Hajdrihova 19, 1000, Ljubljana, Slovenia
[2]Ruđer Bošković Institute, Division for Marine and Environmental Research, Bijenička Cesta 54, 10000, Zagreb, Croatia

irena.grgic@ki.s

Brown carbon (BrC) as a major component of organic aerosol (OA), strongly absorbs solar radiation over a broad range of wavelengths, affecting the Earth's radiation balance, atmospheric chemistry, and air quality (Laskin et al., 2015). Nitroaromatics (NACs) are a group of aromatic compounds that strongly absorb light in the near-ultraviolet (300-400 nm) and visible range (400-550 nm), making them representative of BrC. They were often determined in atmospheric particulate matter (PM), with higher concentrations typically observed during winter months. These elevated levels are largely attributed to biomass burning (BB) emissions. Although NACs typically make up less than 3% of aerosol mass, they can have a significant impact on the light absorption properties of aerosols (Frka et al., 2022). Recent research has demonstrated that certain NACs, such as nitrophenols (NPs), nitrocatechol (NC), and methylnitrocatechols (MNCs) can be produced via gas-phase (photo)chemical reactions in the atmosphere. However, secondary formation through aqueous-phase reactions may also contribute to the overall abundance of these compounds (Vidović et al., 2020).

We investigated size-segregated NACs in ambient aerosols from the urban background environment in Ljubljana, Slovenia. The research focused on the optical properties of NACs and their contribution to water-soluble BrC. Of the 20 identified NACs present in $PM_{15.6}$, more than 74% of their contribution was to submicron aerosol fraction. It was observed that the contribution of NACs to the light absorption of aqueous extracts was up to 10-times higher than their mass contributions to water-soluble organic carbon (WSOC). These results confirm that the identified NACs are strong chromophores, contributing significantly to the overall light absorption properties of water-soluble BrC.

In addition, an example of aqueous-phase transformation of 3-methylcatechol (3MC), as important precursor to MNC will be shown. The influence of different reaction conditions on BrC formation/decomposition under atmospheric sunlight conditions was quantified by a mass absorption coefficient (MAC in $m^2\ g^{-1}$), using to describe the evolution of BrC during the solution aging. Our findings showed that the aqueous-phase processing of 3MC in the presence of HNO_2/NO_2^-, both under the sunlight and in the dark, might significantly contribute to secondary organic aerosol light absorption.

References

Laskin, A. et al. (2015) Chemistry of atmospheric brown carbon. Chem. Rev. 115, 4335–4382.

Frka, S. et al. (2022) Seasonal variability of nitroaromatic compounds in ambient aerosols: Mass size distribution, possible sources and contribution to water-soluble brown carbon light absorption. Chemosphere 299, 134381, https://doi.org/10.1016/j.chemosphere.

Vidović, K. et al. (2020) Aqueous-phase brown carbon formation from aromatic precursors under sunlight conditions. Atmosphere 11, 131; doi: 10.3390/atmos11020131.

Vertical Distribution of Organic Aerosols Under Temperature Inversions: Measurement by Using Tethered Balloons

C. Jaén[1]*, I. Díez[1], B. L. van Drooge[1], E. Marco[1], J. O. Grimalt[1], P. Fernández[1]

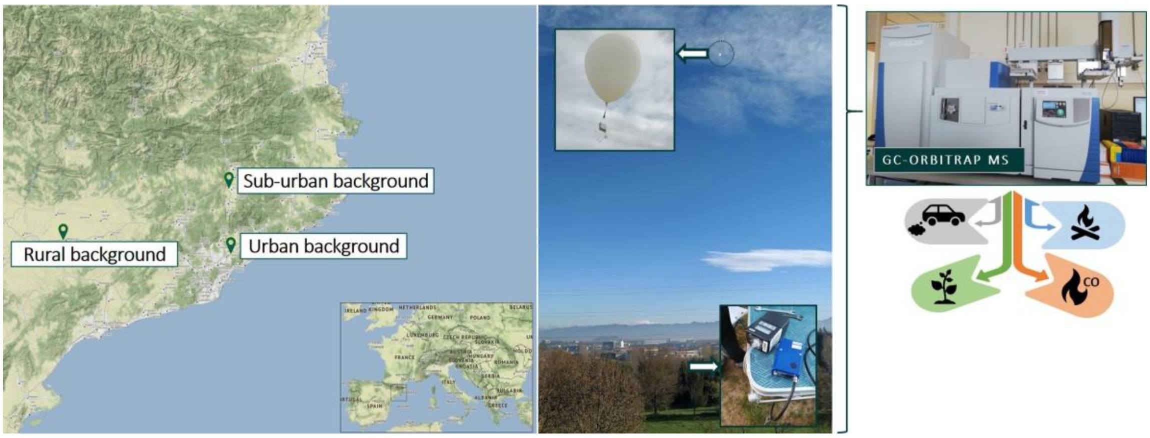
[1]Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, 08034, Catalonia, Spain

clara.jaen@idaea.csic.es

Atmospheric conditions are a key factor in the evolution and intensity of air pollution episodes. Stagnant conditions and thermal inversions are often related to these episodes, as they restrict the diffusion of pollutants and cause their accumulation in the lower layers of the atmosphere. In addition, photooxidation in the upper layers of the air generates qualitative and quantitative changes of aerosols with formation of secondary organic aerosols (SOA), in which still unknown processes are involved. The present study aims to analyze the vertical distribution of particle-bound organic compounds and Black Carbon (BC) under temperature inversions and standard ambient lapse rates.

Tethered balloons were used to locate air filtration pumps above the temperature inversions in diverse environments such as urban, sub-urban and rural background sites. Ground level samples were analyzed in parallel. In addition, sampling was also carried out at two heights in the city of Barcelona.

The analysis of particle-bound organic molecular compounds in the low volume samples (<1 m^3) was performed with a high-resolution Q Exactive GC Orbitrap MS including, anhydrosaccharides, hopanes, phthalates, SOA compounds and polycyclic aromatic hydrocarbons (PAHs) and their oxy and nitro derivatives. The results allow us to describe what are the population exposure increments under these temperature inversion conditions, specifically those related to exposure to primary sources. It has also been observed that the SOA products mix in the atmosphere and can be accumulated in the noctural residual layer.



PM and BC sampling methodology by using tethered balloons.

References

Jaén, C. et al. (2021) Source apportionment and toxicity of PM in urban, sub-urban, and rural air quality network stations in Catalonia, Atmosphere, 12 (6), p 744. https://doi.org/10.3390/atmos12060744.

Van Drooge, B.L. et al. (2023). Determination of subpicogram levels of airborne polycyclic aromatic hydrocarbons for personal exposure monitoring assessment. Journal of Environmental Monitoring and Assessment, 195:368, https://doi.org/10.1007/s10661-023-10953-z.

Unique Environmental Conditions at Dragon Eye Marine Lake (Croatia) Promoting New Particle Formation

K. Vidovic[1,2]*, Irena Grgić[1], S. Hočevar[1], A. Gregorič[3 4], Balint Alfoldy[3], Irena Ciglenečki-Jusic[2]

[1]National Institute of Chemistry, Department of Analytical Chemistry, Hajdrihova 19, 1000, Ljubljana, Slovenia
[2]Ruđer Bošković Institute, Division for Marine and Environmental Research, Laboratory for physical chemistry of aquatic systems, Bijenička Cesta 54, 10000, Zagreb, Croatia
[3]Aerosol d.o.o., Kamniška ulica 39a, 1000, Ljubljana, Slovenia
[4]University of Nova Gorica, Center for Atmospheric Research,Glavni trg 8, 5271, Vipava, Slovenia

kristijan.vidovic@ki.si

Atmospheric new particle formation (NPF) is a dominant contributor to the abundance of atmospheric particles on a global scale. As they increase in size, these particles are capable of acting as cloud condensation nuclei (CCN) (Kulmala et al., 2004). The climatic significance of newly-formed particles depends on their rate of growth and removal via different processes. Particles smaller than 20 nm are particularly noteworthy, as they are more susceptible to being scavenged by larger pre-existing particles through coagulation. The growth of newly-formed particles has been observed across diverse environments worldwide, including urban, rural, remote, coastal, arctic, and Antarctic regions (Kerminen et a., 2018).

Marine and coastal NPF events are particularly interesting due to their significant role in regulating the global aerosol number population through secondary gas-to-particle conversion processes. However, the extent of this phenomenon remains poorly understood (O'Down et al., 2002). The purpose of this study is to characterize, classify, and identify the main components of NPF events at the Dragon Eye lake area in Rogoznica, Croatia using a combination of online (SMPS and Aethalometer) and offline (Berner impactor and $PM_{2.5}$ sampler) instruments. While the results indicate a higher frequency of NPF occurrence (70%), we have also observed different types of events, including regional, local, tail events, and pollution-related NPF events.The relatively low particle number concentration (<2000 #/cm³) suggests that coagulation is not significant. It is worth noting that the 99% calculated overall growth rate specifically refers to the condensation growth rate, indicating that condensation is the primary mechanism driving particle growth. Nevertheless, it should be acknowledged that surface-active substances (SAS) might play a significant role in particle growth. Additionally, the results suggest that this group of compounds is responsible for the shrinkage process.

References

Kulmala, M., et al. (2004) Formation and growth rates of ultrafine atmospheric particles: a review of observations. J. Aerosol Sci. 35, 143-176.

Kerminen, V.-M., et al. (2018) Atmospheric new particle formation and growth: review of field observations. Environ. Res. Lett. 13, 103003.

O'Down, C. D., et al. (2002) A dedicated study of New Particle Formation and Fate in the Coastal Environment (PARFORCE): Overview of objectives and achievements. J. Geophys. Res.: Atmos. 107.D19: PAR 1-1-PAR 1-16.

Fast and Cost Efficient Analysis of Organic Molecular Tracer Compounds in PM for Source Apportionment Studies

B. L. van Drooge[1]*, C. Jaén1, R.M. Prats[1]

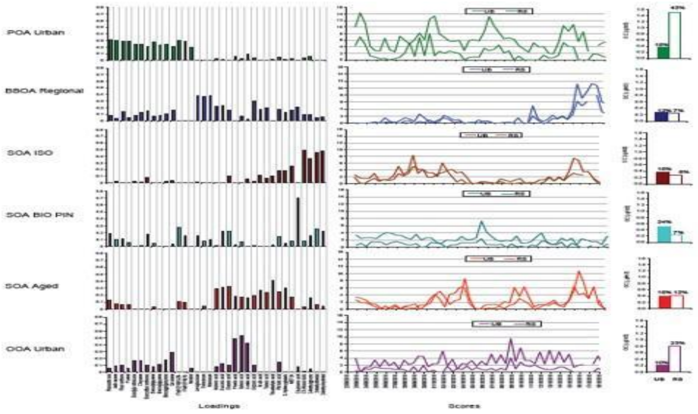
[1]Institute of Environmental Assessment and Water Research - Spanish National Research Council (IDAEA-CSIC)

barend.vandrooge@idaea.csic.es

The Geosciences & Pollution Group of IDAEA-CSIC developed a fast and cost-efficient methodology to analyze organic molecular tracer compounds in atmospheric particulate matter collected on quartz filter after high- or low-volume sampling in indoor- or outdoor environments. The method allows the processing of 20 samples/h, and another hour per sample to analyze by GC-MS 30 tracer compounds that are related to air pollution and major emission sources, such as biomass burning, plastics, personal care products, food cooking, soil dust, traffic, and secondary organic aerosol formation processes. These compounds can be used independently for source apportionment analysis, or by analyzed in combination with data from air quality, meteorology, or toxicity.

Overall, the developed methodology provides fast acquisition of data; saving time and consumables in the analysis respect to conventional methods, which is very relevant for long term air pollution monitoring. Moreover, only a very small fraction of the whole filter sample (<1 m^3 eq.sample volume) is used for analysis, which offers the possibility of further analyses in these filters, such as toxicity tests.

We present examples from several studies in indoor environments, such as school classroom, living rooms and subway-platforms, and outdoor environments, such as rural, background and urban traffic sites.



Chemical profiles (left) and scores (right) of organic aerosol in urban background and traffic sites in Barcelona.

References

B.L. van Drooge, et al. (2023). Determination of subpicogram levels of airborne polycyclic aromatic hydrocarbons for personal exposure monitoring assessment. Journal of Environmental Monitoring and Assessment, 195:368, https://doi.org/10.1007/s10661-023-10953-z

C. Jaén et al. (2021). Source apportionment and toxicity of PM in urban, sub-urban, and rural air quality network stations in Catalonia. Atmosphere 2021, 12, 744. https://doi.org/10.3390/atmos12060744 ge.

Antibiotic Resistance Genes and Air Pollution in a Primary School in Barcelona

B. L. van Drooge[1*], Jessica Subirats[1]

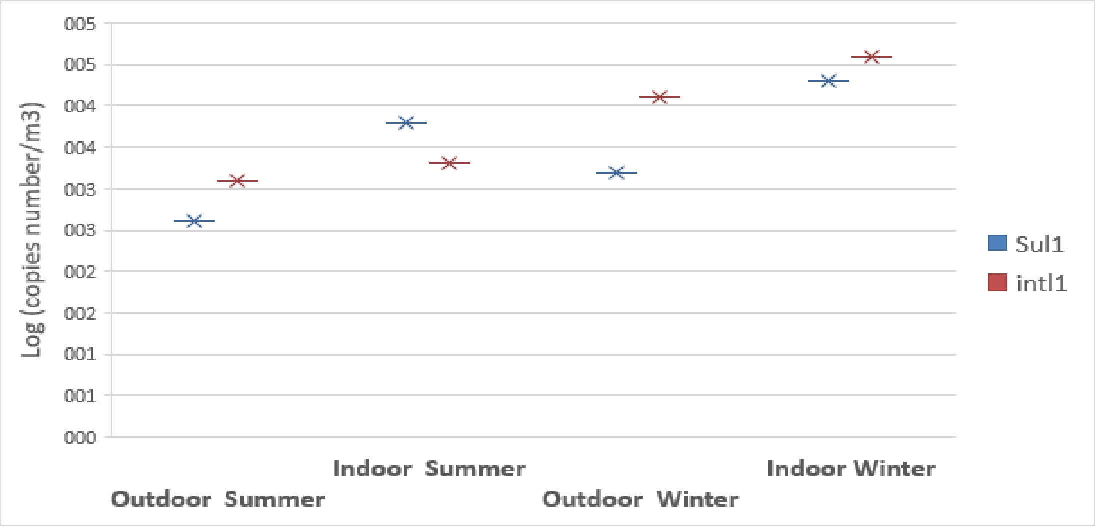
[1.]Institute of Environmental Assessment and Water Research - Spanish National Research Council (IDAEA-CSIC)

barend.vandrooge@idaea.csic.es

Antibiotic resistance and Air Pollution are two of the biggest public health challenges of our time. Recently, there has been increasing concern regarding airborne antibiotic resistance genes (ARGs), particularly from a "One health perspective". ARGs are carried by antibiotic-resistant bacteria (ARBs) that can be absorbed into aerosol particles and pose a risk to human health when inhaled, especially if the genes are carried by pathogenic bacteria. To assess human exposure and health risks posed by airborne ARGs it is essential to understand the factors that impact the occurrence, diversity, and dispersal of airborne ARGs. Here we focus on indoor air in a primary school compared to outdoor air in Barcelona. Aerosol samples (PM10) were collected by hivol-sampling in four spaces in the school and an outdoor urban background site in summer and winter.

The study of the bacterial communities and the profile of ARGs was carried out using a metagenomic analysis (shotgun metagenomic sequencing) and quantification of target ARGs by real-time PCR (qPCR). Organic tracer compounds were analyzed by GC-MS.

The abundance of twelve selected gene targets associated with antibiotic resistance (qnrS, mecA, tetM, tetW, blaTEM, blaCTXm, blaOXA, blaKPC, sul1 , sul2, ermB and ermF) or horizontal gene transfer (intI1) was quantified by Real time PCR (quantitative qPCR). Only sul1 and intl1 were detected in both the outdoor and indoor environments during the winter and summer seasons, with higher abundance in indoor environment in winter related to air pollution.



ARGs sul1 and intl1 were detected in both the outdoor and indoor environments

References

W. Gwenzi et al. (2022). The air-borne antibiotic resistome: Occurrence, health risks, and future directions. the Science of the Total Environment, 804, 150154. https://doi.org/10.1016/j.scitotenv.2021.150154.

Re-Emissions of Nitrated and Oxygenated PAHs From Land and Sea Surfaces in Source and Receptor Areas

J.K. Mwangi[1], B.A.M. Bandowe[2], P. Bohlin Nizzetto[3], C. Degrendele[1,4], A.K. Halse[3], M. Iakovides[5], P. Kukučka[1], M. Kyprianou[5], J. Martiník[1], B. Palátová Nežiková[1], P. Přibylová[1], R. Prokeš[1], M. Sáňka[1], J. Sobotka[1], M. Tannous[1], J. Vinkler[1], M. Wietzoreck[2], H. Harder[6], J. Lelieveld[5,6], U. Pöschl[2], E.G. Stephanou[5,7], M. Tsapakis[8], B. Vrana[1], G. Lammel[1,2*]

[1]Masaryk University, Faculty of Science, RECETOX, Kamenice 5, 62500 Brno, Czech Republic
[2]Max Planck Institute for Chemistry, Multiphase Chemistry Dept., Hahn-Meitner-Weg 1, 55128 Mainz, Germany
[3]Norwegian Institute for Air Research, POB 100, 2027 Kjeller, Norway
[4]Aix-Marseille University, Laboratory of Chemistry and Environment, CNRS, 3 Pl. Victor Hugo, 13003 Marseille, France
[5]Cyprus Institute, Climate and Atmosphere Research Centre, 2121 Nicosia, Cyprus
[6]Max Planck Institute for Chemistry, Air Chemistry Dept., Hahn-Meitner-Weg 1, 55128 Mainz, Germany
[7]University of Crete, Dept. of Chemistry, 70013 Heraklion, Greece
[8]Hellenic Centre for Marine Research, Institute of Oceanography, POB 2214, 71003 Gournes-Pediados, Greece

gerhard.lammel@recetox.muni.cz

Most nitrated and oxygenated polycyclic aromatic hydrocarbons (NPAHs, OPAHs) are semivolatile compounds with toxic and ecotoxic properties. They are co-emitted with PAHs from fossil fuel and biomass combustion processes or formed in photochemical and microbiological reactions of PAHs in air and soil. However, little is known about their atmospheric lifetimes and environmental fate. As semivolatiles resisting biodegradation in soils and surface waters, their long-range transport potential could be enhanced by multihopping, as observed for PAHs (grasshopper effect; Mulder et al., 2014).

We determined the concentration of 10 OPAHs and 17 NPAHs along with parent PAHs during summer in air and soils at a rural and near-coastal north European site (Birkenes, southern Norway), a central European rural background site (Košetice, Czech Republic), and in air and surface seawater at two off-shore sites in the Aegean Sea and along transects across the Mediterranean Sea. We also analysed recent monitoring data from 3 summers at Košetice (Nežiková et al., 2021; Wietzoreck et al., 2022). Directions of diffusive air-soil and air-sea exchanges were derived from the fugacities.

In the source area (central Europe), the diffusive vertical fluxes of 2-nitronaphthalene and a number of 3-4 ring OPAHs were upward and the carcinogen 1-nitropyrene was found close to phase equilibrium. In the receptor area (northern Europe), two 3-4 ring OPAHs, dibenzofuran and 6H-benzo(c)chromen-6-one, were found to volatilise, and 2-nitrofluoranthene close to phase equilibrium. In the Mediterranean Sea, 2-nitronaphthalene and few 3-4 ring OPAHs were found to volatilise from the sea surface or being close to equilibrium. These findings suggest that land and sea areas even far from the primary sources may indeed act as secondary sources for NPAHs and OPAHs in the atmosphere and enable global transport by multihopping.

References

Mulder, M.D. *et al.* (2014) ‚Air-sea exchange and gas-particle partitioning of polycyclic aromatic hydrocarbons in the Mediterranean' *Atmos. Chem. Phys.*, 14, p. 8905. doi.org/10.5194/acp-14-8905-2014

Nežiková, B. et al. (2021) 'Three years of atmospheric concentrations of nitrated and oxygenated polycyclic aromatic hydrocarbons and oxygen heterocycles at a central European background site' *Chemosphere,* 269, 128738. doi.org/10.1016/j.chemosphere.2020.128738

Wietzoreck, M. et al. (2022) 'Nitro- and oxy-PAHs in grassland soils from decade-long sampling in central Europe' *Environ. Geochem. Health,* 44, p. 2743. doi.org/10.1007/s10653-021-01066-y.

Quaternary Ammoniums Compounds in Indoor Environment: Links Between Biocidal Uses and Contamination

P. Martinache[1]*, R. Moilleron[1], A. Bressy[1]

[1]Univ Paris Est Creteil, Ecole des Ponts, LEESU, Marne-la-Vallée, France

pierre.martinache@enpc.fr

Quaternary ammoniums compounds (QACs) are broadly used in our daily life in PPCPs, household products or buildings materials. QACs are known to have impacts on health and environment: asthma, antibiotic resistance, and genotoxic effects on aquatic organisms at low concentrations (Mohapatra et al., 2023). It is therefore important to assess both the health and environmental risks linked to QACs released from indoor practices. Our objectives were to fill the gap about QAC contamination of indoor environment based on a dual approach coupling study of consumption practices and monitoring campaigns. Institutional database concerning QAC sales in France was questioned. Formulation of products from supermarkets and DIY stores were studied (n=3490). Sociological survey about practices and risk perception were conducted among the population (n=200). Five QACs were quantified in indoor settled dust from 19 Parisian dwellings and greywaters from a collective catering building (n=8). In France between 2019 and 2020, QAC consumption has increased by 100% due to the Covid-19 pandemic (Fig. 1). QACs appear to be ubiquitous in indoor environment with a quantification frequency above 75% for all the compounds and matrices, except for C18 in dust. Contents in dust vary from 410 to 25,000 ng/g.dw (median) and reach for C16 more than 73,000 ng/g.dw (Fig. 1). In greywaters, concentrations vary from 36 to 74,000 ng/L. The somehow high QAC levels in samples are explained by the results of consumption surveys and open the door to source reduction to limit the sanitary and environmental risks.

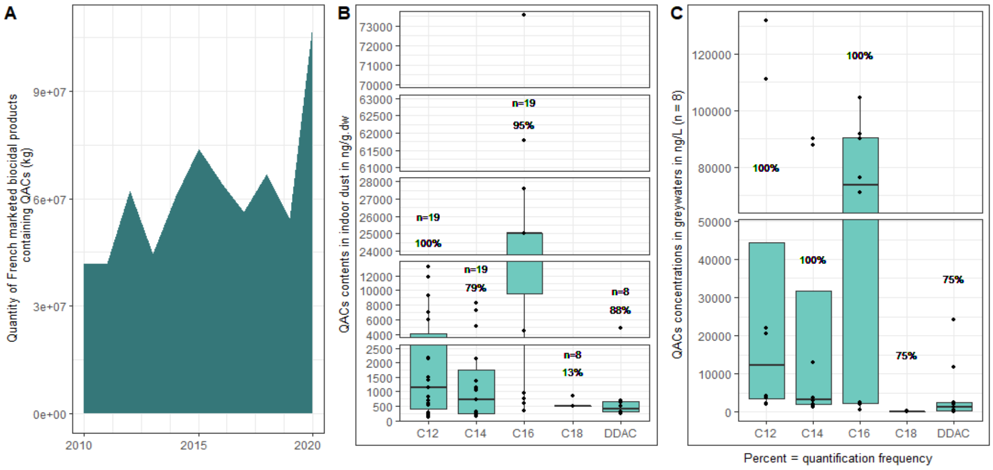


Fig. 1: (A) Evolution of QAC consumption in France according to Simmbad (B) QAC contents in domestic dust (C) QAC concentrations in greywaters

References

Mohapatra, S. et al. (2023) ‘Quaternary ammonium compounds of emerging concern: Classification, occurrence, fate, toxicity and antimicrobial resistance’, Journal of Hazardous Materials, 445, p. 130393. Available at: https://doi.org/10.1016/j.jhazmat.2022.130393.

Physico-Chemical Characterization of Ultrafine Particles Emitted by Different Transport Modes at Different European Cities

S. Ridolfo[1]*, F. Teoldi[2], C. Colombi[3], G. Lanzani[3], A. Karanasiou[1], X. Querol[1], A. Alastuey[1], N. Perez[1], U. Olofsson[4], M. Tu[4], E. Bergseth[4], M. Norman[5], J. Cortes[6], I. Hernandez[7], and F. Amato[1]

[1]Institute of Environmental Assessment and Water Research, CSIC, Barcelona, 08034, Spain
[2]Mario Negri Institute for Pharmacological Research, Milan, 20156, Italy
[3]Arpa Lombardia, Milan, 20124, Italy
[4]KTH, Stockholm, 10044, Sweden.
[5]SLB-analys, Stockholm, 10420, Sweden.
[6]Port of Barcelona, Barcelona, 08039, Spain.
[7]Governement of Catalonia, Barcelona, 08036, Spain.

sharon.ridolfo@idaea.csic.es

The nPETS (Nanoparticle Emissions from The Transport Sector: https://www.npets-project.eu/) is a H2020 project, that aims to monitor and sample the ultrafine particles (UFP, diameter<100 nm) emitted from different transport modes, in four European cities (Barcelona, Stockholm, Milan and Thessaloniki). Within nPETS, field studies take place at 4 urban background, 4 road traffic, 3 airports, 2 harbours and 2 railway sites, during two seasons of 4 weeks duration each. The deployed instrumentation includes ELPI+ and DGIs impactors for particle number size distribution (PNSD) and sampling, often coupled to CPC/SMPS/FMPS/EEPS, high volume PM_1 and PM_{10} samplers, aethalometers, and gaseous pollutant analysers. Sampled filters undergo inorganic and organic chemical speciation (by means of ICP-AES, ICP-MS and GC-MS), animal and human toxicology tests, as well as microscopic (SEM and TEM) analysis. For each monitoring site, a distinction between freshly emitted and secondary particles is performed following the method proposed by Rodríguez and Cuevas (2007). In addition, PMF multivariate analysis method (Rivas et al., 2020) is performed for source apportionment using PNSD data > 2.5 nm. Results reveal that particle number concentrations (PNC) reached highest values at the Stockholm road tunnel (87’500 pp/cc in cold season and 47’000 pp/cc in warm season), about 4 times higher than the outdoor road sites in Barcelona and Milan and up to one order of magnitude higher than the urban background and subway rail environments. Urban background sites showed mean PNC between 4’000 and 16’000 particles/cc, with the urban background site in Barcelona being more polluted due to the higher photo nucleation processes. UFP contribute very little to the overall PM mass and no correlation is found between PN (pp/cc) and UFP mass ($\mu g/m^3$). In the urban background sites unimodal PNSDs are observed. In Barcelona, due to photo-nucleation, the PNSD peaks at 3 nm (in warm season) to 14 nm (in cold season). For Stockholm urban background the peak is observed between 47-58 nm in summer, in the Aitken mode, while in Milan the PNSD shows the peak at around 250 nm, in the accumulation mode, revealing the higher aging of secondary particles. All traffic sites show the peak of PNSD between 6-13 nm, indicating the high prevalence of nucleation particles, both primary and secondary from traffic-related gaseous precursors. Interestingly, it was observed that the size distribution does not change significantly between the road tunnel and the underground tunnel, although absolute concentrations are much higher in the road tunnel. This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 954377.

References

Rodríguez, S. and Cuevas, E. (2007) 'The contributions of “minimum primary emissions” and “new particle formation enhancements” to the particle number concentration in urban air', Journal of Aerosol Science, Volume 38, Issue 12, p. 1207-1219. doi: https://doi.org/10.1016/j.jaerosci.2007.09.001.

Rivas, I. et al. (2020) 'Source apportionment of particle number size distribution in urban background and traffic stations in four European cities', Environment International, Volume 135, 105345. doi: https://doi.org/10.1016/j.envint.2019.105345.

Aerosol Characterization in a Central-West Site of Brazil: Influence of Farming Activities and Toxicity

P. C. Vasconcellos[1]*, Y. J. Parra[1], G. M. Pereira[1,2] and C. Alves[3]

[1] Universidade de São Paulo, Departamento de Química Fundamental, Instituto de Química, 05508-000, São Paulo, Brazil.
[2]Departamento de Ciências Atmosféricas, Instituto de Astronomia, Geofísica e Ciências Atmosféricas, Universidade de São Paulo, 05508-090, São Paulo, Brazil.
[3]University of Aveiro, Department of Environment and Planning, Centre for Environmental and Marine Studies (CESAM), 3810-193, Aveiro, Portugal.

perola@iq.usp.br

The central region of Brazil presents important and large ecosystems. Different anthropogenic activities such as biomass burning, land use, and vehicular emissions release hundreds of compounds into the atmosphere that can reach large urban sites. This research aimed to study the seasonal variations of the PM10 concentration (2008-2014) in Cuiabá (Brazil), investigate the chemical composition, toxicity, and evaluate the contribution of the different emission sources.

One hundred fifty samples were collected (110 dry season and 40 rainy season) using quartz fiber filters and a high-volume sampler. Organic and elemental carbon (OC, EC) were quantified by thermo-optical analysis. The concentrations of water-soluble ions (WSI) were obtained using an ion chromatograph after ultrasonic agitation extraction. Different organic compounds (n-alkanes, polycyclic aromatic hydrocarbons (PAH), and their derivatives (nitro and oxy-PAH)) were determined too. The n-alkanes concentrations were determined by GC-FID, while the PAH and derivatives were quantified by GC-MS. Emission sources and toxicity were determined using species ratios, correlations, the Positive Matrix Factorization (PMF) receptor model, and Rstudio software.

High concentrations of PM10 were found throughout the period (70 µg m-3), being higher in the dry season, where 87% of the samples exceeded the value recommended by the WHO (WHO, 2021). The WSI presented a greater contribution to the mass of PM10 in the dry season (19%) compared to the wet season (10%). Na+, SO42-, NO3-, Ca2+, and K+ were the most abundant species and are associated with soil resuspension sources and biomass burning (Pereira et Al, 2017). The concentration of OC and EC was higher during the less rainy period. The OC/EC ratio was similar in both periods (2.7) and these values are attributed to the contributions of secondary aerosols and biomass burning (Pereira et Al, 2017). High concentrations of aliphatic compounds emitted mainly by vegetable wax (C27, C29, C31 and C33) and other n-alkanes (C20-C26) associated with vehicle exhaust gases were found. BkF was the PAH with the highest concentration, representing 16 and 19% (wet and dry season), followed by BeP, InP, BbF and DahA, showing a predominance of pyrogenic sources (fuel and biomass combustion) (Pereira et Al, 2017) 4-Npyr (carcinogenic) and 2-MAQ (suspected carcinogenic to humans) presented the highest concentrations, both with a detection frequency greater than 90%. The calculated values for the benzo(a)pyrene equivalent carcinogenic, mutagenic, and estimated lifetime risk of cancer (ILCR) were higher than those recommended by the US EPA (EPA, 2011). In children, adolescents, and adults, the ILCR results calculated with contribution to dermic exposure were higher compared to ingestion and inhalation exposure. The main source of emission was the burning of biomass and soil resuspension, they showed a mixture of loads of different species such as OC, EC, Na+, K+, Ca2+, Cl-, SO42- and NO3- and increased with northwesterly winds. Another important contribution was made by vehicles (light and heavy), with emissions of Flt, Chry, BeP, BaP, Cor and BbF, which increased with the southerly winds.

References

WHO, 2021. WHO global air quality guidelines. Coast. Estuar. Process. 1–360.

Pereira, G. M. et al. (2017) 'Particulate pollutants in the Brazilian city of Saõ Paulo: 1-year investigation for the chemical composition and source apportionment', Atmospheric Chemistry and Physics, 17(19), pp. 11943–11969. doi: 10.5194/acp-17-11943-2017.

EPA, 2011. Exposure Factors Handbook: 2011 Edition. U.S. Environ. Prot. Agency EPA/600/R-, 1–1466. https://doi.org/EPA/600/R-090/052F.

Spatial and Temporal Variation of Particulate Matter at Micro Level in Different Types of Urban Hotspots in an Indian Metropolis.

D. Madayil[1]*, S. M. Shiva Nagendraa[1]

[1]Indian Institute of Technology (IIT), Department of Civil Engineering, Madras, Chennai, India-600036

madayildiya@gmail.com

Air pollution hotspots are areas where pollution concentrations are several times greater than acceptable ambient air quality levels and cause significant health risks. In this study, mobile monitoring of particulate matter (PM10, PM2.5, and PM1) was conducted at four different types of hotspots (construction sites, traffic junctions, restaurants, and commercial corridors) and one residential site (as background site) during January –February 2021. The monitoring was carried out for three days at each location covering morning, afternoon, and evening traffic flows. A GPS logger with a time resolution of 6 sec was synchronized with the PM instrument during the campaign. The PM10 concentrations were observed to be50±12, 155±47.5, 250±75, 120±32, and 312±115 µg/m3 at residential, construction, traffic, restaurant, and commercial sites, respectively. In comparison to a traffic site, the mean PM10 concentrations at commercial locations were 2.6 times greater. In all of the monitoring locations, a considerable drop in PM10 concentrations was noted spatially. At 100 meters away from the restaurant, traffic junction, and construction sites, the reduction of PM10 was observed to be 25, 40, and 52%, respectively. Further, at 500 meters away from these sites, a substantial reduction of 50, 60, and 61% was seen. However, as we move away from a residential neighborhood, the PM10 concentrations were initially shown to be modestly reducing, and then gradually rising due to the influence of other sources. Furthermore, the temporal variation of PM indicated that concentrations were more than twice the morning/evening (peak) hours than afternoon (non-peak) hours. The higher PM2.5/PM10 ratios at residential (average), restaurant (average), and traffic (average) sites in comparison to construction (average) and commercial (average) sites indicate the influence of combustion-generated particles. The constant exposure to such finer particle fractions would cause negative health consequences, especially to employees on-site.

References

Prachi Goyal, Sunil Gulia, S.K. Goyal, Identification of air pollution hotspots in urban areas - An innovative approach using monitored concentrations data, Science of The Total Environment, Volume 798, 2021, 149143, ISSN 0048-9697, https://doi.org/10.1016/j.scitotenv.2021.149143 .

Jyothi S. Menon & S.M. Shiva Nagendra (2018) Personal exposure to fine particulate matter concentrations in central business district of a tropical coastal city, Journal of the Air & Waste Management Association, 68:5, 415-429, https://doi.org/10.1080/10962247.2017.1407837

New Approach Methodologies and Chemometrics to Study the Effects of Airborne Pollution on Lung Health: Application to Air Samples from Suburban and Rural Backgrounds

A. Pavlidou[1], M. Pyambri[1], C. Jaén[1], B. L. van Drooge[1] and C. Bedia[1]*

[1]Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Department of Environmental Chemistry.
Jordi Girona 18-26, 08034 Barcelona, Spain

carmen.bedia@idaea.csic.es

Airborne particulate matter (PM) pollution has raised great concern since its exposure has been associated with adverse respiratory outcomes, such as exacerbations of asthma and chronic obstructive pulmonary disease, pulmonary fibrosis and lung cancer (Jaen et Al., 2021). However, the causality between specific chemical exposures and their effects on lungs health and their mechanism of action remain mostly unknown.

To avoid the use of animals, a variety of approaches called New Approach Methodologies (NAMs) have been developed and progressively introduced to improve understanding of toxic effects of chemicals. In this work, we propose the use of NAMs, i.e. 3D cell cultures, high throughput screening (HTS) methods (viability assays, ELISA), metabolomics and lipidomics to assess the biological effects of chemical extracts from environmental air samples. In addition, we apply chemometrics to find relationships between the chemical composition data of air samples and the biological effects on cell cultures.

In this work, filter samples collected from July to December 2019 from two air quality monitoring stations of Catalonia, i.e., Manlleu and Bellver de Cerdanya, which are representative sites of sub-urban and a rural background pollution, respectively, were employed. The air toxicity of non-urban backgrounds is often disregarded, but previous reports indicate that air pollutants from these sites can elicit damage to cells (Jaen et Al., 2021).

Cell spheroids of the lung cancer cell line A549 were exposed to air filter extracts for 72h, and cell viability, the induction of reactive oxygen species (ROS), and release of interleukin 8 (IL-8) were assessed using HTS methods. In addition, the ability of air sample extracts to induce epithelial to mesenchymal transition (EMT), a process associated to the acquisition of a malignant phenotype (Yang et Al. 2020), was evaluated using a fluorimetric HTS assay. Extracts of exposed cells were analysed through metabolomics and lipidomics workflows and the chemometric analysis revealed that almost all the samples induced significant changes on the metabolite and lipid profiles, and that these were more accentuated in October and November than in summer samples. To perform a joint analysis, data fusion of chemical composition of filters, and all the biological data obtained from both phenotypic assays and omics analyses was carried out. Fused data was further analysed using multivariate curve resolution (MCR) (Tauler et Al., 1995) to reveal the relationship between specific compounds or sources of pollution and changes in lung cells phenotype. For instance, some biomolecular pathways related to cell death induction were associated to chemical features characteristic of biomass burning. Overall, the combined use of physiologically relevant cell cultures, HTS methods, lipidomics and metabolomics, and chemometrics methods has enabled a better understanding of the biological impact of air pollution in sub-urban and rural areas and has been useful to point out the potential toxicity of some compounds present in these disregarded air pollution backgrounds.

References

Jaén, C. et al. (2021) Source Apportionment and Toxicity of PM in Urban,Sub-Urban, and Rural Air Quality Network Stations in Catalonia. Atmosphere, 12(6), 744; https://doi.org/10.3390/atmos12060744

Yang, J., et al. (2020) Guidelines and definitions for research on epithelial–mesenchymal transition. Nat Rev Mol Cell Biol 21, p. 341. https://doi.org/10.1038/s41580-020-0237-9

Tauler, R. (1995) Multivariate curve resolution applied to second order data, Chemom. Intell. Lab. Syst. 30, p.133. https://doi.org/10.1016/0169-7439(95)00047-X.

The Investigation of Biomass Burning Events in the Arctic Using Optical and Chemical Measurements

S. Pulimeno[1], F. Bruschi[2], M. Feltracco[1], S. Gilardoni[3], M. Mazzola[3], S. Crocchianti[2], D. Cappelletti[2,3], C. Barbante[3,1], A. Gambaro[1,3] E. Barbaro[3,1]*

[1]Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino, 155 - 30172 Venice Mestre (VE), Italy
[2]Università degli Studi di Perugia, Dipartimento di Chimica, Biologia e Biotecnologie, Via Elce Di Sotto 8, 06123 Perugia, Italy
[3]National Research Council (CNR-ISP), Institute of Polar Sciences, Via Torino, 155 - 30172 Venice Mestre (VE), Italy

elena.barbaro@cnr.it

Biomass burning aerosols influence the climate system by affecting the Earth's solar balance, acting as cloud condensation nuclei, and influencing snow albedo. Biomass burning is the most important source of black carbon and one of the main sources of organic aerosols, whose deposition on the Arctic snow can decrease the albedo and diminish the Arctic sea ice extent (Keywood et al., 2013). However, biomass burning aerosols' transport, evolution, and sinks are poorly understood. In recent years, the pan-Arctic region has experienced an increasing frequency of extreme fire events (Stohl et l., 2006).

Summer 2019 is remembered as one of the most intense biomass burning seasons on record. Based on the aerosol observations recorded at the Gruvebadet laboratory in Ny Alesund (Svalbard), we propose to identify the most intense burning events during the second half of 2019, from mid-June to the end of December, overlaying the obtained data with those from the MOSAiC Expedition.

Our proposed approach combines the atmospheric aerosols' optical parameters (e.g., scattering and absorption coefficients, single scattering albedo, and Ångström absorption exponent) with the chemical analysis of aerosol samples collected at the atmospheric laboratory of Gruvebadet (Ny-Ålesund, Svalbard 78°55′03″N, 11°53′39″E, 50 m a.s.l.). Moreover, a back-trajectories analysis has been carried out to pinpoint the area of origin of the air masses containing burning particles arriving at Svalbard.

We started with the identification of biomass burning events using aerosol optical properties. Then, each specific event is evaluated through air mass trajectory analysis to identify the areal sources. Furthermore, chemical characterization of each event is carried out using specific biomass burning tracers, such as levoglucosan, its isomers, and phenolic compounds. Finally, a source apportionment using positive matrix factorization is performed using the chemical dataset obtained from the aerosol samples. In particular, major ions, MSA, carboxylic acids, levoglucosan, arabitol and mannitol, glucose, L and D-amino acids, pinic and pinonic acids are used to identify five factors: 1) sea salts, 2) long-range components, 3) fungal spores, 4) secondary organic aerosol, 5) biomass burning. For each factor, particle size distribution and temporal trend are obtained to complete the characterization of each biomass burning event.

These results contribute to the aims of the project "Boundary layer Evolution Through Harmonization of Aerosol measurements at Ny-Ålesund research stations - BETHA-NyÅ" (PRA2021_0020)

References

Stohl, A. et al. (2006) 'Pan-Arctic enhancements of light absorbing aerosol concentrations due to North American boreal forest fires during summer 2004', Journal of Geoghysical Research, 111, D22214. doi:10.1029/2006JD007216.

Keywood, M. et al. (2013) 'Fire in the Air: Biomass Burning Impacts in a Changing Climate', Critical Reviews in Environmental Science and Technology, 43(1), pp. 40-83. doi:10.1080/10643389.2011.604248.

Hammond, M. R. et al. (2008). Identifying the source of a strong fullerene envelope arising from laser desorption mass spectrometric analysis of meteoritic insoluble organic matter. Geochim. Cosmochim. Acta 72, 5521–5529. doi: 10.1016/j.gca.2008.08.008.

Biomass Burning Traces in the Arctic Atmosphere in Winter, Fairbanks (Alaska)

R. Zangrando[1]*, E. Barbaro[1], M. Feltracco[2], F. Scoto[3], S. Decesari[3], G. Pappaccogli[3], A. Donateo[3], A. Gambaro[2]

[1]Institute of Polar Sciences, National Research Council (CNR-ISP), Via Torino, 155, 30172, Venice Mestre (VE), Italy
[2]Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino 155, 30170, Mestre (VE), Italy
[3]Institute of Atmospheric Sciences and Climate, National Research Council (CNR-ISAC),via Gobetti 101, 40129, Bologna (BO), Italy

roberta.zangrando@cnr.it

About 7 million people live in the Arctic, with 45% of them living in urban areas of at least 50000 inhabitants. This study is part of a field study carry out in the town of in Fairbanks (Alaska). Urbanization, high energy consumption for transport and domestic heating and widespread use of cheap fuels (wood, diesel) explain the rising concern about urban air pollution in the Arctic. The problem is exacerbated by the peculiar weather in these areas such as thermal inversions to occur at only 10 – 30 m above the ground, hence largely limiting the dispersion of pollutants, increasing of PM2.5 concentrations and prolonging the lifetime of pollutants in the atmosphere. At the same time, on the days with strongest surface cooling - which are the coldest ones - the emissions from domestic heating and power production increase, hence further enhancing PM levels. As a consequence, PM2.5 concentrations in Fairbanks, with a total population of 100000, exceeds the US EPA 35 ug/m³ threshold limit about 7 days per month in winter. Such levels are found in the mid-latitudes in much more densely populated areas, like the Po Valley with a population of 20 million.

Measurements of the chemical composition of PM2.5 in Fairbanks show that carbonaceous particles emitted by residential burning account for more than 60% of the mass, with smaller contributions from traffic and inorganic secondary compounds. In order to assess the impact of wood combustion on the particulate matter, biomass burning tracers including anhydrosugars and phenolic compounds have been determined.

The atmospheric aerosol samples were collected at the Fairbanks site (Alaska), in the period between 01/21/2022 and 02/17/2022, extracted and analyzed by IC-MS and HPLC – MS/MS, using the internal standard method for quantification. The anhydrous sugars levoglucosan, mannosan and galactosan which are specific indicators of the combustion of cellulose (levoglucosan) and hemicellulose (mannosan and galactosan) were determined in the aqueous extract. In the atmospheric aerosol, the most present compound was lavoglucosan with an average concentration of 70 ng/m³. Mannosan and galactosan are present at a lower concentration of 15 ng/m³ and 3 ng/m³. The observed levels are compatible with those in urban aerosols. The ratio between levoglucosan and mannosan is of 4.71 close to the range of 3.6–3.9 indicative of the combustion of conifers. Phenolic compounds (vanillin, syringic acid, p-coumaric acid, coniferyl aldehyde, vanillic acid, syringaldehyde, acetovanillone, acetosyringone), are generated by the combustion of lignin. The total mean concentration of phenols in the particulate matter is of 7 ng/m³. Vanillic compounds are indicators of predominantly of softwood burning, while syringic compounds indicate combustion of hardwood. The relative abundance between vanillic and syringic compounds indicates a percentage of 62% and 37% respectively, confirming a prevalent combustion of conifers in this area.

These results are part of the projectPRA2019-0069 “A-PAW”, “Air Pollution in the Arctic Winter (A-PAW): an Italian contribution to the ALPACA field experiment”.

Atmospheric Sink Mechanism of 4-Isobutylacetophenone, a Toxic Intermediate Product from Ibuprofen Decomposition

C. Roman[1,2], A. G. Negru[1,2], C. Amarandei[1,2], C. Arsene[1,2], I. G. Bejan[1,2], D. Vione[3*], R. I. Olariu[1,2*]

[1]"Alexandru Ioan Cuza" University of Iasi, Integrated Centre of Environmental Science Studies in the North Eastern Region (CERNESIM), 11 Carol I, 700506 Iasi, Romania
[2]"Alexandru Ioan Cuza" University of Iasi, Center with Integrated Techniques for Atmospheric Aerosol Investigation in Romania (RECENT AIR), 11 Carol I, 700506 Iasi, Romania
[3] Università degli Studi di Torino, Dipartimento di Chimica, Via Pietro Giuria 5, 10125 Torino, Italy

oromeo@uaic.ro

The atmospheric fate of 4-isobutylacetophenone was investigated under simulated tropospheric conditions using the 760 L cylindrical Environmental Simulation Chamber made of Quartz from "Alexandru Ioan Cuza" University of Iasi (ESC-Q-UAIC) facilities (Roman *et al.*, 2022). Recent studies have shown that misconduct in drug storage and disposal, in particular of ibuprofen rich pharmaceutical formulations, could lead to surface water and air pollution with a potential toxic intermediate known as 4-isobutylacetophenone (Ruggeri *et al.*, 2013). This compound is stable in surface waters and can undergo phase-transition into the gas-phase where it might react with atmospheric oxidants such as OH radicals, thus leading to the formation of secondary organic aerosols (SOA) (Arsene *et al.*, 2022).
State of the art instruments such as PTR-ToF-MS equipped with CHARON technique were used for real-time aerosol and volatile organic compounds (VOCs) monitoring during the gas-phase reaction of 4-isobutylacetophenone with OH radicals. The investigations were also being assessed by long-path FT-IR spectroscopy and Scanning Mobility Particle Sizer (SMPS) spectrometry. Current data suggest that the OH-initiated gas-phase reaction is the main atmospheric degradation pathway for this compound. The gas-phase oxidation occurs via the H-atom abstraction channel from the side carbon-chain, with acetone emerging in a molar yield of (20.80±0.61) %. IR and MS products spectra support the gas-phase formation of aromatic dicarbonylic compounds with complementary mass-to-charge ratios of those corresponding to acetone and acetaldehyde. In high NOx conditions, relevant to urban troposphere, a mass formation yield of (4.7±0.3) % for the SOA has been estimated. The gas-phase mechanism of atmospheric degradation of 4-isobutylacetophenone by OH radicals is discussed. Investigations carried out through this study, where 4-isobutylacetophenone was identified and chosen as a master-example of pharmaceuticals usage related water and air pollutant, reveal the potential environmental harmful effects of a common and heavily used nonsteroidal anti-inflammatory drug such as ibuprofen.

Acknowledgements: C.A., I.G.B., R.I.O., and D.V. acknowledge the financial support from European Union's Horizon 2020 Research and Innovation Framework Program through the EUROCHAMP-2020 Infrastructure Activity Grant (grant agreement no. 730997). C.R., A.G.N., C.A., C.A., I.G.B. and R.I.O. acknowledge the Operational Program Competitiveness 2014−2020, Axis 1, under POC/448/1/1 research infrastructure projects for public R&D institutions/sections F 2018, through the Research Center with Integrated Techniques for Atmospheric Aerosol Investigation in Romania (RECENT AIR) project, under grant agreement MySMIS no. 127324, and PN-III-P4-PCE2021-0673 (acronym ATMO-SOS) and PN-III-P2-2.1-PED2021-4119 (acronym SOA-REACTOR) UEFISCDI projects for their co-support.

References

Arsene, C. *et al.* (2022) 'Evaluation of the environmental fate of a semivolatile transformation product of ibuprofen based on a simple two-media fate model', Environ. Sci. & Technol., 56(22), p. 15650. doi:10.1021/acs.est.2c04867.

Roman, C. *et al.* (2022) 'Investigations into the gas-phase photolysis and OH radical kinetics of nitrocatechols: Implications of intramolecular interactions on their atmospheric behaviour', Atmos. Chem. Phys., 22(4), p. 2203. doi: 10.5194/acp-22-2203-2022.

Ruggeri, G. *et al.* (2013) 'Photochemical transformation of ibuprofen into harmful 4-isobutylacetophenone: Pathways, kinetics, and significance for surface waters', Water Res., 47, p. 6109. doi:10.1016/j.watres.2013.07.031

Tracking Long-Term Gaseous Elemental Mercury Concentrations by Passive Air Sampling at an Abandoned Mining Site and Nearby Urban Area

F. Monaci[1]*, D. Baroni[2], D. Rappuoli[3], F. Wania[4]

[1]University of Siena, Dept. of Life Science, Via Mattioli 4, 53100 Siena, Italy
[2]University of Siena, Dept. of Physical Sciences, Earth and Environment, Via Mattioli 4, 53100 Siena, Italy
[3]Unione dei Comuni Amiata Val d'Orcia, Unità di Bonifica, Via Grossetana 209, 53025, Piancastagnaio, Siena, Italy
[4]University of Toronto Scarborough, Dept. of Physical and Environmental Sciences, 1265 Military Trail, Toronto, Canada

fabrizio.monaci@unisi.it

Mercury (Hg) is a global pollutant causing pervasive environmental impacts especially through its gaseous elemental form (GEM). Long-term quantitative assessment of GEM pollution is a challenge, due to the difficulties in producing adequate spatially distributed and temporally resolved measurements. However, such measurements are essential to appropriately capture the dispersal of highly fluctuating Hg in air and to evaluate chronic human exposure through inhalation. This is particularly important around strong point sources.

To resolve these issues, a precise, low-cost, and practical passive sampler (PAS) for GEM monitoring has been conceived (McLagan et al., 2016). Since 2015, we tested the suitability of this PAS for long-term surveillance of GEM exposure in the urban area of Abbadia San Salvatore, central Italy, which is impacted by a nearby abandoned Hg mining and metallurgic facility. GEM concentrations were determined on a seasonal basis at 13 sites located along three transects originating in the area of the metallurgical buildings and extending towards the East, South-East and North-East, which have been identified as the main directions for GEM dispersal from the mine (McLagan et al., 2019). Here, the data from five years (2015 – 2019) of monitoring are reported. Time-weighted average concentrations determined at the 13 PAS deployment sites varied over two orders of magnitude, from 3.7 to 342 ng/m^3. Such an extended range reflects the varying concentrations that characterize the investigated area (McLagan et. al, 2019; Vaselli et al., 2013) and reveals a steep gradient of GEM concentrations in relation to the distance from the mining site, the direction and intensity of winds as well as different seasonal temperatures. Clearly, using three-months deployment times, the PAS was found suitable to record different ranges of GEM concentrations, from background values (2-5 ng/m^3) typical of the study area, up to concentrations exceeding the non-occupational Minimal Risk Level (200 ng/m^3; USATSDR), thereby proving the usefulness of these samplers for the long term tracking of GEM at concentration ranges needed for chronic human exposure assessment. GEM monitoring in Abbadia San Salvatore using passive sampling is presently continuing with the aim of ascertaining the variations in GEM concentrations expected in the urban area, arising from mitigation activities which have started at the mining site in 2018.

References

McLagan, et al. (2016) ‘A High-Precision Passive Air Sampler for Gaseous Mercury’. Environ. Sci. Technol. Lett. 3, p. 24–29. doi.org/10.1021/acs.estlett.5b00319

McLagan, et al. (2019) ‘Characterization and Quantification of Atmospheric Mercury Sources Using Passive Air Samplers’ J. Geophys. Res. Atmos. 124, p. 2351–2362. doi.org/10.1029/2018JD029373

Vaselli, et al. (2013) ‘Distribution of gaseous Hg in the Mercury mining district of Mt. Amiata (Central Italy): A geochemical survey prior the reclamation project’ Environ. Res. 125, p. 179–87. doi.org/10.1016/j.envres.2012.12.010.

Pollutant Emissions from Wood-Fired Pizza Ovens

A. Bergomi[1]*, S. Chiavarini[2], C. Morreale[3], S. Bertagna[3], P. Fermo[1], T. La Torretta[4], A. Malaguti[4], M. Stracquadanio[2] and G. Migliavacca[3]

[1]University of Milan, Department of Chemistry, Via Golgi 19, 20133, Milan, Italy
[2]ENEA, Division Protection and Enhancement of the Natural Capital, Via Anguillarese, 30100123, Santa Maria di Galeria (RM), Italy
[3]Innovhub Stazioni Sperimentali per l'Industria, Area Combustibili, Via Galilei 1, 20097, San Donato Milanese (MI) , Italy
[4] ENEA, Atmospheric Pollution Laboratory, Via Martiri di Monte Sole 4, 40129, Bologna, Italy

andrea.bergomi@unimi.it

Recent studies estimate that a non-negligible percentage of atmospheric particulate matter (PM) collected (sampled) in urban areas can be attributed to emissions deriving from the combustion of solid biomass for uses other than heating (Hugony,2020). One of the activities that could be responsible for these emissions are pizzerias with wood-burning ovens, which are active all the year and are highly concentrated in Italian large cities. However, measurements of the emission factors of these devices have never been performed in practice. In this study, experimental tests were carried out on a traditional wood-fired oven using two different fuels (beechwood logs and briquettes) in order to determine the pollutant emissions of the device. The sampling system employed (Fig. 1) was constructed by referring to the UNI EN 16510-1:2019 technical standard and enabled the simultaneous measurement of pollutants and other substances on the hot and cold flue gases. The pollutants measured during the tests were: carbon monoxide (CO), nitrogen oxides (NOx), organic gaseous carbon (OGC), PM, and polycyclic aromatic hydrocarbon (PAHs). A sampling protocol and appropriate combustion cycles were established in order to simulate, as far as possible, the real-life operating conditions of an oven within a public establishment. The results show that the pollutant emissions of the wood-fired oven fall within the wide range of values observed in literature for other wood-burning appliances, such as stoves and fireplaces (Tomlin,2021), indicating these devices as relevant air pollution sources in urban areas.

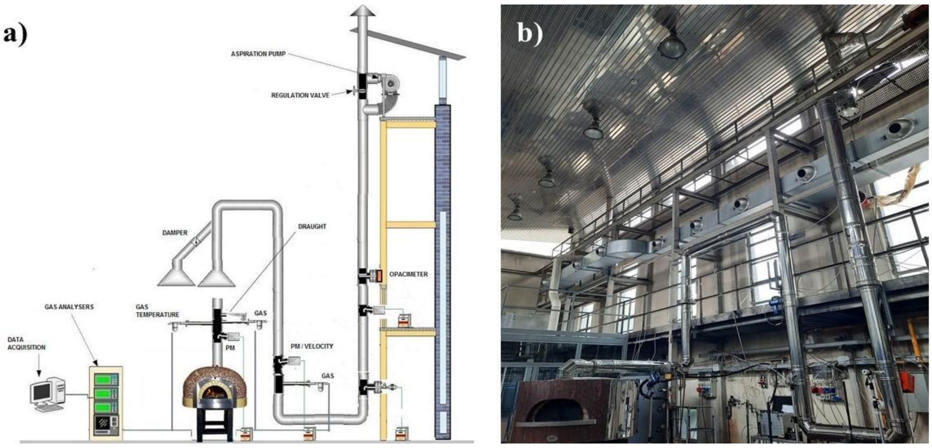


Figure 1. a)Sampling system scheme (not to scale)(Bergomi,2022) b)Real-life sampling system.

References

Hugony F. (2020) 'Progetto Metropizza', Seminar, Città metropolitana di Milano – ENEA, Milano, IT.

Tomlin A. S. (2021) 'Air Quality and Climate Impacts of Biomass Use as an Energy Source: A Review', Energy & Fuels, 35, p. 14213–14240. https://doi.org/10.1021/acs.energyfuels.1c01523.

Bergomi, A. *et al*. (2022) 'Determination of pollutants emissions from wood-fired pizza ovens', Chemical Engineering Transactions, 92, p. 499-504. DOI:10.3303/CET2292084.

Good News: Some Insecticides Have been Virtually Eliminated in the Air near the Great Lakes

M. Venier[1]*, R. Hites[1]

[1]Indiana University, O'Neill School of Public and Environmental Affairs, Bloomington, Indiana, USA

mvenier@indiana.edu

Persistent insecticides have been classic environmental problems for 60−70 years perhaps starting with Rachel Carson's indictment of DDT. Both national and international regulations have been put in place over the last 20−30 years to eventually eliminate these compounds from the environment. One focus is the atmosphere, which acts as a major long-range transport route of these pollutants from their numerous sources to many ecosystems.

A modified Anderson high volume air sampler was used to collect air samples for 24 h once every 12 days (except at Point Petre, where the frequency was once every 36 days) at a flow rate giving a total sample volume of about 820 m^3. The particle phase organic compounds were collected on a 20 × 25 cm quartz fiber filter. This was followed by Amberlite XAD-2 resin held in a stainless-steel cartridge to collect the vapor phase organics. This paper is focused on six classic insecticides measured in samples collected since about 1990 as part of the Integrated Atmospheric Deposition Network, a US-Canada Binational program funded by the US Environmental Protection Agency (EPA). Concentrations were analyzed using a linear regression model that accounts for both linear temporal trends and seasonal effects[1]. Halving or doubling times were calculated for each chemical at each site.

The calculated halving times ranged from ~5 years for lindane to ~17 years for DDTs. Halving times were not significant for octachlorostyrene and hexachlorobenzene. Results show that some of these compounds (lindane, α-HCH, and endosulfans) are well on their way to being virtually eliminated, while the concentrations of others (DDT, chlordane, and hexachlorobenzene) have not changed much. We speculate that this difference in elimination is a result of soil compaction in cities (DDT, etc.) versus soil mixing in rural areas (lindane, etc.). These findings, with clear implications on health for both biota and the local human population, especially in urban areas, can be expanded to other areas in the world. The lessons learned from the fate, transport, and degradation processes of legacy pesticides should be used to address current chemical threats.

References

[1]Venier, M.; Hites, R. A. Regression model of partial pressures of PCBs, PAHs, and organochlorine pesticides in the Great Lakes' atmosphere. Environ. Sci. Technol. 2010, 44, 618−623.

Monitoring of Dioxin Levels in Air, in the Major Cities of Cyprus

L. Eleftheriou[1]*, C. Papastephanou[1] and P. Eleftheriou[2]

[1]CP Foodlab Ltd, 19 Viomichanias str. 2326, Nicosia, Cyprus
[2]Cyprus University of Technology, Department of Mechanical Engineering and Materials Science Engineering, 30 Arch. Kyprianos str. 3036, Limassol, Cyprus

lygia@foodlab.com.cy

Dioxins, a term used to describe molecules which consist of two benzene rings connected by a third oxygenated ring, belong to persistent environmental pollutants (POPs) and have been previously linked with behavioral, reproductive, developmental, endocrine, neurologic, and immunologic adverse health effects. Their sampling, as well as analysis are quite challenging, with only a few available protocols offering reproducible results, rendering their study even more urgent.

The dioxin levels in air in the major cities of Cyprus were measured during a two-year period (2020-2022). Sampling was performed using highly specialized PUF Air Samplers with both PUF and quartz filters. An extraction method through the DEXTech Plus was validated and performed according to ISO17025 provisions, while targeted GC-MS/MS analysis was utilized for identification and quantification of the dioxin molecules of interest (2,3,7,8 – TCDD, 1,2,3,7,8 – PeCDD, 1,2,3,4,7,8 – HxCDD, 1,2,3,6,7,8 – HxCDD, 1,2,3,7,8,9 – HxCDD, 1,2,3,4,6,7,8 – HpCDD, OCDD, 2,3,7,8 – TCDF, 1,2,3,7,8 – PeCDF, 2,3,4,7,8 – PeCDF, 1,2,3,4,7,8 – HxCDF, 1,2,3,6,7,8 – HxCDF, 2,3,4,6,7,8 – HxCDF, 1,2,3,7,8,9 – HxCDF, 1,2,3,4,6,7,8 – HpCDF, 1,2,3,4,7,8,9 – HpCDF, OCDF). The findings showed higher levels of dioxins in industrial areas (31.92 TEQ fg/m^3 as the average), with the city centres and locations with high traffic coming next (24.24 TEQ fg/m^3) and residential areas showing the lowest concentrations (4.86 TEQ fg/m^3). All sampling and analysis were in accordance with the EU legislation for pollutants in air, while the results were compared to those of other countries around the world (Dopico and Gomez, 2015) and were at the low end of the range for all sites tested (industrial, residential, high traffic).

References

Dopico, M. and Gomez, A. (2015) 'Review of the current state and main sources of dioxins around the world.' J Air Waste Manag Assoc, 65(9), 1033:1049.

A Multi-Analytical Approach for the Identification of Pollutant Sources on Cultural Heritage

M. Ricciardi[1]*, A. Faggiano[1], C. Pironti[2], V. Comite[3], P. Fermo[3], M. Carotenuto[1], O. Motta[2] and A. Proto[1]

[1]University of Salerno, Department of Chemistry and Biology, via Giovanni Paolo II 132, 84084 Fisciano, SA, Italy;
[2]University of Salerno, Department of Medicine and Surgery, via S. Allende, 84081 Baronissi, SA, Italy;
[3]University of Milan, Department of Chemistry, Via Golgi 19, 20133 Milan, Italy

mricciardi@unisa.it

The degradation of cultural heritage caused by exposure to atmospheric pollutants (e.g., CO_2, NOx and SOx) is a growing concern, especially for buildings and monuments located in the historic centers of large cities. The chemical interaction of stone surfaces of historical buildings with such atmospheric pollutants (i.e., SO_2) can originate dark-colored deposits called black crusts (BCs) (Comite et al., 2020). BCs are referred to the areas where atmospheric deposition accumulates together with the products of the chemical transformation of materials, and their formation is one of the most dangerous phenomena that occurs in architectural heritage. Different pollutants can be detected on BCs, including organic matter, metals, and polycyclic aromatic hydrocarbons (Rivas et al., 2014).

Characterizing the nature and sources of degradation products is an important aspect to identify proper strategies to prevent damaging of cultural heritage. In this context, stable isotope ratio is a valuable tool to assess the origin and sources of pollutants, and it is employed in several fields of environmental science. Sulphur and oxygen isotope ratio have been used for the identification of the source of sulfur in black crusts and efflorescence formed on stone surfaces of monuments and buildings (Rivas et al., 2014). Generally, the most important source of sulfur is SO_2 emissions from fossil fuels combustion by road vehicles and factories, although other sources such as biological ones and construction materials cannot be overlooked. It is important to note that different pollutants, including carbonaceous particles, heavy metals, and polycyclic aromatic hydrocarbons (Orecchio et al., 2010), are incorporated in black crusts during their formation and accumulated over time.

The present study concerns the characterization of sources of pollutants on black crust samples collected from the Monumental Cemetery of Milan (Northern Italy). In detail, polycyclic aromatic hydrocarbons were detected on Soxhlet extracts by high performance liquid chromatography (HPLC), while stable isotope ratios of sulfur ($\delta^{34}S$), oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) are measured by isotope ratio mass spectrometry (IRMS). Carbon stable isotope ratio was used to evaluate the sources of carbonaceous pollutants on black crust samples, and its value was correlated to the organic matter and polycyclic aromatic hydrocarbons content. Sulfur and oxygen stable isotope ratio are instead employed to assess the origin of sulfates.

The proposed multi-analytical approach can be useful for the identification of sources of hazardous pollutants accumulated on black crust samples.

References

Comite, V. et al. (2020) "A multi-analytical approach for the characterization of black crusts on the facade of an historical cathedral”, Microchemical Journal, 158, 105121, 10.1016/j.microc.2020.105121.

Rivas, T. et al. (2014) "Sulphur and oxygen isotope analysis to identify sources of sulphur in gypsum-rich black crusts developed on granites", Science of the Total Environment, 482–483, 137–147, 10.1016/j.scitotenv.2014.02.128.

Orecchio, S. et al (2010) "Analytical method, pattern and sources of polycyclic aromatic hydrocarbons (PAHs) in the stone of the Temples of Agrigento (Italy)", Journal of Hazardous Materials, 176, 339–347, 10.1016/j.jhazmat.2009.11.033.

Study of CO_2 Adsorption on Activated Carbon Spheres

I. Pełech [1]*, K.S. Sobczuk[1], D. Sibera[1,2], P. Staciwa[1], A.W. Morawski[1], E. Kusiak-Nejman[1], U. Narkiewicz[1]

[1]West Pomeranian University of Technology in Szczecin, Department of Inorganic Chemical Technology and Environment Engineering, Faculty of Chemical Technology and Engineering, Pułaskiego 10, 70-322 Szczecin, Poland
[2]West Pomeranian University of Technology in Szczecin, Faculty of Civil and Environmental Engineering, Piastów 50a, 70-311 Szczecin, Poland

ipelech@zut.edu.pl

Carbon dioxide is the major anthropogenic factor related to climate change, affecting the healthy functioning of the biosphere. The increased CO_2 concentration in the atmosphere is connected with development of the energy industry, progressive urbanization and combustion of fossil fuels. For this reason, various materials have been tested as solid sorbents for CO_2 capture: zeolites, silica, activated carbons, ordered porous carbons, activated carbon fibers, and microporous carbon materials including carbon spheres. The increase of interest in these materials is due to their unique chemical and physical properties, such as high specific surface area, large porous volume, well-defined pore size distribution, chemical stability, the possibility for modification with heteroatoms, and high affinity for carbon dioxide. In order to develop the surface area and improve the adsorption capacity of carbon materials, physical and chemical activation is one of the most frequently used methods. Therefore, the aim of this work is to investigate the effect of the activation of carbon spheres on CO_2 adsorption process. Carbon spheres were obtained with different textural characteristics and the dependency between the obtained values and CO_2 adsorption have been designated.

In order to prepare carbon spheres, resorcinol was dissolved in an aqueous alcohol solution and then formaldehyde was added. After 24 h of stirring, the mixture was transferred into a microwave reactor, and the treatment was carried out for 15 min under a reaction pressure of 20 atm. Next, the products were carbonized under argon atmosphere at 700 ºC. To the activation of carbon materials various kinds of activating agents: potassium hydroxide, sodium hydroxide, potassium oxalate, sodium carbonate, potassium carbonate and zinc chloride were used. Activation proceed in a high-temperature furnace under argon atmosphere at 700 ºC for 5 min.

For the obtained materials N_2 adsorption/desorption isotherms at -196 ºC were measured. The surface area was determined in the relative pressure range of 0.05–0.3 and calculated based on Brunauer–Emmett–Teller (BET) equation. The total pore volume (TPV) was calculated from the volume of nitrogen held at the highest relative pressure (p/p0 = 0.99). The volume of micropores Vm with diameter below 2 nm was calculated as a result of integrating the pore volume distribution function using the DFT method; the volume of mesopores Vmeso with diameter from 2 to 50 nm was calculated from the difference in the total pore volume TPV and the volume of micropores Vm. Carbon dioxide adsorption isotherms at 0 ºC and 25 ºC were measured in the pressure range between 0.01 and 0.98 bar. From CO_2 adsorption, the isotherms at 0 ºC, pore size distribution (PSD), and the volume of ultra-micropores Vs below 1.0 nm were determined and calculated by integrating the pore volume distribution function using the NLDFT method.

Acknowledgments
The research leading to these results has received funding from the Norway Grants 2014-2021 via the National Centre for Research and Development under the grant number NOR/POLNORCCS/PhotoRed/0007/2019-00.

Exploring the Chemical Transformations of Biomass Burning and Diesel Exhausts at the EUPHORE Simulation Chamber

M. Ródenas[1]*, M. Rigler[2], A. Gregorič[2], B. Alfoldy[2], T. Vera[1], E. Borrás[1], R. Soler[1], T. Gómez[1], E. Yubero[3], J. Crespo[3], R. Climent[1], A. Muñoz[1]

[1]Fundación CEAM. EUPHORE lab, C/ Charles R. Darwin 14, 46980, Paterna, Spain
[2]Aerosol d.o.o., Research & Development Department, Kamniska, 39 A, SI-1000, Ljubljana, Slovenia
[3]Miguel Hernández University, Atmospheric Pollution Laboratory, Avda. Universidad, s/n, 03202, Elche, Spain

rodenas_mil@gva.es

Biomass burning (BB), both in the form of open fires and residential burning, produces important amounts of gas and particle emissions that are released into the atmosphere. Its impact on air quality, climate, and human health has led to increasing concern and interest in the last decade. Indeed, BB is one of the main sources of primary particulate matter, and a source of organic aerosols, black and brown carbon. Besides, organic compounds emitted by BB can react with oxidants present in the atmosphere leading to the formation of new products. Nevertheless, most of the studies only focus on a characterization of the emissions but do not assess their chemical evolution and the emission sources and formation processes remain poorly understood and under-represented in climate and air quality models (Kasthuriarachchi et al., 2020).

Within this context, emissions and their chemical transformation from different sources, including wood burning (orange, beech, and vineyard) and vehicle exhausts, were studied at the EUPHORE simulation chamber (200 m3, Muñoz et al., 2011). Various analytical instruments were used to characterize both the optical properties and chemical composition of the particle phase (Aethalometers, TCA08 for black carbon and total carbon measurements, OPC, PM2.5 sampler, nephelometer, filters for offline analysis, SMPS, TEOM) and the gas phase (optical equipment, chromatographs and monitors, and high-resolution state-of-the-art spectrometers: PTR-ToF-MS, API-ToF-CIMS + Figaero), which allowed a detailed examination of the chemical composition, aging and transformation of the emissions when exposed to oxidants, simulating real day and night conditions. The experiments also allowed the exploration of spectral chemical fingerprints for identifying sources of BB and the successful test of the new AE36s and TC-BC method (Rigler et al., 2020) to determine organic carbon. The analysis of data revealed different patterns in the air composition as a function of the emission source, burning phase (flaming vs smoldering), and aging conditions (night vs day).

This knowledge is essential for developing effective mitigation policies and for improving air quality models and to better quantify wood combustion secondary organic aerosols (SOA) in ambient air. It can also aid in designing educational and mitigation programs for more efficient use of domestic wood-burning practices.

This work is part of a project that is supported by the EC under the Horizon 2020 – R&I FP, through the ATMO-ACCESS Integrating Activity under GA N. 101008004.Abstract (max 3200 characters – spaces included or 29 lines)

References

Kasthuriarachchi, N.Y. et al, (2020), 'Light absorbing properties of primary and secondary brown carbon in a tropical urban environment' Environ. Sci. Technol. 54, 17, 10808–1081, https://doi.org/10.1021/acs.est.0c02414

Muñoz, A. et al. (2011), 'Studies on the Atmospheric degradation of Chorpyrifos methyl', Env. Sci. Tech., 45,1880-1886, https://doi.org/10.1021/es103572j

Rigler, M. et al. (2020), 'The new instrument using a TC–BC (total carbon–black carbon) method for the online measurement of carbonaceous aerosols', Atm. Meas. Tech. 13, 4333–4351, https://doi.org/10.5194/amt-13-4333-2020

Epidemiological Studies and Characterization of Indoor Air Pollutants at Six Hospitals of Lucknow City-a Longitudinal Research

A. Taushiba[1,2]*, A. Lawrence[1], R.R. Khan[2]

[1]Isabella Thoburn College, Department of Chemistry, Lucknow, India
[2]Integral University, Department of Environmental Science, Lucknow, India

ataushiba2626@gmail.com

The current study was carried out in three different microenvironments, namely residential (AB), commercial (CD), and industrial (EF), in Lucknow city from 25th October 2022 to 28th February 2023. Two hospitals from each microenvironment were selected for indoor and outdoor monitoring of microbial contaminants, PM2.5, PM>2.5, PM1.0-2.5, PM0.50-1.0, PM0.25-0.50 and PM<0.25. According to the study's observation, Hospital E and F, which were located in an industrial area, had the highest outdoor concentrations of PM2.5 i.e., 207.17 and 228.60 µg/m3 and PM1.0 - 2.5, PM0.50 - 1.0, PM0.25 - 0.50, and PM0.25, were 35.44 µg/m3, 40.49 µg/m3, 58.08 µg/m3, 45.44 µg/m3, 65.08 µg/m3, 68.9 µg/m3, 75.50 µg/m3 and 90.9 µg/m3, respectively in an indoor and outdoor environment. Nevertheless, for PM>2.5, Hospital A and B, located in the city's residential area, had the highest indoor and outdoor concentrations i.e., 30.7 µg/m3, 35.8 µg/m3, 40.45 µg/m3, 50.05 µg/m3. Regarding PM2.5, hospital C and hospital D located in the commercial area, reported the highest indoor concentrations of 149.40 µg/m3 and 227.50 µg/m3, respectively. The current investigation also found that Hospital A and B had a high bacterial load of 1507.1 CFU/m3, and 1179.5 CFU/m3, while Hospital E and F had the greatest fungal load at 602.86, 511.12 CFU/m3. The results of this work will aid to increase familiarity with indoor air quality (IAQ) with respect to size-determined particles and biological contaminants in the most delicate microenvironments i.e., hospitals. The study's results will help field professionals and policymakers in drafting specific guidelines and mitigation techniques for hospitals owing to the presence of a variety of microbial contaminants along with sub-micron particles and also provides insightful findings about the temporal dynamics of interior PM2.5 and sub-micron concentrations.

References

Kumar, P., Singh, A. B., & Singh, R. (2021). Seasonal variation and size distribution in the airborne indoor microbial concentration of residential houses in Delhi and its impact on health. Aerobiologia, 37(4), 719-732 https://doi.org/10.1007/s10453-021-09718-3

Slezakova, K., da Conceição Alvim-Ferraz, M., & do Carmo Pereira, M. (2012). Elemental characterization of indoor breathable particles at a Portuguese urban hospital. Journal of Toxicology and Environmental Health, Part A, 75(13-15), 909-919 http://doi.org/10.1080/15287394.2012.690707

Presence and Impact of Volatile Methylsiloxanes in the Air of a WWTP and other Indoor Environments

F. Sánchez-Soberón[1,2], C. Rodrigues[1], N. Ratola[1,3]*

[1]University of Porto, Faculty of Engineering, LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2]Institute of Health Carlos III, Dep. of Atmospheric Pollution. Ctra. Majadahonda-Pozuelo, Km 2. 28220 Madrid, Spain
[3]University of Porto, Faculty of Engineering, ALiCE - Associate Laboratory in Chemical Engineering, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

nrneto@fe.up.pt

Volatile methyl siloxanes (VMSs) are anthropogenic chemicals of emerging concern that are ubiquitous in industrial and consumer products. With particular relevance in the formulations of personal care products (PCPs), cleaning items and lubricants, among others, VMSs have raised concern among the scientific community and two of the congeners (D4 and D5) are already restricted in the European Union in wash-off products, after evidence of potential harm to humans and the environment (ECHA, 2019).

Given their use and volatile nature, VMSs are strongly emitted in indoor environments by the use of PCPs and cleaning products and in WWTPs, entering via the urban and industrial wastewaters. For this reason, in this study, indoor and outdoor locations on WWTP and in 18 different work/home environments were subjected to passive air sampling for 14 days with XAD-2 sorbent to determine the levels and seasonality of 7 VMSs (the linear L3-L5 and the cyclic D3-D6). Furthermore, sampling rates taken from literature were used to estimate the potential human exposure to D4-D6. In the WWTP, results revealed seasonality of VMSs outdoors in general, with the highest values obtained in Summer. The congener profiles remained fairly constant along the year, with a predominance of D5 outdoors and D3 and D4 indoors. Overall, outdoor sites (0.32-0.49 m3/day) had higher VMSs concentrations in air than indoors (0.16-0.21 m3/day). The exposure to D4-D6 was higher for maintenance technicians and lower for laboratory personnel, but still under a safe inhalation threshold of 150 µg/(kg·day) (Sánchez-Soberón and Ratola, 2022).

In the work/home spaces, the highest total VMS concentration was found in a private bedroom (14095 ng/day), followed by a hair salon (6880 ng/day), with D5 prevailing, which is in line with a strong use of PCPs (Dudzina et al., 2014). As expected, the two background outdoor sites had the lowest levels (0.79 and 56 ng/day). Regarding the estimation of the human exposure, women are apparently more susceptible to higher inhalation doses than men, due to their physiology. The highest exposure levels estimated were found for hairdressers workers (1183 ng/kg bw·day). More than 50% of this dose is inhaled at home, which makes our daily routine a key part in the exposure process and its changes in extreme situations such as the CoViD pandemic. Nevertheless, the estimated exposure by ingestion of dust contaminated by VMSs (0.027 mg/bw·day) was shown to be higher than inhalation (0.005 mg/kg bw·day) for babies.

This work was financially supported by: (i) LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE – Laboratory for Process Engineering, Environment, Biotechnology and Energy), funded by national funds through FCT/MCTES (PIDDAC); (ii) Project LANSILOT (PTDC/CTA-AMB/32084/2017; POCI-01–0145-FEDER-032084) funded by FEDER through COMPETE2020 - POCI and by national funds (PIDDAC) through FCT/MCTES. The authors wish to express their appreciation to the volunteers that helped in the setting-up and collection of the samples.

References

Dudzina, T. et al. (2014) 'Concentrations of cyclic volatile methylsiloxanes in European cosmetics and personal care products: Prerequisite for human and environmental exposure assessment', Environment International,62, p. 86-94. doi: 10.1016/j.envint.2013.10.002.

ECHA (2019). 'Annex XV - Restriction report: D4, D5 and D6'. European Chemicals Agency.

Sánchez-Soberón, F. et al. (2022) 'Seasonal occurrence, concentrations, and occupational exposure to VMSs in different environments of a WWTP', Environmental Pollution, 315, p. 120423, doi:10.1016/j.envpol.2022.120423

Comparison of Source Apportionment Methods: Receptor Models - PMF and Dispersion Models - Camx/PSAT in Po Valley (Italy) and Catalonia (Spain)

F. Ippolito[1]*, E. De Angelis[2], G. Pirovano[2], P. M. Costa[2], C. Colombi[3], G. Lanzani[3], E. Cuccia[3], G. Maffeis[4], M. Bedogni[5], X. Querol[1], A. Alastuey[1], C. Reche[1], N. Perez[1], In't Veld M.[1] and F. Amato[1]

[1]Institute of Environmental Assessment and Water Research, IDAEA, Spanish Research Council (CSIC), 08034 Barcelona, Spain
[2] RSE SpA, Milano, 20134, Italy
[3]Arpa Lombardia, 20124 Milano, Italy
[4] TerrAria s.r.l., 20125 Milano, Italy
[5]AMAT, Milano, Italy

federica.ippolito@idaea.csic.es

Source apportionment (SA) is a widely used technique to understand the origin of ambient air particulate matter (PM) levels identifying and quantifying the sources that contribute most to concentration levels and evaluate the efficiency of mitigation strategies. Receptor Models and Dispersion Models are the most common approaches to perform source apportionment analyses. Dispersion models are commonly affected by large uncertainties which hamper the SA analysis. Hence, it is important to reduce the existing uncertainties of dispersion models by means of the comparison with receptor modelling results (Belis et al. 2020). Therefore, a comparison between two different SA tools was carried out in Po Valley (Italy) and Catalonia (Spain), both at urban background and rural sites. Receptor modelling has been performed by means of Positive Matrix Factorization (PMF, Paatero e Tapper (1994)) using the EPA-PMF 5.0 software on PM10 and PM2.5 chemical speciation data collected over several years including elements, ions, OC/EC and, in the case of Po Valley, also levoglucosan. Dispersion modelling has been performed by the CAMx/PSAT model tool: from a regional domain (ITA domain: 4x4 km2; CAT domain: 0.05° x 0.05°) to an urban domain (MI domain: 1x1 km2- BCN domain: 0.01° x 0.01°). The obtained PMF factors (7 in Milan and 8 in Barcelona for PM10 (in't Veld et al. 2021)) can be interpreted either as "PMF sources" (e.g., road traffic) and as "atmospheric secondary processes". Only a small fraction of secondary inorganic aerosols (SIA) and secondary organics aerosols (SOA) is actually apportioned by PMF to individual sources, while most of their concentrations is typically explained by one or more "atmospheric secondary processes" factor(s) while CAMx/PSAT apportions the totality of modelled secondary aerosols to the sources listed in the inventory (MI: European EMEP 2010 inventory – BCN: European EMEP 2017 inventory). Therefore, the methodology for comparison is structured as:

1) For "PMF sources" the comparison is made between the total contribution obtained by PMF with the contribution obtained by CAMx/PSAT excluding those secondary species which are not included in the PMF profile. Such discarded secondary species of the CAMx/PSAT contribution go to an additional CAMx category labelled as "Remaining".

2) For nitrate, sulphate, and ammonium two comparisons are made: one between the "Remaining nitrate" (or sulphate) and the "PMF Secondary nitrate" (or sulphate) and one between the CAMx modelled SIA concentration and the observed SIA concentrations.

Results highlight some key uncertainties in the CAMx/PSAT approach: i) the lack of road dust resuspension emissions; ii) SOA are largely underestimated at both regions; iii) Residential heating is largely overestimated in Barcelona iv) traffic exhaust contributions are also underestimated; v) shipping contributions are overestimated in Barcelona. In addition, PMF slightly underestimates biomass burning source probably due to thermic instability of levoglucosan. This work was carried out in the framework of the LIFE REMY project (PRE/IT000004).

References

Belis, C.A. et al. (2020) 'Evaluation of receptor and chemical transport models for PM10 source apportionment', Atmospheric Environment: X, 5. Available at: https://doi.org/10.1016/j.aeaoa.2019.100053.

Paatero, P. and Tapper, U. (1994) 'Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values', Environmetrics, 5(2). Available at: https://doi.org/10.1002/env.3170050203.

Veld, M. in t. et al. (2021) 'Compositional changes of PM2.5 in NE Spain during 2009–2018: A trend analysis of the chemical composition and source apportionment', Science of the Total Environment, 795. Available at: https://doi.org/10.1016/j.scitotenv.2021.148728.

CO_2 Concentration Monitoring inside Educational Buildings as a Strategic Tool to Reduce the Risk of Sars-Cov-2 Airborne Transmission

J. Palmisani[1*†], A. Di Gilio[1†], M. Pulimeno[2], F. Cerino[3], A. Miani[4], P. Piscitelli[4], G. de Gennaro[1]

[1]University of Bari, Department of Biosciences, Biotechnologies and Environment, via Orabona 4, 70126, Bari, Italy
[2] UNESCO Chair on Health Education and Sustainable Development, University of Naples ‘Federico II’, 80138, Naples, Italy
[3] Befreest srl, Viale Virgilio 113, 74121, Taranto, Italy
[4] Italian Society of Environmental Medicine (SIMA), Viale di Porta Vercellina, 9, 20123, Milan, Italy

jolanda.palmisani@uniba.it †Co-first author

In order to prevent SARS-CoV-2 transmission inside educational buildings, on 2020 the Italian Government in accordance with the WHO recommendations adopted a contingency plan based on specific infection control practices. However, although mandatory measures, educational buildings may fail in contagion containment especially when a high number of students is present inside the classrooms for several hours a day. In such conditions, the probability a subject re-inhales the air exhaled by another bystander may result not negligible (Allen and Marr, 2020; Minguillón et al., 2020; Morawska et al., 2020). Therefore, the present study reports the outcomes of a pilot surveillance study based on the real-time monitoring of CO_2 airborne levels as a proxy of SARS-CoV-2 transmission risk. A total of 9 educational buildings and 11 naturally-ventilated classrooms, differentiated for educational level and located in several provinces of Apulia Region in the South of Italy, were enrolled in the study. The monitoring activity was performed for 3 consecutive weeks starting from 18th January to 8th February 2021. High temporal resolution monitoring of CO2 concentration (ppm), temperature (°C) and relative humidity (%) was performed through the deployment of several units of an integrated IAQ monitoring system (Nose, Befreest srl, Italy). The experimental design was developed based on a two-stage evaluation approach. The first 2-3 days of the monitoring activity were intentionally dedicated to a preliminary evaluation addressed to define the initial scenario inside the classroom e.g., CO2 daily concentration pattern under the specific air ventilation and human occupancy conditions. Afterwards, a detailed protocol was provided to the school administrators to promote air ventilation i.e., door and windows opening in terms of timing and frequency and use of a sensor mobile application providing CO_2 real-time concentration data. During the first evaluation stage and according to the discretionary ventilation strategy of the school administrators, 6 (54%) classrooms showed mean values of CO2 higher than 1000 ppm and all classrooms exceeded the recommended CO2 concentration limit value of 700 ppm. On the contrary, in all the classrooms where the teachers rigorously applied the operating protocol in the second-stage evaluation, an overall improvement of CO2 levels was observed. In few specific cases, despite the air ventilation protocol and the improvement with respect to the initial scenario, due to the building structural limits, the only mechanical ventilation system was identified as the effective tool to guarantee proper air exchanges. Finally, a 4 level-risk classification scheme was developed with specific corrective actions at each level (1-4) with the purpose to provide a useful tool to ensure adequate air ventilation and reduce SARS-CoV-2 transmission risk. In conclusion, evidence-based outcomes of the present study demonstrate, with the only exception of building structural limits, that real-time visualization of CO_2 concentrations and the implementation of an effective air ventilation protocol is a strategic approach to promote air ventilation inside classrooms and to potentially reduce SARS-CoV-2 transmission.

References

Allen, J.G. and Marr, L.C. (2020). ‘Recognizing and controlling airborne transmission of SARS-COV-2 in indoor environments’. *Indoor Air* 30, 557-558. https://doi.org/10.1111/ina.12697

Minguillón, M.C. *et al.*, (2020). ‘Guide for ventilation towards healthy classrooms’. COST Action CA17136 report. CSIC publications. http://hdl.handle.net/10261/225519.

Morawska, L. *et al.*, (2020). ‘How can airborne transmission of COVID-19 indoors be minimised?’ *Environment International* 142, 105832. https://doi.org/10.1016/j.envint.2020.105832

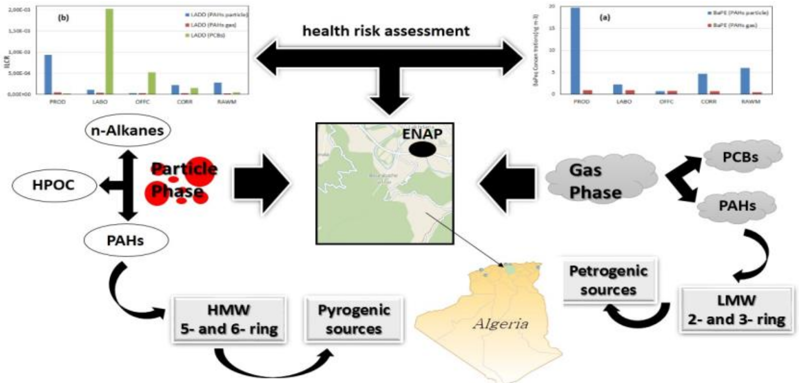
Chemical Characteristics and Gas–Particle Partitioning of Organic Aerosols from a Paint Manufacturing Location in Algeria; Health and Carcinogenic Risk Assessment to Workers

S. Khedidji[1,2]*, C. Balducci[3], L. Rabhi[1,4], A. Cecinato[3], R. Ladji[4] and N.Yassaa[1,5]

[1]University of Akli Mohand Oulhadj Bouira, Department of Chemistry, Algeria
[2]University of Science and Technology Houari Boumediene, Faculty of Chemistry, Algiers, Algeria
[3]National Research Council of Italy, Institute of Atmospheric Pollution Research -CNR-IIA, Roma, Italy
[4]Centre for Scientific and Technical Research in Physico-Chemical Analysis -CRAPC, Algeria
[5]Commission for Renewable Energies and Energy Efficiency CEREFE, Algieria

s.khedidji@univ-bouira.dz

The daily variation of organic compounds associated with PM10, i.e., atmospheric particulate matter with aerodynamic diameter less than 10 µm and occurring in gas phase was investigated inside the National Company of Paintings. Chemical characterization of organic compounds comprising n-alkanes, polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs) and highly-polar organic compounds (HPOCs) was carried out indoors. The concentrations of gaseous PCBs were higher to those reported in other Algerian and European cities. The distribution of PAHs between the particle and gas phase was investigated and it was found that low molecular weight (LMW)-PAHs (2 ring, 95.1% rate) were associated primarily with the gas phase, three ring PAHs were distributed almost equally between the two phases and high molecular weight (HMW)- PAHs (6 ring, 43.9%) were mainly associated with the particle phase.
The source reconciliation of organic contaminants through principal compound analysis (PCA) demonstrated that the principal ones were petroleum combustion, industrial manufacture, tobacco smoking and vehicular traffic. The health risks for workers exposed to PAHs and PCBs in PM10 were quantitatively assessed by BaP equivalent concentration (BaPeq) and the incremental lifetime cancer risk (ILCR). The ILCR values of particulate PAHs indicate higher cancer risk to workers.



The partitioning and health risk assessment of gaseous and particulate organic compounds

References

Khedidji S, Konrad M, Rabhi L, Spindler G, Fomba KW, Van Pinxteren D, Yassaa N, Herrmann H (2020) Chemical Characterization of Marine Aerosols in a South Mediterranean Coastal Area Located in Bou Ismaïl, Algeria. Aerosol Air Qual Res 20: 2448–2473

Khedidji S, Balducci C, Ladji R, Cecinato A, Perilli M, Yassaa N (2017a) Chemical composition of particulate organic matter at industrial, university and forest areas located in Bouira province, Algeria. Atmos Pollut Res. 8:474-482.

An Approach to Assess the Biological Effects of Semi-Volatile Organic Chemicals in Indoor Air

A. K. Halse[1]*, E. Longhin[1], P. Bohlin-Nizzetto[1], E. Mariussen[2], A.R. Borgen[1], N. Warner[3]

[1]Norwegian Institute for Air Researh (NILU)
[2]Norwegian Institute of Public Heath (NIPH)
[3]Thermo Fisher Scientific (Bremen)

akh@nilu.no

Air pollution is known as a main cause for the onset of adverse health outcomes in Europe. As we spend as much as up to 90 % of our time in indoor environment, indoor air quality is of crucial importance for our health. The various materials and products present in indoor environments contain a wide range of organic pollutants, e.g., halogenated flame retardants, bisphenols, chlorinated paraffins, which may, over time, be emitted from the materials to indoor air. Some of these compounds are known to be persistent, bio-accumulative, and toxic, with reported endocrine disruptive potential, and capability to increase reactive oxygen species (ROS) production and oxidative stress, finally leading to genotoxicity. In this study we collected air samples from different indoor sites, analyzed the levels of various organic pollutants and investigated their potential to induce endocrine disrupting potential and alter cellular ROS levels. A selection of air sampling devices was co-deployed at five indoor locations in Tromsø, of which three public (the high north Research Centre for Climate and the Environment (Fram Centre)) and two residential locations. Two types of commonly used passive air samplers (PAS) were deployed: i) XAD-PAS and ii) polyurethane foam (PUF)-PAS, together with a low volume air sampler using ABN as adsorbent. Duplicate samplers were deployed side by side at all locations, to enable chemical analysis and toxicity testing on the same type of air (same exposure) in parallel. Targeted chemical analysis of chlorinated paraffins (SCCP and MCCP), novel flame retardants, together with polybrominated flameretardants (PBDE) and bisphenols was performed, along with toxicity assays to assess the estrogenic activity with U2-OS CALUX (BDS-company) assay, and ROS formation by the DCFH-DA assay. Interestingly, samples from different indoor environments elicited diverse responses on endocrine disruption activity and ROS formation, suggesting that different chemicals and biological mechanisms are involved in the endpoints investigated. Correlation analyses were performed between the results of the chemical analysis and the toxicity assays. Based on these analyses further investigations can be selected to identify the chemicals responsible for the observed biological responses.

Assessing a Mobile Urban Street Cleaning Activity

A. Brunelli[1]*, S. Breda[2], P. Scanferla[2], L. Calgaro[1], A. Marcomini[1], E. Badetti[1]

[1]Ca' Foscari University of Venice, DAIS - Department of Environmental Sciences, Informatics and Statistics, Venice, Italy
[2]Fondazione Università Ca' Foscari Venezia, Venice, Italy

andrea.brunelli@unive.it

An experimental methodology to assess the human exposure of a street cleaning service, performed by a worker handling a leaf blower followed by a water-flushing sweeper, was developed. The sampling campaign was achieved by considering data from road dust (RD), personal air sampling and particulate matter detector. The experimental design allowed to obtain qualitative and quantitative information on the chemical composition of RD, the size and chemical composition of potentially inhalable particles suspended during the street cleaning activity, as well as the duration of the particles' suspension effect. The methodology showed: i) the compliance with the occupational exposure threshold values for the total inhalable dust and with the occupational exposure limit values according to national-international regulatory approaches for PAH and inorganic elements; ii) a good agreement of the metals concentrations from the RD (i.e., Ca, Mg, K, Fe, Al and Na) with those from the material collected by the personal air sampler, highlighting the negligible effect of the investigated sweeping activity compared to the material already present on the road; iii) a similar pattern of inorganic elements within the three different monitoring areas; iv) a "dust wave" effect detected by the particle counter lasting no more than 2 min. The results showed that performing the urban sweeping activity in the early mornings, when there is a low PM10-PM2.5 average concentration, low traffic intensity, and the almost absence of passers-by, lead to a low probability of citizens' exposure.

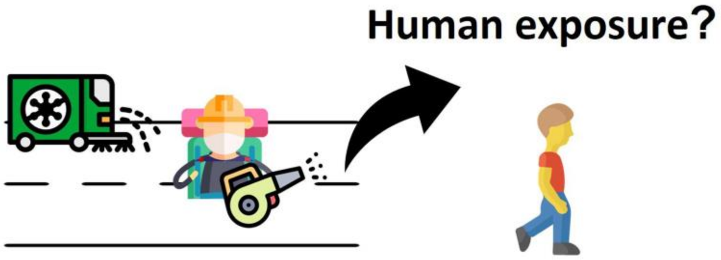


Figure 1 - Experimental methodology to assess the human exposure of a street cleaning service

Indoor air Pollution in Central India: Past, Current and Future Perspectives

N. K. Jaiswal[1]*

[1]School of Engineering and Research, ITM University Raipur CG

nitinkjaiswal@hotmail.com

Air pollution is known to cause local problems including damage to materials, and human health, and sometimes creates zero visibility among a particular region as well as on geographical and global scales such as ozone depletion and climate change. According to a WHO report, Air pollution (both outdoor and indoor air pollution) alone kills over around 4.2 million every year: 90% of it in low and middle-income countries where wood, agricultural residues, and charcoal are the primary source of domestic energy (WHO, 2014). In the central part of India, fuels i.e., wood, charcoal, dung, crop residue, LPG, kerosene, etc. are used for energy generation in houses while incense materials and mosquito repelling coils are frequently fumed for ceremonial purposes, and insects' protection, respectively (Jaiswal et al., 2019). The indoor air becomes contaminated due to the incomplete combustion of hydrocarbons and generates heavy smoke with a complex mixture of particulate matter, black carbon, organic carbon, polycyclic aromatic hydrocarbon, trace elements, etc. The mass concentration of PM10 in an indoor environment ranged from 464-15767 µg m-3. Black carbon, organic carbon, polycyclic aromatic hydrocarbon in Particulate matter, and their correlations are discussed.

References

WHO 2014. http: //www.who.int/mediacentre/news/releases/2014air-pollution/en/

N. K. Jaiswal et al., "Winter Particulate Pollution over Raipur, India," J Hazard Toxic Radioact Waste, vol. 23, no. 4, 2019, doi: 10.1061/(ASCE)HZ.2153-5515.0000444.)

Passive Air Sampling of Volatile Methylsiloxanes, Synthetic Musks and Pahs in Latin America

D. Armada[1,3], F. Sánchez-Soberón[1,4], M. Llompart[3], M. Celeiro[3], A. Azevedo[5], G. Fillmann[5], N. Ratola[1,2]*

[1]University of Porto, LEPABE - Faculty of Engineering, 4200-465 Porto, Portugal
[2]University of Porto, ALiCE - Faculty of Engineering, 4200-465 Porto, Portugal
[3]CRETUS - University of Santiago de Compostela, E-15782, Spain
[4]Institute of Health Carlos III, 28220, Majadahonda, Madrid, Spain
[5]Instituto de Oceanografia, Universidade Federal do Rio Grande, 96201-900 Rio Grande, RS, Brazil

nrneto@fe.up.pt

Air pollution is one of the biggest problems due to the effects on human health and environment (Kampa and Castanas, 2008). According to the Panamerican World Health Organization (PAHO/WHO), the Americas are regions where air pollution is the main public health hazard leading to an increase in the risk of respiratory and heart diseases or lung cancer, among others, especially in vulnerable people (children, elderly and women) (PAHO, 2022). Recently, the European Environmental Agency (EEA) indicated that atmospheric pollution causes around 1% of all cancer cases in Europe and is the source of about 2% of all cancer deaths (EEA, 2022). In the present study, chemicals of emerging concern such as volatile methyl siloxanes (VMSs) and synthetic musks, and polycylic aromatic hydrocarbons (PAHs) were studied in air samples collected in different Latin American countries, taking advantage of the Latin American Passive Atmospheric Sampling Network (LAPAN). To this objective, a simple analytical methodology based on the precepts of green analytical chemistry, was developed to be able to determine 33 analytes of interest belonging to the above-mentioned families. A solid-liquid extraction was selected as extraction technique to isolate the target substances prior to an analysis by gas chromatography coupled to mass spectrometry. Some preliminary experiments were carried out to optimize the sample preparation step, and the method was validated in terms of linearity, sensitivity, precision, and accuracy, obtaining satisfactory results for most of the studied compounds. Once validated, 42 air samples collected in 9 Latin American countries were analyzed. In these samples, compounds from all families were detected, including carcinogenic, priority pollutants compounds, bioaccumnulative, persistent and toxic, among others harmful properties. Differences in the chemicals occurrence and concentration were related to the land-use profile with the higher concentrations associated to suburban and urban areas. Finally, analysis of variance and principal component analysis were performed in an attempt to find chemical markers to identify the possible geographical or environmental origin of the analysed samples and possibly identify the main emission sources.

This work was financially supported by: (i) LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE – Laboratory for Process Engineering, Environment, Biotechnology and Energy), funded by national funds through FCT/MCTES (PIDDAC).

References

EEA (2022) 'Exposure to pollution causes 10% of all cancer cases in Europe'. European Environment Agency. https://www.eea.europa.eu/highlights/pollution-and-cancer (accessed 2022-07-07)

Kampa, M. et al. (2008) 'Human health effects of air pollution', Environmental Pollution, 151, p. 362-367. doi: 10.1016/j.envpol.2007.06.012

PAHO (2022) 'Air Quality - PAHO/WHO', Pan American Health Organization. https://www.paho.org/en/topics/air-quality (accessed 2022-07-07)

Principles and Best Practices for Measurements and Data Interpretation of Pesticides in Air

S. Mayer[1], D.M. Brown[2], A. Terry[2], J. Rüdiger[3], T. Hoffmann[4], M. Brüggemann[1*]

[1]Bayer AG, Crop Science Division, Alfred Nobel Strasse 50, 40789 Monheim am Rhein, Germany
[2]Cambridge Environmental Assessments, RSK ADAS Ltd., Battlegate Road, Boxworth, CB23 4NN, United Kingdom
[3]Air Monitoring Network, German Environment Agency, 63225 Langen, Germany
[4]Chemistry Department, Johannes Gutenberg University, 55128 Mainz, Germany

martin.brueggemann@bayer.com

Pesticides are essential in maintaining productivity in modern farming as part of an integrated approach to pest, weed and disease management. During their application, they can be emitted into the atmosphere by volatilisation, spray drift and by wind erosion of particles on which the pesticide is sorbed (FOCUS, 2008). As the atmosphere represents the largest and most dynamic environmental compartment, pesticides can be transported far from their application areas. Since there are only limited regulations for pesticides in ambient air and their potential impact on human health and the environment is getting more and more attention, there is a growing interest in monitoring for their presence and concentrations in the atmosphere.

Pesticides in air have been sampled using numerous methods and approaches, and data are often generated with a range of objectives in mind. This lack of standardisation has created a diverse array of information that needs to be understood and better organised to improve future air monitoring programmes and to analyse and interpret previously collected data appropriately.

This study presents the results of an in-depth review of the different approaches used to measure and interpret pesticides in air. It highlights the major differences in these approaches and how they influence both the setup of studies and the interpretation of data. The work also introduces a number of principles (study setup, data quality assessment, data interpretation, etc.) that are expected to form the basis of best practices for pesticide detection and measurement in air. It is hoped that these principles will inform both data generators (pesticide air sampling practitioners) and data users during their work and initiate improvements to the standardisation of monitoring pesticides in air.

References

FOCUS (2008) “Pesticides in Air: Considerations for Exposure Assessment”. Report of the FOCUS Working Group on Pesticides in Air, EC Document Reference SANCO/10553/2006 Rev 2 June 2008. 327 pp.

Long-Range Atmospheric Transport of Currently-Used Pesticides Over Europe

L. Mayer[1]*, P. Šenk[1], P. Přibilová[1], P. Kukučka[1], A. Durand[2], S. Ravier[2], J. Klánová[1], G. Lammel[1 3], C. Degrendele[1 2] and 59 more co-authors representing monitoring networks

[1]Masaryk University, RECETOX, Faculty of Science, Kotlarska 2, 61137, Brno, Czech Republic
[2]Aix-Marseille University, CNRS, LCE, 13003 Marseille, France
[3]Max Planck Institute for Chemistry, Multiphase Chemistry Dept., Hahn-Meitner-Weg 1, 55128 Mainz, Germany

ludovic.mayer@recetox.muni.cz

Currently-used pesticides (CUPs) are semi-volatile organic compounds that have been widely used in agriculture over the last 30 years (FAO, 2022). Several CUPs previously had been detected in air of remote locations such as in the Arctic, showcasing their potential for long-range atmospheric transport (Balmer et al., 2019; Röhler et al., 2020). However, for most CUPs, their potential for long-range atmospheric transport has never been investigated. The aims of this study are (i) to report on the atmospheric levels of CUPs on the regional European scale and (ii) to identify the CUPs prone to long-range atmospheric transport.

To this end, a sampling campaign took place simultaneously at 16 rural, 4 coastal, 6 mountain and 3 polar sites in 17 European countries in spring 2020. About 120 samples were collected using active air samplers and were extracted and analysed by LC- and GC-MS×MS. In total, 76 CUPs were analysed, including 35 herbicides, 22 insecticides and 19 fungicides.

Among the 76 CUPs targeted, 58 were quantified in the European atmosphere. In particular, six fungicides, six herbicides and one insecticide, which are all, except one, authorized for agricultural use in Europe, were found in more than 50% of the sampling sites. Overall, 22 out of the 76 CUPs investigated in this study were identified as prone to long-range atmospheric transport. Indeed, at the polar sites, 19 CUPs were quantified in air. In addition, in the five samples which collected free tropospheric air at mountain sites, 14 CUPs were quantified, of which 11 that were also found at the polar sites. Out of the 22 CUPs identified as prone to long-range atmospheric transport, 15 are currently authorized for agricultural use in Europe, suggesting a need to revise the registration criteria in terms of long-range atmospheric transport.

References

Balmer, J.E. et al. (2019) ‘Levels and trends of current-use pesticides (CUPs) in the arctic: An updated review, 2010–2018’, Emerging Contaminants, 5, pp. 70–88. doi:10.1016/j.emcon.2019.02.002.

FAO (2022) FAOSTAT: Pesticides use. URL: http://www.fao.org/faostat/en/#data/RP.

Röhler, L. et al. (2020) ‘Non-target and suspect characterisation of organic contaminants in Arctic air - Part 2: Application of a new tool for identification and prioritisation of chemicals of emerging Arctic concern in air’, Atmospheric Chemistry and Physics, 20(14), pp. 9031–9049. doi:10.5194/acp-20-9031-2020.

Improving Knowledge on the Atmospheric Fate of Current-Use Pesticides: A Case Study in Central Europe

L. Mayer[1]*, G. Lammel[1,2], P. Šenk[1], J. Vinkler[1], M. Šudoma[1], P. Přibylová[1] and C. Degrendele[1,3]

[1]RECETOX, Faculty of Science, Masaryk University, Kotlarska 2, 61137, Brno, Czech Republic
[2]Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany
[3]Aix-Marseille University, Laboratory of Chemistry and Environment (LCE), CNRS, 13003 Marseille, France

ludovic.mayer@recetox.muni.cz

After the ban of organochlorine pesticides (OCPs) in the 1970s, current-use pesticides (CUPs) were considered as an environmentally friendly replacement alternative due to their degradability and to their lower toxicity for non-target organisms compared to OCPs. However, several studies have shown that several CUPs can pose a serious threat to the environment and health (Kim et al., 2017). In particular, despite the increase in the global use of CUPs over the last 30 years, the knowledge on their atmospheric fate, and the key processes governing it has remained rather scarce. The aims of this study were to fill this gap by characterizing (i) the particle size distribution of CUPs, (ii) their gas-particle partitioning and (iii) their air-surface exchange (volatilisation, deposition).

For this, a sampling campaign occurred during the main pesticide application season in April 2020 at an urban site located in Brno, in the Czech Republic. Firstly, to assess the gas-particle partitioning of CUPs, a combination of high- and low-volume air samplers were used with different sampling configuration in order to evaluate the importance of sampling artefacts on this partitioning. The particle size distribution of CUPs was assessed using a cascade impactor separating particles onto six size fractions. In order to assess the gaseous air-surface exchange, a soil fugacity sampler was deployed (Cabrerizo et al., 2009). In addition, the deposition of CUPs (dry, wet and bulk) was also determined. In total, 50 samples were collected, extracted with methanol and 53 pesticides were analysed by means of high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS).

Overall, out of the 53 pesticides targeted, 41 pesticides were quantified in at least one of the sample collected. Some CUPs were found to be only present in the particulate phase (e.g., fenpropimorph, fenpropidin, spiroxamine, …) or in the gaseous phase (e.g., prosulfocarb, pendimethalin, S-metolachlor), whereas some CUPs were found to be partitioning between the two phases (e.g., 2,4-D, mecoprop, terbuthylazine). Surprisingly, the majority of CUPs were present on particles larger than 1 µm, which suggests a lower potential for long-range atmospheric transport due to more efficient wet and dry deposition for these particle sizes and a lower potential to reach the deepest regions of the respiratory system. Finally, 24, 28 and 35 CUPs were quantified in the dry, wet and bulk deposition samples highlighting the importance of this process towards the contamination of surfaces in the city.

References

Cabrerizo, A., Dachs, J. and Barceló, D. (2009) ‘Development of a soil fugacity sampler for determination of air - soil partitioning of persistent organic pollutants under field-controlled conditions’, Environmental Science and Technology, 43(21), pp. 8257–8263. doi:10.1021/es9020525.

Kim, K.H., Kabir, E. and Jahan, S.A. (2017) ‘Exposure to pesticides and the associated human health effects’, Science of the Total Environment. Elsevier B.V., pp. 525–535. doi:10.1016/j.scitotenv.2016.09.009.

Residential Contamination by Agricultural Pesticides in the Bordeaux Wine Region

R. Teysseire[1,2]* A. Roudil[2], E. Barron[3], C. Bedos[4], H. Budzinski[3], A. Chazeaubeny[3], K. Le Menach[3], P. Pardon[3], I. Baldi[1,2] and F. Delva[1,2]

[1]University of Bordeaux, Bordeaux Population Health Research Center, Inserm UMR1219, 33000 Bordeaux, France
[2]Bordeaux Hospital, Department of Occupational and Environmental Medicine, 33000 Bordeaux, France
[3]University of Bordeaux, CNRS, UMR5805 EPOC-LPTC, 33400 Talence, France
[4]Université Paris-Saclay, INRAE, AgroParisTech, UMR ECOSYS, 91120 Palaiseau, France

raphaelle.teysseire@chu-bordeaux.fr

Pesticides emitted into the atmosphere during field applications (spray drift) but also after treatments (volatilization) are likely to reach residential areas. Grapevine is one of the most treated crops in France, with about 20 treatments per year (Simonovici, 2019). Vineyards also have the particularity of being closely intertwined with residential areas (Guilpart et al., 2022). To assess residential contamination by fungicides applied to vineyards, we conducted an observational measurement study in the Bordeaux wine region.

METHODS

Indoor and outdoor surface wipes were collected during the summers of 2020 and 2021 in 31 homes bordering vineyards (n=986 samples) and in two homes located 5 and 25 km from the vineyards (n=17 samples). Wipe samples were ultrasonically extracted with acetonitrile. Final extracts were analyzed by LC/MS/MS or GC/MS/MS using the multiple reaction monitoring (MRM) mode. Eight fungicides were selected because of their used on grapevines: benalaxyl, boscalid, cyflufenamide, cymoxanil, folpel, pyraclostrobin, tebuconazole, trifloxystrobin (no domestic use except tebuconazole). The limits of quantification per sample ranged from 0.02 ng for trifloxystrobin to 5 ng for folpel. A questionnaire was used to collect data related to the surfaces.

RESULTS

Inside homes near vineyards, trifloxystrobin, tebuconazole and cyflufenamide were quantified in more than 90% of the surface samples, while the other fungicides were found less frequently (from 20% for cymoxanil to 68% for boscalid), with median surface loadings (SLs) of pesticides ranging from 5 ng/m^2 for pyraclostrobin to 469 ng/m^2 for folpel (n=706 samples). Outdoors (n=280 samples), median SLs ranged from 0.8 ng/m^2 for pyraclostrobin to 422 ng/m^2 for folpel. For all pesticides, median SLs were higher indoors than outdoors and the highest median SLs were found in the main entrance. The lowest indoor SLs were found for floor samples, while the highest concentrations were measured on high horizontal dusted surfaces. Median SLs tended to decrease with a recent cleaning. For most pesticides, the highest median SLs were found on surfaces cleaned by sweeping or wiping and the lowest on vacuumed surfaces. In homes located away from fields, the highest median SLs were found for folpel (134 ng/m^2), whereas cymoxanil was never quantified. For all pesticides, median SLs were lower than in homes located near vineyards.

CONCLUSION

Analytical performances influenced pesticide detection frequencies and SLs in the samples. Other factors such as the local use of pesticides, the type of surface sampled, the room itself, and the cleaning habits appear to influence indoor pesticide SLs. These initial descriptive results need to be consolidated by further analysis, but they confirm the residential contamination by agricultural pesticides and could be used to identify measures to reduce pesticide exposure in rural populations.

References

Guilpart, N. et al. (2022) ‘How much agricultural land is there close to residential areas? An assessment at the national scale in France’, Building and Environment, 226, p. 109662. doi:10.1016/j.buildenv.2022.109662.

Simonovici, M. (2019) ‘Enquête Pratiques phytosanitaires en viticulture en 2016 - Nombre de traitements et indicateurs de fréquence de traitement’, Agreste Les Dossiers, 2, p. 50.

Assessment of Atmospheric Organochlorine Pesticides over a Decade in Spain (2008-2019)

J. Muñoz-Arnanz[1], P. Colomer-Vidal[1], M. Ros[1], A. Vicente [1], C. Salcedo[1], A. Bartalini[1], B. Jiménez[1]*

[1]Institute of Organic Chemistry (IQOG-CSIC), Juan de la Cierva 3, 28006, Madrid, Spain

bjimenez@iqog.csic.es

Over the past 30 years, both national and international regulations have been implemented to protect the human health and the environment from toxic chemicals such as persistent organic pollutants (POPs). Awareness of the risks that POPs pose worldwide led the international community to enact the Stockholm Convention (SC) in 2001 under the United Nations Environment Program. A continuous and long term monitoring of POPs is essential in determining the effectiveness of the SC. The atmosphere acts as crucial route of transport of these pollutants, so air monitoring represents an important tool to contribute to this evaluation. In this study, we evaluate data on chlorinated pesticides (HCHs, PeCB, HCB, DDTs and Endosulfan) in air samples, from 2008 to 2019, obtained every three months by means of passive samplers.

Despite the wide range of concentrations measured for most contaminants, based on median concentrations, a common pattern of relative abundance could be observed: HCB ≈ ∑HCHs > ∑DDTs >> ∑Endosulfan > PeCB. Median concentrations in background locations (EMEP stations) varied according to HCB > ∑HCHs > ∑DDTs > ∑Endosulfan > PeCB, while in urban locations ∑HCHs > HCB ≈ ∑DDTs >> ∑Endosulfan > PeCB.

In general, statistically significant (Mann-Whitney, $p<0.05$) higher levels of total pesticides were found in urban than in background locations, which underpinned the role of the former as main source for most target pesticides (∑DDTs, and ∑HCHs). Conversely, no significant differences could be found for HCB, ∑Endosulfan and PeCB between background and urban locations. Among urban locations, Barcelona exhibited the highest median concentration of total pesticides (155 pg/m3) and Huelva the lowest (55.8 pg/m3), although this trend was not uniform for all families of pesticides. Regarding background stations, Cap de Creus exhibited the highest median concentration of total pesticides (127 pg/m3) and O Saviñao the lowest (37.1 pg/m3).

Significant seasonal variations were detected for the study pesticides. These patterns can be generally explained according to seasonal variations in pesticide sources as well as based on the environmental behavior of the compounds according to their temperature-dependent physicochemical properties. Seasonal variations were statistically significant (Kruskal-Wallis, $p<0.05$) for all families except for ∑HCHs.

Global pesticide concentrations measured in Spain from 2008 to 2019 showed a non significant decreasing trend. This trend was neither homogeneous in the entire monitoring program, nor for the whole collection of target pesticides. While only ∑Endosulfan exhibited statistically significant (Spearman, $p<0.05$) decreases in its concentration, air levels of PeCB, HCB, DDTs and HCHs showed no clear trends. Given the absence of a clear decreasing pattern, it seems necessary to widen the number of monitoring years to crystalize the expected decline of airborne chlorinated pesticides and to better understand the influence of re-emissions, ongoing sources, and long-range atmospheric transport.

New Insights into Pesticide Droplets Dispersion Modelling with a Coupled Lagrangian Stochastic and Second Order Turbulence Model. Comparison with a New French Dispersion Dataset

B. Loubet[1]*, M. R. Vuolo[2], C. Bedos[1], M. Djoury[3], M. Voltz[3], F. Verpont[4], Y. Hudebine[4], B. Perriot[5],
A. Verges[6], J.-P. Douzals[7], M. Sellam[8]

[1]Univ. Paris-Saclay, ECOSYS, INRAE - AgroParisTech - France
[2]Uptofarm s.r.l. Italy
[3] Univ. Montpellier-INRAE-IRD-Institut Agro, LISAH, France
[4]CTIFL Lanxade, France
[5]ARVALIS-Institut du végétal Boigneville, France
[6]IFV Montpelier, France
[7]ITAP, INRAE-Institut Agro, France
[8]ACTA Paris, France

Benjamin.Loubet@inrae.fr

Pesticides usage has been expanding since the 1950s, levelling to around 4 Mt since 2010 (FAO, 2020). In 2018, pesticides use consisted in 30% herbicides, 13% fungicides, 10% insecticides and 45% others, worldwide 1. Asia was at that time the largest consumer (52%), before the Americas (32%) and Europe (12%), while Africa and Oceania only consumed 2% each of the global production. Their usage is now known for decades to produce adverse effects on both human and environmental health (WHO, 2019 and references therein). Therefore, controlling the spread of pesticides in the environment is a key question for scientists. Measuring pesticide spread is essential but still challenging due the required experimental setups and the costs of multiplying measurements. Models are therefore of great interest to investigate pesticide fate in the environment.

A Lagrangian stochastic dispersion model has been coupled to a k-epsilon atmospheric turbulence model to reproduce pesticides droplets dispersion after spreading in the field. The model takes as input the pesticides droplets initial velocity and diameter distribution, as well as the turbulence induced by the application and mimic the physical processes of dispersion in the atmosphere and in the canopy, droplets evaporation and deposition by impaction and settling to the ground and on the vegetation. The model was applied to the three main types of agricultural sectors: annual crops, vineyard and orchards, by adapting the representation of the vegetation characteristics (leaf area density and heights) and application techniques (by adjusting droplets initial velocity and diameter distributions, as well as applicator turbulence). The model outputs the droplets deposition in and downwind from the applied field, but also the concentration in the atmosphere in the modelled domain.

In this study the sensitivity of the modelled concentration and deposition against droplet initial diameter and velocity, crop characteristics and turbulence, is presented. The effect of hedges on droplet dispersion and deposition is also studied. The model is also tested against a very new dataset gathered in 2021 and 2022 in France for the three main agricultural sectors. Preliminary results show a good qualitative agreement between the measured and modelled droplet deposition, but some discrepancies in the quantitative values. This, together with the sensitivity analysis suggests that the particle initial diameter and velocity distributions are key parameters that are not well known and need further attention in future experiments. This study stresses the need for measurements of droplets size distributions in ambient air downwind from the application, together with the turbulence characteristics.

References

FAO. Inputs (ed Food and Agriculture Organization of the United States (FAO)) (Food and Agriculture Organization of the United States (FAO), 2020).

WHO, 2019: WHO recommended classification of pesticides by hazard and guidelines to classification, 2019 edition.

Formation of Ozone and Secondary Organic Aerosol from the Atmospheric Degradation of Insecticides Mixed with Terpenes Emitted by Citrus and Vineyard Crops

A. Muñoz[1]* A, E. Borrás[1], T. Vera M. Ródenas[1], T. Gómez[1], H. Calvete-Sogo[1]

[1]Fundación CEAM. EUPHORE, Lab, C/ Charles R. Darwin 14, 46980, Paterna (Valencia), Spain

munyozama@gva.es

Pesticides are key elements in the development of modern cropping systems. However, only a fraction of them reaches the target plant surfaces while the rest remains in the surrounding areas contaminating water, soils, and air. Complex reactions can take place in the presence of pesticides in the atmosphere. Those reactions depend on the atmospheric conditions and on the presence of other pollutants. Commercial pesticides include in their formulation the so called “inert” ingredients from the point of view of activity against plagues, but not from the point of view of atmospheric reactivity. In addition, crop vegetation can release several biogenic organic compounds (BVOCs) to the atmosphere that can also be transformed into secondary pollutants.

In this work, we studied the atmospheric chemical behavior of a commercial insecticide, Karate Zeon, which contains lambda-Cyhalothrin as an active substance, as well as other insecticides commonly used in the Mediterranean agriculture, in the presence of selected BVOCs emitted by citrus and vineyard crops.

We used the EUropean PHOtoREactor (EUPHORE) to investigate the atmospheric reactions and formation of secondary products of insecticides and their interaction with mixtures of selected BVOCs, mainly monoterpenes. EUPHORE is a high-volume (200 m3) atmospheric outdoor simulation chamber equipped with outstanding equipment for the measurement of gas and particulate phases in air. Different types of experiments have been carried out, including photolysis using natural sunlight at different VOC/NOx ratios in order to simulate typical rural conditions, and experiments in dark conditions with ozone (O3).

Significant secondary organic aerosol (SOA) formation was observed during the photolysis or reaction with ozone in the presence of BVOCs, which was higher than the sum of the production of SOA from the compounds by separate. The highest values were obtained when a mixture of karate zeon and vineyard BVOCs was tested. On the other hand, we also studied the formation of O3 in the photolysis experiments. In this case, the highest O3 values were obtained from the mixture of citrus BVOCs and karate zeon.

In summary, atmospheric reactions of BVOCs emitted by crops lead to the formation of secondary pollutants. This formation can be increased when pesticides are used. The results of our study will allow to better understand the chemistry involved in the use of pesticides and to make a more rational use of them.

Acknowledgement
This research has been supported by the European Commission LIFE Programme (PERFECT LIFE: LIFE17 ENV/ES/000205)

References

Borrás et al., 2017. Sci.Tot.Environ. 579, 1-9.

Muñoz et al., 2023 Atmospheric Environment 295 119541.

Comparative Analysis of Drift in Air Between Conventional and Optimized Application of Pesticides

E. Borrás [1], A. Muñoz[1]*, H. Calvete-Sogo[1], T. Vera[1], M. Ródenas[1], T. Gómez[1], C. Coscollá[2], E. Fuentes[2], A. López[2], C. Garcerá[3], P. Chueca[3]

[1]Fundación CEAM. EUPHORE lab, C/ Charles R. Darwin 14, 46980, Paterna (Valencia), Spain
[2]Foundation for the Promotion of Health and Biomedical Research in the Valencia Region, FISABIO-Public Health, 21, Avenida Catalunya, 46020 Valencia, Spain
[3]Centro de Agroingeniería, Instituto Valenciano de Investigaciones Agrarias (IVIA), CV-315, Km 10.7, Moncada, 46113 Valencia, Spain

munyozama@gva.es

Pesticides constitute fundamental components in the advancement of modern agricultural practices. Nonetheless, a mere fraction of these substances effectively reaches the plant surfaces, while the remainder spreads their surroundings, inducing contamination of water, soil, and air. Furthermore, the composition of commercial pesticides includes “inert” ingredients that may lead to numerous chemical reactions. To mitigate the effects of this contamination and optimize the use of pesticides in crops, proper tools and methods must be used in their application.

The present study presents a comparative analysis of pesticide drift in air between conventional and optimized applications, the latter based on the use of diverse tools optimized in the LIFE-PERFECT project to mitigate the use of pesticides and their subsequent diffusion in the atmosphere. The utilized optimized tools are Optimal Volume Rate Adjustment (OVRA) and Spray Drift Reducing Tools and Techniques (SDRTs) [1]. Our findings are based on direct measurements of losses obtained from gas active samplers and are derived from citrus field trials conducted between September 2020 and September 2021. Lambda-cyhalothrin, the active ingredient of the commercial pesticide Karate Zeon, was the selected active substance model used for the tests in our study.

Two automated devices were developed by the CEAM team to sample various organic compounds, including coadjuvants from the Karate Zeon formula, as well as other compounds emitted by the crops during pesticide application. The systems were placed in the orchard following different configurations: downwind and upwind and also at both sides of the application swath. While charcoal cartridges are capable of measuring a wide range of air pollutants, this study focused specifically on compounds previously identified at the EUPHORE Photo-Reactor[2] [3] as being released into the atmosphere by the studied pesticide. Additionally, organic compounds emitted by citrus and vineyards were included in the study. The concentrations of the three categories of compounds examined (HVOCs, Biogenics, and Karate Zeon Coadjuvants) were found to be lower in the optimized treatment than in the conventional one. Results indicated a reduction of 37% for HVOCs, 78% for Biogenics, and 57% for Karate Zeon Coadjuvants emissions in the optimized application, as compared to the conventional method. These findings clearly demonstrate the effectiveness of the optimized treatment in reducing pollutant emissions during pesticide application.

References

https://perfectlifeproject.eu/perfect-tools.

Muñoz et al., 2023 Atmospheric Environment 295 119541.

Abstract submitted to ICEE. Muñoz et al. 2023 “Formation of ozone and secondary organic aerosol from the atmospheric degradation of insecticides mixed with terpenes emitted by citrus and vineyard crops".

Long-Range Atmospheric Transport of Current-Use Plant Protection Products (PPPs) through the Analysis of Sediment Cores from Alpine Lakes

S. Cirelli[1]*, E. Schaad[1], M. Grosjean[1], A. C. Chiaia-Hernández R.[1]

[1]University of Bern, Institute of Geography & Oeschger Center for Climate Change Research, Hallerstrasse 12, 3012, Bern, Switzerland

sergio.cirelli@giub.unibe.ch

The processes governing the transportation of current-use Plant Protection Products (PPPs) through the atmosphere and their potential impact on health and the environment are not yet fully understood. Although current-use PPPs are designed to degrade rapidly in the environment, several studies have shown that some PPPs can be quite persistent in the atmosphere. For example, PPPs have been detected in remote regions in the arctic (Hageman et al., 2006). These areas are not in direct contact with potential contamination sources, therefore, some atmospheric processes must play an important role. Moreover, several degradation reactions during PPPs' residence time in the atmosphere might result in the formation of transformation products (TPs) which can be more toxic and persistent than the parent compounds (Anagnostopoulou et al., 2022). Thus, it is surprising that until now there is still very little information on the fate of PPPs and their TPs in the atmospheric compartment.

Recent studies have exploited innovative techniques for the detection and quantification of PPPs in complex environmental matrices such as sediments (Chiaia-Hernández et al., 2020). This study has shown that sediment cores can provide an accurate historical record of PPPs concentration since the first emissions of these compounds into the environment in the mid-20th century. The detected PPPs are particularly stable in this matrix due to the anoxic conditions in the hypolimnion and surface sediments.

In this study, we use an innovative and original approach to investigate the long-range atmospheric transport of PPPs and their TPs in the environment by creating and analyzing concentration time series of PPPs in sediment cores from Alpine lakes. Sediment cores from three lakes at different distances and along an elevation gradient from the Swiss Plateau are investigated. The selected lakes are in areas with high precipitation rates, relatively constant sedimentation rates, and are not in direct contact with potential contamination sources from agricultural or urban areas. Thus, any contamination detected in the sediment will derive from atmospheric transport and deposition. Concentration time series of PPPs, TPs, and unknown anthropogenic contaminants over the past 100 years are constructed. Furthermore, clusters of the detected compounds for data exploration and visualization are combined with sedimentological data to contextualize the findings. Liquid chromatography and gas chromatography combined with a triple quadrupole (QqQ) unit and high-resolution mass spectrometer are used to sort known and unknown contaminants with identical time series to differentiate anthropogenic and non-anthropogenic compounds. Concentrations of PPPs obtained from different lakes will disclose patterns of contamination due to increasing distance or elevation. The obtained patterns will help us to identify persistent and mobile compounds based on their ubiquitous presence in all lakes or by identifying their TPs among sediment cores.

This study will provide a fundamental building block to gain a comprehensive overview of how PPPs move and transform across the environment and their fate.

References

Anagnostopoulou, K. et al. (2022) 'Overarching issues on relevant pesticide transformation products in the aquatic environment: A review', Science of The Total Environment, 815, p. 152863.DOI: 10.1016/j.scitotenv.2021.152863.

Chiaia-Hernández, A.C. et al. (2020) 'High-Resolution Historical Record of Plant Protection Product Deposition Documented by Target and Nontarget Trend Analysis in a Swiss Lake under Anthropogenic Pressure', Environmental Science & Technology, 54(20), pp. 13090–13100. DOI: 10.1021/acs.est.0c04842.

Hageman, K.J. et al. (2006) 'Atmospheric Deposition of Current-Use and Historic-Use Pesticides in Snow at National Parks in the Western United States', Environmental Science & Technology, 40(10), pp. 3174–3180. DOI: 10.1021/es060157c.

Pesticide Inhalation Exposure and Urinary Metabolites Risk Assessment using Conventional and Innovative Cropping Systems in Citrus and Vineyard Crops

E. Fuentes[1]*, A. López[1], P. Chueca[2], C. Garcerá[2], M. Grella[3], F. Gioelli[3], P. Maruco[3], A. Muñoz[4], H. Calvete-Sogo[4], E. Borrás[4], T. Vera[4], M. Ibáñez[5] and C. Coscollà[1]

[1]Foundation for the Promotion of Health and Biomedical Research in the Valencia Region, Valencia, Spain
[2]Instituto Valenciano de Investigaciones Agrarias (IVIA); Valencia, Spain
[3]Università degli Studi di Torino, Department of Agricultural, Forest and Food Sciences (DiSAFA), Grugliasco (TO), Italy
[4]d Fundación CEAM, Valencia, Spain
[5]University Jaume I, Research Institute for Pesticides Pesticides and Water; Castellò, Spain

fuentes_estfer@gva.es

A total of 350 000 tons of pesticide were sold to France, Spain, Italy and Germany during the period 2011-2020 which is considered the two thirds of total pesticide sales in the EU (EUROSTAT, 2022). These countries are known to be the main agricultural producers in the European Union (EU) and for this reason they are leaders in pesticide application to avoid crops infestations and diseases. However, exhaustive pesticide application results in pesticides human and environmental exposure that could produce human health risk and environmental pollution.

This work provides results in the frame of a European LIFE project, called Pesticide Reduction using Friendly and Environmentally Controlled Technologies (PERFECT LIFE) which aims to demonstrate the reduction of environmental pesticides contamination using optimized application techniques based on Optimal Volume Rate Adjustment tools (OVRA) and drift reducing tools (SDRT) (Perfect Life, 2023).

Lambda-cyhalothrin applications using conventional and optimized systems were performed in two types of crops (citrus and vineyards) and in two different European countries (Spain and Italy). During field trials air samplers and human volunteers (acting as applicators and bystanders) were directly exposed to this pesticide and two types of samples were collected: (i) air samples which were analysed by Gas Chromatography coupled to tandem Mass Spectrometry (GC-MS/MS); (ii) and urine samples, from which two target pesticide metabolites (CFMP and 3-PBA) were analysed using Liquid Chromatography coupled to tandem Mass Spectrometry (LC-MS/MS).

Obtained results were processed and human risk assessment of applicators and bystanders was performed. Human inhalation exposure provides Hazard Quotients (HQs) lower than one in all cases, which means that the exposed concentrations of pesticide in air do not pose a potential health risk. In the same line, pesticide metabolites in urine also provide HQs that do not indicate health risk. Nevertheless, calculated Hazard Quotients showed in most cases that lower health risk is provided when optimized application techniques are use. Bystanders inhalation exposure can be reduced around 80 % and 50% in citrus and vineyards, respectively, using OVRA and SDRT tools. Moreover, 3-PBA metabolite exposure is reduced in citrus field trails approximately 70% and 60% in applicators and bystanders respectively and in vineyard field trials around 30% and 60% in applicators and bystanders respectively, if low drift application techniques were used.

References

Statistics Explained article on agri-environmental indicator: consumption of pesticides, (EUROSTAT 2022). Available online: https://ec.europa.eu/eurostat/en/web/products-eurostat-news/-/ddn-20220502-1 (accessed on 24th March 2023).

Perfect Life "Pesticide Reduction using Friendly and Environmental Controlled Technologies". Available online: https://perfectlifeproject.eu (accessed on 24th March 2023).

Microplastics Detection Using Chemical Ionization MS With Multi-Scheme Chemical Ionization Inlet (MION)

J. Mikkilä[1], J. Mikkilä[1], J. Kontro[1], F. Partovi[1,2], H.J. Jost[1], E. Lattouf[1]*

[1]Karsa Ltd., A. I. Virtasen aukio 1, 00560 Helsinki, Finland
[2]Tampere University, Aerosol Physics Laboratory, Physics Unit, Faculty of Engineering and Natural Sciences, 33720 Tampere, Finland

elie.lattouf@karsa.fi

The process of Chemical Ionization (CI) involves using a chemical reagent to create ions that will charge a gaseous sample through ion-molecule reactions. This method is considered to be gentle and specific, but traditional CI and Electrospray Ionization have some drawbacks such as neutral reagent vapors/droplets that can negatively affect the sample chemistry and result in adverse matrix effects. However, the MION approach overcomes these limitations by using ion injection to allow only charged reagents to enter the sample flow and providing the ability to rapidly sample ions in both polarities. The system combines filters thermal desorption (TD), a MION source, and an orbitrap mass spectrometer (LTQ Velos pro) for substance identification. The aim of this work is to demonstrate that plastic compounds can be desorbed, ionized, and detected with Karsa TD-MION-Orbitrap setup without chromatographic separation.

Two methods were used for sample introduction to the system: polystyrene was in suspension in water and polypropylene in the form of solid beads. The first was introduced to the filters by injecting 2 µl of the solution and the second by rubbing the solid beads against the filters. The MION source was used with dibromomethane reagent gas leading to the formation of Br- reagents ions (Rissanen et al., 2019).

Results show that polystyrene and polypropylene containing samples are being desorbed, ionized and detected with TD-MION-Orbitrap setup. The filters have the potential to be used for collection of airborne plastic nanoparticles, and other applications.

References

M. P. Rissanen, et al., https://doi.org/10.5194/amt-12-6635-2019

Immobilised Carbon Nitride for the Photocatalytic Elimination of Psychoactive Pharmaceuticals

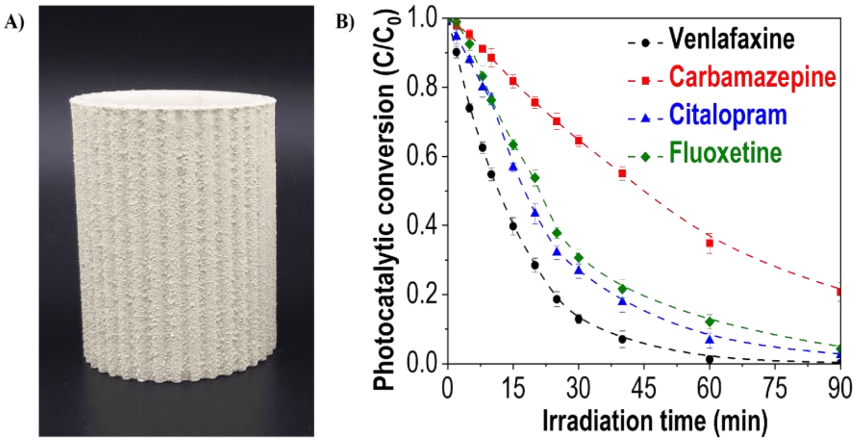
M. Peñas-Garzón[1,2], M.J. Sampaio[1,2], Y. Manrique[1,2], C.G. Silva[1,2], J.L. Faria[1,2]*

[1]University of Porto, LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2]University of Porto, ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

jlfaria@fe.up.pt

The increased consumption of psychoactive pharmaceuticals not only represents a serious public health problem but also directly affects the presence of these substances in surface waters, such as those reaching wastewater treatment plants (WWTPs) (Chaves et al., 2022). Furthermore, secondary biological treatment in WWTP can often not achieve conversion rates of these compounds above 50%. Among the advanced oxidation processes, heterogeneous photocatalysis can be considered a promising tertiary treatment for removing refractory pollutants in wastewater (Sampaio et al., 2023). In this study, carbon nitride (g-C_3N_4) was immobilized on cylindrical support prepared from poly(lactic acid), overcoming two common problems associated with photocatalysis: light-harvesting under visible light irradiation and easy recovery of the photocatalyst after the reaction. The supported photocatalyst (Figure A) showed remarkable photocatalytic performance for removing psychoactive drug mixtures, including commonly prescribed antidepressants such as venlafaxine, carbamazepine, citalopram, and fluoxetine under LEDs illumination (Figure B). The immobilized material exhibited modular character and good stability in terms of conversion rate and optical and electronic properties after consecutive reuse, thus providing a promising and straightforward set-and-use approach for removing challenging substances with an impact on aquatic ecosystems.

Work financially supported by LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC).



A) Picture of the immobilized g-C_3N_4; B) Removal of different psychoactive drugs using immobilized g-C_3N_4 (Initial concentration ≈ 2.0 µM each one)

References

Chaves, M.d.J.S. et al. (2022)'Updated knowledge (…) of pharmaceuticals and personal care products in global aquatic environments', Environmental Science: Processes & Impacts, 24(11), 1982-2008. Doi:10.1039/D2EM00132B

Sampaio,M.J., (2023) 'A technological approach using a metal-free immobilized photocatalyst for the removal of pharmaceutical substances from urban wastewaters', Chemical Engineering Journal, 459, 141617.

Influence of Bromide and pH Adjustment Strategies on Micropollutant Degradation in the UV/NH_2Cl and UV/$NHCl_2$ Processes

K. Wang[1]*, Y. Xiang[1,2] and C. Shang[1,3]

[1]The Hong Kong University of Science and Technology, Department of Civil and Environmental Engineering, Clear Water Bay, Kowloon, Hong Kong
[2]Université de Poitiers, Institut de Chimie des Milieux et des Matériaux IC2MP UMR 7285 CNRS, France
[3]Hong Kong Branch of Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, Hong Kong

kwangbo@connect.ust.hk

The UV/monochloramine (NH_2Cl) process is a promising advanced oxidation process (AOP) for degrading micropollutants that are poorly rejected by reverse osmosis (RO) in potable reuse. However, $NHCl_2$ may coexist with NH_2Cl in RO permeate due to the rejection of NH_4^+ and the decrease in pH. Consequently, the subsequent AOP consists of both the UV/NH_2Cl and UV/$NHCl_2$ processes. The radical generation in the UV/chloramine(s) process could be greatly affected by water matrix components (e.g., bromide) and operating strategies (e.g., pH adjustment with bicarbonate). In this study, the influence of bromide and two pH adjustment strategies using bicarbonate (i.e., one-step strategy: adjusting the pH of RO permeate directly to 8 prior to the AOP; and two-step strategy: adjusting the pH to 7 prior to the AOP and then to 8 after the AOP) on micropollutant degradation and radical generation were quantitatively evaluated in the UV/NH_2Cl and UV/$NHCl_2$ processes. Caffeine (CAF), N,N-diethyl-3-toluamide (DEET), and acetaminophen (ACP) were used as model micropollutants due to their varying reactivity towards reactive species. In the presence of 20 µM bromide, the steady-state concentration of HO• ([HO•]ss) decreased by 38% and 24% in the UV/NH_2Cl and UV/$NHCl_2$ processes, respectively, at pH 5.5 compared to that in the absence of bromide. The pseudo-first-order rate constant of CAF degradation by reactive haloamine species (RHS) and reactive nitrogen species (RNS) (k´RHS+RNS) decreased by 65% and 68% in the UV/NH_2Cl and UV/$NHCl_2$ processes, respectively. The significant decrease of [HO•]ss and k´RHS+RNS could be attributed to the shift in radical speciation from HO• and Cl• towards reactive bromine species (RBS), which are less reactive with CAF than HO• and Cl•. The changes of k´RHS+RNS of DEET in the presence of bromide followed a similar trend to that of CAF. The k´RHS+RNS of ACP, which is highly reactive with RBS, showed a 38% decrease in the UV/NH_2Cl process upon addition of bromide, while remained unchanged in the UV/$NHCl_2$ process. Additionally, the effect of pH adjustment strategies on micropollutant degradation in the two processes was investigated in the presence of bromide. Compared to the one-step strategy, the pseudo-first-order rate constant of CAF and DEET degradation increased by 26% and 19%, respectively, using the two-step strategy in the UV/NH_2Cl process, while that of ACP degradation decreased by 21%. This can be explained by the reduced scavenging effect of bicarbonate towards HO• and RHS by the two-step strategy, which hindered the generation of $CO_3^{\bullet-}$ that has high reactivity with ACP. Interestingly, the degradation of ACP in the UV/$NHCl_2$ process using the one-step strategy was predominantly driven by reactive species generated from $NHCl_2$ decomposition under dark conditions (i.e., 89%), and the contribution remained unaffected by bromide. This study provides fundamental knowledge on the influence of bromide on micropollutant degradation in the UV/NH_2Cl and UV/$NHCl_2$ processes, and assists in selecting the appropriate pH adjustment strategy in potable reuse facilities.

Driving Resource Resilience: Layered Double Hydroxides for Antibiotic Remediation from Wastewaters

A. Johnston[1]*, E. Lester[1], O. Williams[1], RL. Gomes[1]

[1]University of Nottingham, Faculty of Engineering, University Park, Nottingham, NG7 2RD, United Kingdom

amy-louise.johnston@nottingham.ac.uk

Widespread consumption of antibiotics (AB), coupled with human activities, has resulted in their uncontrolled release into the environment. This pollution is of global concern, causing environmental toxicity and spread of antimicrobial resistance. ABs are emerging contaminants, hence advanced wastewater treatment approaches are required for their removal from the environment. Sorption, including by Layered Double Hydroxides (LDHs), is suggested as a suitable remediation technology for removal of ABs from wastewaters. However, few studies consider suitability of LDHs for applications away from idealised conditions. This work investigates behaviour of ABs in the presence of LDHs at environmentally relevant concentrations (µg/L) in wastewater effluent (WWE). A batch sorption set-up was used with continuously synthesised MgAl-NO_3-LDH and this LDHs suitability for remediating sulfamethoxazole (SMX) and amoxicillin (AMX) evaluated. Findings show the nature of the aqueous matrix and AB properties have significant impacts on sorption behaviour. SMX (Fig 1.a.) shows a sorption/release mechanism over 24h in ultrapure (UP) H_2O. Unintended NO_3^- release into UP H_2O, caused by the LDH, results in SMX displacement from LDH. However, a successful >95% removal of AMX (Fig 1.b.) is observed from UP H_2O over 24h. Further, AB removal by LDHs is greatly inhibited by competition from components present in WWE, with no removal observed from WWE for either AB. This work reinforces the importance of research being carried out in environmental waters early in the development of sorbent materials.

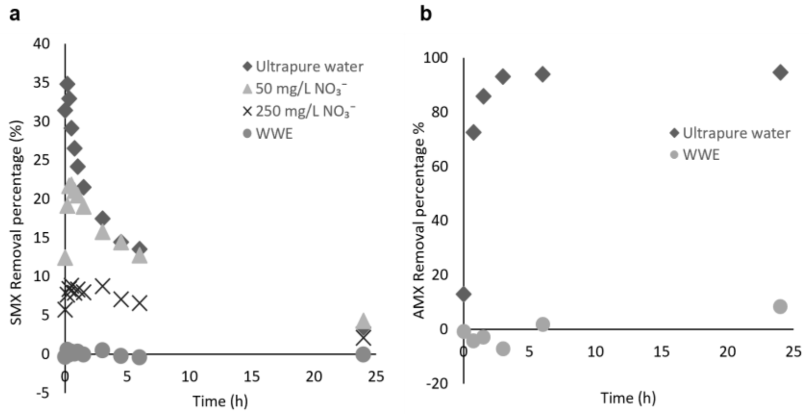


Figure 1. Removal of (a) SMX and (b) AMX (100 µg/L) by MgAl-NO_3-LDH from varying aqueous matrices. Conditions:continuous stirring, dark, 20˚C.

References

Felis, E. et al. (2020) ‘Antimicrobial pharmaceuticals in the aquatic environment - occurrence and environmental implications’, European Journal of Pharmacology, 866, p. 172813. doi: 10.1016/j.ejphar.2019.172813.

Johnston, A.-L. et al. (2021) ‘Understanding Layered Double Hydroxide properties as sorbent materials for removing organic pollutants from environmental waters’, Journal of Environmental Chemical Engineering, 9(4), p. 105197. doi: 10.1016/j.jece.2021.105197.

Advancing the Reactive Nitrogen Species Pathway for N-Nitrosodimethylamine (NDMA) Formation in Chloramine Systems: Nitrogen and Oxygen Mass Balances from Dichloramine Decay

J. L. Fairey[1*], H. T. Pham[1], and D. G. Wahman[2]

[1]University of Arkansas, Department of Civil Engineering, 4190 BELL, Fayetteville, AR, 72701, USA
[2]U.S. Environmental Protection Agency, Drinking Water Treatment and Distribution Branch, Water Infrastructure Division, Center for Environmental Solutions & Emergency Response, 26 West Martin Luther King Drive, Cincinnati, OH, 45268, USA

julianf@uark.edu

The reaction mechanism for dichloramine decomposition has remained unresolved for several decades. Previous studies have focused on the fate of the chloramine species, free ammonia, and nitrogen gas rather than the minor intermediates and decay products that comprise less than 5% of the nitrogen mass balance under typical chloramination conditions. We recently showed that nitroxyl formed by dichloramine hydrolysis and was the key missing intermediate in the N-nitrosodimethylamine (NDMA) formation pathway (Pham et. 2021). In this reaction scheme, nitroxyl reacts with dissolved oxygen (DO) to form peroxynitrite which reacts with dimethylamine (DMA) to form NDMA. We revised the Unified Model (UF) of Chloramine Chemistry to include nitroxyl as the product of dichloramine hydrolysis and added existing reaction schemes for nitroxyl and peroxynitrite chemistry. The resultant UF+RNS model kinetically simulated dichloramine decay, monochloramine formation, DO decomposition, and NDMA formation at pH 7–10. However, nitrous oxide formation—a product of nitroxyl reacting with itself followed by a dehydration reaction—was undersimulated at pH 7–9 and oversimulated at pH 10, prompting additional studies to assess the nitroxyl fate during dichloramine decay. Nitrogen and oxygen mass balances were performed under ambient and low DO conditions in the presence and absence of DMA. This presentation will focus on key findings from these mass balances, which include (1) a revision to nitroxyl chemistry to better simulate nitrous oxide formation at pH 7–10 while maintaining fits for dichloramine, monochloramine, DO, and NDMA and (2) identification of peroxynitrite decay products that react with DMA to form NDMA. These findings help resolve the dichloramine decomposition pathway and its role in NDMA formation in chloramine systems and shed light on the reaction pathway for the so-called Unidentified Product of chloramine chemistry in the absence of DMA. This Unidentified Product contains nitrogen, chlorine, and oxygen and is an inorganic disinfection byproduct of unknown health significance. The practical implications of these findings will be discussed in terms of chloramine formation and stability.

References

Pham HT, Wahman DG, and Fairey JL (2021), 'Updated Reaction Pathway for Dichloramine Decomposition: Formation of Reactive Nitrogen Species and N-Nitrosodimethylamine", Environmental Science & Technology, 55(3), 1740–1749. doi: 10.1021/acs.est.0c06456.

Enhancing and Sustaining Arsenic Removal in a Zerovalent Iron-Based Magnetic Flow-Through Water Treatment System

Y. Wu[1], D. Zhong, Y. Jiang[1*]

[1] The Hong Kong Polytechnic University, Department of Civil and Environmental Engineering, Hong Kong, China

yi-cee.jiang@polyu.edu.hk

Arsenic contamination in groundwater occurs worldwide and poses severe adverse health effects. Zerovalent iron (ZVI) is a promising material for arsenic removal because it not only induces As(III) oxidation via generated oxidizing species, but also enables effective arsenic sequestration by its corrosion products. However, practical applications of ZVI for arsenic removal are hindered by a few challenges, especially when applied in packed bed reactors (e.g., ZVI/sand filter). The formed iron corrosion products result in ZVI surface passivation and consequent loss of its oxidation and sequestration capabilities over time, and also clogging of the reactor. This project describes a magnetic confinement-enabled flow-through column reactor (MCCR) that can enhance and sustain ZVI reactivity for arsenic removal from water. Distinctive from conventional ZVI/sand filters, the as-developed treatment system employs a parallel magnetic field (simply created by two parallel permanent magnets) to stabilize and disperse ZVI microparticles in the column. The magnetically confined ZVI microparticles have high/enhanced reactivity due to excellent spatial dispersion and accelerated iron corrosion in the strong magnetic field. By coupling in situ periodic ultrasonic depassivation (PUD), the ZVI reactivity is constantly rejuvenated to sustain the arsenic removal performance. The flowrate of the conventional ZVI/sand filter rapidly decreased, but that of the MCCR remained stable and high (ca. 14-15 mL/min for 7 days). The PUD extended ZVI reactivity, resulting in an increased water treatment volume from 1834 EBV to 7338 EBV before breakthrough (when As >10 µg/L). This value is among the highest, and the EBCT of 1.49 min is also among the shortest reported values. Furthermore, the less toxic form of As(V) was dominant in the effluent, due to effective oxidation of As(III) in the system. Our technology therefore substantially increases the technical feasibility and material economy of ZVI for water treatment.

Reactive Black 5 Dye Removal from Wastewater Using Orange, Banana and Pomegranate Peels as Natural Adsorbents

A. K. Tolkou[1]*, E. Tsoutsa[2], D. G. Trikkaliotis[1], I. A. Katsoyiannis[2] and G. Z. Kyzas[1]

[1] International Hellenic University, Department of Chemistry, Kavala GR-654 04, Greece
[2]Aristotle University of Thessaloniki, Department of Chemistry, Thessaloniki 54124, Greece

tolkatha@chem.ihu.gr

Many industries, such as leather, textile, tanning, plastics, rubber, and cosmetics use huge amounts of synthetic dyes which may be released into the wastewater in dyeing processes. Disposal of these wastewaters into the environment, without efficient treatment, causes serious damage to aquatic life. Furthermore, reactive dyes are recalcitrant, non- biodegradable, stable to oxidizing agents and toxic. Various methods, including physical and chemical treatments, have been used to remove these dyes from the wastewater (Al-Tohamy et al., 2022). Adsorption has been found to be a very efficient technique. In the current work the removal of Reactive Black 5 (RB5), a commercial reactive anionic and anthraquinonic dye, by using natural adsorbents, was studied. Therefore, the aim of this study is to investigate the efficiency of fruits peels as natural adsorbents in treating wastewater (Munagapati et al., 2020). In terms of selection of natural adsorbents, this study focused on the local waste materials, which are banana peels, orange peels and pomegranate peels, collected from local market. These peels were prepared by washing, drying, grinding and finally sieving, thus becoming powder of natural adsorbents ready to be used. Factors affecting the adsorption of RB5 (like dosage, pH solution, initial concentration of RB5, contact time and temperature) were investigated. FTIR, SEM-EDS and BET analysis characterized the adsorbent material. According to the results, the obtained effectiveness order was banana peels>orange peels>pomegranate peels with removal rates 94, 87 and 59 % respectively, by applying 6.0 g/L at pH 2.0±0.1 Adsorption kinetic results evaluated by non-linear pseudo-second-order model, was found to fit well and showed good correlation with the experimental data than the pseudo-first-order model. The experimental equilibrium data evaluated by non-linear Langmuir and Freundlich, equations and the experimental data were well described by the Langmuir isotherm model. Regeneration studies were applied in order to examine the reusability of natural adsorbents and banana peels were found to successfully regenerate by using NaOH treatment for eight cycles. In conclusion, banana peels were found to be an effective, sustainable, economical and reusable material for dye removal.

References

Al-Tohamy, R. et al. (2022) ‘A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety’, Ecotoxicology and Environmental Safety, 231, p. 113160. doi: 10.1016/j.ecoenv.2021.113160.

Munagapati, V. S. et al. (2020) ‘Adsorptive removal of anionic dye (Reactive Black 5) from aqueous solution using chemically modified banana peel powder: kinetic, isotherm, thermodynamic, and reusability studies’, International Journal of Phytoremediation, 22(3), pp. 267–278. doi: 10.1080/15226514.2019.1658709.

Oxidation of Micropollutants During Drinking Water Ozonation: Formation of Transformation Products and their Fate During Biological Post-Filtration

U. von Gunten[1,2*], R. Gulde[1], B. Clerc[1], M. Rutsch[1], J. Helbing[3], Elisabeth Muck[1], C. S. McArdell[1]

[1]Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-8600 Dübendorf, Switzerland
[2]School of Architecture, Civil and Environmental Engineering (ENAC), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
[3]Zürich Water Works, CH-8021 Zürich, Switzerland

vongunten@eawag.ch

Micropollutants (MP) with varying ozone-reactive moieties were spiked to lake water in the influent of a drinking water pilot plant consisting of an ozonation followed by a biological sand filtration. During ozonation, 227 transformation products (OTPs) from 39 of the spiked 51 MPs were detected after solid phase extraction by liquid chromatography high-resolution mass spectrometry (LC-HRMS/MS). Based on the MS/MS data, tentative molecular structures are proposed. Reaction mechanisms for the formation of a large number of OTPs are suggested by combination of the kinetics of formation and abatement and state-of-the-art knowledge on ozone and hydroxyl radical chemistry. OTPs forming as primary or higher generation products from the oxidation of MPs could be differentiated. However, some expected products from the reactions of ozone with activated aromatic compounds and olefins were not detected with the applied analytical procedure. 187 OTPs were present in the sand filtration in sufficiently high concentrations to elucidate their fate in this treatment step. 35 of these OTPs (19%) were abated in the sand filtration step, most likely due to biodegradation. Only 24 (13%) of the OTPs were abated more efficiently than the parent compounds, with a dependency on the functional group of the parent MPs and OTPs. Overall, this study provides evidence, that the common assumption that OTPs are easily abated in biological post-treatment is not generally valid. Nevertheless, it is unknown how the OTPs, which escaped detection, would have behaved in the biological post-treatment.

References

Gulde, R. et al. (2021) 'Oxidation of 51 micropollutants during drinking water ozonation: Formation of transformation products and their fate during biological post-filtration', Water Res., 207, 117812, doi.org/10.1016/j.watres.2021.117812

Wastewater Filtration Using Adsorbents Based on Spent Coffee Grounds

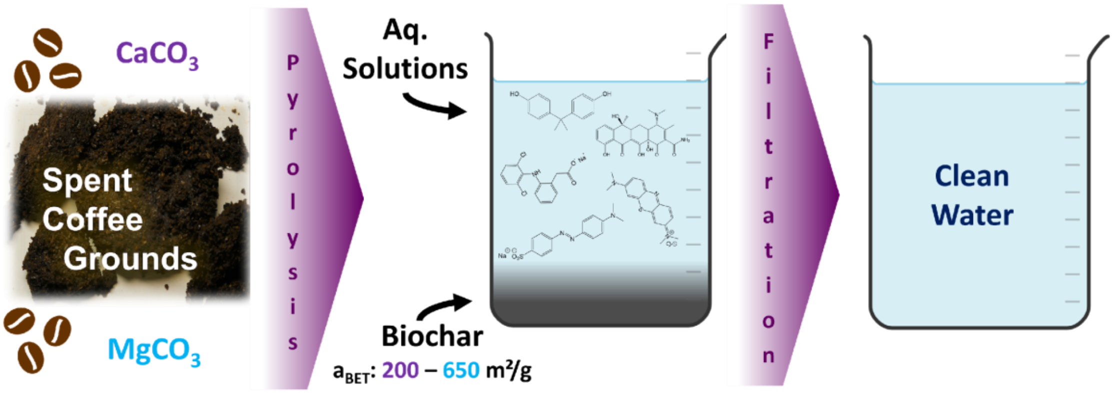
I. Block[1*], L. Holtzheimer[1], C. Günter[2], A. Taubert[1]

[1]Universität Potsdam, Institut für Chemie, Karl-Liebknecht-Straße 24-25, 14476 Potsdam, Germany
[2]Universität Potsdam, Institut für Geowissenschaften, Karl-Liebknecht-Straße 24-25, 14476 Potsdam, Germany

inga.block@uni-potsdam.de

Economically viable and efficient methods to produce clean water for the growing world population gain more and more importance. Adsorption of pollutants using activated carbon (AC) for clean water production is a common step in wastewater treatment. An abundant and cheap raw material is spent coffee (SC) which is daily disposed worldwide in large amounts. It is already known for removal of e.g. heavy metals, dyes or organic acids (Cerino-Córdova, F. J. et al 2013, Block, I. et al 2021).

In our group we focus on the easy and quick preparation of carbon adsorbents for water treatment from SC using calcium carbonate or magnesium carbonate as activators. The materials show surface areas starting at 200 m²/g up to 650 m²/g and good to excellent adsorption qualities. Contaminants of interest are the organic dyes methylene blue and methyl orange, but also the pharmaceuticals diclofenac and tetracycline as well as the commonly known pollutant bisphenol-A. The adsorption capacities of these biochars are studied using UV/Vis-spectroscopy. To improve water purification processes we are also developing magnetic materials which can be removed from solutions using a simple magnet.. The overall goal is to make production of adsorbents less complex as well as the development of filtration processes, that are easily carried out removing the adsorbens and eventually regenerating it for further adsorption application.



Adsorption of organic contaminants from aq. solutions using biochars.

References

Cerino-Córdova, F. J. et al (2013) 'Biosorption of Cu(II) and Pb(II) from aqueous solutions by chemically modified spent coffee grains' Int. J. Environ. Sci. Technol., 10, 611–622, doi:10.1007/s13762-013-0198-z

Block, I. et al (2021); Carbon Adsorbents from Spent Coffee for Removal of Methylene Blue and Methyl Orange from Water, MDPI Materials, 14, 3996, doi: 10.3390/ma14143996

Application of Persulfate Oxidation for Secundary Wastewater Disinfection

J.P.F. Venâncio, L.M. Madeira, O.C. Nunes, C.S.D. Rodrigues*

University of Porto, LEPABE, Faculty of Engineering, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.
University of Porto, ALiCE, Faculty of Engineering, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.

csdr@fe.up.pt

Current societies are coming across a scarcity of freshwater. Considering that water is essential for life, it is crucial to discover viable solutions to combat this crisis, mainly reusing treated wastewater for the various purposes required by the society. However, treated wastewater has to meet restrictive quality standards for reuse, especially concerning the presence of microorganisms. The limits imposed by current legislation are not reached in conventional wastewater treatment plants (WWTPs). In the literature, several disinfection approaches can be found for inactivating pathogenic microorganisms, involving physical (such as membrane separation or coagulation/flocculation) or chemical methods (e.g. chlorination, ozonation, and ultraviolet radiation). These treatment processes have significant limitations, such as the simple transfer of the pollutant from one phase to the other (instead of their complete elimination), the generation of toxic by-products, and/or high treatment costs. Thus, efficient and viable alternatives for the inactivation of microorganisms must be found. These treatment alternatives can be based on advanced oxidation processes (AOPs), particularly activated persulfate, which is based on the generation of sulfate radicals with high oxidation potential (2.5-3.1 ev Wang, J. et al. 2017); the radicals permanently damage the cell structure and microbial functions, causing cell lysis (Venieri D. et al. 2020, Imlay J. et al. 1988).
This study evaluates the disinfection of secondary wastewater from a WWTP using the iron-activated persulfate process with the main goal of generating treated wastewater with characteristics that permit safe reuse. The influence of several operating conditions (reaction time, pH, temperature, persulfate and iron concentrations) was evaluated. The maximum (91%) inactivation of total heterotrophic organisms was reached when using the following conditions: pH = 7.5, T = 40 ºC, $[Fe^{2+}]$ = 0.75 mM, $[S_2O_8^{2-}]$ = 3 mM and t = 60 min. Moreover, the enumeration of enterococci and enterobacteria with and without ciprofloxacin (antibiotic) resistance was below the detection limit (<10 CFU/100 mL). In addition, after 72 hours of treated wastewater storage only a slight regrowth of total heterotrophs was observed. Also, the physicochemical characteristics of the treated wastewater (pH, total nitrogen, ammonia nitrogen, total phosphates, total suspended solids, turbidity, and biological oxygen demand) met the values imposed in European and Portuguese legislation for wastewater reuse in irrigation and most urban utilities. Such results suggest that activated persulfate-based processes can be good alternatives to conventional tertiary wastewater treatments.

Acknowledgments. This work was financially supported by: UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), and LA/P/0045/2020 (ALiCE) funded by national funds through FCT/MCTES (PIDDAC); Project: NORTE-01-0145-FEDER-000069 supported by NORTE 2020 under the PORTUGAL 2020 Partnership Agreement through ERDF. C.S.D.R. thanks the Portuguese Foundation for Science and Technology (FCT) for the financial support of her work contract through the Scientific Employment Support Program (Norma Transitória DL 57/2017).

References

Wang, J. et al. (2017) Treatment of refractory contaminants by sludge-derived biochar/persulfate system via both adsorption and advanced oxidation process, Chemosphere, 185, p. 754-763. DOI:j.chemosphere.2017.07.084

Venieri, D. et al. (2020) Application of activated persulfate for the inactivation of fecal bacterial indicators in water. Journal of Environmental Management, 261, p. 110223. DOI: j.jenvman.2020.

Imlay, J. et al. (1988) DNA damage and oxygen radical. Science, 240, p. 1302–1309. DOI: 10.1126/science.3287616.

Combined Sewer Overflows - Do Biocides Play a Role?

C. Meier[1*], K. Ziegler[1], L. Kopp[2], F. Sacher[3], S. Fuchs[2]

[1]German Environment Agency (UBA), Section Biocides, Wörlitzer Platz 1, 06448 Dessau-Roßlau, Germany
[2]Karlsruhe Institute of Technology (KIT), Institute for Water and River Basin Management, Gotthard-Franz Straße 3, 76131 Karlsruhe, Germany
[3]Water Technology Center (TZW), Water Chemistry Department, Karlsruher Straße 84, 76139 Karlsruhe, Germany

christiane.meier@uba.de

Several studies show that biocides are often detectable in various environmental matrices. Thus, surface water quality can be affected. Biocides are primarily used in urban areas and are transported via the sewer systems to sewage treatment plants (STP). During heavy rainfall events, however, STPs cannot completely treat the increased sewage volume. Therefore, a part of untreated sewage enters the surface waters via combined sewer overflows (CSO). This may be an important emission pathway of biocides otherwise eliminated in STPs. However, the emission via CSOs is poorly investigated and a monitoring screening program with focus on these substances does not exist in Germany. Therefore, a research project was initiated, in order to generate data for biocide occurrence in CSOs and to assess the relevance of combined sewer overflows in comparison to other urban entry pathways. In an exemplary study area in the city of Karlsruhe eight sampling sites were selected: three sites in the river Alb, two storm water outlets, one combined sewer overflow, one discharge point of various sources and the effluent of the local sewage treatment plant. Based on criteria like physico-chemical properties, ecotoxicity and relevance for surface water pollution a total of 42 biocidal active substances and transformation products (mainly disinfectants, material preservatives and pest control products) were prioritized and are analyzed over a period of a year.
First results show that above all, biocides that are used as material preservatives, e.g. carbendazim, terbutryn, diuron and isoproturon, were detected in approximately 90% of all samples. But also the insecticides imidacloprid, acetamiprid and permethrin show a high number of detections (10-40% of all samples). While the mentioned material preservatives were detected in all sample types, the insecticides were measured mainly in the CSO samples. For example, permethrin concentrations of the CSO samples were generally above the regulatory relevant environmental quality criteria PNEC (predicted no effect concentration) for surface water. Even if a regulatory dilution factor of 10 for the discharge into surface waters is considered the PNEC is still exceeded. This can be seen as an indication that pyrethroids used in urban areas are mainly transported into surface waters via CSOs, where they may pose a risk to aquatic organisms. However, the findings of a part of the substances investigated cannot be attributed clearly to a biocidal application, since the same substances are also used in a different context e,g. as human or veterinary pharmaceuticals. Nevertheless, the project provided important insights into the occurrence of biocides in urban runoff components and identified combined sewer overflows as a relevant emission pathway in urban areas which needs to be investigated further.

Efficient Removal of AB74 Dye From Wastewater Using Hybrid Catalysts: Comparative Studies on Ce-LDH-GO and Mo-LDH-GO Composites

R. Zavoianu[1]*, A.-E. Stamate[1], O.D. Pavel[1], A. Cruceanu[1], R. Birjega[2], I.A. Brezestean[3], A. Ciorita[3]

[1]University of Bucharest, Faculty of Chemistry, Bd. Regina Elisabeta, 4-12, 030018, Bucharest, ROMANIA
[2]National Institute for Lasers, Plasma and Radiation Physics, Street Atomistilor, 409, 077125, Măgurele, ROMANIA
[3]National Institute for Research and Development of Isotopic and Molecular Technologies, Street Donat, 67-103, 400293 Cluj-Napoca, ROMANIA

rodica.zavoianu@chimie.unibuc.ro

Conventional water treatment technology cannot eliminate the dyes used in the textile industry, making them some of the most problematic water pollutants to remove. Acid Blue 74 (AB74) is an indigoid water-soluble dye commonly used in the dyeing of the popular blue-denim fabrics (Wambuguh D. et al. 2008). Previous attempts to remove AB74 using advanced photo- or electro-oxidation catalytic processes have been limited due to the high cost of equipment (Vidya Lekshmi, K. P.et al. 2018). This contribution brings new insights on the catalytic activity of hybrid materials that combine a layered double hydroxide (LDH) and graphene oxide (GO). Two different types of LDH, one modified with Ce in the brucite type layer $Mg_3Ce_{0.25}Al_{0.75}$ (abbreviated as Ce-LDH) and one modified with molybdate in the interlayer Mg_3Al-(MoO_4) (abbreviated as Mo-LDH), were combined with GO obtained by Hummers method. Ten hybrids (five with each type of LDH) were synthesized by precipitating the LDH phase in the appropriate amount of GO suspension (4g/L) in order to reach different concentrations of GO in the resulting solids in the range of 5-25 wt.%. Raman spectra have proved the incorporation of GO in the composites, and the XRD patterns of the solids have revealed the formation of nanocomposites with fine particles embedded in the 2D layered structure of Ce-LDH-GO or Mo-LDH-GO. Synthetic wastewater samples were prepared using AB74 from Merck. The initial concentrations of AB74 in the simulated wastewaters were chosen to be in a similar range as in the industrial wastewaters coming from the textile industry (e.g. 0.098-2.1 g/L, Wambuguh D. et al. 2008). H_2O_2 was used as oxidation agent at different concentrations varying from the required stoichiometric amount up to 5 fold excess of H_2O_2. The catalytic tests were performed in batch systems at 25ºC, under magnetic stirring (150 rpm) during 2 h, using 1 g/L of catalyst. Wastewater samples were analyzed by Visible spectrometry, for determining the dye concentration, COD, TOC and the amount of unreacted H_2O_2. The most active hybrid catalysts were found to be Ce-LDH-15%GO and Mo-LDH-20%GO which achieved a removal extent of AB74 higher than 90% when performing the reactions with 1.5 fold excess of H_2O_2. The quality of the treated wastewater met the european legislation standards (91/271/EEC) for the discharge of the treated water into natural receptors. The catalytic activity of each type of LDH-GO hybrid catalyst was strongly correlated with their textural properties and basicity. The presence of CeO_2 nanocrystallites revealed by XRD in the structure of Ce-LDH-GO composites and the increased dispersion of Mo-sites in Mo-LDH-GO (as revealed by XRF and BET) were found to play the main role in influencing catalytic activity. SEM analyses highlighted that the size of the solid particles decreased with the increase of GO content for Ce-LDH-GO, while the opposite effect was observed for Mo-LDH-GO. Recyclability tests demonstrated that the catalytic activity was maintained without a significant loss (-5%) for eight reaction cycles in the case of Mo-LDH-20%GO and four reaction cycles in the case of Ce-LDH-15%GO.

References

Wambuguh, D. et al. (2008) 'Indigo dye waste recovery from blue denim textile effluent: a by-product synergy approach', New J. Chem., 32, p. 2189. doi: 10.1039/B806213G.

Vidya Lekshmi, K. P.et al. (2018) 'MnO_2 efficiently removes indigo carmine dyes from polluted water', Heliyon 4, p. e00897. doi: 10.1016/j.heliyon.2018.e00897.

Removal of Organic Micropollutants and Heavy Metals in Electrodialysis Treatment for Nutrient Recovery from Nitrified MBR Filtrate

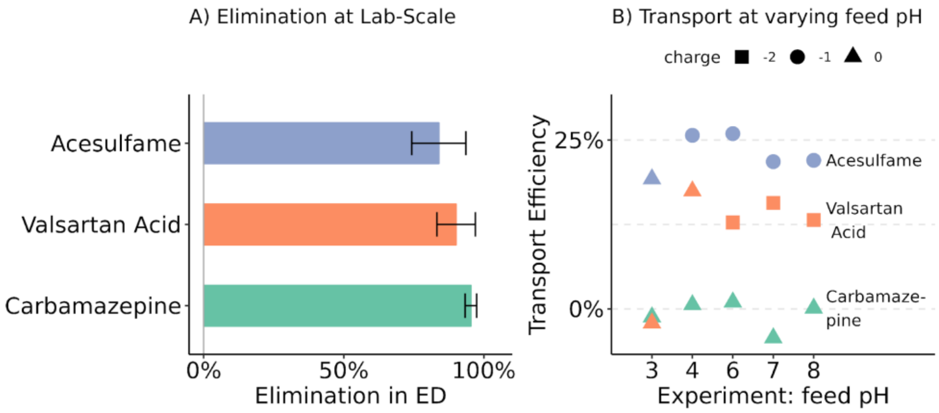
P. Genz[1*], V. Katayama[2], T. Reemtsma[1 3]

[1]Helmholtz-Centre for Environmental Research, Permoserstrasse 15, 04017 Leipzig, Germany
[2]Fraunhofer UMSICHT, Osterfelder Straße 3, 46047 Oberhausen, Germany
[3]University of Leipzig, Institute of Analytical Chemistry, Linnéstrasse 3, 04103 Leipzig, Germany

paul.genz@ufz.de

Nutrient recovery from municipal wastewater may become a component of sustainable agriculture Electrodialysis (ED), a membrane-based technology used for desalination (Strathmann, 2010), is gaining attention also for nutrient recovery (Arola et al., 2019). We have studied the extent of rejection of ionic organic micropollutants and heavy metal cations, to avoid contamination of the nutrient solution. A lab-scale conventional ED-system was operated over a two-year period for nutrient recovery from nitrified MBR filtrate. The retention of 29 micropollutants (i.e. pharmaceuticals, industrial chemicals and others), that may be taken up by plants, was monitored. Moreover, the effect of feed pH on retention of organic micropollutants was investigated, as rejection may be affected the by pH dependent speciation of micropollutants.

Results showed >90% median retention of the investigated organic micropollutants. Some small and polar compounds such as acesulfame were retained only incompletely. Moreover, it was not possible to improve retention by adjusting feed pH, supposedly due to formation of internal pH gradients in the ED that are difficult to control. Heavy metal retention ranged from 6% for Pb to 94% for Cu. To further improve retention, better understanding of the internal processes in ED are needed. Despite incomplete micropollutant retention, the recovered nutrient solution meets EU legislative requirements for wastewater reuse. Therefore, electrodialysis is a suitable process for nutrient recovery from wastewater.



A)Elimination of micropollutants in electrodialysis B)Transport efficiency in electrodialysis normalized to Na & Cl transport, at various feed pH.

References

Arola, K. et al. (2019) ‘Transport of pharmaceuticals during electrodialysis treatment of wastewater’, Water Res., 161, pp. 496–504. doi: https://doi.org/10.1016/j.watres.2019.06.031.

Strathmann, H. (2010) ‘Electrodialysis, a mature technology with a multitude of new applications’, Desalination, 264(3), pp. 268–288. doi: https://doi.org/10.1016/j.desal.2010.04.069.

Micropollutants Abatement from Wastewater by Using Alkali-Activated Foams as Catalyst Supports in Advanced Oxidation Processes.

M. Rabbil[1*], M.A.H. Bhuyan[1], E. Adesanya[1], T. Luukkonen[1]

[1]University of Oulu, Faculty of Technology, Fiber and Particles Engineering Research Unit, PO Box 4300, 90014 Finland

Mehedi.rabbil@oulu.fi

The increasing use of pharmaceuticals and other organic daily chemicals is a growing concern as they end up in aqueous systems as micropollutants. The abatement of micropollutants from wastewater by using alkali-activated materials as catalyst supports in advanced oxidation process (AOPs) is a relatively new research topic. Alkali-activated materials are synthesized through the reaction of aluminosilicate precursors with high-pH alkali-activator solutions and have been considered as sustainable alternative materials in wastewater treatment for the last decade. In this study, alkali-activated foams (AAFs) were prepared from different low-cost aluminosilicates to be utilized as heterogeneous catalyst supports in AOPs. Four AAFs were prepared with the direct foaming method using metakaolin, blast furnace slag, glass wool, stone wool, or their mixtures as the precursors. The stone wool-based foam resulted the highest compressive strength (3.07 MPa) while the metakaolin-based foam yielded the highest porosity (86%). The nanostructure of the foams varied from low-Ca zeolite-like aluminosilicate networks to high-Ca tobermorite-like chain structures. The AAFs were neutralized by flushing with 0.1M acetic acid and deionized water and then the leaching of Al, Ca, Mg, Na, S, and Si from the foams were analyzed. There, the metakaolin based foams showed the lowest leaching. Based on the characterization results, the optimum foam will be modified with catalytically active transition metals (i.e., Fe(II), Co(II), Cu(II), or Mn(II)) by using ion exchange and calcination. The modified foams will be compared in the activation of peracetic acid ($CH_3C(O)OOH$) to abate phenol. The effect of pH, contact time with the foams, and dose of the oxidizer will be optimized by using synthetic wastewater. This study will provide insights into the development of AAFs as catalyst supports in AOPs.

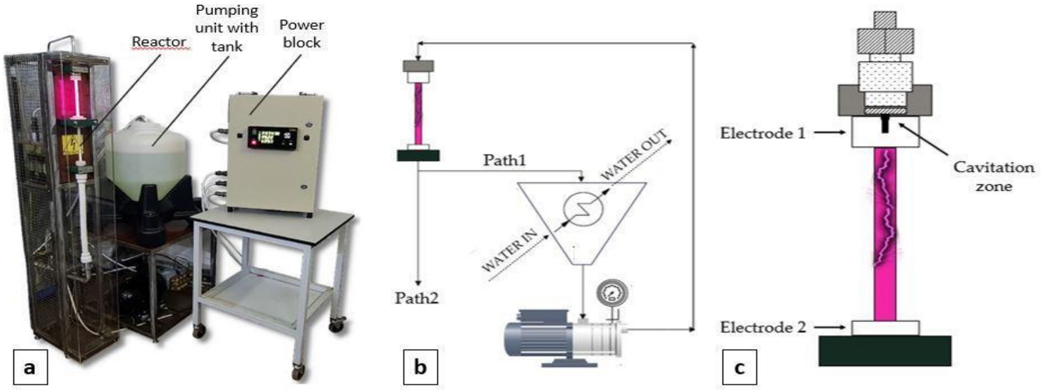
Oxidants and Catalysts Free Fast Antibiotics Degradation in Water by Hydrodynamic Cavitation (HC) Treatment Combined With in Situ Generated Electrical Discharge Plasma

F. Verdini[1]*, E. Calcio Gaudino[1], E. M. M. Flores[2], T. C. Pereira[2], G. Cravotto[1]

[1]University of Turin, Department of drug science and technology, Via P. Giuria 9, 10125, Turin, Italy
[2]Federal University of Santa Maria, Department of Chemistry, Av. Roraima 1000, Cidade Universitária Bairro - Camobi, Santa Maria - RS, 97105-900, Brasil

federico.verdini@unito.it

Tetracyclines and metrodinazole are widely used antibiotics that are often carelessly released into the environment, posing a potential threat to the ecosystem (Gros M. et al. 2023). Due to the lack of efficient methods to remove tetracyclines and metrodinazole from wastewater, a remarkable research effort on the remediation of antibiotics has been undertaken. The production of hydroxyl radicals, hydrogen peroxide, ozone, UV light, and shock waves promoted by the synergistic effect of hydrodynamic cavitation (HC) and electrical discharge (ED) plasma has been studied for the intensification of tetracycline hydrochloride (TC), doxycycline hyclate (DC), oxytetracycline dihydrate (OC) and metrodinazole (MNZ) degradation process. Catalyst- and oxidant-free processes have been carried out using a new pilot-scale hybrid device (HC/ED plasma) (Abramov V. O. et al. 2021) working in flow-through mode (330 L/h). Degradation tests were performed on 5 L water solution at various antibiotic concentrations both in flow and loop configuration. Near quantitative TC (> 98%), DC (98%), OC (95%) and MNZ (90%) degradation was documented after only 15 min of combined HC/ED plasma treatment. A sonochemical dosimetry assay showed the formation of oxidizing species of 0.00015 mmol/L during HC alone and 13.426 mmol/L in the hybrid HC/ED plasma. This study demonstrates the impressive efficiency of hybrid HC/ED plasma technology in degrading recalcitrant antibiotics in wastewater without the need for catalysts and oxidants provided useful information on the synergistic effect between hydrodynamic cavitation and ED plasma.



Pilot scale hybrid device. a) Picture of the system b) Scheme of the hybrid reactor set-up c) Detail of the reaction chamber

References

Gros, M. et al. (2023) 'Antibiotics, antibiotic resistance and associated risk in natural springs from an agroecosystem environment', Science of The Total Environment, 857, 159202.
doi:10.1016/j.scitotenv.2022.159202.

Abramov, V. O. et al. (2021) 'Flow-mode water treatment under simultaneous hydrodynamic cavitation and plasma', Ultrasonics - Sonochemistry, 70, 105323.
doi: 10.1016/j.ultsonch.2020.105323

Study of A High-Rejection, Aquaporin-Inside Lab-Scale Hollow Fiber Module for Osmotic Dewatering: Three-Dimensional CFD Modeling and Experiments

S. Rampriyan[1]*, K. Mahawer[2], B. Ray[1]

[1]Indian Institute of Technology Delhi, Department of Mechanical Engineering, Hauz Khas, 110016, New Delhi, India
[2]Indian Institute of Technology Delhi, Department of Chemical Engineering, Hauz Khas, 110016, New Delhi, India

shivangrp@mech.iitd.ac.in

In recent years, hollow fiber membrane contactors/modules have attracted significant attention from the scientific community. A hollow fiber membrane module essentially contains the following components: a hollow fiber bundle which is responsible for mass transfer, tubesheet(s) for separating the fluids inside and outside the fibers, end cap(s) that contain ports used as fluid inlets or outlets, and a shell housing that contains the three components as mentioned. Hollow fiber membrane modules are widely used for filtration (micro-/nano-/ultra-), forward/reverse osmosis, gas separation and stripping, pervaporation, membrane distillation, and dialysis applications (Wan et al., 2017). On an industrial scale, hollow fiber modules are used in the food industry for juice concentration, pharma industries for active pharmaceutical ingredient separation from wastewater, brine management, zero liquid discharge and seawater desalination (Francis et al., 2020). To improve the design and efficiency of the hollow fiber membrane modules, it is, therefore, necessary to have reliable modeling strategies for quantifying their performance.

In a hollow fiber membrane contactor, the shell-side hydrodynamics significantly influences the mass transfer of the module. This is attributed to the presence of preferential fluid flow pathways, non-uniform fiber distribution, dead zones, and fluid recirculation zones, which produce heterogenized concentration distribution in the solutions, and, consequently, a non-uniform water flux. One-dimensional and two-dimensional mechanistic models involve numerous simplifying assumptions and have a limited capability to evaluate the physical phenomena occurring inside an actual lab-scale module. To address this shortcoming, this study proposes a module-scale three-dimensional CFD-based mathematical model capable of analyzing the performance of hollow fiber modules in detail. Using the model, we analyze the performance characteristics of a high-rejection, lab-scale forward osmosis (FO) module. The model is validated through extensive experimentation, and the results agree with our experiments. A non-destructive characterization method is developed to evaluate the gross porosity of the membrane fibers. Optical microscopy is used to ascertain the module's fiber distribution, which helps group the fibers into fiber clusters for ease of further computational studies. Performance trends due to variations in popular system parameters, like flow rates and concentrations of the flowing streams, are analyzed and justified based on the concentration polarization phenomena observed near the membrane surface inside the module. The insights provided in this paper may be leveraged for designing, validating, and optimizing other hollow fiber modules commonly used for sustainable separation applications—especially osmotic dewatering.

References

Francis, L. et al. (2020) 'A comprehensive review of forward osmosis and niche applications', Environmental Science: Water Research and Technology, 6(8), pp. 1986–2015. Available at: https://doi.org/10.1039/d0ew00181c.

Wan, C.F. et al. (2017) 'Design and fabrication of hollow fiber membrane modules', Journal of Membrane Science, 538, pp. 96–107. Available at: https://doi.org/10.1016/j.memsci.2017.05.047.

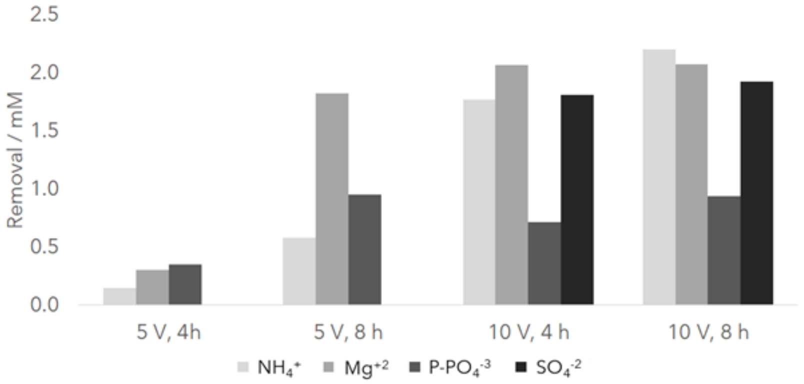
Electrochemical Removal of Phosphorus from Simulated Wastewater

C. Sousa[1], A. Lopes[1]*, A. Amaro[1], M.J. Pacheco[1], L. Ciríaco[1], A. Fernandes[1]

[1]Universidade da Beira Interior, FibEnTech, Rua Marquês D'Ávila e Bolama, 6201-001, Covilhã, Portugal

analopes@ubi.pt

The population growth from the 20th century onwards has boosted the use of synthetic fertilizers in agriculture, inducing environmental problems like the depletion of raw materials such as phosphate rock and a higher release of nutrients into water bodies (Wangg et al., 2022). Electrochemical removal of phosphorus has been studied as a technology capable of reducing the need for phosphate rock and decreasing the phosphorus load in water ecosystems, but only a few systematic research studied the viability of the process (Ren et al., 2022). We studied the effect of the applied current and of the treatment time on phosphorus removal efficiency. The tests were performed in a potentiostat/galvanostat, using a conventional one-compartment, three electrodes cell, with Ag/AgCl as reference electrode (ref), and boron-doped diamond (BDD) plates as both working electrode and counter electrode. The synthetic effluent containing ammonium, magnesium, phosphate and sulfate was treated with potentials of 5, 7.5 and 10 V vs ref for 4 hours, reaching phosphorus removals of 8.9, 16.7 and 18.1%, respectively, showing that increasing the potential above 7.5 V is poorly significant. However, by increasing the treatment time to 8 hours, the highest efficiency was obtained at 5 V, with 24.1% of phosphorus removal. Since no sulfur was detected by EDX on the precipitated, it was assumed that higher potentials favor sulfate oxidation, that competes with the phosphate electroprecipitation. Also, the composition of the solids obtained showed that phosphorus removal is more affected by treatment time than by applied potential.



Molar removal of ammonium, magnesium, phosphate and sulfate in the experiments.

References

Wang, Y. et al (2022). ‘Electrochemically mediated precipitation of phosphate minerals for phosphorus removal and recovery: Progress and perspective’, Water Ressearch, 209, p. 1-14, doi: 10.1016/j.watres.2021.117891.

Ren, Y. et al (2022). ‘Recent advances in electrochemical removal and recovery of phosphorus from water: A review’, Environmental Funcional Materials, 1, 1, p. 10-20, doi: 10.1016/j.efmat.2022.04.003.

Development of Membrane Introduction Mass Spectrometry Method for the Quantification of Bromochloramines

Y. Xiang[1]*, F. Berne[1], S. Soreau[2], H. Gallard[1]

[1]Université de Poitiers, Institut de Chimie des Milieux et des Matériaux de Poitiers IC2MP UMR 7285 CNRS, ENSI Poitiers, 1 rue Marcel Doré TSA 41105, 86 073 Cedex 9, Poitiers, France
[2]EDF - Recherche et Développement, Laboratoire National d′Hydraulique et Environnement (LNHE), 6 quai Watier, 78401 Chatou Cedex, France

yingying.xiang@univ-poitiers.fr

Chlorination is a widely employed process for fouling control and disinfection in various scenarios, such as seawater cooling systems, desalination plants, and ocean-fed swimming pools. In such scenarios, the coexistence of chlorine, ammonia, and bromide results in the formation of bromochloramines. However, due to the high instability of dibromochloramine (NBr_2Cl) and bromodichloramine ($NBrCl_2$), there is currently no accurate analytical method available for their quantification. The kinetics of their formation and decomposition during seawater chlorination, as well as their reactivity toward dissolved organic compounds, remain a puzzle. In this study, we developed an analytical method for the quantification of bromochloramines using membrane introduction mass spectrometry (MIMS). The molar absorption coefficients of NBr_2Cl at 242 nm and 300 nm were obtained by monitoring the decay of NBr_2Cl (with a half-life of < 5 min), which was synthesized by reacting dichloramine (NH_2Cl) and HOBr at a molar ratio of 1:2 at pH 6 (Gazda and Margerum, 1994), with UV-vis measurements. The decay of NBr_2Cl followed second-order kinetics (R^2 of > 0.997), and the molar absorption coefficients of NBr_2Cl at 242 nm and 300 nm were determined to be 4907 $M^{-1}cm^{-1}$ and 601 $M^{-1}cm^{-1}$, respectively. To establish the calibration curve of NBr_2Cl in MIMS, the concentrations of NBr_2Cl obtained by direct UV measurements (using the molar absorption coefficient obtained by this study) were compared to the MIMS signal recorded at m/z 207 ($N^{79}Br_2{}^{35}Cl^{\bullet+}$) and m/z 209 ($N^{79}Br^{81}Br^{35}Cl^{\bullet+}$ and $N^{79}Br_2{}^{37}Cl^{\bullet+}$). The limit of detection of NBr_2Cl at m/z 207 and m/z 209 was calculated to be 2.26 µM (472 µg/L) and 0.99 µM (207 µg/L), respectively. This newly developed MIMS method enables the unambiguous quantification of NBr_2Cl, which allows for the further development of the kinetic model of the ammonia-chlorine-bromide system by including NBr_2Cl. It also facilitates the investigation of the reactivity of NBr_2Cl with dissolved organic compounds, which may lead to the formation of undesirable disinfection byproducts. A quantification method for $NBrCl_2$ using MIMS is currently under development and will be presented at the conference.

References

Gazda, M. and Margerum, D. W. (1994) ‘Reactions of Monochloramine with Br2, Br3-, HoBr, OBr-: Formation of Bromochloramines’, Inorganic Chemistry, 33(1), p. 118–123. doi: 10.1021/ic00079a022.

Magnetic-Nanocomposite-Tio$_2$ Immobilized Poly(Ethylene Terephthalate) Beads as Photocatalysts for Removal of Antidepressants Under UV Irradiation at Pilot Plant Scale

E. Evgenidou[1,2]*, N. M. Ainali[1,2], A. Rapti[1], R. Bikiaris[1], D. Gkika[3], V. Tsekeridis[1], G. Kyzas[3], D. Lambropoulou[1,2]

[1]Aristotle University of Thessaloniki, Department of Chemistry, GR 54124, Thessaloniki, Greece
[2]Centre for Interdisciplinary Research and Innovation (CIRI-AUTH), Balkan Center, Thessaloniki, 10th km Thessaloniki-Thermi Rd, GR 57001, Greece
[3]International Hellenic University, Department of Chemistry, Kavala, 65404, Greece

evgenido@chem.auth.gr

Advanced oxidation processes (AOPs), such as TiO_2 heterogeneous photocatalysis, which can be used either as post- or pre-treatment methods, have been proved as a powerful, ecofriendly tool for the degradation of many organic compounds in wastewater or landfill leachates. However, the difficult recyclability of catalysts largely hinders their applications. In this regard, the present study assessed removal of microcontaminants such as antidepressants (Venlafaxin, Bupropion, Sertraline) from different water matrices (natural water, wastewater, leachate) using magnetic-Nanocomposite-TiO_2 Immobilized Poly(Ethylene Terephthalate) beads as photocatalysts. To this end, TiO_2 nanoparticles were decorated with magnetic Fe_3O_4 nanoparticles, and then embedded into poly(ethylene terephthalate) (PET) matrix, which originated from post-consumer bottles, to form PET-TiO_2/Fe_3O_4 composite beads, in three different compositions of inorganic fillers. The newly synthesized beads were investigated for their successful synthesis, employing several materials characterization techniques, including spectroscopic, crystallographic, thermal, and microscopic ones. At first, the performance of the new synthesized materials were tested and optimized in laboratory-scale experiments set-up by using an irradiation simulator system. Secondly, the optimized process were valuated under different operating conditions in a novel, automated photocatalytic pilot-scale plant. The plant has a maximum capacity of 100 L, maximum flow rate of 12 L/min of treated water, and 160 W of UV-C power, serving for heterogeneous photocatalysis employing PET-TiO_2/Fe_3O_4 composite beads with UV irradiation. Pilot tests with different water matrices under continuous operation were carried out for the assessment of the pilot unit performance. Different operating parameters and conditions were tested. Namely, the flow rate of the reactor (1, 5 and 10 L/min), the concentration of the model compounds, the PET-TiO_2/Fe_3O_4 composite beads loading and the UV-C irradiation dose were assessed to define the optimum parameters of the plant performance for both the degradation of antidepressants compounds and TOC mineralization. According to the results, the removal of antidepressants was affected by the catalyst loading, while the flow rate had rather a negligible effect. The identification of transformation products formed during the photocatalytic process was performed by using an Orbitrap Q Exactive Focus™ high-resolution mass spectrometry system. Thanks to the Compound Discoverer software (version 3.1), more than 30 TPs were identified with the view to untangle the possible reaction pathways involved with pharmaceutical mineralization. Finally, the overall cost of treatment process was evaluated in detail to visualize the practical feasibility of the presented performance reactor system.

Funding
This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship, and Innovation, under the call RESEARCH – CREATE – INNOVATE (2nd Cycle) (Project acronym: UV-LEACH; Project code: T2EDK-00137).

References

Belessi, V., et. al., (2009). Structure and photocatalytic performance of magnetically separable titania photocatalysts for the degradation of propachlor. Applied Catalysis B: Environmental, 87(3-4), 181-189. doi:10.1016/j.apcatb.2008.09.012.

Evgenidou, E., et. al., (2023). Photocatalytic degradation of the antiviral drug abacavir using titania-graphene oxide nanocomposites in landfill leachate. Journal of Photochemistry and Photobiology A: Chemistry, 439 doi:10.1016/j.jphotochem.2023.114628.

Efficiency of Buoyant TiO2-Immobilized Poly (Ethylene Terephthalate) Beads towards Pregabalin Photocatalytic Degradation

N. M. Ainali[1,2]* A. Rapti[1], R. Bikiaris[1], Ch. Nannou[3], E. Evgenidou[1,2] and D. Lambropoulou[1,2]

[1]Aristotle University of Thessaloniki, GR Department of Chemistry, 54124, Thessaloniki, Greece
[2]Centre for Interdisciplinary Research and Innovation (CIRI-AUTH), Balkan Center, Thessaloniki, 10th km Thessaloniki-Thermi Rd, GR 57001, Greece
[3]International Hellenic University, Department of Chemistry, Kavala, 65404, Greece

nsainali@chem.auth.gr

Among different AOPs, heterogeneous photocatalysis employing nano size TiO_2 has been an attractive research and development subject in aqueous matrices treatment owing to its proven capability in the degradation of bio-recalcitrant organic contaminants (Gopinath et. al., 2020). However, the application of suspended TiO_2 is limited at full-scale since the small size of the catalyst complicates its recovery at the end of the treatment, reducing its potential reuse and compromising the quality of treated effluent (Ainali, et. al. 2021; Falah et. al., 2020; Xing et. al., 2018). In this light, the synthesis and application of composite materials, which contain polymeric and inorganic units such as TiO_2, has gained much attention in the field of treatment processes, due to their better (and more practical) performance parameters. To this end, the main objective of this study was to assess the application of a promising configuration based on immobilized TiO_2 on recycled poly(ethylene terephthalate) beads, during photocatalytic treatment of different aqueous matrices (groundwater, wastewater effluent, leachate), focusing on the elimination of pregabalin. The novel PET/TiO_2 beads were prepared using a non-solvent technique and their properties were thoroughly investigated using various characterization techniques (e.g., FTIR, XRD, SEM etc). The photocatalytic performance of the fabricated composite PET/TiO_2 beads was evaluated under different irradiation systems for the degradation a pregabalin, showing their efficiency towards pharmaceutical removal. The effect of operation parameters like load of catalyst, drug concentration, aqueous matrices, concentration of oxidants (e.g H_2O_2, $S_2O_8^{2-}$) etc were investigated and optimized. Powerful analytical techniques such as ultra- performance liquid chromatography (UPLC)-electrospray ionization (ESI)-high resolution mass spectrometry (HRMS) were used to identify transformation products and propose the mechanism of transformation. The reusability of PET/TiO_2 beads and the mechanism of the photocatalytic pregabalin transformation were also investigated.

Funding
This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship, and Innovation, under the call RESEARCH – CREATE – INNOVATE (2nd Cycle) (Project acronym: UV-LEACH; Project code: T2EDK-00137).

References

Gopinath, K. P., et. al., (2020). Present applications of titanium dioxide for the photocatalytic removal of pollutants from water: A review. Journal of Environmental Manageme, Ainali, N.M.et., al., (2021). Insights into Biodegradable Polymer-Supported Titanium Dioxide Photocatalysts for Environmental Remediation, Macromol 2021, 1(3), 201-233; https://doi.org/10.3390/macromol1030015.

Falah, M., et. al., (2020). Photocatalytic nanocomposite materials based on inorganic polymers (geopolymers): A review. Catalysts, 10(10), 1-20. doi:10.3390/catal10101158.

Xing, Z., et. al.,. (2018). Recent advances in floating TiO2-based photocatalysts for environmental application. Applied Catalysis B: Environmental, 225, 452-467. doi:10.1016/j.apcatb.2017.12.005.

Photocatalytic ZnO Molecular Foams for the Degradation of Micropollutants

Z. Warren[1]*, T.T. Guaraldo[1,2], J. Wenk[1], D. Mattia[1]

[1]University of Bath, Department of Chemical Engineering, Claverton Down, BA2 7AY, Bath, United Kingdom.
[2]University of Coventry, Department of Engineering, Priory St, Coventry CV1 5FB, Coventry, Unitied Kingdom

zw799@bath.ac.uk

Micropollutants such as pharmaceuticals have been detected in water supplies across the globe, (Wilkinson et al., 2022) and are of concern to public health, as these compounds can bioaccumulate, impacting health resisting current water treatment methods. Photocatalysis shows promise as a solution to this problem but is hindered in two main ways: slurries require downstream separation, while supported photocatalysts suffer from low exposed surface areas and efficiencies. This novel work solves both issues associated with photocatalysts, as the highly porous monoliths show high surface area, similar to a slurry, while having a structure of ZnO only, removes binding interactions between catalyst and support, with no risk of leaching.

This work presents a novel ZnO photocatalytic foam (Warren et al., 2022). Briefly, the synthesis is based on sol gel synthesis of ZnO, incorporating direct aeration during gel formation followed by high temperature sintering to form a highly porous yet mechanically stable ZnO structure as macroscale foam monoliths without foaming agents nor supercritical drying. These molecular foams or "MolFoams" were used in the photocatalytic degradation of carbamazepine as a model pollutant in recirculating systems. The MolFoams were characterised as wurtzite ZnO showing high porosity and a hierarchical structure, which shows promise for the degradation of pollutants. FE-SEM shows a structure consisting of channels and smaller pores, allowing for flow through the foam and a reactive surface for degradation to occur at.

Altering the concentration of surfactant used in the formulation of the gels allowed controlling the size of the macropores of the MolFoam in the 0.69 – 0.84 mm range. Smaller macropores within the MolFoam structure were highly beneficial for the degradation of carbamazepine with pseudo first-order degradation kinetics of 5.43 x10-3 min-1 for the MolFoams with the smallest macropore size. The best foams were tested in a recirculating reactor, with an optimal flow rate of 250 mL min-1, resulting in a quantum yield of 2.63 X 10-3 and an electrical energy per order of 21.34 KWh m-3 order-1, exceeding values reported for slurries and supported catalysts, in addition to high mechanical and chemical stability. Furthermore, the versatility of the synthesis allowed for doping of transition metals into the ZnO lattice (Warren et al., 2023) resulting in a significant increase in stability and resistance to photocorrosion, a key drawback of ZnO. The doped foams showed 60-80% decrease in Zn leaching after irradiation, albeit with a reduction in photocatalytic activity. A full suite of analysis identified the cause of the reduction to be shifting of the band edge positions of the doped foams providing a pathway to significantly reduce the photocorrosion of ZnO in water, with further work required to maintain the photocatalytic activity of undoped ZnO.

These results show promise for the potential application of photocatalytic foam structures as a tertiary wastewater treatment step for the removal of currently persistent micropollutants. The proposed 3D structure combines the advantages of slurries and immobilised catalysts while simultaneously addressing drawbacks.

References

Wilkinson, J. L. et al. (2022) 'Pharmaceutical pollution of the world's rivers', Proc Natl Acad Sci U S A, 119(8).

Warren, Z et al. (2022) 'Synthesis of photocatalytic pore size-tuned ZnO molecular foams', Journal of Materials Chemistry A, 10(21), pp. 11542-11552.

Warren, Z et al. (2023) 'Increased photocorrosion resistance of ZnO foams via transition metal doping', RSC Advances, 13(4), pp. 2438-2450.

Photocatalytic ZnO Molecular Foams for the Degradation of Micropollutants

Z. Warren[1]*, T.T. Guaraldo[1,2], J. Wenk[1], D. Mattia[1]

[1]University of Bath, Department of Chemical Engineering, Claverton Down, BA2 7AY, Bath, United Kingdom.
[2]University of Coventry, Department of Engineering, Priory St, Coventry CV1 5FB, Coventry, Unitied Kingdom

zw799@bath.ac.uk

Micropollutants such as pharmaceuticals have been detected in water supplies across the globe, (Wilkinson et al., 2022) and are of concern to public health, as these compounds can bioaccumulate, impacting health resisting current water treatment methods. Photocatalysis shows promise as a solution to this problem but is hindered in two main ways: slurries require downstream separation, while supported photocatalysts suffer from low exposed surface areas and efficiencies. This novel work solves both issues associated with photocatalysts, as the highly porous monoliths show high surface area, similar to a slurry, while having a structure of ZnO only, removes binding interactions between catalyst and support, with no risk of leaching.

This work presents a novel ZnO photocatalytic foam (Warren et al., 2022). Briefly, the synthesis is based on sol gel synthesis of ZnO, incorporating direct aeration during gel formation followed by high temperature sintering to form a highly porous yet mechanically stable ZnO structure as macroscale foam monoliths without foaming agents nor supercritical drying. These molecular foams or “MolFoams” were used in the photocatalytic degradation of carbamazepine as a model pollutant in recirculating systems. The MolFoams were characterised as wurtzite ZnO showing high porosity and a hierarchical structure, which shows promise for the degradation of pollutants. FE-SEM shows a structure consisting of channels and smaller pores, allowing for flow through the foam and a reactive surface for degradation to occur at.

Altering the concentration of surfactant used in the formulation of the gels allowed controlling the size of the macropores of the MolFoam in the 0.69 – 0.84 mm range. Smaller macropores within the MolFoam structure were highly beneficial for the degradation of carbamazepine with pseudo first-order degradation kinetics of 5.43 x10-3 min-1 for the MolFoams with the smallest macropore size. The best foams were tested in a recirculating reactor, with an optimal flow rate of 250 mL min-1, resulting in a quantum yield of 2.63 X 10-3 and an electrical energy per order of 21.34 KWh m-3 order-1, exceeding values reported for slurries and supported catalysts, in addition to high mechanical and chemical stability. Furthermore, the versatility of the synthesis allowed for doping of transition metals into the ZnO lattice (Warren et al., 2023) resulting in a significant increase in stability and resistance to photocorrosion, a key drawback of ZnO. The doped foams showed 60-80% decrease in Zn leaching after irradiation, albeit with a reduction in photocatalytic activity. A full suite of analysis identified the cause of the reduction to be shifting of the band edge positions of the doped foams providing a pathway to significantly reduce the photocorrosion of ZnO in water, with further work required to maintain the photocatalytic activity of undoped ZnO.

These results show promise for the potential application of photocatalytic foam structures as a tertiary wastewater treatment step for the removal of currently persistent micropollutants. The proposed 3D structure combines the advantages of slurries and immobilised catalysts while simultaneously addressing drawbacks.

References

Wilkinson, J. L. et al. (2022) 'Pharmaceutical pollution of the world's rivers', Proc Natl Acad Sci U S A, 119(8).

Warren, Z et al. (2022) 'Synthesis of photocatalytic pore size-tuned ZnO molecular foams', Journal of Materials Chemistry A, 10(21), pp. 11542-11552.

Warren, Z et al. (2023) 'Increased photocorrosion resistance of ZnO foams via transition metal doping', RSC Advances, 13(4), pp. 2438-2450.

Treating Waste with Waste – the Use of Spent Tea and Coffee Wastes as Adsorption Media for Wastewater Treatment

T.I.J. Dugmore[1]*

[1]University of York, Department of Chemistry, Green Chemistry Centre of Excellent, York, YO10 5DD, UK

tom.dugmore@york.ac.uk

The issue of waste generation is an inevitable problem in many industrial processes that comes at a cost to the manufacturing companies in terms of its safe treatment and disposal. Unfortunately, these processes can often require virgin chemicals and materials that compete with other manufacturing sectors. This work therefore seeks to address these problems by employing one waste stream to treat another – notably to use the residues from tea and coffee production to remove pollutants (metals, dyes) from wastewater.

Spent Coffee Grounds in particular are noted for their high oil content, which can be extracted for use in fields such as biodiesel and cosmetics, with the added bonus that the extraction process leaves behind a porous structure. This structure can then be fixed in place in the process of conversion to activated carbon under relatively mild pyrolysis conditions (600 oC, 1 hour). This has the result of producing an activated carbon that is not just high in surface area, but also in mesoporosity (2-50 nm wide) which makes them ideal for adsorption of large pollutants.

The materials have shown comparable adsorption capacity under standard conditions for Cr(VI) and Mn(VII) when compared to commercially available activated carbon and a ten-fold increase in adsorption capacity for Au (III) which is attributed to mesopore volumes of ~0.5 cm3 g-1.

Previous work on mesoporous carbons as adsorbents has shown good promise for subsequent desorption of pollutants which in turn shows potential for recovery and recycling of materials. This is particularly important for adsorption of metals for re-use given the scarcity of known reserves for many elements crucial to modern-day technologies. Future work will therefore seek to achieve and optimize desorption of adsorbed pollutants for recovery and re-use.

References

Dugmore, T.I.J et al., (2019) Superior Mesoporosity of Lipid-Free Spent Coffee Ground Residues, ChemSusChem, 12(17), 4074-4081. https://doi.org/10.1002/cssc.201901232.

Bansal, M. et al., (2020) Adsorption of Eriochrome Black-T (EBT) using tea waste as a low cost adsorbent by batch studies: A green approach for dye effluent treatments,Current Research in Green and Sustainable Chemistry, 3, 100036.

Bose, S. et al (2022) Mesoporous-rich calcium and potassium-activated carbons prepared from degreased spent coffee grounds for efficient removal of MnO42− in aqueous media. RSC Advances, 12(30), 19417-19423.

Structured Graphitic Carbon Nitride Films for The Removal of Micropollutants from Urban Wastewaters

M. J. Sampaio[1,2]*, A. R. L. Ribeiro[1,2], C. Ribeiro[3,4], M. F. Pedrosa[1,2], A. M.T. Silva[1,2], C. G. Silva[1,2] J. L. Faria[1,2]

[1]University of Porto, Faculty of Engineering, LSRE-LCM – Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Rua Dr. Roberto Frias, Porto, 4200-465, Portugal
[2]University of Porto, Faculty of Engineering, ALiCE – Associate Laboratory in Chemical Engineering, Rua Dr. Roberto Frias, Porto, 4200-465, Portugal
[3]University Institute of Health Sciences, TOXRUN – Toxicology Research Unit, CESPU, CRL, Gandra, 4585-116, Portugal
[4]Interdisciplinary Center for Marine and Environmental Research (CIIMAR), Port of Leixões Cruise Terminal, Av. General Norton de Matos, s/n, Matosinhos, Portugal

mjsampaio@fe.up.pt

Despite the progressive advances in technologies employed in Urban Wastewater Treatment Plants - UWWTPs (e.g., filtration, disinfection, oxidation and biological processes), the presence of organic micropollutants (MPs) in the environment has been raising a great concern, in particular those found in surface waters (levels of ng L^{-1} and μg L^{-1}) (Ribeiro et al., 2021). Thus, the exploitation of far-sighted and holistic technologies to attenuate harmful emerging pollutants in water are imperative nowadays. As a similar alternative concept to photosynthesis, photo-assisted systems can excite molecules in the presence of optical semiconductors in aqueous media, accelerating their photodegradation (Sampaio et al., 2023). However, in most photocatalytic applications, the catalysts are used as slurries, and several practical problems arise from the use of a catalyst in powder form, such as difficult separation of the catalyst, aggregation of particles, and the difficulty of applying this technology in continuous flow processes. Here, we proposed an efficient photocatalytic system based on an immobilized polymeric carbon nitride material to remove 2 MPs (metoprolol and venlafaxine), which are pharmaceutical compounds commonly found in actual wastewaters. The photocatalytic efficiency of GCN-T/PVDF film was examined under batch and continuous flow modes using a Light-Emitting-Diode (LED) system as the radiation source at a fixed wavelength (417 nm).

This work was financially supported by LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC). The authors also thank the projects ClimActic and Healthy Waters. MJS thanks FCT funding under the Scientific Employment Stimulus - Institutional Call (CEECINST/00010/2021).

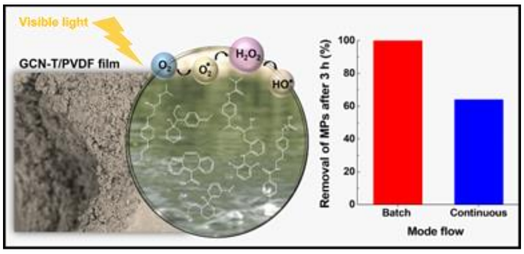


Figure 1 - Schematic representation of the photocatalytic system.

References

A.R.L. Ribeiro, et al., Current Opinion in Green and Sustainable Chemistry, 31 (2021) 100507.

M.J. Sampaio, et al., Chem. Eng. J., 459 (2023) 141617.

Photochemical Transformation of Thiophenes in the Aquatic Environment

O. Yushchenko[1]*, M. Amacha[1] and K. McNeill[1]

[1]Institute of Biogeochemistry and Pollutant Dynamics (IBP), Department of Environmental Systems Science, ETH Zurich, 8092 Zurich, Switzerland

oleksandr.yushchenko@usys.ethz.ch

Thiophenes are an important class of sulfur containing heteroatomic compounds. They make up a significant portion of organosulfur containing compounds found in petroleum and other products derived from fossil fuels. Thiophenes have also gained interest in medicine, in which they possess a wide range of therapeutic properties, such as antibacterial, anti-inflammatory, analgesic, anti-anxiety, antidepressant, antipsychotic and anticancer.

Oil spills and pharmaceutical waste are major pathways through which thiophenes are released into the aquatic environment. Several studies have shown that the metabolism of thiophene-containing substrates lead to toxic products. On the other hand, there is lack of fundamental understanding of the thiophene photoreactivity in aquatic systems. Few studies have been primarily focused on the reaction of thiophenes with singlet oxygen ($^1O_2$) but in organic solvents.

In this study, we investigated the photoreactivity of a series of model thiophenes with varying number and position of alkyl groups. This has been done in the presence of model and natural sensitizers, namely chromophoric dissolved organic matter (CDOM), the light absorbing fraction of naturally occurring organic molecules in aquatic systems. The photoreactivity of thiophenes with reactive intermediates produced from CDOM (such as $^1O_2$ and excited triplet states of CDOM), its efficiency, mechanism and the effect of alkyl substitutions have been investigated and will be discussed in detail. These results are important for evaluating the environmental fate of an understudied but important class of organosulfur containing compounds.

Ultrasound-Enhanced Carbocatalysis Using Iron-Activated Biochar and Peroxymonosulfate: Effect of Frequency on the Removal of Acetaminophen from Waters

S. Estrada-Flórez[1], E. Serna-Galvis[1], J. Lee[2] and R. Torres-Palma[1]*

[1]Universidad de Antioquia (UdeA), Grupo de Investigación en Remediación Ambiental y Biocatálisis (GIRAB), Instituto de Química, Facultad de Ciencias Exactas y Naturales, Calle 70 No. 52-21, Medellín, Colombia
[2]University of Surrey, Chemical and Process Engineering, Guildford, GU27XH, United Kingdom

ricardo.torres@udea.edu.co

The combination of ultrasound (US) and carbocatalysis has recently been investigated with excellent results (Grilla et al., 2020; Chu et al., 2021). Here, US was combined with potassium peroxymonosulfate (PMS), and iron-activated biochar (Fe-BC) for the removal of acetaminophen (ACE). The US/Fe-BC/PMS system was compared with the other possible systems (US, oxidation by PMS, Fe-BC adsorption, Fe-BC/PMS, US/PMS, and US/Fe-BC). Besides, the effect of frequency (40, 375, and 1135 kHz) on the kinetics and synergy was evaluated in all sonochemical systems. The results (see Fig. 1) showed that in the US system, the kinetics was favored at 375 kHz due to the increased production of hydroxyl radicals, and interesting synergistic and antagonistic effects were observed at the low and high frequencies where mechanical effects prevail. On the other hand, the US/Fe-BC/PMS at 40 kHz was the most efficient system obtaining 95% ACE removal in the first 10 minutes of the treatment, with high synergy (S = 10.30). At this frequency, the US has mechanical effects that contribute to biochar disaggregation, which increases the availability of catalytic sites that promote PMS activation. This system was also evaluated in real water matrices: Hospital wastewater (HWW), urine, and seawater (SW) evidencing the competition of organic matter by the sonogenerated species and the intensification of the removal when chloride ions are present. It was also verified that although the US/Fe-BC/PMS is not a mineralizing system, it generates by-products less toxic than the parent molecule and is effective after three cycles of reuse.

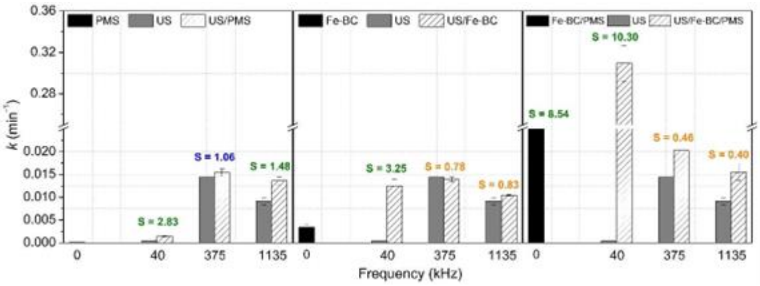


Fig 1. Effect of the US frequency on the kinetics (k) and synergy (S) of the ACE removal. Green: Synergistic, Blue: Additive, Orange: Antagonistic.

References

Grilla, E. et al. (2020) Activation of persulfate by biochar from spent malt rootlets for the degradation of trimethoprim in the presence of inorganic ions, J. Chem. Technol. Biotechnol. 95, 2348–2358. doi: 10.1002/jctb.6513.

Chu, J. et al. (2021) Enhanced sonocatalytic degradation of bisphenol A with a magnetically recoverable biochar composite using rice husk and rice bran as substrate, J. Environ. Chem. Eng. 9, 105284. doi: 10.1016/j.jece.2021.105284.

Comprehensive Assessment of Zero-Liquid-Discharge Treatments for Indirect Potable Reuse of Tertiary Wastewater Using Advanced Oxidation Processes Versus Conventional Treatments: Fate of Microbiological Parameters and Compounds of Emerging Concern

S. Murgolo[1]*, O. De Giglio[2], C. De Ceglie[1], F. Triggiano[2], F. Apollonio[2], C. Calia[3], C. Pousis[3], A. Marzella[3], F. Fasano[2], M. E. Giordano[4], M. G. Lionetto[4], D. Santoro[5], O. Santoro[5], C. Di Iaconi[1], M. De Sanctis[1], M. T. Montagna[2], G. Mascolo[1,6]

[1]CNR-Istituto di Ricerca Sulle Acque, Bari, Italy
[2]Department of Interdisciplinary Medicine, Hygiene Section, University of Bari Aldo Moro, Bari, Italy
[3]Department of Biomedical Science and Human Oncology, University of Bari Aldo Moro, Bari, Italy
[4]Department of Biological and Environmental Sciences and Technologies, University of Salento, Lecce, Italy
[5]AquaSoil S.r.l., Fasano, Brindisi, Italy
[6]CNR-IRPI, Bari, Italy

sapia.murgolo@ba.irsa.cnr.it

Two advanced oxidation processes (AOPs), namely ozone/H_2O_2 and UV/H_2O_2, were tested at pilot scale as zero-liquid-discharge alternative treatments for the removal of microbiological (bacteria and viruses), chemical (compounds of emerging concern (CECs)) and genotoxic responses from tertiary municipal wastewater for indirect potable reuse (IPR). The AOP treated effluents were further subjected to GAC filtration and UV disinfection, following the concept of multiple treatment barriers. As a reference, a consolidated advanced wastewater treatment train consisting of ultrafiltration, UV disinfection, and reverse osmosis was also employed.

The results showed that, for the same electrical energy applied, the ozone/H_2O_2 treatment was more effective than the UV/H_2O_2 treatment in removing CECs. Specifically, the ozone/H_2O_2 treatment achieved an average CECs removal efficiency of 66.8%, compared to 18.4% for the UV/H_2O_2 treatment. The subsequent GAC filtration step, applied downstream the AOPs, further improved the removal efficiency of the whole treatment trains, achieving rates of 98.5% and 96.8% for the ozone/H_2O_2 and UV/H_2O_2 treatments, respectively. In contrast, the ultrafiltration step of the reference treatment train only achieved a removal percentage of 22.5%, which increased to 99% when reverse osmosis was used as the final step.

Microbiological investigations showed that all three wastewater treatment lines displayed good performance in the complete removal of mandatory (Escherichia coli, coliforms and Enterococci) and optional parameters (Salmonella spp, S.aureus and Clostridium perfringens), according to national Legislative Decree 31/2001 and new European Directive 2020/2184 on the quality of water intended for human consumption. Only P. aeruginosa (not foreseen by new European Directive) resulted resistant to all treatments with a higher removal by UV/H_2O_2 when higher UV dose was applied. In addition, E. coli STEC/VTEC and enteric viruses (HAV, HEV, Adenovirus, Enterovirus, Norovirus and Rotavirus), were found to be completely removed in all tested treatments. No genotoxic activity was detected in any effluent even when concentration factors up to 1000-time was applied.

When the chemical cost associated with using 11-12 mg/L of H_2O_2 (equivalent to 0.130 €/m^3) was added to the cost calculations, the overall operational cost (energy plus chemical) required to achieve 50% average CECs removal in tertiary effluent for an hypothetical full-scale plant of 250 m^3/h (or 25,000 inhabitants) was 0.183 €/m^3 for the ozone/H_2O_2 treatment train, and 0.425 €/m^3 for the UV/H_2O_2 treatment train.

A New Combination of Dye-Surfactant To Bring Down The Methyl Violet Dye Waste, an Industrial Pollutant: A Pilot Study

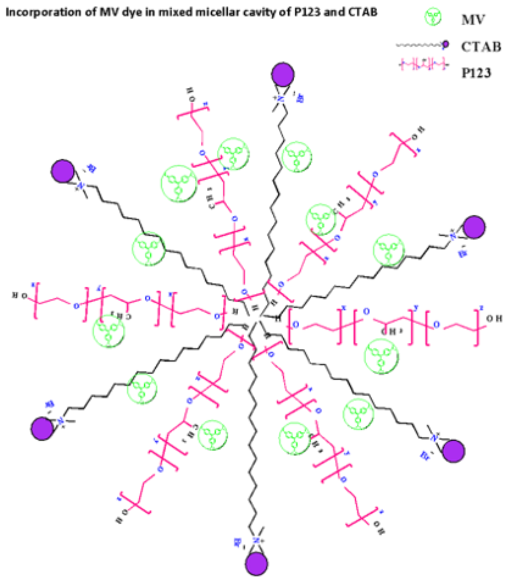
I. Tumbas[1*]

ivana.ivancev-tumbas@dh.uns.ac.rs

Methyl Violet (MV) is a common hazardous dye polluting water. Increasing the solubility of this dye will bring down the quantity of dye necessary for dyeing. This will automatically reduce the quantity of dye waste which will directly reduce the industrial pollution. Surfactants are known to enhance solubilization of dyes. For enhancing solubility of MV, a cationic dye, it is generally combined with micellar system of anionic surfactants, which are oppositely charged. We attempted to test the effect of solubility of MV dye by combining it with mixed cationic-nonionic micellar systems. The first micellar system employed was a combination of Pluronic P123(P123), a non-ionic surfactant and Cetyltrimethyl ammonium bromide (CTAB), a cationic surfactant. The second micellar system employed was a combination of P123, a non-ionic surfactant and Cetylpyrinidium bromide (CPB), a cationic surfactant. The binary systems were investigated through UV-visible Spectroscopy, Conductivity and FT-IR studies. Negative values of free energy of micellization were obtained for both the systems viz. P123+CTAB and P123+CPB, which is suggestive of spontaneous binding between MV and both the micellar systems, thus, enhanced solubilization. There is potential application of this process in industry. This is a pilot study and further study is recommended.

GRAPHICAL ABSTRACT

Incorporation of MV dye in mixed micellar cavity of P123 and CTAB



Venlafaxine and Tramadol Produce Different Ozonation Products in Pure and Wastewater

S.harel[1], P. R. Tentscher[2] and K. Bester[1]

[1]Environmental Science, Aarhus University
[2]Dortmund, Germany

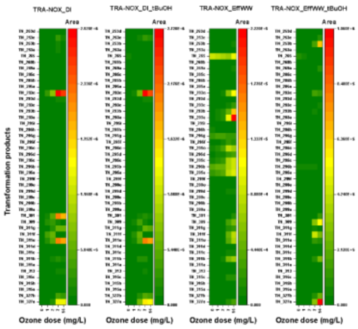
Ozonation is one of the predominant technologies to remove micropollutants from wastewater. One of the major challenges in this area is to understand the formation of ozonation products from the micropollutants which are usually oxidized but not mineralized. Identification of ozonation products is usually done in pure water, to avoid overwhelming signals from the TOC of the water (ozonation by-products).

In the present study, we selected venlafaxine and tramadol *N*-oxides as model compounds for primary ozonation products that can be further reacted during water treatment (Kharel et al., 2022). The ozonation reaction and product formation of these *N*-oxides was analysed, using either pure water or effluent wastewater. Our results show that for these moderately ozone-reactive compounds, matrix effects on the qualitative and quantitative product formation are pronounced.

For moderately ozone-reactive compounds, both ozone and OH radicals generated in situ during ozonation can contribute to the abatement. The majority of the differences in observed products can be attributed to different concentrations of OH radical, which are controlled by the DOC in the respective water, which can be demonstrated by utilizing quenchers of OH radicals such as *tert*-butanol.

The formation of some second tier ozonation products (TN_301) can be completely suppressed both by *tert*-butanol and the DOC of the wastewater. The formation of other ozonation products (TN_295a-g) occurs only in the effluent wastewater and not in pure water, but can be suppressed by *tert*-butanol.

Conclusion: It is not sufficient to do the ozonation product identification in pure water, when assessing ozonation of wastewater. Even pollutants that are highly reactive towards ozone may produce primary products that are only moderately reactive, and for their further degradation HO radical and thus matrix effects cannot be neglected. Identifying ozonation products in reactions conducted in wastewater is needed as a second experiment.



References

Kharel, S., et al. 2022. Further transformation of the primary ozonation products of tramadol- and venlafaxine *N*-oxide: Mechanistic and structural considerations, Science of the Total Environment, 845, 157259.

Long-Term Drift in Several Properties of Newer Pharmaceuticals: Are They Increasingly Recalcitrant to Removal in Wastewater Treatment?

J. O. Straub[1], J. Le Roux[2] and D. Tedoldi[3]*

[1]ERA Competence, CH–4123, Allschwil, Switzerland
[2]Univ Paris Est Creteil, LEESU, 61 avenue du Général de Gaulle, F–94010, Creteil, France
[3]Univ Lyon, INSA Lyon, DEEP, EA7429, 11 rue de la Physique, F–69621, Villeurbanne, France

damien.tedoldi@insa-lyon.fr

This study investigates whether newer pharmaceutical organic active substances (OASs) are more recalcitrant to biodegradation than older ones, and examines possible consequences in terms of removal in wastewater treatment plants (WWTPs). 1850 unique small-molecule OASs were considered; for 1641 of them a year of introduction was found, ranging from 1840 to present. Experimental data on (i) n-octanol/water partition coefficients (logKow), (ii) ready biodegradability – as defined by the OECD Test Guidelines 301 (1992) – and (iii) removal in WWTPs, were collected from the literature as well as chemical databases; then the dataset was expanded using the common, free, quantitative structure-property software EPISuite (US EPA, 2017). After checking the goodness of fit of EPISuite predictions against the available experimental data, time series statistics were applied to the dataset.

Molecular mass and logKow values displayed a positive shift over time with newly introduced OASs (Figure 1), hardly compatible with the hypothesis of same parent distributions. Readily biodegradable compounds were found to represent a relatively small proportion of all OASs, and this proportion tended to decrease over time. However, despite newer OASs being less biodegradable, the EPISuite-predicted removal in WWTPs showed an increase over time for the upper half of the values, reflecting an expected increase in adsorption to sludge. Likely reasons for this result will be discussed, together with the value of modelling tools like EPISuite for basic, initial environmental fate estimation for OASs.

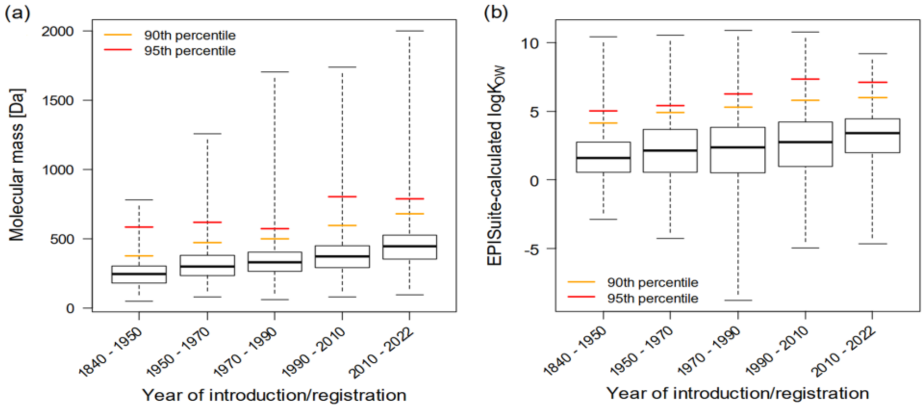


Figure 1 – Year of first registration/introduction to the market versus (a) molecular mass and (b) logKow (dataset split into time series groups).

References

OECD (1992) ‘Test No. 301: Ready Biodegradability’, OECD Guidelines for the Testing of Chemicals, Section 3, OECD Publishing, Paris, France. https://doi.org/10.1787/9789264070349-en

US EPA (2017) ‘Estimation Program Interface Suite (EPISuite)’, United States Environmental Protection Agency, Office of Pollution Prevention and Toxic Risk Assessment Division, Washington, DC, USA.

Attenuation of Trace Organic Compounds Along Specific Hyporheic Flow Paths

C. J. Reith[1,2] *, S. Spahr[1], M. Posselt[3], A. Putschew[2], and J. Lewandowski[1] [5]

[1]Leibniz Institute of Freshwater Ecology and Inland Fisheries, Berlin, Germany
[2]Technical University of Berlin, Berlin, Germany
[3]Stockholm University, Stockholm, Sweden
[5]Humboldt University, Berlin, Germany

christoph.reith@igb-berlin.de

The hyporheic zone of a stream, i.e. the streambed, is characterized by steep redox gradients, high microbial activity, and high turnover rates of chemicals, such as dissolved organic carbon, nutrients, or trace organic compounds. Studying the turnover processes in field experiments is challenging, as high spatial heterogeneity leads to unknown inhomogeneous flow paths. To tackle this problem, we developed and tested an experimental setup which presets short (40 cm), U-shaped hyporheic flow paths that enable sampling of the same pore water parcel at flow distances of 5, 15, 25, and 35 cm from the sediment-water interface. This setup was implemented in triplicates downstream a wastewater treatment plant in the hyporheic zone of the urban lowland River Erpe (Brandenburg, Germany). During 14 consecutive hours, we took pore water samples, which were analyzed for redox properties and 18 different trace organic compounds including pharmaceuticals, an artificial sweetener, iodinated X-ray contrast media, corrosion inhibitors, and three transformation products. As water flowed along the flow paths, we observed a clear redox zonation with denitrification and a propagation of an electrical conductivity signal from the wastewater treatment plant along the flow paths. Median residence times were 11.67 or 16.92 hours, respectively, for different specific flow paths. The relative attenuation of trace organic compounds along the whole flow paths could be divided into four groups: strong attenuation (5 of the 18 trace organic compounds), moderate attenuation (7 compounds), slight to no attenuation (5 compounds), and formation (1 compound). The attenuation was strongest in the first 5 to 15 cm, which corresponded to the oxic sections of the flow paths. Our work shows the relevance of knowing hyporheic flow paths to better assess hyporheic chemical turnover processes. Furthermore, the presented setup can be used in field experiments when it is necessary to know the hyporheic flow path, to sample along this path, or to intentionally manipulate flow path properties (e.g., the sediment).

A Survey of Industrial N-Nitrosamine Discharges in Switzerland

F. Breider[1*], C. Gachet Acquillon[1] and U. von Gunten[2]

[1]Ecole Polytechnique Fédérale de Lausanne (EPFL), ENAC, IIE, CH-1015 Lausanne, Switzerland
[2]Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-8600 Dübendorf, Switzerland

florian.breider@epfl.ch

N-nitrosamines are formed during different industrial processes and are of significant concern due to their carcinogenic and mutagenic properties. For instance, the formation of N-nitrosamines has been associated with rubber manufacturing and processing, leather tanning, metal casting, metalworking using cutting fluids, electronic industry and food processing. Recently several studies have also shown that N-nitrosamines are unintentionally formed during the production process of certain pharmaceuticals. N-nitrosodimethylamine (NDMA) concentrations in Swiss primary and secondary effluents of municipal WWTPs are usually in the ng/L range, with peak concentrations of in the µg/L range (Krauss et al., 2009). Such concentration peaks are suspected to be caused by industrial discharges, resulting in highly variable N-nitrosamine concentrations in municipal wastewater. This study reports concentrations of N-nitrosamines in eight different industrial wastewater treatment plants in Switzerland and the variability of their abundance (Breider, Gachet Aquillon and von Gunten, 2023). Only four N-nitrosamine species, NDMA, N-nitrosodiethylamine (NDEA), N-nitrosodibutylamine (NDBA) and N-nitrosomorpholine (NMOR) were above the limit of quantification in this campaign. Remarkably high concentrations (i.e. up to 975 µg NDMA/L, 90.7 µg NDEA/L, 1.6 µg NDBA/L and 710 µg NMOR/L) of these N-nitrosamines were detected at seven of eight sites. These concentrations are two to five orders of magnitude higher than those typically detected in municipal wastewater effluents. These results suggest that industrial effluents may be a major source of N-nitrosamines. Although very high concentrations of N-nitrosamines have been detected in industrial discharges, various processes in surface water can partially mitigate their concentrations (e.g. photolysis, biodegradation and volatilization) and hence the risk to human health and aquatic ecosystems. Nevertheless, there is little information on long-term effects on aquatic organisms and therefore the discharge of N-nitrosamines to the environment should be avoided until the impact on ecosystems is assessed.

References

Krauss, M. et al. (2009) ‘Occurrence and removal of N-nitrosamines in wastewater treatment plants’, Water Research, 43(17), pp. 4381–4391. doi:10.1016/j.watres.2009.06.048.

Breider, F., et al. (2023) ‘A survey of industrial N-nitrosamine discharges in Switzerland’, Journal of Hazardous Materials, 450, p. 131094. doi:10.1016/j.jhazmat.2023.131094.

Synergistic Removal of Pharmaceuticals and Emerging Contaminants from Aqueous Solutions: an Investigation of Bi-Metal Catalysts, Magnesium, and Green Hydrogen as Efficient Degradation Agents

V. Birke[1*], R. Singh[1], O. Prang[1], L. Vigelahn[1], K. Bläsing[1]

[1]Hochschule Wismar – University of Applied Sciences, Technology, Business and Design, Faculty of Engineering Science, Department of Mechanical, Process and Environmental Engineering, Philipp-Müller-Str. 14, 23966 Wismar, Germany

volker.birke@hs-wismar.de

This research aims to investigate highly efficient methods for removing emerging contaminants such as pharmaceuticals, personal care products, and drugs from contaminated wastewater. The study has evaluated the use of micro and nano-iron particles, iron bimetals, magnesium and magnesium catalyst combinations in the removal of diclofenac (DCF), ibuprofen (IBP), bisphenol A (BPA) and 17α-ethinylestradiol (EE2) from aqueous solutions, using laboratory-scale batch experiments. The iron bimetal systems were developed by depositing Co, Cu, In, Ni and Sn on the surface of Fe. Results showed that DCF was removed from the solution through adsorption on a Fe-Cu or Fe-Ni bimetal and/or iron hydroxide formed during corrosion, with at least 46 % and 25 % removal rates, respectively. When Mg was combined with Rh, a hydrogenation degradation reaction decreased all sample substance concentrations, with virtually no adsorption observed. Similarly, using Pd catalysts led to rapid decreases in concentrations of DCF and EE2 within minutes.

A kinetic model was fitted simultaneously to all four data sets, which indicated that the degradation of DCF on the Rh-HK surface followed a modified first-order kinetics. An activation energy of 59.6 kJ/mol was calculated using the Arrhenius equation, consistent with similar results reported in the literature (Park et al., 2020). Overall, these findings suggest that using micro-iron particles, iron bimetals, magnesium and magnesium catalyst combinations could be highly effective methods for removing emerging contaminants from wastewater.

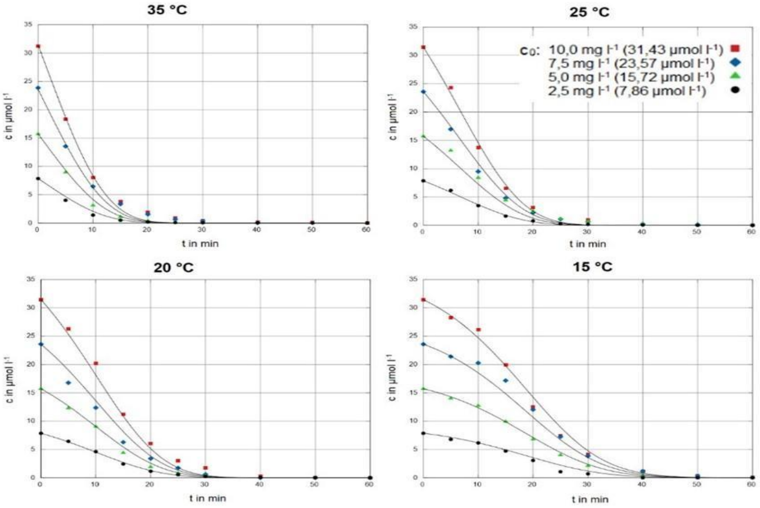


Fig. 1 Simultaneous fits of data sets for DCF concentration curves with magnesium and Rh-HK at different temperatures (35 °C, 25 °C, 20 °C, 15 °C).

References

Park, J. et al. (2020). Exploring reductive degradation of fluorinated pharmaceuticals using Al2O3-supported Pt-group metallic catalysts: Catalytic reactivity, reaction pathways, and toxicity assessment. Water Research, 185, p.116242.

Coupled Physical and Chemical Fouling Control Methods in Submerged Anaerobic Ceramic Membrane Bioreactor System Treating High Strength Food Wastewater

Y. Lee[1], C. Jung[1], H. Kim[1], and S. Lee[1*]

[1]Sunkyunkwan University, Department of Water Resources, Graduate School of Water Resources, Suwon 16419, Korea.

sookim@skku.edu

The treatment of high strength food wastewater presents a significant challenge due to the high organic and nutrient content. Anaerobic ceramic membrane bioreactors (AnCMBRs) have been demonstrated to be effective for treating this type of wastewater, but membrane fouling remains a major issue that can negatively impact system performance, This study investigates the effectiveness of coupled physical and chemical fouling control methods in an AnCMBR system treating high strength food wastewater.

The physical fouling control method in this study applies a movable rubber blade between flat-sheet ceramic membranes immersed in an anaerobic reactor and arranged at regular intervals. These movable rubber blades prevent membrane fouling from deepening by scraping off membrane foulants. The study examines whether the physical membrane fouling control method using a movable rubber blade affects the treatment efficiency of high-concentration food wastewater in the anaerobic MBR system, considering COD removal efficiency, methane production rate, and changes in microbial species in anaerobic reactors.

The chemical fouling control method in this study applies salt assisted backwash (SAB). This method uses the combination of three salts of NaOCl, $MgCl_2$, and $NaHCO_3$. These mixed salts solution is used during backwashing, and it passes through the membrane fouling layer accumulated on the surface of the ceramic membrane through backwashing, weakening the cohesion of the membrane fouling layer through osmotic swelling so that the membrane fouling layer can be easily removed. Each salt has another purpose: NaOCl helps destroy the biofouling layer, $MgCl_2$ contributes to reducing the phosphorus concentration in the effluent of the anaerobic reactor by combining with phosphorus in the food wastewater to form struvite, and $NaHCO_3$ contributes to keeping optimal pH condition of anaerobic MBR. The study examines whether this chemical membrane fouling control method using the salt-assisted backwash affects the treatment efficiency of high-concentration food wastewater in the anaerobic MBR system, considering COD removal efficiency, methane production rate, and changes in microbial species in anaerobic reactors.

A Novel Concept of Environmental Samplers Based on Functionalized Membranes for the Control of Organic and Inorganic Pollutants in Water

C. Fontàs[1]*, B. Alcalde[1], E. Anticó[1]

[1]University of Girona (UdG), Department of Chemistry, Faculty of Science, Maria Aurèlia Capmany 69, 17003, Girona, Spain

claudia.fontas@udg.edu

There is a need for simple and efficient techniques to improve the analysis of pollutants in environmental samples. Therefore, the design of simple devices that facilitate the monitoring of pollutants is mandatory to obtain reliable and significant data concerning contamination in aquatic environments. Polymer inclusion membranes (PIMs), a type of functionalized membranes consisting of an extractant embedded in a polymeric matrix, are easy to prepare and are stable materials useful to perform in situ extraction.

In the present study, we will present new samplers based on functionalized membranes for the monitoring of both metals and organic compounds in rivers. The composition of the membranes will depend on the analytes to be measured. In the case of metals, we have investigated two different extractants to be incorporated in a PIM: the commercial ionic liquid (IL) Cyphos 104 and the task-specific IL TOMATS. PIMs were prepared mixing the extractant and the polymer cellulose triacetate (CTA) and were mounted in teflon holders to be used as monitoring samplers. One of the study sites was the Osor river, situated in North-East Catalonia (Spain), which is influenced by continuous (effluent) and diffuse (run-off) metal inputs from a disused mine (Anticó, E. et al. 2020). PIM-samplers were deployed for 24 h, and once retrieved, they were directly analyzed by a low-power benchtop Energy Dispersive XRF (EDXRF) spectrometer. This new methodology allowed the easy detection of Zn in the river water.

Also, the preconcentration of three antibiotics of the family of sulfonamides (SF) has been successfully achieved using functionalized membranes. PIMs were prepared using three different polymers (CTA, poly(vinyl) chloride (PVC), and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)) and two different ionic liquids anion-exchangers as extractants (trihexyltetradecylphosphonium chloride and methyltrioctylammonium chloride (Aliquat 336)). Among the different membranes tested, it was found that the PIM made of 50% PVC and 50% trihexyltetradecylphosphonium chloride allowed a quantitative extraction for sulfathiazole (STZ), sulfamethazine (SMZ), and sulfamethoxazole (SMX).

The financial support of the Spanish Government (research project PID2019-107033GB-C22) is acknowledged.

References

Anticó, E. et al. (2020) A novel Cyphos IL 104-based polymer inclusion membrane (PIM) probe to minim biofilm zinc accumulation, Science of the Total Environment, 715, 136938. doi: 10.1016/j.scitotenv.2020.136938.

Rocher, V., Azimi, S. (Eds.), 2021. 'Effectiveness of Disinfecting Wastewater Treatment Plant Discharges: Case of chemical disinfection using performic acid'. IWA Publishing. https://doi.org/10.2166/9781789062106

Formation of Nitrogenous Disinfection by-Products Under Various Climate Change Scenarios

A. Kozari[1]*, D. Voutsa[1]

[1]Aristotle University of Thessaloniki, School of Chemistry, Environmental Pollution Control Laboratory, Ethnikis Amynis 41, 546 35, Thessaloniki, Greece

akozaria@chem.auth.gr

Climate change has an enormous impact on water resources. The ongoing rise of temperature, heavy rainfall incidents, extended dry periods and sea level rise are the major factors affecting the availability and quality of them. Heavy precipitation events are likely to become even more intense and frequent in the future. Extreme weather conditions, driven by climate change, increase external or internal derived precursors such as natural organic matter in water reservoirs, leading to the rise of Disinfection By-Products (DBPs). More than 600 DBPs are known so far and some of them are mentioned as highly toxic, carcinogenic and mutagenic. Besides the regulated DBPs -triahalomethanes and haloacetic acids -, there are also the emerging DBPs including Nitrogenous-DBPs (N-DBPs), which appear to be more toxic.

The aim of this study is to investigate the formation of N-DBPs under extreme conditions caused by climate change. For this reason, four scenarios were adapted: 1. sea level rise leading to increase of water salinity, 2. heavy rainfall incidents leading to flooding events, 3. water blooming and 4. water enrichment by humic substances. The target-compounds were Haloacetonitriles (HANs), Haloacetamides (HAcAms) and Halonitromethane (TCNM). In all cases, chlorination and chloramination were chosen as disinfection techniques. The results showed enhancement on the formation of N-DBPs and changes in the profile of them, as well as in their cyto- and geno-toxicity.

References

Bertels, D. and Willems, P. (2022) 'Climate change impact on salinization of drinking water inlets along the Campine Canals, Belgium', Journal of Hydrology: Regional Studies, 42, 101129, doi: 10.1016/j.ejrh.2022.101129.

Majidzadeh, H. et al. (2020) 'Hurricane resulted in releasing more nitrogenous than carbonaceous disinfection byproduct precursors in coastal watersheds', Science of the Total Environment, 705, 135785, doi: 10.1016/j.scitotenv.2019.135785.

Plewa, M.J. et al. (2017) 'TIC-TOX: A preliminary discussion on identifying the forcing agents of DBP-mediated toxicity of disinfected water' Journal of Environmental Sciences, 58, 208-216, doi: 10.1016/j.jes.2017.04.014.

Application of Chemometric Approaches to a Photocatalytic Pilot Plant for Environmental Issues and Study of the Material Recovery

N. Ghibaudo[1*], S. Alberti[1], E. Al-Hetlani[2], M. O. Amin[2], M. Madkour[3] and M. Ferretti[1]

[1]Chemistry and Industrial Chemistry Department, via Dodecaneso 31, 16146, Genova (Ge), Italy
[2]Kuwait University, Chemistry Department, Faculty of Science, P.O. Box 5969, Safat 13060, Kuwait
[3]Arish University, Chemistry Department, Faculty of Science, Al-Arish 45511, Egypt

nicolo.ghibaudo@edu.unige.it

Environmental problems related to the presence of emerging pollutants within the environment is finally receiving the proper attention, due to the dangerous side-effects that arise due to the presence of these biologically active compounds (pharmaceuticals and personal care products, PPCPs). Therefore, it's mandatory to find proper water treatment technologies able to efficiently counteract the spread of these new contaminants, because actual wastewater treatments are not able to deal with micro-contaminants (Rueda-Marquez et al., 2020). In this work, the performance of powdered TiO2-based photocatalysts for the degradation of different dyes has been evaluated in a photocatalytic pilot plant (Figure 1), with an investigated volume of 1L and solar simulated light as the irradiation source. Five different materials were tested in the pilot plant, and to study and evaluate the significance of the parameters which could affect the photocatalytic process, a chemometric approach was applied, selecting a model (D-Optimal) to simultaneously monitor a large number of variables (7, in this work), both qualitative and quantitative, on a wide range of levels. Also a different chemometric approach (Full Factorial model) has been implemented to compare the photocatlytic performances of each tested material on a different scale. Finally, the recovery of the photocatalyst was studied following a promising recuperation method, by reaching the isoelectric point (pHPZC) of each sample by means of pH modifications for the precipitation of TiO2 nanoparticles, annulling their surface charge (Azeez et al., 2018).

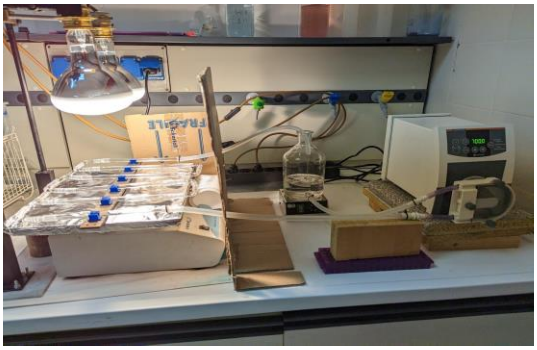


Figure 1: Photocatalytic pilot plant and its components: reactor, peristaltic pump and glass coil

References

Rueda-Marquez, J.J. et al. (2020) 'A critical review on application of photocatalysis for toxicity reduction of real wastewaters', Journal of Cleaner Production, 258, p. 120694. doi:10.1016/j.jclepro.2020.120694.

Azeez, F. et al. (2018) 'The effect of surface charge on photocatalytic degradation of methylene blue dye using chargeable titania nanoparticles', Scientific Reports, 8(1), p. 7104. doi:10.1038/s41598-018-25673-5.

Effect of Molecular Weight of Polyethylenimine on Chromate and Arsenate Adsorption Capacity of Polyethylenimine-Silica Composite Material in Aqueous Media

M. Xanthopoulou[1*], D. Gkiliopoulos[1], K. Triantafyllidis[1], M. Kostoglou[1], and I. A. Katsoyiannis[1]

[1]Aristotle University of Thessaloniki, Department of Chemistry, Box 116, 54124 Thessaloniki, Greece

mariaxanth@chem.auth.gr

Environmental pollution is a worldwide problem and heavy metals constitute one of the most important pollutant challenges. Long exposure to toxic heavy metals can lead to serious human health problems such as muscular, physical, and neurological degenerative processes. Chromium and arsenic are two of the most toxic and carcinogenic heavy metals widely present in water and wastewater (Zamora-Ledezma et al., 2021). Chromium and arsenic usually coexist in natural waters, which are released through natural causes such as soil corrosion and anthropogenic activity such as mining and alloy industries. In aqueous media, chromium and arsenic can exist in several anionic species, mainly as chromate (CrO_4^{2-} or $Cr_2O_7^{2-}$) and arsenate ($HAsO_4^{2-}$ or AsO_4^{3-}) (Baranik et al., 2018). Heavy metal ions are among the most released contaminants, and for this reason, they are particularly worrisome.

Adsorption is among the best methods to remove a wide variety of contaminants from water, including heavy metals. Among its advantages, we can highlight a high removal capacity, relatively low energy consumption and technical requirements for operation, and the possibility of avoiding major secondary pollution (Zamora-Ledezma et al., 2021). In our study, we prepare and use a polyethylenimine-silica composite material (SiO_2-PEI) as an adsorbent. Polyethylenimine (PEI) is a polymer with a high cationic charge. It can easily bind negatively charged chromate and arsenate due to the electrostatic interaction between PEI and anions. In our previous work, we proved that the adsorption capacity of SiO_2-PEI is affected by the molecular weight of PEI used in the adsorbent synthesis concerning phosphate ions adsorption (Xanthopoulou et al., 2021).

In this study, we examine the effect of the molecular weight of polyethylenimine on chromate and arsenate adsorption capacity of polyethylenimine-silica composite material in aqueous media. We use PEI of three different molecular weights, 800, 25000, and 70000 for the synthesis of SiO_2-PEI adsorbents, examining in parallel the performance of the synthesis process using different ratios of the primary component materials. Initial results showed that SiO_2-PEI materials of PEI 25000 and 70000 have been efficient in removing chromate and arsenate from aqueous media. The purpose of the study is to investigate the most efficient synthesis of the adsorbent material that would be more effective in the simultaneous removal of chromate and arsenate from aqueous media.

References

Baranik, A. et al. (2018) ‘Determination and speciation of ultratrace arsenic and chromium species using aluminium oxide supported on graphene oxide’, Talanta, 185, pp. 264–274. doi:10.1016/J.TALANTA.2018.03.090.

Xanthopoulou, M. et al. (2021) ‘Phosphate Removal Using Polyethylenimine Functionalized Silica-Based Materials’, Sustainability 2021, Vol. 13, Page 1502, 13(3), p. 1502. doi:10.3390/SU13031502.

Zamora-Ledezma, C. et al. (2021) ‘Heavy metal water pollution: A fresh look about hazards, novel and conventional remediation methods’, Environmental Technology & Innovation, 22, p. 101504. doi:10.1016/J.ETI.2021.101504.

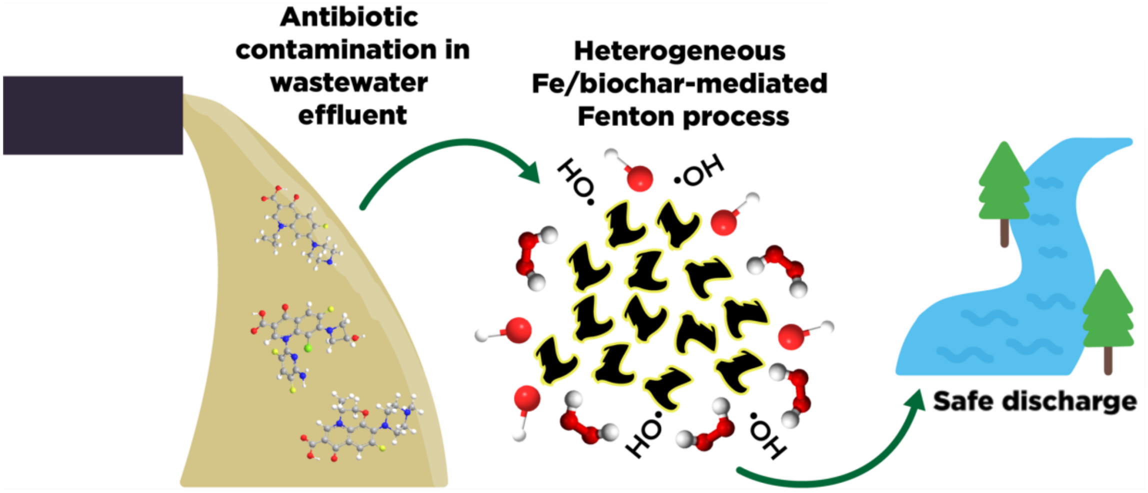
Removal of Fluoroquinolone Antibiotics from Water by Heterogeneous Fenton Process with Iron Sulphate Modified Biochar

A. Fiorentino[1*], A. Faggiano[1], M. Carotenuto[1], O. Motta[2], A. Proto[1]

[1]University of Salerno, Department of Chemistry and Biology “Adolfo Zambelli”, Via Giovanni Paolo II 132, 84084 Fisciano, SA, Italy
[2]University of Salerno, Department of Medicine Surgery and Dentistry “Scuola Medica Salernitana", Via S. Allende 1, 84081, Baronissi, Italy

afiorentino@unisa.it

In recent years, the increasing use of antibiotics (ABs), both on farms and for human use, has generated an environmental problem linked to the presence of these compounds in sewage effluents. Fluoroquinolones (FQs) are among of the most used ABs, as this class of ABs has proven effective in counteracting complications due to the SARS-CoV-2 virus, such as bacterial respiratory tract infections, i.e., pneumonia. Conventional treatments in use in civil sewage treatment plants are not suitable to eliminate these compounds. To prevent the spread of ABs in the environment, several innovative purification technologies are under investigation. Among these, advanced oxidation processes (AOPs) are gaining increasing interest in the removal of ABs and in particular FQs. Among AOPs, the heterogeneous Fenton process, using carbonaceous material as a support for the metal catalyst, appears to be an excellent alternative to homogenous Fenton, due to certain advantages such as good efficiency even at more neutral pH and lower catalyst consumption. In this work, the removal of FQs was investigated by the use of Biochar (BC), a secondary raw material, and iron-impregnated BC (Fe-BC) as Fenton catalysts. In order to optimize the operating conditions, i.e., pH, oxidant concentration (H_2O_2), a response surface methodology approach was used by two-level factorial design. FQs removals in excess of 99.99% in less than 30 min were obtained under neutral pH conditions. Moreover, Fe-BC reuse tests showed that this technology is very promising in the removal of ABs from wastewater.



FQs degradation through heterogeneous Fe/biochar-mediated Fenton process

References

Fiorentino, A. et al. (2022) ‘Neutral (Fe3+-NTA) and acidic (Fe2+) pH solar photo-Fenton Vs chlorination: Effective urban wastewater disinfection does not mean control of antibiotic resistance’, Journal of Environmental Chemical Engineering, 10(6), p. 108777. doi:10.1016/j.jece.2022.10877

Van Doorslaer, X. et al. (2014) ‘Fluoroquinolone antibiotics: An emerging class of environmental micropollutants’, Science of The Total Environment, 500–501, pp. 250–269. doi:10.1016/j.scitotenv.2014.08.075.

Characterizing Inorganic Elements in Urban Treated Wastewater for Sustainable Management: Variability and Fractionation of Metals

E. Varennes[1*], D. Blanc[2], A. Azaïs[1], J.-M. Choubert[1]

[1]INRAE, UR REVERSAAL, 5 Rue de La Doua, Villeurbanne, CS 20244, F-69625, France

[2]Univ Lyon, INSA Lyon, DEEP, EA7429, 69621 Villeurbanne, France

elodie.varennes@inrae.fr

The urban wastewater treatment plant is the receptacle for various materials, including metals and metalloids, with concentration varying from 80 mg.L-1 (Na) to 0.2 µg.L-1 (Cr) (Vriens et al., 2017). The treated wastewater output (TWW) still contains the majority of metal fluxes of the input, in particular for alkali and alkaline-earth metals (Ca, K, Li, Mg, Na, Sr). To move towards a circular economy in urban wastewater management via either TWW reuse or metal recovery, it is essential to improve the characterization of metals and metalloids. This study focuses on a deeper TWW inorganic characterization by measuring fifteen metals' concentrations for variability and fractionation. Compartments for fractionation are defined as particulate matter (superior to 0.45 µm), high colloid (between 0.45 µm and 30 kDa), low colloid (between 30 kDa and 3 kDa) and truly dissolved (inferior to 3 kDa).

Metals concentrations were measured by ICP AES or ICP MS after filtration with 0.45 µm cellulose acetate membrane. For fractionation, mineralization and ultrafiltrations at 30 kDa and 3 kDa were performed. Principal Components Analysis (PCA) was used to investigate TWW variability of eighty-nine different TWW samples collected at the outlet of a nitrifying-denitrifying activated sludge plant during dry weather conditions (thirteen sampling campaigns over two years).

According to their median relative deviation, cobalt shows highest dispersion (71%) and silicon lowest dispersion (8%) between campaigns. PCA shows that potassium variability is correlated neither to chromium nor to zinc variabilities. Sodium, magnesium, cobalt and silicon variabilities are the most correlated to each other. Concentration variability intra-campaign and inter-campaign seems to be of the same order of magnitude (up to a multiplying factor of five between lowest and highest concentration). However, investigation is still needed to understand if variabilities are correlated with other traditional characterization parameters (pH, COD, conductivity…).

Most of metals is truly dissolved (more than 60% of their concentration is in the fraction inferior to 3 kDa) except for iron and aluminum. This means the larger molecular weight fraction of metals in urban wastewater goes in the sludge output. It corroborates results from other studies (Choubert et al., 2011) for partitioning metals in wastewater treatment plant. Nevertheless, a few metals (Al, Fe, Mn, Mo) are present as particulate matter and 5 to 10% of silicon and zinc is present in the high colloidal fraction.

Results can be used to discriminate between processes that depends on size to separate metals from TWW. Ion exchangers should be the better equipped to remove truly dissolved metals (more than 95% inferior to 3 kDa) such as calcium, potassium, strontium and magnesium, whereas adsorbents should be a better choice for metals present in the colloidal fraction. Although other factors like charge are involved, we confirmed those hypotheses by removing more than 95% of calcium, magnesium and strontium from TWW with a weak cation exchanger and more than 90% of molybdenum with ironiron hydroxide grains.

References

Choubert, J.-M. et al. (2011) 'Influent concentrations and removal performances of metals through municipal wastewater treatment processes', Water Science and Technology, 63(9), pp. 1967–1973. doi:10.2166/wst.2011.126.

Vriens, B. et al. (2017) 'Quantification of Element Fluxes in Wastewaters: A Nationwide Survey in Switzerland', Environ. Sci. Technol., 51(19), pp. 10943–10953. doi:10.1021/acs.est.7b01731

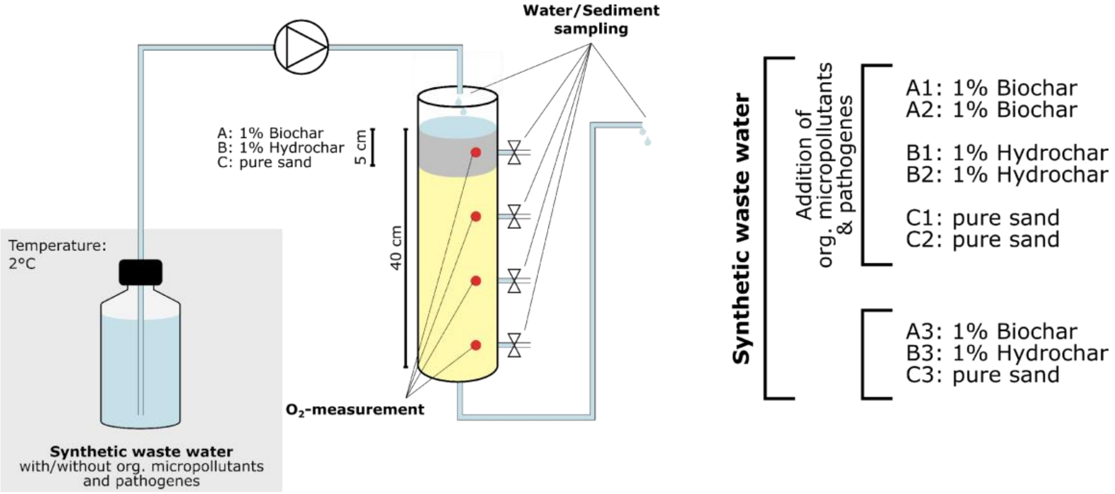
Hydrochar or Biochar Amendments to Increase the Retention of Organic Micropollutants and Pathogens in Managed Aquifer Recharge Systems (MAR)

U. E. Bollmann[1*], T. B. Bech[1], N. Vermaak[2], A. Magingi[3], S. Clarke[4], A. M. Smith[5], M. Gambino[6], and J. Aamand[1]

[1]Geological Survey of Denmark and Greenland (GEUS), Dep. of Geochemistry, Copenhagen, DK
[2]University of the Free State, Centre for Environmental Management, Bloemfontein, ZA
[3]Department for Water and Sanitation, Pretoria, ZA
[4]University of the Western Cape, Earth Science Dep., Bellville, ZA
[5]Aarhus University, Dep. of Biolog. and Chem. Engineering, Aarhus, DK
[6]Copenhagen University, Dep. of Veterinary and Animal Sciences, Frederiksberg, DK

ueb@geus.dk

Managed Aquifer Recharge (MAR) is a commonly used technique to improve water quality and to store water for later use in areas with precipitation seasonality, and it is a low-energy and low-cost water-recycling technology used worldwide (Dillon et al., 2019). The present study assessed the effects of a reactive barrier with 1% biochar or hydrochar on the leaching of organic micropollutants (22 pesticides and pharmaceuticals) and pathogens (S. Senftenberg, two model bacteriophages infecting E. coli) in laboratory column experiments (see figure below). The columns were run continuously for 4 months, and samples were analysed by HPLC-MS/MS and plate counting.
Biochar has a higher sorption capacity for most tested organic micropollutants than hydrochar and considerably higher than pure sand. Thus, the leaching of micropollutants was delayed in the amended columns compared to pure sand (biochar > hydrochar > sand). Degradation seemed slightly increased when hydrochar was used as a barrier compared to pure sand, while biochar did not affect the degradation efficiency. This is in accordance with a higher biological activity detected in the hydrochar amended columns compared to the biochar and sand columns.
Pathogen adhesion revealed strong adhesion of S. Senftenberg to all three materials, while the bacteriophages adhered most to biochar and limited adhesion was observed to hydrochar or sand. The leaching of the three pathogens was influenced by cell size, while the reactive barrier did not influence the leaching.



Experimental setup - 9 parallel columns with/without amendments and with/without feeding with organic micropollutants and pathogens

References

Dillon, P., et al. (2019). Sixty years of global progress in managed aquifer recharge. Hydrology Journal 27,1-30.

Ozonation of Secondary Metabolites from Cyanobacteria: Simultaneous Multi-Compound Competition Kinetic Measurements

V. Rougé[1*], A. Dax, U. von Gunten[1], E.M.-L. Janssen[1]

[1]Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-8600, Dübendorf, Switzerland

valentin.rouge@eawag.ch

Cyanobacterial blooms increase in frequency and intensity worldwide, notably in freshwaters that are serving as water supplies. During such bloom events, a diverse array of secondary metabolites (cyanopeptides) is produced and may reach drinking water treatment trains (He et al., 2016). Ozone (O_3) is commonly used as an initial and intermediate treatment step and its interaction with cyanopeptides is still largely unknown except for a few microcystins (Kim and Lee, 2019). Cyanopeptides are usually not commercially available and are currently only produced as complex mixtures from laboratory-grown bacterial strains. Studying the O_3 reactivity of individual compounds would require labour-intensive separation processes and kinetic experiments. Instead, the ozonation kinetics of cyanopeptides were assessed as a mixture, using several competitors (mostly micropollutants such as bezafibrate, clofibric acid or carbamazepine, with well-known apparent second-order rate constants, kapp) covering a wide range of O_3 reactivities.

The cyanopeptide mixtures were extracted from laboratory-grown Planktothrix rubescens and Microcystis aeruginosa cultures. Cyanopeptides were identified by HPLC coupled with high-resolution tandem mass spectrometry using suspect screening against the database CyanoMetDB (Jones et al., 2021), and confirmed by MS^2 fragmentation annotation. Competitors, buffer (phosphate/borate) and tert-butanol were added to the aqueous extract and various doses of O_3 (0.002-0.4 $mgO_3/mgDOC$) were spiked under vigorous stirring to the reaction solutions. The abatement of cyanopeptides and competitors was monitored by HPLC-HRMS/MS.

First, the 15 competitors were tested against each other, which demonstrated that the kapp needed to be within an order of magnitude to obtain a good correlation ($R^2 > 0.9$). As competitors with overlapping reactivities were selected, a more quantitative assessment could be done. Clofibric acid was the only competitor over one order of magnitude less reactive than expected while the others were within a factor 1.2-3 of their expected reactivity. The kapp values measured for the reactions of cyanopeptides with O_3 by the selected competitors generally agreed well with their expected reactivity, based on their reactive functional groups. For example, olefin- and phenol-containing cyanopeptides had kapp around $10^5\ M^{-1}\ s^{-1}$ at pH 7 and around 10^5 and $10^8\ M^{-1}\ s^{-1}$, respectively, at pH 9. For thioether and tryptophan-containing, kapp remained around 10^7-$10^8\ M^{-1}\ s^{-1}$ at pH 7-9.

The good correlation between abatement of cyanopeptides and competitors during ozonation demonstrates the possibility of performing competition kinetics in a complex mixture and with large concentration differences between the compounds. Some cyanopeptides with kapp obtained from a mixture will also be determined by more traditional kinetic experiments to assess the accuracy of the kapp estimates. In addition, some losses of linearity and descripancies between expected and measured reactivities need to be further evaluated. With a careful experimental design, this method with multiple competitors can be applied as a high-throughput kinetic screening method.

References

He, X. et al. (2016) 'Toxic cyanobacteria and drinking water: Impacts, detection, and treatment', Harmful Algae, 54, pp. 174-193. DOI: 10.1016/j.hal.2016.01.001.

Jones, M. R. et al. (2021) 'CyanoMetDB, a comprehensive public database of secondary metabolites from cyanobacteria', Water Research, 196, pp. 117017. DOI: 10.1016/j.watres.2021.117017.

Kim, M. S. and Lee, C. (2019) 'Ozonation of Microcystins: Kinetics and Toxicity Decrease', Environmental Science & Technology, 53(11), pp. 6427-6435. DOI: 10.1021/acs.est.8b06645.

Analysis of Disinfection By-Products (DBPs) In Laboratory Disinfection Simulations and From Genuine Disinfection Uses – Analytical Challenges and Factors Influencing DBP Formation

M. Hüben[1]*, M. Usman[2] and V. Linnemann[2]

[1]Fraunhofer Institute for Molecular Bology and Applied Ecology IME, Auf dem Aberg 1, 57392 Schmallenberg, Germany
[2]RWTH Aachen University, Institute of Environmental Engineering, Mies-van-der-Rohe-Str. 1, 52074 Aachen, Germany

michael.hueben@ime.fraunhofer.de

Disinfection by-products (DBPs) may be formed during disinfection applications, especially if organic matter is present. The environmental risk of DBPs must be considered in course of the authorization process of biocidal active substances in the EU, as stated in the EU Biocides Regulation 528/2012 (Regulation (EU) No 528/2012, 2012). Over the years and with advancing capability of the analytical techniques, several hundreds of DBPs have been detected after applications of biocides used for disinfection. The specific disinfection uses, and the reaction conditions have great influence on the formation of DBPs making regulatory approaches challenging and the complex matrices present during the applications prevent a simple and general analytical approach.

The goal of the project was to define worst-case conditions for environmental risk assessment of DBPs. As a result of a literature search, 61 DBPs were chosen as target analytes in laboratory disinfection simulations and from genuine disinfection uses. The laboratory disinfection simulations were performed using two matrix compositions, one focusing on disinfection uses in swimming pools and one containing organic matter that can be generally expected for other disinfection uses. Simulations were performed both in aqueous solutions and considering surface disinfection uses. Rection conditions influencing DBP were evaluated by variation of experimental parameters. Samples from genuine disinfection uses encompassed samples from swimming pools, pools within a thermal spa and samples from cooling systems. The analytical results of the laboratory simulations showed the complex system of reactions taking place after applying active substance in presence of matrix. The system was too interconnected to define worst-case conditions, even in controlled laboratory experiments. Conditions leading to a high formation of a specific class of DBPs might at the same time lead to a decreased formation of another DBP class changing the composition of the formed DBPs. The genuine samples from real disinfection processes underlined this finding, showing that in reality, even more factors partially characteristic for a specific disinfection use influenced the formation of DBPs. The presentation shows analytical problems that were faced in course of the experiments and focuses on the results obtained for DPBs in the various scenarios.

References

Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products.

Metal-Organic Frameworks as Efficient Adsorbents of Drinking Water Disinfection By-Products

G. Sanchez-Cano[1,2]*, P. Cristobal-Cueto[2], A. Lastra[1], L. Saez[1], S. Rojas[3], P. Horcajada[2]

[1]R&D&I Department, Canal de Isabell II, Square of Descubridor Diego de Ordás 3, 28003, Madrid, Spain
[2]Advanced Porous Materials Unit (APMU), IMDEA Energy Institute, Av. Ramón de la Sagra 3, 28935, Móstoles, Madrid, Spain
[3]University of Granada, Inorganic Chemistry Department, Faculty of Science, Av. Fuentenueva s/n, 18071, Granada, Spain

gabrielsanchezcano@canal.madrid

Water disinfection is a crucial process in drinking water treatment plants (DWTPs) to eliminate harmful microorganisms. Chlorination, a widely used effective, and low-cost method, can lead to the formation of potentially toxic species (i.e., chlorite and chlorate). In this sense, their concentration in water has been limited to 250 $\mu g \cdot L^{-1}$ by the European Council Directive 2020/2184. (The European Parliament and the Council of the European Union, 2020) In DWTPs, activated carbons are commonly used as adsorbent materials due to their low cost and mild operating conditions. However, their ability to retain ClO_3^- is limited and novel strategies to eliminate these by-products in drinking water are required.

In this regard, Metal-Organic Frameworks (MOFs), a family of porous hybrid crystalline materials, are gaining great attention due to their exceptional porosity and versatile composition/topology compared to traditional adsorbents. In this work, we propose a series of environmentally friendly Fe-terephthalate MOFs (MIL-101(Fe), MIL-88B(Fe), and MIL-53(Fe)) and their amine-derivatives (-NH_2) exhibiting high porosity for the selective adsorption of $ClO_3^-$and ClO_2^- from disinfected drinking water. (Tamames-Tabar et al., 2014) The MIL-88B(Fe)-NH_2 with flexible porosity exhibits remarkable efficiency in removing ClO_2^- and ClO_3^- from water, up to 100 and 40%, respectively, in just 10 minutes (Figure 1). Moreover, these MOFs exhibit exceptional stability in freshwater conditions with less than 1% degradation, showing a high potential for their use in freshwater treatment.

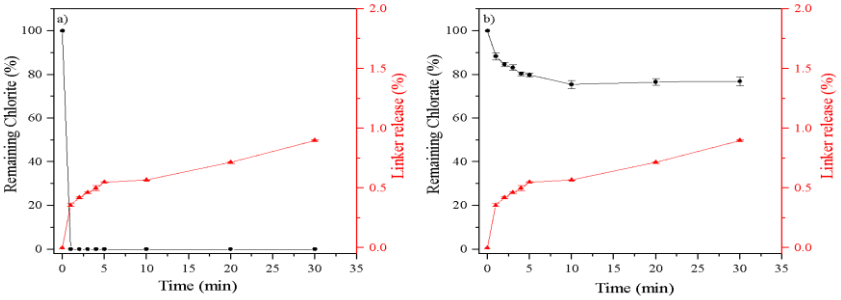


Figure 1. a) Chlorite (ClO_2^-) and b) chlorate (ClO_3^-) adsorption kinetics (black lines) and linker release (red lines) of MIL-88B(Fe)-NH_2 in water.

References

The European Parliament and the Council of the European Union (2020) Directive (EU) 2020/2184, EU (revised) Drinking Water Directive. Annex 1. Part B., Official Journal of the European Communities. Available at: https://eur lex.europa.eu/eli/dir/2020/2184/oj.

Tamames-Tabar, C. et al. (2014) 'Cytotoxicity of nanoscaled metal-organic frameworks', Journal of Materials Chemistry B, 2(3), pp. 262–271. Available at: https://doi.org/10.1039/c3tb20832j.

Innovative Technologies for Potential Toxic Elements Water Treatment

E. Pereira[1]*, J. Jacinto[1], N. Ferreira[1], T. Viana[1], J. Pinto[1], F. Monteiro[1], D. Tavares[1], B. Henriques[1]

[1]University of Aveiro, LAQV-REQUIMTE, Department of Chemistry, Aveiro, 3810-193 Portugal

eduper@ua.pt

Water is one of the most precious resources in our life. As a consequence of rapid population growth and industrial development, the contamination of water results in the presence of a wide variety of potential toxic elements (PTEs). Even at low concentrations, these elements show high toxicity, persistent character, bio-accumulation and bio-amplification along food chain. Mercury (Hg), arsenic (As), cadmium (Cd) and lead (Pb) continue to be at the top of the list of priority hazardous substances that must be reduced/eliminated from water (ATSDR, 2022), and a variety of processes, such as chemical precipitation, membrane processes, ion exchange and sorption have been used. However, most of these technologies are expensive, involve high operation costs and are ineffective in low metal concentration systems. Sorption is considered a good alternative in water treatment since it is eco-friendly, economic and allows to treat wastewater in trace realistic concentrations. In this work sorption has been focused on the use of synthetic (nanoparticles and mesoporous materials) and natural materials in their natural form (industrial and agricultural wastes, seaweeds) to develop new technologies for water treatment. Synthetic materials have been an important class of sorbents that can be designed with high sorption capacity for specific PTEs, and an innovative strategy to remove simultaneously different elements is the combination of different type of materials on the sorption process. Here, magnetic nanoparticles $Fe_3O_4@SiO_2/SiDTC$, $Fe_3O_4@SiO_2/EDTA$ and $CoFe_2O_4$ have shown good performance in the removal of PTEs in mono-elemental solutions, and the combination of nanoparticles allows to remove simultaneously several PTEs from contaminated waters. 2,5 mg/L of $Fe_3O_4@SiO_2/SiDTC$ nanoparticles were able to remove 99,9 % of Hg(II) (50 µg/L) in 8 hours and $CoFe_2O_4$ nanoparticles remove 92% of As(V) (1000 µg/L) in 48h. The combination of 60 mg/L of $Fe_3O_4@SiO_2/SiDTC$ and 60 mg/L of $CoFe_2O_4$ allows to remove simultaneously more than 80 % of As(V) (1000 µg/L), Cd(II) (200 µg/L), Hg(II) (50 µg/L) and Pb(II) (1000 µg/L) from water in 48 hours. On the other hand, natural materials are considered an area of great potential and an attractive alternative for the removal of PTEs from contaminated water, due to the low cost and high availability, and can be considered, in most cases, an "environment-friendly" process. In this work the ability of agricultural wastes as banana and potato peels, eggshells, eucalyptus bark and coffee waste has been carried out in order to determine their removal performance in contaminated water with PTEs. Banana peels were the best sorbent for Hg, an amount of 0,5 g/L eliminate more than 99% of the Hg in 24h hours (Fabre et al., 2021). Green (Ulva intestinalis and Ulva lactuca), brown (Fucus spiralis and Fucus vesiculas), and red (Gracilaria sp. and Osmundea pinnatifida) marine macroalgae also showed good removal of PTEs from waters (Fabre et al., 2021). In general, 6 g/L of all species removed 69,8 - 99,9 % of Hg (II) (50 g/L) in 24h.

References

ATSDR. Priority List of Hazardous Substances 2022. https://www.atsdr.cdc.gov/spl/index.html#2022spl (accessed march, 2023).

Fabre, E. et al. (2021) "Sustainable water treatment: Use of agricultural and industrial wastes to remove mercury by biosorption", Water, Air and Soil Pollution, 232, p. 1-17. doi:10.1007/s11270-021-05165-5.

Fabre, E. et al. (2021) "Bioaccumulation processes for mercury removal from saline waters by green, brown and red living marine macroalgae", Environmental Science and Pollution Research, 28, p. 30255-30266. doi:10.1007/s11356-021-12687-2

Advanced Treatment of WWTP Effluent for the Removal of Contaminants of Emerging Concern: Laboratory and Full-Scale Studies

A. Chiavola[1]*, C. Di Marcantonio[1], M.R. Boni[1], G. Cecchni[2], A. Frugis[2], S. Leoni[2], M. Lazzazzara[2], G. Valentina[2], M. Spizzirri[3]

[1]Sapienza University of Rome, Department of Civil, Building and Environmental Engineering, Via Eudossiana 18, 00184 Rome, Italy
[2]Acea Elabori, Via Vitorchiano 165, Rome, Italy
[3]ACEA ATO 2 SpA, Viale di Porta Ardeatina 129, 00154 Rome, Italy

agostina.chiavola@uniroma1.it

Contaminants of Emerging Concern (CECs) represent a class of pollutants which has received in the last years increasing attention due to their extremely wide diffusion in the environment, persistence and still uncomplete knowledge about their fate and behavior and effect on the ecosystem and human health. The Wastewater Treatment Plants (WWTPs) for domestic sewage with preliminary, primary and secondary treatments only are unable to remove effectively many of them, as observed by the authors in their previous studies. Tertiary treatments have proven to be able to reduce the concentrations of some CECS found in the secondary treated effluent. However, their efficiency depends on several factors, such as operating conditions, matrix composition, characteristics of the contaminant. The present study was carried out jointly with one of the largest Italian utility with the aim to investigate the capability of adsorption, ozonation and disinfection as advanced treatments for the abatement of CECs in the effluent. Activated carbon adsorption and ozonation were both studied at laboratory scale to predict the behavior of a single contaminant and a mixed solution under controlled conditions, focusing on the following CECs, selected based on previous studies by the same authors: sulfamethoxazole (SMX), carbamazepine (CBZ), 1H-Benzotriazolo (BTR) and 5-Metil-1H-Benzotriazolo (MBTR). Both equilibrium and column adsorption tests highlighted the following scale of removal: BTR-MBTR>CBZ>SMX. The ozonation tests conducted at different dosages showed a rapid and high removal of CBZ and SMX (>80%) at dosages comparable with those reported in the literature studies, whereas BTR and MBTR required higher dosages to achieve the same abatement level. Three types of disinfecting agents were investigated for a wide range of CECs by monitoring three different full-scale WWTPs: (1) peracetic acid, (2) sand filtration+UV radiation and (3) sodium hypochlorite. All of the disinfection processes did not provide a high removal rate, with the worst performance achieved by NaOCl. Peracetic acid was able to better remove methamphetamine and trimethoprim (TMT) only; when the dosage was increased significantly (in laboratory tests), the removal of lincomycin increased up to 61%. Combination of filtration and UV disinfection showed higher removal for SMX, ketoprophene and TMT only. Finally, the risk assessment was conducted on the effluent from these treatments. It was highlighted an ecological risk from low to medium depending on the final release, i.e. river or soil, respectively. The sanitary risk assessment showed a low risk for the reuse of the treated effluent in agriculture. These results provide an important contribution to the advancement in the knowledge of the processes for CECs reduction in the final effluent of WWTPs. Further studies are ongoing to optimize the adsorption and ozonation processes, which demonstrated to achieve better performance.Abstract (max 3200 characters – spaces included or 29 lines)

References

Di Marcantonio, C. et al. (2023) A step forward on site-specific environmental risk assessment and insight into the main influencing factors of CECs removal from wastewater, Journal of Environmental Management, 325, 116541, doi.org/10.1016/j.jenvman.2022.116541.

Di Marcantonio, C. et al. (2021) Evaluation of removal of illicit drugs, pharmaceuticals and caffeine in a wastewater reclamation plant and related health risk for non-potable applications. Process Safety and Environmental Protection, 152, 391-403, doi.org/10.1016/j.psep.2021.06.024.

Efficient Magnetic Sorbentes for Cleaning Rare Earth Elements from Water

D. S. Tavares[1]*, R. Fernandes[1], D. Branco[1], J.P. Pinto[1], L. Carvalho[2], T. Trindade[1], B. Henriques[1], E. Pereira[1]

[1]University of Aveiro, LAQV-REQUIMTE, Department of Chemistry, Aveiro, 3810-193, Portugal
[2]University of Aveiro, LCA, Department of Chemistry, Aveiro, 3810-193, Portugal

danielatavares@ua.pt

Rare earth elements (REEs) are emerging contaminants whose increasing use in technological applications causes risk of environmental contamination (Brewer et al., 2022). Electronic waste (e-waste) accounts for the fastest growing solid waste stream in the world and could be a major source of REE. In most cases, e-waste is disposed in landfills without any treatment leading to an increase of the levels of these elements in water and health effects already been shown in aquatic organisms (Freitas et al., 2020).

Efficient removal of contaminants from waters is necessary for human and environmental well-being. Conventional water treatment technologies are found inadequate for the effective removal at low concentration and therefore advanced treatments are necessary. Sorption is one of the most efficient techniques used due to its simple design and ease operation. The main aim of the present work was to evaluate and optimize the sorption efficiency of magnetic nanoparticles ($MnFe_2O_4$) for the removal of REE from contaminated water. The influence of sorption parameters such as sorbent dose, time, pH, ionic strengh and REE concentration was investigated. The sorbent shows high capacity to removal La, Ce, Y, Eu, Dy, Pr, Nd, Gd and Y in mixtures. Optimal conditions shows that 200 mg/L of $MnFe_2O_4$ nanoparticles were able to remove 100 % of the REE mixture with an initial element concentration of 5µmol/L, at pH 8 and in 6 hours. The use of magnetic sorbents shows an additional advantage, because they can be easily separated from water, by applying an external magnetic field.

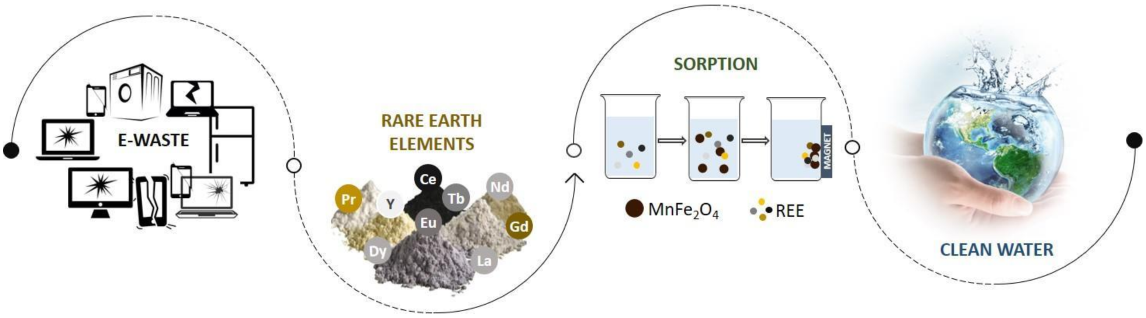


Figure 1 - Schematc representation of magnetic nanoparticles removal of REE from water

References

Brewer, A. et al. (2022) "Electronic waste as a source of rare earth element pollution: Leaching, transport in porous media, and the effects of nanoparticles", Chemosphere, 287, p. 1-8. doi:10.1016/j.chemosphere.2021.132217.

Freitas, R et al. (2020) " New insights on the impacts of e-waste towards marine bivalves: The case of the rare earth element Dysprosium". Environmental Pollution, 260, p. 1-10. doi:10.1016/J.ENVPOL.2019.113859

Efficient Cadmium Removal from Aqueous Solution Using Sustainable Clay/Polymer Composite Beads: Kinetic, Equilibrium and thermodynamic Study

K. Achchatar[1,2,3]*, S. Valange[1], B. Gregoire[1], A. Kherbeche[2], K. Draoui[3], H. Gallard[1]

[1]Université de Poitiers, Institut de Chimie des Milieux et des Matériaux de Poitiers, ENSI Poitiers, 1 rue Marcel Doré TSA 41105, 86 073 Cedex9, Poitiers, France
[2]Laboratoire de Matériaux, Procédés, Catalyse et Environnement (LMPCE), École supérieure de technologie, USMBA, Route d'Imouzzar BP2427, Fès, Maroc
[3]Laboratoire de Matériaux, et systèmes interfaciaux (LMSI), Faculté des sciences, Université Abdelmalek Essaadi, 93000, Tètouan, Maroc

khadija.achchatar@univ-poitiers.fr

Cadmium is a hazardous heavy metal that poses a significant risk to human health and environment quality. This toxic metal can enter the environment through various sources, including industrial waste, the use of fertilizers and pesticides in agriculture. Cadmium contamination in water resources can lead to severe health issues such as kidney damage, osteoporosis, and cancer.

Therefore, the development of efficient and sustainable adsorbents is crucial for the remediation of cadmium-contaminated water. In recent years, nanocomposites based on clay and biopolymers have emerged as promising adsorbents for heavy metals due to their high surface area, porosity, and biocompatibility. In this study we investigated the effectiveness of clay/polymer composite beads in cadmium removal from aqueous solution by adsorption process, an easy, efficient, and cost-effective water treatment technique.

The effect of various physicochemical parameters on the adsorption capacity of clay/polymer beads for Cd(II) ions was examined. The parameters studied included the adsorbent dosage (10-80 mg), contact time (30-360 min), initial pH (2-7), initial concentration of Cadmium (20-200 mg/L), and temperature (25-40°C). Results showed an adsorption capacity of 60 mg/g for the non-modified clay whereas clay/polymer beads had a higher adsorption capacity of 105 mg/g, in addition the thermodynamic parameters free energy ΔG°, enthalpy ΔH°, and the entropy ΔS° indicate that the adsorption of Cd (II) onto clay/polymer beads is a physical, spontaneous, and endothermic process)

References

Amari, A. et al. (2021) 'Clay-Polymer Nanocomposites: Preparations and Utilization for Pollutants Removal', Materials, 14(6), p. 1365. Available at: https://doi.org/10.3390/ma14061365

Ayouch, I. et al. (2020) 'Improved recovery of cadmium from aqueous medium by alginate composite beads filled by bentonite and phosphate washing sludge', Colloids and Surfaces A: Physicochemical and Engineering Aspects, 604, p. 125305. Available at: https://doi.org/10.1016/j.colsurfa.2020.125305.

Aziz, F. et al. (2020) 'Composites with alginate beads: A novel design of nano-adsorbents impregnation for large-scale continuous flow wastewater treatment pilots', Saudi Journal of Biological Sciences, 27(10), pp. 2499–2508. Available at: https://doi.org/10.1016/j.sjbs.2019.11.019.

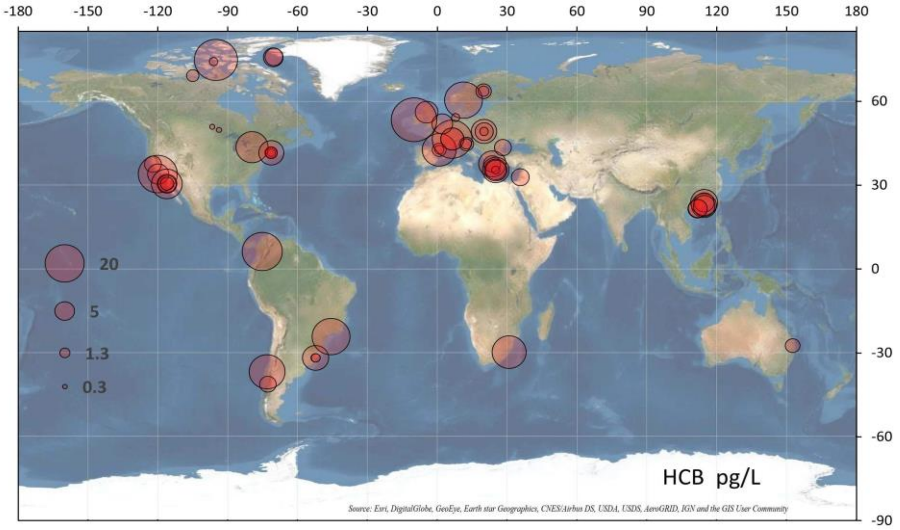
Passive Sampler-Derived Concentrations of Pops in the Waters of the World – First Results from the AQUA-GAPS/MONET Network

B. Vrana[1]*, R. Lohmann[2], D. Muir[3], F. Smedes[1], and J. Sobotka[1]

[1]Masaryk University, Faculty of Science, RECETOX, Kotlarska 2, 61137 Brno, Czech Republic
[2]University of Rhode Island, Graduate School of Oceanography, Narragansett, Rhode Island 02882-1197, United States
[3]Environment and Climate Change Canada, Aquatic Contaminants Research Division, 867 Lakeshore Road, Burlington, Ontario, Canada L7S 1A1

branislav.vrana@recetox.muni.cz

Persistent organic pollutants (POPs) are recognized as pollutants of global concern, but so far, information on legacy POPs' trends in the waters of the world has been missing due to logistical, analytical, and financial reasons. Passive samplers have emerged as an attractive alternative to active water sampling methods as they accumulate POPs, represent time-weighted average concentrations, and can easily be shipped and deployed. As part of the AQUA-GAPS/MONET network, passive samplers were deployed at 40 globally distributed sites between 2016-2020. In total, 61 exposed samplers were obtained from 21 freshwater and 40 marine deployments. Results from silicone passive samplers showed α-hexachlorocyclohexane (HCH) and γ-HCH displaying the greatest concentrations in the northern latitudes/ Arctic Ocean, in stark contrast to the more persistent penta (PeCB)- and hexachlorobenzene (HCB), which approached equilibrium. Enthalpies derived from the correlation of the logarithm of dissolved concentrations of PeCB and HCB versus reciprocal temperature were similar to those estimated for air-water exchange. Geospatial patterns of polychlorinated biphenyl (PCBs) aqueous concentrations closely matched original estimates of production and use, implying limited global transport. Positive correlations between log-transformed concentrations of $\sum_7$PCB, ∑DDTs, ∑endosulfan and ∑chlordane, but not ∑HCH, and the log of population density ($p<0.05$) within 5 and 10 km of the sampling sites also supported limited transport from use sites.



Aqueous concentrations of hexachlorobenzene at 40 marine and freshwater surface water sites, derived from passive sampling with silicone

References

Lohmann, R. et al. (2017) 'Aquatic Global Passive Sampling (AQUA-GAPS) Revisited: First Steps toward a Network of Networks for Monitoring Organic Contaminants in the Aquatic Environment', ES&T, 51(3), pp. 1060–1067. doi: 10.1021/acs.est.6b05159.

Sodium Alginate/Β-Cyclodextrin Immobilized Multi-Walled Carbon Nanotubes Hydrogel Adsorbent for Nickel (II) Metal Ion Removal

A. F. Zakaria[1], S. Kamaruzaman[1,2]*, and N. A. Rahman[1,3]

[1] Universiti Putra Malaysia, Department of Chemistry, Faculty of Science, 43400, UPM Serdang Selangor, Malaysia
[2] Universiti Putra Malaysia,Natural Medicines and Product Research Laboratory (NaturMeds), Institute of Bioscience (IBS), 43400, UPM Serdang Selangor, Malaysia
[3] Universiti Putra Malaysia, Materials Processing and Technology Laboratory, Institute of Advanced Technology, UPM Serdang, Selangor, 43400, Malaysia

sazlinda@upm.edu.my

Heavy metal ions contamination has endangered water body quality, possibly accelerating water diseases and sicknesses. Nickel(II) ion is one of the heavy metals frequently detected at alarming levels in many water environments as a consequence of negligent manufacturing companies improperly throwing it into main water reservoirs. In that course, this research work has been emphasized to develop a sustainable hydrogel adsorbent incorporating several biopolymers such as sodium alginate, β-cyclodextrin, and multi-walled carbon nanotubes. The removal of nickel(II) ions by hydrogel adsorbent of sodium alginate immobilized β-cyclodextrin and multi-walled carbon nanotubes (SA-β-CD/CNTs) was thoroughly studied in a batch experiment process using several adsorptive parameters such as initial concentration, pH, contact time, temperature, and dosage amount. The optimum adsorption conditions were comprehensively reported and showed an impressive percentage removal of up to 79.86 % when the concentration of nickel ion solution was maintained at 100 ppm, pH 5, 303K, and contacted for 120 minutes with 1000 mg adsorbent dosage. Moreover, the main interaction mechanism, such as coordination binding, surface complexation, and electrostatic attraction between the cationic sites of nickel ion and oxygenated functional groups of the hydrogel adsorbent during the adsorption process has been discussed. Therefore, this study successfully investigated the feasible approach to developing a single functionalized adsorbent for nickel(II) removal.

References

Mitra, S.et al. (2022) Impact of heavy metals on the environment and human health: Novel therapeutic insights to counter the toxicity. J. King Saud Univ. Sci., 34, 101865. https://doi.org/10.1016/j.jksus.2022.101865.

Lan, M. et al. (2022) Bio-accumulation effects of heavy metals Pb, Zn and Cd on Prococidochares utilis parasitism to Eupatorium adenophorum at Suzu metal mines, Yunnan. Heliyon 2022, 8, e10381. https://doi.org/10.1016/j.heliyon.2022.e10381.

Attar, K. et al. Sorption and Desorption Studies of Pb(II) and Ni(II) from Aqueous Soluti

Analysis of Glyphosate, Glufosinate and AMPA in Environmental Water with Direct Injection

J. de Alwis[1], B. Wuyts[1] and C. Pinto[1]

[1]*Waters Corporation*

Monitoring highly polar, small organic pesticides in waters as well as in food presents an analytical challenge. The purpose of this work was to demonstrate a direct injection UHPLC-MS/MS method for the determination of highly polar anionic pesticides in drinking and environmental waters. The method performance study was completed on an ACQUITY^{TM} UPLC^{TM} I-Class PLUS System with a Xevo^{TM} TQ Absolute Mass Spectrometer.

A method validation study was carried out on drinking, reservoir, river, and ground water. The method performance was assessed for glyphosate, AMPA and glufosinate using 2 spike levels at 20 and 60 ng/L for all analytes, with 11 replicates through inter-day and intra-day testing. The coefficients of determination (r2>0.999) and residuals (<10%) were all excellent. Average method performance for trueness was between 95 and 103% across all matrices, while the RSDs were below 11%.

This poster demonstrates the performance of a method, combining stable retention on Waters' Anionic Polar Pesticide Column (APPC), ultra-performance chromatography on the ACQUITY I-Class System and absolute MS power with the Xevo^{TM} TQ Absolute Mass Spectrometer to provide a fast and robust solution to one of the most challenging and time-consuming applications in environmental analysis.

Alginate Biopolymer Stabilized Pickering Emulsion Liquid Membrane for Methylene Blue Extraction from Aqueous Solution

A. Bidkar[1], M. Jerold[1]*

[1]National Institute of Technology Warangal, Department of Biotechnology, Warangal – 506004, Telangana State, India

jerold@nitw.ac.in

Membrane technology is one of the emerging technologies for the recovery of toxic elements from wastewater. Liquid membrane is gaining more importance due to its various salient features such less expensive, more permeability, higher diffusivity coefficient, and one step operation. Emulsion liquid membrane (ELM) was first introduced Norman N. Li in 1968 for the recovery of hydrocarbons. ELM is an advanced and alternative form of conventional liquid-liquid extraction technique which has high interfacial area and able to selectively recover solute from aqueous phase. ELM techniques was successfully used for the extraction of heavy metals or precious metals, dyes, Organic acids and other compounds. PELM is the modified version of ELM in which the emulsions are stabilized by colloidal solid particles. In PELM, the solid particles with a balance of hydrophilic and hydrophobic surface properties could strongly absorb at interfaces and stabilize emulsions have emerged in recent years. Pickering stabilization is the phenomena that solid particles employed on the interface of droplets to provide resistance to opposing coalescences, fusion and coarsening. In the present investigation, alginate biopolymer stabilized Pickering emulsion liquid membrane (PELM) was employed for the extraction of Methylene blue (MB) from aqueous solution. The novel PELM composed of aliquot 336 as a carrier, potassium hydroxide (KOH) as a stripping agent, and waste cooking oil (WCO) as the green diluent. WCO is a non-toxic organic solvent was used as substitution of petroleum based organic solvent in the preparation of PELM. The optimum conditions for the maximum removal of MB were: Emulsifier concentration – 2.3 (v/v %), Carrier concentration – 5.6 (v/v%), Treat ratio – 12, internal phase concentration – 0.92 M, initial external feed phase concentration – 100 ppm, O/A ratio – 1. The mechanism of MB extraction was also presented. At optimized condition, the maximum extraction of 98.8% was recorded. Kinetic analysis shows that the MB extraction by PELM follows first-order reaction. Furthermore, the thermodynamic analysis reveals that the extraction process was an endothermic, and spontaneous in nature.

References

Das, C., Rungta, M., Arya, G., DasGupta, S., & De, S. (2008). Removal of dyes and their mixtures from aqueous solution using liquid emulsion membrane. Journal of Hazardous Materials, 159(2–3), 365–371. https://doi.org/10.1016/j.jhazmat.2008.02.027.

Ramsden, W. (1904). Separation of solids in the surface-layers of solutions and“suspensions” (observations on surface-membranes, bubbles, emulsions, andmechanical coagulation). Preliminary account. Proceedings of the Royal Societyof London, 72, 156–164.

Pickering, S. U. (1907). Cxcvi.—emulsions. Journal of the Chemical Society,Transactions, 91, 2001–2021
Tong Zhang, Fuguo Liu, Jie Wu, To Ngai, Pickering emulsions stabilized by biocompatible particles: A review of preparation, bioapplication, and perspective, Particuology, Volume 64.

Investigation of Mutagenic Aromatic Amines in Municipal Wastewaters Using Passive Sampling

S. Krupčíková[1], M. Stiborek[1], Z. Šimek[1] and B. Vrana[1]

[1]Masaryk University, Faculty of Science, Centre RECETOX, Czech Republic

simona.krupcikova@recetox.muni.cz

Aromatic amines (AAs) represent an environmentally and industrially important group of compounds, including known and suspected mutagens. They often enter surface water and rivers directly from industrial emissions or indirectly as the metabolites of pesticides and have the potential to endanger aquatic ecosystems. Municipal wastewaters (WW) present a not yet-investigated potential emission source of AAs. This study aims to develop a representative method for monitoring AAs in WW and recipient surface water using passive sampling. We designed a hydrogel-based passive sampler (HPS) comprising a combination of AttractSPE™ SDB-RPS (styrene-divinylbenzene copolymer modified with sulphonic functional groups) sorption disk and a diffusive agarose hydrogel layer that is designed to control the AA mass transfer from water to the passive sampler (PS). The PS was tested for monitoring AAs in influent and effluent of a municipal wastewater treatment plant (WWTP) serving the city of Brno (Czech Republic), with a capacity of 500,000 equivalent inhabitants. PS were deployed for 1, 2, 3 and 4 weeks, using various overlapping deployment combinations to assess the performance characteristics of HPS. The uptake of AA to HPS was compared with their content in 24-hour composite water samples. The targeted analysis of samples included about 50 AAs with potential to cause adverse effects. Further, suspect screening of AAs on samples was performed. The performance of HPS will be discussed in terms of AAs uptake characteristics and a comparison of AAs detection in passive samplers and WW samples.

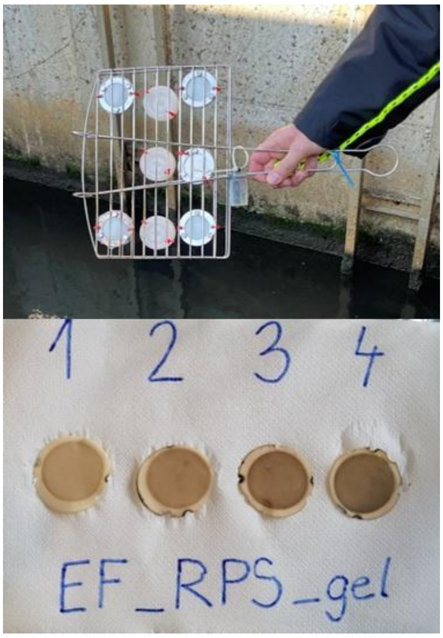


Figure - Passive samplers deployment - PS in stainless steel tray (up), appearance of SDB-RPS disk after placement to WWTP effluent for 1 - 4 weeks

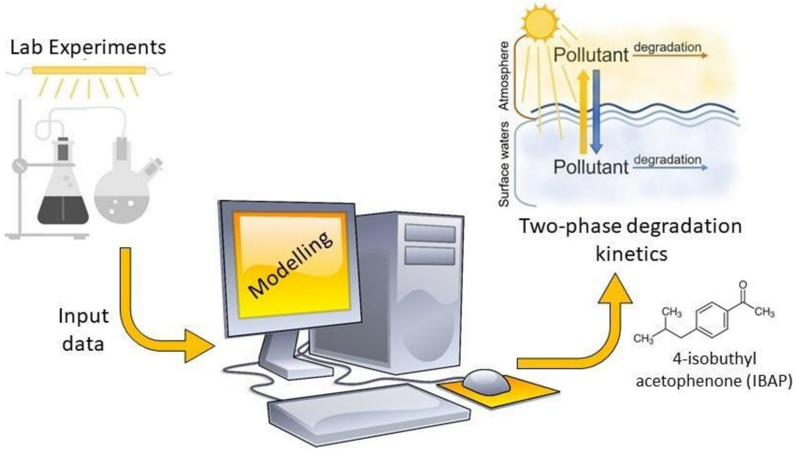
Use of a Simple Two-Media Degradation Model to Evelauate the Environmental Fate of a Semivolatile Transformation Product of Ibuprofen

M. Minella[1*], C. Arsene[2,3,4], I. G. Bejan[2,3,4], C. Roman[2,3,4], R. I. Olariu[2,3,4], M. Passananti[1,5], L. Carena[1], D. Vione[1]

[1]Università di Torino, Dipartimento di Chimica, Via Pietro Giuria 7 10125 Torino, Italy
[2]University of Iasi, Department of Chemistry, Faculty of Chemistry, 11 Carol I, 700506 Iasi, Romania
[3]University of Iasi, CERNESIM, 11 Carol I, 700506 Iasi, Romania
[4]University of Iasi, RECENT AIR, 11 Carol I, 700506 Iasi, Romania
[5]University of Helsinki, Institute for Atmospheric and Earth System Research (INAR), PL 64 00014 Helsinki, Finland

marco.minella@unito.it

The partitioning of semivolatile contaminants between surface waters and the atmosphere is an important process that influences their fate and transport (Atkinson, 2000). In this work, we used a simple methodology that combines experimental data and modeling to investigate the degradation of 4-Isobutylacetophenone (IBAP) in a two-phase system (surface water and atmosphere). IBAP is a semivolatile toxic pollutant that was chosen as model contaminant. IBAP is a transformation product of the widely use non-steroidal, anti-inflammatory drug ibuprofen (IBP), and it may occur in expired IBP formulations or photochemically formed in sunlit surface waters, mostly upon IBP direct photolysis, and reaction with the triplet states of chromophoric dissolved organic matter (^{3}CDOM*) (Vione et al., 2018).
The atmospheric behavior of IBAP would mainly be characterized by its degradation with OH radicals, while degradation initiated by NO_3 radicals or direct photolysis would be negligible. Furthermore, the gas-phase reactivity of IBAP with OH is faster compared to the likely kinetics of volatilization from aqueous systems. Therefore, it would be extremely difficult to detect gas-phase IBAP. Nevertheless, up to 60% of IBAP occurring in a deep and DOC-rich water body might be degraded via volatilization, and subsequent reaction with gas-phase OH. In conclusion, the present study suggests that the gas-phase chemistry of the semivolatile organic compounds initially occurring in surface waters (like IBAP) is potentially very important in some environmental conditions.



Graphical description of the experimenatl and modelling approach used to evaluate the environmental fate of IBAP

References

Atkinson, R. (2000) Atmospheric chemistry of VOCs and NOx. Atmospheric Environment 34, 12-14, p. 2063.

Vione. D. et al. (2018) A model assessment of the potential of river water to induce the photochemical attenuation of pharmaceuticals downstream of a wastewater treatment plant (Guadiana River, Badajoz, Spain). Chemosphere 198, p. 473.

Assessing the Temporal Trends of Halogenated Flame Retardants in Air, Precipitation, Herring Gull Eggs and Lake Trout in Lake Ontario, Canada

W.-L. Li[1], H. Hung[1]*, T. V. McDaniel[2], S. R. de Solla[2], L. E. Bradley[3], A. Dove[3], D. McGoldrick[3], P. Helm[4]

[1]Environment and Climate Change Canada (ECCC), Air Quality Processes Research Section, Toronto, ON M3H 5T4, Canada
[2]ECCC,Water Quality Monitoring and Surveillance Directorate, Burlington, ON L7S 1A1, Canada
[3]ECCC,Wildlife and Landscape Science Directorate, Canada Centre for Inland Waters, Burlington, ON, L7S 1A1, Canada
[4]Ontario Ministry of the Environment, Conservation and Parks, 125 Resources Rd., Toronto, ON M9P 3V6, Canada

hayley.hung@ec.gc.ca

Persistent Organic Pollutants (POPs) and Chemicals of Emerging Concern (CEC) are being monitored in Canada's Great Lakes Basin (GLB) in support of the Canada/US Great Lakes Water Quality Agreement and the United Nations Environment Programme (UNEP) Stockholm Convention on POPs. In 2006, halogenated flame retardants (HFRs) were included in the Canadian Government's Chemical Management Program (CMP) to protect the health of Canadians. Polybrominated diphenyl ethers (PBDEs) were traditionally the most widely used HFRs. Since the listing of PBDEs for global regulation under the Stockholm Convention, many alternative HFRs were introduced into the market to reduce the flammability of commercial products. For example, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiphenylethane (DBDPE) were introduced to the market to replace commercial octa-BDE and deca-BDE formulations, respectively (Hoh et al. 2005, Kierkegaard et al. 2004).

PBDEs and alternative HFRs were measured in air (2005-2017), precipitation (2006-2018), lake trout (1997-2019) and herring gull eggs (2008-2018) in the GLB. All targeted HFRs were detected in one or more air [detection frequency (DF): 0.80-98%], precipitation (DF: 6.4-97%), lake trout (DF: 34-100%), and herring egg (DF: 8.3-100%) samples. Declining trends for PBDEs were observed in air, precipitation and lake trout since mid-2000. However, little or no change in trends was observed in herring gull eggs. Temporal trends of non-PBDE HFRs were more variable with no clear increasing or decreasing trends.

Hexabromocyclododecane (HBCDD) was the only non-PBDE HFR that was found in all four media. While the concentrations of HBCDD decreased from 2006 to 2011, increasing trends were observed in air and precipitation after 2011. However, no trends for HBCDD were observed in biotic species. Atmospheric concentrations of HBCDD are influenced directly by emissions from sources, while concentrations in biota are affected by multiple factors, including chemical bioavailability, diet, metabolism and excretion rates. This may explain the differing trends of HBCDD in biota and in air and precipitation.

A multimedia environmental model, the modified Quantitative Water Air Sediment Interaction (QWASI) model, was used to better understand the observed trends and environmental fate of HFRs in Lake Ontario. Results suggest that input from tributaries and wastewater effluent were primary sources of PBDEs and HFRs into the lake. The atmosphere is an important source of lower molecular weight HFRs in Lake Ontario. The major pathways for the removal of BDE 47, 209 and HBCDD were degradation in water and sediment, followed by sediment burial.

References

Hoh, E., Hites, R. A. (2005) 'Brominated flame retardants in the atmosphere of the east-central United States', Environ. Sci. Technol. 39, p. 7794-7802

Kierkegaard, A. et al. (2004) 'Identification of the flame regardant decabromodipheyl ethane in the environment', Environ. Sci. Technol. 38, p. 3247-3253

Controlling Trichloroethene Aerobic Cometabolism Rate and Microbial Biomass Using Acetylene

J. Skinner[1,3*], C. McLaughlin[1,2], R. Koenig[1,2], J. Chu[3], A.G. Delgado[1,2]

[1]Arizona State University, Swette Center for Evironmental Biotechnology, 1001 S. McAllister Ave, Tempe, Arizona, 85281 USA
[2] Arizona State University, Engineering Research Center for Bio-mediated and Bio-inspired Geotechnics (CBBG), 650 E Tyler Mall, Tempe, Arizona 85281, USA
[3]Haley & Aldrich, 400 E Van Buren St #545 Phoenix, Arizona, 85004 USA

jpskinne@asu.edu

Bioremediation of large diffuse trichloroethene (TCE) plumes via aerobic cometabolism often experiences excessive microbial growth near substrate injection points, which leads to bioclogging. Bioclogging decreases permeability and effectiveness of in-situ bioremediation. To minimize bioclogging, chemicals may be used to deter microbial growth allowing for better operational control. In this project, we investigated the effect of acetylene, a microbial inhibitor, on cometabolic biodegradation of TCE in soil-free microcosms and soil columns containing sediment and groundwater from a contaminated site.
In the first phase of the project, batch studies were conducted using two microbial cultures - a pure culture of the hydrocarbon degrading Mycobacterium austroafricanum JOB5 and a propane-oxidizing and TCE-cometabolizing mixed culture named COMET1. These cultures were exposed to the monooxygenase-inhibiting acetylene gas at 5% v/v for differing lengths of time (no exposure, 1 day, 2 days, 4 days, and 8 days) to verify if microbial growth and TCE cometabolic capacities were altered. In the second phase of the project, soil columns filled with sediment from a TCE-contaminated site were bioaugmented with a mixture of the two cultures. Flow through the columns consisted of groundwater from the contaminated site with either O_2, O_2 and propane, or O_2, propane, and acetylene. TCE was added at 50 µM.

In batch studies, both cultures displayed the capacity to aerobically degrade TCE through cometabolism and exhibited time-dependent relationships between acetylene exposure and microbial growth, O_2 consumption, and propane consumption. TCE degradation, microbial growth, and substate consumption rates decreased as a function of increasing exposure to acetylene. Microbial community analysis of COMET1 microcosms at T_0 showed decreases in the relative abundance of propanotrphic bacteria from known TCE cometabolizing families in the acetylene exposed treaments. In the second phase, the soil columns without propane showed minimal TCE removal, as expected. Columns fed with propane + acetylene showed significant TCE degradation, but to a lower extent than the columns with propane but without acetylene. Consitent with our batch studies, acetylene decreased the rates of TCE degradation and propane consumption. The biomass profile in the soil columns clearly revealed that less biomass was formed in the acetylene exposed columns near the inlet, where substrate injection occurred. Overall, our data stongly support that acetylene can be used to control excessive biomass growth during aerobic cometabolism in groundwater.

A Meta-Analysis of Urban Stormwater Events to Evaluate the Role of Site and Storm Characteristics on Organic Contaminant Concentrations

L. Graves[1]*, S. Spahr[2], C. Zarfl[1]

[1]Eberhard Karls University of Tübingen, Schnarrenbergstr. 94-96, 72076 Tübingen, Germany
[2]Leibniz Institute of Freshwater Ecology and Inland Fisheries (IGB), Müggelseedamm 301, 12587 Berlin, Germany

lana.graves@uni-tuebingen.de

As the intensities, frequencies, and spatial distribution of rain events continue to change in response to the climate, the challenge of monitoring, modeling, and managing stormwater contaminant loads will increase. It is therefore critical to harness knowledge we gain from individual studies and monitoring programs that investigate stormwater quality, particularly those that report organic contaminant concentrations, which are less commonly measured than other water quality parameters and contaminants. However, the comparability of results from stormwater studies is often limited due not only to the actual heterogeneity of sample collection conditions (i.e., site and storm characteristics) and methods, but also how and which information about these parameters is communicated. This lack of standardization for reporting conditions surrounding sample collection, in addition to the details about sample collection and analysis methodology, limits our understanding of what controls contaminant discharges and may lead to misinterpretation of results. Site characteristics include impervious area percentages, land cover and land use categories, and vehicle related metrics, which have all been previously demonstrated to correlate with organic contaminant concentrations in stormwater. In order to determine the relative importance of specific site and storm characteristics, a meta-analysis of data from literature and database sources that include contaminant event mean concentrations in urban stormwater discharges was conducted. Information was compiled and standardized for more than 250 organic contaminants, resulting in ~25,000 concentration records (including data < detection/quantification limit) from the following compound groups: herbicides, fungicides, insecticides, alkylphenols, benzotriazoles, phthalates, PAHs, PBDEs, PCBs, and PFASs, as well as pharmaceuticals and other household/industrial chemicals. Additionally, publicly available and spatially explicit data were processed with the software QGIS to supplement information provided in individual studies, particularly for creating standardized land cover related calculations. With this compiled data, data-driven, statistical analyses of the most significant site and storm characteristics was conducted. Trends in herbicide concentrations show alignment with the agricultural growing season in cold climates without a dry season. However, the impact of drainage areas' individual characteristic constellations cannot be understated. A better understanding of the parameters that influence the mobilization of contaminants from different sites will support (1) standardization of future stormwater sampling campaign design and reporting, and (2) implementation of better suited treatment measures to avoid discharge of contaminated stormwater into surface waters or enable safe stormwater harvesting.

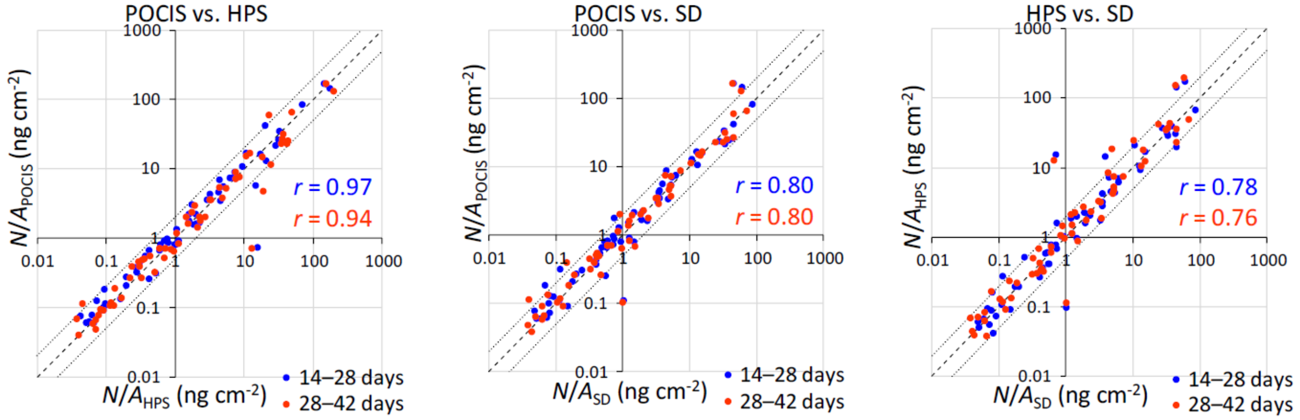
Performance Comparison of Three Passive Samplers for Monitoring of Polar Organic Contaminants in Treated Municipal Wastewater

P. Fialová[1]*, K. Šverclová[1], K. Grabicová[2], R. Grabic[2], B. Vrana[1]

[1]Masaryk University,RECETOX, Faculty of Science, Kotlarska 2, 61137, Brno, Czech Republic
[2]University of South Bohemia in České Budějovice, Faculty of Fisheries and Protection of Waters, South Bohemian Research Center of Aquaculture and Biodiversity of Hydrocenoses, Zátiší 728/II, 38925, Vodňany, Czech Republic

pavla.fialova@recetox.muni.cz

Over the past decades, several types of passive samplers (PSs) have been developed for the monitoring of polar compounds. For representative monitoring, a PS must meet several criteria; it should accumulate compounds covering the desired range of physicochemical properties, its uptake should be robust (independent of environmental conditions), and it should sample in a time-integrative manner over a long period of time. The objective of this study was to compare the performance of three PSs: the Polar Organic Chemical Integrative Sampler (POCIS; the pesticide variant), the Hydrogel-based Passive Sampler (HPS) consisting of Oasis HLB sorbent and agarose diffusion hydrogel, and the Bakerbond Speedisk (SD; the hydrophilic variant). These PSs were deployed in the treated effluent of a large municipal wastewater treatment plant in Brno, Czech Republic for varying periods of up to 28 days for POCIS and HPS, and up to 42 days for SD. Daily composite water samples were also collected and analyzed along with PS extracts for 78 pharmaceuticals, 29 PFASs, 110 anticorrosives, pesticides, and metabolites. PSs captured similar numbers and patterns of compounds from water, and compound uptake was time-integrative for up to 14 days for POCIS and HPS, and up to 42 days for SD. Comparison of the surface-specific uptake N/A (accumulated amount/surface area; ng cm^{-2}) for compounds sampled integratively by all three PSs for 14 days showed good correlation. Since the N/A was comparable for all three PSs, it appears that the uptake is controlled similarly and the PSs may be interchangeable.



N/A comparison for compounds sampled integratively in all three PSs for 14 days, lines define 2-fold difference, and r is correlation coefficient.

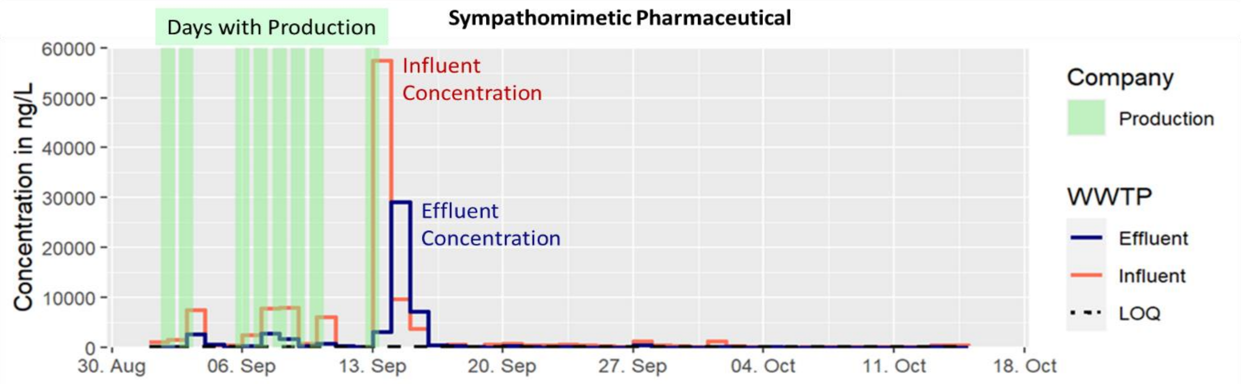
Active Ingredient Emissions Via Wastewater from Pharmaceutical Formulation Sites – A Reason for Concern?

J. Bosshard[1*], Fabienne Eugster[2], Rebekka Gulde[2], Heinz Singer[1]

[1]Department of Environmental Chemistry, Eawag, Ueberlandstrasse 133, 8600 Dübendorf, Switzerland;
[2]Association of Swiss Wastewater and Water Protection Professionals, Europastrasse 3, 8152 Glattbrugg, Switzerland

julian.bosshard@eawag.ch

Pharmaceutical production sites can cause peak concentrations of active pharmaceutical ingredients (APIs) in wastewater treatment plants (WWTPs). This is problematic because elevated concentrations can be toxic to aquatic organisms and – in case of antibiotics production – it promotes the development of antibiotic resistance (Larsson, 2014). Until now, studies focused on emissions from API synthesis or drug production in general. However, very little is known on emissions from the formulation of APIs into the medical end product. This is a challenge in an increasing number of countries, especially now with the emerging call for more local production due to disrupted delivery chains. To address this knowledge gap, we investigated API emissions from nine formulating companies spread across Switzerland. We measured daily composite samples of the influent and effluent of the respective WWTPs during 1.5 months. Thanks to the collaboration with the companies, we could verify industrial emissions with the production plan and calculate loss rates from production. Emissions from formulation were found at all investigated sites both for liquid and solid dosage forms. Maximum concentrations in the effluent of the WWTPs reached up to 0.5 mg/L. Loss rates without pretreatment were usually between 0.1-1% while pretreatment including activated carbon filtration reduced it <0.03%. In conclusion, this study provides comprehensive data with extensive time series on emissions from formulation which is fundamental knowledge for regulation and supports companies in their risk assessment.



Concentration of a sympathomimetic pharmaceutical in a WWTP influent and effluent. The green bars indicate the days on which this API was processed.

References

Larsson, D. J. (2014). Pollution from drug manufacturing: review and perspectives. Philosophical Transactions of the Royal Society B: Biological Sciences, 369(1656). https://doi.org/10.1098/rstb.2013.0571.

A Metatranscriptomics-Derived Laccase-Mediator System for Organic Pollutants Bioremediation: From Experimental Observations to Quantum Chemical Predictions

Y. Yu[1]*, V.-M. Steiner[2], N. F. Trottmann[3], S. Robinson[3], H. Satoh[2], J. Hutter[2], K. Fenner[12]

[1]Eawag, Department of Environmental Chemistry, Überlandstrasse 133, 8600 Dübendorf, Switzerland
[2]University of Zürich, Department of Environmental Chemistry, Rämistrasse 71, 8006 Zürich,Switzerland
[3]Eawag, Department of Environmental Microbiology, Überlandstrasse 133, 8600 Dübendorf, Switzerland

yaochun.yu@eawag.ch

Trace organic contaminants (TrOCs) pose an increasing threat to natural and drinking water resources. Biotransformation of TrOCs has shown potential for reducing chemical load reaching ecosystems. In our previous study[1], a bacterial multicopper oxidase (i.e., laccase) identified from metatranscriptomics sequencing of activated sludge microbial consortia was shown to effectively biotransform selected TrOCs in a laccase-mediator system (LMS). The enzyme was later identified to originate from an ammonium-oxidizing bacterium Nitrosomonas sp. Although ammonium-oxidizing bacteria (AOB) are known for their roles in initiating nitrification and biotransforming some TrOCs, previous studies mostly emphasized the role of ammonia monooxygenase, overlooking the potential contributions of other enzymes. To address this knowledge gap and further explore the potential of AOB-related laccases in TrOCs removal, we tested its activity against 182 wastewater-related contaminants. The LMS exhibited significant removal for 53 compounds. The transformation products of selected compounds were analyzed and compared with those found in previous activated sludge studies. In the LMS, the mediator, once oxidized by laccase to stable radicals, can oxidize compounds that might not be direct substrates of laccase, thereby broadening the range of recalcitrant organic contaminants that can be transformed by the system. Considering the chemical nature of the reaction between the oxidized mediator and TrOCs, we further applied quantum chemical (QC) approaches to predict different indicators of the TrOCs' oxidation potential and used them to develop and test models to predict TrOCs' reactivity in the LMS. This proof-of-concept study demonstrates the potential of environmental laccase-mediated biotransformation in removing TrOCs and highlights the use of ab initio (QC) descriptors as a tool for predicting the fate of contaminants under environmental conditions.

References

Athanasakoglou, A. et al. (2021) Toward Characterizing the Genetic Basis of Trace Organic Contaminant Biotransformation in Activated Sludge: The Role of Multicopper Oxidases as a Case Study. Environ. Sci. Technol., 56, 1, 313–324. doi:10.1021/acs.est.1c05803.

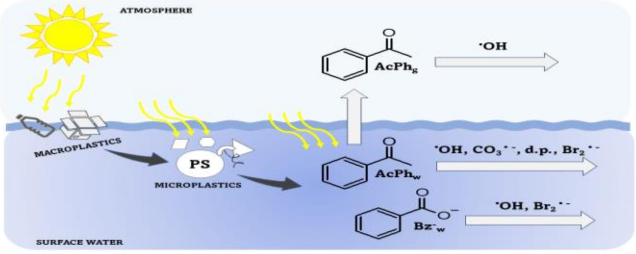
Double Role of Photochemistry as Source and Sink of Nanoplastic Dissolution Products in Aqueous Environments

D. Vione[1]*, D. Fabbri[1], L. Carena[1], D. Bertone[1], M. Brigante[2], M. Passananti[1,3]

[1]Università di Torino, Dipartimento di Chimica, Via Pietro Giuria 5, 10125 Torino, Italy
[2]Université Clermont Auvergne, CNRS, INP Clermont Auvergne, Institut de Chimie de Clermont-Ferrand, F-63000 Clermont-Ferrand, France
[3]University of Helsinki, Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, FI-00014 Helsinki, Finland

davide.vione@unito.it

Irradiation by sunlight plays an important role in the weathering of plastics in water, leading to fragmentation into smaller particles and to dissolution (Andrady, A. L. et al. 2022, Zhu, L. et al. 2020) In particular, polystyrene nanoplastics have been shown to produce a range of dissolved compounds upon sunlight exposure, among which benzoate (Bz-) and acetophenone (AcPh) have been detected as important transformation products in water (Bianco, A. et al. 2020). These compounds might be used as markers of polystyrene pollution, depending on their environmental persistence and mobility. Interestingly, both Bz- and AcPh would undergo further photochemical processing in natural surface waters. Here we show that Bz- would mainly be degraded by hydroxyl radicals (•OH), while AcPh would react with •OH, carbonate radicals, and (to a minor extent) by direct photolysis. In the case of non-volatile Bz-, elevated values of the dissolved organic carbon (DOC) in water environments would be an important protective factor from •OH-mediated oxidation. For semivolatile AcPh, partitioning to the gas phase followed by reaction with gas-phase •OH would be very competitive with aqueous-phase photodegradation. Both Bz- and AcPh react with the dibromine radical (a reactive halogen species in seawater) to a significant extent, but reaction rate constants are two orders of magnitude lower compared to those with •OH. Therefore, •OH scavenging by bromide in seawater would considerably slow down photodegradation of both Bz- and AcPh, compared to surface freshwaters. Overall, photochemistry is expected to play key roles in both Bz-/AcPh formation from polystyrene, and their further degradation in aquatic environments.



Schematic of Bz- and AcPh photodegradation in environmental waters and for AcPh) in the gas phase as well

References

Andrady, A. L. et al. (2022) Oxidation and fragmentation of plastics in a changing environment. Sci. Total Environ. 851(2), 158022.

Zhu, L. et al. (2020) Photochemical dissolution of buoyant microplastics to dissolved organic carbon. J. Hazard. Mater. 383, 121065.

Bianco, A. et al. (2020) Degradation of nanoplastics in the environment: Reactivity and impact on atmospheric and surface waters. Sci. Total Environ. 2020, 742, 140413.

Photochemical Degradation of Common Xanthene Diagnostic Dyes: What is the Fate of Fluorescein, Eosin and Rose Bengal?

P. Šebej[1*], M. Martínek[1], M. Šranková[2], L. Muchová[2], L. Ludvíková[1], J. Huzlík[3],P. Klán[1,4], L. Vítek[2]

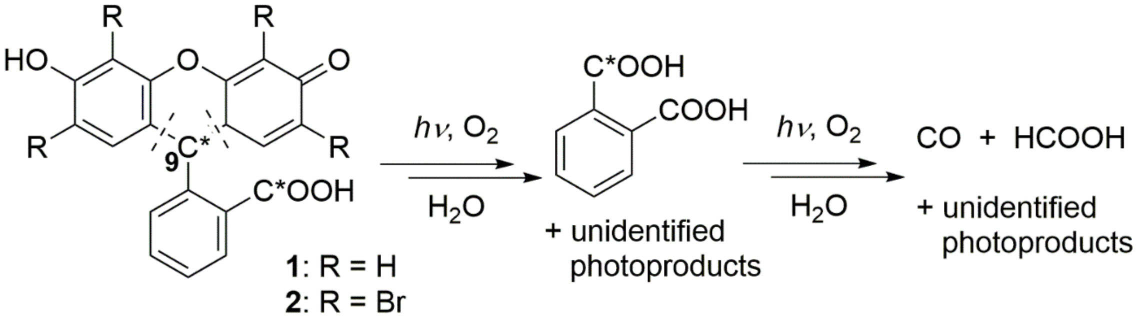
[1]Masaryk University, RECETOX, and 4Department of Chemistry, Faculty of Science, Kamenice 5; 625 00 Brno, Czech Republic
[2]Charles University in Prague, Institute of Medical Biochemistry and Laboratory Diagnostics, 1st Faculty of Medicine, Na Bojišti 3, 121 08 Praha 2, Czech Republic
[3]Transport Research Centre (CDV), Líšeňská 33a, 636 00 Brno-Líšeň, Czech Republic

sebej@recetox.muni.cz

Dyes are used in many areas of human acitivity, for coloring and visualization in various contexts. In (bio)medicine and research fluorescent dyes are often used as tags, reporters or diagnostic agents. Their degradation in environment proceeds either thermally, e.g. by hydrolysis, or photochemically.

We investigated the primary photoinduced chemistry of some of the most common such diagnostic dyes: fluorescein, eosin Y, and rose bengal; and major products of their photodegradation using a variety of techniques, e.g. optical spectroscopy, NMR, chromatography and mass spectroscopy. We found these substances, usually considered (photo)chemically stable, to liberate carbon monoxide (a bioactive gas with potential benefits) in 40–80% chemical yields upon extensive irradiation with visible light in aqueous solutions during their multistep concomitant degradation processes (Scheme 1). In addition, other low-mass secondary photoproducts, such as phthalic and formic acids, were identified in the irradiated mixtures (Martínek, 2022). Using an experimental cell line model, we also demonstrated that these photodegradation pathways could have potential biological implications (Šranková, 2022).

This work was supported by the Czech Science Foundation (GJ20-30004Y; GA21-01799S), First Faculty of Medicine, Charles University, Prague (GAUK 314621), Czech Ministry of Health (MH-DRO-VFN64165), CETOCOEN EXCELLENCE Teaming 2 (02.1.01/0.0/0.0/18_046/0015975) and RECETOX RI (LM2018121).



Scheme 1. Multistep visible light induced photochemical degradation of xanthenes (fluorescein 1, and eosin Y 2) in aerated protic environment.

References

Martínek, M., et al. (2023) "Common xanthene fluorescent dyes are visible-light activatable CO-releasing molecules" Org. Biomol. Chem, 21, 93, doi: 10.1039/D2OB01823C.

Šranková, M., et al. (2022) "Antiproliferative and Cytotoxic Activities of Fluorescein—A Diagnostic Angiography Dye" Int. J. Mol. Sci. 23, 1504, doi: 10.3390/ijms23031504.

Impacts of Oxygen Depleted Zones on the Transformation of Halogenated Pharmaceuticals

K. Gerundt[1]*, L. Adrian[2], J. Lewandowski[3,4], F. Hellweger[1], A. Putschew[1]

[1]Technische Universität Berlin, Chair of Water Quality Engineering, Straße des 17. Juni 135, 10623 Berlin, Germany
[2]Helmholtz Centre for Environmental Research – UFZ, Department Environmental Biotechnology, Permoserstraße 15, 04318 Leipzig Germany
[3]Institute of Freshwater Ecology and Inland Fisheries, Mueggelseedamm 310, 12587 Berlin, Germany
[4]Humboldt University Berlin, Geography Department, Rudower Chaussee 16,
12489 Berlin, Germany

k.gerundt@tu-berlin.de

Refractory iodinated organic compounds, including the widely used iodinated x-ray contrast media (ICM), can be transformed by deiodination under reducing conditions (Redeker et al., 2014; El-Athman et al., 2019). The deiodination is a key reaction enabling better sorption to sandy aquifer material (Bartels et al., 2023) and potentially mineralization (Redeker et al., 2014). The aim of the present study is to investigate if abiotic corrinoid-catalyzed dehalogenation under reducing conditions is also able to transform fluorinated, chlorinated and brominated pharmaceuticals. We are interested in that because (i) the oxygen concentration in the water bodies might decrease with climate change and with that, the anoxic/anaerobic zone will develop earlier, making reactions under oxygen free conditions more important. (ii) We hypothesize that the anaerobic transformation results in products better removable, e.g., during infiltration or drinking water treatment as found for ICM.

Initial batch tests (n=3) were done with a mixture of selected multiple halogenated pharmaceuticals including ICM in an oxygen free glovebox. Titanium(III)citrate was added as a reducing agent and cyanocobalamin (vitamin B12) as catalyst. Additionally, different halogenated benzoic acids were investigated. Samples were taken over a period of three months and were analyzed using LC-UV, IC-DC and LC-ESI-MS/MS.

A concentration decrease was observed for all selected halogenated compounds. Transformation of tested ICM (iopromide, iopamidol) was fastest and the completely deiodinated transformation product (TP) was detected as main product. Iodide quantification confirmed complete deiodination. The transformation of the di-brominated compound (ambroxol) was slower. Bromide quantification showed that the bromine atoms were sequentially released. Based on the bromine isotopic pattern an unknown mono-brominated TP was recognized by LC-MS screening. Transformation was examined for three chlorinated compounds (diclofenac, sertraline, hydrochlorothiazide), resulting in different concentration decreases. Chloride used for titanium(III)citrate production interfered with the quantification of released chloride, but LC MS/MS analyses for TPs are in progress. For the fluorinated sitagliptin fluctuating concentrations with a marginal decrease were observed. Fluoride was not detectable, but traces of a defluorinated TP by LC-MS which still needs to be confirmed. Results show the possibility of abiotic reductive dehalogenation for pharmaceuticals besides ICM.

References

Bartels, Y. *et al.* (2023) 'Can reductive deiodination improve the sorption of iodinated X-ray contrast media to aquifer material during bank filtration?' *Chemosphere*, accepted.

El-Athman, F. *et al.* (2019) 'Abiotic reductive deiodination of iodinated organic compounds and X-ray contrast media catalyzed by free corrinoids', *Chemosphere*, 221, pp. 212–218. doi: 10.1016/j.chemosphere.2019.01.003.

Redeker, M. *et al.* (2014) 'Removal of the Iodinated X-ray Contrast Medium Diatrizoate by Anaerobic Transformation', ES&T , 48. doi: 10.1021/es5014714.

Benzothiazoles as a Molecular Markers for Automobile Tire-Derived Inputs: Occurrence and Phase Distribution in Highway Runoff and Road Dust

M. Feltracco[1], G. Mazzi[1], E. Barbaro[2,1], B. Rosso[1], C. Barbante[2,1], A. Gambaro[1,2]

[1] Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino, 155 - 30172 Venice Mestre (VE), Italy
[2] National Research Council (CNR-ISP), Institute of Polar Sciences, Via Torino, 155 - 30172 Venice Mestre (VE), Italy

matteo.feltracco@unive.it

Over the past several decades, discharges of both wastewater and stormwater have been identified as one of the major causes of the deterioration observed in receiving waters (Lamprea and Ruban, 2011). The major sources are vehicle emissions, motor oil, tyre and brake wear, and road particles in urban environments. During rainfall events contaminants are washed into the stormwater system and then discharged. The Italian legislation (Legislative Decree no. 152 of 11 May 1999) provides a complete program for the protection of water bodies from pollution. The decree implements the community directive 91/271/EEC concerning the treatment of urban wastewater, that constitutes the reference standard for the EU member states. The Italian law focuses on the quality of the receiving water body with several monitoring activities for determining the environmental damage. Despite these steps forward, several pollutants are not determined and their impact and fate in the environment are unknown. Furthermore, a comprehensive determination of contaminants of emerging concern (CECs) is crucial to understand the distribution of target compounds in dissolved phase and suspended particulate matter (Feltracco et al., 2022). The accumulation of road dust itself also serves as a notable pollutant source because it can be transported by runoff, and the associated pollutants could adversely affect the water ecosystem. Among the hazardous pollutants in dissolved phase, suspended particulate matter and road dust particles originating from tires, rubbers, and microplastics are often observed (Rosso et al., 2022), together with benzothiazoles. A total of eight benzothiazoles were determined in highway stormwater runoff and road collected from February to April 2022 near Venice (Casale sul Sile, Veneto Region, Italy). A full validated method is presented, by using an ultra-high pressure liquid chromatography coupled to a triple quadrupole mass spectrometer. The target compounds were determined in both dissolved phase and suspended particulate matter of runoff. The road dust samples were divided in seven fractions depending on particles diameters to evaluate the fraction partitioning. The results underline that SO_3H-BTH was the most concentrated benzothiazole derivate in all the analysed substrates, suggesting the presence of tires debris as main source because it is used in the vulcanization processes. The three major compounds in the dissolved phase were inversely correlated with precipitation amount and positively correlated with the number of days after last rain event, while no correlation were found with suspended particulate matter. The road dust samples indicated a clear trend of the majority of benzothiazoles to distribute in the finest fraction (<63 µm). The distribution of 2-SCNMeS-BTH was opposite to the other benzothiazoles, suggesting a different source and environmental behaviour.

References

Lamprea, K. and Ruban, V. (2011) 'Pollutant concentrations and fluxes in both stormwater and wastewater at the outlet of two urban watersheds in Nantes (France)', Urban Water Journal, 8(4), pp. 219–231. doi:10.1080/1573062X.2011.596211

Feltracco, M. et al. (2022) 'The Occurrence of Glyphosate and its Degradation Products in the Urban Stormwater: A Short Review', Water, Air, and Soil Pollution. Institute for Ionics. doi:10.1007/s11270-022-05973-3

Rosso, B. et al. (2022) 'Quantification and characterization of additives, plasticizers, and small microplastics (5–100 µm) in highway stormwater runoff', Journal of Environmental Management, 324. doi:10.1016/j.jenvman.2022.116348.

Biodegradation of Water-Soluble Polymers in Wastewater Systems: Process Insights and Implications for Testing

M. Zumstein[1]* and A. Kintzi[1]

[1]University of Vienna, Division of Environmental Geosciences, Centre for Microbiology and Environmental Systems Science, Josef-Holaubek-Platz 2, 1090 Vienna, Austria

michael.zumstein@univie.ac.at

Water-soluble polymers (WSPs) provide a broad range of functionalities and are thus widely used in numerous applications. After their use, for example in home- and personal care products, WSPs are often released into wastewater systems (Arp, H.P. et al. 2020). Because the recovery of WSPs from wastewater is not feasible, biodegradability in receiving environments is a desired property for WSPs used in such applications (Zumstein, M. et al. 2022). Currently, the biodegradation of chemicals is typically assesed according to OECD testing guidelines. However, these guidelines were developed for small molecules and their suitability for polymers requires validation. Biodegradation testing protocols should, for example, be re-considered with respect to the role of extracellular enzymes given that extracellular breakdown into molecules sufficiently small for cellular uptake is an important step in the biodegradation of polymers (Zumstein, M. et al. 2022). Here, we assessed the biodegradation of selected WSPs (with a focus on polyamino acids) using incubation experiments coupled to respirometric analysis. Thereby, we addressed key aspects regarding both the process of WSP biodegradation, as well as the testing protocol. First, we tested how WSP biodegradation dynamics are affected by a pre-incubation of WSPs with cell-free wastewater extracts. For some of the tested WSPs, these pre-incubations reduced the lag phase duration (i.e., the time between WSP addition and the onset of detectable biodegradation). Notably, the effect was in some cases also observed for autoclaved extracts, indicating that the effect is not always due to enzymatic activity in the extracts, but presumably linked to the adsorption of WSPs to components of the wastewater matrix. Second, we tested how WSP biodegradation is affected by often-conducted pre-treatments of the biological inoculum prior WSP addition (i.e., aeration and washing). We expected both pre-treatments to reduce the availability and activity of extracellular enzymes and thus decrease WSP biodegradation rates. Our experimental data showed an effect of pre-treatments on the biodegradation process of some WSPs, while the biodegradation of other WSPs was unaffected. Third, we tested how WSP concentrations affected the biodegradation dynamics. Overall, we present promising data on the biodegradation of selected WSPs in wastewater systems and discuss process-level insights that we expect to inform both the design of sustainable WSPs and the development of testing protocols required for a realistic, yet feasible, assessment of WSP biodegradation.

References

Arp, H.P. et al. (2020), 'Could We Spare a Moment of the Spotlight for Persistent, Water-Soluble Polymers?', Environ. Sci. Technol., 54, p. 3, doi: 10.1021/acs.est.9b07089

Zumstein, M. et al. (2022), 'Environmental Biodegradation of Water-Soluble Polymers: Key Considerations and Ways Forward', Acc. Chem. Res., 55, p. 2163, doi: 10.1021/acs.accounts.2c00232.

A New Concept to Classify the Biodegradability of Chemical Substances with a Microbial Array

G. Thouand[1]*, M. Cregut [1,2], C. Sweetlove[3], M.J. Durand[1], J.C. Chenèble[3], A. Taze[3], O. Dufour[3], M. Léonard[3], J. L'Haridon[3]

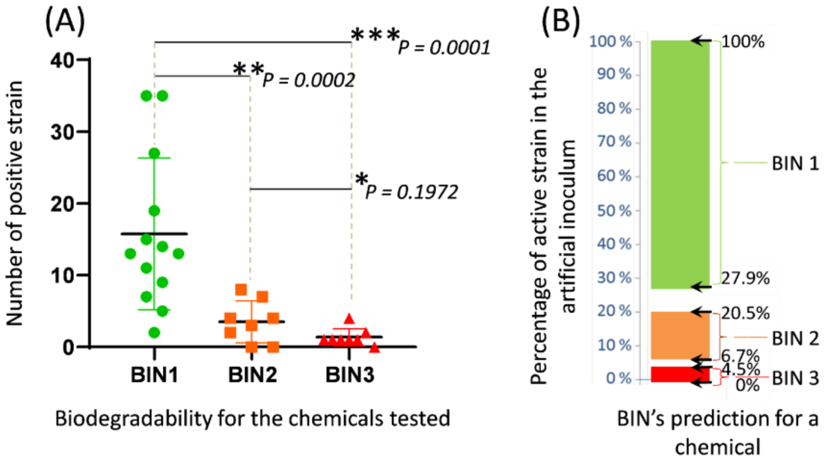
[1]University of Nantes, Oniris, CNRS, GEPEA, UMR 6144, F-85000 La Roche sur Yon, France
[2]University of Nantes, CAPACITES, 26 Bd Vincent Gâche, F-44200 Nantes, France
[3]L'Oréal, 1 ave Eugène Schueller, 93600 Aulnay-sous-Bois, France

gerald.thouand@univ-nantes.fr

In REACH, Ready Biodegradation Tests are the cornerstone for biodegradation of xenobiotics. Since the 1980s, numerous studies have reported on the variability of biodegradation tests, which has an impact on the evaluation of a chemical substance. We propose a concept based on the selection of 44 microorganisms representative of the microbial diversity of an activated sludge and their individual use in a miniaturized biodegradation test leading to a "fingerprint" of biodegradability of a substance. To validate the concept, 30 BIN 1,2,3 chemical substances were tested to determine the ability of the artificial inoculum to predict their biodegradability.

The 3960 individual biodegradation tests carried out over 28 days allowed a prediction in BIN 1 to 92%. For BIN 2 and BIN 3 type substances, the prediction of the artificial inoculum accurately classified 75% of the substances tested. Prediction errors tend to lower the BIN of the substance. Also, some BIN 2 type substances were classified as BIN 3. Indeed, among the 9 substances considered as BIN 2 in this study, 4 were classified as BIN 2 according to the artificial inoculum method and 4 as BIN 3, including DMSO, diethylene glycol, polyethylene glycol. Finally, our screening test classified 100% of the 8 substances recognized as BIN 3 in the literature.

This concept is highly reproducible, do not need any environmental sampling and may finds an application in the design of new substances all along their conception to test their biodegradation.



(A) Classification of the artificial inoculum according to the known biodegradability of the chemical substances (B) Statistical analysis

Target and Suspect Screening of Organic Contaminants in Sediments by Pressurized Liquid Extraction and GC-APGC-Q-Tof-MS

M. L. Tovar-Salvador[1]*, P. A. Lara-Martín[1], M. G. Pintado-Herrera[1]

[1]University of Cadiz, Physical Chemistry Department, Faculty of Marine and Environmental Sciences, International Campus of Excellence of the Sea, Cadiz, 11510 (Spain)

luz.tovar@uca.es

Contamination of aquatic systems by regulated and emerging organic compounds represents a rising concern. Indeed, new substances are constantly being developed and released to the environment with adverse effects. In that sense, high-resolution mass spectrometry (HRMS) coupled to gas chromatography can be a very valuable tool for a more comprehensive analysis of organic contaminants in the environment than using more widely used low resolution instruments. In this research, we have developed and optimized of a multiresidue method for the GC-HRMS determination of target and suspect compounds in sediment matrices after pressurized liquid extraction (PLE). First, PLE was tested using different types of solvents and clean-up sorbents in three types of sediment matrices with different granulometry. The optimized extraction protocol using dichloromethane as solvent and silica as sorbent showed good recovery percentages (70-100%) for a wide range of target chemicals, including legacy and emerging compounds such as polycyclic aromatic hydrocarbons (PAHs), UV filters, fragrances, organophosphorus flame retardants (OPFRs), polybrominated diphenyl ethers (PBDEs), phthalates, pyrethroids, etc. Besides target compounds, suspect screening was performed to identify tentative compounds and reveal a more complete profile of organic contaminants depending on the selected solvent and clean-up sorbent. Full MS scan and all ions MS/MS modes were performed on a GC-APGC-Q-ToF-MS instrument (Bruker Impact II) for the suspect analysis and the processing was performed using Metaboscape (Bruker) and available MS/MS library databases that include industrial and household chemicals (MassBank EU). The method was applied to the analysis of sediment samples collected in 2022 from Guadalete Estuary river (Cadiz, Spain). The most prevalent target contaminants were PAHs (anthracene or phenanthrene). Traces of UV-filters (4-MBC or octocrylene) and fragrances (tonalide or galaxolide) were also found, suggesting inputs from domestic wastewater sources in the study area. Tentative identification of more than twenty features was the main result from the suspect analysis performed, allowing to the extend the number of contaminants known in coastal systems.

References

Barco-Bonilla, N. et al. (2009) ‘Comparison of ultrasonic and pressurized liquid extraction for the analysis of polycyclic aromatic compounds in soil samples by gas chromatography coupled to tandem mass spectrometry’, Talanta, 78(1), pp. 156–164. doi: 10.1016/j.talanta.2008.10.048.

Cheng, Z. et al. (2016) ‘Atmospheric pressure gas chromatography quadrupole-time-of-flight mass spectrometry for simultaneous determination of fifteen organochlorine pesticides in soil and water’, Journal of Chromatography A, 1435, pp. 115–124. doi: 10.1016/J.CHROMA.2016.01.025.

Leaching of Degradation Products DMS and DMSA from Cyazofamid Shows Shortcomings in EFSA Risk Assessment

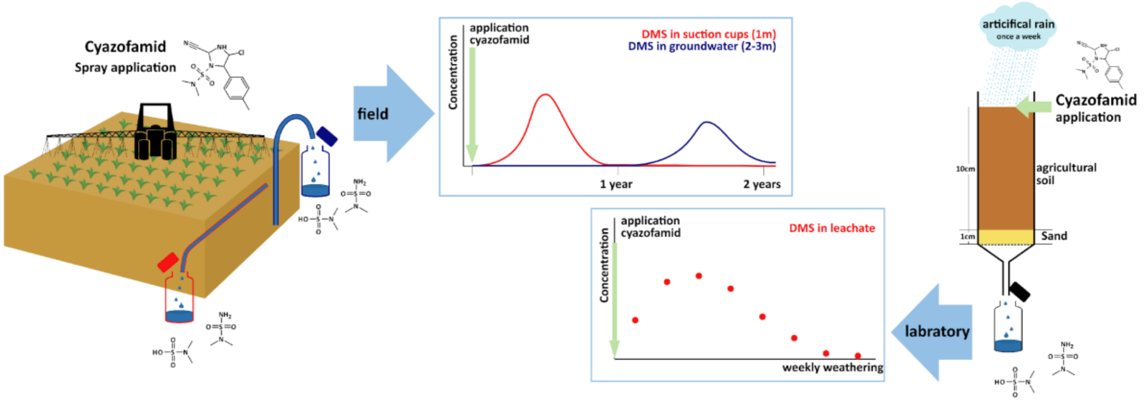
N. Badawi[1]*, U.E. Bollmann[1], E.B. Harder[1], C.N. Albers[1], K. Kørup[2] and S. Karan[1]

[1]Geological Survey of Denmark and Greenland (GEUS), Oester Voldgade 10, DK 1350, Denmark
[2] Aarhus University, Department of Agroecology, Blichers Allé 20, 8830 Tjele, Denmark

nba@geus.dk

The fungicide cyazofamid was applied in a potato crop as part of the Danish pesticide leaching assessment programme (www.plap.dk). Leaching of N,N-dimethylsulfamid (DMS), dimethylsulfamic acid (DMSA), 4-chloro-5-(4-methylphenyl)-1H-imidazole-2-carbonitrile (CCIM), and 4-chloro-5-(4-methylphenyl)-1H-imidazole-2-carboxylicacid (CTCA) was monitored in water from the variably saturated zone (suction cups) and groundwater for two years. Supplementary laboratory studies were executed in parallel with the field monitoring study. Here, formation of the four degradation products was studied in a soil batch experiment in combination with a leaching experiment with packed soil columns.

In the EFSA conclusion (EFSA 2020) on cyazofamid, CCIM and CTCA are mentioned as major relevant metabolites; DMS is not mentioned in the risk assessment at all and DMSA is only included in acute oral toxicity studies and an in vitro bacterial mutation assay. In contrast, our studies revealed no leaching or formation of the two major metabolites, CTCA and CCIM, but instead major leaching and formation of DMS and DMSA in both the field and laboratory studies. Both DMS and DMSA leached to the groundwater in concentrations > 0.1 µg/L for more than half a year. Usage of cyazofamid is now banned in Denmark coming into force on May 1, 2023.



Experimental field setup of the PLAP-system (left) and supplementary laboratory-setup with packed soil columns (right)

References

EFSA 2020. Updated peer review of the pesticide risk assessment of the active substance cyazofamid. EFSA Journal 2020;18(9):6232. Doi: 10.2903/j.efsa.2020.6232.

Removal of Contaminants of Emerging Concern From Sewage: Activated Sludge vs. Biofilter Technology

M. De Sanctis[1]*, C. De Ceglie*, V.G. Altieri[1], S. Murgolo[1], G. Mascolo[1], C. Di Iaconi[1]

[1]Water Research Institute, C.N.R, Viale F. De Blasio 5, 70132, Bari, Italy

marco.desanctis@ba.irsa.cnr.it, cristina.deceglie@ba.irsa.cnr.it

Globally, over 350,000 chemical compounds and mixtures have been registered so far [Wang et al., 2020]. This represents a serious threat, due to their massive release in the environment and typical low removal in conventional wastewater treatment plants (WWTP). Many of them, including pharmaceuticals, pesticides, personal care products, surfactants, endocrine-disruptors, antibiotics, and hormones, have been recently classified as contaminants of emerging concern (CECs), because they might cause undesired effects to aquatic environments and human health.

In this study two biological treatment strategies based on activated sludge process and on an innovative biofilter technology (known as MULESL) were compared, in terms of removal efficiencies of 46 compounds in the wastewater entering the Putignano WWTP during a 5-month campaign.

For more than half of the compounds taken into account (Fig.1), the removal efficiencies showed by MULESL technology were considerably higher than those obtained by the conventional strategy, with more than a dozen of substances efficiently removed by the two approaches considered. In particular, MULESL performances in removing carbamazepine (55.4%), carbamazepine 10,11 epoxide (84.4%) and flecainide (58.5%) appear noteworthy, since these contaminants are well known to be very difficult to remove by means of conventional treatments. This result was attributed to the long SRT and low food-to-microorganism ratio in MULESL that force microorganisms to use also slowly biodegradable carbon sources.

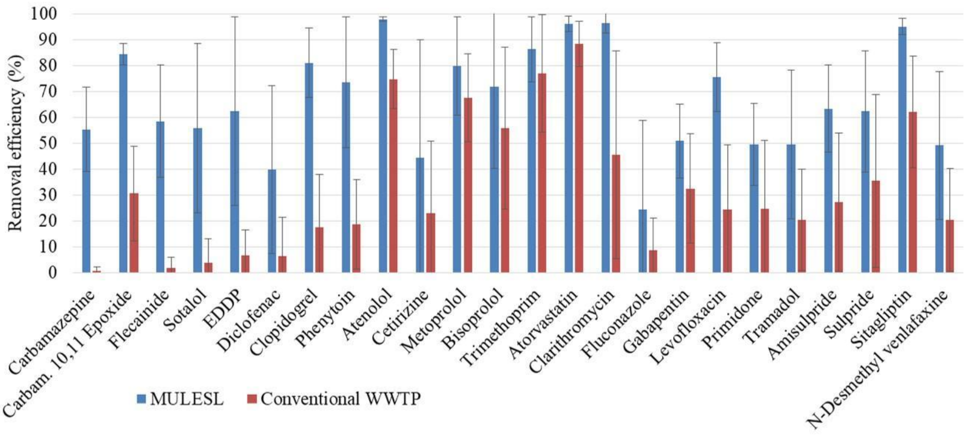


Fig.1. Mean removal efficiency of CECs by MULESL and conventinal WWTP (primary and secondary section).

References

Wang, Z. et al (2020) "Toward a Global Understanding of Chemical Pollution: A First Comprehensive Analysis of National and Regional Chemical Inventories", Environmental Science & Technology, 54, pp. 2575-2584. doi: 10.1021/acs.est.9b06379.

Investigation of the Adsorption of a Low-Molecular-Weight Sodium Polyacrylate on Calcite

M. Bey-Zekkoub[1]*, P. Tassi[1], C. Lorthioir[2], N. Chhim[3], M. Bretaud[3], A. Harnichard[3], D. Bontemps[3]

[1]Electricité De France (EDF), Saint-Venant Hydraulics Laboratory
[2] Sorbonne Université, CNRS, Laboratoire de Chimie de la Matière Condensée de Paris
[3]Electricité De France (EDF)

mohamed.bey-zekkoub@edf.fr

Sodium polyacrylate is well known for its application in various industrial fields such as hygiene products, agriculture and wastewater treatment. Low-molecular-weight polyacrylates (2000-4000 g/mol) is one of the most common used compounds as scale inhibitor and dispersing agents due to its high adsorption capability (Lamarche et al., 1983). When released into a river, the sodium polyacrylate has a high tendency to adsorb onto suspended matter (sketched in Fig. 1.) and its environmental behavior depends mainly on the sediment composition, water properties (pH, ionic strength, temperature), and flow characteristics. Given the use level of this polymer in water treatment and its low degradation (Wilske et al., 2014), it is important to consider its environmental fate. Mathematical modeling is a powerful tool for understanding the distribution and transport of chemical substances in rivers. In this study, we implemented an external diffusion model to describe adsorption, based on mass transfer through the external layer which surrounds the calcite particle and the mass balance equation. Laboratory experiments were performed to investigate the adsorption properties of this polymer on calcite under different conditions (ionic strength, pH and calcite concentration). The results provided by the mathematical model are found to be in agreement with the experimental data, but only at low polymer concentrations. Overall, our study provides an original approach to model adsorption at low polymer concentrations. Furthermore, it can be applied to correlate the adsorption kinetic data for other systems at low adsorbate concentrations.

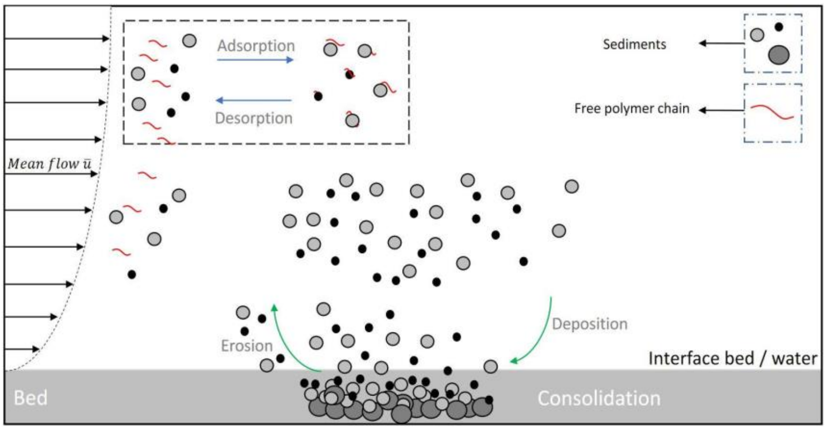


Fig. 1. *Adsorption and transport of sodium polyacrylate in a river*

References

Wilske, B., Bai, M., Lindenstruth, B. et al. (2015) ‘Biodegradability of a polyacrylate superabsorbent in agricultural soil’, Environmental Science and Pollution Research , 21, p. 9453--9460 . Doi: https://doi.org/10.1007/s11356-013-2103-1.

Lamarche et al. (1983) ‘Influence of molecular weight of sodium polyacrylate in calcium carbonate aqueous dispersions’, Industrial & Engineering Chemistry Product Research and Development, 1, p. 123—126. Doi: https://doi.org/10.1021/i300009a028

First Groundwater Monitoring for Modern Pesticides in Mayabeque, Cuba

D. Sosa[1]*, I. Hilber[2], K. Hórnak[2], V. Vegas[1], B. Peña[1], A.C. Escobar[1], M G.A. van der Heijden[3,4] and T.D. Bucheli[2]

[1]Centro Nacional de Sanidad Agropecuaria, Departamento de Salud Animal, Apartado 10, CP 32700, San José de las Lajas, Cuba.
[2]Agroscope, Methods Development and Analytics, Reckenholzstrasse 191, CH-8046, Zurich, Switzerland
[3]Agroscope, Plant-Soil-Interactions Research Group, Reckenholzstrasse 191, CH-8046, Zurich, Switzerland
[4]University of Zurich, Department of Plant and Microbial Biology, Zollikerstrasse 107, CH-8008, Zurich, Switzerland

dayanasosap@gmail.com

Ground water (gw) in Cuba has many purposes, amongst others it is an important drinking water as well as irrigation source. Particularly in the Mayabeque province, Cuba, some of the gw abstraction sites are located in areas of intensive agricultural production with high pesticide use. This may lead to gw contamination and exposure of humans to pesticides. For instance, the European Directive (ED) sets a maximum concentration (MC) of 100 ng/L for individual pesticides and 500 ng/L for the sum of different compounds in a sample (EC, 2006)). Cuba has a Water Quality Network (RedCal) and an official norm for drinking water (NC-827:2017), which does, however, not mention modern pesticides (MPs) and/or transformation products (TPs). Recently, a systematic study on pesticides and some TPs in potato cultivation in the same study area (Quivicán and Batabanó department of Mayabeque) revealed sum compound concentrations of 0.1 to 658 µg/kg of soil. The main objective of this study was to develop the first gw monitoring study in Cuba, determining and quantifying MPs and TPs in gw from Mayabeque (CUBAGUA). We selected RedCal water well sites in Quivicán (n=18) and Batabanó (n=8) where grab samples were taken according to the RedCal protocol during the dry and wet season in 2022. One liter was frozen (-20 ºC). When thawed, a) 500 mL gw were adjusted to pH 6.5, b) filtered through cellulose 0.45 µm filter c) spiked with a mix of isotopically labelled standards (0.004 ng/mLgw), d) passed through solid-phase extraction (SPE) cartridges of Oasis HLB that were conditioned prior to use, and frozen e) they were transported to Switzerland, and f) cartridge kept frozen until analysis. The thawed cartridges were a) washed with 5 mL of ultra-pure water and dried by air during 20 min, b) eluated with 5 mL methanol and formic-acid 0.1%, v/v. The extract was dried with air and reconstituted in 1 mL of ultra-pure water and methanol (9:1 v/v). Finally, 46 MPs and 10 TPs identified and quantified by liquid chromatography-tandem mass spectrometry. Most important figures of merit were: $R^2 > 0.99$ for all analytes in a matrix matched Milli-Q water calibration curve (0.5, 1, 2, 5, 10, 20, 50 ng/L), a quantification limit of 0.006 to 2.5 ng/L, and an absolute recovery in gw samples of 50 to 86% for 51 of 56 analytes. Preliminary results revealed 11 MPs and six TPs in gw sites (n=13). From the 11 MPs quantified, 28% were herbicides (H), 36% fungicides (F) and 36% insecticides (I). Median concentration ranges (ng/L) and frequency (%) of MPs were for H: 1.1-1.7 and 8-46, F: 0.7-1.8 and 15-23, I: 0.2-6.9 and 8-54 and of TPs of atrazine (H): 2-14 and 62-100, desnitro imidacloprid: 2 and 15, metribuzin desamino: 1 and 8, and trifloxystrobin CGA: 2 and 15. Pesticide concentrations were lower than the MC established by the ED and thus representing a low risk to human health. These results shed first light on the quality of Cuban gw and thereby serves as a basis for a risk assessment of human health in Cuba.

References

European Parliament and Council. (2006) “Directive 2006/118/EC of 12 December 2006 on the protection of groundwater against pollution and deterioration,” Official Journal of the European Union L. 2006. p. 12.
NC-827:2017. (2017) "Agua Potable. Requisitos Sanitarios". Third Edition. Cuban National Bureau of Standards.

Analysis of Poly- and Perfluoroalkyl Substances (PFASs) in the Danube River Water Samples from Serbia

N. Đurišić-Mladenović[1*], M. Farré[2], J. Živančev[1], M. Llorca[2], I. Antić[1], M. Buljovčić[1] and D. Rakić[1]

[1]University of Novi Sad, Faculty of Technology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia
[2]Environmental Chemistry Dept., IDÆA-CSIC, Jordi Girona 18, 08034 Barcelona, Spain

natasadjm@tf.uns.ac.rs

Poly- and perfluoroalkyl substances (PFASs) form an important group of synthetic chemicals that have found multiple industrial and domestic applications and are widely distributed on the world market. For these reasons, PFASs have a global distribution in the environment and affect ecosystems and human health. Moreover, PFASs have been detected in waste, surface, and ground waters, as well as in other environmental compartments such as soils, sediments, and biota. Literature data indicate that the dominant sources of PFASs into the environment are manufacturing facilities, followed by wastewater treatment plants (WWTPs), which have been found to be ineffective in removing these compounds from wastewater influents. Previous investigations on PFASs were based on analytical methods for the determination of PFASs such as perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) in various environmental matrices. Recent research is focused on the identification of other PFASs produced as alternatives for PFOS and PFOA and the development of methods that can cover a wide range of PFAS species. Accordingly, current knowledge suggests that progress in the identification of PFASs in environmental samples has been achieved through the successful application of high-resolution mass spectrometry (HRMS) techniques. Although the presence of PFASs has been reported in surface waters throughout Europe, the need for their constant monitoring and fresh data is the motive for numerous ongoing studies.

Within this context, the main aim of this study was to assess the occurrence and environmental fate of a wide range of PFASs in water samples taken at selected locations along the Danube River through Serbia. Water samples were successfully prepared with Oasis WAX cartridges, while ultra-high performance liquid chromatography coupled with high-resolution mass spectrometry was employed for instrumental analysis. The results of this study will provide insight into trends and patterns in PFAS occurrence in the surface water of the Danube from the region with frequent discharges of untreated municipal wastewaters, which will be compared with those available in the literature, indicating potential risks that may be caused by these contaminants.

Acknowledgements: Funded by the European Union. Views and opinions expressed are, however, those of the author(s) only and do not necessarily reflect those of the European Union or EU executive agency. Neither the European Union nor the granting authority can be held responsible for them. This work is conducted under the project TwiNSol-CECs that has received funding from Horizon Europe program under grant agreement no.101059867.

Wide-Scope Target Screening of Pharmaceuticals in the Danube River Water Samples by Ultra-Performance Liquid Chromatography Coupled with High-Resolution Mass Spectrometry

J. Živančev[1*], O. Gómez-Navarro[2], N. Montemurro[2], S. Pérez[2], I. Antić[1], M. Buljovčić[1], D. Rakić[1] and N. Đurišić-Mladenović[1]

[1]University of Novi Sad, Faculty of Technology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia
[2]ONHEALTH, Dept. Environmental Chemistry, IDAEA-CSIC, Jordi-Girona 18-26, 08034, Barcelona, Spain

jelena.zivancev@tf.uns.ac.rs

Water resources, such as rivers and other water bodies, are at great risk of becoming more contaminated by various pollutants, among which contaminants of emerging concern (CECs) attract a lot of attention from the scientific community and the general public due to their potential long-term adverse effects as well as degradation of the quality of water resources. This imposes the need to understand their occurrence, levels, and spatiotemporal distribution in water resources and to establish effective and efficient long-term surveillance of their presence in water systems. In this context, high-resolution mass spectrometry (HRMS) offers full-spectrum acquisition and represents a promising and powerful technique for screening different classes of pharmaceuticals in water resources, enabling target, suspect, and unknown screening approaches.

Based on the aforementioned, the main goal of this study was to provide insight into the occurrence and distribution of a broad set of pharmaceuticals in water samples of the Danube River from Serbia by applying advanced high-resolution mass spectrometry. The research is focused on the Danube River, as it is the second-largest river basin in Europe and is under the constant pressure of introduction the of different classes of pharmaceuticals, particularly in Serbia where the direct discharge of municipal wastewater occurs frequently as less than 10% of the population in Serbia is linked to wastewater treatment plants with the most frequently applied method of the secondary treatment. Thus, samples were collected at selected locations along almost the entire course of the Danube River through Serbia and prepared using homemade multilayer SPE cartridges. The obtained extracts were analyzed by reversed-phase ultra-high performance liquid chromatography coupled to high-resolution mass spectrometry (RP-UHPLC–HRMS), while collected HRMS data are under processing by the dedicated advanced software tool. The results obtained in this research will be compared with previous ones obtained and available for the Danube River Basin at different river stretches, indicating that surface water screening by RP-UHPLC–HRMS is a powerful approach for the rapid collection of comprehensive information on the pharmaceuticals presence in water resources. The information provided by the screening approach may contribute to the preservation of the good ecological status of water resources or may indicate the necessity of triggering mitigation measures.

Acknowledgements: Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or EU executive agency. Neither the European Union nor the granting authority can be held responsible for them. This work is conducted under the project TwiNSol-CECs that has received funding from Horizon Europe program under grant agreement no.101059867.

Enzyme@Metal-Organic Framework Composites as a Future Alternative for Plastic Degradation in Polluted Waters

I. Rincon[1]*, T.Hidalgo[1], S.Rojas[1,2], P.Horcajada[1]

[1]IMDEA Energy Institute, Advanced Porous Materials Unit, Avda.Ramón de la Sagra 3, E-28935 Móstoles, Madrid, Spain
[2] University of Granada, Department of Inorganic Chemistry, Av. Fuentenueva S/N, 18071 Granada, Spain.

irene.rincon@imdea.org

Plastic pollution is one of the main current worldwide environmental concerns. Nowadays, the society lifestyle involves a persistent plastic consumption, aggravating the low efficiency of wastewater treatment plants (WWTPs) for the water removal of micro/nanoplastics (Lambert and Wagner, 2017). These pollutants can be accumulated in living beings, which makes necessary to seek novel water remediation strategies to avoid their harmful effects. Enzymes (e.g., Candida Rugosa-CrL) are known to play as natural plastic degraders, acting as biocatalysts for depolymerization reactions (Carniel et al., 2017). However, their practical use is limited by their stability, recyclability, and economical costs. Here, a new plastic degradation approach is originally presented: enzyme immobilization in Metal-Organic Frameworks (CrL@MOF composites) (Rafiei et al., 2018) for boosting plastic decomposition in aqueous systems, allowing the catalyst cyclability. In particular, the bis-(hydroxyethyl) terephthalate (BHET) was selected as model substrate for decontamination experiments for being the main polyethylene terephthalate (PET) degradation product. Once suspended in contaminated water, CrL@MOF composites can eliminate BHET (up to 37% in 24 h), following two complementary mechanisms: enzymatic degradation (CrL action) and adsorption (MOF effect). As a proof of concept, recyclability and BHET degradation products were also tested with highly promising results. The composite keeps up to 20% its relative catalytic activity after 2 degradation cycles being also able to adsorb BHET degradation byproducts and other organic pollutants present in wastewater.

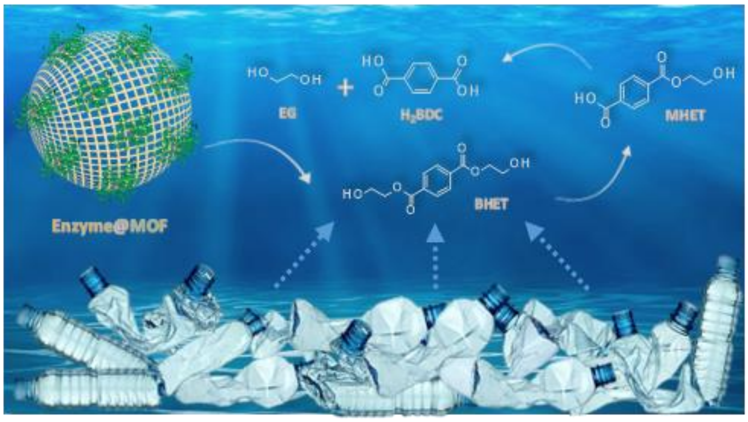


Figure 1:Schematic view of CrL@MOF composite actvity in BHET degradation reactions

References

Lambert, S. and Wagner, M. (2017) "Microplastics Are Contaminants of Emerging Concern in Freshwater Environments: An Overview," The Handbook of Environmental Chemistry. Springer International Publishing.

Carniel, A. et al. (2017) "Lipase from Candida antarctica (CALB) and cutinase from Humicola insolens act synergi".

Rafiei, S. et al. (2018) "Efficient biodiesel production using a lipase@ZIF-67 nanobioreactor," Chemical Engineering Journal. Elsevier BV. doi:10.1016/j.cej.2017.10.

Assessing the Contamination and Tidal Influence of Emerging Contaminants in the Guadalquivir River Estuary, SW Spain

R. Rios-Quintero[1]*, N. R. Colás-Ruiza[1], M. Luz Tovar-Salvador[1], P. Lara-Martín[1], M. G. Pintado-Herrera[1]

[1]University of Cadiz, Physical Chemistry Department, Faculty of Marine and Environmental Sciences, International campus of Excellence of the Sea, University of Cadiz, 11510 Cadiz, Spain

ruben.rios@uca.es

The human influence on surface runoff has significant effects on aquatic systems. A study was conducted on the lower part of the Guadalquivir River in southwest Spain, which flows into the Atlantic Ocean. This navigable river is affected by various anthropogenic activities including maritime traffic, agriculture, fish farming, and urban areas. To extract and analyze different groups of contaminants of emerging concern (CECs), such as pharmaceutically active compounds, sweeteners and illegal drugs, a multiresidue method based on solid-phase extraction (SPE) followed by ultra-performance liquid chromatography-triple quadrupole spectrometry (UPLC-QqQ-MS/MS) was used. Seventeen surface water samples were collected from various sampling sites, and tidal cycle sampling was conducted at two sampling sites to elucidate tidally associated variations. For this, 150 compounds were analyzed.

This study observed the dilution effect of most of the compounds detected towards the ocean. Higher concentrations of PhACs and illegal drugs were detected in upstream areas closer to wastewater discharges, as well as differences along the tidal cycle for some compounds, such as gemfibrozil (from 340 to 5 ng/L) or sucralose (from 1200 to 3 µg/L), respectively. Furthermore, the results showed the presence of some psychiatric drugs such as caffeine and carbamazepine, anti-inflammatory drugs such as ketoprofen, and illegal drugs such as benzoylecgonine, the main metabolite of cocaine, among others.

To our knowledge, the presence of some CECs in the selected area has been demonstrated for the first time, highlighting the importance of the monitoring of aquatic systems to evaluate the distribution as well as the persistence of some chemicals in surface waters.

References

Baena-Nogueras, R.M. et al. (2016) 'Determination of pharmaceuticals in coastal systems using solid phase extraction (SPE) followed by ultra-performance liquid chromatography–tandem mass spectrometry (UPLC-MS/MS)', Current Analytical Chemistry, 12, pp.183-201. doi: 10.2174/1573411012666151009193254.

Robles-Molina, J. et al. (2014) 'Monitoring of selected priority and emerging contaminants in the Guadalquivir River and other related surface waters in the province of Jaén, South East Spain', Science of the Total Environment, 479, pp.247-257. doi:10.1016/j.scitotenv.2014.01.121.

Removal of Pesticide and Pharmaceutical Residues During Riverbank Filtration

D.Drożdżyński[1]*, R. Kruć-Fijałkowska[2], K. Dragon[2]

[1]Institute of Plant Protection – National Research Institute, Department of Pesticide Residue Research,
Władysława Węgorka St. 20, Poznań, Poland
[2]Adam Mickiewicz University, Department of Hydrogeology and Water Protection, Bogumiła Krygowskiego St. 12,
Poznań, Poland

d.drozdzynski@iorpib.poznan.pl

The growing demand for water and the need to protect ground water resources makes it necessary to search for alternative methods of obtaining drinking water. One of the methods used to enrich water resources is river bank filtration (RBF). RBF is a cost-effective and sustainable natural water treatment process. In RBF systems, surface water infiltrates through the river bank/riverbed and then flows through the aquifer media from the source (river) to the wells. As a result, processes occur that improve surface water quality, such as dilution, filtration, adsorption, biodegradation and redox reactions. RBF systems significantly reduce concentrations of chemical and biological pollutants in the water and effectively reduce emerging contaminant concentrations such as pesticides and pharmaceuticals.

Occurrence of pesticide residues were studied in river and RBF water at the Mosina-Krajkowo site (Wielkopolska, Poland), in 7 sampling campaigns between August 2017 and August 2018, while pharmaceutical concentration levels in the same sampling points were investigated in 6 sampling campaigns from November 2019 to June 2020. Eight sampling points were selected for this study - Warta river, horizontal well (HW) and six vertical wells (VWs) located on the flood plain and higher terrace (11–680 m at a distance from the river bank). During the research, a total of 25 pesticide active substances and their metabolites were detected. Based on previous studies (Dragon et al., 2018, 2019), ten of the most frequently detected pharmaceuticals that occur in the highest concentrations in this area were selected for analyses. All of the ten pharmaceutical compounds tested for were detected in the river and HW water samples. The highest concentrations of both pesticide and pharmaceutical residues were observed in surface waters. There was a reduction in their levels in HW with drains located below the river bottom, averaging 17–19%. Significantly higher reductions were observed in vertical wells (VWs). Mixing, sorption and biodegradation were distinguished as processes conditioning the reduction of organic micropollutants flow paths from the river to the wells. Their reduction in the HW occurs due to sorption onto fine sediments with high organic matter content and aerobic biodegradation, while in the VWs it is the effect of aerobic biodegradation and water mixing with unpolluted ground water. Sorption on riverbed fine sediments can also occur, especially during low water levels in the river. VWs located at similar distances from the river yielded different concentrations of pesticides and pharmaceuticals. At greater distances of the wells from the river, the removal of pesticide and pharmaceutical residues was in the range of 55–68% and 52–66%, respectively. The highest removal of pharmaceutical residues and pesticides was found in a well located 250 m from the river and no micropollutants were detected in a well located 680 m from the river. The results provide evidence of the high efficacy of riverbank filtration for contaminant removal.

References

Dragon, K. et al. (2018) Removal of natural organic matter and organic micropollutants during river bank filtration in Krajkowo, Poland, Water, 10 (10): 1457. doi: 10.3390/w10101457.

Dragon, K. et al. (2019) The migration of pesticide residues in groundwater at a bank filtration site (Krajkowo well field, Poland), Environmental Earth Science, 78 (20): 593. doi: 10.1007/s12665-019-8598-0.

Spatial and Temporal Trends of 64 Pesticides and Their Removal from Australian Wastewater

ER. Knight[1]*, R. Verhagen[1], JF. Mueller[1], BJ. Tscharke[1]

[1]The University of Queensland, Queensland Alliance for Environmental Health Sciences (QAEHS), 20 Cornwall Street, Woolloongabba, 4102, Brisbane, Australia

emma.knight@niva.no

Pesticides are necessary for the control of pest plant, fungi and insect species. After use some pesticides are retained in the environment and can find their way into waste streams, including municipal sewage. There is no clear source or mechanism defined for their occurrence in wastewater, and their spatio-temporal distribution has also not been well characterised. To further understand the spatio-temporal distribution and to evaluate potential sources and fate after treatment, 64 pesticides were analysed in matched influents and effluents of 22 wastewater treatment plants (WWTPs) from 7 states or territories of Australia. The total population served by the 22 sites was equivalent to approximately 41% of the Australian population. The pesticides consisted of 30 herbicides and 8 herbicide metabolites or transformation products, 16 insecticides and 10 fungicides. Archived samples were chosen from within the Australian Environmental Specimen Bank and consisted of 1,084 24-hr composite samples pooled into 113 samples. Pools represented 2 influent pools and 1 effluent pool at each of 22 WWTP sites in 2019 (i.e., spatial trend), and 2 influent pools per year from 2009 – 2021 at a subset of 2 locations to evaluate the temporal trend. Using established analytical methods, LC-MS/MS (Hageman et al. 2019, Thai et al. 2020), 25 of the 64 pesticides were detected with maximum concentrations of 100 µg/L in influent and 16 µg/L in effluent, both for the herbicide 2,4-D. Some WWTPs had higher population-normalised mass loads of several pesticides compared to other sites potentially indicating point source contamination. Removal efficiencies varied considerably for different pesticides, ranging between <-100% (effluent higher than influent, potential formation during treatment) and 100%, with some indications of greater removal with tertiary over primary treatments. The total mass of pesticides was extrapolated to Australia, suggesting approximately 33 kg of pesticides entered WWTP influent annually nation-wide, with 14 kg emitted into effluents annually. Temporal trends varied, with some pesticides concentrations decreasing over time (diuron and simazine hydroxy), increasing concentration over time (hexazinone), and some pesticides with no change (thiamethoxam, imidacloprid, DEET, and metalaxyl) over the 11 year period. Of the 63,000 tons of pesticides used in Australia in 2019 we estimated 0.05% of the total pesticides end up in influent and 0.02% to effluents, indicating the small endpoint of the chemical class. Similar proportions of the total pesticide mass loads were attributable to herbicides, insecticides and fungicides (approximately 60%, 35%, 5% of total pesticide loads) as pesticide use data (70%, 22% and 7%, respectively). Understanding the tempo-spatial trends of pesticides in wastewater can help to characterise sources of pesticides and enable prevention, or possible pre-treatment of pesticide-containing wastewater entering WWTPs.

References

Hageman, K. J., et al. (2019) 'Current-use pesticides in New Zealand streams: comparing results from grab samples and three types of passive samplers', Environmental Pollution, 254, pp. 112973. doi: 10.1016/j.envpol.2019.112973.

Thai, P., et al. (2020) 'Marine Monitoring Program: Annual Report for inshore pesticide monitoring 2018–19'.

Toxins in Biofilms of Lakes and Rivers, an Emerging Threat for Public Health in a Scenario of Climate Changes

L. Cerasino[1]*

[1]Fondazione Edmund Mach, Research and Innovation Centre, via e. Mach, 1, 38098, San Michele all'Adige (TN), Italy

leonardo.cerasino@fmach.it

Cyanobacteria constitute a health hazard in freshwater environments due to the ability to produce toxic metabolites. Animals and humans can be harmed upon exposure to water containing high levels of cyanotoxins that can occur during intense blooms. Toxin cyanobacteria blooms represent a relevant problem in many lakes and reservoirs worldwide and they are therefore routinely monitored by health/environmental authorities. Microcystins and anatoxins are the most common toxins produced by planktonic cyanobacteria. In the last years more and more reports are being published about the occurrence of toxic cyanobacteria in benthic mats (biofilms) growing on rocks, sediment, or macrophytes on the shores of lakes or rivers. The concentration of toxins in biofilm (especially of anatoxins) can reach very high levels, sufficient to cause the death of dogs and cattle. Differently from planktonic cyanobacteria, there is no regular monitoring of benthic cyanobacteria by authorities. It is therefore important to conduct more studies aimed at assessing the real relevance of this phenomenon in aquatic environments. Additionally, the impact of ongoing climate changes on the ecological aspects of these organisms are needed. Recent investigations conducted in the frame of local and international projects (i.e., Eco-AlpsWater project, financed by the EU-Interreg Alpine Space program) has offered the occasion of running a survey on some lakes and rivers in Europe, in particular in the Alpine region. Results have demonstrated that toxic cyanobacteria are present in biofilm collected from stones on the shores of some lakes. A comprehensive analytical effort was conducted by means of LC-MS/MS, which showed that anatoxins are the most relevant toxins in biofilms. In particular, two congeners were found to be the most represented: anatoxin-a and homoanatoxin-a. The toxin content in samples showed also a big spatial heterogeneity with up to two orders of magnitudes differences from samples taken meters away from each other.

References

Wood, S. et al. (2020) "Toxic benthic freshwater cyanobacterial proliferations: Challenges and solutions for enhancing knowledge and improving monitoring and mitigation", Freshwater Biology, 65(10), 1812-1842. doi: 10.1111/fwb.13532.

Fastner, J. et al. (2018) "Fatal Neurotoxicosis in Dogs Associated with Tychoplanktic, Anatoxin-a Producing Tychonema sp. in Mesotrophic Lake Tegel, Berlin", Toxins, 10(2): 60. doi: 10.3390/toxins10020060.

Cerasino, L. et al. (2020), "Co-occurrence of anatoxin-a and microcystins in Lake Garda and other deep perialpine lakes", Advances in Oceanography and Limnology, 11, 8677. doi: 10.4081/aiol.2020.8677

Biodegradation of Benzalkonium Compounds (BACs) Under Different Conditions – Pathways, Kinetics and Removal

Y. Larsson[1], A. Mongelli[1], K. Bester[1]

Aarhus University, Environmental Science

Benzalkonium compounds (BAC) are among the most commonly sold biocides in Europe and several thousand tons are marketed every year for use in human and veterinary hygiene, wood protection as well as other applications. Most of them will be introduced into wastewater treatment or manure treatments. However, their degradation kinetics and pathways as well as generally fate are not fully established at this moment.

We have studied the degradation pathways for multispecies biofilm systems and single species fungal systems by means of HPLC-HRMS.

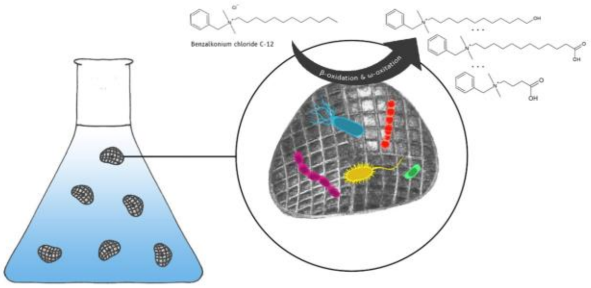
For each BAC several pathways with a multitude of metabolites are detected, however at least BAC 12 and BAC 14 show the same degradation pathways in each system. The main pathways are including Ω- and β-oxidations.

To transfer that knowledge to wastewater treatment, biodegradation rate constants for a large variety of BACs in sludge were determined in incubation experiments. The resulting half-lives are ranging from 1.5-60 h. Concerning the BAC of highest environmental relevance the half-lives were: 13 h (BAC-16) and 14 h (BAC-14), 31 h DDAC-12 and 49 h (BAC-12).

These results are compared to mass balances in wastewater treatment plants: Inflow and effluent concentrations of the parent compounds were determined by means of HPLC-MS/MS from 24 h composite samples from three smaller WWTPs. The highest BAC concentrations in WWTP influents were measured for BAC-12 (900-2200 ng/L), BAC-16 (88-217 ng/L) and BAC-14 (25-100 ng/L). As the removal in the tested WWTPs was high (exceeding 99%), the effluent concentrations were very small.

Probably the main removal mechanism is a two-step process: sorption to sludge of the parent compound, followed by a (slower) biodegradation of the sorbed BAC.

Conclusions: There are two issues concerning the emissions of WWWTPs: a) the parent compounds as sorbed to sludge pose a risk for terrestrial ecosystems, when the sludge is amended on land as is typically the case in Scandinavia. The formed metabolites are more water soluble than the parent compounds and might well be discharged with the effluent water to a relative high extent and have impact on aquatic life.



Comparative Phenotypic and Molecular Characterization of Clinical and Aquatic Multidrug Resistant Acinetobacter Baumannii Circulating Clones Isolated in Romania for Four Consecutive Years

I. Gheorghe-Barbu*[1], I. Czobor Barbu[1], V.M. Corbu[1], G.A. Grigore[1], O.C. Vrâncianu[1], M. Surleac[2], S. Paraschiv[2], L. Bănică[2], A.M. Muntean[3], I. Pecete[1], L. Măruțescu[1], M. Popa[1], M.I. Popa[3], D. Oțelea[2], M.C. Chifiriuc[1 2 4]

[1]University of Bucharest, Faculty of Biology, Intr. Portocalelor no 1-3, 060101, Bucharest, Romania,
[2]National Institute of Infectiosus Diseases "Matei Bals", Dr. Calistrat Grozovici no 1, 021105, Bucharest, Romania
[3]National Institute of Research & Development for Microbiology & Immunology Cantacuzino, Spl. Independenței no 103, 50097, Bucharest, Romania
[4]Romanian Academy, 13 Septembrie no 1-55, 50711, Bucharest, Romania

irina.gheorghe@bio.unibuc.ro

Background: Romania is one of the European countries with the highest rates of multidrug-resistance (MDR) in Acinetobacter baumannii (AB) clinical isolates. According to ECDC, in 2021 Romania reported the highest resistance levels for fluoroquinolones, carbapenems and aminoglycosides, the available data being limited to the capital city and few regions of the country (ECDC, 2023). This study aims to assess the phenotypic and molecular resistance of AB strains isolated for four consecutive years (2019-2022) from intra-hospital infections and different aquatic compartments [wastewater (WW) and surface water (SW) network] from 3 geographical regions of Romania (2 of them not currently covered by national reports), and to highlight the genetic virulence markers (VM) in MDR strains producing carbapenemases (CP) and extended spectrum β-lactamases (ESBL).
Methods: The strains were isolated on chromogenic media from WW and SW samples and identified by MALDI-TOF-MS. Antibiotic susceptibility testing was followed by confirmation of CP and ESBL phenotypes and investigation of resistance and virulence genotypes by PCR and NGS sequencing.
Results: From a total number of 168 WWs and SW samples collected from 7 geographical locations of Romania during 2019-2022 were isolated and identified a total of 587 AB strains, the highest frequency being associated with water samples recovered from large cities, county seat [Bucharest (23.16%), Târgoviște (20.95%); and respectively Galați (18.56%), a city located on the lower course of the Danube river, considered the future central axis of the European Union. The comparative analysis of the AR profiles according to the isolation source and the geographical location of AB strains demonstrated comparable levels: the strains isolated from intra-hospital infections before the pandemic/after-pandemic period showed the highest resistance level to carbapenems (CR) (IMP, MEM) in all geographical regions; in the case of the strains isolated from the water samples, the CR resistance level varied, with the region, the CR resistance being higher in postpandemic isolates from Bucharest (41.1%/64.7% and respectively 12.12%/18.18%) and Iași (50%/100% and respectively 42.8%/94.9%). The genotypic study of CR and cephalosporin resistance demonstrated the presence of international high risk clones ST2, ST492, ST63, ST79 and ST1 carrying CP encoding genes blaOXA-66, blaOXA-23, blaOXA-72 and ESBL encoding genes blaTEM-1, blaTEM-12, blaADC-5,-25,-73,-74,-81,-154,-167 and blaPER-1 circulating between the hospitals and the water network; in the case of AB strains isolated in 2022 from WW and SW samples, the CP and ESBL encoding genes were associated with the presence of VMs (ompA, csuE and bfmS). Conclusions: We report here the first dynamic long term comparative description of the phenotypic and genetic background of AR and VMs in MDR AB relevant clones circulating in the hospital and WW environments in Romania.
We acknowledge the financial support of PN-III-P4-ID-PCCF-2016-0114, PN-III-P1-1.1-TE-2021-1515 (TE112/2022), PN-III-P1-1.1-PD-2021-0540 (PD102/2022) and ERANET 243/2021 research projects awarded by UEFISCDI.

References

The European Centre for Disease Prevention and Control (ECDC) (2023) Surveillance Atlas of Infectious Diseases Available at: http://atlas.ecdc.europa.eu/public/index.aspx (Accessed: 12 March 2023).

Pharmaceuticals From Wastewater in Plants: Lettuce as an Antidepressant?

H. Švecová[1*], R. Kodešová[2], A. Nikodem[2], A. Klement[2], M. Fér[2], G. Fedorova[1], R. Grabic[1]

[1]University of South Bohemia in České Budějovice, Faculty of Fisheries and Protection of Waters, South Bohemian Research Center of Aquaculture and Biodiversity of Hydrocenoses, Zátiší 728/II, CZ 389 25 Vodňany, Czech Republic
[2]Czech University of Life Sciences Prague, Faculty of Agrobiology, Food and Natural Resources, Dept. of Soil Science and Soil Protection, Kamýcká 129, CZ-165 00 Prague – Suchdol, Czech Republic

hsvecova@frov.jcu.cz

The reuse of wastewater is an emerging topic following global climate change. However, conventionally treated wastewater from municipal wastewater treatment plants (WWTP) still contains several micropollutants, such as pharmaceuticals or personal care products (PPCPs) or their transformation products (Golovko et al., 2014). Partitioning between water and solid phases along the WWTP leads to PPCPs occurrence in the sludge. When applying wastewater or sludge in agriculture, these substances can consequently leak into groundwater or pass into plants. This study focused on the behavior of selected micropollutants in a natural water-soil-plant system.

During a project funded by the Ministry of Agriculture of the Czech Republic (QK21020080), flower beds with different types of soil (cambisol and regosol) were constructed at WWTP and planted with lettuce. Part of the beds was irrigated with outgoing wastewater (effluent), and part with drinking water. After harvest, the plants were freeze-dried and extracted with a mixture of acetonitrile: water (1:1 v/v) with 0.1% formic acid. The extracts were analyzed by liquid chromatography coupled with high-resolution mass spectrometry. Effluent, used for irrigation of flower beds, was analyzed by liquid chromatography with in-line solid phase extraction coupled with mass spectrometry. Concentrations of 56 and 74 micropollutants were evaluated in plants and wastewater.

Of the 74 substances analyzed, 56 compounds were found above the detection limit in effluent samples. Psychoactive substances were the most represented group, of which the highest average concentration was found for gabapentin (600 ng/l), venlafaxine and its metabolite O-desmethyl venlafaxine (260 and 570 ng/l, resp.), carbamazepine and its metabolite trans-10,11 -dihydro-10,11-dihydroxy carbamazepine (270 and 490 ng/L, resp.) and lamotrigine (440 ng/L). High average concentrations were also found for telmisartan (890 ng/l), diclofenac (590 ng/l), 1H-benzotriazole (560 ng/l), and UV filter PBSA (580 ng/l). Lettuce was grown in green and red variants. Of the 56 monitored substances, 19 compounds were found in green lettuce and only ten in red. The most frequently represented psychoactive substances were gabapentin (3.2-19 ng/g), carbamazepine (6.3-16 ng/g), tramadol (3.4-18 ng/g), and venlafaxine (1.3-8 ng /g). Significant differences were observed between red lettuce grown in cambisol and regosol. The uptake of gabapentin was more than fivefold higher in regosol compared to cambisol. The content of carbamazepine in lettuce grown in regosol was 1.3 and 2.7 times higher for the green and red variants, resp. The higher adsorption of carbamazepine in cambisol than in regosol may explain this phenomenon (Kodešová et al., 2109).

Although plants significantly accumulated and metabolized several drugs from irrigation in laboratory conditions, this accumulation is considerably lower than in natural conditions. One of the factors why the uptake was low in the field study was the significant atmospheric precipitation, which diluted and washed the monitored compounds from the test beds. Another factor could be the different distribution of the roots.

References

Golovko, O. et al. (2014) Seasonal changes in antibiotics, antidepressants/psychiatric drugs, antihistamines and lipid regulators in a wastewater treatment plant. Chemosphere 111, p. 418-426. https://doi.org/10.1016/j.chemosphere.2014.03.132

Kodešová, R. et al. (2019) Root uptake of atenolol, sulfamethoxazole and carbamazepine, and their transformation in three soils and four plants. Environ Sci Pollut Res 26, p. 9876-9891. https://doi.org/10.1007/s11356-019-04333-9.

Bioinformatic Insights into Resistant Escherichia Coli Isolated from Different Aquatic Environments in Romania

M. Surleac[1,3]*, I. Czobor Barbu[2,3], S. Paraschiv[1], I. Gheorghe-Barbu[2,3], D. Oțelea[1], M.C. Chifiriuc[2,3]

[1]National Institute for Infectious Diseases, Matei Balș, Bucharest, Romania
[2]University of Bucharest, Faculty of Biology, Intr. Portocalelor, no. 1-3, 060101, Bucharest, Romania
[3]University of Bucharest, Research Institute of the University of Bucharest, Bucharest, Romania

marius.surleac@gmail.com

Romania is among the European countries with the highest rates of multidrug resistant (MDR) pathogens (e.g., the species from the ESKAPE group) that become more & more resistant to the last-resort antimicrobials (such as colistin, vancomycin, imipenem, etc.). The use of WGS techniques provides the means to monitor various aspects of resistance transmission, the emergence and spread into the natural environment of high-risk pathogens harboring antibiotic resistance genes (ARGs), especially the ones acquired by mobile genetic elements (MGE).

Methods: A total of 144 E. coli isolates have been collected between 2018-2020 from some of the largest and polluted cities in Romania, covering the main geographic regions of the country. The isolation sources span from clinical settings (n = 14) to wastewater treatment plants (WWTP) (n = 101) and isolates from the WWTP's upstream (n = 8) and downstream (n = 21) surface waters. A detailed analysis pipeline has been performed on these isolates: WGS sequencing using MiSeq Illumina technology and continuing with de novo assembly using shovill; and other predictions on ARGs and MGEs.

Results: The 144 E. coli isolates from this study harbor a huge repertoire of resistance determinant for antibiotics and biocides, as well as MGEs. Most of the surface water strains belong to commensal phylogroup A, but there are a few from phylogroup D (known to be associated with increased virulence in E. coli), while in the wastewaters we noticed that 10% from this set belong to phylogroup D clustered in the West of Romania. There is also a difference in the distribution of E. coli subtypes in the environment, ST540 being the most frequent in the West of Romania while in the South the most frequent ones were ST167 (known to be a high-risk clone emerging in human clinical isolates) and ST607. Looking at the wastewaters, the most abundant were ST167 & ST131 in the South of Romania, while in the East the most frequent was ST10. All the analyzed isolates (no matter the isolation source) carry a consistent set of MGEs, such as insertions sequences (e.g. IS1A, ISSen9), transposons (e.g. Tn6011, Tn6024 (associated with colistin resistance), etc. The most abundant ARGs were found in WWTP influent isolates. Some of the most abundant genes include blaOXA-48, blaTEM-1 and blaEC-15, among others. When comparing the IS in the surface water isolates between 2019 and 2020, we notice increased levels of IS for almost all isolates from 2019 compared to the ones from 2020. This could be due to the stricter sanitary regulations implemented during the SARS-CoV-2 pandemics.

We acknowledge the financial support of UEFISCDI funded projects: PN-III-P1-1.1-PD-2021-0540 (PD102/2022), PN-III-P1-1.1-TE-2021-1515 (TE112/2022), COFUND-AQUATIC POLLUTANTS-BIOCIDE (ERANET 243/2021), PN-III-P4-ID-PCCF-2016-0114.

Pharmaceuticals From Wastewater in Plants: Lettuce as an Antidepressant?

H. Švecová[1*], R. Kodešová[2], A. Nikodem[2], A. Klement[2], M. Fér[2], G. Fedorova[1], R. Grabic[1]

[1]University of South Bohemia in České Budějovice, Faculty of Fisheries and Protection of Waters, South Bohemian Research Center of Aquaculture and Biodiversity of Hydrocenoses, Zátiší 728/II, CZ 389 25 Vodňany, Czech Republic
[2]Czech University of Life Sciences Prague, Faculty of Agrobiology, Food and Natural Resources, Dept. of Soil Science and Soil Protection, Kamýcká 129, CZ-165 00 Prague – Suchdol, Czech Republic

hsvecova@frov.jcu.cz

The reuse of wastewater is an emerging topic following global climate change. However, conventionally treated wastewater from municipal wastewater treatment plants (WWTP) still contains several micropollutants, such as pharmaceuticals or personal care products (PPCPs) or their transformation products (Golovko et al., 2014). Partitioning between water and solid phases along the WWTP leads to PPCPs occurrence in the sludge. When applying wastewater or sludge in agriculture, these substances can consequently leak into groundwater or pass into plants. This study focused on the behavior of selected micropollutants in a natural water-soil-plant system.

During a project funded by the Ministry of Agriculture of the Czech Republic (QK21020080), flower beds with different types of soil (cambisol and regosol) were constructed at WWTP and planted with lettuce. Part of the beds was irrigated with outgoing wastewater (effluent), and part with drinking water. After harvest, the plants were freeze-dried and extracted with a mixture of acetonitrile: water (1:1 v/v) with 0.1% formic acid. The extracts were analyzed by liquid chromatography coupled with high-resolution mass spectrometry. Effluent, used for irrigation of flower beds, was analyzed by liquid chromatography with in-line solid phase extraction coupled with mass spectrometry. Concentrations of 56 and 74 micropollutants were evaluated in plants and wastewater.

Of the 74 substances analyzed, 56 compounds were found above the detection limit in effluent samples. Psychoactive substances were the most represented group, of which the highest average concentration was found for gabapentin (600 ng/l), venlafaxine and its metabolite O-desmethyl venlafaxine (260 and 570 ng/l, resp.), carbamazepine and its metabolite trans-10,11 -dihydro-10,11-dihydroxy carbamazepine (270 and 490 ng/L, resp.) and lamotrigine (440 ng/L). High average concentrations were also found for telmisartan (890 ng/l), diclofenac (590 ng/l), 1H-benzotriazole (560 ng/l), and UV filter PBSA (580 ng/l). Lettuce was grown in green and red variants. Of the 56 monitored substances, 19 compounds were found in green lettuce and only ten in red. The most frequently represented psychoactive substances were gabapentin (3.2-19 ng/g), carbamazepine (6.3-16 ng/g), tramadol (3.4-18 ng/g), and venlafaxine (1.3-8 ng /g). Significant differences were observed between red lettuce grown in cambisol and regosol. The uptake of gabapentin was more than fivefold higher in regosol compared to cambisol. The content of carbamazepine in lettuce grown in regosol was 1.3 and 2.7 times higher for the green and red variants, resp. The higher adsorption of carbamazepine in cambisol than in regosol may explain this phenomenon (Kodešová et al., 2109).

Although plants significantly accumulated and metabolized several drugs from irrigation in laboratory conditions, this accumulation is considerably lower than in natural conditions. One of the factors why the uptake was low in the field study was the significant atmospheric precipitation, which diluted and washed the monitored compounds from the test beds. Another factor could be the different distribution of the roots.

References

Golovko, O. et al. (2014) Seasonal changes in antibiotics, antidepressants/psychiatric drugs, antihistamines and lipid regulators in a wastewater treatment plant. Chemosphere 111, p. 418-426. https://doi.org/10.1016/j.chemosphere.2014.03.132

Kodešová, R. et al. (2019) Root uptake of atenolol, sulfamethoxazole and carbamazepine, and their transformation in three soils and four plants. Environ Sci Pollut Res 26, p. 9876-9891. https://doi.org/10.1007/s11356-019-04333-9

Estimating Annual PFAS Loads in WWTP Influent Using a Source-Based Modelling Approach

N. Krlovic[1]*, E. Saracevic[1], M. Zessner[1] and O. Zoboli[1]

Institute for Water Quality and Resource Management, TU Wien, Austria

nikola.krlovic@tuwien.ac.at

Per- and polyfluoroalkyl substances (PFAS) are a class of persistent chemicals, whose impact has been observed in various environmental compartments. Wastewater treatment plants (WWTPs) are a major emission pathway of PFAS into the aquatic environment. Given the various sources of these chemicals that can contribute to WWTP loads, including a broad variety of consumer product use (Glüge et al., 2020), as well as recirculated PFAS from the environment (Cousins et al., 2022), it is important to properly quantify and assess the relevance of individual contributions of different sources in the wastewater influent.

The goal of this study was to develop a scalable, source-based modelling framework of PFAS load quantification within the municipal wastewater influent, and afterwards apply and validate it on a case study urban environment in a large central European city. 5 carboxylic (PFCA) and 2 sulfonic (PFSA) based groups were selected, including PFHxA, PFHpA, PFOA, PFNA, PFDA , PFHxS and PFOS. This set of chemicals was selected in order to assess compounds that are represented by differing chemical properties, and due to the fact that these compounds are well represented in the literature in terms of source concentrations, allowing for a reliable mass balance calculation. The quantification of individual loads was carried out by coupling an extensive literature review on prior research results pertaining to the concentration of PFAS in various media with location-specific data including water consumption and detailed water balance of the WWTP catchment, consumer statistics and paved surface area, among others. To validate the resulting Material Flow Analysis (MFA) model, a year long sampling campaign of both the influent and effluent of the WWTP of the studied area was conducted in 2022, and samples analysed using liquid chromatography mass spectrometry (LCMS).

The percentage of annual loads were explained in the range of 40% to 90% of influent loads measured at the WWTP, with PFCAs yielding higher explained percentages compared to the PFSAs. This approach allowed for an insight into the proportion of different contributors in terms of loading, with respect to different PFAS. Preliminary results indicate that PFCAs have a higher degree of variability of sources. For example, PFOA exhibited a 60% load contribution from recirculated sources, and 40% stemming from consumer products. Conversely, PFSA loads consisted mostly of recirculated PFAS (>90%). Additionally, the study found that the load attributed to consumer products depended on the magnitude of precursor transformation, individual chemical characteristics and the resulting stock accumulation of substances in the system during product lifetime, indicating a need to include an array of variables when computing the final load entering the WWTP in a given year. Lastly, the sampling campaign in this study confirmed prior findings relating to poor removal of PFAS in the WWTP effluent (Lenka, Kah and Padhye, 2021), (Kruskall-Wallis test, $p > 0.05$), meaning that assessment of PFAS originating from WWTP can be initiated at the source of entry into the sewer system, rather than at the effluent.

References

Cousins, I.T. et al. (2022) ‘Outside the Safe Operating Space of a New Planetary Boundary for Per- and Polyfluoroalkyl Substances (PFAS)’, Environmental Sience & Technology, 56(16), pp. 11172–11179. Available at: https://doi.org/10.1021/acs.est.2c02765.

Glüge, J. et al. (2020) ‘An overview of the uses of per- and polyfluoroalkyl substances (PFAS)’, Environmental Science: Processes & Impacts, 22(12), pp. 2345–2373. Available at: https://doi.org/10.1039/D0EM00291G.

Lenka, S.P. et al. (2021) ‘A review of the occurrence, transformation, and removal of poly- and perfluoroalkyl substances (PFAS) in wastewater treatment plants’, Water Research, 199, p. 117187. Available at: https://doi.org/10.1016/j.watres.2021.117187.

Pathways to Zero Fluoro-Pollution

Z. Wei[1]*

[1]Centre for Water Technology (WATEC), Department of Biological and Chemical Engineering, Aarhus University, Universitetsbyen 36, 8000 Aarhus C, Denmark

zwei@bce.au.dk

The consensus of removing per- and polyfluoroalkyl substances (PFAS) from the environment is widely recognized and enlightened by the recent near-zero health advisories by the U.S. EPA in 2022. The only way to achieve the goal of eliminating PFAS pollution is to fully defluorinate or mineralize PFAS (i.e., converting PFAS to innocuous H2O, CO2, and F- ions), but current technologies only partially defluorinate a limited number of PFAS, which can lead to the creation of potentially more toxic short-chain intermediates (M.G. Evich et al. 2022, H. Li et al. 2022, J.A. Juve et al. 2022) Therefore, this talk will discuss the need to broaden the scope of tested PFAS and summarize the state-of-the-art degradation technologies including oxidation, reduction, photocatalysis, sonication, etc. Besides fundamental knowledge gaps in defluorination reactions, technical gaps in the aspects of water matrix effects, pilot tests, and cost analysis also limit the application and comparison of different treatment technologies. Despite these challenges, we should endeavor to advance next-generation water purification technologies that enable the complete destruction of PFAS in water.

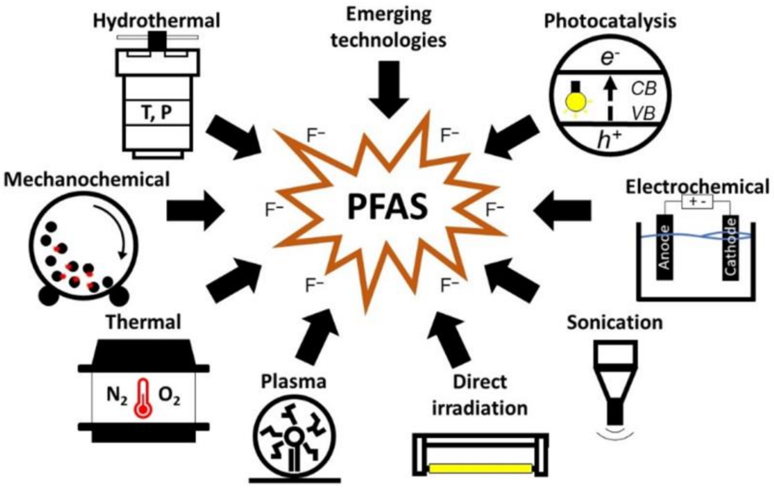


Figure 1: Summary of PFAS removal and defluorination technologies.

References

M.G. Evich et al. (2022) Per- and polyfluoroalkyl substances in the environment, Science 375, 1–14.

H. Li et al. (2022) A recent overview of per- and polyfluoroalkyl substances (PFAS) removal by unctional framework materials, Chem. Eng. J. 452, 139202.

J.A. Juve et al. (2022) Concentrate and degrade PFOA with a photo-regenerable composite of In-doped TNTs@AC, Chemosphere. 300, 134495.

Highly PFAS Contaminated Field Side in Germany: Non-Target Screening Via Fragment Mass Differences and Kendrick Mass Defect Analysis

J. Zweigle[1*], B. Bugsel[1], C. Zwiener[1]

[1]Universität Tübingen, Environmental Analytical Chemistry, Department of Geosciences, Schnarrenbergstr. 94-96, 72076 Tübingen, Germany

jonathan.zweigle@uni-tuebingen.de

Per- and polyfluoroalkyl substances are a very diverse group of anthropogenic chemicals with unique properties. Therefore, they are used in countless industrial processes and consumer products. Due to their intrinsic persistence in combination with extensive use, selected PFAS can be detected globally in various media. While long-chain perfluoroalkyl acids (PFAAs) are almost phased out, there are large numbers of not well characterized alternative PFAS in current use that can eventually transform into persistent end products (Evich et al. 2022). Due to the shear number of PFAS, comprehensive measurements with authentic reference standards are not possible which is why non-target screening (NTS) approaches based on high-resolution mass spectrometry (HRMS) are necessary to characterize complex PFAS contaminations. Since highly fluorinated PFAS typically have common molecular moeties such as perfluoroalkyl- or perfluoroether chains, they form characteristic fragment mass differences during MS/MS fragmentation. Those mass differences have the advantage that they are more generic than specific diagnostic fragments and they can often still be applied to transformation products (different mass) were specific fragments might change while fragment differences can persist.

With the use of PFAS standards, extracts of PFAS impregnated papers and contaminated soil as well as the online MS/MS library MassBank (~20000 spectra), we investigated the occurrence of specific mass differences for efficient detection of highly probable PFAS spectra. The effect of parameters such as mass tolerance and intensity threshold on false positive detection were analyzed. After optimization, an open-source algorithm (FindPFΔS) was developed to search for mass differences in vendor independent MS/MS raw data (*.ms2 files) (Zweigle et al. 2022).

The FindPFΔS workflow in combination with Kendrick mass defect (KMD) analysis was applied to an extract of a composite soil sample from a highly contaminated field site in north-western Germany (Brilon-Scharfenberg; BS) were presumably 20 years ago contaminated waste was applied to agricultural fields. In 2006, PFAAs were detected in surface waters, drinking water and the adjustent population in the vicinity of this contamination, however, to date no NTS approach was applied to the soil to comprehensively charcterize the occurrence of PFAS. Therefore, the soil extract and an eluate after precursor oxidation (TOP assay) were measured with iterative data-dependent acquisition by high-performance liquid chromatograpy time-of-flight mass spectrometry. After in-depth data analysis (FindPFΔS and KMD), in total, 10 further PFAS classes (73 single PFAS) were identified in the soil from BS including one novel PFAS class. Due to structural similaries (all PFAS classes comprised sulfonic acid groups) they were semi-quantified with perfluoroalkyl sulfonic acid (PFSA) reference standards. The results showed that ~97% of the present PFAS are perfluorinated and only ~3% are precursors which was in good agreement to the TOP assay results. Overall the PFAS concentration was estimated to be >30 mg/kg with SF5-PFSA being the dominant class (> 40%).

References

Evich, M. G. et al. (2022) Per- and polyfluoroalkyl substances in the environment. Science 375 (6580):eabg9065. doi:10.1126/science.abg9065

Zweigle J. et al. (2022) FindPFAS: Non-Target Screening for PFAS - Comprehensive Data Mining for MS2 Fragment Mass Differences. Anal Chem 94 (30):10788-10796. doi:10.1021/acs.analchem.2c01521.

3D Printed In_2O_3 Superstructures: a New Adsorptive Photocatalyst for Removal of PFAS in Water

A. S. Martins[1*], T. T. Guaraldo[1], G. Zoumpouli[1], J. Wenk[1], D. Mattia[1]

[1]University of Bath, Department of Chemical Engineering, Claverton Down, BA2 7AY, Bath, United Kingdom

asm205@bath.ac.uk

Semiconductors based on In_2O_3 have demonstrated photocatalytic effectiveness for the removal of perfluorooctanoic acid (PFOA), an extraordinary persistent compound among per- and polyfluoroalkyl substances (PFAS), resistant to conventional treatment, and widely detected in the aquatic environment (Dickman, R. A. et al. 2022). In_2O_3 has a high adsorption capacity towards PFOA via tight coordination through bidentate/bridging configuration (Li, X. et al. 2012). Strong adsorption capacity is critical for photocatalytic degradation of PFOA which occurs at the surface of In_2O_3 via direct oxidation by photogenerated holes. However, little data on the synergetic effect of adsorption and photocatalytic PFOA degradation is available with mostly inconsistent results. 3D printing allows the production of self-supporting In_2O_3 photocatalysts, with large surface areas, defined geometry and porosity. Use of 3D printed solid photocatalytic structures can overcome the disadvantages of photocatalytic slurries that have been extensively studied for PFOA degradation (Friedmann, D. et al. 2021) such as the requirement of catalyst separation, and the impacts of their release into the environment. In this work, we have investigated an extrusion-based 3D printing approach to fabricate a novel self-supported In_2O_3 photocatalyst with high adsorptive capacity towards PFOA. In_2O_3 powder was mixed into a printable paste via dispersing in a binder surfactant solution (15% Pluronic F-127). The printed structure exhibited high open porosity (80%) with high chemical and mechanical stability, in the shape of a cylindrical scaffold structure (20 mm Ø), patterned layer by layer. This geometry was designed for a flow-through reactor for optimised photocatalytic active surface area, light penetration, adsorption sites, and mass transfer, while minimising pressure drop. The printed photocatalyst was tested in a recirculating batch reactor under dark and UV-light (254 nm) for PFOA removal (10 µM), with a goal of achieving low energy consumption and high quantum yield. Preliminary studies demonstrated the effectiveness of the adsorption process in dark conditions for the 3D printed In_2O_3 structures, exhibiting 5-27% of PFOA adsorption after 3 h for sintering at 1100 and 500 °C, respectively. The scaffold structure was unchanged, showing excellent mechanical and chemical stability, which facilitates catalyst reuse. Up to 70% of PFOA removal adsorption was observed after 9 h, and the subsequent photocatalytic degradation led to a high PFOA oxidation rate, generating shorter carbon chain by-products. Ongoing experiments (flow rate effect, photocatalyst height, and sintering conditions) aim to optimise the synergy of adsorption and photocatalysis to improve the role of the photogenerated holes of In_2O_3 and minimise the photogenerated pair recombination, targeting not only PFOA removal, but the complete decomposition of its intermediates. This effective strategy for the fabrication of self-supported photocatalysts opens the way to reusable and scaled-up materials to meet the urgent challenge of PFAS removal from the aquatic environment.

References

Dickman, R. A. et al. (2022) A Review of Recent Studies on Toxicity, Sequestration, and Degradation of Per- and Polyfluoroalkyl Substances (PFAS), Journal of Hazardous Materials, (436) 129120, pp. 1-14. doi: 10.1016/j.jhazmat.2022.129120.

Li, X. et al. (2012), Efficient Photocatalytic Decomposition of Perfluorooctanoic Acid by Indium Oxide and Its Mechanism, Environmental Science & Technology, (46), pp. 5528−5534. doi: 10.1021/es204279u

Friedmann, D. et al. (2021) Indium Oxides and Related Indium-based Photocatalysts for Water Treatment: Materials Studied, Photocatalytic Performance, and Special Highlights, Solar RRL, 5(1), pp. 1-24. doi: 10.1002/solr.202100086.

Application of a Novel PFAS Prioritization Technique (MD/C-M/C Approach) to Identify Microbial Transformation Products of The Aqueous Film-Forming Foam (AFFF) Component Capstone A

B. Bugsel[1*], J. Zweigle[1], M. Schneider[1], C. Zwiener[1]

[1]Universität Tübingen,Environmental Analytical Chemistry, Department of Geosciences, Schnarrenbergstr. 94-96, 72076 Tübingen, Germany

boris.bugsel@uni-tuebingen.de

Per- and polyfluorinated alkyl substances (PFAS) are a class of compounds consisting of several thousand known individual representatives. PFAS have a wide range of applications, from industrial processes to consumer products. Typical applications of PFAS involve lubricants, aqueous film-forming foams (AFFFs), electroplating baths and cleaning agents. Due to their high thermal and chemical stability, PFASs are particularly durable. The combination of a wide range of applications and the longevity of the substances has led to a worldwide detection of PFAS in various environmental compartments. Some PFAS can be considered degradable under environmental conditions (so-called precursors), but are often degraded to perfluorinated transformation products (TP) such as perfluorinated carboxylic acids (PFCA) or perfluorinated sulfonic acids (PFSA), which are considered highly persistent under environmental conditions. Since TPs are typically more mobile than their precursors, a characterization of the transformation potential of precursors under environmental conditions is crucial. Due to the wide range of applications of PFAS, analytical screening approaches using high-resolution mass spectrometry (HRMS) coupled to liquid or gas chromatography are of great interest. Here, we present a novel approach to reveal PFAS in non-target HRMS data that was first proposed by Kaufmann et al. (2022) and further systematically evaluated by Zweigle et al. (2023).

In the first part, the new approach to separate selected PFAS from sample matrix features works by plotting the mass defect (MD) normalized to the number of carbons (MD/C) vs. the mass normalized to the number of C (m/C) is presented. The basic idea behind the powerful m/C dimension is that PFAS tend to be heavier molecules compared to their hydrocarbon counterpart with the same number of carbon atoms. Since the number of carbon atoms can be estimated relatively easily by the M+1 isotope in HRMS scan data, this information allows a highly efficient prioritization of features when screening for PFAS.

In the second part, the MD/C-m/C approach is used and applied to bench-scale biotransformation batch experiments with the precursor AFFF component Capstone A. Two different types of PFAS-free standardized soils (one sand and one clay, 10 g each) were spiked with Capstone A, mixed with 100 mL water and placed on a horizontal shaker. Additionally, autoclaved controls were prepared to distinguish biotic from abiotic transformation processes. Samples were taken weekly over the course of three months. Target analysis by triple-quadrupole mass spectrometry showed the production of PFCAs in the live, but not the autoclaved samples. Transformation to PFCAs occurred more rapidly in the clay than in the sand. In addition, the samples were measured by HRMS. The application of the MD/C-m/C plot then revealed several further transformation products which could efficiently be separated from the sample matrix. Among the TPs, 6:2 fluorotelomer sulfonamide could be identified which was also confirmed by MS/MS measurements.

References

Kaufmann, A. et al. (2022) Simplifying nontargeted analysis of PFAS in complex food matrixes. J AOAC Int. 105(5):1280-1287. doi: 10.1093/jaoacint/qsac071

Zweigle, J. et al. (2023) Efficient PFAS prioritization in non-target HRMS data: systematic evaluation of the novel MD/Cm/C approach. Anal Bioanal Chem. doi:10.1007/s00216-023-04601-1.

Using the Northern Gannet (*Morus Bassanus*) as a Sentinel of Environmental Changes of Pfas Prior and After Restrictions

M. Glória Pereira[1], Lee A. Walker[1] and Silvia Lacorte [2],

[1]UK Centre for Ecology and Hydrology, Lancaster Environment Centre, Library Avenue, Bailrigg, Lancaster, LA1 4AP, UK.
[2]Department of Environmental Chemistry, Institute of Environmental Diagnostics and Water Studies, CSIC, Jordi Girona 18-26, 08034 Barcelona, Catalonia, Spain.

Perfluoroalkyl substances (PFAS) are a large group of man-made compounds, produced since the 1950's, with chemical and thermal stability. Because of their persistence, ubiquity in the environment, bioaccumulation potential and toxicity they are considered compounds of concern: PFOS (perfluorooctanesulfonic acid) and its related compounds are listed in the in the Stockholm Convention (2009).

We analysed long term trends of eight Perfluorinated Carboxylic Acids (PFCAs) and three perfluorinated sulfonates (PFSAs) in a marine sentinel species, the Northern gannet, in two UK colonies (Ailsa Craig, and Bass Rock) between 1977 and 2014.

We found no significant differences in the ∑PFAS between both colonies also that they were dominated by the ∑PFSAs which accounted for >80% of the total load measured in the eggs. By contrast, the ∑PFCAs was slightly, but significantly higher in Ailsa Craig (2-34.5 ng/g w.w.) than in Bass Rock (1.6- 26.4 ng/g w.w). This group of compounds was dominated by perfluorotridecanoate (PFTriDA), perfluoroundecanoate (PFUnA) and perfluorooctanoic acid (PFOA), with these compounds comprising 90% and 82% of the total in Ailsa Craig and Bass Rock, respectively. No significant difference in the ∑PFSAs (16.5 - 165 ng/g w.w.) were found between the colonies. PFOS dominated the PFSAs, accounting for 99% of the total concentration of sulfonates.

The ∑PFSAs and ∑PFCAs had very different temporal trends. The ∑PFSAs increased significantly in eggs of both colonies in the earlier part of the study. However, from the 1990s onwards there was a significant declined, possibly as a result of the phasing out of PFOS production in 2000. By contrast, in the 1970s and 1980s the concentrations of PFCAs were low and remained low, suggesting not much usage of these compounds. Then, their levels increased significantly in both colonies until the end of the study. The increase in ∑PFCAs was linked to the rise in large chain, namely odd, perfluorinated carboxylic acids. PFOA, the best known of the PFCAs, had a different temporal trend from the other predominant acids, showing a slow decline in the last 15 years of the study. In the first 20 years, PFSAs accounted for >90% ΣPFAS in eggs but from 1994 onwards, this proportion decreased to 62% - 73%, suggesting a temporal decline of PFSAs combined with increase of PFCAs.

HR-CS-GFMAS a Versatile Screening Tool for Pfas in Various Environmental Samples

F. Simon[1]*, L. Gehrenkemper[1], I. Rühl[1], B. Meermann[1]

[1]Federal Institute for Materials Research and Testing (BAM), Division 1.1. “Inorganic Trace Analysis”, Richard-Willstätter-Straße 11, 12489 Berlin, Germany

Michael-Fabian.Simon@bam.de

Per- and polyfluoroalkyl substances (PFASs) are a group of anthropogenic contaminates associated with persistent, bioaccumulative and toxic properties. Mostly, target-based approaches (e.g., LC-MS/MS) are utilized for the analysis of PFASs in the environment. Target approaches are limited to a few selected PFASs and therefore underestimate the total PFAS burden. Analytical approaches based on total fluorine for PFAS sum parameter analysis become increasingly important to indicate realistic PFAS pollution levels.

Recently high resolution-continuum source-graphite furnace molecular absorption spectrometry (HR-CS-GFMAS) turned out to be a sensitive and highly selective tool for fluorine determination. The method is based on the in situ formation of diatomic gallium-mono fluoride (GaF) in a graphite furnace at a temperature of 1550°C. The molecular absorption of GaF can be detected at its most sensitive wavelength at 211.248 nm providing limits of quantification in the low µg F/L range. HR-CS-GFMAS analysis can be combined with the extractable organically bound fluorine (EOF) approach whereas PFASs are extracted from liquid or solid samples using organic solvents and/or solid phase extraction (SPE).

In this presentation the applicability of HR-CS-GFMAS for organic fluorine analysis in various environmental sample including (1) water samples, (2) soil samples and (3) plant samples is demonstrated.

(1) We investigated EOF concentrations in water bodies in Berlin, Germany and used additional PFAS target analysis for a PFAS mass balance approach. EOF concentrations were in the expected range for an urban river system. However, downstream of an effluent discharge, the EOF increased by one order of magnitude from 40 to 574 ng F/L. Target analysis determined mostly short-chained perfluorinated carboxylic acids and sulfonic acids, which however only made up less than 10% of the EOF. This study highlights that EOF screening using HR-CS-GFMAS is useful and advantageous compared to target analysis to identify pollution sites in urban water systems (Nxumalo T. et al. 2023).

(2) For soil samples, we optimized a fast and simple PFAS extraction method for EOF determination. The developed extraction method consists of a liquid-solid extraction without any additional SPE for fluoride removal. We investigated different soil samples using the optimized method with and without an additional SPE clean-up step and revealed a drastic underestimation of EOF mass fractions using SPE. The optimized method is a valuable screening tool for fast PFAS monitoring (Simon F. et al. 2022).

(3) For plant samples, we conducted a study on the uptake and fate of PFASs in bean plants. For PFAS mass balancing HR-CS-GFMAS analysis was combined with LC-MS/MS analysis. PFASs were spiked as mixtures of known and unknown composition. Short-chained PFASs were determined with high mass fractions mainly in the fruits of the investigated plants while long-chained PFASs were mainly determined in roots. Overall, both methods indicate comparable results with target analysis being more reliable for known PFAS contamination and EOF/HR-CS-GFMAS analysis being more valuable to identify PFAS exposure of unknown composition (Gehrenkemper L. 2023).

References

Nxumalo, T. et al. (2023) EOF and target PFAS analysis in surface waters affected by sewage treatment effluents in Berlin, Germany, Anal Bioanal Chem, 415, p. 1195–1204. doi: https://doi.org/10.1007/s00216-022-04500-x

Simon, F. et al. (2022) A fast and simple PFAS extraction method utilizing HR–CS–GFMAS for soil samples, Chemosphere, 295, 133922. doi: https://doi.org/10.1016/j.chemosphere.2022.133922

Gehrenkemper, L. (2023) Investigating the uptake and fate of per- and polyfluoroalkylated substances (PFAS) in bean plants (Phaseolus vulgaris) – Comparison between target MS and sum parameter analysis via HR-CS-GFMAS, submitted manuscript.

Electrosorption of Perfluoroalkyl Acids - A Strategy for More Sustainable Water Treatment

A. Georgi[1*], N. Saeidi[1], S. Sühnholz[1], R. Köhler[1] and K. Mackenzie[1]

[1]Helmholtz Centre for Environmental Research – UFZ, Department of Environmental Engineering, Permoserstr. 15, 04318 Leipzig, Germany

anett.georgi@ufz.de

Short-chain perfluoroalkyl acids and other ionic organic compounds challenge state-of-the art adsorption technologies. Due to their highly hydrophilic nature which results in insufficient removal and/or shortened operation times, e.g. activated carbon (AC) fixed-bed adsorbers have to replaced frequently. At the same time, phase out of fossil fuels and replacement by decentralized and local renewable energy creates strong advantages for electricity-driven approaches in sorbent regeneration. As current high-temperature regeneration of AC (the most widely applied technical adsorbent) cannot be easily electrified, novel materials and alternative regeneration approaches are expected to become increasingly important in the years to come.

Electrosorption can be considered an advanced adsorption process for certain types of contaminants as it allows controlling adsorption and desorption by applying mild electric potential to high-surface area, conductive carbon-based electrodes. In this way, AC performance for ionic organic compounds can be enhanced by applying potential of opposite charge to the adsorbent. Even more importantly, the adsorbent can be regenerated on-site simply by switching potential and thus enriching contaminants in a low volume concentrate.

This study presents results on electrosorption of perfluoroalkyl acids (PFAAs) using conductive activated carbon felts - from proof of principle in miniaturized flow cells towards upscaling of electrosorption modules to 8 m² active electrode area. This upscaled electrosorption module is applied within a German collaborative project (FABEKO, 2023) for removing PFAAs from soil washing water. Single-point adsorption coefficients Kd of perfluorooctanoic acid (PFOA) at environmentally relevant concentrations vary between 650,000 L/kg at positive potentials and 14,800 L/kg at negative potentials (≤ ±1 V vs. Ag/AgCl), i.e. by a factor of 44. 2) The differences are even higher (factor of 100) for perfluorobutanoic acid (PFBA). A first estimation of the achievable concentration factor for PFOA in a fixed-bed electrosorption unit with potential swings results in values ≥ 40, which is competitive with other pre-concentration technologies such as membrane filtration. Flow-cell (250 mL volume) experiments with PFBA proved that electrosorption/desorption cycles can be operated with complete PFBA desorption and stable performance in ad-/desorption over multiple cycles. In addition, first results of the up-scaled electrosorption module (40 L volume) will be presented. Our results illustrate the great potential of electrosorption for I) on-site adsorbent regeneration and II) as pre-concentration step which is mandatory for cost- and energy-efficient PFAA destruction technologies such as electrooxidation.

References

FABEKO (2023): Groundwater protection through areal treatment of PFAS-contaminated soils by on-site soil elution and water treatment by electrostimulated activated carbon, German collaborative project funded by BMBF, https://www.fabeko.de/

Saeidi, et al. (2021) 'Controlling adsorption of perfluoroalkyl acids on activated carbon felt by means of electrical potentials' Chem. Eng. J., 416, 129070, https://doi.org/10.1016/j.cej.2021.129070.

Coupling Low Pressure RO Membrane with Anodic Electro-Oxidation for the Treatment of PFAS Contaminated Water

L. Saleh[1]*, J.-C. Coutanceau[1], P. Westerhoff[2], H. Budzinski[3], and J.-P. Croué[1]

[1]Université de Poitiers, Institut de Chimie des Milieux et des Matériaux, France.
[2]Arizona State University, School of Sustainable Engineering and the Built Environment, Tempe, USA.
[3]Université de Bordeaux, Laboratoire de Physico- & Toxico-Chimie de l'environnement, France.

lama.saleh@univ-poitiers.fr

Per- and polyfluoroalkyl substances (PFAS) are commonly found in everyday products such as food packaging and fire-fighting foams. Due to their high chemical stability, these substances can accumulate in ecosystems. The presence of PFAS in natural water systems is therefore a major environmental issue, due to their potentially harmful impact on human health. Anodic electro-oxidation (AEO) is a promising technique for water contaminated with PFAS, as it involves radical reactions at the electrode surface. Previous studies have demonstrated that boron-doped diamond (BDD) electrodes can effectively increase the efficiency of AEO, particularly for water with high PFAS content, due to the importance of the diffusion phenomenon in electrochemical oxidation (Zhuo Q. et al. 2012). The decontamination of polluted water, particularly by PFAS, can be achieved by implementing treatment processes that include a pre-concentration phase followed by a degradation step. Low-pressure reverse osmosis (RO) membranes are gaining interest because they have a lower energy cost than traditional RO membranes while offering higher efficiency than nanofiltration (NF) membranes (Diawara C.K. et al. 2011). Therefore it is essential to verify their effectiveness, especially for low molecular weight PFAS. Additionally, the role of organic fouling and biofouling, on the rejection efficacy of RO membranes is still not fully understood and requires further research.
Under our experimental conditions, filtration conducted on membrane coupons using synthetic solutions and real waters confirmed the high rejection efficiency of virgin RO membranes for both long and short-chain PFAS, with approximately 98% retention (Liu C. et al. 2022). Similar results were obtained with fouled membrane coupons (same membrane type) recovered from modules harvested in a RO treatment train installed in drinking water production plants. The presence of biofilm (membrane autopsy was performed) does not seem to have a significant impact on the PFAS retention efficiency of RO membrane.
The experiments conducted using a BDD electro-oxidation cell in recirculation mode using synthetic PFAS solutions (9 perfluoroalkyl carboxylic and sulfonic acids from C4 to C9) demonstrated that the degradation kinetics of these molecules increase with the length of the carbon chain. The degradation of PFAS leads to the formation of by-products resulting from the successive loss of -CF2. Furthermore, hydroxide salts are as effective as sulfate and carbonate salts in degrading PFOA (C8), and the type of cation in the electrolyte has no impact on the degradation and defluorination of PFOA. The presence of dissolved organic matter, such as humic substances isolated from surface waters, in solution with concentrations between 5 and 20 mg/L has little impact on the degradation kinetics of PFHxA (C6, 50 µg/L), regardless of the aromatic character of the DOM (SUVA = 1 to 5). Further research is being conducted on reverse osmosis concentrates generated from the filtration of contaminated ground waters.

References

Zhuo, Q. et al. (2012) 'Degradation of perfluorinated compounds on a boron-doped diamond electrode', Electrochimica Acta, 77, pp. 17–22. Available at: https://doi.org/10.1016/j.electacta.2012.04.145.

Diawara, C.K. et al. (2011) 'Performance of Nanofiltration (NF) and Low-Pressure Reverse Osmosis (LPRO) Membranes in the Removal of Fluorine and Salinity from Brackish Drinking Water', Journal of Water Resource and Protection, 03(12), pp. 912–917. Available at: https://doi.org/10.4236/jwarp.2011.312101.

Liu, C. et al. (2022) 'Evaluating the efficiency of nanofiltration and reverse osmosis membrane processes for the removal of per- and polyfluoroalkyl substances from water: A critical review', Separation and Purification Technology, 302, p. 122161.

Performance of Colloidal Activated Carbon as In-Situ Sorbent for PFAS Contaminated Sites

A. Schierz[1]*, M. Balda[1], J. Beihsner[1], S. Sühnholz[1], K. Mackenzie[1] and A. Georgi[1]

[1]Helmholtz-Centre for Environmental Research, Department of Environmental Engineering, Permoser Str. 15, 04318 Leipzig, Germany

ariette.schierz@ufz.de

Due to their extreme persistence, often combined with high aqueous mobility, per- and polyfluoroalkyl substances (PFAS) are challenging to remediate and remove from the environment. The in-situ application of colloidal activated carbon (CAC) aims at an adsorptive barrier effect against the further spread of PFAS within the aquifer. This requires high-performance activated carbon materials that ensure high retardation of PFAS at low aquifer sediment loading (0.1-1 mass%) and thus long lifetimes even for shorter-chain PFAS in the order of decades.

Here, we will discuss the development and testing of injectable CAC for in-situ sorption barriers. Our studies include a commercially available CAC (Intraplex®) and very uniform activated carbon spheres (aCS) – an AC at the research stage. Activated carbon spheres are produced by bottom-up synthesis based on sucrose, a locally available, cheap renewable raw feedstock, using hydrothermal carbonization and subsequent thermal activation with low water vapor dosage (Balda et al. 2023). This route allowed the production of high-purity spherical carbon particles with a mean diameter of about 1 µm and a microporous structure. In comparison, commercial CAC products are produced by top-down synthesis by wet-grinding of granular/powdered AC produced from raw feedstock such as hard coal, which leaves a considerable carbon footprint.

In the first part, we present the results of the retardation of various PFAS by immobilized commercial CAC from column tests and a field trial at a former airport site (Georgi et al. 2020). These results were used to predict the long-term performance and lifetime of in-situ barriers in contaminated aquifers. Assessments show that in-situ sorption barriers based on CAC are particularly suitable for contaminants with long-chain PFAS (> 6 C atoms) and in the range of low concentrations (< 10 µg/l). The barriers provide long-term retention from many decades to several hundred years. This indicate that PFAS plumes, in particular plumes with high mobility or hydrogeological displacement dynamics, can be reliably contained. In critical cases, this can buy valuable time for the actors involved.

In the second part, we evaluate the potential of aCS for the application as an in-situ sorbent. Therefore, batch experiments to characterize the sorption performance for PFAS and the suspension stability as well as columns studies to evaluate the mobility were performed with aCS compared to the commercial CAC.

References

Balda, M. et al. (2023): Bottom-up synthesis of de-functionalized and dispersible activated carbon spheres as colloidal adsorbent, Int. J. Mol. Sci., 24 (4), art. 3831.

Georgi, A. et al (2020): Kolloidale Aktivkohle für die In-situ Sanierung von PFAS-kontaminierten Grundwasserleitern, Altlasten Spektrum, 29, 232-237.

Gulls (Larus Michahellis) as Biomonitors of PFASs Pollution: What we Find and What are the Environmental Implications

B. Oró-Nolla[1*], M. Dulsat-Masvidal[1], A. Bertolero[2], A. López-Antía[1], S. Lacorte[1]

[1]IDAEA-CSIC, Department of Environmental Chemistry, Jordi Girona 18-26, 08034, Barcelona, Spain
[2] Associació Picampall de les Terres de l'Ebre, Amposta, Spain

bonqam@idaea.csic.es

Perfluoroalkyl substances (PFASs) comprise a chemical family of more than 4000 compounds that are known to bioaccumulate in wildlife and trigger toxic effects (Sebastiano et al., 2021). Marine birds e.g, Larus michahellis are excellent bioindicators of environmental pollution and provide information on the presence and impact of contaminants in areas of ecological importance. This study explores the use of L. michahellis eggs and blood as non-invasive matrices to determine in a quantitative way 25 PFASs and identify other potential PFASs present in these samples. Blood samples (n=30) and eggs (n=25) were collected in 2022 in the Ebro Delta Natural Park, an area affected by PFASs. Samples were solid-liquid extracted and analyzed by ultra-high-performance liquid chromatography coupled to a Bruker Impact II Q-TOF mass spectrometer with negative electrospray ionization. Data-independent acquisition (DIA) was obtained through a full-scan acquisition to obtain MS1 at 6 eV and MS2 at 30 eV to confirm the presence of PFASs and allow for suspect screening. Data were processed in a target-untargeted approach where: i) PFASs were determined using internal standard quantification using a 9-mass labelled PFASs mixture solution; ii) other PFAS were identified using the accurate mass in MS1 with mass tolerance < 5 ppm and ensuring the presence of at least one qualifier or diagnostic fragment ion in the MS2 spectra and using the high-resolution Per- and perfluoroalkyl substances library database (NORMAN, 2023). By this new optimized method, PFBA, PFHxA, PFNA, PFOS, PFDA, PFUdA, PFDoA, PFTrDA and PFTeDA were identified in eggs and blood from 0.50 to 110 ng/g wet weight, evidencing that birds from the Ebro Delta are still exposed to these contaminants. 2-(Perfluorohexyl)ethanol (6:2FTOH, CAS number 647-42-7) and perfluoro-p-ethylcyclohexylsulfonic acid (PFECHS, CAS number 646-83-3) were detected in L. michahellis eggs and blood. Ten more compounds from the PFASs family with different polar groups and long fluorinated chains were tentatively identified by their molecular ions at exact mass. Our study reveals that PFASs are transferred from gulls to the eggs and these findings could be extrapolated to other bird species inhabiting in the area. Biomonitoring with gull eggs or blood enlarges the number of PFAS detected, including their precursors, and provides essential information to determine exposure to these contaminants and potential risks in birds.

Acknowledgments

This work was supported by the Spanish Ministry of Science and Innovation Project TED2021-131552B-C21, Excelencia Severo Ochoa Project CEX2018-000794-S and project PID2019-105732GB-C21.

References

Sebastiano, M., et al. (2021) 'High levels of fluoroalkyl substances and potential disruption of thyroid hormones in three gull species from South Western France' Sci. Total Environ. 765, 144611., https://doi.org/10.1016/j.scitotenv.2020.144611

NORMAN, Per- and perfluoroalkyl substances - NORMAN SusDat [21 March 2023], available from www.norman-network.com/nds/susdat/

Levels and Trends of Perfluoroalkyl Substances Regulated Under the Stockholm Convention in Water from the Duero Basin in Spain

P. Colomer-Vidal[1*], J.L. Roscales[1], J. Muñoz-Arnanz[1], M. Ros[1], A. Vicente[1] and B. Jiménez[1]

[1]Institute of Organic Chemistry (IQOG-CSICI), Calle Juan de la Cierva 3, 28006, Madrid, Spain

pere.colomer@iqog.csic.es

Perfluoroalkyl substances (PFAS) are a large family of synthetic chemicals with excellent thermal and chemical stability. These chemicals have been used as polymers, surfactants, stain repellents, and flame retardants in several products such as carpets, leather paper, textiles, fire-fighting foams (FFF), etc. PFAS are ubiquitous in the environment due to discharges from various sources such as manufacturing and processing industries, military areas, use of FFF, wastewater discharges and landfills. The Stockholm Convention (SC) on Persistent Organic Pollutants (POPs) included perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorohexanesulfonic acid (PFHxS), their salts and related products on the restriction and elimination list in 2009, 2019 and 2022, respectively.

The present study aimed to assess the presence of PFOS, PFOA and PFHxS in riverine water from the Duero basin in Spain to evaluate the spatiotemporal and seasonal variation, sources of pollution and the effectiveness of the implementation of SC regulations.

Four sampling locations were selected in the Duero basin which run across the mid-north Iberian Peninsula with ca. 20% located in Portugal and 80% in Spain. Samples were seasonally collected (mid-February for winter, mid-May for spring, mid-August for summer, and mid-November for fall) from 2013 to 2022. The first sampling point (W1) is located in an area with low human activity, W2 and W3 are located near industrial and populated areas, and W4 is located in a background reservoir in the lower part of the basin next to Portugal.

Obtained data showed median PFOS, PFOA and PFHxS concentrations were 0.596, 0.353 and 0.193 ng/L respectively, being PFOS the most abundant (up to 90%). Conversely, PFOA was dominant in W1. Detected values ranged from below the limits of quantification (LOQ) to 24.2, 2.04 and 0.725 ng/L, respectively. The highest levels of ∑PFAS and most of the individual compounds were detected in the following order W2>W3>W4>W1, and statistically significant differences were found and between locations in most of the chemicals (Kruskal-Wallis, $p<0.05$; Dunn Pairwise test, $p<0.05$). PFOS differed statistically between all locations; PFOA in W1 vs all remaining locations, and W4 vs W2 and W3; and PFHxS only for W1 vs all locations. Levels detected in W2 and W3 (located after the cities of Burgos and Valladolid, respectively) are attributed to numerous industries related to the manufacture of articles of pulp, paper and paperboard; waste management sites, and coating of metals.

The seasonality did not seem to influence the PFAS levels from the Duero basin, while from a temporal perspective, the Duero basin trend exhibited a negative statistically significant trend for ∑PFAS (Spearman, $p<0.05$). Moreover, W2, W3 and W4, separately, evidenced a negative statistically significant decrease for ∑PFAS and PFOS (Spearman, $p<0.05$), which may be reelated to its ban in 2009. Our results highlight the role of research and monitoring in the evaluation of public policies and the protecition of health. Further efforts are nedeed to track the tendencies of PFOA and PFHxS as they have been recently regulations.

Unveiling the Molecular Basis of Long and Short Chain Pfass-Binding to Serum Albumin and their Potential Applications

G. Moro[1], F. Vascon[2], S. De Felice[2], S. Linciano[1], C. Foresta[3], A. Di Nisio[3], L. Cendron[2], L. De Toni[3], A. Angelini[1,4]*

[1]Ca' Foscary University of Venice, Department of Molecular Sciences and Nanosystems, Via Torino 155, 30172, Venice Mestre, Italy.
[2]University of Padua, Department of Biology, Viale G. Colombo 3, 35131 Padua, Italy.
[3]University of Padua, Department of Medicine, Via Giustiniani 2, 35128 Padua, Italy.
[4]European Centre for Living Technology (ECLT), Ca' Bottacin, Dorsoduro 3911, Calle Crosera, 30123 Venice, Italy.

alessandro.angelini@unive.it

Poly- and per-fluorinated alkyl substances (PFAS) are man-made organic compounds widely found in consumer and industrial products as well as in food items. Their high resistance to degradation, in combination with their ubiquity and global distribution, gives rise to an increasing public concern over their potential risks to human health and impact on the environment. Currently, there are no proved medical interventions to facilitate the removal of persistent PFASs from the body. In recent years, a number of toxicokinetic studies in humans and animals reported that PFAS show low elimination rates and high accumulation levels in the blood and in vital organs such as liver, kidney and lung. Indeed, the average half-life values for serum elimination of some PFAS in environmentally exposed human populations are estimated to be in the order of years. The primary binding protein for PFASs in the blood is serum albumin, the most abundant protein in plasma. In recent years the binding of PFAS to serum albumin has been characterized using multiple analytical techniques and while considerable insights have been accumulated, our understanding of these interactions is far from complete.

To fill this gap, we applied X-ray crystallography and isothermal titration calorimetry (ITC) to investigate the nature and locations of the albumin-binding sites of three representive short and long, branmched and linear, PFAS molecules such as HPFO-DA, C6O4 and PFOA (Maso L. et al. 2021, Moro G. et al. 2022). Competition experiments with known albumin-binding drugs allowed locating binding sites with different affinities (Maso L. et al. 2021, Moro G. et al. 2022). These findings were further applied in the desing of albumin-based sensors for monitoring PFOA levels in water (Moro, G. et al. 2020).

Although many challenges still remain, the elucidation of the interaction between PFAS and serum albumin might provide a better assessment of the absorption and elimination mechanisms of these compounds in vivo. Moreover, in light of the urgent need to implement better strategies to detect and reduce exposure to PFAS, our studies are also expected to have implications for the development of novel albumin-based bioreceptors for multiple applications.

References

Maso, L. et al. (2021), Unveiling the binding mode of perfluorooctanoic acid to human serum albumin, Prot. Scien., 30, p. 830, doi: 10.1002/pro.4036.

Moro, G. et al. (2022), Investigation of the Interaction between Human Serum Albumin and Branched Short-Chain Perfluoroalkyl Compounds, Chem. Res. in Toxicol., 35, p. 2049, doi: 10.1021/acs.chemrestox.2c00211.

Moro, G. et al. (2020), Covalent immobilization of delipidated human serum albumin on poly(pyrrole-2-carboxylic) acid film for the impedimetric detection of perfluorooctanoic acid, Bioelctrochem.,134,p. 107540,doi:10.1016/j.bioelechem.2020.107540.

Perlfuoroalky Substances: from the Epidemiological Evidence to The Novel Models of Toxicodynamics

G. Moro[1,3], F. Vascon[2], S. Linciano[1], S. De Felice[2], C. Foresta[3], A. Di Nisio[3], L. Cendron[2], A. Angelini[1,4], N. Ferri[3], L. De Toni[3]*

[1]Ca' Foscari University of Venice, Department of Molecular Sciences and Nanosystems, Via Torino 155, 30172 Venice, Italy
[2]University of Padua, Department of Biology, Viale G. Colombo 3, 35131 Padua, Italy
[3]University of Padua, Department of Medicine, Unit of Andrology and Reproductive Medicine, Via Giustiniani 2, 35128 Padua, Italy
[4]European Centre for Living Technology (ECLT), Ca' Bottacin, Dorsoduro 3911, Calle Crosera, 30123 Venice, Italy

luca.detoni@unipd.it

In the last decades, great attention has been paid to disclose the possible effects of various chemicals that interfere with hormonal function, collectively known as endocrine-disrupting chemicals (EDCs), on human health. Among EDCs, poly- and per-fluorinated alkyl substances (PFAS) are raising health concerns worldwide (Di Nisio, G. et al. 2022). PFAS are a group of more than 4,700 man-made chemi-cals, widely used for their unique chemical and physical stability, having the legacy compounds per-fluoro-octanoic acid (PFOA) and perfluoro-octane sulfonic acid (PFOS) among the most widespread in the environment and in human specimens. The exposure to PFAS raises concerns for their impact on human health since it has been associated, among the others, with metabolic derangements and impairment of the endocrine and nervous system. One of major characteristics of PFAS is their persistence in the environment and in living being, so much so that the estimated half-life for these compounds in humans is 3-5 years (Giesy J.P. et al. 2002).
Our group has been studying PFAS toxicity since the late 2010s. During this pluriannual research activity, due to the presence in the Veneto region of Italy of a wide area with high environmental exposure (HEE) to man-made PFAS, the complexity of the clinical manifestations associated with their exposure has been investigated. In addition to an almost doubled risk of death from diabetes-related causes, we reported that people residing in HEE areas showed an increased risk of couple infertility for both an impairment of semen parameters and increased miscarriage rate (Di Nisio A. et al. 2019, Di Nisio A. et al. 2020). Through an extensive use of in vitro cell models, we showed that the possible mechanisms of cell toxicity related to PFAS expsosure not only relies on a "classical" interference with the signaling of steroid hormones, observed for other calsses of pollutants, but is also related with different modalities in which a key element is represented with the surfactant nature of PFAS and their disruption with the cell membrane. According to this models, PFAS alter membranes biophysical properties, such as fluidity, permeability to ion and modification of the molecular environment of surface receptors. Under this novel point of view, additional risk for coagulation derangements, thyroid disfunction, hyperlipidemia and altered neuronal development have been described in association with the exposure to PFAS (Šabović I. et al. 2020, Minuz P. et al. 2021, De Toni L. et al. 2022, Di Nisio A. et al. 2022). In this review communication, the main highlights of this field of scientific investigation will be described.

References

Di Nisio, G. et al. (2022), Impairment of human dopaminergic neurons at different developmental stages by perfluoro-octanoic acid (PFOA) and differential human brain areas accumulation of perfluoroalkyl chemicals, Env. Int. 158. https://doi.org/10.1016/j.envint.2021.106982.

Di Nisio, A. et al. (2020) Chemosphere, Perfluorooctanoic acid alters progesterone activity in human endometrial cells and induces reproductive alterations in young women, 242, p125208.
doi: 10.1016/j.chemosphere.2019.125208.

Šabović, I. et al. (2020) J Endocrinol Invest., Perfluoro-octanoic acid impairs sperm motility through the alteration of plasma membrane, 43, p641.
doi: 10.1007/s40618-019-01152-0.

Transfer of PFAS From Soil into Plants and its Relevance for PFAS Regulation in Germany

L. Gehrenkemper[1]*, A. Schmidt[1], L. Lesmeister[2], R. Boeddinghaus[3], J. Breuer[3], M. Scheurer[2], A. Biegel-Engler[1]

[1]German Environment Agency (UBA), Department II 2.6, Measures of Soil Protection Wörlitzer Platz 1, 06844 Dessau-Roßlau, Germany
[2]German Water Centre (TZW), Karlsruher Str. 84, 76139 Karlsruhe, Germany
[3]Center for Agricultural Technology Augustenberg (LTZ), Section Agroecology, Neßlerstr. 25 76227 Karlsruhe, Germany.

lennart.gehrenkemper@uba.de

PFAS are ubiquitously found in the environment due to their persistence and their wide spread uses. Humans take up PFAS mainly via food or contaminated drinking water. PFAS may enter into food either via contaminated soil, air or water or during food processing and food packaging. This presentation focusses on the transfer of PFAS from soil into plants. In a recently published review the available data have been summarized (Lesmeister *et al.*, 2021). This review discussed critically various factors influencing substance specific transfer factors. Up to now two problems arise while looking for PFAS transfer factors: 1st most studies focus on PFAAs - historically mainly on PFOA and PFOS - resulting in a huge knowledge gap for PFAA precursors and short-chain PFAS. 2nd existing studies are based on a brought variety of set-up designs, resulting in questionable comparability.
Therefore, further experiments were performed within the Fluortransfer project (Scheurer *et al.*, 2022) to investigate the transfer of certain PFAS into three different plant species grown on three different soil types. The results show that trends known from literature regarding chain length and plant compartment/plant species dependency were confirmed, i,e, short-chain PFAA showed higher plant uptake then long-chain PFAA. In addition, PFAS-uptake depended on plant species. A correlation of PFAS uptake and soil type could be identified, i. e. uptake was lower the higher the clay content of soil. During the literature research, different practices regarding the time point of soil sampling to determine soil PFAS concentration were observed. By multiple soil sampling in the Fluortransfer experiments, a relevant influence of sampling time on the resulting transfer factors was determined. Also, a time dependency of PFCA concentration in plants as products of a spiked precursor was observed. Taking all these observations together, the establishment of transfer factors for PFAS becomes very challenging. Reviewed data combined with own results have further been analyzed in order to compare PFAS data pairs from plants and corresponding soils of various set-ups as in-lab experiments, field experiment or lysimeters. Additionally, different exposure conditions as spiking or samples from contaminating events were studied to discuss the comparability of different transfer-study approaches. The results shall be used to derive threshold values for PFAS in soils used for food and feed production.Additionally, we suggest a criteria catalogue for future transfer studies to improve comparability and relevance of such for regulation of PFAS and other emerging pollutants. This criteria catalogue can have an important impact to close identified knowledge gaps for PFAS transfer and improve the comparability of future soil-plant-transfer studies in general.

References

Lesmeister, L. *et al.* (2021) Extending the knowledge about PFAS bioaccumulation factors for agricultural plants – A review, Science of the Total Environment, 766, p. 142640. doi: https://doi.org/10.1016/j.scitotenv.2020.142640.

Scheurer, M., *et al.* (2022) final report Fluortransfer, Umweltbundesamt, Texte | 77/2022, https://www.umweltbundesamt.de/publikationen/erarbeitung-von-fachlichen-grundlagen-fuer-die.

Adaptation of Large Panels of Per- and Polyfluoronated Alkyl Substances (PFAS) for Routine Analysis in Drinking and Environmental Waters by Direct Injection Using UHPLC-MS/MS

J. Davies[1]*, JD. Alwis[1] and C. Pinto[1]

[1]Water corporations

jenny_davies@waters.com

Per- and Polyfluoroalkyl Substances (PFAS), are extremely persistent in the environment. Their production and use have resulted in severe contamination of soil, water and food. To protect public health, advisory and regulatory limits continue to be created and updated. Consequently, routine PFAS analysis has become challenging as not only low detection limits are required, but extensive compound coverage is a prerequisite nowadays.
The purpose of this work was to demonstrate a direct injection UHPLC-MS/MS method for the ultra-low-level determination of multiple PFAS compounds in drinking and environmental waters. The method performance study was completed on an ACQUITYTM Premier System with a XevoTM TQ Absolute Mass Spectrometer and UniSprayTM Ion Source. Samples were prepared by dilution with an acidified organic solution.

A method validation study was carried out on 2 common drinking water and 2 surface water matrices. The method performance was assessed using 3 spike levels at 1, 5, and 10 ng/L for all analytes, with 6 replicates at each level. Average method performance for trueness, repeatability, linearity, and sensitivity was assessed.
.
Improvements in both the analytical and isolator column technologies demonstrated in this work, as well as enhancements in negative ion sensitivity from the Xevo TQ Absolute Mass Spectrometer are helping to support ongoing efforts in PFAS analysis. This allows for easier, more robust, and accurate options as PFAS analysis continues into the future.

HRMS Workflows Reveal Target and Suspect PFAS in Landfill Leachates: Identification and Evaluation of their Potential Risk to Environment

L.-A. Koronaiou[1,2], S. Petromelidou[1,2]*, E. Evgenidou[1,2], D. A. Lambropoulou[1,2]

[1]Aristotle University of Thessaloniki, Laboratory of Environmental Pollution Control, Department of Chemistry, Thessaloniki, Greece
[2]Center for Interdisciplinary Research and Innovation (CIRI-AUTH), Balkan Center, Thessaloniki, Greece

spetrome@chem.auth.gr

Sanitary landfill leachates are a by-product of water percolation through the collected materials that are directed to landfills as well as the product of biotic and abiotic processes occurring naturally during solid waste decomposition. Landfill leachates are a complex matrix characterized by high organic loading, which includes a wide variety of emerging organic contaminants among them being PFAS, varying from a few ng/L to several μg/L, thus leachates may present as a route for these compounds into the environment. Such pollutants are present in a wide variety of everyday products and include numerous chemical compounds such as perfluoroalkyl and polyfluoroalkyl substances (Nika et al., 2022). PFAS are a concerning diverse group of man-made compounds with numerous applications varying from consumer products (nonstick cookware, food packaging) to industrial uses (fire-fighting foams, carpeting, apparels, and metal plating). The main goal of the present study is to investigate the occurrence of PFAS in raw landfill leachates across a 7-month period and predict the possible environmental risk they pose to the aquatic environment. To this end, raw leachate samples were collected from a Greek sanitary landfill located in Western Macedonia. A mixed-mode solid phase extraction was employed in sample preparation (Koronaiou et al., 2022) in order to assess maximum number of pollutants. Analysis was performed in a high-resolution mass spectrometer, namely a Q Exactive Focus Orbitrap equipped with a heated ESI source operated in negative ionization mode, providing fragment-rich data and high mass accuracy measurements, thus enabling not only target but also suspect screening. Extensive in-house databases involving, characteristic fragmentation pattern, chromatographic behavior, etc. were built for PFAS and suspect screening workflows were employed in real samples for the tentative identification of these newly emerging contaminants. The application of the method in leachates a revealed 100% detection frequency of L-PFBS, PFOA and PFHxA with maximum concentration of latter reaching 5.3 μg/L. Finally, to investigate the ecotoxicity of the compounds, for which an analytical standard was available, acute and chronic toxicity data were estimated using the Ecological Structure Activity Relationships (ECOSAR) Class Program for three trophic levels of organisms (namely fish, daphnids and algae). The current study suggests that landfill leachates are an important source of PFAS in the aquatic environment and further investigation is required in order to provide a basis for setting up risk management measures.

Funding: This research was funded by the Greek Ministry of Development and Investments (General Secretariat for Research and Technology) through the research project “Research-Create-Innovate” (Grant no: T2EΔK-00137).

References

Nika, M.C. et al. (2020) ‘Wide-scope target analysis of emerging contaminants in landfill leachates and risk assessment using Risk Quotient methodology’, Journal of Hazardous Materials, 394(March), p. 122493. doi:10.1016/j.jhazmat.2020.122493.

Koronaiou, L.A. et al. (2022) ‘High-resolution mass spectrometry-based strategies for the target analysis and suspect screening of per- and polyfluoroalkyl substances in aqueous matrices’, Microchemical Journal, 179(February), p. 107457. doi:10.1016/j.microc.2022.107457.

What's in my Wastewater? Tracing 'Forever Chemicals': the Fate of PFAS throughout the Urban WWTP Process

L.Dockx[1]*, B. Raes[1], M. Stevens[1] and R. Delgado[1]

[1]Aquafin NV, Dijkstraat 8, 2630 Aartselaar, Belgium

lennert.dockx@aquafin.be

PFAS (Per- and PolyFluoroAlkyl Substances) are a large group (+/- 5000) of synthesized, highly fluorinated chemicals posing a serious environmental concern. PFAS are chemical and thermal resistant, resulting in an effective diffusion in the environment (Ebrahimi et al., 2021). Despite The Stockholm Convention (2009) PFAS are still used in many industrial applications and consumer products, e.g., coatings, fire-fighting foams, textile, food packaging (Winchell et al., 2021). To obtain a better understanding of the overall distribution of these contaminants, research towards PFAS in (side) streams of different urban domestic wastewater treatment plants (WWTPs) in Flanders (BE) was conducted. By applying commercially available target analysis, including up to 46 different PFAS, almost no PFAS were found in the WWTP's influent with total concentration ranges between 0 and 676 ng.L^{-1}. However, much higher concentrations of up to 1516 ng.L^{-1} where found in the effluent, especially short-chain PFAS. In addition, results indicated an excessive sorption behavior of long-chain PFAS (10 – 265 µg.kgdm^{-1}) in sewage sludge. This outcome assumes the extensive role of unknown precursors in the overall PFAS load of domestic WW. As precursors are not stable, they are converted in stable PFAS throughout the WW treatment process. Furthermore these results suggest that by further exploring non-target PFAS analysis, urban WW could be used as indicator regarding upcoming regulatory perspectives concerning the restricted production and application of PFAS.

Current commercially available target analysis are, due to the presence of precursors, not applicable to set up a PFAS mass balance at an urban WWTP.

References

Ebrahimi, F. et al. (2021) 'Linking PFAS partitioning behavior in sewage solids to the solid characteristics, solution chemistry, and treatment processes', Chemosphere, p. 271. doi: 10.1016/j.chemosphere.2020.129530.

Winchell, LJ. et al. (2021) 'Per- and polyfluoroalkyl substances thermal destruction at water resource recovery facilities: A state of the science review', Water Environ Res, p. 826-843. doi: 10.1002/wer.1483.

PFAS, from here to Eternity - or maybe not

K. Kasalica[1], B. Jimenez[2], A. Yamamoto[3], H. Inui[4], M. Lješević[1], N. Radić[1], G. Gojgić-Cvijović[1], L. Slavković Beškoski[5], J. Radulović[5], T. Nakano[6], V.P. Beškoski[7]*

[1]University of Belgrade - Institute of Chemistry, Technology and Metallurgy, Njegoseva 12, Belgrade, Serbia
[2]Institute of Organic Chemistry (IQOG-CSIC), Juan de la Cierva 3, 28006, Madrid, Spain
[3]Tottori University of Environmental Studies, Tottori, Japan
[4]Kobe University, Biosignal Research Center - Japan
[5]Anahem laboratory ltd, Mocartova 10, Serbia
[6]Osaka University, Japan
[7]University of Belgrade-Faculty of Chemistry, St. trg. 12, Serbia

vbeskoski@chem.bg.ac.rs

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic chemicals with extremely strong C-F bonds. Due to their thermal stability, acid resistance, and high surface activity, they have been widely used for several decades in various consumer products. PFAS has been detected in water, soil, sediment, air, food, and biota samples on all continents and due to this are recognized as environmental and human health risk (Carlson et al. 2022). In the last decade, several available technologies were tested for the remediation of PFAS-polluted environments, such as adsorption, filtration, thermal destruction, oxidation/reduction, and soil washing, but several disadvantages were reported (Bolan et al., 2021).

We hypothesize that by using advanced oxidation techniques followed by microbial treatment decrease in the concentration of PFOA as a PFAS model compound will occur. In the beginning, we tested separately abiotic and biotic degradation of PFOA. Target LC-MS/MS was used for quantitative analysis of PFOA decrease, and for detecting degradation products, non-targeted LC-MS/MS analysis was used.

In the photocatalysis study, we used selected Ti and Al-based photocatalysts. The experiments were conducted at 20 °C in an open cylindrical polypropylene reactor, and a simulated solar radiation lamp (Solimed BH Quarzlampen) was used as a light source.

Microbial communities were isolated from the locations in Serbia, Japan, and Italy known for their pollution with PFAS, and enrichment was conducted on the media supplemented with ppm values of PFOA (Beskoski et al., 2018). Microbial communities were used as inoculum in the PFOA biodegradation study.

Phododegradion of PFOA using Ti and Al-based photocatalysts ranged between 50 and 80% depending on the catalyst used. On some catalysts, sorption was observed, which additionally speeded up the degradation reaction. Based on the non-targeted analysis, shorter chain homologs of PFOA were detected, and their concentration increased during photocatalysis which was followed by a decrease in the parent compound. Free Fluoride ions were detected using ion selective electrode and ionic chromatography. In addition, a polyfluorinated compound with m/z 395 was detected as standard contamination, and a decrease of the concentration of this compound was also detected, suggesting that the applied technology is also active not only to per- but also to polyfluorinated compounds.

In the biodegradation study, the PFOA concentration decreased from 21 to 36% using the most active microbial consortia.
From the enrichment, more than 30 pure colonies were isolated.

Our results confirmed that photocatalysis could be used for a decrease of PFOA and that microorganisms isolated from an environment polluted with PFAS chemicals can not only survive in this harsh environment but can also conduct the degradation of these chemicals under specific conditions. Further study will focus on optimization and a combination of these techniques.

References

Beškoski V.P. et al. (2018) 'Defluorination of perfluoroalkyl acids is followed by production of monofluorinated fatty acids', Science of the Total Environment 636, 355–359. doi: 10.1016/j.scitotenv.2018.04.243.

Bolan et al., (2021) 'Remediation of poly- and perfluoroalkyl substances (PFAS) contaminated soils – To mobilize or to immobilize or to degrade?', Journal of Hazardous Materials, 401, p.123892. doi:10.1016/j.jhazmat.2020.123892.

Carlson L.M. et al. (2022), 'Systematic Evidence map for over one hundred and fifty per- and polyfluoroalkyl substances (PFAS)', Environ. Health Perspect., 130(5), p.56001. doi:10.1289/EHP10343.

Solving the PFAS Challenge: Comprehensive Screening in a Single Run from Organisms at Different Trophic Levels

G. Gkotsis[1], D. E. Damalas[1], M. C. Nika[1], N. Van Den Borg[2]*, C. Baessmann[2], R. Galvin[2], G. Labella[2], N. S. Thomaidis[1]

[1]National and Kapodistrian University of Athens, Athens, Greece
[2]Bruker Daltonik GmbH, Bremen, Germany

noud.van_der_borg@bruker.com

Per- and Polyfluoroalkyl Substances (PFAS) are known as "forever chemicals" due to their persistent, bio-accumulative, toxic (PBT) properties and ubiquitous presence in the environment and organisms. Ca. 5,000 PFAS are marketed worldwide, making their systematic environmental monitoring an extremely challenging task. Adding trapped ion mobility spectrometry (TIMS) to LC-HRMS allows the very comprehensive monitoring of organic micropollutants in complex environmental matrices such as biota, through targeted and untargeted workflows.
Presented here is a complete solution for PFAS characterization in environmental samples, combining ion mobility supported target analysis with wide scope suspect and non-target screening,

Extracts suitable for untargeted screening were generated through a generic sample preparation protocol developed for the simultaneous extraction of 56 PFAS from different sub-groups. The analysis was conducted using LC-TIMS-QTOF. Data independent (bbCID) acquisition and PASEF, an efficient data-dependent acquisition mode, were used for targeted and untargeted workflows, respectively. The target analysis based on four independent criteria was run on the target list of 56 PFAS. In the untargeted data processing workflow, the raw data was transformed into a comprehensive feature table. Then the detected features were lined up by Kendrick mass analysis and annotated using a PFAS suspect list of ca. 5,000 compounds. In-silico prediction of MS/MS spectra and CCS values for the suspected compounds was performed for their identification.

Due to the PFAS structure there is a high probability of isomers, making their separation and structure elucidation very demanding. TIMS capabilities were evaluated to separate coeluting isobaric and isomeric analytes. The ion mobility filtrating resulted in higher sensitivity and lower detection limits of the targeted PFAS as well as significantly higher quality of full-scan MS and bbCID MS/MS spectra. The use of collisional cross sections (CCS) as additional identification criteria enhanced the identification confidence.
A feature table containing thousands of entries was created in the untargeted workflow. Kendrick mass defect analysis filtered features as potential PFAS from the matrix background, based on high fluorine content (repeating CF2 units). Wide-scope suspect screening of 5,000 PFAS using in-silico MS/MS and CCS value prediction was evaluated as a comprehensive approach for a fast and efficient identification.
The proposed workflow provides a comprehensive solution for the characterization of 1000s of PFAS compounds in complex environmental matrices. Therefore, it will assist in understanding the chemical universe of PFAS in the environment and protecting environment, wildlife, and human health.

Residues of Drugs of Abuse in an Urban Aquifer: Chemical Analysis and Solute Transport Modelling

T. Verovšek[1],[2]*, M. Janža[3], D. Heath[1], A. Šuštarič[4], H. Prosen[4], E. Heath[1],[2]

[1]Jožef Stefan Institute, Jamove 39, 1000 Ljubljana, Slovenia
[2]Jožef Stefan International Postgraduate School, Jamove 39, 1000 Ljubljana, Slovenia
[3]Geological Survey of Slovenia, Dimičeva ulica 14, 1000 Ljubljana
[4]Faculty of Chemistry and Chemical Technology, Večna pot 113, 1000 Ljubljana, Slovenia

ester.heath@ijs.si

Groundwater is considered a high-quality primary source of freshwater that typically requires only minimal treatment for use as drinking water. Its quality for human consumption is regulated according to various directives, but many anthropogenic compounds (including emerging contaminants), increasingly present in the environment due to population growth and urbanisation, are not currently regulated. Emerging contaminants also include residues of drugs of abuse, which are pseudo-persistent and have been shown to have adverse effects on aquatic organisms. Furthermore, their physiochemical properties facilitate their movement through water, enabling their entry into groundwater and drinking water, potentially posing a risk to human health. Regardless, the occurrence and sources of drug residues in groundwater are poorly studied since obtaining representative groundwater samples across the aquifer is not always feasible.

In this study, 17 drug residues of two licit drugs (nicotine and alcohol), four medications of abuse (morphine, codeine, methadone and ketamine) and six illicit drugs (cannabis, cocaine, amphetamine, methamphetamine, ecstasy and heroin) were studied in an unconfined intergranular aquifer (Ljubljansko polje, Slovenia), aquifer-recharging river water (Sava River) and raw wastewater from the main municipal wastewater treatment plant serving the city of Ljubljana. Drug residues were extracted using liquid-liquid extraction into acetonitrile (alcohol residues) and solid-phase extraction (Oasis MCX) and analysed using LC-MS/MS (Verovšek et al., 2023). In addition, a solute transport model designed to predict nitrate concentrations in groundwater was used to predict the sources and distribution of drug residues within the aquifer.

Targeted drug residues were ubiquitous in raw wastewater (ng/L to µg/L), while nicotine residues (nicotine, cotinine, trans-3'-hydroxycotinine - HCOT), cocaine residues (cocaine and benzoylecgonine) and methadone residues (methadone and 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine - EDDP), 3,4-methylenedioxymethamphetamine (MDMA) and codeine were detected in the Sava River (ng/L range). Seven drug residues were detected in the ng/L range in groundwater samples, with nicotine, cotinine and benzoylecgonine having the highest detection frequency (>55% of the samples). Both, solute transport modelling and chemical analysis, showed that although drug residues were present in the aquifer recharging the Sava River, the river itself was not a significant contributor to drug residues in groundwater. Instead, a leaky sewer system was identified as the primary source. The good agreement between predicted and measured concentrations of drug residues suggests that the modelling can be used to assess groundwater contamination by drug residues and evaluate their sources.

References

Verovšek, T. et al. (2023) 'Removal of residues of psychoactive substances during wastewater treatment, their occurrence in receiving river waters and environmental risk assessment', Science of The Total Environment, 866, 161257. https://doi.org/10.1016/j.scitotenv.2022.161257.

Quorum-Sensing Based Electrode as a Promising Technique for Biofilm Detections

W. S. Gado[1*], A.-r. Gamal[1], M. S. E. M. Badawy[2], A. Labena[1], Khaled Zakaria[1], K. I. Kabel[1]

[1]Egyptian Petroleum Research Institute (EPRI), Nasr City 11727, Cairo, Egypt.
[2]Al-Azhar University, Department of Microbiology and Immunology, Faculty of Pharmacy (Girls), Cairo, Egypt.

Walaa_shabaan86@yahoo.com

Homoserine lactone (HSL) is a chemical signal that bacteria use to communicate. It is well known that, n-hexanoyl-l-homoserine lactone (C6-HSL), one of the HSL family produced mostly by Gram-negative bacteria, is a distinctive signal that used for sporulation, virulence, conjugation, competence and biofilm formation as a cell-to-cell communication. Oil and gas companies in fact are suffering from many problems that totally attributed to sulfate-reducing bacteria (SRB) in bulk phase (planktonic) and on metal surface (biofilm-formation) (D. Jiang, et al. 2017). SRB-biofilms induced sever pitting corrosion in comparison to planktonic counterpart and the scientist till now are looking for a method that can detect SRB-biofilms when they formed (D Jiang, et al. 2018). Metal oxides (MOx) interlaced polymers matrix, particularly conducting polymers (CPs), senses HSL effectively due to its ability to form a coordination bond, high selectivity and organic molecules absorbance capability. Therefore, this work was directed to apply a biofilm sensing technique to distinguish invisible SRB-biofilms attached to metal surface, two different MOx/Polyaniline-Dodecyl benzene sulfonic acid (PANI-DBSA) composites; ZnO/PANI-DBSA and Fe_2O_3/PANI-DBSA were successfully synthesized and applied with carbon paste 1 % by weight over carbon working electrode to detect the C6-HSL via electrochemical qualitative and quantitative analysis. The synthesized composites were confirmed structurally. The electrochemical impedance spectroscopy (EIS) verified the ability of the obtained composites to monitoring C6-HSL produced by SRB-biofilm in comparison to the standard. The monitoring composites achieved that worthily where the observation swapping from 50 ppm to 1000 ppm of C6-HSL. SRB-biofilm was confirmed by color change colorimetry as well as EIS and the outcomes were compatible with each other's.

References

D. Jiang, et al. (2017), Preliminary study on an innovative, simple mast cell-based electrochemical method for detecting foodborne pathogenic bacterial quorum signaling molecules (N-acyl-homoserine-lactones)Biosensors and Bioelectronics, 90: 436. Doi:https://doi.org/10.1016/j.bios.2016.09.096

D Jiang, et al. (2018), A novel screen-printed mast cell-based electrochemical sensor for detecting spoilage bacterial quorum signaling molecules (N-acyl-homoserine-lactones) in freshwater fish, Biosensors and Bioelectronics 102: 396. Doi:https://doi.org/10.1016/j.bios.2017.11.040

Possibilities and Limitations of Modern Electroanalytical Methods in Environmental Analysis

J. Barek[1]

[1]Charles University, Faculty of Science, Department of Analytical Chemistry, UNESCO Laboratory of Environmental Electrochemistry, Albertov 6, CZ 12843 Prague 2, Czech Republic

barek@natur.cuni.cz

The advantages of electroanalytical methods in environmental analysis (low cost, possibility of miniaturization, portability compatible with on-site measurements, point of care devices, large scale monitoring, compatibility with green and white analytical chemistry, user-friendliness, reasonable sensitivity and selectivity, etc.) and some limitations (problems with working electrode passivation (Barek, J. 2021), limited qualitative information obtainable from electroanalytical methods, problems with more complicated mixtures) will be discussed. Possibilities of modern electroanalytical methods in combination with separation methods (high performance liquid chromatography and/or capillary zone electrophoresis with electrochemical detection to increase selectivity) (Tvorynska S., et al. 2021) or flow injection and/or sequential injection analysis (to increase through-put) (Jiranek,I., Barek J. 2021) will be demonstrated. An attempt to compare fascinating possibilities of modern separation and spectrometric methods with modern electroanalytical methods from the point of view of practical applicability under different situation will be done together with evaluation of their practical applicability to answer different questions in modern environmental analytical chemistry. The obvious and imaginary disadvantages of electroanalytical methods will be discussed together with their possible overcoming. At the end a personal view on future development in the field of modern electroanalytical methods will be discussed with the focus on novel electrode materials and arrangements and preliminary separation and preconcentration.

Acknowledgement
This research was financially supported by the Grant Agency of the Czech Republic (project GACR 20-01589S). We appreciate material, technical and intellectual support of Metrohm.CZ (www.metrohm.com/cs-cz/).

References

Barek, J. (2021) "How to Improve the Performance of Electrochemical Sensors via Minimization of Electrode Passivation", Chemosensors, 9,12. https://doi.org/10.3390/chemosensors9010012.

Tvorynska S., et al. (2021) "Flow Amperometric Uric Acid Biosensors Based on Different Enzymatic Minireactors",Sensors and Acuators B. Chemical, 344, 130252.
https://doi.org/10.1016/j.snb.2021.130252.

Jiranek,I., Barek J. (2021) "The Use of Non-traditional Carbon Film Electrode Based on Microcrystalline Natural Graphite – Polystyrene Composite Film for Amperometric Determination of 5-Aminoquinoline Using Flow Injection Analysis Minimising Electrode Fouling", Journal of Electroanalytical Chemistry 885, 115085.
https://doi.org/10.1016/j.jelechem.2021.115085.

Greener Sample Preparation Method for Direct Determination of Toxic Metals in River Sediments Using Functionalized Ionic Liquids

S. Ražić[1*], J. Mušović[2], M. Vraneš[3], S. Papović[3], S. Gadžurić[3] and T. Trtić-Petrović[2]

[1] University of Belgrade, Faculty of Pharmacy, Department of Analytical Chemistry, Vojvode Stepe, 450, Belgrade, Serbia
[2] University of Belgrade, Laboratory of Physics, Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia, Mike Petrović Alasa 12-14, Belgrade, Serbia
[3]University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića, 3, Novi Sad, Serbia

Despite amazing advances in analytical methods and instrumentation, sample pretreatment is still considered the bottleneck of the entire analytical process. In recent decades, the main interest of the scientific community in the field of sample preparation has been the evaluation of novel extraction agents that can reduce the cost of extraction and the volume of solvents, and make the whole process more environmentally friendly within the principles of sustainable chemistry. Simple sample preparation based on low-cost and non-hazardous materials is essential for a sustainable and environmentally friendly approach. In this presentation, an aqueous biphasic system based on functionalized ionic liquids will be presented and discussed as a promising alternative to conventional extraction methods. The main advantage is the replacement of organic solvents by dilute aqueous ionic liquids. Two water-soluble functionalized ionic liquids based on the 2-mercaptobenzothiazole anion, [mbt]: butyl-3-methylimidazolium [mbt] ([bmim][mbt]) and 1-ethyl-3-methylimidazolium [mbt] ([emim][mbt]) were designed and synthesized to selectively extract cadmium and lead from river sediment. Direct extraction was studied, and the following optimal conditions were determined: direct contact of the aqueous solution of [bmim][mbt] and the sediment sample at 90 °C, 60 minutes, followed by the formation of an aqueous biphasic system with potassium citrate. The environmental performance of the proposed method for direct extraction of Cd(II) and Pb(II) from sediment was determined by applying the metric approach based on the following software/tools: NEMI, GAPI, AGRE, and AGREEprep.

Development of Enzyme-Based Amperometric Nitrite Biosensor Using Films of Chitosan and Multi-walled Carbon Nanotubes

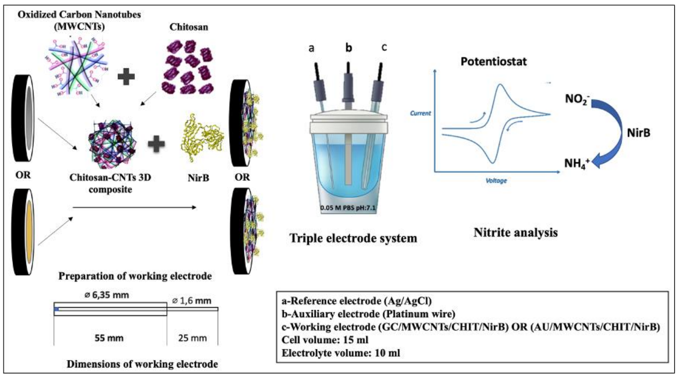
M. Özkan[1*], H. Yilmaz[1], E. M. Erdoğan[1] and P. Ergenekon[1]

[1]Gebze Technical University, Department of Environmental Engineering, Kocaeli, Turkey

mozkan@gtu.edu.tr

Nitrite (NO_2^-) is an unstable nitrogen form that is frequently present in the environment, and nitrogen-based fertilizers and agricultural chemicals are the main sources of nitrite in rivers and lakes (Molayemraftar et al. 2022, Lucas S. B. et al. (2022). Various techniques such as spectrophotometric methods based on the Griess reaction (Ellis G., et al.1998, Rubio M. A., et al. 2002) and ion chromatography (Zuo Y. et al., 2006) are commonly used for nitrite analysis in environmental samples. However, these methods are not suitable for speedy on-site detection. Biosensors have a high potential to be used for on-site environmental measurements. In the present study, an electrochemical amperometric nitrite biosensor was prepared with a recombinant assimilatory nitrite reductase (NirB) enzyme of *Escherichia coli*, which was cloned and characterized for the first time in our previous study (H. Yılmaz H.N. et al. 2022). The glassy carbon (NirB/ MWCNTs/CHIT/GCE) and gold (NirB/MWCNTs/CHIT/Au) electrodes were prepared by immobilization of the enzyme in carbon nanotube chitosan layers (CHIT-MWCNT). The NirB/MWCNTs/CHIT/GCE showed a sensitivity of 31.1 mA/M/cm^2 with a response time ($t_{95\%}$) of 10 sec, while the NirB/MWCNTs/CHIT/Au had a sensitivity of 46.7 mA/M/cm^2 with 7.7 sec response time ($t_{95\%}$) The minimum measured nitrite concentration was observed to be 2µM with the NirB/MWCNTs/CHIT/Au while the NirB/MWCNTs/CHIT/GCE electrode's minimum measured nitrite concentration was 5µM. The MWCNTs/CHIT electrodes developed in this study have the potential to be used for low concentrations of NO_2^- in environmental samples.

Keywords: Biosensor, nitrite reductase, NirB



References

Molayemraftar, et al. (2022). Single and combined effects of ammonia and nitrite on common carp, Cyprinus carpio: Toxicity, hematological parameters, antioxidant defenses, acetylcholinesterase, and acid phosphatase activities. Aquaculture, 548, 737676. https://doi.org/10.1016/J.AQUACULTURE.2021.737676.

Lucas, S. B. et al. (2022). Nitrite Determination in Environmental Water Samples Using Microchip Electrophoresis Coupled with Amperometric Detection. Micromachines, 13(10), 1736. https://doi.org/10.3390/MI13101736/S1
Ellis, G., et al. (1998). Nitrite and Nitrate Analyses: A Clinical Biochemistry Perspective. Clinical Biochemistry, 31(4), 195–220. https://doi.org/10.1016/S0009-9120(98)00015-0.

Rubio, M. A., et al. (2002). Nitrite in rain and dew in Santiago city, Chile. It's possible impact on the early morning start of the photochemical smog. Atmospheric Environment, 36(2), 293–297. https://doi.org/10.1016/S1352-2310(01)00356-9.

Identification and Quantification of Synthetic Musks Fragrances in Freshwaters

S. Tasselli[1]* and L. Guzzella[1]

[1]National Research Council - Water Research Institute (CNR-IRSA), Via del Mulino 19, 20861, Brugherio (MB) Italy

stefano.tasselli@irsa.cnr.it

Synthetic musks or Polycyclic Musk Fragrances (PMFs) are compounds incorporated in detergents, perfumes, and house-cleaning products. Within PMFs there are Galaxolide, its metabolite Galaxolidone, Tonalide, Celestolide and Phantolide. They are released every day in large amounts into sewage systems and can enter aquatic ecosystems through wastewater treatment plant (WWTP) effluents (Clara et al., 2011). The exposure of aquatic environments to the continuous discharge of PMFs is raising many concerns about their possible chronic toxicity and future impacts. In fact, these chemicals proved to be lipophilic, persistent, and highly bioaccumulative since they easily adsorb onto organic matter and can be accumulate in sediments and organisms. Various toxic effects of synthetic musks, as interferences with steroidal and xenobiotic metabolism in fish and acute toxicity in invertebrates have been highlighted (Tumová et al., 2019). Data regarding PMFs in Italy are scarce even if this is the EU-Member State with the highest consumption of these chemicals. In this study, a new analytical method in GC-MS/MS was developed to measure PMFs in freshwater samples. Filtered samples of 0.5 L were spiked with internal standard, solid-phase extracted using C_{18} cartridges and eluted with opportune solvents. Samples were then concentrated at 30°C using N_2 flux and transferred in micro-vials for GC-MS/MS analysis in multiple reaction monitoring mode. Method validation was performed considering linearity, limits of detection, precision and accuracy. Linearity was checked by injection of six standard samples containing all PCMs at different concentration levels, corresponding to sample concentrations 0.5-2000 ng/L. Instrumental limit of detection was calculated based on the signal-to-noise ratio (S/N) of individual peaks. Precision and accuracy were evaluated by spiking real water samples in triplicate at different concentration levels to cover the entire concentration range of the analysed samples. Intra-day and inter-day precision resulted in a relative standard deviation below 13% while recoveries were always above 80% for all compounds. PMF presence was then assessed in surface waters of the main tributaries of an Italian anthropized subalpine lake. PMFs were detected up to hundreds of ng/L especially in small rivers where dilution could not affect concentrations discharged through WWTP effluents. A common temporal trend was evidenced in all rivers, probably due to the effect of rainfall. The highest concentrations were recorded in the smaller rivers that cross anthropized areas. Galaxolide, its metabolite Galaxolidone and Tonalide were the most abundant compounds. The developed method allowed to detect synthetic fragrances in some Italian rivers, thus filling the gap of knowledge regarding the presence of these chemicals in Italy. Measured concentrations evidenced discharges impacts especially on small rivers and, from here, the need to improve water purification with additional and innovative methodologies to improve the quality of receiving water bodies.

References

Clara, M. et al. (2011) ‘Occurrence of polycyclic musks in wastewater and receiving water bodies and fate during wastewater treatment’, Chemosphere, 82(8), pp. 1116–1123. doi:10.1016/j.chemosphere.2010.11.041.

Tumová, J. et al. (2019) ‘Effect of polycyclic musk compounds on aquatic organisms: A critical literature review supplemented by own data’, Science of The Total Environment, 651, pp. 2235–2246. doi:10.1016/j.scitotenv.2018.10.028.

X-Ray Absorption Spectroscopy for Food Safety: Assessment of Arsenic Uptake and Accumulation in Grapevine

C. Petroselli[1]*, R. Baraldi[2], M. V., Salomon[4], F. d'Acapito[3], P. Piccoli[4]

[1]University of Perugia, Department of Chemistry, Biology and Biotechnology, via Elce di Sotto 8, 06123, Perugia, Italy
[2]National Research Council (CNR), Institute of BioEconomy (IBE), via P. Gobetti 101, 40129, Bologna, Italy
[3]National Research Council (CNR), IOM-OGG c/o ESRF, Avenue des Martyrs 71, 38043, Grenoble, France
[4]National University of Cuyo, IBAM-CCT-Mendoza, Almirante Brown 500, M5528AHB, Mendoza, Argentina

chiara.petroselli@unipg.it

Arsenic (As) contamination of agricultural soils poses a widespread threat to human health, affecting roughly 1/60 of the global population. The Rio Jáchal valley in Argentina is an area vocated to grapevine and onion cultivation, however, due to natural groundwater contamination, As concentrations in soils reach values that are 10 times higher than the limits established by the Argentinian regulations (20 ppm). A fundamental aspect of arsenic toxicity is that it is not only concentration dependent, but rather determined by As speciation. In fact, speciation can change As solubility, bioavailability and also the uptake and transport pathways activated in the plant. The most common forms of As in the environment are inorganic arsenite (As(III)) and arsenate (As(V)), and organic methylated forms (MMA, DMA) mainly produced by microbial activity. Inorganic As species are more toxic than organic ones because they are more mobile and more easily absorbed by plant tissues via the phosphate channels in the case of As(V) or via the bidirectional aquaporin transporters for As(III). Once inside the plant, As will undergo different detoxification mechanisms depending on its speciation, that range from redox reactions (e.g. As(V) reduction to As(III)) with production of Reactive Oxygen Species (ROS) and subsequent oxidative stress for the plant organism, to immobilisation into root tissues or translocation to aerial biomass (shoots and leaves).

Arsenic is a non-essential metalloid that exhibits toxic potential at any concentration inside a living organism, and it is therefore able to reduce plant growth and crops yield. The beneficial effect of Plant Growth Promoting Rhizobacteria (PGPR) in increasing As-tolerance in grapevine was demonstrated (Pinter M. I. F. et al. 2018), however, the involved mechanisms are not fully understood.

This work aims at investigating As accumulation and speciation in grapevine tissues of plants cultivated in-vitro and subjected to As treatment and PGPR inoculation. Implemented treatments are: As-only, PGPR-only, As+PGPR, control. After 40 days of treatment, the plants were dissected into roots, shoots and leaves and as concentrations were determined by Inductively Coupled Plasma - tandem Mass Spectrometry (ICP-MS/MS) after acid digestion. Plant tissues solid samples were also analysed by X-ray Absorption Spectroscopy (XAS) at the LISA beamline (BM08) of the European Synchrotron Radiation Facility (ESRF). Both the XANES (X-ray Absorption Near Edge Structure) and the EXAFS (Extended X-ray Absorption Fine Structure) parts of the spectrum were acquired, providing information on the oxidation state, the nature of the ligands and the bond distances. Results highlight a different accumulation and translocation pattern for inoculated plants compared to uninoculated ones. Moreover, a change in As speciation was observed going from belowground to aboveground tissues, which is also affected by PGPR inoculation. Overall, PGPR inoculation has a beneficial effect on plant growth and productivity, however, it seems to promote translocation to aboveground biomass potentially threatening food safety.

References

Pinter, M. I. F. et al. (2018) ‘Plant growth promoting rhizobacteria alleviate stress by AsIII in grapevine’, Agriculture, Ecosystems & Environment, 267, 100-108. doi: 10.1016/j.agee.2018.08.015.

Residues of Modern Pesticides in Soils and Potatoes from Tropical Agroecosystems in Mayabeque, Cuba

B. Peña[1]*, I. Hilber[2], D. Sosa[1], N. Perez[3], A.C. Escobar[1], T.D. Bucheli[2]

[1]Centro Nacional de Sanidad Agropecuaria (CENSA), Departamento de Salud Animal, Apartado 10, CP 32700 San José de las Lajas, Mayabeque Cuba
[2]Agroscope, Environmental Analytics, Reckenholzstrasse 191, 8046 Zurich, Switzerland
[3]Agrarian University of Havana, Plant Health Department, Autopista Nacional km 22, CP 32700 San José de las Lajas, Mayabeque, Cuba

brizeidipe@gmail.com

Despite the increasing pesticide usage in tropical countries, monitoring programs for modern pesticides (MPs) in tropical agricultural soils are scarce. Solanum tuberosum L. (potato) is an important crop worldwide and their cultivation requires high amounts of pesticides. In Mayabeque province, one of the major potato-producing regions in Cuba, as many as 52 active ingredients (a.i.) were used in potato production, at annual range between 2.3-8.9 kg a.i./ha in 2011-2013. In Batabanó (BT) and Quivicán (QV) (two counties in Mayabeque), were applied 44 a.i. (4.8-27.9 kg a.i./ha) in 2018-2021. However, there are no reports of MPs residues in soil and there grown potato tubers. The objectives of this study were to: (i) sample field soils and there grown potato tubers over four consecutive years in BT and QV, (ii) determine a.i. selected according to application records of farmers and some transformation products (TPs) in the two matrices, and (iii) evaluate residue concentrations, if possible, also concerning regulatory limits. Soil samples (n=152) were taken from 2018-2022 at three times per year (before planting, high application time and harvest) and the potatoes were also sampled (n=50). Thirty-one MPs and eight TPs were extracted by QuEChERS (Quick, Easy, Cheap, Robust, and Safe) method, and quantified by Gas Chromatography tandem Mass Spectrometry (GC-MS/MS). More than 93% of soil samples had ≥1 MPs/TPs residue and ≥5 residues co-occurred in 101 soil samples. Median values of individual MPs/TPs were 5.7 µg/kgsoil and minimum (min) and maximum (max) concentrations 0.1 and 658 µg/kgsoil, respectively. Pesticide residues most frequently detected were s-metolachlor (72% of samples, min=1.1, max=658 µg/kgsoil), dicofol (71%, 0.1-35 µg/kgsoil), and azoxystrobin (69%, 0.2-293 µg/kgsoil). In 59% of samples, at least one pesticide was present at ≥10 µg/kgsoil; this value represents the generic soil limit for individual non-chlorinated (No-Cl) pesticides used in the Czech Republic. The sum of co-occurring pesticides exceeded the Dutch limit (70 µg/kgsoil) and the Czech limit (100 µg/kgsoil) in 49% and 41% of soils, respectively (Hvězdová et al. 2018). The intervention value for total No-Cl pesticides by Dutch legislation (500 µg/kgsoil) (VROM, 2006) was not surpassed in any soil sample. In potato tubers, 11 MPs/TPs were quantified over the four years in 50% of the samples. Median values of individual MPs/TPs were 2.7 µg/ kgfresh weight (fw) with a range 0.04-17.5 µg/kgfw. Trifloxystrobin, metribuzin desamino and boscalid were the most frequently present MPs/TPs, with detections in 18%, 18%, and 10% of potato samples, respectively. All concentrations were below of any guide values including Cuban Regulation (NC902:2012). This study is the first report about MPs/TPs in soil and potato samples under real field conditions in Cuba. The results contribute to establish a regulatory guide value for MPs in Cuban agricultural soils that are currently non-existent, which holds for many other tropical countries too. The food safety of potatoes was not affected, but monitoring programs for the tubers but also for other cash crops should still become standard.

References

Hvězdová, M. et al. (2018) ‘Currently and recently used pesticides in Central European arable soils’, Science of the Total Environment, p.361-370. doi: http://dx.doi.org/10.1016/j.scitotenv.2017.09.049.

NC902:2012. Plaguicidas en alimentos — requisitos sanitarios generales. Oficina Nacional de Normalización. Consejo Norma Cubana. http://www.nc.cubaindustria.cu/index.html.

VROM, 2006. Soil Quality Regulation. Ministry of Housing, Planning and the Environment, the Netherlands.References.

Historical Records of Plant Protection Product Deposition in Lakes under Anthropogenic Pressure

A. C. Chiaia-Hernández[1]*, E. Schadd[1], N. Fahrni[1], N. Gosain[1], and M. Grosjean[1]

[1]University of Bern, Institute of Geography and Oeschger Center for Climate Change Research, Hallerstrasse 12, 3012, Switzerland

aurea.hernandez@giub.unibe.ch

Until today, there has been little understanding of the emissions, environmental disturbances, or toxic effects of plant protection products (PPPs) in lake systems or of their concentration in sediments, despite the fact that sediments serve as habitats and spawning sites for many organisms and are hotspots of biodiversity in general (Chiaia-Hernández et al., 2020). Although many studies have analyzed the losses of diffuse PPPs from agricultural fields to surface water (e.g., rivers and creeks) (Moschet et al., 2014a, 2014b), so far, few attempts have been made to gain a comprehensive picture of the transport and deposition of current-use PPPs in freshwater lake systems, largely due to the complexity of sediment analysis and the missing link to paleolimnological methods.

This work present for the first time the use of multiproxy-workflows to assess a wide range of current-use PPPs in sediment samples from different Swiss lakes under heavy agricultural pressure. The applied analytical methods using LC-MS/MS and LC-HRMS helped to identify more polar and mobile compounds than previously reported in PPP sediment analysis (>30 PPPs per lake). Our findings confirm that PPP embedded in sediments are often quite stable, especially under anaerobic conditions. By adopting paleolimnological methods (e.g., chronology, hyperspectral measurements of sedimentary green pigments and µXRF), our work reveals that PPP fluxes are not related to sedimentological processes such as soil erosion (Ti counts, µXRF scans) or lake biogeochemistry like precipitation of calcite or lake productivity (green pigments, HSI). As a result, post-depositional processes or variations in sediment binding do not majorly influence PPP fluxes over time and PPP behavior can be related mainly to sales (used as a proxy for PPP application) or bans.

Sediment records indicate PPP start appearing in Swiss lakes for the first time in the early 1960s. The detection in recent sediment layers of PPP that are not yet reported in other environmental compartments (e.g., groundwater) can help identify possible persistent compounds in the future. Nontarget analysis reveals significant inputs of contaminants to the lakes starting in the 1970s, followed by a decrease of contaminants at the beginning of the 1990s and a constant increase of different type of contaminants since the year 2000.
Lake systems like the lakes studied are abundant in the Swiss plateau and Europe and are often used as freshwater supplies. Therefore, our findings are likely representative of many agriculturally influenced lakes in Europe. The present study calls for further studies to investigate the mechanisms of organic contaminants in sediments, particularly, how PPP and other organic contaminants are reaching lakes and the lake sediments, and if these compounds can be remobilized.

References

Chiaia-Hernández, A. C. et al. (2020) 'A high-resolution historical record of plant protection products deposition documented by target and nontarget trend analysis in a Swiss lake under anthropogenic pressure'. Environmental Science & Technology, 54, 20, 13090-13100. doi:10.1021/acs.est.0c04842.

Moschet, C. et al. (2014) 'Picogram per liter detections of pyrethroids and organophosphates in surface waters using passive sampling', Water Research, 66, 411-422. doi:10.1016/j.watres.2014.08.032.

Moschet, C. et al. (2014) 'How a Complete Pesticide Screening Changes the Assessment of Surface Water Quality', Environmental Science & Technology, 48, (10), 5423-5432. doi: 10.1021/es500371t.

The Rare Earth Elements Distribution in Lake Sediments as an Indicator of Surface Water Redox Potential and Micropollution

L.V. Soroaga[1,2], C. Amarandei[1,2,3], A. G. Negru[1,2], C. Arsene[1,2,3], R. I. Olariu[1,2,3]*

[1]University of Iasi, Alexandru Ioan Cuza, Integrated Centre of Environmental Science Studies in the North Eastern Region (CERNESIM), 11 Carol I, 700506, Iasi, Romania
[2]University of Iasi, Alexandru Ioan Cuza, Center with Integrated Techniques for Atmospheric Aerosol Investigation in Romania (RECENT AIR), 11 Carol I, 700506, Iasi, Romania
[3]University of Iasi, Alexandru Ioan Cuza, Faculty of Chemistry, 11 Carol I, 700506, Iasi, Romania

oromeo@uaic.ro

The REEs (Sc, Y, and the lanthanides) form the largest group of elements with similar physical and chemical properties from the periodic table. This is important for the indirect evaluation of the redox conditions of surface water bodies as the REEs chemistry in aqueous solutions involves almost exclusively the trivalent oxidation state, with Ce^{4+} and Eu^{2+} being the only species of significant importance in different oxidation state. Compounds formed by these two species may lead to fractionation from the trivalent state, especially important as the oxidation of Ce^{3+} to Ce^{4+} takes place in well oxygenated aqueous environments and the tetravalent state is mostly associated with water insoluble solid phase. This leads to depletion of Ce from the water column and, thus, a variation from the normal REEs distribution (Soroaga *et al.*, 2022). The process can be easily identified by REEs concentration normalization to Chondrite and/or Upper Continental Crust (UCC) values. Moreover, any variation from the normal distribution of REEs in the sediment samples may highlight micropollution, as the REEs are extensively being used in new technologies and the emission of REEs into natural waters from fertilizers, industry and medical applications is continuously increasing (Sojka *et al.*, 2021).

In this study, the concentration of 15 REEs and other trace elements was determined from sediment samples collected from Podu Iloaiei Dam Lake, one of the most important water resources used for aquaculture from NE Romania (Amarandei *et al.*, 2021). Two sampling sessions corresponding to warm and cold seasons have been performed. The sample preparation steps included solid-state dissolution by sintering with Na_2O_2. The analysis was performed on 7700 x Series ICP-MS (Agilent Technologies) using the aerosol dilution mode.

The UCC-normalized REEs concentration allowed the identification of a Ce anomaly ranging from 0.33 to 0.78 in July and from 0.37 to 0.92 in October, which indicates a higher oxidizing potential of the aqueous environment in October in comparison to July. This is also correlated with the distribution of Mn, another redox-sensitive element. For all other REEs a low variability was observed.

The distribution of the UCC-normalized REEs concentration allowed the observation of a positive anomaly for Gd that may be an indicator of Gd micropollution and could be related to the use of Gd-chelating agents in Magnetic Resonance Imaging (MRI).

Acknowledgements: The authors acknowledge the Operational Program Competitiveness 2014−2020, Axis 1, under POC/448/1/1 research infrastructure projects for public R&D institutions/sections F 2018, through the Research Center with Integrated Techniques for Atmospheric Aerosol Investigation in Romania (RECENT AIR) project, under grant agreement MySMIS no. 127324, and PN-III-P4-PCE2021-0673 (acronym ATMO-SOS) UEFISCDI project for their co-support.

References

Amarandei, C., *et al.* (2021) 'Assessment of Surface Water Quality in the Podu Iloaiei Dam Lake (North-Eastern Romania): Potential Implications for Aquaculture Activities in the Area', Water, 13(17), p. 2395. doi:10.3390/w13172395.

Sojka, M., *et al.* (2021) 'Causes of variations of trace and rare earth elements concentration in lakes bottom sediments in the Bory Tucholskie National Park, Poland', Scientific Reports, 11, p. 244. doi:10.1038/s41598-020-80137-z.

Soroaga, L.V. *et al.* (2022) 'Assessment of the Anthropogenic Impact and Distribution of Potentially Toxic and Rare Earth

Elements in Lake Sediments from North-Eastern Romania',Toxics, 10(5), p. 242. doi:10.3390/toxics10050242.

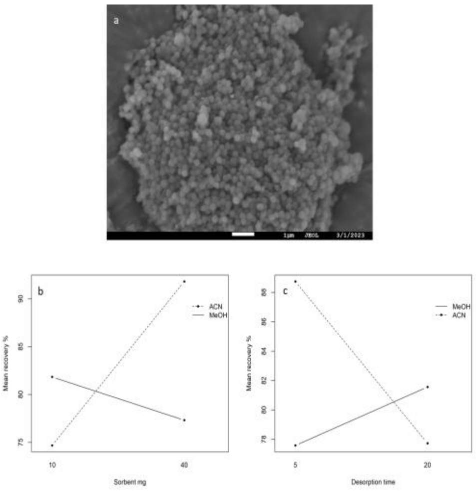
An Efficient d-SPE Method for Multi-Residue Fungicides Enrichment from River Water Samples Based on a Newly Synthesized Chitosan Derivative

L. Martello[1,2]*, A. Rapti[3], D. Bikiaris[3] , D. Lambropoulou[1,2]

[1]Aristotle University of Thessaloniki, Laboratory of Environmental Pollution Control, Department of Chemistry, GR-541 24 Thessaloniki, Greece
[2]Centre for Interdisciplinary Research and Innovation (CIRI-AUTH), Thessaloniki, 10th km Thessaloniki-Thermi Rd, GR 57001, Greece
[3]Aristotle University of Thessaloniki, Laboratory of Polymer Chemistry and Technology, Department of Chemistry, GR-541 24 Thessaloniki, Greece

martello@chem.auth.gr

The use of preventive or therapeutic fungicides on crops is constantly growing. A large number of fungicides used in agriculture are characterized by high persistence in the environment and proved toxicity, representing an element of concern (Pacholak et al., 2022). Investigation on new sorbent materials to apply in environmental analysis for sample pre-treatment is an active research field, and chitosan, which easily establishes electrostatic interactions thanks to its amino and hydroxyl groups, seems a promising material for this purpose (Rinaudo, 2006).In the present study a new, inexpensive co-polymer of chitosan grafted with N-isopropylacrylamide, acrylic acid and triethylene glycol dimethacrylate was synthesized through free-radical polymerization. The material was studied through Fourier transform infrared spectroscopy, scanning electron microscopy (SEM) and nitrogen adsorption, showing a morphology marked by an aggregation of nanoparticles with high surface area. The sorbent was tested as innovative sorbent for dispersive solid phase extraction (d-SPE) followed by LC-MS analysis on river water (sampled from Litheos river, Central Greece) spiked at trace level with 10 widespread agricultural fungicides belonging to different chemical classes. Some important parameters (sorbent amount, desorption solvent and desorption time) were screened and optimized through design of experiments, leading to an extraction procedure characterized by satisfactory methodological indices (LOD < 20 µg l for most of the analytes, recovery in the range 88%-106%; RSD < 5).



a) Sorbent SEM image; b,c) Effects interaction plots on recovery for: sorbent amount (mg), desorption time (min) and solvent (acetonitrile, methanol).

References

Pacholak, A. et al. (2022) 'Azole fungicides: (Bio)degradation, transformation products and toxicity elucidation', Science of the Total Environment, 802. doi:10.1016/j.scitotenv.2021.149917.

Rinaudo, M. (2006) 'Chitin and chitosan: Properties and applications', Progress in Polymer Science (Oxford), pp. 603–632.

doi:10.1016/j.progpolymsci.2006.06.001.

Residues of Modern Pesticides in Soils and Potatoes from Tropical Agroecosystems in Mayabeque, Cuba

B. Peña[1]*, I. Hilber[2], D. Sosa[1], N. Perez[3], A.C. Escobar[1], T.D. Bucheli[2]

[1]Centro Nacional de Sanidad Agropecuaria (CENSA), Departamento de Salud Animal, Apartado 10, CP 32700 San José de las Lajas, Mayabeque Cuba
[2]Agroscope, Environmental Analytics, Reckenholzstrasse 191, 8046 Zurich, Switzerland
[3]Agrarian University of Havana, Plant Health Department, Autopista Nacional km 22, CP 32700 San José de las Lajas, Mayabeque, Cuba

brizeidipe@gmail.com

Despite the increasing pesticide usage in tropical countries, monitoring programs for modern pesticides (MPs) in tropical agricultural soils are scarce. Solanum tuberosum L. (potato) is an important crop worldwide and their cultivation requires high amounts of pesticides. In Mayabeque province, one of the major potato-producing region in Cuba, as many as 52 active ingredients (a.i.) were used in potato production, at annual range between 2.3-8.9 kg a.i./ha in 2011-2013. In Batabanó (BT) and Quivicán (QV) (two counties in Mayabeque), were applied 44 a.i. (4.8-27.9 kg a.i./ha) in 2018-2021. However, there are no reports of MPs residues in soil and there grown potato tubers. The objectives of this study were to: (i) sample field soils and there grown potato tubers over four consecutive years in BT and QV, (ii) determine a.i. selected according to application records of farmers and some transformation products (TPs) in the two matrices, and (iii) evaluate residue concentrations, if possible, also concerning regulatory limits. Soil samples (n=152) were taken from 2018-2022 at three times per year (before planting, high application time and harvest) and the potatoes were also sampled (n=50). Thirty-one MPs and eight TPs were extracted by QuEChERS (Quick, Easy, Cheap, Robust, and Safe) method, and quantified by Gas Chromatography tandem Mass Spectrometry (GC-MS/MS). More than 93% of soil samples had ≥1 MPs/TPs residue and ≥5 residues co-occurred in 101 soil samples. Median values of individual MPs/TPs were 5.7 µg/kgsoil and minimum (min) and maximum (max) concentrations 0.1 and 658 µg/kgsoil, respectively. Pesticide residues most frequently detected were s-metolachlor (72% of samples, min=1.1, max=658 µg/kgsoil), dicofol (71%, 0.1-35 µg/kgsoil), and azoxystrobin (69%, 0.2-293 µg/kgsoil). In 59% of samples, at least one pesticide was present at ≥10 µg/kgsoil; this value represents the generic soil limit for individual non-chlorinated (No-Cl) pesticides used in the Czech Republic. The sum of co-occurring pesticides exceeded the Dutch limit (70 µg/kgsoil) and the Czech limit (100 µg/kgsoil) in 49% and 41% of soils, respectively (Hvězdová et al. 2018). The intervention value for total No-Cl pesticides by Dutch legislation (500 µg/kgsoil) (VROM, 2006) was not surpassed in any soil sample. In potato tubers, 11 MPs/TPs were quantified over the four years in 50% of the samples. Median values of individual MPs/TPs were 2.7 µg/ kgfresh weight (fw) with a range 0.04-17.5 µg/kgfw. Trifloxystrobin, metribuzin desamino and boscalid were the most frequently present MPs/TPs, with detections in 18%, 18%, and 10% of potato samples, respectively. All concentrations were below of any guide values including Cuban Regulation (NC902:2012). This study is the first report about MPs/TPs in soil and potato samples under real field conditions in Cuba. The results contribute to establish a regulatory guide value for MPs in Cuban agricultural soils that are currently non-existent, which holds for many other tropical countries too. The food safety of potatoes was not affected, but monitoring programs for the tubers but also for other cash crops should still become a standard.

References

Hvězdová, M. et al. (2018) ‘Currently and recently used pesticides in Central European arable soils’, Science of the Total Environment, p.361-370. doi: http://dx.doi.org/10.1016/j.scitotenv.2017.09.049.

NC902:2012. Plaguicidas en alimentos — requisitos sanitarios generales. Oficina Nacional de Normalización. Consejo Norma Cubana. http://www.nc.cubaindustria.cu/index.html.

VROM, 2006. Soil Quality Regulation. Ministry of Housing, Planning and the Environment, the Netherlands.References.

Towards Community Health Surveillance in Wastewater Treatment Plants and more – Setting Up Methods and Chasing Antibiotics, Microorganisms and AMR in Untreated Waters and Bioaerosols

A. S. Gaetano[1], S. Semeraro[1], S. Fornasaro[1], S. Licen[1], V. Gelao[2], S. Briguglio[2], S. De Martin[2], C. Ametrano[3], F. Malfatti[3], A. Cain[4], F. Barbone[5], A. Pallavicini[3], P. Barbieri[1]*

[1]Dept. of Chemical and Pharmaceutical Sciences @ University of Trieste, via L.Giorgieri. 1, 34127, Trieste, Italy
[2]SOC Laboratorio Multisito ARPA FVG. Via Colugna, 42. 33100, Udine, Italy
[3]University of Trieste, Dept. of Life Sciences, via L.Giorgieri. 5, 34127, Trieste, Italy
[4]ACEGASAPS AMGA Via degli Alti Forni, 11
[5]University of Trieste, Dept. of Medicine, Surgery &Health Sciences, via Pietà 2/2, 34129, Trieste, Italy

barbierp@units.it

Urban waste waters treatment plants are collectors and repositories of chemical and microbiological information relevant as community health determinants (Rizzo, 2013). Thus, modern unsupervised analytical (Kosma, 2020) and genetic approaches applied on properly collected samples can provide snapshots or monitoring tools for getting chemical and microbial fingerprints of the population served by the WWTP.

A short pilot study, at the wastewater treatment plant of the municipally of Trieste (Italy) has allowed us to develop a workflow for detecting antibiotics and other pharmaceuticals in waters, together with microbes that are aerosolized from untreated wastewater and coupled antimicrobial resistance genes. Analytical determinations on water samples have been performed by an Orbitrap Q-Exactive Focus spectrometer and data treatment by Compound Discoverer 3.2 software.

Considering the lack of standardized bioaerosol sampling procedures, an intercomparison between bioaerosol samplers was conducted at the aeration tank of untreated effluents at the wastewater treament plant in the municipally of Trieste (Italy), by bacteria rRNA 16S metabarcoding highlighting pros and limits of different instruments (AD ViVAS, Sartorius MD8 Airport, SKC BioSampler and more) and procedures. Unsuspected presence of pathogens in sampled aerosols has been detected.

The search of anti-microbial resistance genes is performed after NGS (Yadav, 2021) on Illumina NovaSeq platform and the analysis is supported with an extensive integrated access to multiple AMR databases including Comprehensive Antimicrobial Resistance Database (CARD), ResFinder, ARG-ANNOT, NCBI Bacterial Antimicrobial Resistance Reference Gene Database, PointFinder and VFDB databases.

New integrated sampling procedures at WWTP and technological analytical MS and genetic NGS platforms have been designed and tested for provideng new insights on AMR, highlighting the strength of links between analytical, environmental and health sciences, for providing sound advice to public health decision makers.

This study was carried out within the Interconnected Nord-Est Innovation Ecosystem (iNEST) and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.5 – D.D. 1058 23/06/2022, ECS00000043)

References

Rizzo L, Manaia C, Merlin C, Schwartz T, Dagot C, Ploy MC, Michael I, Fatta-Kassinos D. (2013) 'Urban wastewater treatment plants as hotspots for antibiotic resistant bacteria and genes spread into the environment: a review'. Sci Total Environ. ;447:345-60. doi: 10.1016/j.scitotenv.2013.01.032.

Kosma, C. I., Kapsi, M. G., Konstas, P. G., Trantopoulos, E. P., Boti, V. I., Konstantinou, I. K., & Albanis, T. A. (2020). Assessment of multiclass pharmaceutical active compounds (PhACs) in hospital WWTP influent and effluent samples by UHPLC-Orbitrap MS: Temporal variation, removals and environmental risk assessment. Environmental research.

Yadav S, Kapley A. (2021) Antibiotic resistance: Global health crisis and metagenomics. Biotechnol Rep (Amst). ;29:e00604. doi: 10.1016/j.btre.2021.e00604 .

Biomonitoring Strategies to Determine Legacy and Emerging Contaminants for Environmental Protection Purposes

S. Lacorte[1]*, A. Bertolero[2], B. Oro-Nolla[1], P. Zapata[1], P. Colomer-Vidal[1], F. J. Santos[3]

[1]IDAEA-CSIC, Department of Environmental Chemistry, c/Jordi Girona 18, 08034 Barcelona, Catalonia, Spain
[2]Associació Ornitològica Picampall de les Terres de l'Ebre, Amposta, Catalonia, Spain
[3]University of Barcelona, Department of Chemical Engineering and Analytical Chemistry, Martí i Franquès 1, 08028 Barcelona, Catalonia, Spain

silvia.lacorte@idaea.csic.es

Biomonitoring is the measurement of chemical compounds and/or their metabolites accumulated in biological systems, and is used around the world as reflect the quality of the environment. Long-term biomonitoring can, in addition, identify changes in population exposure over time and relate it to potential adverse effects and causative agents, which can be used thereafter to provide a comprehensive diagnostic assessment of ecological impacts. Biomonitoring strategies are gaining importance within the context of the Birds and Habitats Directives (2009/147/EC and 92/43/EEC), the Zero Pollution Action Plan and the new European Biodiversity Strategy aimed at reversing biodiversity loss in the EU. Several organisms are used as biomonitors of environmental pollution, most typically fish, mussels, crustaceans, macroalgae, macroinvertebrates, and plants, among others. In this study, we propose the use of gull eggs (Larus michahellis) as biomonitors of legacy and emerging contaminants (Zapata et al., 2018; Colomer-Vidal et al., 2022). Gulls are long-lived, have a wide distribution and are tolerant to environmental pollution, thus reflecting contaminant variability over a protracted period. Our biomonitoring strategy includes the annual sampling of gull eggs since 2009 in 4 colonies in Spain to determine multiple contaminants such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), perfluoroalkyl substances (PFASs), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), dechlorane plus, short-chain chlorinated paraffins and phthalates. Several solid-liquid extraction protocols have been optimized and validated to determine the different chemical families. Analysis is performed with gas and liquid chromatography coupled to tandem mass spectrometry (LC or GC-MS/MS) to quantify the different contaminants. Also, GC and LC coupled to high-resolution mass spectrometry with an Orbitrap or time of flight mass analyzers has been used in a targeted and non-targeted approach for quantitative analysis and to extend the number of other potential contaminants present in the samples. Our results reveal specific geographical contamination patterns according to the anthropogenic pressures in each sampled colony and time variations related to the use and prohibitions of several commercial formulations. Also, the use of gull eggs as biomonitors permit to evaluate the impact of environmental pollutants in other species sharing habitat and with similar diet, as observed for protected gull species (Larus audouinii), flamingos (Phoenicopterus roseus) or shearwaters (Calonectris diomedea). Overall, we propose the use of gull eggs as environmental biomonitors to identify the pollution status of areas of high ecological interest and to contribute to the implementation of management and conservation actions against chemical pollution.

Acknowledgements
This work was supported by the Spanish Ministry of Science and Innovation with the Excelencia Severo Ochoa Project CEX2018-000794-S and project PID2019-105732GB-C21.

References

Zapata et al. Presence and impact of Stockholm Convention POPs in gull eggs from Spanish and Portuguese natural and national Parks (2018). Sci. Total. Env. 633, p. 704. https://doi.org/10.1016/j.scitotenv.2018.03.081.

Colomer-Vidal, P. et al. Distribution and ten-year temporal trends (2009-2018) of perfluoroalkyl substances in gull eggs from spanish breeding colonies (2022). Environmental Pollution, 293, p. 118555. https://doi.org/10.1016/j.envpol.2020.118555.

Targeted and Non-Targeted PFAS Analysis in Environmental Matrices by LC/Q-TOF

L. Zingaro [1]*, Nicola Cimino [1], Sophie Tirat [1], Tarun Anumol [2]

[1] Agilent Technologies, Cernusco S/N, Milano, Italy
[2] Agilent Technologies, Inc. Wilmington, DE, USA

lorenzo_zingaro@agilent.com

Per and Polyfluoroalkyl Substances (PFAS) have been recognized as emerging contaminants by several organizations around the world. New regulations have been issued to address and report analysis of these compounds in many matrixes according to specific limits (LOD). Current deterction limits, matrices variety and chemistry complexity for these compounds make the method development a challenge for most of laboratories. In this work we present analytical solution to perform a robust and reliable method by targeted and non targeted approach using High Resolution LC/MS system.
This work shows an instrument demonstration of the Agilent 6546 quadrupole time-of-flight LC/MS for the analysis of PFAS compounds to meet sensitivity levels and all performance criteria mentioned in US EPA Method 533, while also allowing users to perform screening of other PFAS or nontargeted identification of unknown and emerging PFAS with LC-Q/TOF.
The analysis of PFAS is usually perfumed using LC/TQ to achieve the regulated extraction recovery, method reporting levels, and precision. We replace the detector and use an LC/Q-TOF instead of TQ to show performance criteria for EPA Method 533 met with the Agilent 6546 LC/Q-TOF.

References

K. Hunt, R. Hindle, T. Anumol, J. Pyke, C. Klein, Quantification of Per and Polyfluoroalkyl Substances in Drinking Water, Agilent Application Note 5994-3648EN

K. Hunt, R. Hindle, T. Anumol, J. Pyke, C. Klein, Quadrupole-Resolved All Ions (Q-RAI) Analysis of Select PFAS Chemicals on an Agilent 6546 LC/Q-TOF, Agilent Application Note 5994-3966EN

K. Hunt, R. Hindle, T. Anumol, EPA Method 533 for Analysis of Per/Polyfluoroalkyl Substances in Drinking Water Using Agilent 6470 Triple Quadrupole LC/MS, Agilent Application Note 5994-1628EN

Pesticide Occurrence in Edible Insects from Asia, Europe and Africa Using Liquid Chromatography Coupled to High-Resolution or Tandem Mass Spectrometry

A. M. Schönleben[1]*, S. Yin[1], L. Belova[1], Y. Ait Bamai[1], A. van Nuijs[1], G. Poma[1], A. Covaci[1].

[1] University of Antwerp, Toxicological Centre, Universiteitsplein 1, 2610 Wilrijk, Belgium

AliciaMacanSchonleben@uantwerpen.be

With a continuously growing world population, alternative food sources with high nutritional value are becoming increasingly important and will be a crucial factor in the global food system (FAO, 2018a). Insects have already proven to be a valuable protein alternative, due to their high nutritional value, their limited use of resources and reduced emission of greenhouse gases compared to common livestock (FAO, 2013). In the past years, the European Union has added edible insects to the list of novel foods, allowing an increasing number of insect-based food products into the European market. With insects gaining more popularity in the Western world, it is crucial to investigate their chemical food safety and to move forward with this novel protein source.

In this study, we investigated the occurrence of current-use pesticides (CUPs) in edible insects (n=49) purchased from Africa, Asia and Europe, by applying suspect screening and semi-quantification approaches. The analysis for the suspect screening was carried out using liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS). A suspect list was developed containing different pesticide classes and the results were then confirmed by matching against open-source databases (MassBank, mzCloud) and in silico prediction tools (MS Fragmenter, CFM-ID). For semi-quantification of 50 selected CUPs liquid chromatography-tandem mass spectrometry (LC-MS) was used. For the extraction of the insect samples, a QuEChERS method was performed, using acetonitrile and an additional hexane fraction for removal of lipids.

A total of 26 CUPs were identified using suspect screening, 18 of these with confidence level (CL) 2 and 9 with CL3, according to the classification proposed by Schymanski et al. 2014. With the semi-quantification approach, a total of 30 compounds were detected in the insect samples above the limit of quantification, out of which 9 compounds had a detection frequency higher than 30%. With semi-quantification, the neonicotinoid imidacloprid was detected in 70% of the samples, followed by fipronil with 48%. The highest measured CUP concentration in the samples was piperonyl butoxide, with a concentration of ~500 ng/g wet weight in a giant water bug (Lethocerus americanus) sample purchased from Thailand. While this was only a semi-quantitative approach, it can still be used as an indicator for CUP contamination in edible insects and offers an understanding of the magnitude of pesticide concentrations. When comparing with maximum residue levels (MRLs) for meat, the concentrations of the individual pesticides were generally below the respective internationally defined MRLs. However, the organophosphate dichlorvos was found in the same order of magnitude of the MRL value in three samples. Fipronil was also detected in concentrations close to the MRL value in a cicade from Thailand.

While future work is needed to improve quantification of CUPs in edible insects and to accurately assess their chemical food safety, this study offers novel and useful insights into the occurrence of different CUPs and their contamination levels in diverse edible insect species from around the world.

References

FAO (2018a) ‘Future of Food and Agriculture: Alternative Pathways to 2050.’. Rome.

FAO (2013) Edible insects: Future prospects for food and feed security. (FAO forestry paper, 171). Rome: Food and Agriculture Organization of the United Nations. Available at: http://www.fao.org/docrep/018/i3253e/i3253e.pdf.

Schymanski, E.L. et al. (2014) ‘Identifying small molecules via high resolution mass spectrometry: communicating confidence’, Environmental Science & Technology, 48(4), pp. 2097–2098. doi: 10.1021/es5002105.

Prioritizing Molecular Formulae Identified by Non-Target Analysis Through High-Throughput Modelling: Application to Identify Compounds with High Human Accumulation Potential from House Dust

F. Wania[1]*, Z. Zhang[1,2], L. Li[1,2], H. Peng[3]

[1]University of Toronto Scarborough, Department of Physical and Environmental Sciences, 1265 Military Trail, Toronto, Ontario, Canada M1C 1A4
[2]University of Nevada Reno, Reno, School of Public Health, Nevada, USA
[3]University of Toronto, Department of Chemistry, 80 St. George Street, Toronto, Ontario, Canada M5S 3H4

frank.wania@utoronto.ca

Non-target analysis (NTA) is gaining popularity as a screening-level analytical technique due to its ability to efficiently detect tens of thousands of chemicals in environmental samples with minimal pre-treatment. One of the key challenges during NTA is the sheer number of chemical features present in a sample, which is typically too large to pursue compound identification efforts for all of them. This creates the need for tools that aid in the prioritisation of such features. Here we introduce a strategy that may be useful in selecting features worthy of efforts to ascertain their molecular identity. This strategy seeks to rank chemical features based on a model derived metric that quantifies an attribute of a feature that makes it desirable to elucidate its structure, e.g., properties that lead to a high potential to cause human or wildlife exposure.

We start with the molecular formulae assigned to chemical features detected through NTA of a particular type of sample. The next step involves the identification of isomers that could plausibly represent each of these formulae. For each identified isomer, the properties required in the calculation of the prioritization metric are predicted using high-throughput methods. The prioritization metric for each molecular formula is calculated either by using in the model the average properties of the isomers representing that formula or by averaging the model-calculated metrics of those isomers. Finally, the molecular formulae are ranked based on the numerical values of the prioritization metric. The chemical features with the highest ranked molecular formulae are then singled out for structure elucidation.

In a proof-of-concept study we applied this workflow to 558 chemical features identified in house dust samples, using as the prioritization metric a model predicted blood-to-dust ratio (R), which is a unitless quotient between chemical concentrations in human blood and dust. The sampling and analysis of the house dust was described in Dhunagana et al. (2019). The assignment of 558 molecular formulae to these chemical features was accomplished with the DIPIC-Frag method (Hui et al. 2015). We assembled collections of isomers for these molecular formulae through a PubChem search that was automated using python code. Using chemical partitioning and biotransformation properties for these isomers predicted from molecular structure using quantitative structure property relationships based on the Iterative Fragment Selection algorithm, we estimated R. Finally, we identify the molecular formulae with the highest R and compare the calculated R with those of compounds that are known to bioaccumulate in humans as a result of exposure to house dust.

Our premise is that the higher the average R calculated for a molecular formula, the more likely this formula corresponds to a molecule that can accumulate in the human body, and therefore a structure elucidation is warranted. If the average R predicted for a collection of isomers is small, we infer that the concern associated with that formula is not high and the elucidation of its exact structure is of lower priority.

References

Dhungana, B. et al. (2019) 'Abundances and concentrations of brominated azo dyes detected in indoor dust', Environ. Pollut. 252, p. 784-793.

Peng, H. et al. (2015) 'Untargeted identification of organo-bromine compounds in lake sediments by ultrahigh-resolution mass spectrometry with the data-independent precursor isolation and characteristic fragment method', Anal. Chem. 87, p. 10237-1-246.

Analysis of Fish Samples by GC-Orbitrap Applying the ROIMCR Chemometric Approach

A. Queral-Beltran[1]*, R. Tauler[1], P. Pastorino[2] and S. Lacorte[1]

[1]Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Department of Environmental Chemistry,
Carrer de Jordi Girona 18-26, Barcelona, Spain
[2]The Veterinary Medical Research Institute for Piemonte, Liguria and Valle d'Aosta, via Bologna 148, 10154 Torino, Italy

aina.queral@idaea.csic.es

Fish samples from two high-altitude lakes in the Alps (Upper and Lower Balma Lakes, Cottian Alps, Italy) were analyzed because of their potential use as indicators of overall environmental change and "early warning systems" for the mountain environment. The objective was to determine the presence of legacy Persistent Organic Pollutants (POPs) and emerging contaminants associated to long range transport or human footprint.

Fish samples were homogenized, weighed and spiked with a mixture of labeled surrogate internal standards. A generic extraction method in an ultrasonic bath was performed with hexane:dichloromethane 1:1 (v/v) and clean-up with Florisil Solid Phase Extraction (SPE) cartridges using hexane:dicholomethane. The eluate was evaporated and reconstituted with 500 µL of isooctane. Analysis was performed using a TRACE 1310 Gas Chromatograph coupled to a ThermoScientific Q Exactive Orbitrap with electron ionization at 70 eV. Chromatographic separation was carried out on an Agilent HP-5MS UI (30 m length x 0.25 mm internal diameter x 0.25 µm film thickness) fused-silica capillary column. Data were acquired in full scan mode, using a mass range from 70 to 1000 m/z and at a resolution of 60000.

All analytical data generated was processed using the ROIMCR chemometrics method (de Juan & Tauler, 2016; Dalmau et al., 2018) in order to solve and identify in a non-target approach the chemical compounds detected in the samples. This procedure was first validated using spiked fish samples and permitted to determine with confidence 41 POPs and to quantify them using internal standard calibration. Thereafter, the fish samples collected from both lakes were processed in the same way and a suite of 17 emerging contaminants were tentatively identified. Results also revealed that fish from the Alps contained endrin, dieldrin, 4,4'-DDE, hexachlorobenzene, hexachlorobutadiene, various polychlorinated biphenyls (PCBs), among others, at concentrations ranging from 0.01 to 98 ng/g wet weight (w.w.).

This study highlights the potential of ROIMCR for the non-target screening of GC-Orbitrap-MS data to identify emerging contaminants and POPs in biota samples, which even at low concentrations can have an environmental impact. The results herein obtained indicate that theoretically pristine remote areas are affected by chemical pollution.

References

de Juan, A. et al., (2016) 'Multivariate Curve Resolution-Alternating Least Squares for Spectroscopic Data', Data Handling in Science and Technology, 30, pp. 5–51. doi:10.1016/B978-0-444-63638-6.00002-4.

Dalmau, N., et al. (2018) 'Validation of the Regions of Interest Multivariate Curve Resolution (ROIMCR) procedure for untargeted LC-MS lipidomic analysis', Analytica Chimica Acta, 1025, pp. 80–91. doi:10.1016/J.ACA.2018.04.003.

Regulatory Use of Non-Target Screening Data in the Aquatic Environment

A. L. Kronsbein[1]*, A. Badry[1], K. S. Jewell[2], N. Bandow[1], J. Koschorreck[1]

[1]German Environment Agency (Umweltbundesamt), Department of Water and Soil, Woerlitzer Platz 06844, Dessau-Roßlau, Germany
[2]Federal Institute of Hydrology, Department of Aquatic Chemistry, Am Mainzer Tor 1, 56068 Koblenz, Germany

AnnaLena.Kronsbein@uba.de

With its Zero Pollution Ambition the EU Green Deal aims for a toxic-free environment and a better protection of human health from hazardous substances. However, current environmental programs monitor chemicals with conventional target analysis that only capture a small part of the marketed substances in water bodies. Comprehensive analytical methods such as Non-Target Screening (NTS) provide a broader overview on contaminants of emerging concern (CECs) in the aquatic environment but are not yet routinely implemented on a regulatory scale. So far, NTS data are challenging for authorities, e.g. because guidance is still missing for the use of non-quantitative data. Environmental monitoring programs, in turn, frequently lack regulatory information on CECs such as hazard parameters, use categories, or production volumes. Up to now, there is no such curated substance information available that provides data across substance legislations. In 2022, the German Environment Agency (UBA) initiated the project ‘Ad-hoc assessment for water monitoring of the future’ to overcome this shortcoming and add specific regulatory information to the German database ‘NTS Portal’. In this project, we intend to develop ad-hoc risk assessment options for CECs identified by NTS and provide tools for rapid prioritization according to their persistence, bioaccumulation and toxicity. In addition to individual CECs we also aim to characterise their mixtures, ubiquitous compounds, point sources, and temporal trends in riverine samples. Here, we present examples from different EU chemical legislations (e.g. biocides, pharmaceuticals, plant protection products, REACH) for an ad-hoc assessment of substances that were identified and prioritised using established NTS workflows. Linking substance hazard information with environmental monitoring data in a centralised database is crucial for dealing with the registered/authorised substances on the EU market and will strengthen the connection between regulation and science.

Analytical Workflow for Chemical Exposomics in Human Plasma by Gas Chromatography High Resolution Mass Spectrometry

H. Xie[1], K. Sdougkou[1], S. Papazian[1], J. W. Martin[1]

[1] Stockholm University,Science for Life Laboratory, Department of Environmental Science, Stockholm, 114 18 Sweden

The challenge of the human exposome is to comprehensively quantify all environmental exposures throughout an individual's lifespan (Wild, 2005) with knowledge that most chronic diseases have an environmental etiology (Rappaport, 2010), techniques to measure the exposome (i.e. exposomics) are of increasing importance. The chemical exposome is a particularly complex challenge due to over 350,000 chemicals in commerce today, and only a few hundred of these have historically been biomonitored in human biofluids by targeted methods (Wang, 2020). Here, a workflow was developed that combines sensitive nontarget molecular discovery with multi-target quantification of 103 priority environmental contaminants in small volumes of individual blood plasma. A major objective was to minimize interference by lipids, which have not been addressed by existing methods, to enable injecting larger extract volumes (i.e. 25 µL) on-column and achieve better sensitivity by gas chromatography (GC) - high resolution mass spectrometry (Orbitrap). The extraction and cleanup were optimized for the wide range of target analytes (log K_{ow} range, 1.7 - 11.2) from 6 classes, including polychlorinated biphenyls, halogenated flame retardants, dioxins, polycyclic aromatic hydrocarbons, organochlorine pesticides, and phthalates. Validated method quantification limits were as low as 0.005 ng/mL (with a mean value at 0.118 ng/mL) for a 200 µL plasma sample. The developed workflow had high sensitivity, recovery, and reproducibility for target analytes and enabled nontarget contaminant discovery by open source data processing (MS-DIAL) with spectral matching to multiple spectral libraries (NIST, MassBank, GNPS). Application of the method to Swedish cohort studies revealed inter- and intra-individual variability of the chemical exposome, including based on lifestyle and dietary habits.

References

Wild, C. P.(2005) *Cancer Epidemiol. Biomarkers Prev.*, 14(8), 1847–1850.

Rappaport , S. M. (2010) *Science*, 330(6003), 460–461.

Wang, Z. (2020) *Environ. Sci. Technol.*, 54(5), 2575–2584.

Ice Cores: Unique Environmental Archives for Non-Target Screening Reconstructions of Natural and Anthropogenic Aerosol Compounds

F. Burgay[1,2*], D. Salionov[3], T. Singer[1,2,4], C. Huber[1,2,4], A. Eichler[1,2], S. Bjelić[3] & M.Schwikowski[1]

[1]Laboratory of Environmental Chemistry, Paul Scherrer Institut, 5232 Villigen, Switzerland
[2]Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland
[3]Bioenergy and Catalysis Laboratory, Paul Scherrer Institut, 5232 Villigen, Switzerland
[4]Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Bern, Switzerland

francois.burgay@psi.ch

Ice cores are unique environmental archives for reconstructing past climate and environmental conditions. To date, research has focused on inorganic aerosol components, whereas only a few specific organic compounds, like biomass burning tracers, marine phytoplankton oxidation products, low-molecular weight carboxylic acids and persistent organic pollutants have been studied. These compounds represent only a small fraction of the overall organic burden preserved in ice-core samples, meaning that the identity of the large majority of molecules remains unknown. Today, advances in high-resolution mass spectrometry (HRMS) unlock the possibility to explore a wider chemical space through the application of non-target screening (NTS) workflows, with great implications on our understanding of the Earth's system and on the anthropogenic impact on the environment.

Considering the broad physical and chemical properties of the molecules present in environmental samples, the definition of an appropriate sample preparation strategy and instrumental set-up is key to define the organic molecular classes that will be addressed. Additionally, since organic molecules in ice cores are usually present at sub-ppb levels, a pre-concentration step is often required for their instrumental detection.

We developed a method that includes a solid-phase extraction (SPE) enrichment followed by NTS using Ultra-High Performance Liquid Chromatography HRMS. The method is particularly suitable for the detection of water-soluble molecules and it was successfully applied on 50 meters of the Belukha ice core (Siberian Altai, 4072 m. a.sl.), providing the first NTS study of an ice-core record that embraces both the pre-industrial and industrial periods. The sampling site is mainly influenced by biogenic emissions, especially from herbs and conifers. Nevertheless, a significant increase in sulphate concentration (i.e. a proxy for the combustion of fossil fuels, mainly coal and oil) has been observed since the 1950s, meaning that the ice core tracks past (and present) environmental pollution mainly from Eastern Europe. Following a NTS workflow, we identified more than 4000 profiles. The application of hierarchical cluster analysis on the dataset allowed the identification of two clear temporal clusters (i.e. pre-industrial and industrial periods), as well as six distinct groups of molecules with different trends. Four of them are likely linked to anthropogenic activities (directly or indirectly) with significant increasing trends since the 1950s, consistent with other environmental contamination proxies.

With this work, we show the unique potential that ice cores have in reconstructing the temporal evolution of the molecular composition of both natural and anthropogenic aerosols, paving the way for future interdisciplinary NTS investigations on these environmental media.

Open and FAIR Transformation Product Data for Improved Suspect/Non-Target Screening: REFTPs in the NORMAN-SLE, Pubchem and Patroon

P. Chirsir[1]*, R. Helmus[2], E. E. Bolton[3], P. A. Thiessen[3], J. Zhang[3], E. L. Schymanski[1]

[1]Luxembourg Centre for Systems Biomedicine (LCSB), University of Luxembourg, 6 avenue du Swing, L-4367, Belvaux, Luxembourg
[2]Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, P.O. Box 94240, 1090 GE, Amsterdam, The Netherlands
[3]National Center for Biotechnology Information, National Library of Medicine, National Institutes of Health, Bethesda, MD, 20894, USA

parviel.chirsir@uni.lu

Non-target screening with high resolution mass spectrometry is widely used to identify chemicals in environmental, food and human samples. Processing this complex data includes both suspect and full non-target screening, which relies on the availability of machine-actionable chemical information in databases to help annotate potential compounds of interest in the data. Extremely valuable chemical information, including transformation product (TP) formation is often hidden in literature (e.g., in .pdf files, see Fig 1A), which poses a challenge to machine-actionability of such data. Making chemical data FAIR (findable, accessible, interoperable and reusable) in open databases (e.g., PubChem, Fig. 1B-C) will help improve the detection of chemicals and their TPs in the environment. Here we show how a FAIR dataset, REFTPs in NORMAN Suspect List Exchange (NORMAN-SLE) (Mohammed Taha et al., 2022), created to fill TP gaps in open databases, is applied to wastewater treatment plant samples from Pétange in Luxembourg (Fig 1D) using patRoon (Helmus et al., 2022) (Fig 1E) to identify chemicals of emerging concern, including PFOA and possible TPs (Fig 1F). This work demonstrates how connecting FAIR and Open resources helps provide seamless non-target mass spectrometry workflows for many use cases.

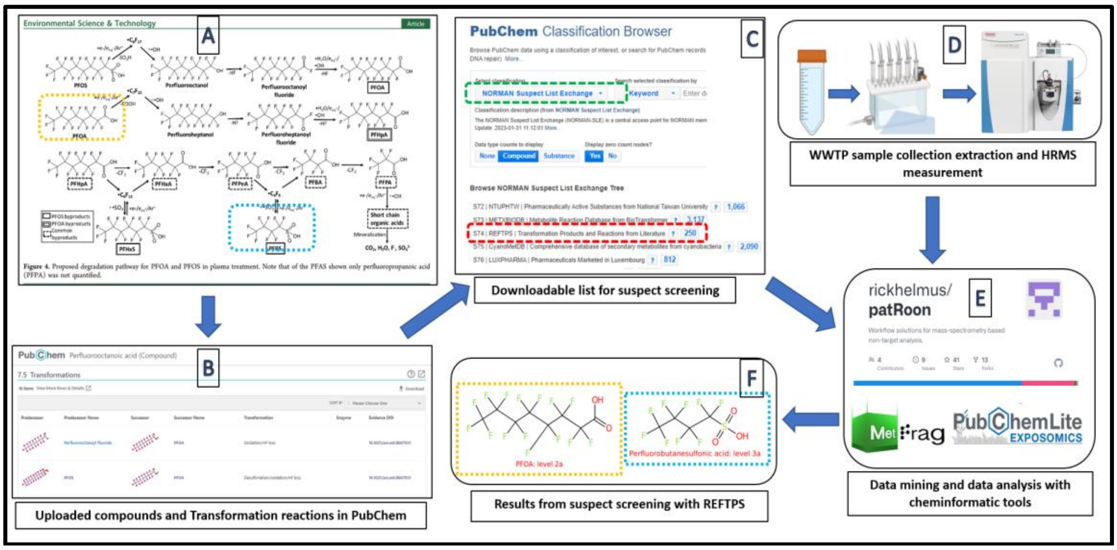


Figure 1: The Open and FAIR transformation product screening workflow

References

Helmus, R. et al. (2022) ‘patRoon 2.0: Improved non-target analysis workflows including automated transformation product screening’, Journal of Open Source Software, 7(71), p. 4029. doi:10.21105/joss.04029.

Mohammed Taha, H. et al. (2022) ‘The NORMAN Suspect List Exchange (NORMAN-SLE): facilitating European and worldwide collaboration on suspect screening in high resolution mass spectrometry’, Environmental Sciences Europe, 34(1), p. 104. doi:10.1186/s12302-022-00680-6.

Doxazosin Degradation – Photocatalytic Degradation Versus Gamma Irradiation

P. Trebše[1,2], M. B. Kralj[1], A. Lebedev[2]

[1]University of Ljubljana, Faculty of Health Sciences, Zdravstvena pot 5, 1000 Ljubljana, Slovenia
[2]Masseco d.o.o., Erazmova 20, 6230 Postojna, Slovenia

Polonca.trebse@zf.uni-lj.si

Pharmaceuticals and pharmaceutical active substances used in human and veterinary medicine (such as painkillers, antibiotics, hormones, anti-inflammatory drugs, lipid regulators, beta blockers, anti-cancer drugs) and represent a group of new pollutants, so called emerging pollutants. Their continuous release from communal wastewater effluents to the environment as complex mixtures can result in higher concentrations, long-term and negative effects on aquatic and terrestrial organisms. For these reasons various degradation pathways of pharmaceuticals have been studied by different methods to deepen the understanding of their fate in the aquatic compartments

Doxazosin, a selective alpha blocker, is widely used in medical therapy as an effective antihypertensive agent. It is very frequently prescribed drug and for this reason, environmental and ecotoxicological research is of great importance in terms of exposure and risk for both aquatic species and humans. In this study we focused on degradation of doxazosin using TiO2 photocatalysis as well as gamma irradiation, with the emphasis on identification of degradation products.

TiO2 photocatalytic and photolytic (without TiO2) experiments were performed in photoreactor equipped with polychromatic low-pressure mercury lamps (1.6 mW/cm2 of UVA (300 - 400 nm)) and have been carried out under constant oxygen flow (Tartaro Bujak et al., 2020). On the other hand, gamma irradiation experiments have been performed in a panoramic type 60Co-γ irradiation chamber. The applied dose rates were 0.65 Gy/s and 6,9 Gy/s. Doxazosin aqueous solutions were irradiated with 100 and 200 Gy in equilibrium with the air and the temperature was kept constant during the irradiation process at 20 ± 2 °C (Tartaro Bujak et al., 2023).

Selected samples have been further analyzed by LC-HRMS, which proved the formation of several degradation products, depending on reaction conditions (presence, absence of oxygen, photocatalysis, gamma irradiation).

Based on the exact masses, isotopic distribution, fragmentation pathways, and elemental compositions of the ions in the mass spectrum, the transformation products were identified. In the case of photocatalysis, dominated the products: C17H21N5O3 and C17H23N5O4 (cleavage of the dioxane cycle), and C23H25N5O7 (hydroxylation), while in the case of gamma irradiation C22H21N5O8 (demethylation and oxidation), C17H23N5O5 and C17H23N5O6 (cleavage of the dioxane cycle), C23H25N5O6 (hydroxylation), and C15H21N5O5 (cleavage of both dioxane and piperidine cycle). The detailed degradation pathway has been proposed and will be presented.

References

Tartaro Bujak, I. (2020) Photolytic and photocatalytic degradation of doxazosin in aqueous solution. Science of the total environment. 740, 140131-1-1401316-8, DOI: 10.1016/j.scitotenv.2020.140131.

Tartaro Bujak, I., et al. (2023) Radiation-induced degradation of doxazosin : role of reactive species, toxicity, mineralization and degradation pathways. Journal of water process engineering. 51, 1-12, DOI: 10.1016/j.jwpe.2022.103401.

Time-Trend Guided Non-Target Screening of Baltic Sea Blue Mussel (1994–2017) and Eelpout (1994–2017) by Gas Chromatography–High-Resolution Mass Spectrometry

A. Rebryk[1*] and P. Haglund[1]

[1]Umeå University, Department of Chemistry, Chemical Biological Centre (KBC), Linnaeus väg 6, 901 87, Umeå, Sweden

andriy.rebryk@umu.se

After restrictions were applied in 1970–1980s, the levels of regulated persistent organic pollutants (POPs) have declined drastically (Nyberg, E. et al. 2015). However, the levels of the contaminants of emerging concern (CECs), that in many cases suppose to serve as substitutions for the regulated ones, often increase in environmental samples (Rebryk, A. et al. 2022). To track these changes in two important Baltic Sea species, blue mussel and eelpout, a time-trend study was carried out using a gas chromatography–high-resolution mass spectrometry (GC-HRMS) based non-target screening (NTS). Data were acquired using electron ionization (EI) and electron capture negative ion chemical ionization (ECNI) and time-trend analysis was done using an improved version of previously published NTS data processing workflow (Rebryk, A. et al. 2022). This work revealed temporal trends for >170 tentatively identified compounds in blue mussel and >200 in eelpout as well as a number of compounds that demonstrated significant temporal trends but were not possible to identify (No ID); see Fig. 1. As was expected, regulated substances, such as PCBs, organochlorine pesticides (OCPs), and many polybrominated diphenyl ethers (PBDEs), demonstrated significant declining trends. Their rates of decline were in good agreement with published scientific data. In contrast, many CECs, some polycyclic aromatic compounds (PAHs), and hydrocarbons demonstrated increasing trends. Four CECs, namely, 4-isopropoxyaniline, bilobol dimethyl ether, 2-ethylhexyl stearate, and 1,2,3,5-tetrabromobenzene, were reported in marine biota for the first time, to the best of our knowledge.

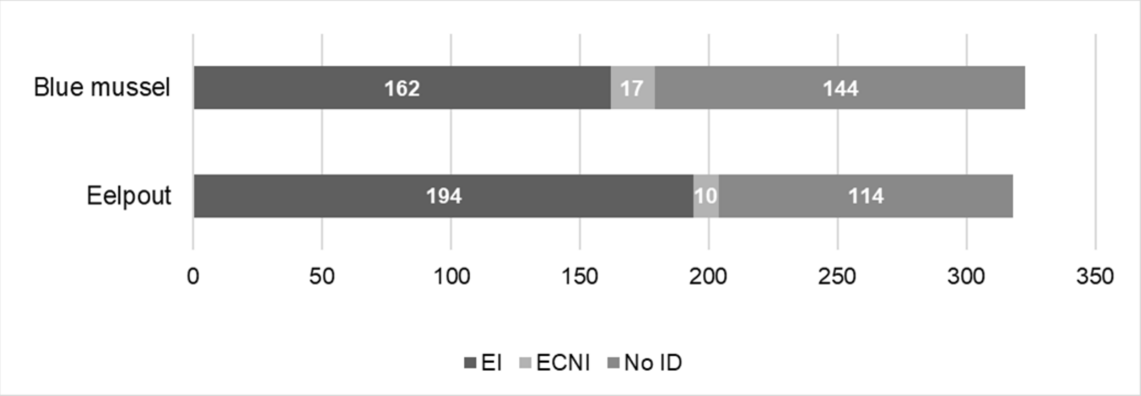


Fig. 1. Number of features with significant time-trends detected using EI and ECNI in Baltic blue mussel and eelpout.

References

Nyberg, E. et al. (2015) ‘Temporal and spatial trends of PCBs, DDTs, HCHs, and HCB in Swedish marine biota 1969–2012’, AMBIO, 44, p. 484-497.

Rebryk, A. et al. (2022) ‘A time-trend guided non-target screening study of organic contaminants in Baltic Sea harbor porpoise (1988-2019), guillemot (1986-2019), and white-tailed sea eagle (1965-2017) using gas chromatography-high-resolution mass spectrometry’, Sci Total Environ, 829, 154620.

Resolving Complex Mixtures of Microplastics, Plasticizers and Associated Contaminants in Air Samples Using Pyr-GC-Orbitrap

A. Torres-Aguló[1]*, R. Tauler[1], A. Karanasiou[1], S. Lacorte[1]

[1]Institute of Environmental Assessment and Water Research of the Spanish Research Council (IDAEA-CSIC), Jordi Girona 18-26, 08034, Barcelona, Spain.

ana.torres@idaea.csic.es

Microplastics (MP) in air is a matter of concern due to human health implications (Prata, 2018). The objective of the present study was to develop a non-targeted methodology to identify different MP polymers, associated additives and sorbed pollutants in particulate matter air samples by a pyrolysis process coupled to a gas chromatography-orbitrap mass spectrometer (Pyr-GC-Orbitrap). Optimization on multiple Pyr-GC-Orbitrap parameters was performed using ten different polymers (polyethylene terephthalate (PET), polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS), polycarbonate (PC), acrylonitrile butadiene styrene (ABS), poly(methyl methacrylate) (PMMA), nitrile rubber (NBR), and polyamide (PA)). Mass spectrometric large datasets were processed using the regions of interest multivariate curve resolution (ROIMCR) consisting in five-step identification procedure: i) data acquisition and conversion; ii) slicing across the chromatographic time and column-wise augmentation; iii) mass and time compression; iv) peak resolution and v) chemical identification. With this procedure, a significant reduction of the computer storage requirements without any significant loss of spectral resolution nor of accuracy on the measures is achieved. Finally, the optimized method was applied to different real indoor air samples, including department stores and gyms. As a result, volatile organic compounds (VOCs), plasticizers, flame retardants, and UV-light stabilizers were found in the samples. This work provides a detailed identification procedure in the ROIMCR non-target analysis, where a fast resolution of elution and spectra profiles is performed with no additional data pretreatment needed. The developed methodology permits the comprehensive characterizations of microplastics in air and associated contaminants to be further applied in a large air monitoring campaign to determine main contaminants, human exposure and risks.

This work was supported by the Spanish Ministry of Science and Innovation Project TED2021-131552B-C21, Excelencia Severo Ochoa Project CEX2018-000794-S and project PID2019-105732GB-C21. A. Torres-Agullo also acknowledges this Ministry for its financial support (predoctoral grant PRE2021-097960).

References

Prata, J.C. (2018) 'Airborne microplastics: consequences to human health?' Environ. Pollut. 234, 115–126. doi: https://doi.org/10.1016/j.envpol.2017.11.043.

Headspace-Solid Phase Microextraction Followed by Gas Chromatography Mass Spectrometry for Microplastics Identification and Quantification

U. Šunta [1], P. Trebše [1], M. Bavcon Kralj [1*]

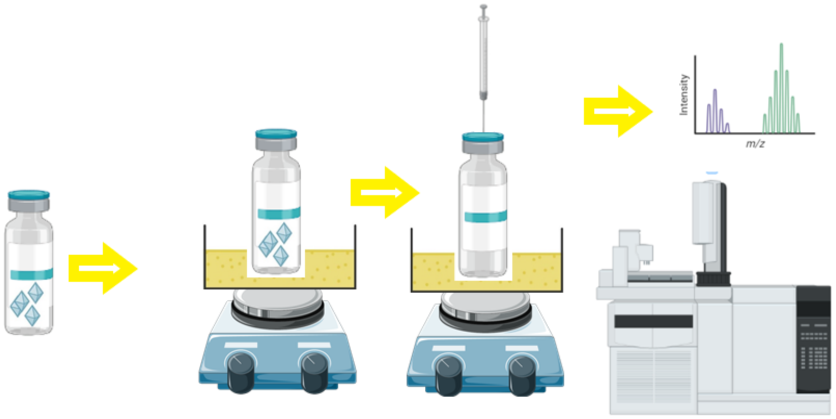
[1]University of Ljubljana, Faculty of Health Sciences, Department of Sanitary engineering, Zdravstvena pot 5, 1000 Ljubljana, Slovenia

mojca.kralj@zf.uni-lj.si

Microplastics (MPs) have gained significant attention predominately in the marine environment, lately, however, their presence, routes of entry, and impacts on the biota are raising scientific curiosity in the soil environment as well. One of the main issues in the study of MPs in soil is a lack of standardized methods for their identification and quantification. Commonly used techniques are Fourier-transform infrared spectroscopy (FTIR) and pyrolysis followed by gas chromatography mass spectrometry GC–MS.

In this study, the headspace-solid phase microextraction followed by GC–MS usually employed for food and aroma studies, was efficiently applied in the identification and quantification of polymers. During the well-controlled melting process of MPs from different polymers, characteristic compounds were formed (for PET: dimethyl terephthalate, for PS: styrene and dimer trans(cis)-1,2-diphenylcyclobutane, for PVC: chlorooctane, for PE: eicosane). A high linear relationship ($0.80 < R2 < 0.99$) between the signals of characteristic compounds and their number was observed in the case of all four types of polymers tested. Finally, the method was upgraded for the identification and quantification in different matrices (from compost, alluvial soil, algae biomass, and intestines from fishes) and showed promising results. This method could be thus, proposed as a simple and widely applicable for the determination of commonly present polymers in soils worldwide.

Acknowledgements: The Slovenian Research Agency (ARRS): No. P3-0388, Young researchers' programme (ARRS 1000-22-0510).



MPs melting, head space solid phase micro extraction, GC-MS identification

References

Šunta, U. et al. (2021), Simply Applicable Method for Microplastics Determination in Environmental Samples, Molecules, 26, p. 1840. doi.org/10.3390/molecules26071840

Prosenc, F. et al. (2021), Extraction and Identification of a Wide Range of Microplastic Polymers in Soil and Compost Polymers, 13, p. 4069. doi.org/10.3390/polym13234069.

Addressing the Occurrence of Drugs of Abuse and New Psychoactive Substances in Educational Institutions using Wastewater Analysis

T. Verovšek[1,2]*, I. Krizman-Matasic[3], A. Celma[4], L. Bijlsma[5], F. Hernández[5], D. Heath[2], E. Heath[1,2]

[1]Jožef Stefan Institute, Jamove 39, 1000 Ljubljana, Slovenia
[2]Jožef Stefan International Postgraduate School, Jamove 39, 1000 Ljubljana, Slovenia
[3]Rudjer Boskovic Institute, Bijenicka 54, 10000 Zagreb, Croatia
[4]Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, SE-750 07, Uppsala, Sweden
[5]Research Institute for Pesticides and Water, University Jaume I, Avda Sos Baynat s/n, 12006 Castellón, Spain

taja.verovsek@ijs.si

The use of both licit and illicit drugs has a negative impact on the health of young people and can pose challenges to their future success and position. Recently, there has been concern about experimentation with new psychoactive substances (NPS), which are widely available online. However, very little is known about their identity and toxicity, putting NPS users at greater risk of intoxication. Since educational institutions are deemed crucial drug-free zones, surveys and drug testing are implemented to identify and assess drug usage among school-aged children and students. Addressing drug use in this age group is particularly important for establishing effective prevention programs, as risky drug use is connected to early use. Nevertheless, conventional methods have their limitations and ethical considerations; hence, alternative approaches are desirable. Accordingly, in this study, the application of non-invasive wastewater analysis was explored for evaluation of the occurrence of licit drugs, medications of abuse, conventional illicit drugs and NPS in educational institutions.

Forty-four educational institutions were included in the study; 19 primary schools (age: 6–15), 10 secondary schools (age: 15–19), six mixed secondary and higher education institutions (age 15+) and nine higher education institutions (age 19+) from urban and non-urban areas of seven Slovenian municipalities. Raw wastewater samples from the institution's sewer outlets were collected as seven-hour composites during class at the end of the 2018/2019 academic year. After extracting the samples, metabolic residues of two licit drugs (nicotine and alcohol), three medications of abuse (morphine, codeine and methadone) and six illicit drugs (cannabis, cocaine, amphetamine, methamphetamine, ecstasy and heroin) were determined using reverse-phase liquid chromatography coupled to tandem mass spectrometry, LC-MS/MS (Verovšek et al., 2021). In addition, 23 samples from institutions in two municipalities were analysed using liquid chromatography coupled to ion mobility separation and high-resolution mass spectrometry, LC-IMS-HRMS (Celma et al., 2020), and screened using a suspect list of more than 5600 compounds.

Nicotine and alcohol, both licit drugs, were commonly detected in educational institutions (detection frequency, DF ≥ 80%), while among medications of abuse, only morphine (DF=40 %) and codeine (DF=23%) were detected. Cannabis was the most prevalent conventional illicit drug (DF=93%), followed by cocaine (DF ≥50%). The most common NPS were synthetic cathinones, with 3-MMC, ephedrine, 4-chloro-α-PPP and ethcathinone being identified unequivocally. The educational level was the primary factor in the prevalence of both licit and conventional illicit drugs in educational institutions. Conversely, geographic location has the most significant effect on the presence of NPS. While wastewater analysis in its current form can only provide data on the entire institutional population and not individual groups, e.g., schoolchildren, students, staff or visitors, it is still a valuable non-invasive alternative to methods such as drug testing.

References

Celma, A., et al. (2020) 'Improving target and suspect screening high-resolution mass spectrometry workflows in environmental analysis by ion mobility separation', Environmental Science & Technology, 54(23), 15120-15131. https://doi.org/10.1021/acs.est.0c05713.

Verovšek, T. et al. (2021) 'Investigation of drugs of abuse in educational institutions using wastewater analysis, 'Science of The Total Environment, 799, 150013. https://doi.org/10.1016/j.scitotenv.2021.150013.

Chlorinated Organic Compounds in Concrete as Specific Markers for Chlorine Gas Exposure

N. Hamzah[1]*, K. Höjer Holmgren[2], C. Åstot[2], M. J. van der Schans[3], L. De Reuver[3], A. Valtanen[1], H. Hakulinen[1], P. Vanninen[1]

[1]University of Helsinki, Finnish Institute for Verification of the Chemical Weapons Convention (VERIFIN), Department of Chemistry, P.O. Box 55, FI-00014 Helsinki, Finland
[2]The Swedish Defence Research Agency, FOI CBRN Defence and Security, SE-901 82 Umeå, Sweden
[3]TNO Defence, Safety and Security, Dep. CBRN Protection, Lange Kleiweg 137, 2288GJ Rijswijk, The Netherlands

nurhazlina.hamzah@helsinki.fi

Chlorine is a toxic chemical with a dual use for both civil and military purposes. Chlorine is highly reactive, rapidly transforming in environment into various relatively stable products that can serve as markers of chlorine exposure (Zelner and Eyer, 2020). This study has examined the formation of chlorinated organic chemicals in concrete samples after chlorine exposure.

Six concrete samples from different origins and ages were selected since their compositions may vary. Concrete samples were exposed to various types of reactive chlorine, including bleach and chlorine gas. The Recommended Operating Procedures for Analysis in the Verification of Chemical Disarmament (ROP) method was used (Vanninen, 2017). The concrete extracts were first analysed for targeted chlorinated organic chemicals such as chlorophenols by both gas and liquid chromatography-tandem mass spectrometry (GC-MS/MS and LC-MS/MS) in the multiple reaction monitoring (MRM) mode. The same extracts were also then analysed by untargeted screening using high-resolution mass spectrometry (GC-HRMS and LC-HRMS) to look for other chlorinated organic compounds that may have formed. Compound Discoverer version 3.3 was utilized for peak identification, and SIMCA version 17 was used for all multivariate analyses to determine systematic differences between concrete samples and various types of reactive chlorine.

Chlorinated phenols have been suggested as markers when concrete is exposed to reactive chlorine (OPCW, 2023) and this was confirmed by the performed experiments. Additionally, we also propose chlorobenzenes, chloromethoxyphenols, chloromethoxybenzenes, and chlorobenzoquinones as markers to be used in investigations of chlorine exposure. The result also showed that the number of chlorine atoms present in the chlorinated compounds was proportional to the initial chlorine concentration to which the concrete samples were exposed to. Dichlorophenols were present in concrete samples exposed to 500 ppm chlorine gas and trichlorophenol was found when using neat chlorine gas. Among the chlorinated phenols only tetrachlorophenol was specific form after neat chlorine gas exposure. The others as dichlorophenols and trichlorophenol were also produced by bleach. The levels of chlorinated phenols were much higher in two old concrete samples from the 1930s and 1950s exposed to neat chlorine gas. We presumed that phenolic sources originated in the concrete samples from old buildings. These findings were supported when chlorination experiments were performed on two different concrete samples spiked with suspected precursor materials namely phenol and lignin. It is our hypothesis that lignin present in surface pit ballast for concrete production contains enough degraded lignin to provide enough phenolic precursors to produce chlorinated phenols after chlorine exposure.

Among six different concrete samples, old concrete samples from the 1930s and 1950s had the most chlorinated chemicals compared to other concretes types.

References

Zellner, T. and Eyer, F. (2020) ‘Choking agents and chlorine gas – History, pathophysiology, clinical effects and treatment’, Toxicology Letters, 320, pp. 73–79. doi: 10.1016/j.toxlet.2019.12.005.

Vanninen, P. (2017) Recommended Operating Procedures for Analysis in the Verification of Chemical Disarmament (ROP). 2017th edn. University of Helsinki. ISBN: 978-951-51-3917-7.

Technical Secretariat of The Organisation for the Prohibition of Chemical Weapons. (2023) ‘Third Report by the OPCW Investigation and Identification Team Pursuant to Paragraph 10 of Decision C-SS-4/DEC.3 “Addressing the Threat from Chemical Weapons Use”, Douma (Syrian Arab Republic) - 7 April 2018’, Vol. 4124.

Analytical and Effect-Based Methods Available for the Environmental Monitoring of Endocrine Disrupting Compounds at the EU Scale

P. Benoit[1], S. Andrès[2], N. Alygizakis[3], N. Creusot[4], C. Miège[5], S. Aït-Aissa[2], E.L. Schymanski[6], L.I. Bengtström[7],
V. Dulio[2], K. Vorkamp[7]* and the PARC T4.2 EDC group

[1]INRAE, ECOSYS, 91120 Palaiseau, France
[2]INERIS, 60550 Verneuil en Halatte, France
[3]National and Kapodistrian University of Athens, Athens 15772, Greece
[4]INRAE, EABX, 33612 Cestas, France
[5]INRAE, RIVERLY, 60625 Villeurbanne, France
[6]LCSB, University of Luxembourg, 4367 Belvaux, Luxembourg
[7]Aarhus University, Environmental Science, 4000 Roskilde, Denmark

kvo@envs.au.dk

The Partnership for the Assessment of Risks from Chemicals (Marx-Stoelting et al., 2023) includes a pilot project for the establishment of environmental monitoring that focusses on per- and polyfluoroalkyl substances (PFAS) and endocrine disrupting compounds (EDCs). Our ambition for EDCs is to contribute to the first EU baseline in multiple environmental compartments and to identify new key EDCs present in the environment. We intend to integrate approaches based on target analysis, non-target and suspect screening as well as effect-based methods (batteries of multi-receptor in vitro and in vivo bioassays), including their combination in effect-directed analysis (EDA) to identify major toxicants in prioritised samples. A comprehensive list of EDCs was compiled, based on previous assessments by regulatory bodies at EU and national level (e.g. (http://edlists.org) and additional potential EDCs (hormones, bisphenols, etc.), including inputs from ECHA. Furthermore, all substances in the NORMAN SusDat database (https://www.norman-network.com/nds/susdat/) were screened using the EDC prediction models of the (QSAR) VEGA platform (https://www.vegahub.eu/about-qsar/), and the EDC active compounds were added. The final list contained approximately 7300 chemicals. Further information was added, such as physico-chemical properties, functional groups for chemical analysis, modes of action for the application of bioassays, relevant matrices for monitoring, use sectors.

In order to relate the list of EDCs to analytical methods, the compounds on the list were assigned to chemical classes. We worked with 75 chemical classes and assigned invidual compounds according to their chemical structure and SMILES automatic recognition. This information was compiled through a collaborative work of the PARC T4.2 EDC group. Concerning the effect-based methods, a previous review was used to list key information required, such as type of endpoints, species, adverse outcome pathways, thresholds, chemical classes, matrices etc. (Carrere et al., 2021). We have obtained a first comprehensive picture of potential applications of target and suspect screening as well as in vitro and in vivo bioassays for the quantification/detection of EDCs. This work highlights compounds and chemical classes still poorly studied and/or environmental matrices inadequately monitored. Another outcome is a restricted list of standardized methods/assays implementable for routine monitoring. This information will be used to prepare focused and cost-effective monitoring campaigns within this PARC pilot project.

PARC T4.2 EDC group : A. Araja, L. Ahrens, S. Buchinger, C. Coscolla, A. Covaci, M. Creta, G. Dervilly, B. Dewitte, D. Dvorakova, R. Duca, J.P. Ghestem, J. Grimalt, C. Kech, M. Krauss, T. Kosjek, A. Lopez, S. Maletz, C. Moyano, M. Nicolas, J. Pulkrabova, P. Rostkowski, G. Thorsén, J. Trontelj, E. Van Hoeck, R. Duca, M Schlüsener, E. Vermeirssen, J. Viidanoja

This work was carried out in the framework of the European Partnership for the Assessment of Risks from Chemicals (PARC) and has received funding from the European Union’s Horizon Europe research and innovation programme under Grant Agreement No 101057014.

References

Carrere M. et al. (2021) Report to the Common Implementation Strategy (CIS) Working Group Chemicals on the outcome of the work performed in the subgroup on Effect-Based Methods (EBM). MANDATE 2016-2018.

Marx-Stoelting P. et al. (2023) A walk in the PARC: developing and implementing 21st century chemical risk assessment in

Europe. Archives of Toxicology, https://doi.org/10.1007/s00204-022-03435-7

Exploring Structure Database, Suspect and Non-Target HRMS Workflows for Comprehensive Screening of Unknown Transformation Products of Pharmaceuticals in Complex Environmental Matrices

L.A. Koronaiou[1,2], C. Nannou[3], E. Evgenidou[1,2], D. P. Abrahamsson[4], D. A. Lambropoulou[1,2]*

[1]Aristotle University of Thessaloniki, Laboratory of Environmental Pollution Control, Department of Chemistry, GR-541 24 Thessaloniki, Greece
[2]International Hellenic University, Center for Interdisciplinary Research and Innovation (CIRI-AUTH), Balkan Center, Thessaloniki, GR-57001, Greece
[3]Department of Chemistry, Kavala, GR-65404, Greece
[4]Department of Pediatrics, NYU Grossman School of Medicine, NY 10016550, New York, USA

dlambro@chem.auth.gr

Through the last decade, a shift in monitoring environmentally relevant compounds has taken place, advancing from targeting known pollutants to non-target analysis (NTA) and suspect screening (SS), thus expanding the range of results to compounds for which the information is limited and would slip through the cracks of NTA, such as transformation products (TPs) (Schymanski, E. L., et. al., 2014). However, ready-to-use non-target workflows present limitations regarding the number of results, when no additional suspect list is considered, when aiming to identify transformation products, especially when the search is based on existing online databases. In this context, a customized overview of transformation of pharmaceuticals in aqueous matrices treated by photo-oxidation is provided as a proof of concept. To this end, the primary goal of the study was to display an integrated strategy by combining the target (parent molecules) and suspect screening approaches (TPs) in order to build an HRMS database able to provide reference information (chromatographic and spectral) for environmental investigations. Furosemide (FUR), a widely prescribed diuretic drug has been used as model compound. High-resolution and high mass accuracy data, isotopic profile, along with characteristic fragments from an HRMS Orbitrap mass analyzer equipped with a heated ESI source operating in negative ionization and ddMS "Discovery" mode, lead to the tentative elucidation of novel TPs and revealed a complex interconnected transformation pathway. Additionally, correlation of the proposed structures with their respected experimental retention time using three prediction models employing logKow, Retip (Bonini et al., 2020), and calculated polyparameter Linear Solvation Energy Relationship (pp-LSER) descriptors as variables provided an additional level of confirmation while highlighting outlier structures that needed further investigation. This holistic approach was applied for the tentative identification of 35 TPs of FRS, 28 of which are reported herein for the first time. Finally, suspect screening based on a comprehensive in-lab database enabled through a step-by-step optimized workflow for the identified TPs in influent and effluent wastewaters led to the tentative identification of 6 TPs, among them, saluamine was detected, a known metabolite of furosemide. On the contrary, non-target analysis performed on the same sample set underlining the important role of extensive databases and suspect screening approaches for the identification of TPs of known emerging contaminants in complex matrices such as wastewaters and landfill leachates.

Funding: This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship, and Innovation, under the call RESEARCH – CREATE – INNOVATE (2nd Cycle) (Project acronym: UV-LEACH; Project code: T2EDK-00137).

References

Schymanski, E. L., et. al., (2014). Identifying small molecules via high resolution mass spectrometry: Communicating confidence. Environmental Science and Technology, 48(4), 2097-2098. doi:10.1021/es5002105.

Bonini, P. et al. (2020) 'Retip: Retention Time Prediction for Compound Annotation in Untargeted Metabolomics', Analytical Chemistry, 92(11), pp. 7515–7522. doi:10.1021/acs.analchem.9b05765.

Landfill Leachates as a Prominent Source of OPFRs and their Transformation Products Based on HRMs Suspect Screening

L.-A. Koronaiou[1,2]*, L. Daktylidi[1,2], E. Evgenidou[1,2], D. A. Lambropoulou[1,2]

[1]Aristotle University of Thessaloniki, Laboratory of Environmental Pollution Control, Department of Chemistry, Thessaloniki, Greece
[2]Center for Interdisciplinary Research and Innovation (CIRI-AUTH), Balkan Center, Thessaloniki, Greece

koronaio@chem.auth.gr

In the last decade, an increased concern in organophosphate flame retardants (OPFRs) has been detected, which can be attributed both to their high production and their increased demand as substitutes for brominated flame retardants, due to the imposed regulation on the latter. OPFRs constitute a group of compounds with a wide range of polarity, solubility, and persistence. OPFRs have been widely used in industrial applications (such as antifoaming plasticizers, anti-wear agents, and lacquers) and consumer products (such as textiles, electronics, furniture, floor polishes) aiming to reduce the danger of fire. The presence of OPFRs has been reported in environmental matrices, where their concentration varies. The pathway OPRFs follow to reach the aquatic environment has not been fully determined, although, landfills, pose as a crucial point of contamination (Qi et al., 2019). To better assess their occurrence in landfill leachates, seven samples were collected in consecutive months and pretreated based on a multilayer solid phase extraction protocol, due to the high complexity of the matrix (Koronaiou et al., 2022). The chemical composition of the collected leachates was explored by a Q Exactive Focus Orbitrap high-resolution mass spectrometer (HRMS) equipped with a heated ESI source was utilized for sample analysis, acquiring high mass accuracy measurements and providing crucial fragmentation data. Target analysis and suspect screening were the selected approaches for data analysis in the present study. The target list consisted of eight compounds while for suspect screening a comprehensive database was constructed containing ionization behavior and characteristic fragments from literature on more than 50 compounds from various OPFRs sub-classes i.e. organophosphite antioxidants and their transformation products (TPs) through natural oxidation, namely organophosphate esters (OPEs). In suspect screening, positive findings were considered as such when a full match in the isotopic profile and at least four characteristic fragments were detected. Results suggest high detection frequency (DF) on OPEs, such as TBEP, TCPP and TnBP. The high DF of OPEs could be attributed to the fact that these compounds are generally not chemically bonded to polymeric materials (i.e. food contact materials, packaging and containers), and thus are easily leaching from such materials and directed into the aquatic environment through waste disposal. Additionally, main findings included alkyl- and aryl- non-halogenated OPEs detected in two forms: organophosphate triesters (OPTEs) and organophosphate diesters (transformation products of OPTEs) i.e. PeBTPHP, TDtBPP and TePeTPhP. This study deepens our understanding of the occurrence of OPFRs and establishes the basis for further investigation.

Funding: This research was funded by the Greek Ministry of Development and Investments (General Secretariat for Research and Technology) through the research project “Research-Create-Innovate” (Grant no: T2EΔK-00137).

References

Qi, C. et al. (2019) ‘Organophosphate flame retardants in leachates from six municipal landfills across China’, Chemosphere, 218, pp. 836–844. doi:10.1016/j.chemosphere.2018.11.150.

Koronaiou, L.A. et al. (2022) ‘High-resolution mass spectrometry-based strategies for the target analysis and suspect screening of per- and polyfluoroalkyl substances in aqueous matrices’, Microchemical Journal, 179(February), p. 107457. doi:10.1016/j.microc.2022.107457.

Compound Specific Isotope Analysis - New Challenges in Environmental and Food Studies

N. Ogrinc[1]*, D. Potočnik[1], L. Strojnik[1]

[1]Jožef Stefan Institute, Dept. Environmental Sciences, Jamova 39, 1000 Ljubljana, Slovenia

nives.ogrinc@ijs.si

Compound Specific Isotope Analysis (CSIA) hold the potential to reveal new insights into the nature, sources and transformation processes of organic compounds including pollutants in the environment and their mobility in ecosystems, food and human health. Determination of isotopic composition of light elements such as C and H at the molecular and atomic levels provides another dimension of information on organic compounds to supplement knowledge of their chemical identity and their concentration.

This presentation deals with the use of CSIA in environmental and food studies. First the theoretical background will be presented followed by the review of current limitations and analytical challenges associated with low concentrations, high polarity of organic compounds and potential isotopic fractionation of the target compound. Selected applications and examples in the environment will include the use of CSIA in source apportionment in natural processes and environmental contaminants such as polycyclic aromatic hydrocarbons. Two different studies will be presented. The sources of PAHs determined in sediments of Lake Bled were mainly attributed to a coal/wood burning source, but PAH from car soot could also contributed. The sources of PAHs determined in air particulate matter at selected locations in Slovenia were liquid fossil fuels, petrogenic sources, and biomass combustion. The application of CSIA in food science will include selected applications including major food groups and how these techniques can be used to detect fraud. For example, the discrimination of olive oil according to the country of origin was much improved by including compound-specific (13C) isotope analysis of fatty acids. The isotope approach can be used to differentiate aroma compounds of natural versus synthetic origin of fruits and vanilla. Indeed, cheap, synthetic, petroleum-derived compounds have different isotope values than their costly natural counterparts. Amino acids can also be used to discriminate between conventionally and organically grown plants, such as wheat and similar commodities. All these examples will be put in the context of relevant projects and infrastructure, including ISO-FOOD, METROFOOD-RI, PROMEDLIFE, FNS-Cloud and FoodTraNet.

The Role of Mass Spectral Libraries in the Circular Economy of Plastics

Y. Simón-Manso[1]*, T. Mak[1], E. P. Erisman[1], K. H. Telu[1], X. Yang1, Y. Liang[1], W. E. Wallace[1], and S. E. Stein[1]

madayildiya@gmail.com

A circular economy aims to eliminate waste by designing durable, reusable, repairable, and refurbish-able products (https://www.nist.gov/circular-economy). For plastics, this circular process, i.e., resource-extraction/manufacturing/selling/using/collecting/sorting/purifying/reprocessing presents many challenges at different levels. For example, plastics sorting is dominated by unreliable manual techniques and only recently spectral-methods have been proposed. The NIST Mass Spectrometry Data Center (MSDC) has been working on a comprehensive approach to the chemical analysis of plastics-related compounds (PRCs) using mass-spectrometry. PRCs represent a heterogeneous group of compounds that usually require many different analytical techniques. In this work, only mass spectrometry, and the corresponding hyphenated methods such as gas (liquid) chromatography and three types of ionizations, ESI, APCI, and EI have been used to develop a diverse number of applications ranging from risk assessment of PCR extractables and leachables (E&Ls) to sorting commercial plastics.

We have started this work by demonstrating that EI, ESI, and APCI ionizations provide full coverage for the analysis of PRCs, including all monomers, processing aids, plasticizers, etc., from the plastic industry. Since then, we have been working on increasing the number of spectra of these compounds in the NIST Mass Spectral Libraries (https://chemdata.nist.gov/). A recent compendium published in ES&T estimated in around 10,000 the number of PCRs. The upcoming 2023 release of the libraries contain spectra of 8000 neat compounds, which allow us to develop simple-and-robust applications for the detection and quantification of PRCs in complex mixtures.

In the context of a circular economy, the first problem we have addressed is a risk assessment of E&Ls. We have developed standard methods for the identification and semi-quantitation of as many PCRs as possible in human biofluid samples such as blood, urine, and breast milk. The samples are NIST Standard Reference Materials (SRMs), so these methods can be reproduced and used as a reference in any laboratory. We can identify most compounds in any material using libraries of annotated unidentified recurrent spectra (ARUS), a technique developed in our group (Telu e al., 2021, 2016; Simón-Manso, 2019). On the other hand, the deconvolution of fingerprints derived from polymer mixtures can be applied to polymer sorting, degradation, pyrolysis, etc., although the implementation may involve some engineering beyond the scope of this work. We have addressed this problem with two different approaches: 1) analyzing extracts from polymer mixtures using LC/MS. 2) analyzing the pyrolysis products using GC/MS. Several mixtures, with a few components ranging from two to five, were extracted using different solvents and temperatures. Multiple runs of each extract were recorded at 6 different collision energies by using gradient elution and two types of ionization, APCI and ESI on a QTOF-6530. LC runs were performed using reversed-phase (C18/2.1x100mm/MPA: water-FA, MPB: methanol-FA). EI spectra were recorded using Agilent 5977-GC/MSD and 8890-GC systems. In-house software was used for clustering, annotating, and building libraries. For the deconvolution of mixtures, a linear combination of the chromatographic profiles of individual polymer extracts acquired under the same conditions was used as a template, and the coefficients were optimized to minimize the variance between the model prediction and the mixture data. Samples of polyethylene, polypropylene, polystyrene, polycaprolactone, and nylon-6 were extracted using isopropanol and hexane at 50 °C for 24 hours at a ratio of 5 mL/g as it was done in previous work for the individual polymers. The GC-MS work is still in progress. The data was processed and the major peaks (above 5% of the base peak) were identified using the most recent versions of the NIST libraries. Retention times and maximum peak intensities have been collected and used for the model. The projected work aims to analyze up to 100 standards of the most used polymers. In most cases, the deconvolution models have confirmed the identities of the polymers and the proportions of the polymers in the mixtures with high precision. The monomers are always present in the extracts with small amounts of other compounds, e.g., nylon-6/isopropanol extract contains, Caprolactam, cis-2-Penten-1-ol, Cyclohexanol, etc. However, more challenging tests, using commercial polymers, random samples, or degraded polymers are still in progress. Eventually, similar work will be performed using pyrolysis data from polymers and polymer mixtures instead of extracts. Software developed for data visualization, organization, and validation of MS data will be described.

References

Telu et al. *Biotechnol. Bioeng*. 2021,1 8, 1491–1510.

Simón-Manso, Y. *Anal. Chem.* 2019, 91, 18, 12021–12029.

Telu et al. RCM 2016, 30, 5, 581-593.

Analysis of Empty Plastic Containers from Pesticide Formulations

P. Tsiantas[1], E. Bempelou[1], G. Balayiannis[1], A. Marousopoulou[1] and E. Karasali[1]*

[1]Benaki Phytopathological Institute, Laboratory of Chemical Control of Pesticides, Scientific Directorate of Pesticides' Control and Phytopharmacy, St. Delta Kifissia 14561, Greece

e.karassali@bpi.gr

The growing awareness of environmental concerns and inadequacy of resources describes the increasing interest respecting the management of plastic waste in general and predominantly hazardous streams. During the last decades and counting the need for greater production yields, agriculture has been intensified with consequent increase of its possible effects on the environment and climate change. Waste originating from agricultural activities is nowadays one of the most dominant waste streams, not only because of their pollutant load but also their wide spatial distribution. In the EU, the possibility for recycling plastic waste continues to be largely unexploited. Recycling of end-of-life plastics is very low, particularly in comparison with other materials. Around 25.8 million tons of plastic waste are produced at EU level every year, while 5% of them has been estimated to be plastic agricultural waste, which is considered hazardous and thus involves special management. The empty pesticide containers are among the main categories of hazardous agricultural waste and significant efforts have been made in recent years to control their disposal, but also for their management based on the principles set out in Directive 2009/128/EC.

An analytical method for the simultaneous determination of 311 active compounds in previously tripled rinsed and shredded plastic containers of various formulations of pesticides was developed and validated. During the sample preparation, the shredded plastic materials obtained from farms all over Greece were further shredded in a cutting mill (Pulverisette 14, Fritsch) to be homogenized, with a series of sieves and with the use of liquid nitrogen and afterwards modified QuEChERS was applied. The determination of the analytes was achieved with the combination of GC-MS/MS and LC-MS/MS techniques. The method was validated in three fortification levels (0.01, 0.05 and 0.1 mg/kg) and all relative parameters, namely accuracy and precision, linearity, sensitivity, and matrix effect were assessed based on EU requirements, providing acceptable results. The LOQ was set at 0.01 μg/g for most of the analytes, while the corresponding calculated LOD values was 0.003 μg/g.

The results indicate that the developed multi-residue method is fit for the purpose of analyzing low levels of pesticides in the specific substrate. The chromatographic analysis of those samples resulted in positive determinations of a plethora of active ingredients at low levels.

References

Ileana Blanco, Rosa Viviana Loisi, Carmela Sica, Evelia Schettini, Giuliano Vox. Agricultural plastic waste mapping using GIS. A case study in Italy. Resources, Conservation and Recycling,
137, 2018, 229-242, ISSN 0921-3449, https://doi.org/10.1016/j.resconrec.2018.06.008

Caterina Picuno, Ayah Alassali, Michel Sundermann, Zoe Godosi, Pietro Picuno, Kerstin Kuchta.
Decontamination and recycling of agrochemical plastic packaging waste, Journal of Hazardous Materials, 381, 2020, 120965, ISSN 0304-3894, https://doi.org/10.1016/j.jhazmat.2019.120965 .

Georgios Garbounis, Dimitrios Komilis. A modeling methodology to predict the generation of wasted plastic pesticide containers: An application to Greece. Waste Management, 131, 2021,
177-186, ISSN 0956-053X, https://doi.org/10.1016/j.wasman.202.

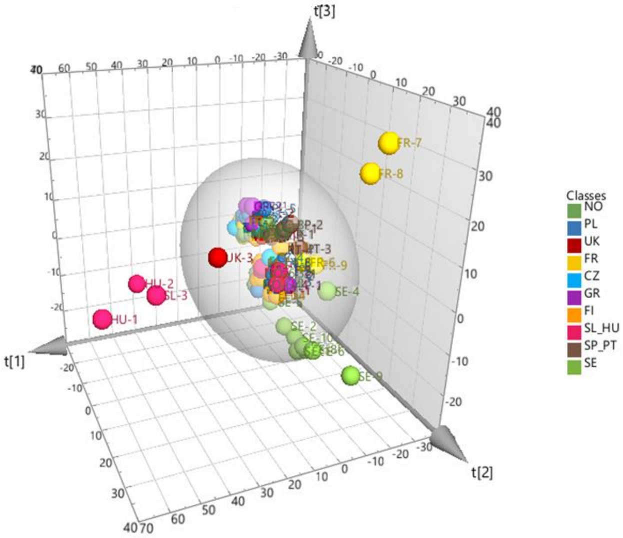
Non-Target Screening and Contaminant Profiling of House Dust Collected Across Europe by Comprehensive Two-Dimensional Gas Chromatography - Mass Spectrometry and Multi-Variate Statistical Evaluation

P. Haglund[1]*

[1]Umeå University, Department of Chemistry, 80187 Umeå, Sweden

peter.haglund@umu.se

Seventy-five house dust samples were collected from 14 countries, spread across Europe, through a collective effort within the Norman research network. The dust was sieved and extracted with acetone:hexane (1:3) and acetone (Moschet et al., 2018). The extracts were pooled and analysis by comprehensive two-dimensional gas chromatography - electron ionization - mass spectrometry (GCxGC-EI-MS). Data evaluation was performed using multi-variate statistical analysis by unsupervised as well as supervised principal component analysis (PCA). Unsupervised PCA was conducted using aligned peak table data (matrix of samples vs. dust contaminant peak volumes), whilst supervised PCA was performed on the raw data utilized Fisher Ratios of chromatographic regions ('tiles') to compare contaminant abundances between groups of samples (Parson et al., 2015), in this case samples from North-Europe, Mid-Europe, and South-Europe. The unsupervised PCA revealed that there are large variations in dust contaminant levels between countries, but also between dust samples originating from the same country. In fact, the within country variability was often as great or even greater than the between country variability. A 3D-score plot of tharethree first principal components is shown in the graph below. Country codes are used to indicate origin. The tile-based data evaluation and supervised PCA revealed a number of compounds that significantly differed between North, Middle and South Europe, including nicotine, fragrances, phthalates, pesticides, and personal care product ingredients.



Unsupervised PCA of GCxGC-MS data from 75 house dust samples. Country codes are used to indicate sample origin.

References

Moschet,C. et al (2018) Household Dust as a Repository of Chemical Accumulation: New Insights from a Comprehensive High-Resolution Mass Spectrometric Study. Environ. Sci. Technol., 52, 5828. doi: 10.1021/acs.est.7b05767.

Parson, B.A. et al. (2015) Tile-Based Fisher Ratio Analysis of Comprehensive Two-Dimensional Gas Chromatography Time-of-Flight Mass Spectrometry (GC × GC–TOFMS) Data Using a Null Distribution Approach. Anal. Chem., 87, 3812. doi: 10.1021/ac504472s.

Wide-Scope Target Screening by LC-HRMS Combined with Fast Ion Mobility – the Answer to Environmental and Human Biomonitoring Challenges

K. S. Diamanti[1]*, R. Aalizadeh[1], D. E. Damalas[1], G. O. Gkotsis1, C. Baessmann[2], B. Galvin[2], G. Labella[2], N. S. Thomaidis[1]

[1]National and Kapodistrian University of Athens, Greece
[2]Bruker Daltonik GmbH, Bremen, Germany

kdiamanti@chem.uoa.gr

Thousands of chemicals are dispersed throughout the environment and may threaten ecosystems and health. Through environmental and human biomonitoring, the exposure to persistent, bio-accumulative and toxic substances can be assessed. Today, various chemical classes can be reliably identified and quantified by target screening with high-resolution mass spectrometry coupled to chromatography. However, the sample complexity often results in high matrix effects, interferences and ion suppression and thus hampers the detection of compounds with low concentration. Therefore, apart from the established target screening protocols using retention time, MS and MS/MS information, an extended workflow and technology is required to identify xenobiotics with high confidence. Presented here is the addition of ion mobility with collisional cross section information for filtering and sensitivity increase of low abundant compounds.

For extracting semi-polar to polar xenobiotics from biota and human biospecimens, generic sample preparations were followed. Reference standards as well as standard addition curves were prepared for a validation dataset at a wide concentration range, which was built considering retention time index, ionization efficiency and ion mobilities. Standards and samples were analyzed using LC-TIMS-QTOFMS in DIA mode (broadband Collision Induced Dissociation (bbCID)), both with ion mobility switched on and off. The performance of a novel vacuum insulated probe-heated electrospray ionization (VIP-HESI) was evaluated compared to the conventional ESI. Comprehensive statistical software was utilized for the screening of xenobiotics (e.g. pesticides and drugs), providing precursor ion formula, RT, MS and MS/MS qualifier ions as well as ion mobility-derived collision cross section (CCS) values.

Results of this study confirm an enhanced sensitivity of the novel ion source for a significant number of analytes, both in standard solutions and real samples. This is crucial for the detection of analytes at low concentration levels, a pain point in the analysis of real samples. The use of an optimized broad mass and mobility transfer bbCID acquisition method improved the resolution of lower m/z ions. The ion mobility filtering provided higher-quality chromatograms and full-scan MS and bbCID MS/MS spectra, since the background signal caused by co-eluting analytes and matrix components was largely reduced. Thus, lower LOD and LOQ values were achieved. The criteria of an allowed CCS window (ΔCCS <2%) was added to the established mass accuracy, RT shift, isotopic pattern fitting and presence of qualifier ions, resulting in an increased overall identification confidence. False positive and negative results were reduced leading to more reliable compound identification.

Investigation of VOCs Sourced from the Poultry Farm Environment

E. Olkowska[1]*, A. Łopatka[2], A. Klimkowicz-Pawlas[2] and L. Wolska[1]

[1]Medical University of Gdansk, Faculty of Health Sciences, Department of Environmental Toxicology, Dębowa Str. 23A, 80-204 Gdansk, Poland
[2]Institute of Soil Science and Plant Cultivation - State Research Institute, Department of Soil Science Erosion and Land Protection, Czartoryskich Str. 8, 24-100 Puławy, Poland

ewa.olkowska@gumed.edu.pl

Poultry industry (mainly chicken meat and eggs production) is an important source of proteins and poultry meat corresponds to approx. 40% of global meat production (FAO, 2022). Growing demand leads to animal rearing in intensive production farms with flocks that count from several thousand up to several hundred thousand birds located in one or more buildings. Such intensive farming leads to emissions that impact various environmental compartments, including air, water and soil. Volatile organic compounds (VOCs) are pollutants connected with different activities on poultry farms (animal exhalation and their waste, feed mixtures, building ventilation, litter composting etc.). This can be connected with large emissions of VOCs, which can affect the local air quality (unpleasant odour problems, contribution in formation of ozone/fine particles) and be harmful for human health even at low levels (Gržinić *et al.*, 2023; Yuan *et al.*, 2017). A comprehensive characterization (identification and quantification, spatial/temporal distribution) of VOCs emitted from poultry farms is needed to evaluate their environmental impact and implement proper mitigation procedures.

In this study, VOCs measurements were performed by collecting air samples (on Tenax sorbent) at 25 locations around the poultry houses, at distances of up to 500 m from the model farm. Meteorological data (temperature, relative humidity, wind direction, wind speed) were also collected. The sampling campaign was performed in summer, when mechanical ventilation of buildings is performed by side wall and roof fans. The desorption and analysis of VOCs (identification and quantitative determination) were carried out by thermal desorption (TD-20, Shimadzu, Japan) and gas chromatography coupled with mass spectrometry (GCMS-QP2010 Ultra, Shimadzu, Japan). The sum of VOCs measured at the various sampling locations ranged from 429 to 1715 $\mu g\ m^{-3}$, while inside the poultry house it was 2039 $\mu g\ m^{-3}$. Three of the sampling points with the highest total VOC levels were located away from the farm buildings, close to the road and crop field. This observation indicates that the used parameter may not properly represent the impact of farm emissions on air composition. Inside the poultry house, the following compounds were identified at highest levels: acetic acid, acetoin, 2-butanol, 3-methyl-butanal, 2-butanone, methyl alcohol. During further analysis of VOCs results, we propose to use acetone levels (50 $\mu g\ m^{-3}$ inside the poultry house) as an indicator of spatial distribution of VOCs sourced from the farm.

Acknowledgements
This study has been financially supported by a grant from the National Science Centre, Poland (Grant No. UMO-2019/35/B/NZ7/04394). The authors would like to thank Mr. Przemysław Gnatowski and Mr. Paweł Szarlej for technical assistance during measurements.

References

FAO (2022) *Food Outlook – Biannual Report on Global Food Markets.* Rome. Available at: https://www.fao.org/documents/card/en/c/cb9427en (Accessed: 06 April 2023).

Gržinić, G., *et al.* (2023) ‘Intensive poultry farming: A review of the impact on the environment and human health’, *Science of The Total Environment,* 858(3) 160014.

Yuan, B., *et al.* (2017) ‘Emissions of volatile organic compounds (VOCs) from concentrated animal feeding operations (CAFOs): chemical compositions and separation of sources’, *Atmospheric Chemistry and Physics*, 17 (8), pp. 4945-4956.

Tire Wear Particles in Coastal Areas: Are there Suitable Chemical Indicators of Exposure in Blue Mussel (Mytilus Edilus)?

A. Foscari[1]*, R. Mowafi[1], B. Seiwert[1], D. Herzke[2], B. De Witte[3], D. Delbare[3], G. B. Heras[4], T. Reemtsma[1,5]

[1]Helmholtz Centre for Environmental Research – UFZ, Department of Analytical Chemistry, Permoserstrasse 15, 04318, Leipzig, Germany
[2]NILU, Norwegian Institute for Air Research, Tromsø, Norway
[3]Institute for Agricultural and Fischeries Research – ILVO, ILVO-marine, Jacobsenstraat 1, 8400 Oostende, Belgium
[4]Instituto Español de Oceanografia - IEO · Centro Oceanográfico de Vigo, Vigo, Spain
[5]University of Leipzig, Institute for Analytical Chemistr

aurelio.foscari@ufz.de

The emission of tire wear particles (TWPs) and of tire related organic contaminants into the environment receives growing attention. However, information regarding the behavior of both TWPs and tire-related compounds in exposed biota is still very scarce. This is particularly true for the marine environment[1],[2].

Here, we present an exposure study of mussels to a cryo-milled tire tread (CMTT) mixture with the aim to investigate to which extent the exposure of mussels to TWP is reflected by internal concentrations of tire-related chemicals. Mussels were exposed for 7 days, followed by additional 7 days of depuration. Both, water and tissues samples were analyzed by UPLC-HRMS and ICP-MS for the detection of organic tire-related chemicals and zinc (Zn) content, respectively.

As a result, a total of 19 tire-related compounds was determined and 17 suspects detected. The concentrations in mussels were directly proportional to the TWPs exposure level for most of the substances, and declining trends were observed during depuration. However, Zn concentrations did not show significant differences compared to the control samples. Additionally, environmental samples from both a high and low contaminated coastal area were analyzed. Results will be presented and it will be explored to which extent tire-related compounds may reflect TWP exposure.

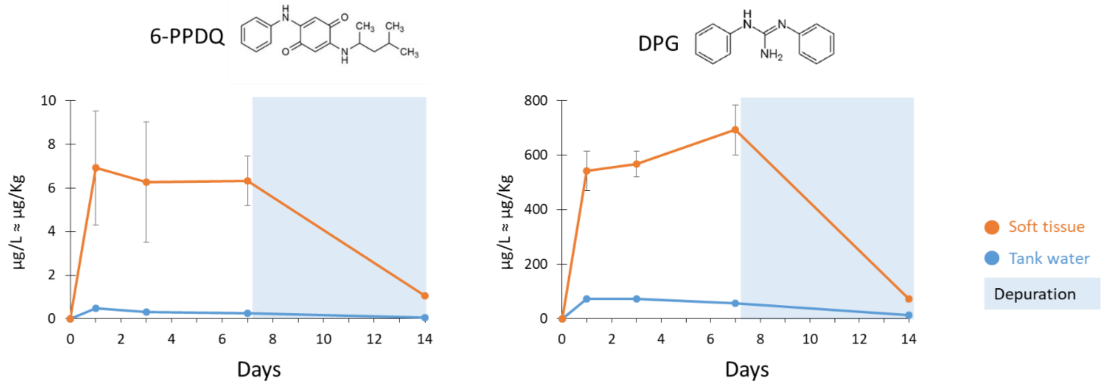


Figure 1. Concentration of 6-PPD quinone (6-PPDQ) and diphenylguanidine (DPG) detected in soft tissue (orange colored) and tank water (blue colored))

References

[1]Müller, K. et al. (2022) ‘Probing the chemical complexity of tires: identification of potential Tire-borne water contaminants with highresolution mass spectrometry’, Sci. Total Environ., 802, p. 149799. doi: 10.1016/j.scitotenv.2021.149799.

[2]Tian, Z. et al. (2021) ‘A ubiquitous Tire rubber-derived chemical induces acute mortality in coho Salmon’, Science, 371, p. 6525. doi: 10.1126/science.abd6951.

How Nematodes Respond to Nanoformulations of Tebuconazole: A Comparison Study in Single Species and Community Level of Nematode

M. EghbaliNejad[1*], S. Höss[2], J. Kotouček[3], J. Hofman[1]

[1] Research Centre for Toxic Compounds in the Environment (RECETOX), Faculty of Science,
[2]Masaryk University Ecossa, Starnberg, Germany
[3]Department of Pharmacology and Toxicology, Veterinary Research Institute, Brno, Czech Republic

Mahleh.eghbalinejad@recetox.muni.cz

In the agriculture sector, nanoformulations of agrochemical are being produced to address the overuse & drawbacks of conventional formulations of agrochemicals e.g., low solubility, degradation, toxicity. To address the demand for healthy and harmless products, nanopesticides (NPs) risk assessment to non-target organisems need to be evaluated carefully to avoid emerging new contaminant. In soil, nematodes, C. elegans is a well-known model species widely used in toxicity testing of chemicals. We tested the toxicity of Tebuconazole (TBZ) in different formulations, two nanoformulations (poly-Ɛ-caprolactone (PCL-NF), nano structured lipid carriers (NLC-NF)), a commercial formulation and TBZ pure on the reproduction of C. elegans. Additionally, the toxicity of nano carriers without TBZ were tested as pesticide-free reference according to ISO (ISO, 2020). Based on the effect concentrations revealed by the single species test, a multi-species microcosom test with soil including the native nematode fauna was conducted. Based on the results, NLC-NF showed higher toxicity on C. elegans compared to PCL-NF, whereas NLC carriers were also more toxic than PCL-Carriers. The effect assessment on nematode community level after 8 weeks of exposure revealed that the tested compounds compared to the control had no strong and significant effect on densities, taxonomic diversity, and maturity indices (Fig1). The current experimes shows the necessity of comprehensive risk assessment of NPs with reliable test guidelines which can be beneficial in providing regulatory frameworks for NPs risk assessment.

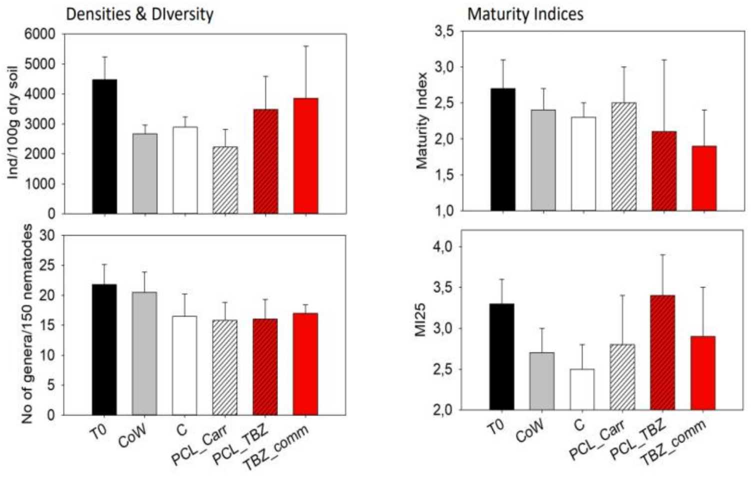


Fig1,(T0=time 0, CoW= control with additional water, C=Control, PCL_Carr = PCL-Carrier, TBZ_Comm=TBZ commercial, No of genera=number of generation)

References

ISO, 2020. Water and Soil Quality - Determination of the Toxic Effect of Sediment and Soil Samples on Growth, Fertility and Reproduction of Caenorhabditis elegans (Nematoda). ISO 10872:2020. International Organization for Standardization, Geneva, Switzerland .

Development and Application of a Two-Dimensional (2D) Particle Analysis Method Based on DMA-Spicp-MS Towards Characterization of Complex Nanoparticles in Wastewater and Airborne Particulate Matters

Y.C. Hsieh[1], C.H. Chang[1], T.C. Hsiao[2], Y.P. Lin[2], W.C. Hou[1]*

[1]National Cheng Kung University, Department of Environmental Engineering, Tainan City 701, Taiwan
[2]National Taiwan University, Graduate Institute of Environmental Engineering, Taipei 106, Taiwan

whou@mail.ncku.edu.tw

Characterizing complex nanoparticles (NPs) in environmental matrices is challenging. This work presents a two-dimensional size analysis method that combines a differential mobility analyzer (DMA) and a single-particle inductively coupled plasma-mass spectrometry (spICP-MS) with an atomizer-enabled sample introduction. spICP-MS is an emerging method that converts single-particle masses to sizes and characterizes environmental NPs at trace levels (Lu, Wang, and Hou, 2022), but its analysis principle still has a difficulty in size characterization of hetero-aggregated NPs. Thus, additional approaches are needed. DMA is common size analysis method of aerosol that accurately selects particle sizes by varying the electric field in the air. Our results indicate the observed tailing in the electrical mobility size distribution measured with DMA was solved by heating the aerosol flow, where water-shelled AuNPs were dehydrated, effectively eliminating the tailing (Hsieh et al., 2022). The improved method has a good sizing performance and can resolve the size fractions of mixed 30 nm and 50 nm AuNPs. It can reliably analyze 7.8×10^5 to 1.9×10^7 # of 50 nm AuNPs (or 4.1×10^5 to 10^7 # NPs/mL, equivalent to 0.6 to 14.3 µg Au/L) with a linear response and a limit of detection of 7.8×10^5 # AuNPs (equivalent to 4.1×10^5 # AuNPs/mL) that is relevant to NP concentrations in surface water and wastewater samples. The potential of this method to analyze environmental samples is demonstrated by characterizing AuNPs and silver nanoparticles (AgNPs) spiked in wastewater, where both NPs were revealed to form hetero-aggregates with colloids existing in wastewater. Inherent nanosized Ag particles in the wastewater can be directly detected by the method even before adding external AgNPs. In this talk, we will also briefly show our recent results of using DMA-spICP-MS to directly characterize airborne particulate metals to demonstrate this method's potential in real-time monitoring of airborne particulate matters.

References

Lu, H.-Y., Wang, Y.-J. and Hou, W.-C. (2022) 'Bioaccumulation and depuration of TiO2 nanoparticles by zebrafish through dietary exposure: Size- and number concentration-resolved analysis using single-particle ICP-MS', Journal of Hazardous Materials, 426, p. 127801. Available at: https://doi.org/10.1016/j.jhazmat.2021.127801.

Hsieh, Y.-C. et al. (2022) 'A two-dimensional nanoparticle characterization method combining differential mobility analyzer and single-particle inductively coupled plasma-mass spectrometry with an atomizer-enabled sample introduction (ATM-DMA-spICP-MS): Toward the analysis of heteroaggregated nanoparticles in wastewater', Science of The Total Environment, 838, p. 156444. Available at: https://doi.org/10.1016/j.scitotenv.2022.156444.

The Stability of Tio$_2$-rGO Self-Cleaning Photocatalytic Coatings for Outdoor Applications

M. Covei[1], I. Tismanar[1]* and T. C. Diamantino[2]

[1]Transilvania University of Brasov, Department of Product Design, Mechatronics and Environment, Eroilor 29, 500036, Brasov, Romania
[2]National Laboratory for Energy and Geology (LNEG), Laboratory of Materials and Coatings, Estr. do Paço do Lumiar 22, Ed.E r/c 1649-038, Lisboa, Portugal

ioana.tismanar@unitbv.ro

Self-cleaning coatings are lately being studied for different applications such as civil buildings (windows, facades, indoor walls, metallic products), the automotive industry (mirrors, windshields, the health field (surgical rooms' walls or tiles) and renewable energies, namely for solar energy (solar reflectors, photovoltaic panel). The self-cleaning occurs through two mechanisms that involve (1) (super)hydrophobic coatings, when the pollutant rolls off the surface without being degraded or (2) (super)hydrophilic coatings, when the pollutant is dissolved in the water sheet and afterwards is degraded through the photocatalytic process (Merai et al., 2019). The most-used photocatalytic material is titanium dioxide (TiO_2) because of its non-toxicity, acceptable production cost and possible anticorrosive properties. The main disadvantage of TiO_2 is related to its UV activation which leads to additional process costs. Recent studies indicate the Vis- or solar-active composite materials (such as TiO_2 - rGO composites) as a solution to overcome the activation problem (Tismanar et al., 2021; Covei et al., 2022). However, for outdoor applications, their stability under environmental conditions (high temperature and humidity or highly corrosive atmospheres) must be analyzed. This research reports on the stability of the TiO_2/TiO_2-rGO double-layered composite thin films deposited on 5x5cm^2 Al substrates using up-scalable and low-cost deposition methods (spray pyrolysis deposition for TiO_2 intermediate layer coupled with sol-gel spraying for the TiO_2-rGO composite second layer). These coatings were subjected to different accelerated ageing tests with different environmental conditions:
(1) highly corrosive artificial atmospheres to check the possible anticorrosive properties using neutral salt spray (NSS) test according to ISO 9227:2017 and sulfur dioxide (SO_2) test in a humid atmosphere according to ISO 22479:2019, method B
(2) high humidity and temperature (40^{o}C and 100% RH with condensation) according to ISO 6270-2:2017.
Before and after the stability tests, the coatings were analyzed in terms of structure, morphology, surface composition and wettability. The results outline that the samples were mostly affected in the salt environment, where the obtained micrographs show large areas of degraded Al surface, indicating that this type of composite may not exhibit high anticorrosive properties. Instead, after high humidity with condensation and temperature tests the results outline the stability of the coatings (structure and surface properties remain almost unchanged). To check the self-cleaning properties the pristine sample and the most damaged samples (the ones exposed to the corrosive environment) were subjected to photocatalytic tests using the standard methylene blue (MB) pollutant (ISO 10678:2010) and simulated solar radiation but at low irradiance value. The results outline promising efficiency considering the irradiance value (up to 30% after 8h of photocatalysis) on the pristine sample. It is significant to note that even if the coatings were affected by the corrosive environment, their photocatalytic efficiencies decreased only by ~3% concluding that the self-cleaning properties were maintained.

Acknowledgements. The work was obtained in the frame of the SFERA-III project SURPF2101300016 (STAB-PHOTOCOAT), Grant Agreement No 823802.

References

Merai, L. et al. (2019) 'Preparation of photocatalytic thin films with composition dependent wetting properties and self-healing ability', Catalysis Today, 328, p. 85-90, doi:10.1016/j.cattod.2018.10.015.

Tismanar, I. et al. (2021) 'VIS-active TiO2 – graphene oxide composite thin films for photocatalytic applications', Applied Surface Science, 538, p. 147833, doi:10.1016/j.apsusc.2020.147833.

Covei, M. et al. (2022) 'Photocatalytic composite thin films with controlled optical properties based on TiO2, WO3 and rGO', Surfaces and Interfaces, 31, p. 102075, doi: 10.1016/j.surfin.2022.102075.

Modeling the Fate and Transport of ZnO Nanoparticles in a River using the Environmental Release Predicted by the Material Flow Analysis

C.H. Chang[1], E. Suhendra[1], Y. Zheng[2], Y.C. Hsieh[1], B. Nowack[2], W.C. Hou[1]*

[1]National Cheng Kung University, Department of Environmental Engineering, Tainan City 701, Taiwan
[2]Technology and Society Lab, Swiss Federal Laboratories for Materials Science and Technology, Gallen, Switzerland

whou@mail.ncku.edu.tw

Modeling work on the fate and transport of nanoparticles in the environment using realistic environmental release data is rare. This talk presents a study to model the fate and transport of ZnO nanoparticles (ZnONPs) in an urban river in southern Taiwan using the combined spatiotemporal river watershed model (i.e., WASP8) and the environmental release model based on the material flow analysis (MFA). The river model considers the hydrology (e.g., flow rate, tide) and ZnONP's fate processes as dissolution, heteroaggregation, sedimentation, etc. The fate and transport in the sediment and of the transformed ZnONP species (e.g., dissolved Zn) are also considered. The MFA accounts for the ZnONP's release into surface waters during the life-cycle stages of ZnONP including production, product manufacturing, trade, usage, end-of-life disposal, and recycling in Taiwan. A probability MFA approach is adopted (Adam et al. 2021). The release of ZnONP into the river comes from the 6 major water drainages serving the watershed areas. The first-order dissolution rate coefficient of ZnONP used for fate modeling was experimentally derived using the actual river water spiked with ZnONP. We found that the spiked ZnONP concentrations significantly affect the dissolution rates. The ZnONP spiked at an environmentally relevant low concentration (50 µg/L) dissolved completely with a greater rate constant and its dissolution level was independent of water quality. In contrast, the extent of dissolution for high concentrations of ZnONP was controlled by the carbonate alkalinity. Preliminary modeling results indicate that dissolution is a potentially important fate process that controls the concentrations of ZnONP in the studied river. Sensitive analysis results will be presented in this talk to identify key factors.

References

Adam, V. et al. (2021) Integrated dynamic probabilistic material flow analysis of engineered materials in all European countries. NanoImpact, 22, 100312. doi: doi.org/10.1016/j.impact.2021.100312

Investigation on the Potential Migration of Multicomponent Nanomaterials into Food Simulants from Food Packaging

A. Brunelli[1]*, C. Salgado[2], J. J. Reinosa[2], J. Fernandez[3], D. Hristozov[4], A. Marcomini[1], E. Badetti[1]

[1]Ca' Foscari University of Venice, DAIS - Department of Environmental Sciences, Informatics and Statistics, Via Torino 155, 30170, Venice, Italy
[2]Encapsulae SL, Lituania 10, 12006, Castellón de la Plana, Spain
[3]Instituto de Ceramica y Vidrio, CSIC. Kelsen 5, 28049 Madrid, Spain.Affiliations
[4]Greendecision S.r.l., Venice, Italy

andrea.brunelli@unive.it

It has been estimated that insect pests annually infect up to 40% of global crop production, and more than 30% of cereals, rice, and legumes, which end up in huge loss of resources and money (each year, plant diseases cost the global economy over $220 billion (FAO, 2021). To tackle this challenge, within the EU funded Horizon 2020 project SUNSHINE, Encapsulae-CSIC-spin off is working on the development of multi component nanomaterials (MCNMs) to extend the shelf life of dry food. These MCNMs are constituted by nanoclays (i.e., sepiolite or bentonite) encapsulating an essential oil and added to a polyethylene film to act as anti-pest against the beetle within the Tenebrionidae family. As this MCNM is classified as food contact material (FCM), a complete consumer safety assessment of this nano-enabled product must be proven before the FCM reaches the market, following the European Food Safety Authority (EFSA) regulations. Within SUNSHINE, the main aim of the activities planned is to support the industry in developing a safe and sustainable FCM. In this regard, the potential migration of MCNMs or elements which constitute the MCNMs from the food packaging film was investigated into different food simulants, according to Regulation (EU) N°10/2011. Moreover, to simulate a natural weathering process, the potential migration of the same components was also studied after accelerated weathering of food packaging film loaded with MCNMs, carried out according to ISO 4892-2-2/2013 method, which has been already used in the literature[2] to perform UV weathering of nano-based plastic materials (Wohlleben and Neubauer, 2016).

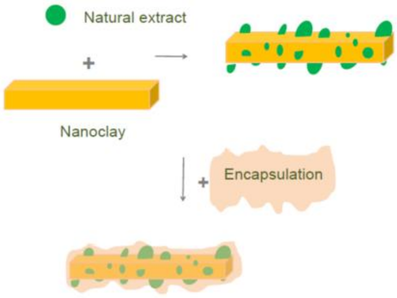


Fig. 1 - The approach used to develop the multicomponent nanomaterial for food packaging application

References

https://www.fao.org/news/story/it/item/1402920/icode/

Wohlleben and Neubauer (2016) 'Quantitative rates of release from weathered nanocomposites are determined across 5 orders of magnitude by the matrix, modulated by the embedded nanomaterial', NanoImpact, 1, 39-45. doi:org/10.1016/j.impact.2016.01.001.

Characterization of Multi-Composite Nanomaterials for Supporting Safe and Sustainable by Design Strategies

E. Badetti[1]*, A. Brunelli[1], M. Blosi[2], A. Costa[2], A. Saccardo[3], S. Doak[3], A. Serrano Lotina[4], M. A. Bañares[4], J. Balbuena[5], J.M. Lloris Cormano[5], D. Hristozov[6], A. Marcomini[1]

[1]Ca' Foscary University of Venice, DAIS, Via Torino 155, 30172, Venice Mestre, Italy
[2]CNR-ISTEC, Via Granarolo 64, 48018 Faenza, Italy
[3]Swansea University, Biomedical Sciences, Singleton Park Swansea SA2 8PP Wales, UK
[4]Instituto de Catalisis y Petroleoquímica. ICP-CSIC, Marie Curie 2, 28049-Madrid, Spain
[5]CIAC, Parque Científico-Tecnológico Rabanales 21,14014, Cordoba, Spain
[6]Greendecision S.r.l., Via Torino 155, Venice, Italy

elena.badetti@unive.it

In recent decades, the development of new technologies has significantly increased the use of engineered nanomaterials in consumer products. Among the most recent materials we find multicomponent nanomaterials (MCNMs), characterized by the integration of two or more nanometer-sized components in a single system, wich are able to give the final product additional innovative properties compared to those with a single component. However, despite the numerous benefits associated with the use of MCNMs, concern is growing about their potential risk to human health and the environment. This concern is related both to their nanometric size and to the complexity of estimating the degradation rates and toxicity of a multi-composite system. Therefore, investigating the interactions between MCNMs and the surrounding media, e.g. dissolution, aggregation/disaggregation and surface ligand adsorption, are of great importance for supporting the risk and safety assessment of these materials (Abdolahpur Monikh et al., 2022).

In this context, this work is framed within the EU funded H2020 SUNSHINE Project and aims at supporting Safe and Sustainable by Design (S&SbD) strategies for mortars incorporating advanced multi-component nanomaterials to photocatalytic NO_x decontamination. In particular, colloidal stability, surface charge and ion release of both single and MCNMs dispersed in different media relevant for (eco)toxicological testing are investigated, as well as the release of ions from mortars. From the combination of different analytical techniques, such as dynamic and electrophoretic light scattering (DLS and ELS), centrifugal separation analysis, Raman spectroscopy, infrared spectroscopy (IR), transmission and scanning electron microscopy (TEM and SEM) and inductively coupled plasma mass spectrometry (ICP-MS), a comprehensive characterization of MCNMs have been performed. The obtained results allow to estimate the qualitative and quantitative stability of the tested dispersions over time, and further significant information for a better correlation with the results from (eco)toxicity studies. The approach presented here can greatly support the development of the environmental risk assessment and management of MCNMs, within a S&SbD approach (Badetti et al., 2021).

References

Abdolahpur Monikh, F., et al. (2022) ‘"Advanced materials" and the challenges on the horizon for testing their (eco)toxicity and assessing their hazard’, Environmental Science: Advances 2(2), pp. 162-170.
doi: 10.1186/s12989-022-00487-6.

Badetti E., et al. (2021) ‘Novel multimethod approach for the determination of the colloidal stability of nanomaterials in complex environmental mixtures using a global stability index: TiO_2 as case study’, STOTEN 801, 149607.
doi: https://doi.org/10.1016/j.scitotenv.2021.149607.

Interaction between Nanomaterials and Perfluorooctanoic Acid in Aqueous Media

F. Calore[1]*, A. Brunelli[1], A. Bonetto[1], S. Calzavara[1], P. Chinellato[1], G. Palombella[1], A. Marcomini[1], E. Badetti[1]

[1]Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino 155,
30172, Venice Mestre, Italy

francesco.calore@unive.it

Recently, multi-component nanomaterials (MCNMs) - i.e. NMs containing more than one component in the nanometric scale - have been produced, with the aim of improving the existing functionality of the single components or to achieve multifunctionality.

(MC)NMs present extremely reactive surfaces, and once reaching the aquatic environment they can undergo several transformations (i.e., dissolution, adsorption of (macro)molecules on the surface, agglomeration/aggregation, ROS generation, etc.), which can affect their fate and behavior by changing, for example, their colloidal stability and bioavailability. More in detail, in the aquatic environments (MC)NMs can interact with salts, natural organic matter, and suspended particles but also with organic molecules, including pollutants. Among the pollutants extensively detected in natural waters are PFAS (per- and polyfluoroalkyl substances), a class of thousands of xenobiotic, persistent, bioaccumulative, and harmful chemicals. They are intentionally produced, as they bestow waterproof, oilproof, and non-stick properties to commercial products. Thus, (E)NMs can interact with PFAS, although information on these interactions is still lacking. ENMs can adsorb pollutants, acting as a "Trojan horse" by carrying and releasing contaminants elsewhere, owing to their high surface reactivity and surface area.

In this context, the interaction between TiO_2-based (MC)NMs (both pristine and core shell structures) and a model PFAS molecule - i.e. perfluorooctanoic acid (PFOA) - have been investigated. Different aqueous media have been used (deionized, artificial fresh, and artificial marine water) to understand how the solution properties could affect such interactions. Centrifugal Separation Analysis (CSA), Dynamic Light Scattering (DLS) and Electrophoretic Light Scattering (ELS) techniques have been used to determine changes in the colloidal stability of (MC)NMs dispersions with respect to different PFOA concentrations and to the different media considered. Adsorption-based interactions have been studied by means of screening batch adsorption studies, for which the concentration of PFOA has been determined via LC-MS analysis.

Potential Applications of Candida Parapsilosis CMGB-YT in Biosurfactant Mediated Bioremediation

O. Csutak[1], V. Corbu[1]*

[1]University of Bucharest, Faculty of Biology, Department of Genetics, Intr. Portocalelor no. 1-3, 060101 Bucharest, Romania;

viorica-maria.corbu@bio.unibuc.ro

Bioremediation represents a fast growing research domain of international interest. The use of microorganisms, including yeasts, in various bioremediation technologies, is based on their ability to degrade a wide range of polluting compounds such as industrial and household wastes (Liu et al., 2022). Many strains belonging to yeast species from the Candida genus (C. tropicalis, C. lipolytica, C. catenulata, C. maltosa and C. parapsilosis) are successfully used in restoration of soil and water contaminated with hydrocarbons from crude-oil and oil derivatives. The assimilation of hydrocarbons in the yeast cells can be facilitated by biosurfactants, amphiphilic molecules able to reduce the tension at hydrocarbon-water interface. Moreover, the yeasts can use various hydrocarbons as sole carbon substrates for production of biosurfactants. Due to their high specificity and biodegradability, the biosurfactants are used in a wide range of biotechnological applications.

Our work deals with the identification of a new yeast strain, Candida parapsilosis CMGB-YT, isolated from oil polluted soil (Pitesti area, Romania), and the characterization of its potential use for production of biosurfactants for bioremediation of hydrocarbon contaminated soil and sediments.

The yeast strain CMGB-YT was preliminary identified using morphological observations, biochemical characterization (Biolog system) and MALDI-TOF mass spectrometry. The taxonomical identification was completed by molecular studies: (1) PCR-RFLP and sequencing of the ITS1-5.8S rDNA-ITS2 region; (2) the RFLP profiles obtained were used for construction of a phylogenetic tree; (3) supplemental PCR-RFLP analysis was performed for the 18S-ITS1 region. The results confirmed that our strain belongs to the species Candida parapsilosis.

The ability to assimilate n-alkanes (n-decane, n-dodecane, n-tetradecane and n-hexadecane), petroleum and toluene was assessed using the cell growth. The highest growth rates were observed on 1% n-alkanes, after six days of incubation.

The biosurfactant obtained from the culture grown on n-hexadecane, emulsified petroleum and fried (burned) vegetable oil, with emuslification index E24% values of 30, respectively, 35%. The biosurfactant was stable at temperatures between 4 and 70oC, at pH values ranging from 6.0 to 12.0, and NaCl concentrations from 8% and 10%, indicating that it could be used in neutral and alkaline environments, under extreme temperature and osmotic stress conditions.

Cell surface hydrophobicity determined using microbial adhesion to the hydrocarbon (MATH) method after six days of incubation in presence of n-hexadecane, suggested that hydrocarbon assimilation takes place both using biosurfactant and cell-hydrophobicity mediated mechanisms.

Crude and concentrated biosurfactants (10 to 40 mg/mL) were able to inhibit the growth of human pathogenic Candida strains possibly found in sediments and soil.

In conclusion, the newly isolated C. parapsilosis strain showed good potential both for bioremediation of oil polluted environments and for developing new efficient strategies based on highly stable biosurfactants to counteract human pathogens.

References

Liu, S. et al. (2022) `Petroleum spill bioremediation by an indigenous constructed bacterial consortium in marine environments` Ecotoxicology and Environmental Safety, 241, 113769, doi:10.1016/j.ecoenv.2022.113769.

End-of-Waste From Pyrite Ashes Contaminated Soils through HPSS Application

P. Scanferla[1]*, R. Quesresmini[2], L. Calgaro[3], R. Pellay[4], G. Ferrari[5], A. Marcomini[3]

[1]Fondazione Università Ca' Foscari, Dorsoduro 3859, 30123 Venezia, VE, Italy
[2]ARPA Lombardia - Waste and Industry Department, via Cantore 20, 25128 Brescia, IBS, taly
[3]Ca'Foscary University of Venice, Department of Environmental Sciences, Via Torino 155, 30172, Venice Mestre, Italy[3]
TEV group srl, statale Romea 8, 30034 Malcontenta di Mira VE, Italy
[4] Mapei Group Spa, via Cafiero 22, 20158 Milano MI, Italy

petra.scanferla@unive.it

A Remediation Project approved in 2014, provided for the use of the term EoW (End-of-waste) for an aggregate produced by a particular solidification/stabilization treatment applied on heavy metal contaminated soil after the implementation of a quality control protocol and a very accurate monitoring plan of the treated material. This case study is particularly relevant because: *i)* the more implemented practices to remediate the heavy metal contaminated soil are landfill disposal or capping, solutions not in agreement with the Circular Economy mandate and *ii)* generally the solidification/stabilization (S/S) treated soil cannot be used outside the site of origin. The area where the technology was applied was an abandoned industrial site heavily contaminated by heavy metals (in particular As, Pb, Cu and Cd) deriving from pyrite ashes resulted from the production of chemical fertilizers. The cement-based solidification/stabilization (S/S) technology used named HPSS- High Performance Solidification Stabilization, transforms the contaminated soil into granular material characterized by high density and mechanical strength and low porosity and leaching of pollutants, which can therefore be reused for environmental restoration (Scanferla et al., 2012, Calgaro et al. 2019). The presentation is related to the monitoring plan and the relative results obtained which have determined defining the contaminated soil after treatment as EoW. The monitoring plan provided for sampling during the soil treatment operations and at the end of the activities on the total treated mass placed on-site (of approximately 19,000 m^3) and provided for analyses on heavy metal leaching, mechanical strength characteristics and a battery of ecotoxicological tests.

Pictures of the excavation front with pyrite ashes (left) and the granulates after treatment (right).

References

Scanferla, P., Marcomini, A., Pellay, R., Girotto, P., Zavan, D., Fabbris, M., Collina, A. (2012). Remediation of a Heavy Metals Contaminated Site with a Botanical Garden: Monitoring Results of the Application of an Advanced S/S Technique. *CET Chem Eng Trans. 28, 113–118*. doi:doi.org/10.3303/CET1228040.

Calgaro, L., Badetti, E., Bonetto. A., Contessi, S., Pellay, R., Ferrari, G., Artioli, G., Marcomini, A. (2019). Consecutive thermal and wet conditioning treatments of sedimentary stabilized cementitious materials from HPSS® technology: Effects on leaching and microstructure. *J Environ Manage. 250*:109503. doi:10.1016/j.jenvman.2019.109503. https://linkinghub.elsevier.com/retrieve/pii/S0301479719312216.

Potentialities of Fungi Bioaugmentation for Improving Bioremediation of Co-Contaminated (PAHs, Trace Metals) Industrial Soils

F. Portet-Koltalo[1*], C. Bassimon[1 2], I. Benjelloun[2], D. Garon[2], F. Baraud[2], L. Leleyter[2], M. Lemoine[2], C. Rafin[3], E. Veignie[3], N. Machour[1] and M. Crampon[4]

[1]Université de Rouen-Normandie, COBRA laboratory, 55 rue St Germain, 27000 Evreux, France
[2]Université de Caen-Normandie, ABTE laboratory, Bd du Maréchal Juin, Campus 2 Bât Sciences 2, 14000 Caen, France
[3]Université Cote d'Opale, UCEIV, MREI 1, 145 avenue Maurice Schumann, 59140 Dunkerque, France
[4]BRGM, 3 avenue Claude Guillemin - BP 36009 - 45060 ORLÉANS Cedex 2, France

florence.koltalo@univ-rouen.fr

Soil pollution is a worldwide problem, co-contamination by organic and metals affecting most of the hazardous sites. Soils containing both trace metals and polycyclic aromatic hydrocarbons (PAHs) are becoming a major concern due to the rapid urbanization and the need to occupy former industrial sites. Bioremediation to clean co-contaminated soils has gained attention, by using bioaugmentation consisting of introducing exogenous species in the soil. The mycoremediation is based on the use of fungi which have the ability to adapt to complex soil matrices and to survive in extreme environmental conditions. The fungi can build up a mycelium network in the soil layer, which can not only contribute to hydrocarbons degradation through metabolization but also to biosorption and/or accumulation of metals. Here are presented the complementary potentialities of two fungal strains: one to biosorb soil metals and thus making them potentially less toxic to other soil microorganisms, and the other to biodegrade high molecular weight PAHs (HMW-PAHs) which are the more toxic and difficult to remove.

A fungal strain was selected for our study, called Absidia cylindrospora (Benjelloun et al., 2023), which was added in an industrial soil highly contaminated with metals and moderately with PAHs. Tests were carried out in soil microcosms with varying incubation times over several months. The effect of this strain on the dissipation of PAHs was quite low, a dissipation trend being observed only after 2 months. In the other hand, even if the total metal concentration remained stable in the soil over 3 months, A. cylindrospora showed a great ability to accumulate Cd, Co, Cu, Ni and Zn, even in the presence of PAHs. The bioaccumulation of these metals within the mycelium increased with the aging of the mycelium. For the majority of metals, the more mobile the element, the greater the increase in content in the mycelium over 3 months. This behavior might be favorable to stabilize the metal, reducing its availability then its potential toxicity, thus promoting the simultaneous degradation of PAHs by other soil bacterial or fungal strains.

In the case of Fusarium solani fungus (Rafin et al., 2000), inoculation in microcosms was first done with a highly PAH-contaminated industrial soil containing only trace metals. Its mycelium extension contributed to improve the degradation of the less water soluble HMW-PAHs (particularly the more toxic Benzo[a]pyrene), which are strongly adsorbed to the organic matter and therefore less available for microbial metabolism. It showed that this fungus could be used in clean-up of long-term contaminated soils by PAHs. In a next step, this fungus was added in an industrial soil with a mixed contamination, containing also high amounts of trace metals. The possible inhibition of mycelium extension and PAH degradation is under observation.

The route for the present research, especially focused on highly co-contaminated soils with metals and PAHs, is the use of a consortium of these two fungi, which is a promising alternative, increasing the metal's accumulation and immobilization capacity, but also improving PAHs degradation potential.

References

Benjelloun, I. et al. (2023). Bioaugmentation effect of Absidia cylindrospora on a PAHs and trace metals co-contaminated soil within a three-month microcosm-experiment. International Journal of Environmental Science and Technology, in press. doi: 10.1007/s13762-023-04842-8.

Rafin, C. et al. (2000). Degradation of Benzo[a]pyrene as sole carbon source by a non white rot fungus, Fusarium solani. Polycyclic Aromatic Compounds, 21, p. 311–329. doi: 10.1080/10406630008028542.

Sediment Quality Assessment of the Begej Canal – Ecotoxicological Tests

T. Tomić[1*], I. Vulin[1], N. Stojanović[1], D. Rađenović[2], N. Slijepčević[2], Đ. Pejin[2], and D. Tomašević Pilipović[2]

[1]University of Novi Sad, Faculty of Sciences, Department of Biology and Ecology, Trg Dositeja Obradovića 2, 21000 Novi Sad, Serbia
[2] University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia

tanja.tunic@dbe.uns.ac.rs

Sediment is an integral part of aquatic ecosystems that receives and deposits pollution from the water phase. As such, it may become a secondary contamination source and potentially pose a risk to human health and ecosystems. In order to establish a more reliable sediment quality assessment, a multidisciplinary approach should be applied which integrates physico-chemical and hydromorphological analysis, benthic fauna monitoring, investigation of biological effects, etc. Ecotoxicological whole sediment contact tests and sediment pore water or eluate tests may provide information about mixture effects and effects of potentially hazardous chemicals that may not be included in chemical analysis of sediments but are bioavailable to aquatic organisms. The Begej canal is an artificial canal that flows as an extension of the Begej River from Temisvar, Romania to its confluence in the Tisa River downstream from Zrenjanin, Serbia. The canal used to serve as a transnational navigable route in the region, but after it was closed to navigation a large amount of sediment has accumulated and due to inflow of industrial and municipal waste waters and run-off from the surrounding agricultural land, water and sediment contamination increased. In order to further manage the Begej canal, the quality of its sediment needs to be evaluated. The aim of this study was to contribute to the toxicity assessment of the Begej canal sediment, applying ecotoxicological tests and analysing biological effects on aquatic organisms from different trophic levels (primary producers – Myriophyllum aquaticum, consumers – Daphnia magna and reducers – Aliivibrio fischeri). Differences between sensitivity of tested models to samples were observed, but in general, results indicate high to moderate toxicity of sediment samples. The applied ecotoxicological tests paired with results of chemical analysis contributed to a more certain sediment quality assessment which provided further Begej sediment management options.

Acknowledgements: The authors gratefully acknowledge the financial support of the Science Fund of the Republic of Serbia, IDEAS call, Grant No. 7753609, BEuSED and the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grant No. 451-03-47/2023-01/200125).

Can the Composition of Plant's Guttation Fluids Be used to Assess the Effectiveness of Soil Remediation? First Evidence from Phytostabilization Experiments

C. Porfido[1*], I. Allegretta[2], R. Terzano[1], C. E. Gattullo[2], M. Garau[3], M. V. Pinna[3], D. Visconti[4], E. Margui[5], M.Fagnano[4], M. Spagnuolo[1]

[1]University of Bari, Dept. of soil, plant and food sciences, Via Amendola 165/A, Bari, IT
[2]University of Salento, Dept. of biological and environmental technologies, Via Monteroni 165, Lecce, IT
[3]University of Sassari, Department of agriculture, Viale Italia 39/A, Sassari, IT
[4]University of Napoli, Dept. of Agriculture, Via Università 100, Portici, IT
[5]University of Girona, Dept. of Chemistry, C/M Capmany 69, Girona, SP

carlo.porfido@uniba.it

When dealing with soils affected by metal(loid)s contamination, especially in the case of low soil organic matter content and poor-fertility conditions (e.g., mine tailings), phytostabilization can be an effective remediation technology, also contrasting soil degradation. In fact, covering polluted sites with herbaceous plants limits the mobility of contaminants by rhizostabilization within the soil, reduces aeolian transport, enhances the microbial activity, increases the organic matter content and decreases soil erosion processes. These effects may lead not only to the reduction of potential risks from hazardous chemical contaminants, but also to an overall improvement of soil chemical, physical and biological properties. In phytostabilization, stress-resistant plants tolerant to high levels of contaminants are commonly used, often in combination with soil amendments that ameliorate and speed up the beneficial effects of the plant cover.

In this study, phytostabilization experiments have been carried out growing Lolium rigidum plants in laboratory mesocosms prepared with tailings from a dismissed silver mining site (Argentiera, Sassari, Italy) and a soil from a former shooting range (Acerra, Napoli, Italy), both characterized by high concentrations of Pb, As, Cd, Sb and Zn. For both soils, the effect of different amendments (compost, biochar and plant growth promoting rhizobacteria-PGPR) on the mobility of the contaminants has been studied through sequential extraction procedures (SEP) and by assessing hazardous elements' uptake in plants' biomass (roots and shoots). Beside these quite conventional analytical approaches, a novel approach has been developed, based on the analysis of polluting and mineral elements in plants' guttation fluids via total reflection X-ray spectrometry (TXRF). Indeed, through guttation many plants exudate droplets of xylem sap by means of specialized foliar structures called hydathodes, located at the tips and at the edges of the leaves. Since the xylem sap is directly translocated from roots to shoots, its analysis allows an indirect measure of the uptake from soil and translocation to the aerial parts of polluting and mineral elements, without the need of uprooting the plant from soil and subsequent sample preparation and analysis. Our first results show that the mineral elements composition of guttation fluids is influenced by soil properties and by the applied amendment; for instance, no Pb is detected in fluids from mesocosms of the shooting range soil (where Pb is mostly stabilized as insoluble phosphates) while it is more concentrated in the sap of plants grown in the soil where Pb is less stabilized (mining tails), especially in PGPR-treated mesocosms with respect to other treatments.

These early evidence suggest that this TXRF-based method can be a non-invasive, reliable and expeditious method to assess hazardous metal(loid)s mobilization from polluted soils and translocation to plants' shoots, useful to evaluate not only the efficiency of phytoremediation experiments as in the present study but also other remediation technologies, where plants are used as bioindicators of soil pollution.

Nanoscale and Microscale Zero-Valent Iron for in Situ Chemical Reduction of Mixed Chlorinated Hydrocarbons at a Petrochemical Site: Preliminary Batch Tests

C. Bianco[1], S. Barbero[1], L. Magherini[1], T. Tosco[1]*, R. Sethi[1]

[1]Politecnico di Torino, DIATI - Department of Environment, Land and Infrastructure Engineering, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

tiziana.tosco@polito.it

The use of zero-valent iron (ZVI) is an effective approach for in-situ remediation of aquifers contaminated by a broad set of contaminants, in particular aliphatic halogenated hydrocarbons, PCBs, pesticides and heavy metals. Traditionally, ZVI has been employed in granular form as filling material in permeable reactive barriers (PRBs), consisting of trenches excavated to intercept the contamination plume, where pollutants are chemically reduced while being transported by natural groundwater flow through the reactive wall. More recently, nanoremediation, consisting of in situ chemical reduction (ISCR) via injection of colloidal nanoscale (NZVI) or microscale (MZVI) zero-valent iron, has been proposed and successfully employed for the targeted remediation of contamination hot spots. Thanks to their reduced size, these materials can be dispersed in colloidal suspensions and injected in the subsoil to form a reactive zone, thus allowing a precise targeting of contamination hot spots and secondary sources. Moreover, they can degrade the contaminants with kinetics orders of magnitude higher than the granular material in PRBs. Surface modification (e.g. sulfidation, polymer coating, doping with a second metal, etc.) is sometimes employed to increase particle longevity and contaminant targeting, and to optimize handling and injectability of the colloidal suspensions.

In this work, laboratory batch degradation tests are presented, aimed at assessing the efficacy of a set of NZVI and MZVI products for the treatment of an aquifer heavily contaminated by a highly concentrated mixture of chlorinated hydrocarbons. The major contaminants include hexachlorobutadiene (HCBD), chlorinated ethenes and ethanes, tetrachloromethane (PCM) and trichloromethane (TCM) at concentrations in the order of tens of mg/L (for HCBD) or µg/L (for the others). Five ZVI samples were tested, namely two nanoscale ZVI (sulfidized, and non-sulfidized), and three microscale ZVI (carbonyl, sulfidized, and non-sulfidized). Contaminated groundwater was collected at the site and used for batch test preparation. Sacrificial vials with no headspace were prepared with site groundwater. Redox potential, pH, electric conductivity and contaminant concentrations were measured at 1, 3, 7, 14 and 21 days.

The results showed a fast degradation rate for most contaminants in contact with all tested materials except for the carbonyl MZVI. The non sulphidized NZVI was identified as the best performing reactant, capable to degrade not only chlorinated ethenes, but also HCBD, 1,1,2,2-TECA, 1,1,2-TCA, PCM and TCM with half life times in the order of 50 h or lower, thus significantly faster than typical values reported in the literature for millimetric ZVI. Despite being only the preliminary step in the design of a full-scale ISCR application, the results of the batch tests herein presented open positive perspectives for the implementation of this technology at the contaminated site under study, confirming the efficacy of NZVI and MZVI also for complex contaminations characterized by highly concentrated mixtures of chlorinated compounds.

References

Sethi, R. and Di Molfetta, A. (2019) ' Groundwater Engineering - A Technical Approach to Hydrogeology, Contaminant Transport and Groundwater Remediation'. Springer Nature.
doi: 10.1007/978-3-030-20516-4, ISBN: 978-3-030-20516-4.

Tosco, T. et al. (2014) 'Nanoscale zerovalent iron particles for groundwater remediation: a review', Journal of Cleaner Production, 77, pp. 10-21.
doi: 10.1016/j.jclepro.2013.12.026.

Elliott, D.W. et al. (2001) 'Field assessment of nanoscale bimetallic particles for groundwater treatment', Environmental Science and Technology, 35(24), pp. 4922–4926.
doi: 10.1021/es0108584. Pure Appl. Chem., 91, p. 851–864.

STAR-LCA: Simplified Tool to Assess Remediation by LCA

M. Menegaldo[1]*, A. Bonfà[2], S. Breda[2], M. Carisi[1], A. Zabeo[1], L. Pizzol[1], P. Scanferla[2], A. Marcomini[2]

[1]GreenDecision s.r.l., Via Torino, 155, 30172 Venice, Mestre, Italy
[2]Fondazione Università Ca' Foscari, Dorsoduro 3859, 30123 Venice, Italy

martina.menegaldo@unive.it

Sustainable remediation is defined as a remedy whose net benefit on human health and the environment is maximized through the judicious use of limited resources (Morais and Delerue-Matos 2010). In the last few decades a growing interest in these practices has emerged in several international and national organizations as well as in sectorial networks and forums (Bardos 2014). Within that context, STAR-LCA, a Simplified Tool to Assess Remediation by Life Cycle Assessment (LCA), has been developed. The aim of the STAR-LCA software is allowing ex-ante simplified environmental assessment of alternative remediation interventions in specific restoration areas. The tool calculates LCA impacts according to ISO 14040-14044 by applying the Recipe 2016 method using data from the Ecoinvent 3.6 database and allows the comparison of alternative solutions. By providing a limited number of conditioning aspects (e.g., surface area, contamination depth) other secondary parameters are automatically calculated and, if needed, can be modified by the user. Once the restoration area is characterized it’s possible to define its available solutions organized according to sub-areas. A solution is identified by a set of one or more technologies applied to a selected subarea alongside the specific waste treatments and transport.

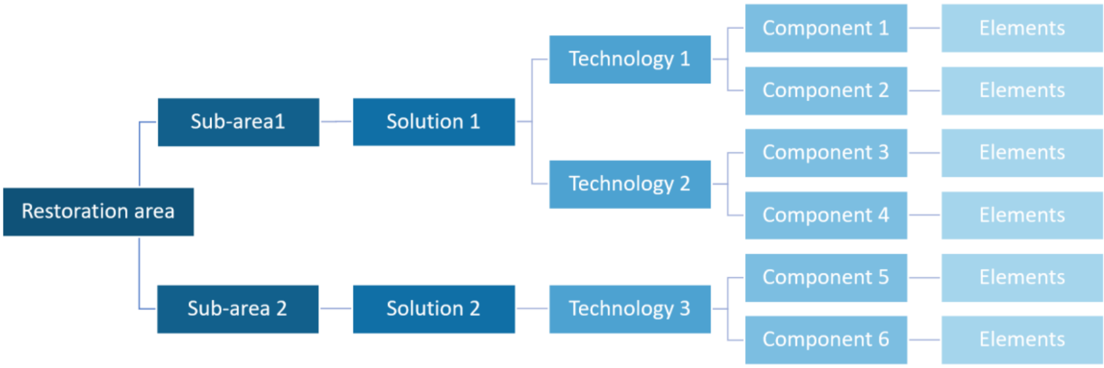


Figure 1: Logical entities involved.

References

Bardos, Paul. 2014. “Progress in Sustainable Remediation.” Remediation Journal 25(1):23–32.
doi: 10.1002/rem.21412.

Morais, Sérgio Alberto, and Cristina Delerue-Matos. 2010. “A Perspective on LCA Application in Site Remediation Services: Critical Review of Challenges.” Journal of Hazardous Materials 175(1–3):12–22.
doi: 10.1016/j.jhazmat.2009.10.041.

Explainable Deep Learning for Early Environmental Safety - Understanding Bioaccumulation of Organic Molecules

S. Schmidt[1]*, H. Heberle[1], F. Montanari[2], L. Zhao[1]

[1]Bayer AG, Crop Science Division, Alfred-Nobel-Str. 50, 40789 Monheim, Germany
[2]Bayer AG, Pharmaceuticals Division, Müllerstr. 178, 13353 Berlin, Germany

sebastian.schmidt1@bayer.com

The rapid evolution of machine learning and explainable artificial intelligence (XAI) methods opened up new opportunities for predictive modelling in the context of molecular design and safety assessments. In the Early Environmental Safety function at Bayer Crop Science we support the discovery and design of new biologically active molecules with benign environmental safety profiles. In this contex, we explored explainable deep learning methods to predict bioaccumulation in fish from molecular structures. Bioaccumulation is an important parameter in the environmental risk assessment of chemicals and new alternative methods are required to reduce vertebrate testing. Despite limited numbers of tested molecules and the complexity of biological systems, artificial intelligence can be useful, especially in combination with human expert mechanistic knowledge.

We developed a multi-task deep learning model for the bioconcentration factor BCF (Zhao 2022). The model is based on a continuous data-driven representation of chemical space that operates on SMILES strings (Winter 2019). In addition to BCF data, we utilized a large dataset for lipophilicity (logD) to improve model performance and extend the applicability domain. Our model is more accurate than previously published models (RMSE of 0.59 log units on an independent test set) and generalizes well to unknown regions of the chemical space. It is purely data-driven and therefore independent from expert-crafted rules or the definition of functional groups.

In addition, we present an explainability approach that provides valuable feedback to the user by highlighting the most influential parts of the molecule (SMILES characters). This additional explainability layer helped during model development, can foster acceptance of the predictions by allowing users to explore the inner workings of the model, supports the design of safe molecules, and can improve mechanistic understanding of the processes involved in bioaccumulation. The explanations can be easily visualized using XSMILES (Heberle 2022), a new library for interactive visualization of atomic and SMILES character scores.

We demonstrate successful applications of the model and point out limitations of the approach. Overall, we aim to contribute to advances in the field of safety predictions and the development of alternatives for animal testing.

References

Heberle, H. et al. (2023) 'XSMILES: interactive visualization for molecules, SMILES and XAI attribution scores', J Cheminform, 15. doi: 10.1186/s13321-022-00673-w.

Winter, R. et al. (2019) 'Learning continuous and data-driven molecular descriptors by translating equivalent chemical representations', Chem Sci, 10, 1692. doi: 10.1039/C8SC04175J.

Zhao, L. et al. (2022) 'Modeling bioconcentration factors in fish with explainable deep learning', Artif Intell Life Sci, 2, 100047. doi: 10.1016/j.ailsci.2022.100047.

New Approaches to Predict Environmental Biodegradation Half-Lives from Structure

J. Hafner[1*], T. W. Lee[2], A. Scheidegger[2], K. Fenner[1,2]

[1] University of Zürich, 8057 Zürich, Switzerland
[2]Swiss Federal Institute of Aquatic Science and Technology (Eawag), 8600 Dübendorf, Zürich, Switzerland

jasmin.hafner@uzh.ch

Predicting a chemical's environmental persistence from its structure is essential to (i) implement benign-by-design principles at an early stage in the design of new chemicals, and (ii) to understand the environmental fate and hence exposure potential of existing micropollutants. However, available biodegradation models are not able to accurately predict the primary biodegradation half-lives of complex structures such as pharmaceuticals, pesticides, or industrial chemicals. This situation is mainly due to the lack of abundant and standardized biodegradation data, which would be crucial to build reliable prediction models.

Here, we address this issue by (i) assembling and curating half-life data obtained from biodegradation experiments with structurally complex small molecules, such as pesticides and pharmaceuticals, in soil and activated sludge, and (ii) by developing new Quantitative Structure-Biodegradation Relationships (QSBRs) to predict biodegradation half-lives. The raw data was obtained from EAWAG-SOIL (S. Latino et al., 2017) and EAWAG-SLUDGE data packages on enviPath, resulting in data sets of 984 and 172 substances with half-life estimates for soil and sludge, respectively. For each substance, we applied a Bayesian inference to include censored data points and to estimate the true mean and standard deviation of the half-life distribution. We then selected the most relevant features from PaDEL descriptors, MACCS fingerprints, and enviPath's biotransformation rules to build machine-learning models that not only predict a half-life, but also assign a confidence metric to each prediction. While no excellent overall model performance could be achieved, we show that the confidence metric can be used to reliably distinguish good from bad predictions, and to point towards chemicals or classes of chemicals for which more experimental data is needed.

Our approach can be expanded in the future to include biodegradation data from other environmental compartments (e.g., water-sediment systems) in the training set, which will improve model performance, increase the coverage of the chemical space, and allow us to predict half-lives in other environments.

(Acknowledgment: JH and KF are members of the Prioritisation and Risk Evaluation of Medicines In the EnviRonment (PREMIER). PREMIER has received funding from the Innovative Medicines Initiative 2 Joint Undertaking under grant agreement No 875508. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme and EFPIA (https://www.imi.europa.eu/).
Disclaimer: This abstract only reflects the author's view and the JU is not responsible for any use that may be made of the information it contains.)

References

S. Latino, D.A.R. et al. (2017) 'Eawag-Soil in enviPath: a new resource for exploring regulatory pesticide soil biodegradation pathways and half-life data', *Environmental Science: Processes & Impacts*, 19(3), pp. 449–464. doi: 10.1039/C6EM00697C.

Automatic Extraction of Optimized Reaction Patterns for the Prediction of Environmental Contaminant Biotransformation Pathways

K. Zhang[1,2*], K. Fenner[1,2]

[1]Eawag, Department of Environmental Chemistry, Überlandstrasse 133, 8600 Dübendorf, Switzerland
[2]University of Zürich, Department of Environmental Chemistry, Rämistrasse 71, 8006 Zürich,Switzerland

kunyang.zhang@eawag.ch

Knowledge on the environmental biotransformation of organic contaminants is essential for chemical risk management, bioremediation of contaminated sites, and the development of green chemical alternatives. Pesticide transformation products (TPs), formed in the environment, can have similar or even more serious adverse environmental effects than parent pesticides. Yet, the analytical identification of TPs is challenging, especially in environmental samples. Several rule-based tools for the in silico prediction of TPs have therefore been developed over the past few decades (e.g., envipath.org) (Wicker J. et al. 2015). One key challenge in developing in silico prediction tools is the extraction of reaction rules from biotransformation reaction databases. Among the rules that are currently available online, the majority of them were manually curated, for example, EAWAG-BBD rules (Gao J., et al. 2010). However, the genericity of manually curated rules is arbitrarily determined, making it difficult to balance between precision and recall of TP prediction. Moreover, with the addition of new pathway information, manually curated rules can be limited in representing the newly added reactions for two main reasons. First, due to the expansion of the chemical space covered, new reaction patterns might be present in the new data sets that are not included in existing rules at all. In the other case, similar reaction patterns are already included but not generalized enough to account for enzyme promiscuity on substrates in new reactions. In our project, we developed an automatic rule generation tool called enviRule, which overcomes the issues caused by arbitrary rule genericity and the addition of new data by extracting and updating rules with three main functional modules, namely, reaction clusterer, reaction adder, and rule generator. It clusters biotransformation reactions into different groups based on the similarities of reaction fingerprints, and then automatically extracts and generalizes rules for each reaction group as SMIRKS. Instead of being arbitrarily determined, the genericity of automatic rules is optimized against the downstream TP prediction task, thus guaranteeing the best possible prediction performance. According to our experiments, the models trained with automatic rules outperformed the models trained with manually curated rules by 30% in the area under curve (AUC) scores of precision-recall curve of TP prediction. Additionally, when new reactions are added, enviRule recognizes which existing rules need to be adapted and which new rules need to be created based on the comparison of reaction fingerprints. The coverage of newly added reactions was increased from 42% to 76% after automatic rule updates by enviRule. To the best of our knowledge, enviRule is the first tool that implements automatic rule updates to deal with the growing number of reported biotransformation reactions.

References

Wicker, J. et al. (2015) 'enviPath – The environmental contaminant biotransformation pathway resource', Nucleic Acids Research, 44(D1), pp. D502–D508. doi:https://doi.org/10.1093/nar/gkv1229.

Gao, J., et al. (2010) 'The University of Minnesota Biocatalysis/Biodegradation Database: improving public access', Nucleic Acids Research, 38(suppl_1), pp. D488–D491. doi:https://doi.org/10.1093/nar/gkp771.

Triclosan and its Metabolites as Potential Thyroid-Disrupting Chemicals: In Silico Analysis

N. Milić[1]*, L.Đurić[1], M. Milanović[1], J. Drljača[1], N. Milošević[1]

[1]University of Novi Sad, Faculty of Medicine, Department of Pharmacy, Hajduk Veljkoa 3, 21000 Novi Sad, Serbia

natasa.milic@mf.uns.ac.rs

Triclosan is a synthetic antimicrobial agent used in disinfectants, cosmetic products, clothing textiles, and other materials. Studies suggest the bioaccumulation potential of triclosan in the environment and thus exposure to triclosan emerged concerns about the possible adverse effects of both parent compound and its metabolites on the endocrine system. The aim of this study was to conduct in silico analysis in order to evaluate if triclosan and its 4 metabolites could be classified as thyroid-disrupting chemicals, considering their binding affinity for thyroid receptors, and molecular and pharmacokinetic properties. Interaction between the analyzed compounds and thyroid receptor alpha (TRalpha; PDB entry code: 1NAV), beta (TRbeta; PDB entry code: 1NAX), and thyroxine-binding globulin (TBG; PDB entry code: 4X30) was determined using GOLD molecular docking tool. Molecular and pharmacokinetic properties were analyzed using SwissADME and admetSAR online tools. Regarding the molecular descriptors, for triclosan and its metabolites, polar surface area was in the range 18.46-49.69 Å², molecular weight 295-315 g/mol, number of rotatable bonds 2-4, number of hydrogen bond acceptors (NHBA) < 4 and number of hydrogen bond donors (NHBD) < 3. Lipophilicity, determined as logP was in the range 3.55-4.68, which indicated good oral bioavailability. Based on the pharmacokinetic analysis, good Caco-2 permeability and penetration via blood-brain barrier could be expected. Binding affinities of the analyzed compounds, using ChemPLP fitness scores, were in the range 69.01-77.77 (co-crystallized ligand affinity-88.89), 55.76-63.15 (co-crystallized ligand affinity-99.00), and 49.86-64.38 (co-crystallized ligand affinity-81.72), for TRalpha, TRbeta, and TBG, respectively. The highest score for TRbeta was observed for triclosan (63.15), while monohydroxilated metabolites showed the highest scores for TRalpha and TBG (77.77 and 65.38, respectively). In compared with the obtained ChemPLP fitness scores for bisphenol A (TRalpha-66.50, TRbeta-65.37, TBG-59.66) the obtained results suggest that triclosan and its metabolites may impair thyroid function.

Acknowledgement
This work was supported by the Provincial Secretariat for Higher Education and Scientific Research, AP Vojvodina, Republic of Serbia [Grant number 142-451- 3120/2022-01].

References

Milanović, M., et al. (2023) Comprehensive insight into triclosan-from widespread occurrence to health outcomes. Environ Sci Pollut Res Int. 10, p.25119-25140. doi: 10.1007/s11356-021-17273-0.

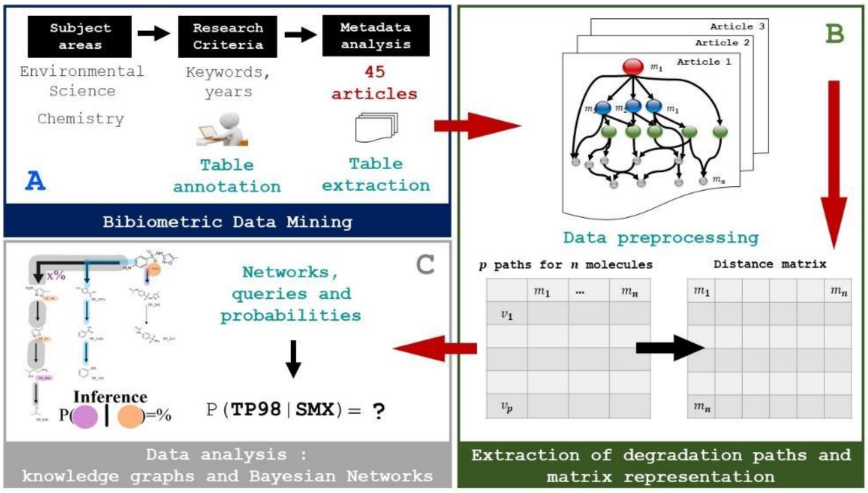
Meta-Analyses for the Elucidation of Micropollutant Degradation Pathways During Wastewater Treatment: Application to Sulfamethoxazole

A. Azaïs[1]*, R. Ouaret[2], A.B. Minta[1], C. Albasi[2], J-M. Choubert[1]

[1]INRAE, UR REVERSAAL, 5 Rue de La Doua, Villeurbanne, CS 20244, F-69625, France
[2]Université de Toulouse,Laboratoire de Génie Chimique, CNRS, INPT, UPS, Toulouse, France

antonin.azais@inrae.fr

The presence of various synthetic molecules (manufactured products), called micropollutants (MPs), in all aquatic compartments (domestic, surface and groundwater) have been pointed out these last decades (Luo et al. 2014). Biological and chemical oxidation do not lead to a complete mineralization of target micropollutants but to transformation products (TPs) with initially similar structures as the parent compounds (Menz et al. 2017). Several micropollutants reaction pathways are proposed in the wastewater treatment literature, these data diverge greatly and, to date, are unexploited. As an innovative alternative, probabilistic graphical models could allow establishing parentage between the most relevant daughter molecules or Transformation Products (TPs). Based on the analysis of an extensive bibliography gathering more than 45 articles (30 for AOPs and 15 dealing with biological processes) for more than 140 molecules, this study proposes an innovative meta-analysis methodology articulated around three complementary parts (see associated figure) and finally based on Knowledge Graphs (KG) and Bayesian Network (BN). For example, probability of the most recurrent pattern in biological processes (SMX > TP98 > TP83 > TP98b > TP60b) can be obtained through a table of calculation of all the modalities taken by the TPs (observed, not observed). In future work, we intend to develop automation of the database mining step and, if possible, data treatment part.



General scheme of the methodology followed for the analysis of the degradation pathways of SMX.

References

Luo, Y. et al. (2014). "A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment". Science of The Total Environment 473-474, 619–641.

Menz, J. et al. (2017). "Transformation products in the water cycle and the unsolved problem of their proactive assessment: A combined in vitro/in silico approach". Environment International 98, 171–180.

Nexus Between Life Cycle Assessment and Environmental Analytical Chemistry

F. Passarini[1,2]*, D. Cespi[1,2], L. Ciacci[1,2], I. Vassura[1,2]

[1]University of Bologna, Department of Industrial Chemistry "Toso Montanari", viale del Risorgimento 4, 40136 Bologna;
[2]CIRI Frame, University of Bologna, via D. Campana 71, 47922 Rimini.

fabrizio.passarini@unibo.it

LCA ("Life Cycle Assessment" or "Analysis") is a powerful tool to quantify the environmental impacts related to products, processes, systems. It has been recognized that this approach, before the term LCA was invented, was first conceived in the industrial chemistry framework (Smith, 1968), even though in the following years this tool was developed much more by other scientific sectors. However, in recent times, a growing importance was recognized to LCA also in the chemical product chain (Maranghi & Brondi, 2020).

The nexus between LCA and environmental analytical chemistry is here investigated, looking for analogies and possible integrations, suggesting common and fruitful areas of interaction.

LCA (ISO 14040/14044) constitutes the environmental analytical branch of the "Life Cycle Thinking" approach, which can provide important information about the consequences of anthropic activities from a systemic point of view. It is aimed at quantifying environmental impacts starting from the collection of many inventory data; thus, similarly to any other scientific analytical methodologies, data quality requirements should address many features, like precision, completeness, representativeness, consistency, reproducibility, uncertainty. Furthermore, in the common industrial practice, process analytical chemistry is a very important tool to monitor the behaviour of different operations and their possible failures, usually through the employment of control charts. The overall sustainability of an industrial process, requiring an LCA approach, is an additional information, whose integration with other conventional parameters has been already suggested in some process data analysis platforms.

Moreover, LCA is used to express synthetic indicators of environmental impact through the elaboration of physico-chemical data. Also, chemometric techniques (commonly considered an integral part of the analytical approach) can be used to process experimental data, in order to recognize patterns, classify and rank different objects, identify properties deriving from the interaction of different variables. Some chemometric studies have been carried out to fill data gaps or to predict unknown environmental indices from the elaboration of various chemical parameters related to molecular structures. Another promising integration between these two methods has been suggested in the field of experimental design, for the optimization of novel technologies in view of improving their environmental performances (Costamagna et al., 2020).

Finally, an increasing attention in recent years has been devoted to the sustainability of the analytical approach itself, to assess its impacts (due to waste generation, energy consumption, contaminant release, use of toxic reagents, etc.) from an environmental point of view. An international conference on Green and Sustainable Analytical Chemistry has recently been launched by EuChemS. Some principles of "green analytical chemistry" have been recently set.

This issue could hopefully be further discussed to better understand potentially profitable integration in chemical expertise, starting from our academic education courses.

References

Smith H., "The Cumulative Energy Requirements of Some Final Products of the Chemical Industry", Transactions of the World Energy Conference, paper n. 188 (Section E), Moscow, 1969.

Maranghi S and Brondi C., "Life Cycle Assessment in the Chemical Product Chain", Springer International Publ., 2020.

Costamagna M., Ciacci L., Paganini M.C., Calza P., Passarini F., "Combining the highest degradation efficiency with the lowest environmental impact in zinc oxide based photocatalytic systems", J. Clean. Prod., 252, Article 119762, 2020.

Investigating Differences in Kinetics of PFAS in a Mixture Exposure Scenario with Physiologically Based Kinetic Modeling

E. Dracheva[1]*, S. Örn[2], L. Ahrens[3], P. L. Andersson[1]

[1]Umeå University, Department of Chemistry, Umeå, Sweden
[2]Swedish University of Agricultural Sciences (SLU), Department of Biomedical Sciences and Veterinary Public Health, Uppsala, Sweden
[3]Swedish University of Agricultural Sciences (SLU), Department of Aquatic Sciences and Assessment, Uppsala, Sweden

elena.dracheva@umu.se

Per- and polyfluoroalkyl substances (PFAS) are a large group of synthetic organic chemicals characterized by extremely strong and stable C-F bond which gives them useful properties such as thermal stability in addition to hydrophobicity and lipophobicity. Due to the properties, PFAS are used extensively in various applications such as textiles, plastics, paper, consumer articles and electronics. Several PFAS are known to be persistent and bioaccumulative and therefore are referred to as “forever chemicals”. Physiologically based kinetic (PBK) models are a means of *in silico* determination of dose-at-target for compounds using information about the organism’s physiology and the chemical properties. Several PBK models have been developed for various PFAS in mammals and fish, few models, however, account for mixture exposure. Most of PBK models tailored for mixture exposure situations cover few chemical classes and are focused on inhalation in rats. (Desalegn et al., 2019) To our knowledge, impact on kinetics for co-exposed PFAS has not been investigated in fish PBK models in ecotoxicology as of today, however, evidence of effects of long-chain PFAS on the kinetics of short-chain PFAS have been reported in fish.

In this study, we aimed to elucidate the changes in kinetic parameters of PFAS in a mixture exposure scenario in adult female zebrafish (*Danio rerio*). To showcase, PFOA was selected based on *in vivo* data availability and environmental relevance. An *in vivo* mixture exposure experiment was performed on adult zebrafish with 7 PFAS (PFBS, PFHxS, PFHpA, PFNA, PFOA, 6:2 FTSA and FOSA) with a nominal water concentration of each chemical being 10 µg/L during 32 days and PFAS levels in brain, liver, ovaries and carcass were quantified. A PBK model was developed and parametrized to represent PFOA kinetics accounting for ionization and uptake and elimination via the gills. The model was fitted to the observed PFOA levels in the four organs and then validated on the whole-body concentration over time using data from Ulhaq et al. (Ulhaq et al., 2015) and the same physico-chemical parameters as those determined in our study. The model showed good agreement with the whole-body concentrations provided from Ulhaq et al., suggesting insignificant or low differences in PFOA kinetics in the studied mixture compared to the single chemical exposure scenario. In addition, we studied another mixture data set (Chen et al., 2016), who exposed zebrafish to 21 PFAS chemicals with perfluorinated chain length from 3 to 18. The predictions showed 2-4 times lower concentrations in the liver and ovaries as compared to the observed levels. These preliminary results suggest changes in kinetic parameters (i.e., gill exchange and blood free fraction) of PFOA in a complex mixture with longer chain PFAS or stronger acids or influence of transformations (formation of PFOA) that could not be captured with our model parametrization. These results highlight the need for further investigations on chemicals kinetics under mixture exposure scenarios, and PBK modeling is a useful tool to test hypotheses on kinetic interactions.

References

Chen, F. F., Gong, Z. Y. and Kelly, B. C. (2016) 'Bioavailability and bioconcentration potential of perfluoroalkyl-phosphinic and -phosphonic acids in zebrafish (Danio rerio): Comparison to perfluorocarboxylates and perfluorosulfonates', Science of the Total Environment, 568, pp. 33-41.

Desalegn, A., Bopp, S., Asturiol, D., Lamon, L., Worth, A. and Paini, A. (2019) 'Role of Physiologically Based Kinetic modelling in addressing environmental chemical mixtures - A review', Comput Toxicol, 10, pp. 158-168.

Ulhaq, M., Sundstrom, M., Larsson, P., Gabrielsson, J., Bergman, A., Norrgren, L. and Orn, S. (2015) 'Tissue uptake, distribution and elimination of (14)C-PFOA in zebrafish (Danio rerio)', Aquat Toxicol, 163, pp. 148-57.

Free in-Silico Tools for the Prediction and Screening of Hazard Properties of Chemicals

E. Papa[1]*, N. Chirico[1], L. Bertato [1,2] and A. Moccia[2]

[1]University of Insubria, Department of Theoretical and Applied Sciences, via J.H. Dunant 3, 21100, Varese Italy.
[2]Suterra Europe Biocontrol S.L., Plaza America 2, 9a 46004, Valencia, Spain

ester.papa@uninsubria.it

The need for in silico tools has grown in the recent years to reduce the impact of animal testing for regulatory and scientific purposes and to speed up chemical screenings and prioritization procedures, which are useful for the early identification of potentially hazardous chemicals and to suggest "safe by design" alternatives (ECHA, 2008). In silico tools (models and software) based on Quantitative Structure-Activity Relationships (QSAR) allow for these purposes; in fact, they can generate predictions based on the molecular structure, and can be applied to evaluate the toxicological profile, physicochemical properties, and properties related to the environmental fate of existing and new compounds (pre-synthesis) (ECHA, 2008). In the last years many QSARs were developed, which predictions are suitable for academic, industrial and regulatory use, therefore it is necessary to ease their dissemination and application with appropriate software.

To this end, since 2018, we have developed a suite of free tools which provide QSAR-based predictions for single and multiple endpoints, along with the technical documentation concerning the quality and predictivity of the models, as required by the regulatory context, reported as QSAR Model Reporting Format (QMRF) compiled and available for each model. The QSARINS-Chem standalone version software (Chirico, 2021) applies individual regression models to predict physico-chemical and fate-related properties (e.g., Koc, Persistence and PBT profiling) in addition to toxicity and in vivo biotransformation. A different version of this software, called QSARINS-Chem ECO.44, is dedicated to the prediction of in vitro intrinsic hepatic clearance in mammals (human and rodents) using QSAR models based on the putative most probable reactions (MPRs) mediated by Cytochrome P450, predicted by the Toxtree Software. The IVBP-Suite (In Vitro Biotransformation Prediction – Suite) software, automatically runs the Toxtree software, to ease the profiling of the in vitro intrinsic hepatic clearance of chemicals providing predictions for multiple endpoints, organisms and chemicals in batch. Finally, the QSAR-ME Profiler (QSAR - Multiple Endpoints Profiler) software combines the possibility to profile chemicals in batch for multiple endpoints (using regression models included in the former software, in addition to new regression and classification models) by means of similarity analysis using fingerprints.

In this presentation we provide a short overview of the four software, with a focus on the application of QSAR-ME Profiler for a case study performed on a set of molecules of interest for industry. The use of these tools is helpful to streamline the prediction of multiple hazard properties of chemicals, by simplifying the application of different QSARs and organizing results in tabular and graphical form.

All the software shown in this presentation are freely downloadable from the internet (http://dunant.dista.uninsubria.it/qsar/).

References

Chirico N. et al, (2021), 'QSARINS-Chem standalone version: A new platform-independent software to profile chemicals for physico-chemical properties, fate, and toxicity', 20, p. 1452. doi:10.1002/jcc.26551.

ECHA (2008), 'Guidance on information requirements and chemical safety assessment Chapter R.6: QSARs and grouping of chemicals' Available at: https://echa.europa.eu/documents/10162/17224/information_requirements_r6_en.pdf/77f49f81-b76d-40ab-8513-4f3a533b6ac9?t=1322594777272 (last accessed 24/03/2023).

An Overview of QSAR Models for the Prediction of Thyroid Disruption-related Endpoints

M. Evangelista[1], N. Chirico[1] and E. Papa[1]*

[1]University of Insubria, Department of Theoretical and Applied Sciences, via J.H. Dunant 3, 21100, Varese Italy.

ester.papa@uninsubria.it

Endocrine disrupting chemicals (EDCs) are structurally heterogeneous hazardous substances with the ability to disrupt the normal functioning of the endocrine system. These chemicals can be found, for instance, in consumer products, industrial substances, pesticides, and biocides. EDCs affect the hormonal systems interfering with the synthesis, the transport, the metabolism, and the binding with several receptors such the estrogen (ER), the androgen (AR), and the thyroid (TR) receptors. This causes several adverse effects to humans and wildlife (e.g., cancer development, reduction of fertility, alteration of the metabolism and of the neurological development) (Diamanti-Kandarakis, 2009). For these reasons, these chemicals need to be regulated in order to identify and manage possible risks for humans and the environment.

Among the approaches recently introduced to support hazard and risk assessment procedures, while reducing the impact of experimental tests in terms of animal lives, time and costs, in silico approaches based on Quantitative Structure Activity Relationships (QSARs) represent a valid alternative to experiments. These tools are useful to help the profiling of existing and new chemicals, and to identify potential hazardous substances and safer alternatives on the basis of the molecular structure (OECD, 2004).

In this poster we focus on the disruption of the thyroid system (TS) which is crucial for the brain development and metabolism regulation. The study provides an overview of the pertinent QSARs reported in the literature in the last 15 years.

The aims of this work are: to create a sound basis for the development of new QSARs specific for the TS, to identify existing approaches and available experimental data for different chemical classes and endpoints, and to highlight possible gaps in data and approaches.

The analysis was conducted using specific keywords in the Web of Science database which led to a total of 44 articles addressing the TS by QSAR models. More than 130 QSARs based on different modelling methods were identified for eight molecular targets specific for the TS (i.e., with the Thyroid Receptor (TR), Transthyretin (TTR), Thyroperoxidase (TPO), Iodothyronine Deiodinases (DIOs), Thyroid-Stimulating Hormone Receptor (TSHR), Thyroid-Releasing Hormone Receptor (TRHR), Sodium-Iodide Symporter (NIS), Sulfotransferases (SULTs)) (Dracheva, 2022).

Finally, the analysis of the results highlighted increasing interest of the scientific community in the modelling of TS.

References

Diamanti-Kandarakis, E. et al, (2009) 'Endocrine-Disrupting Chemicals: An Endocrine Society Scientific Statement', Endocrine Reviews, 4, p. 293. doi: 10.1210/er.2009-0002.

Dracheva, E. et al, (2022), 'In Silico Identification of Potential Thyroid Hormone System Disruptors among Chemicals in Human Serum and Chemicals with a High Exposure Index' Environmental Science and Technology, 12, p. 8363,. doi: 10.1021/acs.est.1c07762.

OECD (2004) 'Principles for the validation, for regulatory purposes, of (quantitative) structure-activity relationship models'. Available at: http://www.oecd.org/dataoecd/33/37/37849783.pdf (last accessed 24/03/2023).

Development of an In Silico Driven Early Warning System for Identification of Potential New Emerging Risk Chemicals in the European Partnership Program PARC

P. L. Andersson[1]*, N. Alygizakis[2], O. Taboureau[3], S. Karaktsios[3]

[1]Umeå University, Department of Chemistry, Umeå, Sweden
[2]National and Kapodistrian University of Athens, Laboratory of Analytical Chemistry, Department of Chemistry, Greece
[3]Universite Paris Cite, INSERM U1133, CNRS UMR 8251, 75006 Patris, France
[4]Aristotle University of Thessaloniki, Department of Chemical Engineering, Environmental Engineer Laboratory, University Campus, Thessaloniki 54,124, Greece

patrik.andersson@umu.se

An early warning system (EWS) for identification of potential new emerging risk chemicals (NERCs) is under development in the new European Horizon Partnership for the Assessment of Risks from Chemicals (PARC). It will include various experimental and computational techniques covering chemical analytical methodologies from target to nontarget analysis, effect driven analysis (EDA) to purely in silico methodologies. The long-term goal and vision is to develop an AI-driven system that is capable of picking up signals of potential risks from different sources of information notifying and triggering risk assessment and management actions. The computer driven component of the EWS aims to derive data to cover exposure and effect properties of identified chemicals to assess risk. It will also include models to describe fate and distribution in the environment and biota including physiologically based toxicokinetic models (PBTK) to estimate dose at target. Data will be derived using read-across approaches and quantitative structure-activity relationship (QSAR) models applying available open-source platforms including machine learning driven models. Text and data mining approaches will be used to identify information in open sources including grey literature, patent information and product and material content data. In addition, bioinformatics tools will be used to screen omics data in open platforms as early indications of interactions in biologicals systems. We will also harvest non-target chemical analytical data making use of digitally archived samples to potentially identify new chemical signatures in different matrices. Signals of different kinds will be filtered and prioritized relative to risk measures to identify potential NERCs to be investigated using higher tier tests including experimental systems and case studies. The system ultimately aims at moving from expert judgments and manual horizon scanning towards an AI-driven, broad scanning and fully automatic precautionary system.

Machine Learning Models for Predicting the Rejection Rates of Organic Contaminants by Forward Osmosis and Reverse Osmosis Membranes

A. Tayara[1]*, Y. Xiang[1,2] and C. Shang[1,3]

[1]The Hong Kong University of Science and Technology, Department of Civil and Environmental Engineering, Clear Water Bay, Kowloon, Hong Kong
[2]Institut de Chimie des Milieux et des Matériaux de Poitiers IC2MP UMR 7285 CNRS Université de Poitiers, ENSI Poitiers, 1 rue Marcel Doré TSA 41105, 86 073 Cedex 9, Poitiers, France
[3]Hong Kong Branch of Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, Hong Kong

atayara@connect.ust.hk

Various organic contaminants, such as pharmaceutical and personal care products, pesticides, lipids, and volatile fatty acids, are commonly present in treated wastewater. Many of these compounds pose a potential threat to human health and act as precursors of undesirable disinfection byproducts, highlighting the importance of their removal for safe potable reuse. Membrane technologies such as forward osmosis (FO) and reverse osmosis (RO) have been demonstrated to be effective in removing organic contaminants in potable reuse scenarios. However, the rejection rates of compounds are highly dependent on their characteristics, membrane properties, and operating conditions, and determining the rejection rates experimentally for each individual compound can be time-consuming and costly. In this study, machine learning (ML) models were established to predict the rejection rates of organic contaminants by FO and RO processes. The input variables for the ML models included molecular descriptors, fingerprints, membrane and compound characteristics, and operating conditions. A total of 616 data points were collected for FO, covering 122 organic compounds and 13 membranes, while 1,101 data points were collected for RO, covering 393 organic compounds and 22 membranes. Among the 14 models established, random forest is the best-performing model for FO with a prediction accuracy (represented by the coefficient of determination, R^2) of 0.85, while XGBoost performed the best for RO with a prediction accuracy of 0.92. Shapley additive explanations (SHAP) analysis was conducted to identify the variables that contributed the most to the prediction. The length of the compound, permeated water flux, and hydrophobicity were the top three contributors for the FO model. For the RO model, the length of the compound and pressure were the top two contributors, and molecular descriptors (e.g., Balaban J and Kappa3) representing branching and complexity of the molecular structure, and fingerprints (e.g., C=C double bonds and carbonyl group) related to $\pi-\pi$ interactions and hydrogen bonding with the membrane, significantly contributed to the prediction accuracy. In addition to the superior prediction performance, the two ML models provided further insights into the rejection mechanisms of compounds by membranes. The significant contribution of the compound length underscores the role of the size exclusion mechanism in both FO and RO models. Furthermore, Balaban J and Kappa3 emphasize the importance of the size exclusion mechanism, whereas the C=C double bonds and carbonyl group highlight the contribution of the adsorption mechanism in the RO model. The findings of this study not only provided predictive models for the removal of organic contaminants but also enhanced the mechanistic understanding of the rejection mechanisms in FO and RO processes.

Bromine, Iodine and Mercury Spatial Variability and Seasonal Accumulation Along the EAIIST Traverse

G. Celli[1*], W.R.L. Cairns[1,2], C Scarchilli[3], C.A. Cuevas[4], A. Saiz-Lopez[4], J. Savarino[5], B. Stenni[1], M. Frezzotti[6], S. Becagli[7,2], B. Delmonte[8], H. Angot[5], R.P. Fernandez[9], A. Spolaor[1,2]

[1]Ca'Foscari University of Venice, Department of Environmental Sciences, Via Torino 155, 30172 Mestre, Italy
[2]CNR-Institute of Polar Sciences, 30172 Mestre, Italy
[3]University of Roma Tre, Department of Science, 00146, Roma, Italy
[4]Institute of Physical Chemistry Rocasolano, Department of Atmospheric Chemistry and Climate, 28006 Madrid, Spain
[5]Univ. Grenoble Alpes, 38000 Grenoble, France
[6]ENEA, C.R. Casaccia, 00123, Roma, Italy
[7]University of Florence, Department of Chemistry, Sesto Fiorentino, 50019, Italy
[8]University of Milano-Bicocca, Department of Environmental Science, 20126 Milan, Italy
[9]Institute for Interdisciplinary Science, National Research Council, Mendoza, 5501, Argentina

giuditta.celli@unive.it

This research investigates the possible influence of the ozone hole on the geochemical cycles, between the cryosphere and the atmosphere, of iodine (I), bromine (Br), and mercury (Hg) in East Antarctica.

Both Br and I promotes the destruction of the tropospheric ozone layer and while iodine is a photoreactive element, bromine is expected to have no significant post-depositional mechanisms in the snowpack.

Hg is a toxic heavy metal present in the environment in several different chemical forms and as iodine, once in the snowpack, it can be photoactivated by the ultraviolet (UV) radiation (280-320 nm mainly) and released from the snowpack into the atmosphere. They have a well-known diurnal cycle of exchange between surface snow and the atmosphere, and here we try to identify the connection between the ozone hole cycle and the Hg and I spatial distribution and seasonal cycle. The increased amounts of UV radiation reaching the snow surface due to ozone layer depletion, could promote the photo-reactivity of mercury and iodine in the photic zone of the snow leading to their higher re-emission from the snow surface.

In surface and bulk snow samples and in shallow core from the East Antarctic International Ice Sheet Traverse project (EAIIST), concentration measurements are performed by ICP-MS and experimental data are compared to data from atmospheric chemical models such as CAM-CHEM.

Concentration results in surface snow show a decreasing trend for mercury and iodine moving inland along the EAIIST route, toward the centre of the ozone hole. Bromine has no significant post-depositional mechanisms and probably the inland surface snow concentration is influenced by spring coastal bromine explosions.

Comparing the bulk and surface samples we can hypothesize that iodine undergoes spring summer snow recycling and accumulates in the snow during the winter months when photochemistry ceases. Mercury instead, seems controlled by an interplay of the oxidative capacity of the atmosphere and surface snow photochemistry emissions.

On going shallow cores analysis are expected to improve our knowledge about the seasonal accumulation of the analytes and what influences them. Moreover, we expect to find a tipping point, a change into the iodine concentration, and possibly the mercury concentration, corresponding with the ozone hole formation. These results would define iodine and/or mercury as proxy for the stratospheric ozone layer.

References

Cairns, W.RL. et al. (2021) 'Mercury in precipitated and surface snow at Dome C and a first estimate of mercury depositional fluxes during the Austral summer on the high Antarctic plateau', *Atmospheric Environment*, 262, p. 118634. doi: https://doi.org/10.1016/j.atmosenv.2021.118634.

Spolaor, A. et al. (2021) 'Antarctic ozone hole modifies iodine geochemistry on the Antarctic Plateau', *Nature Communications*, 12(1), p. 5836. doi: https://doi.org/10.1038/s41467-021-26109-x.

Impact of Temperature and Soil Organic Content on the Mixture Toxicity of Emerging Contaminants on E. Crypticus

A. Waseem[1*], I. Ozturk[1], and E. Topuz[1]

[1]Gebze Technical University,Department of Environmental Engineering, Kocaeli 41400, Turkey

a.waseem2022@gtu.edu.tr

The existence of a large number of Emerging Contaminants (ECs), even at trace levels in the environment, is a source of ongoing concern for human and environmental health and safety. The changes in climate conditions might alter physical, chemical, and biological properties of these ECs, affecting organisms but also the behavior and distribution of chemicals, including pollutants. Hence, this research aimed to identify the impact of temperature (20°C and 25°C), and organic content (biosolids 5g/kg; microplastics 5g/kg) on toxicity of selected ECs, i.e., Diclofenac, anthracene, terbutryn, ciprofloxacin, DEHP, Diphenyl ether, Diuron and EE2, in the soil organisms. The study also evaluated the impact of Ag2S nanoparticles and polyvinyl propylene (PP) microplastics on soil toxicity at these given temperatures. The results indicate that the increase in temperature and soil organic content reduces the survival and reproduction of E. crypticus and therefore affect the toxicity of the polluted soil. The toxicity of emerging pollutants increased with the increase in temperature from 21°C (EC50 6.44±0.6) to 25°C (EC50 4.63±0.8). The optimum temperature of E. crypticus has been stated to be approx. 20ºC, whereas the tolerance limits would be between 15-30ºC. However, in the present study, the toxicity was increased significantly at 25°C. The addition of microplastics, biosolids, and silver nanoparticles increased the temperature effects with the increase of temperature. Traditionally, organic matters in soil and sediment are considered to be the most important adsorbents for organic pollutants. The study showed that even very low concentrations of environmental pollutants, which are non-toxic to organisms, once they adsorb to the microplastic result in significant increase in toxicity at higher temperature (EC50; 3.54±0.6). The EC50 values of mixture were found to be 6.44±0.655, and with addition of biosolids, the EC50 value of mixture stayed at 6.79±0.53. Hovewer, the temperature increase also increased the toxicity of biosolids (EC50 4.36 ±0.2).

Since, organisms in soil environments are often exposed to complex mixtures of emerging pollutants, and ecotoxicity assessments are generally restricted to individual contaminants and rarely are mixtures tested. These emerging pollutants coexist with microplastics, aged microplastics, and environmental nanoparticles. Their co-exposure represents a source of increasing concern as nanoparticles and microplastics have been reported to act as carriers of pollutants due to their high sorption capacity. Our results showed that the impact of temperature and soil organic content on the toxicity of emerging pollutant concentrations in the environment must be regularly monitored to avoid detrimental environments in soil. As a result, changes in soil function and biodiversity loss can be predicted to have a detrimental influence on ecosystem services as temperatures rise. More research is required to study the interaction mechanisms of inorganic-organic co-contaminants, their interaction with soil organic content with different temperatures.

ACKNOWLEDGEMENT
This work was supported by generous grants from the Scientific and Technological Research Council of Turkey under the TUBITAK 2247-A Fellowship for Outstanding Researchers (no. 120C147). However, all scientific contributions made in this project are owned and approved solely by the author.

Water Scarcity and Wastewater Treatment: Effects on Nutrient Concentration and Dynamics in Alpine Streams

S. Bertolotti[1*], M. Macrì[1], A. Marino[1], M. Minella[2], S. Bonetta[1], F. Bona[1,3], E. Falasco[1,3], S. Fenoglio[1,3]

[1]University of Turin, Department of Life Sciences and System Biology, Via Accademia Albertina 13, 10123, Turin, Italy
[2]University of Turin, Department of Chemistry, Via Giuria 5, 10125, Turin, Italy
[3]ALPSTREAM - Alpine Stream Research Center, Località Sant'Antonio 60/A, 12030, Ostana (CN), Italy

silvia.bertolotti@unito.it

Climate change is dramatically affecting water courses more than ever before. The rising temperatures and the altered precipitation patterns are determining heavy reductions in the natural regimes and an overall deterioration of water quality, which conflicts with the increasing demand of this resource (Beniston et al., 2014). In this context, the emissions from anthropogenic sources as wastewater treatment plants (WWTPs) may have a more severe effect on water bodies, as their less dilution power may result into excessive concentration of nutrients, pollutants and pathogens. If the problem has already been addressed in previous studies on intermittent water courses, mainly located in semi-arid or Mediterranean regions (Castelar et al., 2022), few mention has been done on Alpine rivers, always considered the safest and most abundant water sources for Europe and now threatened by increasing droughts.

This study is aimed at investigating the effect of effluents from WWTPs on the concentration of nutrients in alpine-origined streams under water scarcity. The research has involved three rivers (Stura di Lanzo, Malone and Pellice) in Piedmont, NW Italy, a region that could historically rely on a great availability of water thanks to its wide, branched hydrographic network and that is now facing severe water shortage conditions.

A monitoring campaign of one year has been set on the selected rivers, with water samples of 1 dm^3 collected upstream (U), downstream (D) and at the discharge (W) of a local WWTP monthly. The samples have been analyzed for their content in Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, TC, TN, N-NH_3 N-NO_2, SiO_2, P and anionic surfactants. Hydrological data (speed of flow, depth of the water column) have been measured in field, as well as T, pH, conductivity and dissolved oxygen. Data on the flow rates and the precipitations are obtained from Arpa Piedmont.

Possible trends in the budgets of nutrients have been analyzed in relation to the variability of water quantity. Moreover, the biodiversity (density, structural and functional organization of benthic macroinvertebrates and diatom communities) and the microbiological contamination (presence of pathogens, faecal bacterial indicators) have been studied in parallel samplings following the same experimental design.

According to the observations carried out so far, the discharges from the WWTPs are effectively drivers of high amounts of nutrients for most of the analyzed parameters. Their effect, however, is evident only for some species, whose concentrations are higher in D samples than in U samples (e.g. N species), and it is not uniform in all the investigated rivers. The variation in the concentration of nutrients does not seem to follow seasonal trends.

The next steps will include further statistical elaboration of the data, to detect possible correlations between the nutrient loads, the changing hydrology and the biological features of the rivers. The results are expected to shed a new light on how water scarcity and less dilution potential affect the efficiency of WWTPs and on how alpine streams respond both from a chemical and from a more exosystemic point of view.

References

Beniston, M. et al. (2014) ‘Assessing the impacts of climatic change on mountain water resources’. Science of the Total Environment, 493, p. 1129-1137. doi: 10.1016/j.scitotenv.2013.11.122.

Castelar, S. et al. (2022), ‘Wastewater treatment plant effluent inputs influence the temporal variability of nutrient uptake in an intermittent stream’. Urban Ecosystems, 25, p. 1313–1326. doi: 10.1007/s11252-022-01228-5.

Preliminary Study of the Photodegradation of Bisphenol A (BPA) in Artificial Snow Samples

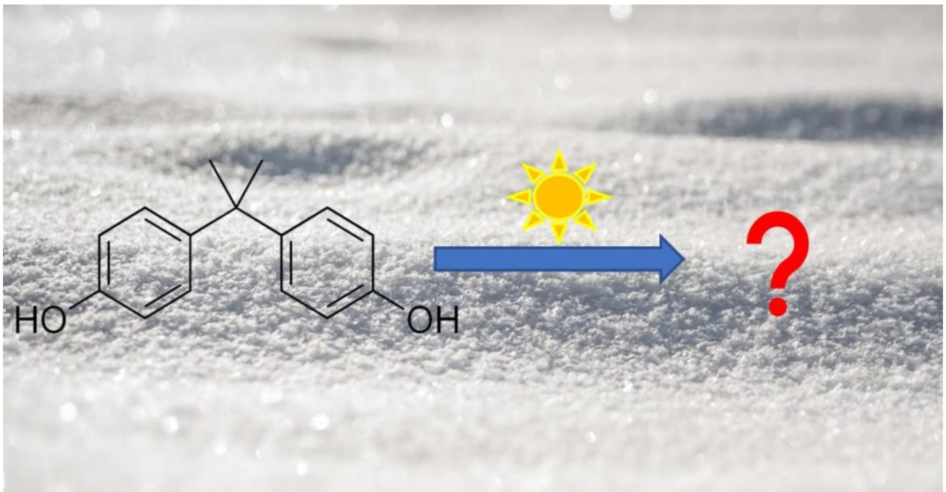
S. Frassati[1*], E. Barbaro[1,2], M. Vecchiato[1, 2], M. Feltracco[1], M. Roman[1], A. Spolaor[1, 2], C. Barbante[1, 2], A. Gambaro[1]

[1]Ca’ Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Venice Mestre, Italy
[2]National Research Council (CNR-ISP), Institute of Polar Science –Venice Mestre, Italy

stefano.frassati@unive.it

Bisphenols (BPs) are organic synthetic compounds formed by two phenolic hydroxyl groups, the most commonly used being bisphenol A (BPA). Traces of BPA have been found in the human body, and this has raised considerable concern since this compound is an interferent of the endocrine system. It is therefore critical to trace this compound within various matrices and to understand its fate in various environmental compartments because it has been found in surface water, marine water, and aerosols1. Since it has been found in the atmosphere, it is plausible that it is transported to remote areas and deposited on the snow surface e, once deposited, photodegradation reactions can occur (direct or indirect).

In this work, we studied the indirect photodegradation of BPA in synthetic ice samples in the presence of rose bengal . This species is usually used to simulate the dissolved organic chromophoric fraction (CDOM), which is able to become excited by visible light and produce singlet oxygen, a strongly oxidizing molecule. Preliminary results showed that BPA is oxidized by singlet oxygen, and various by-products, such as the hydroxylated species (BPA-OH), were identified through analysis using hyphenated techniques with high resolution mass spectrometer (HPLC-Orbitrap).The main aims of these investigation are 1) to understand the degradation kinetic and the main parameters that promote it, 2) to identify the main by-products in order to define their fate and, once the masses of some by-products have been identified, they will be searched in snow samples.



BPA photodegradation in snow

References

Repossi, A., et al. (2016) Bisphenol A in edible part of seafood m er ci on co m us e on on er al. 5.

Rochester, J. R. (2013) Bisphenol A and human health : A review of the literature. Reprod. Toxicol. 42, 132-155.

Bower, J. P. et al. (2014) Degradation of organic pollutants in/on snow and ice by singlet molecular oxygen (1O * 2) and an organic triplet excited state. Environ. Sci. Process. Impacts 16, 748-756.

Machine Learning as a Key Digital Tool for Shaping Environmental Change Processes

E. Furlan[1,2] *, A. Bianconi[1,2], F. Zennaro[1,2], C. Simeoni [1,2], V. Pham [1,2], S. Vascon[1,3], A. Critto[1,2], A. Marcomini[1,2]

[1]Ca' Foscary University of Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino 155, 30172, Venice, Italy
[2]Centro Euro-Mediterraneo sui Cambiamenti Climatici, Risk Assessment and Adaptation Strategies Division, via Marco Biagi 5, 73100 Lecce, Italy
[3]Ca' Foscari University of Venice, European Center for Living Technology, Dorsoduro 3246, 30123 Venice, Italy

elisa.furlan@cmcc.it

The growing availability of geospatial big data, mostly hiling from different sources and in heterogeneous formats, is successfully exploited by machine learning (ML) algorithms across several environmental applications (L'Heureux et al., 2017), such as the prediction of extreme events and natural hazards, water quality monitoring, weather forecasting and climate change (CC) risk assessment (Zennaro et al., 2021).

Within Venezia 2021 and the H2020 MaCoBioS projects, the potential of these models was fully leveraged to analyse environmental dynamics underpinning natural systems' response to CC and human-made pressures. As regards Venezia2021 project, ML and numerical models were combined, exploiting capabilities of both approaches to model water quality (WQ) dynamics in the Venice lagoon, under a baseline and future CC scenarios. Random Forest (RF) algorithm was used to assimilate historical WQ data (i.e., water temperature, salinity and dissolved oxygen) and spatio-temporal information (i.e., monitoring station and acquisition date of WQ data), and to predict changes in chlorophyll-a (Chl-a) conditions. In particular, through a hybrid ML-Biogeochemical framework, this study allowed for a better understanding of the eutrophication issue over the last ten years (2008-2019), and to detect potential critical conditions under future CC scenarios (2049, 2099). Overall, a decreasing trend for the lowest Chl-a values (below 0.85 µg/l, the first quartile) was observed, with an opposite rising trend for the highest ones (above 2.78 µg/l, the fourth quartile). On the seasonal level, summer remains the season reaching the highest Chl-a values in all scenarios, although in 2099 a strong increase in Chl-a is also expected during spring, as Chl-a production will likely rise due to changes in temperature regime. Concerning the MaCoBioS project, the cumulative impacts of both human and CC-related pressures, affecting seagrasses condition in the Mediterranean Sea, was assessed using an RF model. Data collected from different open-source platforms for the 2017 baseline scenario (e.g., data from Copernicus Marine Service) was used to train, validate and test the model. Moreover, future scenario analysis was performed by integrating projections from the CMCC-MedCORDEX model, including sea surface temperature and salinity under 2050 and 2100 timeframes. The results of the analysis showed that the ecological condition and service capacity of seagrass meadows are mainly threatened by human pressures (e.g., distance from main urban areas as proxy of coastal development), as well as by changes in nutrient concentration and sea surface temperature. This aligns with results from the scenario analysis, highlighting a decrease in seagrass coverage and related services capacity, in both 2050 and 2100 timeframes.

In the described applications, ML models provide useful predictive insights on possible future conditions of water bodies and aquatic ecosystems in response to multiple pressures, supporting both the implementation of the EU Water and Marine Strategy Framework Directive and marine planners towards more effective ecosystem-based adaptation and management measures.

References

L'Heureux, A. et al. (2017) "Machine learning with big data: Challenges and approaches" IEEE Access, 5, pp. 7776–7797. Available at: https://doi.org/10.1109/access.2017.2696365.

Zennaro, F. et al. (2021) "Exploring machine learning potential for climate change risk assessment" Earth-Science Reviews, 220, p. 103752. Available at: https://doi.org/10.1016/j.earscirev.2021.103752.

Black Carbon and Organic Carbon Impact in the Tropical Andes: the Case of Shallap Glacier (Cordillera Blanca)

S. Meroni[1*], S. Gilardoni[2], B. Di Mauro[2], P. Fermo[3], P. Bonasoni[4], M. Lasagni[1]

[1]University of Milan - Bicocca, Department of Environmental Sciences, Piazza dell'Ateno Nuovo, 1 - 20125 Milano (MI), Italy
[2]Institute of Polar Sciences, National Research Council, Via Cozzi, 53 - 20125 Milano (MI), Italy
[3]Univerisy of Milan, Department of Chemistry, Via Golgi, 19 - 20133 Milano (MI), Italy
[4]National Research Council, Institute of Atmospheric Sciences and Climate, Via Gobetti, 101 - 40128 Bologna (BO), Italy

s.meroni23@campus.unimib.it

Mountain glaciers are melting at unprecedented rates, with dramatic consequences for the ecosystem and society of the mountain regions. Glacier retreat is due to temperature increase and snow precipitation reduction (IPCC 2019, IPCC 2022). The presence of light absorbing particles (LAPs) on glacier snow surface can further accelerate snow and glacier melting by reducing their surface albedo (McKenzie Skiles 2018). The implementation of effective policy measure to reduce the impact of LAPs on mountain cryosphere requires to know the nature and origin of such particles and to characterize their impact on snow albedo.

In this work we investigated the chemical properties of carbonaceous LAPs, their origin, and their impact on the snow albedo of the Shallap glacier in the Cordillera Blanca (N -9° 29' 26.5’’ E -77° 20' 2.0’’). Snow samples were collected in the ablation and accumulation zone of the glacier every month, from May to December and during multiple years (2017 till 2020).

We measured elemental carbon (equivalent to black carbon or BC) and organic carbon (OC) concentration in snow samples by thermal-optical and thermal analysis. BC and OC concentrations were on average higher in the ablation zone compared to the accumulation zone, due to snow surface processes that lead to the enrichment of impurities on snow surface in the ablation area. In addition, BC and OC concentrations in the accumulation zone were characterized by a clear season variation, with higher values during the dry season, where emissions are expected to be higher.

Then, we investigated the sources of elemental and organic carbon derived from atmospheric deposition by integrating the available emission inventory data with the analysis of the air mass origin using LAGRANTO back trajectories. BC and OC deposition are dominated by open burning during the dry season, and residential combustion and transportation emissions during the wet season.

Finally, we quantified the snow albedo reduction due BC and OC from combustion emissions using the SNICAR model. The albedo reduction due to carbonaceous LAPs varies from 5% in the wet season, up to 36% in the dry season. although the concentration of OC is about one order of magnitude higher than BC, albedo reduction is controlled mainly by BC variability, due to the higher mass absorption efficiency of BC compared to OC.

Results of this study support the identification of effective policy measures to mitigate the impact of anthropogenic activities on the glaciers of the Cordillera Blanca.

References

IPCC Special Report (2019) ‘The ocean and cryosphere in a changing climate’.

IPCC Sixth Assessment Report (2022), doi:10.1017/9781009325844.002.

McKenzi Skiles, S.M. et al. (2018). Radiative forcing by light-absorbing particles in snow. Nat. Clim. Chang. 8 (11), 964–971.

Personal Care Products in Antarctic snow: Regional and Seasonal Distribution

M. Vecchiato[1,2]*, N. Ademollo[1], F. Ardini[3], C. Barbante[1,2], E. Barbaro[1], M. D'Amico[2], A. Gambaro[1 2], G. Genuzio[2], A. Spolaor[1]

[1]Institute of Polar Sciences, CNR-ISP, Via Torino, 155, 30172, Venice-Mestre, Italy
[2]Ca' Foscari University of Venice, DAIS, Via Torino, 155, 30172 Venice-Mestre, Italy
[3]University of Genoa, DCCI, via Dodecaneso 31, 16146, Genoa, Italy

vecchiato@unive.it

Personal Care Products (PCPs) were recently recognized as environmental contaminants of emerging concern emitted by daily human activities: fragrances are ingredients of soaps and detergents, while UV-filters are widely used in sunscreen creams and in outdoor materials. PCPs in the environment are generally associated to direct emissions and are rarely considered among contaminants prone to be atmospherically transported over long distances towards polar regions. Consequently, the distribution of PCPs in Antarctica is still far from being well documented. However, pilot studies recently suggested that the occurrence of fragrances and UV-filters in Antarctic snow may derive from long-range atmospheric transport (Vecchiato et al. 2017; D'Amico et al. 2022). To investigate this hypothesis, in the austral summer 2021-2022 we conducted a comprehensive campaign aimed to describe the distribution of PCPs in Antarctic snow. Surface samples (5 cm) were collected in 16 sites along the Ross Sea coast and in inland sites of the Victoria Land, focusing on representative areas unaffected by local influences from research facilities. Moreover, a snow-pit was dug on the McCarthy ridge (180 cm – 15 cm resolution) to investigate the evolution of PCPs during the last 3 years. Snow samples were processed in clean-room laboratories and analyzed by GC-MS/MS.

PCPs resulted widely distributed in the Antarctic surface snow: repeated samplings showed a significant seasonal variability, with higher levels (> 100 ng/L) detected in summer (mid Dec 2021-Jan 2022), compared to the previous spring samples (≈10 ng/L; early Nov 2021). Higher concentrations were associated to meteorological episodes, suggesting the role of the inputs from synoptic air masses, rather than a transport linked to the Antarctic polar vortex. A similar seasonal variability was found also in the snow-pit samples: the fragrance levels varied by about one order of magnitude at a yearly timeframe, while the UV-filters were changing less markedly. The PCP pattern was centered on salicylate compounds: amyl and hexyl salicylate, followed by benzyl salicylate, resulted the most abundant among the analyzed fragrances, while ethylhexyl salicylate was generally the major UV-filter. Notably, PCPs resulted distributed in the dissolved fraction (generally >90%), except for octocrylene, which was mostly associated to particulate. The levels and the distribution of the PCPs found in Antarctic snow samples are consistent with corresponding data from Arctic surface snow (unpublished). The obtained results lead to two main research priorities: PCPs were so-far overlooked as relevant contaminants in polar areas, while their environmental transport patterns should be better understood, also to reconstruct the anthropic impact in Antarctica during the last decades. Moreover, the possible effects of PCPs - suspected endocrine disrupters - on the fragile marine ecosystem of the Southern Ocean are completely unknown. During few weeks, seasonal melting may lead to contaminant pulses in the coastal areas or amplification phenomena, that may represent analogues of climate-driven snow and ice melting.

References

Vecchiato, M. et al. (2017) 'Fragrances in the seawater of Terra Nova Bay, Antarctica' Sci. Total Environ. 593–594, 375–379, doi:10.1016/j.scitotenv.2017.03.197.

D'Amico, M. et al. (2022) 'Occurrence of the UV-filter 2-Ethylhexyl 4-methoxycinnimate (EHMC) in Antarctic snow: First results' Microchemical Journal 183, 108060. doi:10.1016/j.microc.2022.108060.

Determining the Fate and Behavior of Plant Protection Products (PPPs) in Lakes and Water-Sediment Interface under a Changing Climate Using Passive Sampling

E. Schaad[1]*, S.Cirelli[1], M. Grosjean[1], A. C. Chiaia-Hernández[1]

[1]University of Bern, Institute of Geography & Oeschger Centre for Climate Change Research, Hallerstrasse 12, 3012 Bern, Switzerland

emmanuel.schaad@giub.unibe.ch

The ability to assess plant protection product (PPP) loads in the dissolved and particulate phase is a key issue that has not yet been properly addressed by models due to limited or non-existing data to evaluate deposition and re-emission processes in sediments. Resuspension of organic contaminants to overlaying waters can make them more bioavailable and mobile, leading to erroneous model predictions (e.g. those made based on equilibrium partition theory) of their transport behaviour and availability. PPPs applied to agricultural fields are partly lost to soils and its pore water and subsequently transported to nontarget ecosystems including surface waters such as streams and lakes (Carvalho, 2017). Recently, Chiaia-Hernández et al. (2020) showed that PPPs are very stable once embedded in sediments and more so under anoxic conditions. This is of concern given that the majority of freshwater lakes worldwide show the phenomena of anoxia in the hypolimnion (Jenny et al., 2016). Therefore, stratification and mixing of lake systems will play a key role in understanding the dynamics of PPPs, as these processes control the most important ecological and bio-geochemical processes. Stratification and limited mixing may be of special concern for temperate lakes (particularly under climate warming) given that PPPs are usually heavily applied during late spring and summer. Thus, under enhanced eutrophication and global warming, lake stratification and hypolimnetic anoxia will get stronger and, therefore, reduce PPP degradation. Thus, in the scope of this study, the potential pathways (e.g. sedimentation, remobilization, degradation) of PPPs in a lake under anthropogenic influence is assessed by performing a comprehensive, year-long in-situ study using passive sampling techniques for water and sediment matrices. Firstly, different passive sampling phases are tested for uptake suitability of the targeted PPPs which include polystyrene-divinylbenzene, reversed-phase sulfonated (SDB-RPS) and hydrophilic-lipophilic-balanced (HLB). Then, the samplers are calibrated for different hydrodynamic regimes (flowing/stagnant) for deployment in both the in- and outflow and the water column of the lake. This will allow us to gain a high temporally resolved record of PPPs present in the water phase. The combination of passive sampling with sediment traps and water chemistry will allow to study the sedimentation behavior of PPPs and transformation products in connection with stratification periods. Additionally, freely dissolved fractions of PPPs in the pore water of the topmost sediments will be investigated to assess diffusive fluxes of PPPs to and from the sediment using a novel probe that is able to penetrate the sediment, and consists of a passive sampling phase attached to a hollow cylinder fixed to a tripod.

In conclusion, this study will advance our knowledge on the role of sediment cycling, sinks and sources of PPPs and help improve existing models. Ultimately, this study will give us insights into the pathways and fate of PPPs in lacustrine systems as well as help to create effective risk assessment and management plans now and under future climate scenarios.

References

Carvalho, F.P. (2017) ‘Pesticides, environment, and food safety’, Food and Energy Security, 6(2), pp. 48–60. doi:10.1002/fes3.108.

Chiaia-Hernández, A.C. et al. (2020) ‘High-Resolution Historical Record of Plant Protection Product Deposition Documented by Target and Nontarget Trend Analysis in a Swiss Lake under Anthropogenic Pressure’, Environmental Science and Technology, 54(20), pp. 13090–13100. doi:10.1021/acs.est.0c04842.

Jenny, J.-P. et al. (2016) ‘Global spread of hypoxia in freshwater ecosystems during the last three centuries is caused by rising local human pressure’, Global Change Biology, 22(4), pp. 1481–1489. doi:10.1111/gcb.13193.

Mercury at the Base of Trophic Pyramid in Admiralty Bay, Antarctica

E. Korejwo[1]*, D. Saniewska[2], A. Jędruch[1], M. Saniewski[3], P. Balazy[1], J. Bełdowski[1]

[1]Polish Academy of Sciences, Institute of Oceanology, ul. Powstańców Warszawy 55, 81-712 Sopot, Poland
[2]University of Gdansk, Faculty of Oceanography and Geography, Al. Piłsudskiego 46, 81-378 Gdynia, Poland
[3]Institute of Meteorology and Water Management - National Research Institute, Waszyngtona 42, 81-342 Gdynia, Poland

ewakorejwo@iopan.pl

Recent research has shown that the Antarctic region functions as a sink for mercury (Hg), with unique atmospheric mercury depletion events causing Hg to be deposited and incorporated into the marine food web. Additionally, this metal can be sequestered in the snowpack across the entire continent, making the region a massive cold trap for mercury. However, the West Antarctic ice sheet is currently in a state of dynamical imbalance, with ice loss occurring at a rate five times greater than previously estimated. As a result, the melting ice sheet and glaciers have become an important secondary source of mercury for the Antarctic, leading to an increase in Hg concentration within the marine biota.

The purpose of the study was to identify sources of mercury in Antarctica and determine their potential for accumulation within the marine trophic chain. In December 2018, sampling was conducted at Admiralty Bay, where marine samples including water, suspended particulate matter, phytoplankton, and zooplankton were collected. Total mercury, methylmercury, and labile Hg concentrations were analyzed in the collected samples. The highest Hg values were measured near melting glaciers. While the majority of the mercury in the water was in suspended form, the most toxic form of Hg, methylmercury, was found to be dissolved, which facilitated its accumulation in plankton.

This study has been performed within the framework of a National Science Center projects No. 2019/33/B/ST10/00290 and No. 2017/27/N/ST10/02230.

Climate Change Problem and Implementation of Potential Solutions; Post-Combustion CO_2 Capture with Membranes

P. Gkotsis[1] and A. Zouboulis[1]*

Aristotle University of Thessaloniki, Department of Chemistry, Laboratory of Chemical & Environmental Technology, GR-54124, Thessaloniki, Greece

zouboulis@chem.auth.gr

Climate change and environmental degradation are some of the greatest challenges of humankind, consisting of an existential threat to Europe and the world. In order to overcome these challenges and achieve sustainable development, EU should be transformed into a modern, resource-efficient and competitive economy, and also adopt new strategies that take a holistic and cross-sector policy approach. To do so, in face of the climate emergency a just and fair transition towards carbon neutrality should be carried out. Such a transition can only be delivered in full partnership with all members of society from regional and local authorities, civil society and young people. Becoming the world's first climate-neutral continent requires changes in government policies, business strategies and consumers' behavior. A larger percentage of all national recovery and resilience plans should be also devoted to climate-positive initiatives in order to provide a unique opportunity for the governments to ensure a 'greener' recovery. Under this framework, the Laboratory of Chemical and Environmental Technology (Department of Chemistry, AUTH) in collaboration with other universities and research institutes (NTUA, UNIPD, ELGO-DIMITRA), consulting companies (NEVIS) and power generation companies (PPC and PPC Renewables), aims to develop and demonstrate an innovative, integrated and sustainable industrial process for simultaneous energy storage and CO_2 Capture, Sequestration and Utilization (CCSU), with the implementation of the circular economy program LIFE 'CO_2toCH_4'. The principal idea of LIFE 'CO_2toCH_4' involves the construction, operation and demonstration of an autonomous mobile unit for hybrid energy storage, which uses the exhaust waste gases (flue gases) from a thermo-electric power plant (burning lignite), as well as hydrogen (H_2) produced from water electrolysis (by using renewable energy sources) and subsequently, converts them into (bio)methane (CH_4), i.e., into an alternative energy source. The mobile unit consists of three fundamental sub-units: (i) the electrolyzer (for the production of H_2), (ii) the flue gases cleaning/purification system, and (iii) the bio-methanation unit. Before the main implementation actions, which include the operation, optimization and demonstration of the prototype mobile unit, a detailed technical preparation design of the integrated process elements (i.e., electrolyze, cleaning system, bio-methane reactor) was conducted. The present work, which is part of LIFE 'CO_2toCH_4', provides an overview of the common CCSU strategies and presents the main post-combustion CO_2 capture technologies, with specific regard to membrane separation, as applied both in the context of LIFE 'CO_2toCH_4' (for the purification of flue gases) and in various case studies in Europe and USA as well.

References

Lenton, T. M. et al. (2019). Climate tipping points — too risky to bet against. Nature, 575(7784), 592–595. https://doi.org/10.1038/d41586-019-03595-0.

Steffen, W. et al. (2018). Trajectories of the Earth System in the Anthropocene. Proceedings of the National Academy of Sciences of the United States of America, 115(33), 8252–8259. https://doi.org/10.1073/pnas.1810141115.

Wunderling, N. et al. (2021). Interacting tipping elements increase risk of climate domino effects under global warming. Earth System Dynamics, 12(2), 601–619. https://doi.org/10.5194/esd-12-601-2021.

Impact of Increased Number of High Temperature Days on Atmospheric PM Pollution from Intensive Poultry Farming

G. Gržinić[1]*, A. Łopatka[2], E. Olkowska[1], A. Klimkowicz-Pawlas[2] and L. Wolska[1]

[1]Medical University of Gdansk, Faculty of Health Sciences, Department of Environmental Toxicology, Dębowa Str. 23A, 80-204 Gdansk, Poland
[2]Institute of Soil Science and Plant Cultivation - State Research Institute, Department of Soil Science Erosion and Land Protection, Czartoryskich Str. 8, 24-100 Puławy, Poland

goran.grzinic@gumed.edu.pl

Heat stress is one of the major climatic issues that impacts livestock farming in general, and poultry farming in particular. According to the Polish Institute of Environmental Protection (IOŚ-PIB) Klimada 2.0 climate change database (Institute of Environmental Protection – National Research Institute, 2023), by the year 2100 and based on a moderate future radiative forcing scenario (RCP4.5), the number of hot days (>25^{0}C) in Poland will increase from 35 to 44 and the number of very hot days (>30^{0}C) will double compared to the current decade. In the case of the more pessimistic scenario, based on a continuation of the current developmental path (RCP8.5), the number of hot days will increase from 35 to 65, while the number of very hot days will triple. In order to reduce the negative impact of heat stress on poultry welfare, intensive farming operations resort to various measures such as introduction of more adaptable poultry breeds, adjustments in nutritional strategies and improving housing conditions (Cheng et al., 2022). The latter consists of measures such as increased ventilation and water spraying (misting), in order to reduce heat levels in the poultry house. Unfortunately, such measures lead to increased particulate matter (PM), volatile organic compound (VOC) and bioaerosol emissions from poultry houses and poultry farms in general (Bist and Chai, 2022).
Within the scope of the KURNIK research project, which investigates the impact of intensive poultry farming on the environment and human health, we have studied the PM emissions from a model poultry farm during various seasons of the year, including cases of very hot weather. Using a portable optical-scattering aerosol particle spectrometer, PM concentrations were measured at distances of up to 500 m from the farm in order to ascertain the emissions profile as well as the impact on farm employees and nearby populated areas. The results have shown a multiple fold increase in PM10, PM2.5 and PM1 concentrations during hot and very hot days, with values significantly above WHO suggested limits and those legislated by EU air quality standards, in particular within the bounds of the farm and in close vicinity to it, where values ranging 30.4 - 254.1 µg m^{-3} (PM10), 21.4 - 66.7 µg m^{-3} (PM2.5) and 17.7 - 26.4 µg m^{-3} (PM1) were measured. With the expected increase in frequency of warmer weather and hot days due to ongoing climate change, farm workers and the neighboring population will be exposed to heightened and more frequent PM pollution events. It will therefore be necessary to implement appropriate mitigation strategies to limit the negative environmental and human health effects due to this increase.

Acknowledgements
This study has been financially supported by a grant from the Polish National Science Centre (Grant No. UMO-2019/35/B/NZ7/04394). The authors would like to thank Mr. Przemysław Gnatowski and Mr. Paweł Szarlej for technical assistance during measurements.

References

Bist, R.B. and Chai, L. (2022) 'Advanced Strategies for Mitigating Particulate Matter Generations in Poultry Houses', Applied Sciences 12(22), 11323.

Cheng, M., McCarl, B., Fei, C. (2022) Climate Change and Livestock Production: A Literature Review', Atmosphere 13(1), 140.

Institute of Environmental Protection – National Research Institute (2023) Klimat scenariusze - Klimada 2.0. Available at: https://klimada2.ios.gov.pl/klimat-scenariusze-portal/ (Accessed: 6 April 2023).

Prediction Model for Bioaccumulation of Toxic Metals in Medicinal Plants

G.G. Vasile[1*], N. Vasilache[1], C. Dinu[1], A.G. Tenea[1], V.I.Iancu[1], E.A. Serban[1]

[1]National Research and Development Institute for Industrial Ecology-ECOIND, Pollution Control Department, Drumul Podu Dambovitei Street 57 -73, 060652, Bucharest, Romania

gabriela.vasile@incdecoind.ro

The bioavailability of metals to medicinal plants is controlled by several factors associated with the physical-chemical properties of the soil (pH, organic matter content (CO), redox potential, carbonate, sand content), climatic conditions, metal transfer and speciation processes, the state of oxidation, as well as the type of plant's root (Kohzadi S. et al. 2018).

In the study, a simplified way of predicting bioaccumulation in medicinal plants was developed using the results from bioaccumulation study regarding Thymus serpyllum plants grown in a controlled system and the bioavailability concentration of toxic metals from the cultivated substrate. The use of bioavailability studies obtained through simple chemical extraction procedure, being much more accessible, allow obtaining much faster answers than bioaccumulation studies in plants. Thus, using the prediction model developed in the study and the results of the bioavailability studies, a prediction can be made regarding the accumulation of metals in the various organs of some plants harvested either from the spontaneous flora or agricultural crops. Characterization data of soils contaminated with Cd, As, respectively Cd+As (pH, cationic exchange capacity, CO and total metal concentrations) were used. In addition, the mobile concentration obtained with three different methods (CAT= 0.01 mol/L $CaCl_2$+0.002 mol/L DTPA, 1:5, pH=2.6; DTPA=0.005 mol/L DTPA+ 0.1 mol/L TEA+0.01 mol/L $CaCl_2$, 1:10, pH=7.3, EDTA=1 mol/L CH_3COONH_4 +0.01 mol/L EDTA,1:10, pH=7.1) was used as well as the metal concentration in the plant organs (root, stem, leaves). The indices used in the mathematical modeling of the mobility of metals from soil to plants were the distribution coefficient (Kd) and the plant absorption factor (FAP). The matrix of Pearson correlation coefficients and similarity dendogram in Pearson R-mode were generated with NCSS 2021 statistical analysis software (Liu Z. et al. 2022). To validate the multiple regression model, the parameters R^2, RMSE, Durbin-Watson test were used. EDTA was the recommended method for estimating the mobility of metals from the soil to the plant in the case of soil contamination with As, respectively Cd, while CAT was the most appropriate for prediction model in the case of As+Cd mixture. For example, the Cd concentration accumulated in root could be estimated with the following equation: Cd concentration in root = 0.32xCOsoil + 1.32xCdtotal soil + 0.089xFAP - 1.47xKd (for Cd mobile in EDTA). The predictive models generated in this study can be used in the prediction of As and Cd accumulation in plant organs from areas affected by anthropogenic activities, using soil physical-chemical characterization data, the total and mobile concentrations of metals in the soil.

References

Kohzadi, S. et al. (2018) 'Concentration, source, and potential human health risk of heavy metals in the commonly consumed medicinal plants', Biological Trace Element Research, 1-10, doi:10.1007/s12011-018-1357-3.

Liu, Z. et al. (2022) 'Cadmium Uptake and Growth Responses of Seven Urban Flowering Plants: Hyperaccumulator or Bioindicator?', Sustainability, Vol.14, Issue 2. 619; doi:10.3390/su14020619.

Acknowledgment: The authors acknowledge the financial support offered by the Ministry of Research, Innovation and Digitization of Romania through the Romanian National Research Program “Nucleu” through contract no. 20N/2019, Project code PN 19 04 01 01.

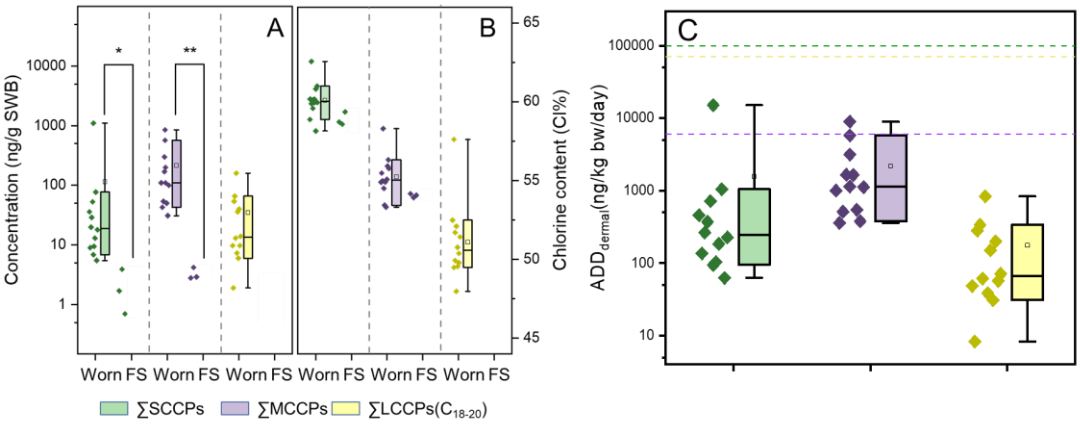
Assessment of Silicone Wristbands for Monitoring Personal Exposure to Chlorinated Paraffins (C8-36): A Pilot Study

S. Yin [1,2*], T.J. McGrath [1], A Cseresznye [1], J Bombeke [1], G Poma [1], A Covaci [1]

[1]University of Antwerp, Toxicological Centre, Universiteitsplein 1, 2610 Wilrijk, Belgium
[2]Key Laboratory of Pollution Exposure and Health Intervention of Zhejiang Province, Interdisciplinary Research Academy (IRA), Zhejiang Shuren University, Hangzhou 310015, China

shanshan.yin@uantwerpen.be

Chlorinated paraffins (CPs) are a major environmental concern due to their ubiquitous presence in the environment.1 Since human exposure to CPs can significantly differ among individuals, it is essential to have an effective tool for monitoring personal exposure to CPs.2 In this pilot study, silicone wristbands (SWBs) were employed as a personal passive sampler to measure time-weighted average exposure to CPs. Twelve participants were asked to wear a pre-cleaned wristband for a week during the summer of 2022, and three field samplers (FSs) in different micro-environments were also deployed. The samples were then analyzed for CP homologs by LC-Q-TOFMS. In worn SWBs, the median concentrations of quantifiable CP classes were 19 ng/g wb, 110 ng/g wb, and 13 ng/g wb for ∑SCCPs, ∑MCCPs, and ∑LCCPs (C18-20), respectively. For the first time, lipid content is reported in worn SWBs, which could be a potential impact factor in the kinetics of the accumulation process for CPs. Results showed that micro-environments were key contributors to dermal exposure to CPs, while a few outliers suggested other sources of exposure. CP exposure via dermal contact showed an increased contribution and thus poses a nonnegligible potential risk to humans in daily life. Results presented here provide proof of concept of the use of SWBs as a cheap and non-invasive personal sampler in exposure studies.



Mass basis concentration (A) and chlorine content (B) of the worn SWBs and FSs of each CP class.(C)ADDdermal for each CP class.

References

McGrath, T.J. et al. (2022) 'Seasonal variation of short-, medium- and long-chain chlorinated paraffin distribution in Belgian indoor dust.' Environ Int 170, 107616.

Waclawik, M.et al. (2022). 'Silicone Wristbands in Exposure Assessment: Analytical Considerations and Comparison with Other Approaches.' Int J Environ Res Public Health 19.

Yuan, B. et al. (2021). 'Human Exposure to Chlorinated Paraffins via Inhalation and Dust Ingestion in a Norwegian Cohort' Environ Sci Technol 55, 1145-1154.

Toxic Organic Chemicals in a Globally Connected World: Quantifying Real and Virtual Flows Embodied in the International Trade of Chemicals, Products and Wastes

F. Wania[1*], K. Tong[1], L. Li[2], K.Breivik[3]

[1]University of Toronto Scarborough, Department of Physical and Environmental Sciences, 1265 Military Trail, Toronto, Ontario, Canada M1C 1A4
[2]School of Public Health, University of Nevada Reno, Reno, Nevada, USA
[3]NILU Norwegian Institute for Air Research, Kjeller, Norway

frank.wania@utoronto.ca

In an increasingly global world, chemical production, product manufacturing, product use and product disposal may all occur in different countries. This global division of labor can lead to an ecologically unequal exchange, as the emissions of a chemical often no longer occur only or largely in the country in which the benefit of the chemical's use is enjoyed. Emissions associated with production, manufacturing and waste disposal occur increasingly in "peripheral" and "semi-core" countries with manufacturing economies, whereas emissions in "core" countries with service-dominated economies are more and more restricted to those occurring during product use. This not only leads to much reduced occupational exposure in core countries, but also to lower emissions to the environment and therefore reduced exposure to the general population. Conversely, manufacturing countries and those involved in the handling of waste are "importing" emissions and, accordingly, are also suffering increased contaminant exposure.

We seek to quantify this unequal exchange embedded in the international trade of chemicals and of the products, wastes and foods containing such chemicals. In doing so, we rely on a toolbox of simulation models that describe contaminant behaviour in the technosphere, the natural environment, in aquatic and terrestrial food chains, in the human residential environment, and in human individuals and populations. In an initial proof-of-concept study, we used "Chemical in Products – Comprehensive Anthropospheric Fate Estimation" (CiP-CAFE), a global scale synamic substance flow analysis model (Li and Wania, 2016) to quantify the emissions of polybrominated diphenyl ethers (PBDEs), a group of flame retardants added to consumer products, that are embodied in the trade between seven world regions over the 2000 to 2020 time period. Specifically, building on the work Abbasi et al. (2019), we quantified the transboundary movement of PBDEs embodied in the trade of neat PBDEs (technical PBDE mixtures and formulations), PBDE-containing products (electronics, foam and carpet, construction, transportation, and textiles), and PBDE-containing waste (mainly electronic waste) (Tong et al., 2022). We find that core regions have off-loaded PBDE emissions, mostly associated with the disposal of electrical and electronic waste (e-waste), to semi-core and peripheral regions in mainland China and the global South. In core regions this results in small emissions that mostly occur during the product use phase, whereas in peripheral regions emissions are much higher and dominated by end of life disposal. Because waste disposal practices vary between regions and e-waste disposal practices prevalent in core countries result in lower PBDE emissions than the more informal disposal practices common in the periphery, international trade also results in an overall increase in the global emissions of PBDEs.

Demonstrating the shared responsibility for contamination between consumers and producers is an essential element for making progress in efforts towards improved chemicals and waste management globally, which is one of the sustainability goals of the United Nations.

References

Abbasi, G. et al. (2019) 'Global historical stocks and emissions of PBDEs', Environ. Sci. Technol. 53, p. 6330–6340
Li, L. & Wania, F. (2016) 'Tracking chemicals in products around the world: introduction of a dynamic substance flow analysis model and application to PCBs', Environ. Int. 94, p. 674–686

Tong, K. et al. (2022) 'Ecological unequal exchange: Quantifying emissions of toxic chemicals embodied in the global trade of chemicals, products, and waste', Environ. Res. Lett. 17, art. 044054.

Wastewater-Derived Organic Contaminants Driven by Reclaimed Wastewater Reuse in Agricultural Irrigation: Dietary Exposure and Potential Risks to the Environment and Human Health

Lúcia H.M.L.M. Santos[1,2]*, S. Semitsoglou Tsiapou[12], M. Castaño-Trias[12], S. Rodríguez-Mozaz[12], G. Buttiglieri[12]

[1]Catalan Institute for Water Research (ICRA-CERCA), C/ Emili Grahit, 101, 17003 Girona, Spain
[2]University of Girona, Girona, Spain

lhsantos@icra.cat

In the last decades, water scarcity has become a challenging issue, specially in arid and semi-arid regions, such as the Mediterranean basin. Agriculture is among the sectors threatened by water scarcity, due to an increasing demand for water in crop production. In fact, it is estimated that agricultural production consumes about 70% of the available water (Ben Mordechay et al., 2022). In this sense, reclaimed wastewater reuse for agricultural irrigation appears as a promising alternative practice to surpass water scarcity. Additionally, it can also compensate for nutrient needs of crop plants, contributing to their growth and development (Christou et al., 2019). However, wastewater-derived organic contaminants, such as pharmaceuticals, may persist in treated wastewater. Thus, reclaimed wastewater reuse in agricultural production raises several uncertainties since these practices represent a potential source of emerging contaminants into the environment and the food chain. Nowadays there is limited data on the impact that wastewater-derived organic contaminants conveyed by reclaimed wastewater reuse in agriculture may have in the environment and even less in the dietary exposure and potential risks to human health due to the consumption of contaminated agricultural products. In this work, two crop plants (lettuce and oregano) were grown in an agricultural field located in Lesvos Island (Greece) and drip irrigated with treated wastewater. The presence of wastewater-derived organic contaminants (e.g., pharmaceuticals) in the irrigation water and crop plants was evaluated. Considering the generated data, the environmental risk assessment of the wastewater-derived organic contaminants detected in irrigation water was assessed. The exposure and human health risk of emerging contaminants due to the ingestion of the reclaimed wastewater irrigated crops was also estimated. Overall, just a few compounds conveyed by irrigation water showed to have a moderate ($0.1 <$ Hazard Quotient (HQ) ≤ 1) to high risk ($HQ > 1$) to the freshwater environment (e.g., diclofenac, ketoprofen, venlafaxine). A much lower number of emerging contaminants was detected in crop plants than in irrigated water, with concentrations <10 ng/g (wet weight). The daily human intake of each emerging contaminant detected in the edible part of crop plants was estimated based on its concentration. In a conventional diet, the Estimated Daily Intake (EDI) for all the detected emerging contaminants showed to be much lower than the Acceptable Daily Intake (ADI), presenting an $HQ < 0.1$. Therefore, detected wastewater-derived organic contaminants would not represent a threat to human health due to their ingestion.

Acknowledgments
This work was funded by the European Union’s Horizon 2020 Research and Innovation programme (HYDROUSA project, GA N° 776643). Gianluigi Buttiglieri acknowledges Spanish State Research Agency of the Spanish Ministry of Science, Innovation and Universities for the Grant to the Creation of a permanent position Ramon y Cajal 2014 (RYC-2014-16754).

References

Ben Mordechay, E. et al., (2022) Wastewater-derived organic contaminants in fresh produce: Dietary exposure and human health concerns. Water Research, 223, 118986, doi: 10.1016/j.watres.2022.118986.

Christou, A. et al., (2019) Ranking of crop plants according to their potential to uptake and accumulate of contaminants of emerging concern. Environmental Research, 170, 422-432, doi: 10.1016/j.envres.2018.12.048.

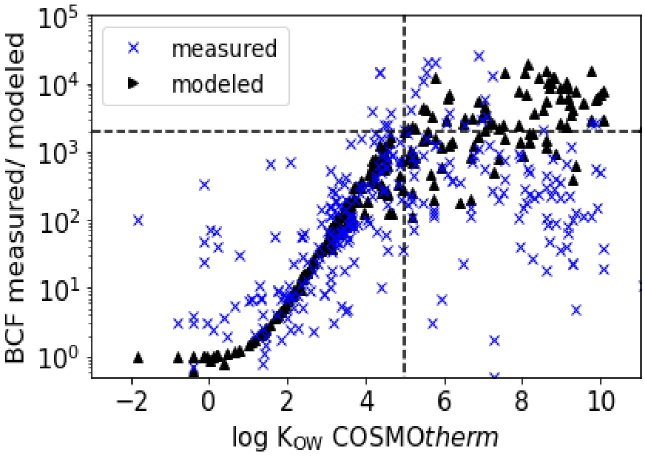
How Error-Prone Bioaccumulation Experiments Affect the Risk Assessment of Hydrophobic Chemicals and What Could be Improved

J. Glüge[1*], B. I. Escher[2,3], M. Scheringer[1,4]

[1] Institute of Biogeochemistry and Pollutant Dynamics, ETH Zürich, Zürich, Switzerland
[2] Department of Cell Toxicology, Helmholtz Centre for Environmental Research–UFZ, Leipzig, Germany
[3] Environmental Toxicology, Department of Geosciences, Eberhard Karls University Tübingen, Tübingen, Germany
[4] RECETOX, Masaryk University, Brno, Czech Republic

juliane.gluege@usys.ethz.ch

Bioaccumulation is one of the hazard criteria for the PBT assessment under the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) in the EU and only if a chemical is persistent (P), bioaccumulative (B), and toxic (T), it is further evaluated and considered as a Substance of Very High Concern. Having reliable bioaccumulation data is therefore of high importance for the regulation of chemicals. The present study investigates the availability and quality of the bioaccumulation data submitted under REACH for neutral substances and identifies potential issues in the data. The data analysis revealed that many of the experimental data, but also the data from QSARs and other calculation methods, underestimate the actual bioaccumulation potential of hydrophobic substances considerably. Using a previously published model for fish (Arnot and Gobas 2003) with chemical specific biotransformation rate constants, we were able to show that between 332 and 584 substances that are registered under REACH are likely to bioaccumulate in the aquatic environment—many more than have so far been identified in the B assessment (Glüge et al. 2022). According to our analysis, a paradigm shift is required for a meaningful assessment of the bioaccumulation potential of hydrophobic substances in the future. This could be done in a weight-of-evidence approach using data from different sources, including data from models, existing biomonitoring studies in humans, mammals, and fish and experimental data using invertebrate species.



Experimental bioconcentration factor (BCF) values from the ECHA database (blue crosses) and modeled BCF values (black triangle).

References

Arnot, J. and Gobas F.A.P.C. (2003) 'A generic QSAR for assessing the bioaccumulation potential of organic chemicals in aquatic food webs.' QSAR Comb Sci. 22(3):337–45 doi: 10.1002/qsar.200390023.

Glüge J. et al. (2022) 'How error-prone bioaccumulation experiments affect the risk assessment of hydrophobic chemicals and what could be improved'. Integr Environ Assess Manag. doi:10.1002/ieam.4714

Analysis of Sixty Environmental Contaminants in Human Adipose Tissue with a Single Extraction–Method Greenness Assessment

S. Sousa[1,2,3]*, P. Paíga[1], M. J. Ramalhosa[1], D. Pestana[2,4], G. Faria[2,5], C. Calhau[2,4], C. Delerue-Matos[1], and V. F. Domingues[1]

[1]REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, 4249-015 Porto, Portugal
[2]Center for Research in Health Technologies and Information Systems, 4200-450 Porto, Portugal
[3] Universidade do Porto, Departamento de Química, Faculdade de Ciências, Portugal
[4]Nutrição e Metabolismo NOVA Medical School, 1169-056 Lisboa, Portugal
[5]Faculty of Medicine, University of Porto, 4200-319 Porto, Portugal

sara.sousa@graq.isep.ipp.pt

Countless environmental contaminants (ECs) are widespread across the environment and several of them are persistent chemicals. These are linked to several hazard effects and biomagnified through the food chain, which makes them an increasing environmental and health issue. As strong lipophilic compounds, these accumulate in biota fat tissue leading to a constant accumulation mostly without excretion or degradation. Polychlorinated biphenyls (PCBs), brominated flame-retardants (BFRs), polycyclic aromatic hydrocarbons (PAHs), organophosphate ester (OPEs), organophosphate pesticides (OPPs) and synthetic musks (SMs) are ECs well documented in the literature (Sousa et al., 2020, 2022).

Global climate change presses the need for environmentally benign, less toxic, biodegradable, natural, and low-cost chemical products, and processes. Hence, reducing or eliminating the use or generation of hazardous substances. Consequently, the demand for cleaner, simple, effective, sustainable, and greener approaches to analytical chemical procedures is continuously increasing (Sousa et al., 2022).

Conventional extraction techniques such as Soxhlet, and liquid-liquid extraction demand large amounts of organic solvents per extraction or energy consumption and are time-consuming procedures. Ultrasound-assisted extraction (UAE) is less time-consuming and has a low amount of sample, solvent, and energy requirement (Sousa et al., 2023).

The present study proposes a quick and simple method using a low amount of organic solvent for the analysis of sixty ECs in adipose tissue using UAE and dispersive solid-phase extraction clean-up(Sousa et al., 2020, 2023). The developed methodology is suitable for the simultaneous extraction of seven OPEs, six OPPs, thirteen PCBs, ten BFRs, six SMs, and eighteen PAHs. Analyte quantification was performed either by gas chromatography (GC) flame photometric detector, GC mass spectrometry (MS), or high-performance liquid chromatography photodiode array and fluorescence detectors inline. Positive samples were confirmed with GC tandem MS. The method was validated according to the European Commission guidelines and in samples of adipose tissue from Portuguese Women (CE146-09). Eco-scale, AGREE and GAPI tools were used to assess the Greenness of the method.

Repeatability, intermediate precision and accuracy were confirmed and low matrix effect, method detection and quantification limits were achieved.

The presented method proves to be suitable and eco-friendly for the assessment of sixty ECs in adipose tissue. Presenting as an easier, quicker, greener alternative to conventional methods.

Acknowledgements: Sara Sousa would like to thank Fundação para a Ciência e Tecnologia (FCT) for the Ph.D. scholarship SFRH/BD/137516/2018 and COVID/BD/153231/2023. The authors thank the General Surgery Department of Hospital de São João (Porto, Portugal) for the human adipose tissue samples and to all patients that consent to participate.

Funding: The authors are thankful to FCT/Ministério da Ciência, Tecnologia e Ensino Superior for the support of this work through projects UIDB/50006/2020, UIDP/50006/2020 and LA/P/0008/2020.

References

Sousa, S. et al. (2020) ‘Method development for the determination of Synthetic Musks and Organophosphorus Pesticides in Human Adipose Tissue’, Journal of Pharmaceutical and Biomedical Analysis, 191, p. 113598. doi: 10.1016/j.jpba.2020.113598.

Sousa, S. et al. (2022) ‘The role of adipose tissue analysis on Environmental Pollutants Biomonitoring in women: The European scenario’, Science of The Total Environment, 806, p. 150922. doi: 10.1016/j.scitotenv.2021.150922.

Sousa, S. et al. (2023) ‘Optimization of a Simple, Effective, and Greener methodology for Polycyclic Aromatic Hydrocarbons extraction from Human Adipose Tissue’, Analytical Methods. doi: 10.1039/D2AY02075K.

Characterization of Dissipation Pathways for Pharmaceuticals in Natural Soils – A Modelling Approach

M. Böckmann[1]*, J. Siemens[2], B. J. Heyde[2], C. Zarfl[1]

[1]Eberhard Karls University of Tübingen, Department of Geosciences, Schnarrenbergstraße 94-96, 72076 Tübingen, Germany
[2]Justus Liebig University Giessen, Institute of Soil Science and Soil Conservation, iFZ, Heinrich-Buff-Ring 26-32, 35392 Giessen, Germany

matthias.boeckmann@uni-tuebingen.de

Reuse of wastewater, e.g. for agricultural irrigation, is an established method of using water resources efficiently, especially when it comes to facing water scarcity. However, especially in countries of the so-called Global South, wastewater is often not or insufficiently treated, so that agricultural soils irrigated with wastewater accumulate organic and inorganic pollutants. These include antibiotics and disinfectants, which are present in the wastewater irrigated soil in relatively low concentrations (10^1 - 10^5 µg·kg^{-1}, Dalkmann et al. 2014, Heyde et al. 2021), but promote the development of resistance in soil microorganisms. Concentrations of pollutants observed in soil water decline over time. However, it is commonly unclear whether this is due to degradation or due to other sequestration-like processes where pollutants analytically cannot be observed but might still persist and thus pose a long-term risk to the soil environment. Therefore, based on combining published concentration data on pharmaceuticals in soils and mathematical models, the objective of this study is to identify and quantify different dissipation pathways using a set of pharmaceuticals like sulfadiazine and sulfamethoxazole as model compounds.

Common extraction methods in the laboratory distinguish between easily extractable and residual pollutant fractions. Hence, the underlying model aims to compare the observed quantities in the dissolved, sorbed and dissipated fractions.

Equilibrium sorption between soil water and particles is represented by the Freundlich model. To consider hysteresis - often observed in sorption processes - intraparticle diffusion is assumed as a diffusion process between different shells of a hypothetical spherical soil particle. Dissipation processes leading to reduced measured total mass are represented by two possible pathways: First, direct loss from the water phase through transformation and mineralization and second, conversion to a non-extractable fraction. Sensitivity analysis and an examination of different model structures are used to identify dominant processes that can explain the observed extraction behavior.

The results suggest that sorption processes, in this case modelled as intra-particle diffusion, play a major role for dissipation of the investigated compounds. Data from radioactively labelled sulfadiazine suggest that large-scale mineralization does not occur. Thus, pollutants dissipated due to sorption processes can be released over longer timescales or due to changes in the boundary conditions and could lead to long-term exposure of microorganisms, even if emissions into the environment are reduced or stopped. After calibration, the model is able to simulate the sampling process while quantifying sorption processes during the sampling procedure that are not directly observable. Based on the underlying data, sorption processes did not distort the sampling of the dissolved fraction for most of the pharmaceuticals, i.e. the easily extractable fraction is representative for the dissolved and thus bioavailable compound fraction.

References

Dalkmann, P. et al. (2014) ‘Does Long-Term Irrigation with Untreated Wastewater Accelerate the Dissipation of Pharmaceuticals in Soil?’ Environ. Sci. Technol. 2014, 48, 9, 4963-4970, https://doi.org/10.1021/es501180x

Heyde, B. et al (2021) ‘Quaternary alkylammonium disinfectant concentrations in soils rise exponentially after long-term wastewater irrigation’ Environ. Res. Lett. 16 064002, https://doi.org/10.1088/1748-9326/abf0cf.

Contribution of RAMAN Spectroscopy to Assess Cadmium Toxicity on Marine Mussel (Mytilus Edulis)

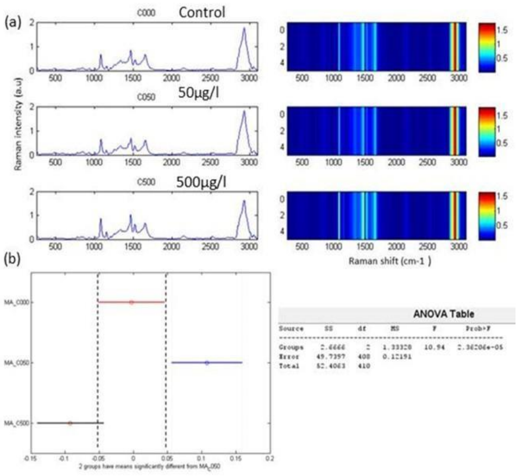
M.J Durand[1]*, A. Assaf[1], A. Pean[1], O. Dib[1], A. Zalouk-Vergnoux[2]
and Thouand[1]

[1]Nantes Université, ONIRIS, CNRS, GEPEA, UMR 6144, La Roche-sur-Yon, F-85000, France
[2]Nantes Université, Institut des Substances et Organismes de la Mer, ISOMer, UR 2160, Nantes, F-44000, France

marie-jose.durand-thouand@univ-nantes.fr

The European Water Framework Directive (WFD) and the Marine Strategy Framework Directive (MSFD) both aim to achieve and maintain a good general water status by 2027. For this, an assessment of the environmental status is necessary, regarding chemical pollution and their effects on living organisms. In this context we propose to use Raman spectroscopy as a diagnostic tool for toxic impact assessment on marine invertebrates.

Raman spectroscopy is used in medical biology as a non-destructive and non-invasive analytical technique (Auner et al., 2018). Except environmental application on microplastic and nanoparticules detection in organism (Lenz et al., 2015), and metal effect on microorganisms (Bittel et al., 2015), no study focuses on invertebrate toxicity analysis. The aim of this study is to evaluate the ability of Raman spectroscopy to assess the health status of sentinel marine organism. To test this hypothesis, mussels were exposed for one week with cadmium, then, the gills, the mantle were analyzed with Raman microspectroscopy (figure: 9 mussels per condition 15 spectra for each tissue). Results show the possibility to discriminate the mantle of the exposed mussels compared to the controls. This study showed that Raman spectrometry is a promising tool in the context of effect assessment and could be also used in Adverse Outcome Pathways study. Additional studies on the optimization of chemometric tool and analysis of biomarkers (lipid peroxidation, SOD…) are currently in progress.



ANOVA Table

Source	SS	df	MS	F	Prob>F
Groups	2.6666	2	1.33328	10.94	2.36206e-05
Error	49.7397	408	0.12191		
Total	52.4063	410			

Raman spectral analysis of mantle from mussels a) Mean Raman spectrum (b) Spectral pre-processing and data analysis

References

Auner G.W. et al. 2018, Cancer Metastasis Rev, 37, 691–717. doi.org/10.1007/s10555-018-9770-9.

Lenz R. et al. 2015, Marine Pollution Bulletin 100, 82–91.

Bittel M. et al. 2015, Environ Sci Technol, 49, 12324-332. doi.org/10.1021/acs.est.5b03013.

Exposure of Organic Micropollutants in Greater Flamingo from the Ebro Delta Natural Park

M. Dulsat-Masvidal[1]*, A. Bertolero[2], R. Mateo[3], S. Lacortel[1]

[1]IDAEA-CSIC, Department of Environmental Chemistry, Jordi Girona, 18-26, 08034 Barcelona, Spain
[2]Associació Ornitològica Picampall de les Terres de l'Ebre, Trinquet 8, 43580 Deltebre, Spain
[3]Institute for Game and Wildlife Research (IREC), CSIC-UCLM-JCCM, Ronda de Toledo, 12, 13071 Ciudad Real, Spain

mdmqam@cid.csic.es

The Ebro delta is a wetland of international importance for water bird conservation. In a relatively small surface, it comprises a great diversity of habitats and species: a total of 343 species of birds have been observed, from which 100 species breed regularly and 15 occasionally. Over the last 150 years the extensive wetland reclamation for rice cultivation has resulted in the loss of 65% of the natural habitats (Prado et al., 2019). Agricultural activities and runoff from industries and wastewater treatment plants are an important source of organic contaminants to Ebro delta. In recent years the presence of pesticides, pharmaceuticals, perfluorinated compounds (PFASs) and organophosphate esters (OPEs) has been reported in soils, sediments and water from Ebro delta (Barbieri et al., 2021). These organic contaminants can be bioaccumulated and transferred along the food chain affecting avifauna. The accumulation of pollutants in Yellow legged gulls and Audouin's gulls from the Ebro delta have been reported in recent years (Zapata et al., 2018). In the present study, we assessed for the first-time the exposure of legacy and emerging organic contaminants to the breeding colony of Greater flamingos (Phoenicopterus roseus) and the potential individual-level adverse effects. The Ebro delta colony of flamingos is one of the few stable breeding places of the species in the western Mediterranean and one of the most emblematic breeding waterbirds of the natural park. 50 whole blood samples from flamingos' chicks (2 months) were analysed for compounds of emerging concern including PFASs, pharmaceuticals, OPEs, and in-used pesticides, and legacy compounds as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCs), and polycyclic aromatic hydrocarbons (PAHs). The concentrations levels were compared to the biometric indexes of the individuals to search alterations in their development.

The results indicate a multi-exposure of flamingo's chicks to organic persistent compounds from a very young age. PFASs were the most ubiquitous compounds and detected in significant high concentration levels, with ∑PFASs ranging from 9.34 to 576 ng/mL. PFOA, PFOS and PFHxS were detected in all samples. ∑PAHs ranged from 0.2 to 422 ng/mL, followed by ∑OCs pesticides ranging from 1.35 to 37.7 ng/mL and ∑PCBs ranging from 1.35 to 53.6 ng/mL. In-use compounds such as pesticides, pharmaceuticals and OPEs were not detected in any sample. PFASs were identified as the most concerning compounds for flamingos breeding colony due to the high exposure. Further research was developed to study the presence of PFASs in sediment and water to determine potential sources of exposure and the potential risk for aquatic organisms in the natural area. The flamingo's filtering behaviour on mud and maternal transfer trough ovo-transference are the more likely routes of exposure of organic micropollutants to flamingos' chicks. The reported levels of micropollutants were not associated with any alternation in the body condition of birds.

Aknowlagments
This work was supported by the Spanish Ministry of Science and Innovation Project PID2019-105732GB-C21 and Excelencia Severo Ochoa Project CEX2018-000794-S.

References

Prado P., et al., (2019). Pristine vs. human-altered Ebro Delta habitats display contrasting resilience to RSLR. Sci Total Environ; 655:1376–86. doi: 10.1016/j.scitotenv.2018.11.318.

Barbieri, M. V., et al., (2021). Evaluation of the occurrence and fate of pesticides in a typical Mediterranean delta ecosystem (Ebro River Delta) and risk assessment for aquatic organisms. Environmental Pollution, 274. https://doi.org/10.1016/j.envpol.2020.115813.

Zapata P., et al. (2018). Presence and impact of Stockholm Convention POPs in gull eggs from Spanish and Portuguese natural and national parks. Sci Total Environ;633:704–15. doi:10.1016/j.scitotenv.2018.03.081.

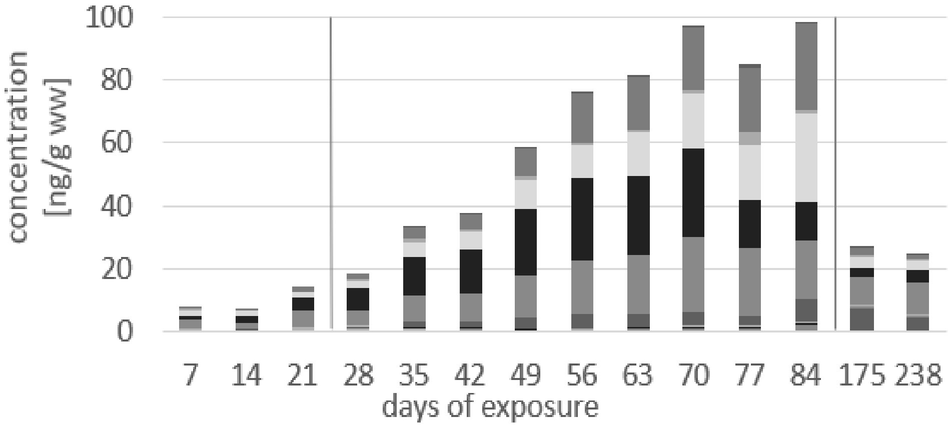
The Bioaccumulation of Pharmaceuticals and their Metabolites in Early Developmental Stages of Brown Trout

K. Grabicová*, N. Zhang, R. Grabic, T. Randák

[1]University of South Bohemia in České Budějovice, Faculty of Fisheries and Protection of Waters, South Bohemian
[2]Research Center of Aquaculture and Biodiversity of Hydrocenoses, Zátiší 728/II, CZ-389 25 Vodňany, Czech Republic)

grabicova@frov.jcu.cz

The emissions of micropollutants from wastewater treatment plants (WWTPs) into the receiving surface water are recognized threats to the aquatic environment. The adverse effects of released chemicals on aquatic organisms belong to the most accented ones. We focused on the bioaccumulation of pharmaceuticals and their selected metabolites (PhACs) in the early developmental stages of brown trout (Salmo trutta) as a promising in situ tool for chronic exposure assessment. The boxes with eggs in the eye stage were deployed in the stream with a high effluent contribution. The same stream but upstream of the WWTP effluent served as a reference locality. The analysis of early developmental stages were sampled in a defined time and analysed for 90 PhACs using liquid chromatography with high-resolution mass spectrometry. Simultaneously, we documented water pollution levels using grab water samples and deploying passive samplers (POCIS).
The development, mortality and sex ratio in tested fish differed in the impacted locality compared to the reference locality. The total concentration of quantified PhACs (64 above limit of quantification) in passive samplers was up to 1000 times higher than in the reference locality. In biota samples, fifteen PhACs were found with clear bioaccumulation trends with time since hatching. The highest concentration was observed for sertraline and its metabolite norsertraline, trazodone (all antidepressants) and telmisartan (cardiovascular drug). The study was conducted under project No. 20-04676X (Czech Science Foundation).



Total concentration of pharmaceuticals and their metabolites in fish samples.

The Effect of Effluent Discharge from a Municipal Wastewater Treatment Plant on the Ecotoxicity of a Relatively Small Watercourse in Aartselaar, Belgium

B. Raes[1]*, M. De Jonge[2] and R. Delgado[1].

[1]Aquafin NV, Dijkstraat 8, 2630 Aartselaar, Belgium
[2]Flemish environmental Agency (VMM), Dokter De Moorstraat 24-26, 9300 Aalst, Belgium

birte.raes@aquafin.be

Urban wastewater treatment plants (UWWTP's) are very successful in removing easily biodegradable organic matter and nutrients from wastewater, however removing all types of contaminants of emerging concern (CEC's) remains a great challenge. The UWWTP of Aartselaar (BE) treats wastewater of about 60.000 p.e. and discharges into the Grote Struisbeek, a relatively small watercourse. In dry periods, the discharge makes up 60% of the receiving water body, therefore contributing significantly to its quality.

To evaluate the contribution of the municipal effluent to the ecotoxicity in the watercourse, the Flemish wastewater treatment utility (Aquafin) and the Flemish Environmental Agency (VMM) started a monitoring campaign on CEC's and ecotoxicity in May 2022. During this campaign, several chemical substances, as well as a selection of both in vivo and in vitro toxicity tests are applied to the effluent and both the upstream and the downstream surface water (Ecofide, 2020). From the results so far it already became clear that for certain chemicals and effects, the toxicity of municipal effluent is influencing the downstream water quality, often exceeding the threshold of the environmental trigger value (de Baat et al., 2021), as is for example the case for estrogenic toxicity, shown in Figure 1. This confirms the need for advanced treatment at certain UWWTP's. A tertiary treatment system for CEC removal is currently being built at the UWWTP of Aartselaar. The monitoring of the effluent and the watercourse will continue to assess the effectiveness of the post-treatment.

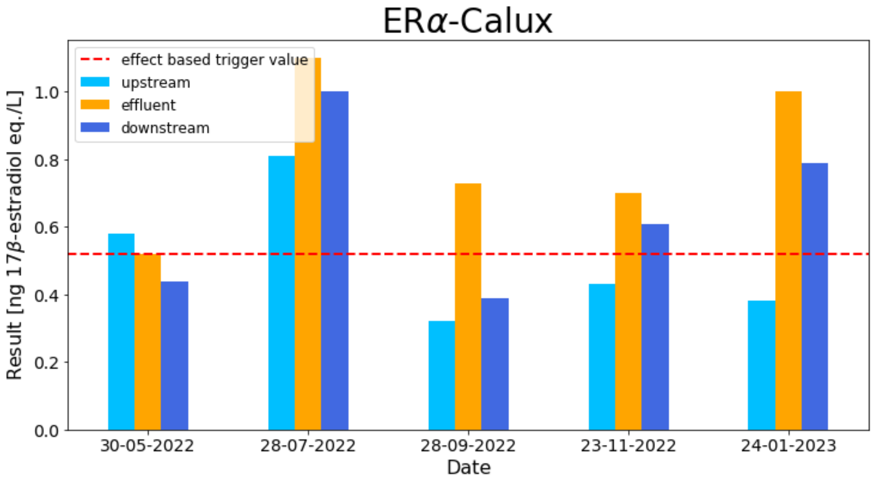


Figure 1: Extrogenic toxicity of municipal effluent, upstream and downstream surface water, compared to the effect based triger value.

References

Ecofide (2020), Handreiking voor uitvoeren van biologische effectmonitoring bij vergaande zuivering van RWZI-effluenten. Versie 0.7 (03/04/2020). The Netherlands.

de Baat, M.L., T.E. Pronk, S.J.P. van den Berg, R. van der Oost (2021) Kalibratie van de risicogrenzen voor interpretatie van bioassays. Version 1, 21 december 2021. Amersfoort, The Netherlands: Kennis Impuls Water Kwaliteit.

Evaluating Environmental Impacts of Different Pest Control Practices Across Europe

F. Soheilifard[1]*, J. Mark[2], P. Fantke[1]

[1]Technical University of Denmark, Quantitative Sustainability Assessment, Department of Environmental and Resource Engineering, Produktionstorvet 424, 2800 Kgs. Lyngby, Denmark
[2]Research Institute of Organic Agriculture (FiBL), Switzerland

farso@dtu.dk

Life cycle assessment (LCA) can be used to assess environmental impacts of pest control practices (Nemecek et al., 2022). However, practices differ across farms in terms of environmental conditions, cropping systems, and pest control options, including the use of pesticides as contributors to (eco-)toxicity impacts. Current LCA models for deriving pesticide emissions and impacts on humans and ecosystems are, however, not adapted to reflect farm-level differences. To address this gap, we propose a framework where life cycle impacts of pest control are evaluated at the farm level, with focus on (eco-)toxicity of pesticides. To compare different conventional, organic and integrated farming practices at farms across 10 European countries, the unit area of produced crop was used as functional unit. Foreground data for pesticide and all involved inputs are derived from farm-level questionnaires and complemented with background data from inventory databases. (Eco-)toxicity impacts from pesticide use are characterized with PestLCI Consensus (emissions), USEtox (emission-related impacts), and dynamiCROP (food crop residue-related impacts) (Fantke et al., 2011). Farm-specific differences in surface areas were considered by mapping emissions and fate-related area fractions to spatialized land use data from Copernicus Landcover. Impacts other than (eco-)toxicity were characterized using ImpactWorld+. Results show that pesticide impacts dominate overall impacts on human health and ecosystem quality across pest control practices. Copper-based fungicides are identified as the main driver for high (eco-)toxicity impacts. Also, high ecotoxicity-related impacts are found for azoxystrobin applied on potatoes in the Netherlands (conventional farming), underlining the special focus on pesticide use for these impact categories. For human toxicity impacts, expsoure to pesticide residues in harvested food crops dominates for most farms and pest control practices. Life cycle impacts (pesticide supply chain and field application, e. g. agricultural machinery) contribute between 15% (human health and ecosystem quality in conventional farming) and 45% (natural resources) in organic farming. Our approach demonstrates that different models can be integrated to assess pest control practices at the farm level, despite limitations in considering spatial characteristics.

References

Nemecek, T., Antón, A., Basset-Mens, C., Gentil-Sergent, C., Renaud-Gentié, C., Melero, C., Naviaux, P., Peña, N., Roux, P. and Fantke, P. (2022). Operationalising emission and toxicity modelling of pesticides in LCA: the OLCA-Pest project contribution. The International Journal of Life Cycle Assessment, 27(4): 527-542. https://doi.org/10.1007/s11367-022-02048-7.

Fantke, P., Charles, R., Alencastro, L.F. de, Friedrich, R., Jolliet, O., 2011a. Plant uptake of pesticides and human health: Dynamic modeling of residues in wheat and ingestion intake. Chemosphere 85, 1639–1647. https://doi.org/10.1016/j.chemosphere.2011.08.030.

Removal Efficacy and Aquatic Hazard Reduction of Psychoactive Drugs by a Pond Treatment System

G. Fedorova[1]*, R. Grabic[1], K. Grabicova[1], J. Turek[1], B. W. Brooks[2] and V. Zlabek[1]

[1]University of South Bohemia in České Budějovice, Faculty of Fisheries and Protection of Water, South Bohemian Research Center of Aquaculture and Biodiversity of Hydrocenoses, Zátiší 728/II, CZ-389 25 Vodňany, Czech Republic
[2]Department of Environmental Science, Institute of Biomedical Studies, Center for Reservoir and Aquatic Systems Research, Baylor University, Waco TX 76798 USA

Pharmaceuticals are introduced to the water environment by anthropogenic inputs, being only partially metabolized by the human body. Especially psychoactive pharmaceuticals are of concern since they are widely prescribed with a continuously increasing trend, resulting in ubiquitous occurrence in surface waters. In developed countries, the primary source of psychoactive drugs is wide population consumption and consequent discharge via wastewater treatment plants (WWTPs). These compounds usually enter waterways via urban wastewater after being excreted.

Recent studies indicate adverse effects of psychoactive drugs on aquatic life at environmentally relevant concentrations. The impacts of pharmaceutical pollution on non-target aquatic organisms that have similarities in the molecular targets with humans raise many concerns. According to the theoretical model of the effects of human pharmaceuticals in fish, they will exhibit similar biological effects across species, if the molecular target has been conserved and effective drug concentrations reach the blood plasma.

In the current study, we employed an ecosystem-based treatment system, specifically employing a treated wastewater pond (TWP), which receives 100% treated WWTP effluent as a tertiary treatment component. We selected a model system for a unique study in which water treated by the TWP is transferred to an aquaculture pond (AP) for common carp production. Here we examined the occurrence of psychoactive drugs within the different locations of the study system and then performed probabilistic environmental hazard assessments to identify the efficacy of different treatment components. Carbamazepine, citalopram, tramadol, and venlafaxine exceeded at least 1 PNEC on at least 1 sampling site. When ecological hazards of psychoactive compounds to fish are considered, PNEC exceedances were observed for citalopram and venlafaxine but not for tramadol and oxazepam. However, these water quality hazards were effectively removed by the TWP-AP system. Based on the approach taken here, the TWP-AP system appears useful as a tertiary treatment step to reduce psychoactive drugs and decrease ecotoxicological water quality hazards prior to beneficial reuse in aquaculture.

Acknowledgment - The authors thank the Czech Science Foundation [No. 22-03754S], the Ministry of Education, Youth and Sports of the Czech Republic - project “CENAKVA” [No. LM2018099]. BWB acknowledges support from United States Department of Agriculture (USDA), National Institute of Food and Agriculture (NIFA) (#20166900725093).

Impact of Beach Recreation on Environmental Quality of Coastal Areas of the Southern Baltic Sea

A. Jędruch[1,2]*, U. Kwasigroch[1], M. Staniszewska[1], Agnieszka Flasińska[3], Grażyna Dembska[3], Piotr Chibowski[4], Małgorzata Suska-Malawska[4], Korejwo[2], D. Narwojsz[2] and J. Bełdowski[2]

[1]University of Gdańsk, Institute of Oceanography, Marszałka Józefa Piłsudskiego 46, 81-378, Gdynia, Poland
[2]Polish Academy of Sciences, Institute of Oceanology, Powstańców Warszawy 55, 81-712, Sopot, Poland
[3]Gdynia Maritime University, Maritime Institute, Trzy Lipy 3, 80-172, Gdańsk, Poland
[4]University of Warsaw, Faculty of Biology, Żwirki i Wigury 101, 02-089, Warszawa, Poland

ajedruch@iopan.pl

The relationship of tourism with the natural environment is complex. In the case of the Baltic Sea a detrimental influence of tourism on its environment was evidenced. The contribution of tourism industry revels through littering, use of non-biodegradable products, discharge of untreated or poorly treated wastewater, as well as increased popularity of recreational boating and personal watercraft. This study (Jędruch et al., 2023) aimed at determining the impact of tourism pressure on environmental quality of coastal areas on the example of one of the most popular tourist area of the southern Baltic, the Puck Bay. Evaluated aspects included: i) water dynamic conditions and depositional processes, ii) composition and origin of sedimentary material, iii) sediment contamination with trace metals, with a focus on mercury, as well as with persistent organic pollutants, including phenolic compounds, polycyclic aromatic hydrocarbons, and total petroleum hydrocarbons, iv) bacterial activity, v) structure of benthic fauna.

Three locations with varying levels of tourism pressure were chosen: Chałupy (minor), Jastarnia (moderate), and Osłonino (strong). Study material was collected during four campaigns at the end of each season: June 2020 (spring), September 2020 (summer), December 2020 (fall), and March 2021 (winter).

The results showed that at Jastarnia and Osłonino, stations with medium and strong tourist pressure, respectively, the condition of the coastal zone environment changed visibly after the end of the summer season. Disruption of the sediment texture and an increase in water turbidity due to intensified water dynamics were evident at both stations. Studies have shown a mixed land-sea sediment origin at all three stations. At the stations in Chałupy and Jastarnia, the 'marine fingerprint' came from beneficial macroalgae and vascular plants, while at Osłonino it was related with the presence of filamentous algae associated with nutrient pollution. In the case of the Osłonino station, sediments collected after the end of the summer season were the most enriched in all investigated contaminants: heavy metals (mercury in particular), phenols (4-tert-octylphenol and bisphenol A in particular), polycyclic aromatic hydrocarbons (phenanthrene, fluoranthene and pyrene in particular), as well as petroleum hydrocarbons. These chemicals can accumulate in tissues and negatively impact marine wildlife, but also humans, causing variety of implications, including carcinogenicity, neurotoxicity, and endocrine-disrupting effects.

Actual sediment pollution from tourist activity in the coastal zone may have been even greater than estimated as the resuspension of the finest sediment particles due to increased water dynamics could cause the release of some pool of contaminants. A significant decrease in the biomass and biodiversity of benthic organisms inhabiting the seabed was also recorded at Osłonino. Increased tourism has also resulted in the emergence of Pseudomonas and Enteric bacteria, which can adversely affect human health.

This work was supported by the National Science Centre grant 2018/31/N/ST10/00214 carried out at the University of Gdańsk.

References

Jędruch, A., et al. (2023), 'Impact of beach recreation on environmental quality of coastal areas of the southern Baltic Sea – a multi-elemental approach', Science of the Total Environment (under review).

Identification of Biological Effect Drivers in Complex Environmental Mixtures using Pull-Down Assay Based on Specific Protein-Ligand Interaction

P. Mikušová[1], L. Sehnal[1], Z. Toušová[1], J. Kuta[1], G.Codling[1], G. Fedorova[2], R. Grabic[2] and K. Hilscherová[1*]

[1]RECETOX, Faculty of Science, , Brno, Czech Republic
[2]South Bohemian Research Center of Aquaculture and Biodiversity of Hydrocenoses, Faculty of Fisheries and Protection of Waters, University of South Bohemia in České Budějovice, Vodňany, Czech Republic

klara.hilscherova@recetox.muni.cz

Chemical pollution is a global threat to aquatic ecosystems and human health. Hundreds of chemicals enter the aquatic environment due to diverse anthropogenic activities. Organic micropollutants, usually related to wastewaters or surface runoff, often occur in low concentrations within highly complex environmental mixtures. These mixtures may elicit "cocktail effects" in biological systems, however, the causative chemicals are largely unknown. Identification of the effect drivers remains a challenging task despite progress in the field of high-throughput bioanalytical techniques, (multidimensional) fractionation schemes, and advanced analytical approaches (Gong *et al.*, 2023).

We present a novel approach for the identification of bioactive compounds in complex environmental mixtures based on protein-ligand interactions. The pull-down assay uses an engineered target protein as a "bait" for compounds, which can be pulled from the complex mixture after binding to the specific protein. The method is based on in-house design, expression and purification of target cellular receptor or transport proteins followed by a pull-down assay and non-target screening of bound ligands. We focus namely on the understudied endocrine disrupting activities that have been detected in aquatic environment, but their drivers are largely unknown. The target proteins are designed to contain either the ligand binding domain of a specific nuclear receptor or whole transport protein, and affinity His-tag for purification purposes. Purified protein is incubated with the extracts from environmental samples to form the protein-ligand complexes, which are bound to magnetic beads and separated from the remaining compounds. Serial elutions enable to retrieve most of the bound protein-ligands complexes. The protein is then denatured to release the ligands, which are subject to identification using a non-target screening workflow (Jia *et al.*, 2022).

The method was developed and optimized for several target proteins (retinoic acid receptor, thyroid hormone receptor and transthyretin). For each protein, specific conditions were optimized to achieve maximum protein yields and avoid precipitation. Functionality of the proteins was examined using standard reference ligands with high affinity to the protein. After achieving sufficient recovery rates of the ligands, confirmed in both targeted analysis and bioassays, the pull-down assays were used to address complex environmental mixtures. Non-target screening workflow was tailored to address the pull-down assay eluates. This workflow uses HPLC-HRMS data for differential analysis of serial eluates of the full pull-down assay employing environmental extracts, and a set of negative controls. We have successfully used this concept to identify known and novel ligands and effect drivers in environmental samples such as retinoids in cyanobacterial biomass extracts as ligands of retinoic acid receptor; or diclofenac and its metabolites, benzydamine, citalopram, telmisartan, lupulone and triclosan sulfate in treated wastewater as ligands of transthyretin. The project is funded by Czech Science Foundation grant GX20-04676X.

References

Gong, Y. *et al.* (2023) 'Building the Environmental Chemical-Protein Interaction Network (eCPIN): An Exposome-Wide Strategy for Bioactive Chemical Contaminant Identification', *Environmental Science and Technology* [Preprint], (February). doi:10.1021/acs.est.2c02751.

Jia, Y. *et al.* (2022) 'Discovery of contaminants with antagonistic activity against retinoic acid receptor in house dust', *Journal of Hazardous Materials*, 426(September 2021), p. 127847. doi:10.1016/j.jhazmat.2021.127847.

Environmental Exposure and Ecotoxicological Properties of a New Generation Fluorosurfactant (Cc6o4): a Comparison with Selected Legacy Perfluoroalkyl Acids

E. C. Bizzotto[1]*, P. Scanferla[1], A. Bonetto[2], A. Marcomini[2], M. Vighi[3]

[1]Foundation Ca' Foscari University, Ca' Dolfin, Calle Larga Ca' Foscari Dorsoduro 3859/A, Venice, 30123, Italy
[2]Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, via Torino 155, 30172 Venice-Mestre, Italy
[3]IMDEA Water Institute, Science and Technology Campus of the University of Alcalá, Avenida Punto Com 2, 28805 Alcalá de Henares, Madrid, Spain

elisachiara.bizzotto@unive.it

The presentation is about cyclic C6O4 (cC6O4, CAS number 1190931-27-1), a new generation polyfluorinated alkyl substance (PFAS) used as polymerisation aid in the synthesis of fluoropolymers and produced in Italy since 2011. Specifically, the presentation aims to provide a comprehensive evaluation of cC6O4 based on all available information (including monitoring data mainly present in the grey literature), in a context of ecological risk assessment.

Monitoring data, mainly referred to surface and groundwater, are available for water bodies close to the production sites as well as for a wider area in the river Po watershed (Northern Italy); few values are also available for concentration in biota (bird eggs and clams). Effect data indicate low toxicity on all tested organisms with NOEC values always higher than the maximum concentrations tested (100 mg/L for acute tests); bioaccumulation potential is also very low. A comparison with selected widely used PFAS with five to eight C atoms indicates that cC6O4 is substantially less dangerous to aquatic organisms. At the time being, an ecological risk for the aquatic ecosystem may be excluded even in directly exposed ecosystems. However, for a complete assessment of the suitability of cC6O4 as substitute of other PFAS (namely PFOA), more comprehensive chronic experiments are necessary, to produce realistic NOECs, as well as higher tier experiments (e.g., mesocosms) capable to provide ecologically relevant endpoints. Moreover, a more accurate evaluation of the environmental persistence would be necessary.

A Novel and Validate Method for Extraction and Analysis of Several Microplastics in Water Samples

V. Cruz Fernandes[1*], R. Garzón-Vidueira[2], D. Rede[1], R. Rial-Otero[2], C. Delerue-Matos[1]

[1]REQUIMTE/LAQV - Instituto Superior de Engenharia do Porto - Rua Dr. António Bernardino de Almeida, 431
4249-015 Porto Portugal
[2]University of Vigo, Food and Health Omics, Department of Analytical and Food Chemistry, Faculty of Science, 32004
Ourense, Spain.

virginiacruz@graq.isep.ipp.pt

Microplastics (MPs) have become a prominent environmental concern over the past few years and their extraction is a scientific challenge that needs to be faced and solved (Martinho S. D. et al. 2022, Martinho S. D., et al. (2022) There is an urgent need to develop methods to extract microplastics from different samples. Standardized and validated protocols for MPs extraction are lacking and the existing methodology is often unable to separate all the types and sizes of microplastics (Lvleva N. P. 2021).

The aim of our research was to develop an oil-based method, inexpensive, simple and safe method to extract MP from water samples. We tested an oil-based extracting technique exploiting the oleophilic properties of plastics. Different oils were tested (olive, sunflower, etc.), even recycled oils in a circular economy perspective. Other parameters influencing the extraction process were tested, namely the temperature of the solutions, the use of a air pump to improve the density separation and the use of NaCl. The extraction experiments were performed in 6 different microplastics with sizes ranging from 50 microm-5mm.

For validating the method, water samples were spiked with six different microplastics: PE (polyethylene), PP (polypropylene), PS (polystyrene), UPVC (unplasticised polyvinyl chloride), PA (polyamide or nylon plastic) and LDPE (low-density polyethylene). The obtained results are promising, and the influencing parameters played a very important role in the extraction efficiency, especially the use of the air pump. The recycled oils also showed good recovery rates. Overall, the recoveries ranged from 70-100%. Microplastics analysis was performed by RAMAN spectrometry. The spectra of the different microplastics were compared before and after extraction using the oils. It was found that the surface of some microplastics was altered after extraction by changes in the bands of the RAMAN spectrum. The best method after validation was applied to river and wastewater treatment water samples for monitoring studies.

References

Martinho, S. D. et al. (2022) 'Microplastic Pollution Focused on Sources, Distribution, Contaminant Interactions, Analytical Methods, and Wastewater Removal Strategies: A Review', International Journal of Environmental Research and Public Health, 19(9), pp. 5610.

Martinho, S. D., et al. (2022) 'Study of the Potential Accumulation of the Pesticide Alpha-Endosulfan by Microplastics in Water Systems', Polymers, 14(17), pp. 3645.

Lvleva, N. P. (2021) 'Chemical Analysis of Microplastics and Nanoplastics: Challenges, Advanced Methods, and Perspectives', Chemical Reviews, 121(19), pp. 11886-11936.

Fertigating Soil with Wood Distillate as a Possible Green Strategy to Mitigate the Impact of Bioplastic on Plants

S. Celletti[1]*, M. Ghorbani[1], R. Fedeli[1], N. Azarnejad[1] and S. Loppi[1 2]

[1]University of Siena, Department of Life Sciences, Via P. A. Mattioli 4, 53100, Siena, Italy
[2]Interuniversity Center for Studies on Bioinspired Agro-Environmental Technology (BAT Center), 80138, Napoli, Italy

silvia.celletti@unisi.it

Interest in ecological sustainability for the use of bioplastics (replacing plastics) and bio-based products is growing significantly in all sectors, including agriculture, as it is strongly supported by the Sustainable Development Goals of the UN 2030 Agenda. However, it is of primary necessity to investigate the impact of bioplastics on the environment, given the massive consumption of bioplastics expected in the near future and given that several studies have recently shown that bioplastic residues are emerging contaminants, which can interfere with soil properties, affecting crop growth and yield, with negative environmental and human health drawbacks (Wang et al., 2022). This study investigated the effect of a starch-based bioplastic on a plant species of economic interest, such as basil (Ocimum basilicum L.). In addition, it also investigated how the possible negative effect of the bioplastic could be mitigated by using wood distillate (WD), which is known in agriculture to be a valuable natural enhancer of plant growth and defense systems (Ofoe et al., 2022). For this purpose, basil plants were grown under controlled conditions for 35 days in soil supplemented with WD and bioplastic, either separately or in combination. Physiological changes of the fresh biomass and chlorophyll content, as well as biochemical changes of the most important biomarkers of adequate growth (protein and soluble sugar content) and oxidative stress (vitamin C and malondialdehyde content) were analyzed at the shoot level, i.e. in the edible parts of the basil. As expected, WD promoted basil development, while bioplastics hindered it. Interestingly, despite the direct correlation between sugar and vitamin C content, WD did not influence sugar levels, while it increased vitamin C levels. This effect can be considered positive, as a change in the sugar level could signal the onset of a stress condition for the plant. Indeed, in the case of the bioplastic, there was a reduction in the sugar content. However, the bioplastic did not change the vitamin C content. This could plausibly be explained by the fact that the reduction in sugars had not reached the threshold level for which a significant reduction in vitamin C content also occurred. In the combined treatment, the addition of WD was effective in mitigating the impact of the bioplastic on basil, except for the sugar and vitamin C content, which were reduced. In this case, the direct correlation between sugar and vitamin C was fulfilled, probably because the sugar level reached the critical threshold of reduction. This study could open up new research perspectives valorizing the use of WD in remediating soils contaminated by bioplastics; however, the mechanisms of WD interaction with bioplastic need to be further explored by studying the effect of different doses and types of bioplastic and WD in various plant species.

References

Wang, Y. et al. (2022) ‘Biodegradable microplastics: a review on the interaction with pollutants and influence to organisms’, Bulletin of Environmental Contamination and Toxicology, 108, p. 1006–1012. doi: 10.1007/s00128-022-03486-7.

Ofoe, R. et al. (2022) ‘Effect of pyroligneous acid on the productivity and nutritional quality of greenhouse tomato’, Plants 11(13), 1650. doi: 10.3390/plants11131650.

Airborne Microplastics in Outdoor and Indoor Environments

G. Zuri[1*], A. Karanasiou[1] and S. Lacorte[1]

[1]Institute of Environmental Assessment and Water Research of the Spanish Research Council (IDAEA-CSIC) Jordi Girona 18-26, 08034 Barcelona

giuseppina.zuri@idaea.csic.es

Microplastics (MP) are ubiquitous and persistent new contaminants which can be suspended in air and transported by wind in long distances away from their source of origin due to their small size and low density. The present study characterized airborne MPs in indoor and outdoor environments in the European regions of Catalunya (Spain) and Sardinia (Italy) which have very different population densities. The relevance of the study relies in the fact that airborne MPs can be inhaled and ingested by humans possibly leading to health effects.

Airborne particles were collected using a 25 mm filter holder (Merck MAWP025AC, Merck Millipore, USA) connected to a Leland Legacy air sampling pump (SKC, UK) with an intake flow rate of 10.0 ± 0.1 L/min. Nylon filters (20 µm pore size, 25 mm diameter, Sigma Aldrich, USA) were used. Sampling duration was 3 h. Qualitative analysis included the assessment of the physical morphology of the particle (dimension, shape, color) by means of a stereomicroscope (Leica S9i, Germany) equipped with a 10 MP CMOS-camera. Polymers were identified using µ-FTIR (Thermo Nicolet iN10 MX/Omnic version 7.3, Waltham, MA, USA) equipped with a mercury cadmium telluride (MCT) array imaging detector in transmission mode with spectra comparison with Hummel Polymer Sample Library. The analysis allowed the identification of the most common plastic polymers, including polypropylene (PP), polystyrene (PS), polyethylene (PE), polyacrylonitrile (PA), polyethylene terephthalate (PET), and nylon. Results showed that:

- the total particle count outdoor was 4 times higher than indoor, but no difference was observed between the concentration of MP per m^3 outdoors and indoors;
- the most abundant particle shape outdoor was fragment while indoor was fiber;
- MPs were present in 90% of the samples collected indoor and outdoor;
- PA and nylon were the most abundant plastic polymers both outdoor and indoor accounting for more than 40% of the total MPs fraction;
- the main sources of MP outdoors are anthropogenic activities while indoors predominant sources include textiles, and construction material.

G. Zuri acknowledges support from “la Caixa” Foundation (ID 100010434) through fellowship LCF/BQ/DI21/11860062. This work was supported by the Spanish Ministry of Science and Innovation (Excelencia Severo Ochoa, Project CEX2018-000794-S and project PID2019-105732GB-C21).

References

Arthur, C., et al. (2009). Proceedings of the International Research Workshop on the Occurrence, Effects, and Fate of Microplastic Marine Debris.

Towards a Quantitative Analysis of Polymer Concentration in Blended Microplastics Using 3-D Micro-Raman Spectroscopy

M. L. Choobbari[1*], J. Ferguson[2], N. Van den Brande[3], T. Smith[2], T. Chalyan[1], W. Meulebroeck[1], and H. Ottevaere[1]

[1]Vrije Universiteit Brussel, Department of Applied Physics and Photonics, Brussels Photonics, Pleinlaan 2, 1050 Brussels, Belgium
[2]Renishaw plc, New Mills, Wotton-under-Edge, Gloucestershire, GL12 8JR, United Kingdom
[3]Vrije Universiteit Brussel, Department of Materials and Chemistry, Physical Chemistry and Polymer Science, Pleinlaan 2, 1050 Brussels, Belgium

Mehrdad.lotfi.choobbari@vub.be

Despite their enormous applications in industry, blended polymers received little attention as an important source to release micro/nano plastics into our ecosystem. Tracking back the source of blended microplastics (B-MPs), that exist down to the nanoscale in the environment, could be a challenging task as different blends form during the recycling process. Moreover, it is yet unclear if B-MPs could form because of different environmental parameters like weathering, erosions, high temperatures, etc. Accordingly, discriminating between microplastics (MPs) that are released from single-type or blended polymers may require a precise analytical approach. In this regard, we are proposing the use of 3-D Raman mapping for the accurate analysis of B-MPs in this study. Valuable information is gained about the morphology of polymers in such complex samples. Moreover, effort is made to quantitatively extract the concentration of each constituent polymer that was present in B-MPs. Considering the correlation between the resolution of Raman mapping and the excitation wavelength, qualitative and quantitative results are obtained and thoroughly compared using three different wavelengths 405, 532, and 633 nm. It is observed that 3-D Raman mapping offers great advantages for the analysis of B-MPs, and it is a suitable approach where high precision is needed.

References

V. D. dos Santos, A. C. et al. (2022) 'Nanoscale chemical characterization of a post-consumer recycled polyolefin blend using tapping mode AFM-IR', Analyst, 147(16), pp. 3741–3747. doi: 10.1039/d2an00823h.

Sánchez-Valdes, S., Ramos-De Valle, L. F. and Manero, O. (2013) Polymer Blends, Handbook of Polymer Synthesis, Characterization, and Processing. doi: 10.1002/9781118480793.ch27.

Witt, W. (1986) 'Polymer blends and their importance as engineering materials', Materials and Design, 7(4), pp. 182–187. doi: 10.1016/0261-3069(86)90119-6.

Occurrence of Microplastic in an Environmentally Protected Wetland Area in Hungary

B. Prikler[1;2*], G. Bordós[1], Z. Palotai[1], A. Micsinai[1], E. Kaszab[2], T. Banga[2], Zs. Lovász[3], S. Szoboszlay[2]

[1]Eurofins Analytical Services Hungary Kft., Anonymus st. 6, 1045, Budapest, Hungary
[2]Institute of Aquaculture and Environmental Safety, Hungarian University of Agriculture and Life Sciences, 2100 Gödöllő, Hungary
[3]West-transdanubian Water Directorate, 9700, Szombathely, Hungary

prikler.bence@laboratorium.hu

Microplastics (MP, plastic waste < 5mm) were first observed in seawater and still there is more data available on their concentration from marine ecosystems, compared to freshwaters. To fill this gap, in the last decades, more and more studies have come to light, that deal with the MP content of freshwaters. The selected area of this study is part of the Balaton Uplands National Park, where the largest shallow lake in Central Europe (Balaton) is located. The wetland habitat and filter zone of the area, called the Kis-Balaton Water Protection System (KBWPS), is unique in Europe and has been recognized as a nature conservation area of international interest. At the same time, the Zala River, which is responsible for almost half of Lake Balaton's water supply, deposits the suspended solids and the associated pollutants in this wetland. This means this area is a suspected hotspot for MPs.

To reveal the microplastic concentration in the Kis-Balaton wetland area, altogether 7 sampling points were designated. For each sample, 2000 L of water was pumped through an in-situ fractionated filtration device previously described by Bordós et al. (2021). Particles between 1000-50 µm size were retained for further analysis. During sample preparation, to reduce the concentration of biogenic organic matter that would disturb FTIR identification of MPs, an oxidation-based removal step was used. The elimination of other, non-plastic particles was performed in a small-volume glass separator (SVGS) using a density-based separation method previously described by Mári et al. (2021). The final, concentrated samples were filtered onto Anodisc filters and were analysed by FTIR imaging microscope.

The results revealed that all of the examined samples contained MPs. The most abundant polymer types were polyethylene and polypropylene. The number of plastic particles in the samples varied between 1.5 and 195.9 per cubic meter, and the average of 7 samples was 55.4 particles. To determine the effectiveness of microplastic removal in this wetland habitat, additional monitoring activities are necessary, including the examination of other environmental matrices such as sediment.

Project no. 2020-1.1.2-PIACI-KFI-2021-00239 has been implemented with the support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the PIACI KFI funding scheme.

References

Bordós G. et al. (2021) 'Validation of pressurized fractionated filtration microplastic sampling in controlled test environment' Water Research 189, 116572, doi: https://doi.org/10.1016/j.watres.2020.116572.

Mári, Á. et al. (2021). Validation of microplastic sample preparation method for freshwater samples. Water Research, 202, 117409. doi:10.1016/j.watres.2021.117409.

Chemical Characterization of Tire Wear Particles (TWPs) Through Cross-Validation of Different Techniques

F. Corami[1*], B. Rosso[2], E. Gregoris[1], L. Litti[3], F. Zorzi[3], M. Fiorini[4], B. Bravo[5], C. Barbante[1], A. Gambaro[2]

[1]Institute of Polar Sciences, CNR-ISP, Via Torino, 155, 30172, Venezia-Mestre, Italy
[2]DAIS Ca' Foscari University of Venice, Via Torino, 155, 30172, Venezia-Mestre, Italy
[3] University of Padova, DCS, Via Marzolo 1, 35131 Padova, Italy
[4] University of Bologna, Department of Civil, Chemical, Environmental and Materials Engineering, Via Terracini 28, Bologna (BO), Italy
[5]Thermo Fisher Scientific, Str. Rivoltana, Km 4 - 20090 Rodano (MI), Italy

fabiana.corami@cnr.it

Tire wear particles (TWPs) are one of the most relevant emission sources of microplastics in the environment. These particles are generated by the abrasion of tire tread against road and highway surfaces and can then accumulate in the road dust. TWPs deposited on roads may be mobilized by wind or during rainfall events. Upon mobilization by runoff, these particles can reach receiving water bodies or soil, posing a risk to aquatic and terrestrial ecosystems (Luo et al., 2021). Due to TWPs' complex chemical mixture composition and the incorporation of material from the surrounding environment, the analytical methods for characterizing TWPs in real samples are challenging. To date, different sampling, pre-treatments, and measurement procedures have been used, resulting in incomparable results, especially in real environmental samples (Rauert et al., 2022). The composition of TWPs varies from brand and purpose; tires are composed of several layers, and their constituents can be different rubber typologies (e.g., styrene-butadiene rubber (SBR) or butadiene rubber (BR)) and additives, such as fillers, softeners, oils, plasticizers, chemicals for vulcanization, and anti-aging agents. Due to TWPs' complex chemical mixture composition, the analytical methods for characterizing TWPs in highway stormwater runoff (HSW) are challenging. In this work, the chemical identification of these particles was carried out in HSW through cross-validation techniques for the first time. HSW was collected along the trafficked highway (Passante of Mestre on the mainland of Venice in Italy) in three different drains along the highway, where three decontaminated glass flasks were located in each drain. Optimization of an oleo-extraction pre-treatment method was provided in a plastic-free Clean Room (Corami et al., 2021). Reagents and procedural blanks were provided for each sample batch. Specific markers were used for TWPs identification comparing FTIR-ATR, Micro-FTIR, and Pyrolysis–gas-chromatography–mass spectrometry (Py-GC/MS). Most of the TWPs analyzed were less than 100 µm in size. The sizes and shapes were also confirmed using a scanning electron microscope (SEM), including the presence of potential nano TWPs in the samples. Further, the complex mixture of these particles was confirmed using the elemental analysis via SEM. An agglomeration of inorganic and organic particles was observed, probably derived from roads and asphalts.

References

RCorami, F., et al., (2021). “Small microplastics (<100 µm), plasticizers and additives in seawater and sediments: Oleo-extraction, purification, quantification, and polymer characterization using Micro-FTIR”, Sci. Total Environ., 797, 148937, 10.1016/j.scitotenv.2021.148937.

Luo, Z., et al., (2021). “Environmental occurrence, fate, impact, and potential solution of tire microplastics: Similarities and differences with tire wear particles”. Sci Total Environ, 795, 148902, https://doi.org/10.1016/j.scitotenv.2021.148902.

Rauert, C., et al., (2022). “Concentrations of Tire Additive Chemicals and Tire Road Wear Particles in an Australian Urban Tributary”. Environ. Sci. Technol. 2022, 56, 4, 2421–2431.

Additives, Plasticizers, Small Microplastics (<100 Mm), and other Microlitter Components in the Gastrointestinal Tract of Commercial Teleost Fish: Method of Extraction, Purification, Quantification, and Characterization Using Micro-FTIR

F.Corami *[1], B. Rosso [2], A.A. Sfriso [3], A. Gambaro [2], M. Mistri [3], C. Munari [3], C. Barbante [1]

[1]Institute of Polar Sciences, CNR-ISP, Via Torino, 155, 30172, Venezia-Mestre, Italy
[2]DAIS Ca' Foscari University of Venice, Via Torino, 155, 30172, Venezia-Mestre, Italy
[3]Department of Chemical, Pharmaceutical, and Agricultural Sciences, University of Ferrara, Via Fossato di Mortara 17, 44121 Ferrara, Italy

fabiana.corami@cnr.it

The concern about plastic pollution is particularly worrisome when considering plastics below 100 µm in size (small microplastics, SMPs). Plastic objects contain additives, plasticizers, and pigments, that can be released into the environment during their fragmentation into macro, meso, and microplastics; these particles are part of micro-litter (MCLs), together with natural and non-plastic synthetic fibers (i.e., rayon). Organisms can ingest microplastics and MCLs according to the size of their mouthparts. Invertebrates, the prey of other organisms in the food web, ingest SMPs and other particles less than 100 µm in size; these particles can then enter the food web and may accumulate and represent a hazard for organisms of higher trophic levels, including human beings. The first goal of this study is to develop a pretreatment method for extracting SMPs and MCLs ingested by fish without further denaturation/degradation of the particles under exam. Another aim of this study is to develop a simultaneous quantification and identification method via Micro-FTIR of MCLs and SMPs ingested. Five of the most widespread commercial fish species in the Northern Adriatic were dissected, and the whole gastrointestinal tract was treated to extract the particles under exam (Figure 1). The distribution of SMPs and MCLs is distinctively different for each species investigated. This study highlights the importance of studying additives and plasticizers that can be used as efficient proxies of the presence of microplastics.

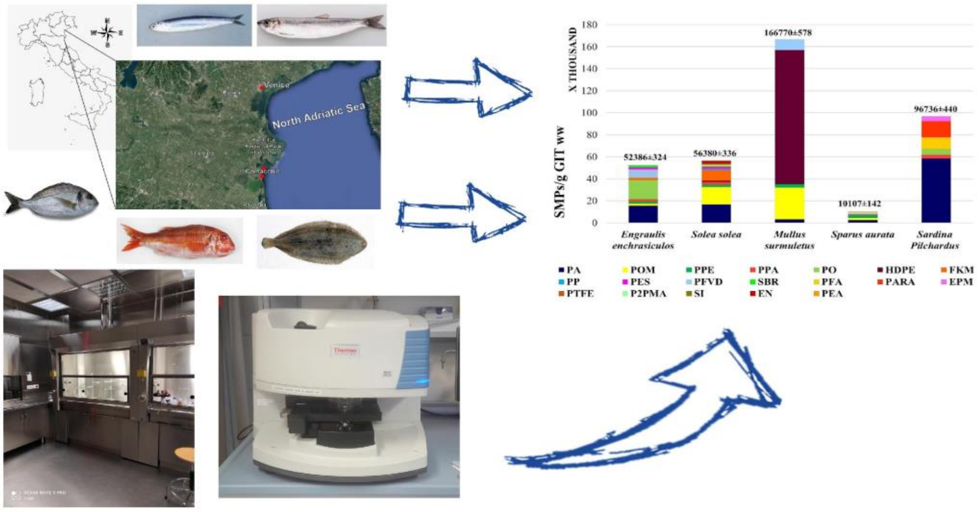


Figure 1: 5 of the most common commercial fish species in the Adriatic Sea were analyzed for ingestion of SMPs and MCLs

References

Corami, F. et al. (2022). Additives, plasticizers, small microplastics (< 100 µm), and other microlitter components in the gastrointestinal tract of commercial teleost fish: Method of extraction, purification, quantification, and characterization using Micro-FTIR. Marine Pollution Bulletin, 177, 113477.

Analysis of Microplastics in Treated Communal Wastewater and the Recipient Surface Waters in the Danube River Basin

G. Bordós[1*], B. Prikler[1,2], Z. Palotai[1], I. Szabó[2], S. Szoboszlay[2], R. Berta[3], Zs. Kovács[4], A. Micsinai[1]

[1]Eurofins Analytical Services Hungary Kft., Anonymus st. 6, 1045, Budapest, Hungary
[2]Hungarian University of Agriculture and Life Sciences, Institute of Aquaculture and Environmental Safety, Páter K. u. 1., 2100 Gödöllő, Hungary
[3]University of Pannonia, Soós Ernő Research and Development Center, Zrínyi M. u. 18., 8800 Nagykanizsa, Hungary
[4]University of Pannonia, Institute of Environmental Engineering, Egyetem u. 10, 8200 Veszprém, Hungary

bordos.gabor@laboratorium.hu

Nowadays it is clear that microplastics (MPs) are abundant and persistent in different environmental matrices such as in rivers, that are the major pathways of the microplastic pollution towards the marine ecosystem. In the past years a common understanding has been formed, that wastewater treatment plants (WWTPs) are a source of riverine microplastics. Still, unified methodology of sample collection from wastewater treatment plants and surface waters, sample preparation and analysis are lacking. That means, results of different studies are hardly comparable. To tackle the global issue of microplastics, it is important to understand microplastics composition and origin through the investigation of treated wastewaters and the recipient rivers.

To get the first overview of MPs in WWTPs and in the associated recipients, ten facilities with different capacities and recipient rivers with different discharges have been investigated in Hungary, in the centre of the Danube River Basin. Samples were collected with on-site fractionated filtration (particles between 1000-50 μm), that is an easy-to-apply, plastic free and closed system described by Bordós et al. (2021). 1000 L of effluent and 2000 L of river water have been sampled. Rivers have been sampled both upstream and downstream of the WWTPs to investigate possible effect of treated wastewater discharge. After sample preparation (oxidation, density separation), full samples have been investigated with FTIR imaging technique.

In the analysed wastewater samples in average 227.7 microplastic particles (range between 29.9-527.7) were found per 1 m^3 water. Surface water samples showed 66.6 MP particles per m^3 (range 3.5-227 MPs/m^3), in upstream samples in average 41.3 MPs/m^3 while in downstream samples in average 91.9 MPs/m^3. Average data highlights, that WWTPs act as a source of MPs, as MP concentration in effluent were always higher than that of upstream samples. Furthermore, in 8 locations out of the 10 sampling area, elevated MP concentration was shown in downstream samples compared to upstream samples, that also indicates significant MP load in surface waters originating from WWTPs. Most abundant polymer types among the indetified MPs were polyethylene (42.3% and 49.2%), polypropylene (34.1% and 22.4%), polystyrene (7.3 and 9.5%) and alkyd polymers (7.2% and 12.6%) in wastewater asn surface water samples, respectively.

This study highlights the importance of future microplastic monitoring programs in wastewater and surface water to better discover time- and geographical location-dependent variations of MP results. Such well defined programs will further improve the common knowledge on microplastic abundance in the environment, thus helping development of other related fields, such as ecotoxycology, human exposure studies and legislation issues.

Project no. 2020-1.1.2-PIACI-KFI-2021-00239 has been implemented with the support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the PIACI KFI funding scheme.

References

Bordós G. et al. (2021) 'Validation of pressurized fractionated filtration microplastic sampling in controlled test environment' Water Research 189, 116572, doi: https://doi.org/10.1016/j.watres.2020.116572.

Plastic-Related Chemicals in the Soil from the Natural Park of Montesinho

D. Rede[1,2], A. Pereira[1], C. Delerue-Matos[1] and V. C. Fernandes[1*]

[1]REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida 431, 4249-015, Porto, Portugal
[2]Departamento de Química, Faculdade de Ciências, Universidade do Porto, 4169– 007, Porto, Portugal

vir@isep.ipp.pt

Plastic materials have shaped modern society improving living conditions through the variety of products in which they are applied, and the jobs associated with production and distribution (Fernandez-Gonzalez et al., 2021). However, high production rates coupled with inadequate management and disposal of plastic waste cause enormous pressure on ecosystems. Under the effect of physical, chemical, and biological drivers, plastic materials can degrade into smaller particles, micronanoplastics (MNPs). These particles have been detected all over the globe, even in remote places such as the Alps (Bergmann et al., 2019). Although the extent of ecological effects is not yet known, MNPs have been detected in food and human biological samples. The hazard posed by MNPs might be related to their ability to sorb/desorb contaminants such as flame retardants or/and pesticides, increasing the bioavailability and toxicity of these chemical compounds in the environment (Fernandez-Gonzalez et al., 2021). This study was designed to monitor the organic pollution in soils around apiaries, improving data on the causes and consequences of pollinator decline. A Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) extraction method was developed for the simultaneous determination of 42 plastic-related chemicals (PRC) (polybrominated diphenyl ethers (PBDEs), polychlorobiphenyls (PCBs), organophosphate esters (OPEs), pyrethroid (PYRs), organochlorine (OCPs), and organophosphorus pesticides (OPPs)). Twenty-one samples were collected near beehives in glass containers from the Natural Park of Montesinho (Portugal). The extraction and quantification of PRC were based on the QuEChERS approach proposed by Fernandes et al. (Fernandes et al., 2013). Briefly, 5 g of soil was weighed into a centrifuge tube, and 3 mL of deionized water plus 7 mL of acetonitrile were added. The mixture was vortexed for 1 min. The QuEChERS salts were added to the tube, which was then vortexed and centrifuged. The supernatant was transferred to a glass vial containing MgSO4, PSA, and C18. The mixture was shaken and centrifuged. The extract was dried, recovered with n-hexane, and injected in a gas chromatograph with a flame photometric detector (OPPs and OPEs) and in a gas chromatograph with an electron capture detector (PBDEs, PCBs, OCPs and PYRs). Matrix-matched calibration standards were prepared, and the method was validated in terms of linearity, matrix effect, recovery percentage, the limit of detection (LOD), the limit of quantitation (LOQ), and precision. The optimized analytical techniques presented good performance with LOQs ranging from 2.15 to 11.87 $\mu g\ kg^{-1}$ and LODs ranging from 0.64 to 3.56 $\mu g\ kg^{-1}$. PCB 101 was quantified in two samples at a concentration of 20.26 and 13.88 $\mu g\ kg^{-1}$. BDE 154 and BDE 100 were quantified in two samples (3.48 and 24.41 $\mu g\ kg^{-1}$) and one sample (8.33 $\mu g\ kg^{-1}$), respectively. The identification and quantification of PRC in remote locations are needed to evaluate the extent of plastic pollution, and prevent ecological risks. In the case of the Natural Park of Montesinho, this cocktail of compounds can ultimately endanger the bees.

References

Bergmann, M. et al. (2019) ‘White and wonderful? Microplastics prevail in snow from the Alps to the Arctic’, Science Advances, 5(8), pp. 1–11. doi: 10.1126/sciadv.aax1157.

Fernandes, V. C. et al. (2013) ‘Multiresidue pesticides analysis in soils using modified QuEChERS with disposable pipette extraction and dispersive solid-phase extraction’, Journal of Separation Science, 36(2), pp. 376–382. doi: 10.1002/jssc.201200673.

Fernandez-Gonzalez, V. et al. (2021) ‘Impact of weathering on the chemical identification of microplastics from usual packaging polymers in the marine environment’, Analytica Chimica Acta, 1142, pp. 179–188. doi:

10.1016/j.aca.2020.11.002.

Detection of Small Microplastics Using Large Area ATR-FTIR

Y. Liu[1*], S. Luettjohann[2], J. Vollertsen[1]

[1]Aalborg University, Department of the Built Environment, Thomas Manns Vej 23, 9220 Aalborg, Denmark
[2]Bruker Optics GmbH & Co. KG, Rudolf-Plank-Straße 27, 76275 Ettlingen, Germany

yuanlil@build.aau.dk

Large area attenuated total reflectance-Fourier transform infrared spectroscopy (LAATR-FTIR) was introduced in this study as a new technology to detect small MPs (<100 µm). Two different LAATR units with Zinc Selenide (ZnSe) and Germanium (Ge) crystal, respectively, were used in µ-FTIR transmission mode, to detect reference MPs smaller than 20 µm and environmental sample (marine samples) collected from Kattegat. The reference MPs and marine samples were deposited on an optical window, and then analyzed in transmission mode through the LAATR unit. The result showed that the LAATR unit performs well for identifying MPs. As an example, the ZnSe unit could detect 10 reference MPs (4.9 – 31.9 µm based on major dimension) in a studied area, while only 3 reference MPs (26.9 – 36.4 µm based on major dimension) were observed in transmission mode. The Ge unit could identify 5 more reference MPs (1.6 – 44.7 µm based on major dimension), which were not detected in transmission mode. For environmental samples, both LAATR units could detect MPs in a sample where no MPs were identified in transmission mode. In other words, both LAATR units could identify small MPs (reference MPs and environmental samples), which could not be identified in transmission mode. These differences might be related to the different measurement techniques, lateral resolution, and spectral quality. It is worth mentioning that LAATR can offer both high-quality spectra and visual image during the process. Hence, considering all these factors, the smallest detectable sizes of micro-particles in transmission mode, LAATR with ZnSe, and Ge crystal were 10 µm, 2.1 µm, and 1.3 µm, respectively. This indicated that the size detection limit of the LAATR units were much better than that of the transmission mode, which can supplement the deficiency of transmission in identifying MPs less than approx. 20 µm. Moreover, the disadvantage and improvements of the application of LAATR in identifying MPs was also discussed. In summary, the LAATR unit with ZnSe crystal and Ge crystal perform well in identifying small MPs.

Analysis of Nanoplastic Contamination in Bottled Water via Infrared Nanospectroscopy

C. Vitali[1,2]*, A. K. Undas[1], H. G. Janssen[2,3], M. W.F. Nielen[1,2], and F. S. Ruggeri[2,4]

[1]Wageningen Food Safety Research, Wageningen University & Research, Akkermaalsbos 2, 6708 WB Wageningen, NL
[2]Wageningen University, Laboratory of Organic Chemistry, Stippeneng 4, 6708WE, Wageningen, NL
[3]Unilever Foods Innovation Centre – Hive, Bronland 14, 6708 WH Wageningen, NL
[4]Wageningen University, Physical Chemistry and Soft Matter, Stippeneng 4, 6708WE, Wageningen, NL

clementina.vitali@wur.nl

In recent years, microplastics (MPs) and nanoplastics (NPs) have emerged as ubiquitous contaminants hinting to a high likelihood of human exposure. NPs have attracted the attention of the scientific community since their sub-micrometre size increases their potential to cross biological membranes, and their translocation and accumulation in human tissues can lead to toxic effects on human body.

The physical and chemical characterization of NPs is key for a better understanding of their exposure, fate, and potential implications for human health. Bulk and micro-scale analytical methods provide rich information about bulk synthetic polymer samples and even single MPs, but lack the spatial resolution required to gather insights into presence of NP contamination.

In this presentation, we demonstrate the capabilities of infrared nanospectroscopy for the nanoscale physico-chemical characterization of NPs. We will showcase the enhanced spectroscopic sensitivity and single-nanoparticle spatial resolution provided by the unique combination of atomic force microscopy and infrared spectroscopy, also in comparison with a range of state of the art micro-analytical techniques. We demonstrate how this method enables a thorough multidimensional study of different synthetic polymers in the form of NPs. We then illustrate the capabilities of this strategy by analysing NP contamination in a set of bottled water samples.

Acknowledgement

MONPLAS has received funds from the European Union’s Horizon 2020 research and Innovation Programme under the Marie Sklodowska Curie Grant Agreement No. 860775

Effects of Natural Weathering of Polystyrene Microplastic on the Leaching of Brominated Flame Retardant Additives and Sorption of PFAS in the Marine Environment: Laboratory and Field Experiments

B. Barhoumi[1], M. Metian[1], F. Oberhaensli[1], N. Mourgkogiannis[2], H. K. Karapanagioti[2], P. Bersuder[1], I. Tolosa[1*]

[1]IAEA Marine Environment Laboratories, 4a Quai Antoine 1er, 98000 Monaco, Principality of Monaco
[2]University of Patras, Department of Chemistry, 26504 Patras, Greece

I.Tolosa@iaea.org

Among the synthetic plastic polymers, polystyrene (PS) which accounts for about 8% of the total plastic production is being used across a large variety of sectors (e.g., packaging, building, electronics, transportation, and maritime), resulting in an increase in mass production of plastic waste (Turner, 2020). In addition to its persistence and long-range transport, PS can contain large amounts of additive brominated flame retardants such as hexabromocyclododecanes (HBCDDs) that can easily leach from the plastic to the marine environment (Aminot et al., 2020). Although, previous studies of plastic debris of PS have shown relatively poor sorption of highly hydrophobic persistent organic pollutants (POPs) compared to other microplastics (e.g. polyethylene and polypropylene), many uncertainties still remain regarding the sorption capacity of PS (Menéndez-Pedriza and Jaumot, 2020), including its ability to sorb other emerging contaminants like amphiphilic per- and polyfluoroalkyl substances (PFAS). Furthermore, how the natural weathering of the PS particles affects the leaching and sorption of these contaminants is poorly understood. So, this study investigates how the natural weathering of the PS particles and the influence of environmental factors such as pH, ionic strength, temperature, and presence of dissolved organic matter (DOM) affect a) the leaching rates of brominated flame retardant additives in seawater and b) the sorption capacity of PS for a variety of PFAS. For that, distinct experimental scenarios using natural weathered PS debris and virgin PS beads were undertaken under seawater field conditions and controlled laboratory conditions. Chemical analyses of brominated flame retardants and PFAS were performed using LC-MS/MS. Scanning electron microscopy (SEM) and attenuated total reflectance−Fourier transform infrared spectrometer (ATR-FTIR) were used to monitor the physical and chemical changes in the weathered PS particles. The empirical results have confirmed higher leaching rates of HBCDDs in the field than in the laboratory experiments, and demonstrated that temperature and DOM concentrations are playing a key role in the leaching rates of these additives. Weathered PS beads were also shown to enhance the sorption capacity of different PFAS compared to pristine PS. Knowledge of the ageing effects and influence of environmental factors on the release of toxic additives from PS and the sorption of PFAS to PS microplastics will improve our understanding on the role and relevance of PS as both a source and a sink or even a dispersing agent of toxic contaminants in the marine environment.

References

Turner, A., (2020) Foamed Polystyrene in the Marine Environment: Sources, Additives, Transport, Behavior, and Impacts. Environ. Sci. Technol. 54, 10411–10420. https://doi.org/10.1021/acs.est.0c03221.

Aminot, Y. et al., (2020) 'Leaching of flame-retardants from polystyrene debris: Bioaccumulation and potential effects on coral', Marine Pollution Bulletin, 151, 110862. https://doi.org/10.1016/j.marpolbul.2019.110862.

Menéndez-Pedriza, A. and Jaumot, J., (2020) 'Interaction of Environmental Pollutants with Microplastics: A Critical Review of Sorption Factors, Bioaccumulation and Ecotoxicological Effects', Toxics, 8(2), 40. https://doi.org/10.3390/toxics8020040

Assessing Applicability of Asymmetric Flow Field-Flow Fractionation as a Tool for Nanoplastics Analysis in Micro- and Macrocosms

M. Hayder[1*], A. van Wezel[2] and G.J.M. Gruter[1,3]

[1]University of Amsterdam, Van't Hoff Institute for Molecular Sciences, Science Park 904, 1098XH, Amsterdam, The Netherlands
[2]University of Amsterdam, Institute for Biodiversity and Ecosystem Dynamics, Science Park 904, 1098XH, Amsterdam, The Netherlands
[3]Avantium Support BV, Zekeringstraat 29, 29, 1014 BV, Amsterdam, The Netherlands

m.w.hayder@uva.nl

With constantly growing plastic production and lack of effective waste treatment, plastic pollution has now become a major environmental issue. Especially minute particles resulting from plastic degradation are potentially hazardous. It is now clear that microplastics (<5 mm) and nanoplastics (<1000 nm) are omnipresent in all environmental compartments, hence the urgent need of accurate analytical methods for their screening (Mitrano et al. 2021). However, while for microplastics analysis many methods have already been established, nanoplastics characterization is still immature.

Estimation of nanoplastics presence in different environmental compartments, such as surface water or sediments, is obviously indispensable for monitoring of the plastic pollution. On the other hand, to understand more about the fate of plastic particles, well-defined samples prepared in the laboratory are used. Both types of samples require different treatment for their successful characterization. One technique allowing to obtain information on sizes of plastic nanoparticles is Asymmetric Flow Field-Flow Fractionation with Multi-Angle Light Scattering detection (AF4-MALS) (el Hadri et al. 2021). This approach has already been suggested as a way of nanoplastics characterization, however, has mostly been applied in proof-of-concept experiments carried out on simple standard polymer mixtures rather than on realistic samples. Therefore, in this work we aim to validate the applicability of AF4-MALS for nanoplastics analysis in highly distinct complex samples.

To fulfill our aim, we use AF4-MALS for size characterization of nanoplastics present in (simulated) real environmental samples. As an example of an environmental nanoplastics reservoir, wastewater treatment plant effluents are analyzed. As a microcosm sample source, polymer standard nanoparticles are subjected to human gastrointestinal conditions simulated in vitro, which includes incubation in highly acidic digestive enzymes solutions in physiological temperature and in the presence of salts. We identified varying difficulties in pretreatment and analysis of both types of samples. For nanoplastics coming from wastewater, the main challenge is to achieve a sufficiently low limit of detection, compatible with the extremely low particle concentrations in the samples. By adding an in-line preconcentration step, we managed to achieve detection limits reaching tens of nanograms and a continuous size distribution down to 150 nm. On the other hand, polymer particles used for in vitro studies require finely tuned, mild conditions to give correct results. With those, we carried out a study on nanoplastic aggregation induced by the human digestive tract and on interactions between plastic particles, digestive enzymes and nutrients. We also elucidate the potential of coupling the AF4 separation with other analytical techniques (DLS and MS) for further characterization of particles.

Our research proves that AF4-MALS is a versatile tool, which allows for sizing nanoplastics from diverse sources. We believe this work will contribute to more feasible nanoplastic analysis and to state-of-the-art plastic pollution monitoring.

References

Mitrano, D.M. et al. (2021) 'Placing nanoplastics in the context of global plastic pollution', Nature Nanotechnology, 16(5), pp. 491–500. doi:10.1038/s41565-021-00888-2.2

el Hadri, H. et al. (2021) 'Fate of nanoplastics in the environment: Implication of the cigarette butts', Environmental Pollution, 268. doi:10.1016/j.envpol.2020.115170.

Exposure of the Aquatic Insect Chironomus Riparius to Cryogenically Milled Tire Tread Leads to Bioaccumulation of Rubber Additives and to Potential Trophic Transfer to Fish

T. Masset[1*], F. Breider[1], W. Dudefoi[3], K. Schirmer[3,4], A.J. Bergmann[2], E. Vermeirssen[2], R. Beauvais[2] and B.J.D. Ferrari[2]

[1] Ecole Polytechnique Fédérale de Lausanne – EPFL, Central Environmental Laboratory, Switzerland.
[2]Ecotox Centre - EPFL, Switzerland
[3]Department Environmental Toxicology, EAWAG, Switzerland
[4]Institute of Biogeochemistry and Pollutant Dynamics, ETHZ, Switzerland

thibault.masset@epfl.ch

Tire and road wear particles (TRWP) are produced by the friction between the tires and road and consist of polymer-containing tread with pavement encrustations. Data gaps have been identified regarding their fate and potential toxicological impact on the aquatic ecosystem. Benthic organisms such as insect larvae could be exposed to TRWP and associated chemicals (e.g. PAHs, metals, antioxidants/antiozonants) through direct contact and/or ingestion. While ecotoxicological studies have mainly focused on pelagic organisms, research concerning organisms living in or on sediment remain scarce. As 6PPD-quinone, an oxidative product of the chemical 6PPD commonly used in tires, has been shown to be highly toxic for salmonid species (Tian et al., 2021), it is of critical importance to identify the different routes of exposure for fish to tire-associated chemicals. Among benthic organisms, chironomid larvae are commonly predated by fish and could participate in the trophic transfer of tire-associated chemicals in aquatic ecosystems.

In this study, stage 4 chironomids larvae were exposed for 4 days to sediment spiked with 0.5 mass% of cryogenically milled tire tread (CMTT) particles as a proxy for TRWP. After exposure, chironomid larvae were collected and half of them underwent gut depuration for 4 hours before being collected, whereas the other half was stored without gut depuration. Non-depurated subsamples were used as a surrogate for fish prey in an in vitro digestion scenario. The scenario reproduced the digestion of chironomids by fish (rainbow trout) for 27 hours using simulated digestive fluids as described in our previous studies (Masset et al., 2021, 2022). Depurated chironomids, non-depurated chironomids and post-digestion gastrointestinal fish fluids were analysed for organic tire-associated chemicals and zinc with LC-MS/MS and ICP-MS/MS, respectively. Our results showed that tire-associated chemicals were transferred to chironomids tissues and biota-sediment accumulation factors ranged from 1.3 to 6.3. Chemical analyses revealed that the tire-associated chemicals were present and bioaccessible in the fish digestive fluids following in vitro digestion of CMTT-exposed chironomids. Comparison of the tire-associated chemical concentration in depurated and non-depurated chironomids showed that non-depurated chironomids exhibited higher concentrations for most compounds. This result is consistent with the presence of CMTT in the guts of non-depurated chironomids. Overall, our results (i) showed the bioavailability of tire-associated chemicals for fish feeding on contaminated prey and (ii) highlighted the potential for trophic transfer of both tire-associated chemicals and tire particles along the aquatic food chain. Future work will aim to elucidate the possibility for formation of potent biotransformation products of tire-associated chemicals along the trophic food chain. The potential for bioaccumulation of tire-associated chemicals in fish following ingestion of contaminated preys will also be studied and will inform on the possibility for biomagnification of bioaccumulative compounds in the aquatic food chain.

References

Masset, T. et al. (2021) ‘In Vitro Digestion of Tire Particles in a Fish Model (Oncorhynchus mykiss): Solubilization Kinetics of Heavy Metals and Effects of Food Coingestion’, Environmental Science & Technology, 55(23), pp. 15788–15796. Available at: https://doi.org/10.1021/acs.est.1c04385.

Masset, T. et al. (2022) ‘Bioaccessibility of Organic Compounds Associated with Tire Particles Using a Fish In Vitro Digestive Model: Solubilization Kinetics and Effects of Food Coingestion’, Environmental Science & Technology, 56(22), pp. 15

Tian, Z. et al. (2021) ‘A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon’, Science, 371(6525), p. 185. Available at: https://doi.org/10.1126/science.abd6951.

Microplastics in a Conventional Wastewater Treatment Plant: Analysis, Distribution, and Environmental Emissions

S. Cavazzoli[1*], R. Ferrentino[1], G. Andreottola[1]

[1]Department of Civil, Environmental and Mechanical Engineering, DICAM, University of Trento, Via Mesiano 77, 38123 Trento, Italy

simone.cavazzoli@unitn.it

Environmental contamination by plastics is a widespread problem on a global scale. In recent years, several studies on micro (< 5 mm)- and nano (< 0.1 µm)- plastics (MNPs) have reported how these contaminants are ubiquitous in different environmental compartments, with main origins inland, and how they can potentially enter the food chain, with negative consequences on the ecosystem and human health. Wastewater treatment plants (WWTPs) can retain most plastic particles, by removing them from the water line and concentrating them in the sewage sludge. Despite this positive phenomenon, the amount of MNPs discharged annually by WWTPs into surface waters is still significant. The study of microplastics (MPs) in these environments is not straightforward, as the matrix to be analysed is complex, and to date, there is still no regulated analytical standard. In this work, wastewater samples entering and leaving a conventional WWTP located in northern Italy were collected and analysed. The 5000 – 2 µm sized MPs contained in these samples were concentrated in stainless-steel cartridge filters mounted on a pump sampling system. The latter also allowed obtaining representative sample volumes, about 10 L for influent and 400 L for effluent, averaged over 24 hours. Grab composite samples of sewage sludge were also collected and analysed. MPs were extracted according to the NOAA method, which was slightly modified to optimise the overall analyte recovery. The chemical-physical characterisation of the extracted MPs and their quantification were performed by using FPA-micro-FTIR and Pyr-GC/MS. The results obtained considering the 24-hour averaged balances of microplastics in/out the WWTP show that the WWTP is indeed able to remove effectively the MPs suspended in the incoming wastewater and accumulate them in the sewage sludge. The calculation of emission factors attributable to the plant also allowed to evaluate its contribution to the MP environmental contamination phenomenon. This study highlights the need to establish verified and harmonized standard methods for sampling and analysis of MNPs in the environment at the European and International levels. It is crucial to monitor the load of MNPs released by WWTPs to evaluate their role in the dispersion of these pollutants into the environment. Furthermore, proper disposal of sewage sludge can prevent additional MNPs dispersion into the environment. Given the extent of plastic contamination in water and soil worldwide and the potential negative impacts on living organisms, we emphasise the need for the application of effective and environmentally sustainable plastic remediation technologies.

References

Mintenig, S.M. et al. (2017) 'Identification of microplastic in effluents of waste water treatment plants using focal plane array-based micro-Fourier-transform infrared imaging', Water Research, 108, pp. 365–372. Available at: https://doi.org/10.1016/j.watres.2016.11.015.

Salmi, P. et al. (2021) 'Particle balance and return loops for microplastics in a tertiary-level wastewater treatment plant', Water Science and Technology, 84(1), pp. 89–100. Available at: https://doi.org/10.2166/wst.2021.209.

Sun, J. et al. (2019) 'Microplastics in wastewater treatment plants: Detection, occurrence and removal', Water Research, 152, pp. 21–37. Available at: https://doi.org/10.1016/j.watres.2018.12.050.

What Can we Learn from Biodegradation of Natural Polymers for Regulation?

S. Hahn[1]*, D. Hennecke[2]

[1]Fraunhofer ITEM, Chemical Safety and Toxicology, Nikolai-Fuchs-Str. 1, 30625 Hannover, Germany
[2]Fraunhofer IME, Applied Ecology, Auf dem Aberg 1, 57392 Schmallenberg, Germany

stefan.hahn@item.fraunhofer.de

Chemical persistence plays a key role in environmental risk assessment and regulation. Synthetic polymers are chemicals of emerging concern for the environment, which is mainly assigned to their persistence. In recent years, several reviews about biodegradation potential of polymers and especially biodegradable polymers are available. Challenges have been identified in the testing but also in the assessment of persistence of polymers. However, polymers exist in nature as well such as natural rubber, cellulose, hemicellulose, starch, lignin, chitin, cutin, etc.. A better understanding of similarities and differences in the environmental fate of natural and synthetic polymers might improve the persistence assessment of synthetic polymers. This may results in information on essential elements to justify persistence assessment of polymers in a weight of evidence, and to give suggestions for future needs and research.

Available literature was reviewed for polymer specific methodologies to identify influencing testing parameters, knowledge gaps and areas of improvement. Natural polymers vary widely in structure, function, and properties. Chemical and enzymatic hydrolysis is the most important process for degradation of natural polymers, which proceeds for particulate material either by bulk or surface erosion. Thus, degradation processes for particulate polymeric materials differ significantly from small molecules, and crystallinity, wettability and surface area are important influencing factors on the biodegradation kinetics. Some natural polymers will be degraded very fast, but in other cases natural polymers show very long time until complete mineralization. These differences in biodegradability are a result of evolution as they must fulfil specific functions in nature which might require certain persistency. Most degradation processes of natural polymers can be transferred and found for synthetic polymers as well.

The presentation summarizes the major findings on biodegradation potential for natural polymers and the learnings for the persistence assessment for synthetic polymers. Many natural polymers have to be regarded as persistent or very persistent (P or vP) if the REACH Annex XIII criteria will be applied. However, those criteria don´t apply to natural polymers which are considered having no concern for the environment for good reasons. This needs to be recognized when assessing synthetic polymers, many of which would fulfil the existing P/vP criteria as well. For this reason, improvement of our methodology of polymer persistence assessment is necessary, for example by establishing polymer specific criteria to enable an adequate hazard assessment of man-made polymers.

References

Hahn, S. and Hennecke, D (2022) Final Report WP4–Comparison between natural and synthetic polymers. http://cefic-lri.org/projects/eco52-bioavailability-complex-substances-and-overall-persistence-bcop-three-themes-to-deliver-a-step-change-in-persistence-assessments/

Quality Assurance and Automation of Microplastics Analysis

J. Stoffel[1]*, R. Kägi[2], N. Ashta[1], G. Crosset-Perrotin[2], M. Philipp[2], C. Hüglin[1]

[1]Swiss Federal Laboratories for Materials Science and Technology (EMPA), Ueberlandstrasse 129, 8600 Dübendorf, Switzerland
[2]Swiss Federal Institute of Aquatic Science and Technology (Eawag), Ueberlandstrasse 133, 8600 Dübendorf, Switzerland

josua.stoffel@empa.ch

Microplastics (MPs) have become an environmental pollutant of global concern (United Nations Environment Assembly, 2022). This calls for reliable and standardized analytical methods to monitor the concentrations of MPs in the environment. Optical microscopy and Fourier transform infrared (FTIR) spectroscopy, often used to analyze microplastics, provide structural as well as morphological information on an individual particle level. However, a quantitative assessment of MPs pollution and the interpretation of spatial and temporal trends requires the implementation of robust quality assurance and quality control (QA/QC) measures. In this context, the use of surrogate standards as suggested by Philipp et al. (2022) is a very promising approach and allows an assessment of sample-specific recoveries and uncertainties associated with the analytical chain. In the work of Philipp et al. (2022), the feasibility of the surrogate standard approach using red polyethylene spheres was demonstrated. However, many processing steps still had to be done manually and were therefore difficult to integrate into large-scale and routine processing of MP samples. We, therefore, developed software integrating the surrogate standard approach as a routine QA/QC measure on a largely automated basis. The software is centered around the following three main features: 1) random generation of sub-sampling areas of multiple samples based on optical images, 2) largely automated FPA-FTIR measurements of randomly generated areas, and 3) calculation of particle number-based recovery rates for (several) mono- and polydispersed surrogate standards and assessment of the uncertainties related to the measurement of the particle sizes. The increased degree of automation will reduce potential biases that arise, for example, from the selection of sub-sampling areas. The integration of the surrogate standard concept into the software on a largely automated basis will greatly facilitate establishing QA/QC measures in routine MP analysis. An assessment of the uncertainties of the particle sizes furthermore will contribute to a better understanding of the current discrepancies between particle number and total mass-based results.

References

Philipp, M., Bucheli, T. D., & Kaegi, R. (2022) 'The use of surrogate standards as a QA/QC tool for routine analysis of microplastics in sewage sludge', Science of The Total Environment, 835, 155485. https://doi.org/10.1016/j.scitotenv.2022.155485.

United Nations Environment Assembly (2022) 5/14. End Plastic Pollution: Towards an International Legally Binding Instrument—Resolution adopted by the United Nations Environment Assembly on 2 March 2022 [UNEP/EA.5/Res.14]. Available at: https://wedocs.unep.org/20.500.11822/40597 (Accessed: 23 March 2023).

Biological Uptake of Organic Contaminants from Car Tire Particles

C. Halsband[1]*, F. Hägg[1,2], Kristin Galtung[2,3], D. Herzke[2,3], A.M. Booth[4], V. Nikoforov[3]

[1]Akvaplan-niva, Fram Centre, N-9296 Tromsø, Norway
[2]UiT - The Arctic University of Norway, N-9037 Tromsø, Norway
[3]NILU – Norwegian Institute for Air Research, Fram Centre, N-9296 Tromsø, Norway
[4]SINTEF Ocean, N-7465 Trondheim, Norway

clh@akvaplan-niva.no

Car tire particles represent an important environmental challenge that is difficult to alleviate. The particles stem from abrasion during driving, so-called tire wear particles (TWPs), down-cycled end-of-life tire granulate, popular as low-cost infill on sports fields, or degradation products from discarded tires. The material contains a variety of additives and chemical residues from the manufacturing process, including metals, especially high concentrations of zinc, polycyclic aromatic hydrocarbons (PAHs), and benzothiazoles (Halsband et al., 2020), but also para-phenylenediamines (PPDs) and numerous other organic chemicals. In urbanized areas, TWPs are emitted from roads, and granulates disperse from artificial sports fields and other urban surfaces to the environment, suggesting that runoff to coastal systems is likely and a route of exposure to marine organisms. Here, we summarize recent experimental studies examining the responses of different marine animals to tire rubber particle exposure, focusing on ingestion and gut evacuation, and the uptake kinetics of tire-related organic chemicals into biological tissues. We present data for different ecological functional groups, including bivalves, crabs, and fish, representing different body sizes, marine habitats, and feeding modes, and thus varying exposure scenarios. Our findings from GC-HRMS SIM chromatography demonstrate that different marine species ingest tire rubber particles, and that several tire additives are taken up into tissues post-ingestion. Although the organic chemicals do not seem to bioaccumulate, mapping of tire rubber particle distributions in coastal systems, dose-response toxicity testing and risk assessments of environmental concentrations are warranted, also with a view to potential trophic transfer and implications for human health.)

References

Halsband, C. et al. (2020) 'Car Tire Crumb Rubber: Does Leaching Produce a Toxic Chemical Cocktail in Coastal Marine Systems?', Frontiers in Environmental Science, 8. doi: 10.3389/fenvs.2020.00125.

Microplastic Records in Sediment Cores in Huguangyan Maar Lake, China

Y.X. Zhang[1,2]*, Q.S. Ji[2], Y. Yang[3], Z.D. Jin[4], M.Y. He[4], H. He[2]

[1]Aarhus University, Aarhus Institute of Advanced Studies, 8000 Aarhus, Denmark
[2]Nanjing Normal University, School of Environment, Nanjing 210023, China
[3]East China Normal University, School of Geographic Sciences, Shanghai 200241, China
[4]Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China

yanxiazhang@envs.au.dk

Microplastics were found to be ubiquitous in different environments (Zalasiewicz et al., 2016). Microplastic records in sediment cores are supposed to reveal anthropogenic influences on the environment (Nakajima et al., 2019). Huguangyan Maar Lake (HML) in the southeast of China (Fig. 1a) is one of the most typical volcanic lakes in the world, with no fluvial inlets or outlets, the sediment core of which is a reliable record of the anthropogenic emissions of microplastics. The objectives were: 1) to detect the abundance, size, and types of microplastics in sediment cores; 2) to reveal the impact factors; 3) to evaluate the possibility of using microplastics as indicators of the Anthropocene. The HML sediment core was sliced into samples at 0.5 cm intervals. The pretreatment of microplastic extraction from the samples included 30% H2O2 digestion, ZnCl2 solution flotation, and 10 µm stainless-steel membrane filtration. Then, the Agilent 8700 LDIR imaging system was adopted to identify and quantify microplastics. The abundance of microplastics largely increased from the 1950s to the 2010s with irregular fluctuations (Fig. 1b), and the maximum occurred in 2013 (465 items g-1). The size of 10-100 µm are the main particles, accounting for around 80% of the total microplastics (Fig. 1c). PE is the most abundant type, followed by PS and PP (Fig. 1d). Agricultural production, precipitation, and wind speed have significant influences on microplastic accumulation. The study fits the theme of nano/microplastic occurrence in the terrestrial environment.

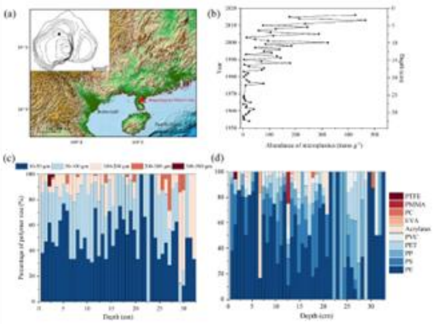


Fig. 1 Microplastic records in the sediment core of Huguangyan Maar Lake. (a) the lake location, (b) the abundance, (c) the partical size, (d) types

References

Zalasiewicz, J. et al., 2016. The geological cycle of plastics and their use as a stratigraphic indicator of the Anthropocene. Anthropocene. 13, 4-17.

Nakajima, R. et al., 2019. A new small device made of glass for separating microplastics from marine and freshwater sediments. PeerJ. 7, e7915.

Technical Aspects for Microplastics Analysis Using Py-GC/MS, Exemplified on a PVC-PMMA Polymer Blend

A. Moraz[1,2]*, J. Tolu[2], G. Crosset-Perrotin[2], R. Kägi[2], and T. D. Bucheli[1]

[1]Swiss Federal Research Station for Agroecology and Agriculture (Agroscope), Environmental Analytics,
Reckenholzstrasse 191, 8046 Zürich, Switzerland
[2]Swiss Federal Institute of Aquatic Science and Technology (Eawag), Process Engineering Department, Überlandstrasse
133, 8600 Dübendorf, Switzerland

angelique.moraz@agroscope.admin.ch

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is one of the first techniques used to characterize polymers and is now used to analyze microplastics (MPs). Pyrolysis is required prior to GC/MS measurement to thermally decompose high molecular weight MPs into volatile compounds. The identification and quantification of MPs rely on specific pyrolysis products, called markers. The selection of specific and usable markers among the large number of compounds formed after pyrolysis can be challenging. In the literature, the identification of polyvinyl chloride (PVC) is commonly reported using unspecific markers such as benzene and (methyl)naphthalene, which are also formed after pyrolysis of organic matter and other synthetic polymers. In this work, several markers were evaluated for their reliability in the identification and quantification of PVC using Py-GC/MS.

Blue PVC was milled down to fragments of 50 µm. Focal plane array - micro - Fourier transform infrared spectroscopy (FPA-µ-FTIR) yielded varying results in terms of identification, with some fragments being identified as PVC, while others were identified as poly(methyl methacrylate) (PMMA) or polyurethane (PU). In addition, the expected chlorine signal was not consistently detected by scanning electron microscopy (SEM). Replicates of 200 µg, corresponding to ca. 2315 blue PVC fragments of 50 µm, were pyrolyzed at 600 °C and subsequently measured by GC/MS. Py-GC/MS mirrored ambivalent results from imaging analyses of particles declared by the provider as PVC and confirmed the presence of PMMA, explaining the unexpected results from FPA-µ-FTIR and SEM analyses. The quantified mass fraction of PVC, using a pure unplasticized PVC reference standard, in blue PVC by Py-GC/MS was dependent on the pyrolysis product used and ion channel selected. The chromatographic peaks associated with candidate markers were evaluated in individual extracted chromatograms corresponding to the mass-to-charge ratios (m/z) of the markers and their fragments. In the present experiment, the most reliable quantification of PVC was obtained using chlorobenzene by monitoring the ion with $m/z = 112$. Using pure PMMA and PVC reference standards, the effect of the presence of PMMA on PVC quantification was also investigated by measuring a constant mass of PVC mixed with an increasing amount of PMMA with Py-GC/MS. This work highlights how different analytical tools can complement each other to characterize polymer blends.

Microplastics Analysis in the Environment - Quantification through a Combination of Optical and Raman Microscopy Enhanced by Machine Learning Evaluation

D. Fischer[1]*, K. Enders[1], R. Lenz[1], F. Fischer[2], E. Kanaki[1], J. Muche[1], B. Hufnagl[3], H. Lohninger[4]

[1]Leibniz-Institut für Polymerforschung Dresden, Germany
[2]Advanced Mask Technology Center GmbH Dresden, Germany
[3]Purency GmbH Wien. Austria
[4]Technische Universität Wien, Austria

fisch@ipfdd.de

Microplastic (MP) analysis in different environment areas is a complex, multi-step process that includes sampling, sample treatment, measurement and data analysis. For each step, various standard operation protocols (SOP) exists, but mandatory standards do not yet exist. Thus, comparability of results is an issue, even if the same methods are used. Result deviations can occur at each point in the process, but to ensure precision and accuracy, it is necessary to evaluate the contribution of each step.

We will focus this lecture on measurement and data analysis of MP. For the measurement, we focus on a combination of optical particle detection and Raman microspectroscopy. For comparison of results of different laboratories, we have developed an interlaboratory test that compares the analytical results by fixing defined particles in a defined area on a filter that can be sent from laboratory to laboratory. Its results, which are very promising, will be presented in the lecture. Furthermore, we will present statistical subsampling strategies (Brandt et al., 2021) and their error limits. For the data analysis, we use the program GEPARD, which is an open-source program (Brandt et al., 2020).

For the assignment of the Raman spectra, a common method is an automated library search that uses comparison algorithms to assign the spectrum with the best match. This is sensitive to effects such as fluorescence or a poor signal to noise ratio. Especially single component library searches, which are suitable for fast analyses and highly automated workflows, may misidentify spectra that contain bands of more than one component. Hence, the result often requires a manual follow-up control, which is time-consuming and prone to introducing human bias.

As an alternative, we developed a machine learning-based approach for the analysis of Raman spectra. We trained a model to identify several of the most common polymer types and compare its performance to the routinely used spectra analysis on the same samples. First the results of this comparison will be shown.

In the second part of the lecture, we will show results obtained with this combination of optical particle detection and Raman spectroscopy on selected samples from different environmental areas. These are the determination of MP along a river, in a sewage treatment plant (influent, sludge, effluent), in an agricultural soil, in the atmosphere and along a production line for mineral water (influent, filling, product).

All these examples show that the presented combination of methods is very well suited to determine MP in various environmental areas and in food.

References

Brandt, J. et al. (2021) 'Assessment of subsampling strategies in microspectroscopy of environmental microplastic samples', Front. Env. Science, 288.
doi.org/10.3389/FENVS.2020.579676.

Brandt, J. et al. (2020) 'High-throughput analyses of microplastic samples using fourier transform infrared and raman spectrometry', Appl. Spec., 74 (9), 1185.
doi.org/10.1177/0003702820932926.

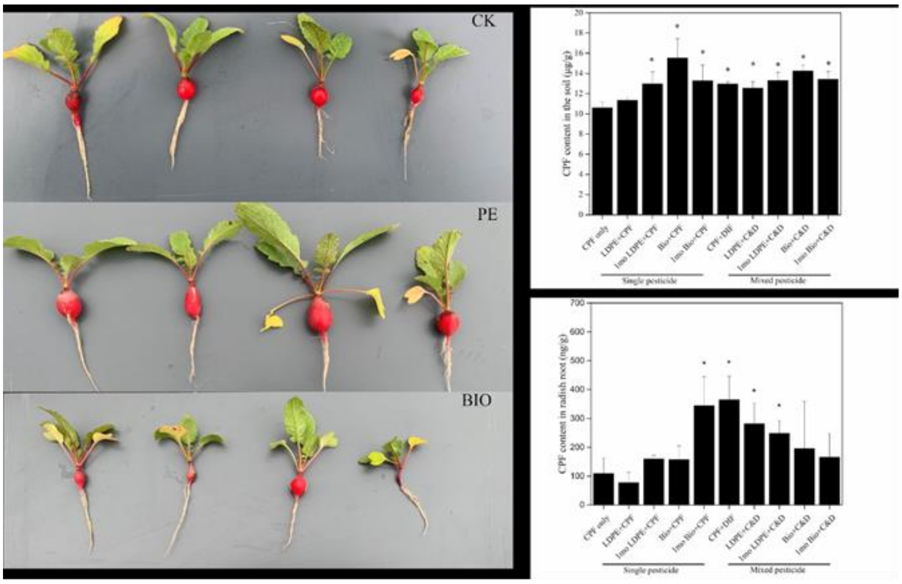
The Effects of MPs on the Radish Production and Bioaccumulation of Pesticides

H. Ju[1]*, X. Yang[1], R. Osman[1], V. Geissen[1]

[1]Wageningen University & Research, Soil Physics and Land Management, 6700AA, Wageningen, the Netherlands

ju.hui@wur.nl

Limited research has focused on the effects of microplastics (MPs) on crop production, especially tuberous plants like radish. In addition, the effects of MPs on the dissipation and plant bioaccumulation of pesticides in soil are still unknown. In this study, we selected two types of MPs (LDPE and biodegradable (Bio), 0.1%, w/w) and three pesticide applications (chlorpyrifos, difenoconazole and mixture of two pesticides), to study the effects of MPs on the yield and pesticide bioaccumulation of radish. Our results showed that the treatment with the addition of LDPE-MPs showed significantly higher yield of radish than control, while in the treatment with Bio-MPs the yield was significantly lower than that in control. This is because MPs changed the soil properties like bulk density and carbon-to-nitrogen ratio. In addition, MPs increased the bioaccumulation of pesticides in radish samples by decreasing the pesticide dissipation in the soil.



Left: Radishes harvested from control, PE-MP and Bio-MP treatments after experiment
Right: The contents of chlorpryfos in soil and radish root

Polyethylene Terephthalate (PET) Photolysis on Surfaces

A. Nobahar[1]*, C. Q. V. da Costa[1], A. Egea-Corbacho[2] and J. P. da Silva[1]

[1]University of the Algarve, Centre of Marine Sciences (CCMAR/CIMAR LA), Gambelas Campus, 8005-139 Faro, Portugal
[2]University of Cadiz, Department of Environmental Technologies, Faculty of Marine and Environmental Sciences, INMAR-Marine Research Institute, Campus Universitario de Puerto Real, 11510 Cádiz, Spain

anobahar@ualg.pt

Polyethylene terephthalate (PET) is a thermoplastic polymer widely used in the production of various consumer goods. Although its known stability, the PET matrix absorbs UV and is therefore expected to undergo direct photodegradation. Exposure to light can lead to its phototransformation through a complex process involving chain scission, crosslinking, and formation of carbonyl and carboxyl groups (Sang et al. 2020). The photodegradation of PET is considered of significant environmental concern due to the potential toxicity of the released degradation products and exposure to these products can have adverse effects on both human health and the environment (Inaner et al. 2022). The extent and rate of PET photodegradation depend on factors such as the wavelength distribution, intensity, and duration of light exposure, as well as the presence of environmental factors such as temperature, humidity, and oxygen (Dhaka et al. 2022). The knowledge of PET photodegradation products, mechanisms and kinetics is therefore crucial for developing efficient strategies for waste management and recycling, as well as for mitigating the environmental impacts.

In this study we present the main photodegradation products of PET observed under Hg lamp irradiation and also under Xe lamp irradiation, the latter source showing a spectral emission similar to sunlight at ground level. PET particles were studied adsorbed on silica and on sand surfaces. For comparison purposes irradiated pure PET particles as well as particles submitted to thermal oxidation were also studied. Products were analysed by LC-HRMS using electrospray (ESI) and atmospheric pressure chemical ionization (APCI). Compounds were annotated using Compound Discoverer 3.3 or assigned based on their spectral information.

Results revealed the release of PET monomer and oligomers, among other compounds. The photoproducts distributions of pure and adsorbed PET particles were slightly different. The observed products, which were detected after extraction of the photolyzed residue with methanol should have been formed after cleavage of two polymer bonds. The annotated compounds are consistent with radical mechanisms involving homolytic cleavages followed by hydrogen abstraction and also decarbonylation, in agreement with results obtained by Sang et al. (2020).

Findings of this study shed light on the fundamental mechanisms of PET degradation on environmental surfaces, namely beach sand surface, and offer potential solutions for the recycling and waste management of PET products. Understanding the nature and extent of the toxicity of PET degradation products is crucial in developing efficient strategies for reducing the environmental impact of PET degradation products. Further research is needed to fully understand the ecotoxicological impact of PET degradation compounds.

References

Dhaka V, Singh S, Anil AG, et al (2022) Occurrence, toxicity and remediation of polyethylene terephthalate plastics. A review. Environ Chem Lett 20:1777–1800. https://doi.org/10.1007/s10311-021-01384-8.

Inaner NB, Demirel B, Yaras A, et al (2022) Improvement of environmental stress cracking performance, load-carrying capacity, and UV light barrier property of polyethylene terephthalate packaging material. Polymers for Advanced Techs 33:2352–2361. https://doi.org/10.1002/pat.5692.

Sang T, Wallis CJ, Hill G, Britovsek GJP (2020) Polyethylene terephthalate degradation under natural and accelerated weathering conditions. European Polymer Journal 136:109873. https://doi.org/10.1016/j.eurpolymj.2020.109873.

Biodegradable Microcapsules as a Repellent Solution for Malaria Control

V. Sousa[1], J. Marques[2], H. Silveira[3], I. Borges[3], J. Gomes[3], A. C. Alves[3], C. Sousa[3], T. Novo[3], C. J. Tavares[1]*

[1]University of Minho and Porto, Centre of Physics, Campus of Azurém, 4804-533 Guimarães, Portugal
[2]Interhigiene - Indústria De Produtos De Higiene Lda., Rua General Humberto Delgado, nº 588 4765-546 Serzedelo (Guimarães), Portugal
[3]University NOVA Lisboa, Institute of Hygiene and Tropical Medicine, Rua da Junqueira, nº 100 1349-008 Lisboa, Portugal

ctavares@fisica.uminho.pt

As microplastics are a growing environmental problem, there is an urgent demand for solutions that prevent and reduce the release of microplastics into the environment. In the area of microencapsulation, various industries are looking for biodegradable alternatives. However, the biggest difficulty in changing a synthetic polymer to a biodegradable polymer is achieving an equal or higher level of performance. It is necessary to meet strict performance criteria in the controlled release of active agents and in the large-scale manufacture of microcapsules.

Malaria represents one of the world's biggest public health problems. Every year, the overall number of new cases of malaria exceeds 230 million, and about 80% of malaria deaths occur in children under 5 years of age (WHO, 2022). There is a global need for products and solutions to control malaria. Preventions such as malaria, which do not have any protective vaccine available, prevention is essential. However, repellents and/or insecticides commonly used in the prevention of diseases transmitted by mosquito bites have several limitations such as reduced uptime or the impossibility of renewal due to their toxicity at high concentrations (Van den Berg et al., 2021). Microencapsulation appears as an alternative to overcome these limitations. The microcapsules act as a vessel for the mosquito repellent, which through a diffusion process releases the encapsulated repellent (Sousa et al., 2022). Cellulose acetate microcapsules were developed with encapsulated citronella oil used as repellent agent against mosquitoes. Through chromatographic analysis coupled to mass spectrometry it was possible to determine the maximum encapsulation capacity of the microencapsulation system developed. The structural analysis performed by Attenuated Total Reflection Fourier Transform Infrared spectroscopy suggests that the encapsulation of the repellent agent was successfully performed. The tests of the repellent efficacy of microcapsules allowed to observe a percentage of repellency above up to 80%. After four months, the microencapsulation system exhibited a repellency percentage of 76.1 (Geometric mean, Geometric SD factor 1.053). This microencapsulation system represents a pioneering application solution in different static supports, which are based on different materials not suitable for the activation of microcapsules by mechanical action.

References

World Health Organisation (2022) 'Malaria'. https://www.who.int/news-room/fact sheets/detail/malaria.

Van den Berg, H. et al. (2021) 'Recent trends in global insecticide use for disease vector control and potential implications for resistance management', Nature, 11. doi:10.1038/s41598-021-03367-9.

Sousa, V.I. et al. (2022) 'Microencapsulation of Essential Oils: A Review', Polymers (Basel), 14. doi:10.3390/polym14091730.

Microplastic Characterization and Screening by Combining DART and High-Resolution Mass Spectrometry

K. Modi[1], W. Fatigane[1], M. Arnould[1], G. Labella[2]*, M. Macht[2]

[1]Bruker Daltonics Ic., Billerica, MA, USA
[2]Bruker Daltonik GmbH, Bremen, Germany

giuseppe.labella@bruker.com

Microplastics are small plastic particles (≤ 5mm) that result from both commercial product development and the breakdown of larger plastics. Microplastics are abundant in our environment and come from a variety of sources. Commercial sources include cosmetics, clothing, and other textiles to other pieces of plastics such as water bottles that breakdown with radiation. Currently microplastics have been detected at an alarming level in our marine life and drinking water.
Direct Analysis in Real Time (DART)-high resolution mass spectrometry allows for rapid fingerprinting of environmental microplastics and the screening of additives. Typical samples of interest are polymers found in the environment like virgin pre-production pellets, microbeads from personal care products, microplastics found in the aquatic environment, and synthetic fibers.

DART was coupled to an impact QTOF (both Bruker, Germany). Traditional GC/MS methods require extensive sample preparation (10-20 minutes) and have long analysis times (> 20 minutes). This new method allows for rapid analysis of polymers (< 5 minutes) with no sample preparation required. DART was coupled to a thermal desorption system (IonRocket, Biochromato Inc., Japan) which delivers temperature gradients from ambient to 600 ºC with ramp rates of 150 ºC/min. A small sample sliver is cut and placed in a copper pot. When the thermal program is started, the QTOF collects MS spectra at 5Hz for the entire run.

The resulting mass spectra display thousands of discrete peaks. Depending on the temperature, different additives, the polymeric basis as well as degradation products are released and detected at different time points during the run.
Here we compared distinct m/z signals as well as general signal patterns of a microplastic material found in water with standard plastic samples such as a soda bottle, a trash bag and packaging material. Some compounds like m/z 411 can be found in all samples, referring to a commonly applied additive for these consumer products. While the soda bottle was made of PET, the microplastic clearly had PE as a basis. Since PE is an insoluble polymer, it is difficult to analyze with other MS-based methods like MALDI. The microplastic material showed most similarity with the trash bag, with regard to both certain distinct marker m/z values as well as the general pattern released by the temperature gradient, so it can very likely be traced back to that origin.
The combination of DART with HRMS allows for rapid fingerprinting of environmental microplastics and the identification of unknown compounds with high resolution and high mass accuracy.

New Insights into Microplastic Pollution Levels at Wastewater Treatment Plant: Removal Efficiency and Distribution Across Treatment Stages

S. Pleskytė[1*], I. Uogintė[1], S. Byčenkienė[1]

[1]Center for Physical Sciences and Technology, Department of Environmental Research, Sauletekio Ave. 3, LT-10257, Vilnius, Lithuania

sonata.pleskyte@ftmc.lt

One of the major concerns in the environmental research community is global microplastic pollution. Microplastics are well-known due to their ubiquitous environmental presence and ability to provide physical and toxicological harm to organisms. The interaction of microplastics with chemical contaminants, antibiotics, and various types of microorganisms exacerbates the threat of a global microplastic pollution crisis. Since 2015, there has been a steady increase in the number of articles reporting extremely high levels of microplastics in wastewater (Marcal et al., 2021).

The key role in reducing microplastic pollution is played by wastewater treatment plants (WWTPs). Even though some WWTPs can remove 69 – 99% of microplastics from wastewater, enormous amounts of these particles still enter water bodies from WWTPs due to the large volume of treated wastes. For example, there might be a daily release of 65,000,000 microplastic particles from a WWTP with a population equivalent to 650,000 people (Murphy et al., 2016). The main physical and chemical properties of microplastics, especially particle density, size, shape, and polymer type determine removal efficiency in WWTPs.

This research aims to analyze the removal efficiency of microplastics across wastewater treatment stages. The research work was conducted in Lithuania, for a three-month sampling campaign, in 2021. All microplastic particles were separated from wastewater samples and examined by microscopic and spectroscopic analytical methods. Microplastics in the size range of 20 – 1000 µm were studied, as well as their shape, color, and chemical composition. The highest level of microplastics has been found in the size range of 50 – 100 µm. A detailed analysis of the microplastic parameter's correlation with removal efficiency in the different treatment stages will be provided and discussed.

New insights into microplastic pollution levels at WWTPs are necessary to better understand how to reduce microplastic pollution in the environment. The suggested correlation between microplastic properties and removal efficiency might be helpful for microplastic removal technologies development.

Acknowledgment: This research is funded by the European Social Fund under the No 09.3.3-LMT-K-712 "Development of Competencies of Scientists, other Researchers, and Students through Practical Research Activities" measure. (Grant No. 09.3.3-LMT-K-712-19-0112).

References

Marcal, J. et al. (2021) 'From pollutant removal to resource recovery: A bibliometric analysis of municipal wastewater research in Europe', Chemosphere, 284. doi:10.1016/j.chemosphere.2021.131267.

Murphy, F. et al. (2016) 'Wastewater Treatment Works (WwTW) as a Source of Microplastics in the Aquatic Environment', Environmental Science and Technology, 50(11), pp. 5800–5808. doi:10.1021/acs.est.5b05416.

A New Approach for Polymers Analysis in Atmospheric Aerosol by Direct Inlet Pyrolysis Gas Chromatography-Mass Spectrometry (Py-GC/MS)

E. Gregoris[1,2], G. Gallo[2], B. Rosso[2], F. Corami[1,2] and A. Gambaro[2]

[1]Institute of Polar Sciences of the National Research Council of Italy, Venice, 30172, Italy
[2]Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Venice, 30172, Italy

Nowadays microplastics are widely dispersed throughout the environment. Although microplastics have been researched in sediments, soil, and freshwaters, the atmosphere has received less attention, even though it can be considered one of the major transport pathways from mid to high latitudes. Due to its effectiveness in chemical characterisation, pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) has been proposed as a promising technique for the analysis of macromolecules, but it has almost never been used for analysing microplastics in atmospheric aerosol yet. In this work, we investigated the potential application of direct inlet Py-GC/MS for detecting polymers in atmospheric aerosol.

Evaluating the matrix interference is crucial when a pre-treatment step is missing. For this purpose, we developed the "organic aerosol baseline" (OAB), which is our initial attempt to calculate the organic aerosol's contribution to the polymer tracer areas. Being aware it does not represent the whole organic aerosol, humic acid was chosen as the representative organic substance for this assessment, as done before in the literature. OAB was estimated for tracers of the most common polymers, using the following equation: $OAB = A_n \cdot OM \cdot PM \cdot V \cdot fr_{sample}$; where A_n is the average tracer normalised areas in the humic acid pyrograms; OM is the typical organic matter fraction in the aerosol in the area and period of sampling; PM is the aerosol concentration; V is the sample volume; fr_{sample} is the fraction of sampling filter introduced in the sample tube. Pyrogram peaks were considered plastic tracers only if their area was over the OAB level.

The novel methodology was applied to total particulate matter (TSP) samples, collected using a AirFlowPUF (Analitica Strumenti, 0.3 m^3 min^{-1}; 48- and 72-samples) and to commercial dust (House SRM2585). Even considering the interference of the matrix, polyethylene, polypropylene, and polystyrene were successfully detected in TSP samples and confirmed by Micro-FTIR analysis. The support analysis by Micro-FTIR also indicated the presence of more polymers that Py-GC/MS had missed. The difference in the results of the two approaches is reduced when the analysis is conducted on pure commercial dust. These first findings suggest that the issue of the matrix presence can be successfully overcome by the evaluation of its baseline and that the crucial point can be represented by the small portion of the filter practically analysable.

Plastics are challenging to extract and usually need specialised equipment. For this reason, the direct analysis represents the ideal screening method for saving time, costs, and waste. This work proposed a quick and simple solution for the identification of plastics in atmospheric aerosol samples, to be applied before other time-consuming techniques for obtaining more detailed information (i.e., quantification). More research is needed to improve this approach for getting the greatest possible efficiency from the analysis.

This work was supported by the EU - Next Generation EU, PNRR under grant IR0000032 (ITINERIS, Italian Integrated Environmental Research Infrastructures System).

Acute Effet of Nanoplastics on *Daphnia* and *Gammarus* Neonates in Comparing Natural Freshwaters

W. Liu[1*], Z. Meng[1], R. Recoura-Massaquant[2], A. Chaumot [2], S. Stol[1]

[1]University of Geneva, Department F.A. Forel for Environmental and Aquatic Sciences, Carl-Vogt 66, CH-1211, Geneva, Switzerland
[2]INRAE, UR RiverLy, Laboratoire d’écotoxicologie, F-69625 Villeurbanne, France

wei.liu@unige.ch

Plastics are ubiquitous in aquatic environments, and are quite persistent due to their chemical inertness (ESPOSITO et al., 2022). More concerning shows that nanoplastics are probably wider distributed and more toxic than microplastics due to their larger surface-to-volume ratio and higher surface reactivity (REDONDO-HASSELERHARM et al., 2020). Despite progress in evaluation of risk assessment, knowledge gaps largely exist understanding the toxicity of nanoplastics in aquatic systems considering nanoplastics surface properties, environmental media characteristics and species ecological traits. In this study, amidine - functionalized polystyrene nanoparticles (PS-NPLs) of different primary sizes of 20, 40, 60 and 100 nm are considered using lake water and mineral water to investigate the behavior and effects in neonate organisms of the plankton Daphnia magna and the benthos Gammarus fossarum. Key parameters including ζ-potential, z-average diameter, conductivity, polydispersity index, pH, viability were investigated. The results shown that PS-NPLs with different initial sizes induced a statistically significant mortality of D. magna and G. fossarum neonates with a dose-time response relationship. More importantly, ecotoxic effects are found driven by both the surface properties of PS-NPLs and environmental factors. The surface charge is also found the most influential toxicity factor of PS-NPLs on D.magna in environmental natural waters, while on G. fossarum the aggregation behavior is the stronger explanatory factor. The combination of the characterization of colloidal stability of nanoparticles and effect assessment in environmental natural waters systems in this work evidenced the relationship between colloidal stability of NPLs, exposure water properties, the species ecological traits and the biological response.

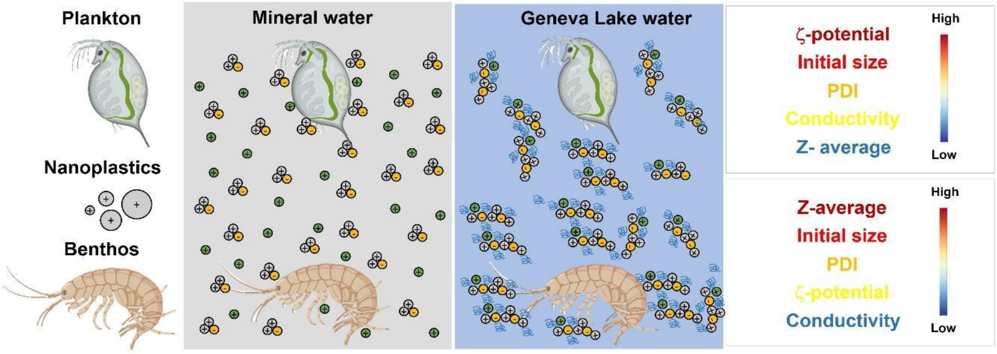


Illustration of PS-NPLs transformation of PS-NPLs under constated exposure scenario to crustaceans, and their main toxicity driver

References

Esposito, G et al. (2022)., Occurrence of microplastics in the gastrointestinal tract of benthic by–catches from an eastern Mediterranean deep–sea environment. Marine pollution bulletin 174: 113231.

Redondo-Hasselerharm, P et al. (2020). Nano-and microplastics affect the composition of freshwater benthic communities in the long term. Science advances 6: eaay4054.

Occurrence of Plastic and Tire Additives and their Transformation Products in the Danube

R.Peng[1]*, C.Henkel[1], V.Wilkeit[1], T Hofmann[1], T Hüffer[1]

[1]University of Vienna, Centre for Microbiology and Environmental Systems Science, Environmental Geosciences EDGE, 1090 Vienna, Austria

ruoting.peng@univie.ac.at

Plastic additives are chemicals that are added to polymer products to improve their properties and performance. Phthalates, a class of plasticizers commonly used to increase the flexibility and durability of plastics, have been associated with potential health hazards, including endocrine disruption. Tire additives are utilized to improve the performance, durability, and safety of rubber tires. Similar to plastic additives, tire additives can also pose environmental risks if they are released into the ecosystem (Tian et, 2021).

In this study, we investigated the occurrence of 18 tire additives and 6 phthalates and their transformation products along the Danube River at 26 locations from Scheer, Germany to Galati, Romania. The sampling locations were designed to allow a thorough assessment of the spatial distribution and transport of plastic-derived compounds and to identify the impact of contamination from major cities along the Danube. Each sample was filtered, and solid-phase extraction was employed to extract the filtrates, while the suspended particles on the filters were extracted via ultrasonication in solvent. The quantification of the target compounds was performed using triple quadrupole liquid chromatography-mass spectrometry (LC-MS/MS).

A total of 16 compounds were detected in water from the Danube River. Phthalic acid, a degradation product of phthatlates, showed the highest maximum concentration of 9820 ng/L. 1,3-Diphenylguanidine (DPG), hexa(methoxymethyl)melamine (HMMM), and aniline were detected in all water samples with concentrations ranging from 10-160 ng/L. Eleven compounds were detected on the suspended particles, while DEHP was detected on the particle at the highest concentration of 48000 ng/L. Tire-derived compounds such as N-(1,3-dimethylbutyl)-N‘-phenyl-1,4-phenylenediamine (6PPD) and N-phenyl-2-naphthyl amine were detected in all suspended particle phase samples with concentrations steadily increasing along the Danube to a maximum level of 3 µg/kg at the Iron Gate, Serbia. Heat maps were created to visualize the distribution of these compounds in both the water phase and suspended particles of the Danube river. The results revealed a clear trend of increasing concentrations of the targeted compounds from Slovakia downstream, which is linked to the decreasing complexity and density of the wastewater treatment systems in the region.

The ecological risks of the detected additives and transformation products in surface waters were assessed according to the technical guidelines of the European Commission (EC, 2008). Di-n-octyl phthalate and HMMM posed a high risk, while other compounds had a low or medium risk when using averaged measured concentrations. With regards to the highest risk quotients, 2,2'-Methylenebis(4-methyl-6-tert-butylphenol) (0.83), 6PPD (0.72), and Phthalic anhydride (0.2) are present at particular sites in concentrations that present a medium risk to aquatic organisms, highlighting the need for further monitoring to prevent adverse health effects on aquatic organisms.

References

EC 2008 Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market Part III.

Tian et al., 2021A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon Science, 371 (6525) (2021), pp. 185-189.

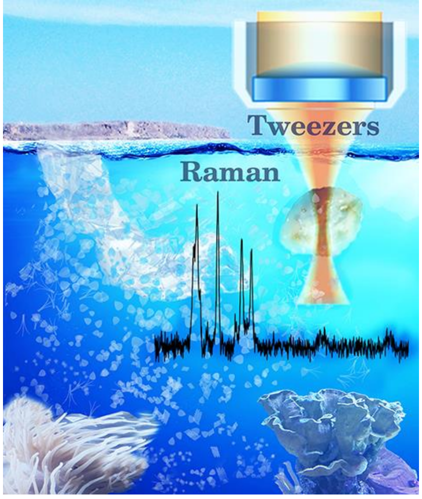
Raman Tweezers for Micro and Nanoplastics Analysis in Watery Ecosystems

A. Foti[1], R. Gillibert[1], A. Magazzù[1], M. G. Donato[1], O. M. Maragò[1], A. Callegari[2], G. Volpe[2], M. Lamy de La Chapelle[3], F. Lagarde[3], and P. G. Gucciardi[1]*

[1]CNR-IPCF, Viale F. Stagno D'Alcontres 37, 98158, Messina, Italy
[2]University of Gothenburg, Department of Physics, 412 96, Gothenburg, Sweeden
[3]Le Mans Université, Institut des Molécules et Matériaux du Mans, UMR 6283 CNRS, 72085, Le Mans, France

gucciardi@ipcf.cnr.it

Hybrid instruments combining Optical Tweezers (OT) with Raman spectroscopy (Raman Tweezers, RT) are becoming increasingly popular, as they enable measurements of size and composition of micro and nanoparticles in a contactless way. RTs are gaining attention as a unique analytical tool for environmental sciences and food analysis, capable of detecting and chemically identifying micro- and nano- plastics (MNPs). Here we show optical trapping and chemical identification of sub-20 µm plastics, down to the 50 nm range by RT (Gillibert et al., 2019). Analysis at the single particle level permits to unambiguously discriminate plastics from organic matter and mineral sediments, overcoming the capacities of standard Raman spectroscopy in liquid, intrinsically limited to ensemble measurements. Applications are shown on both model particles and naturally aged environmental samples, made of common plastic pollutants, including polyethylene, polypropylene, nylon, and polystyrene. Finally, the analysis is extended to samples of tire and road wear particles collected from a brake test platform, where we highlight the presence of sub-micrometric agglomerates of rubber and brake debris, thanks to the presence of additional spectral features other than carbon (Gillibert et al., 2022). RT has the potential to fill the technological gap in MNP detection. In the next years research & development will be oriented towards the exploration of the full potential and limits of RT for applications in environmental sciences (Volpe et al., 2023).



Raman Tweezers enable researchers to trap individual micro and nanoplastics in water ambient, and perform their dimensional and chemical analysis

References

Gillibert R. et al. (2019) "Raman tweezers for small microplastics and nanoplastics identification in seawater" Environ. Sci. Technol. 53, p. 9003. DOI: 10.1021/acs.est.9b03105.

Gillibert R. et al. (2022) "Raman tweezers for tire and road wear micro-and nanoparticles analysis" Environ. Sci.: Nano, 9, 145. DOI: 10.1039/D1EN00553G.

Volpe G. et al. (2023) "Roadmap for Optical Tweezers 2023" J. Phys. Photonics, in press, DOI 10.1088/2515-7647/acb57b.

A New Potential Route of Exposure for Microplastics and Nanoplastics: an Investigation of Common Hygiene Products

L. P. Munoz, D. Purchase, A. G. Baez, H. Jones, H. Garelick

[1]Indian Institute of Technology (IIT), Department of Civil Engineering, Madras, Chennai, India-600036

A growing source of contamination in the environment is the degradation of plastics that leads to fragmentation into microplastics (<5 mm in diameter) and nanoplastics (<100 nm in diameter). Such plastics are known to have potential human health risks through direct contact and through entering the human food chain. The material composition of many personal hygiene products (e.g., wet-wipes, tampons, cosmetic products etc.) is poorly documented. Many such products are made with plastic compounds that can reach the environment when these products are incorrectly disposed or when they fragment into smaller plastics (i.e. microplastics or nanoplastics).

We studied two different personal hygiene products, namely wet-wipes and period products, and analysed the plastic content as well as their fragmentation using infrared spectroscopy (FTIR), confocal Raman microscopy, scanning electron microscopy (FEG-SEM) and nanoparticle tracking analysis (NTA). We found that some products advertised as “flushable” contain plastics and therefore reach the environment as they are flushed. Most “non flushable” products also contain plastics. Unfortunately, “non-flushable” products are also often flushed when disposed, as the consumers may be confused by unclear labelling. In addition, the advertising of “flushable” products may encourage this behaviour.

Investigating other common hygiene products such as tampons, we found evidence for the fragmentation of the microplastics into billions of nanoplastics. We report for the first time that such fragmentation can potentially occur inside the human body. This fragmentation was found to be related to pH only and not due to temperature (37^0C). The potential toxicity of these released particles is currently investigated. Both of our studies demonstrated the presence of synthetic polymers with potential health and environmental impact, such as polyester (polyethylene terephthalate (PET)) in period products, high-density polyethylene (HDPE) and polyethylene/vinyl acetate (PEVA/EVA) in some flushable wipes, and PET in all non-flushable wipes. Other polymers include polypropylene (PP), low-density polyethylene (LDPE), expanded polystyrene (EPS), and polyurethane (PU).

Microplastics in the Environmental Compartments: Occurrence and Characterization

L. Rivoira[1]*, A.E. Carioli[1], M. Castiglioni[1], P. Bracco[1], E. Padoan[2], M. Almeida[3,4], S. Ramos[3,4], S. Beldean Galea[5], T. Vlase[6] and M.C. Bruzzoniti[1]

[1]University of Torino, Department of Chemistry, Torino, Italy
[2]University of Torino, Department of Agricultural, Forest and Food Sciences, Grugliasco, Italy
[3]Faculdade de Ciências da Universidade do Porto, Porto, Portugal
[4]CIIMAR, Matosinhos, Portugal
[5]Babes-Bolyai University, Faculty of Environmental Science and Engineering, Romania
[6]West University of Timisoara, Department of Chemistry, Romania

luca.rivoira@unito.it

Microplastic (MP) contamination has emerged as a global environmental problem due to the spread of plastic debris in various environmental compartments, including oceans, freshwater systems, soil, and air. Microplastics are small plastic particles, less than 5 mm in size, that can be generated from both primary sources, such as microbeads in personal care products, and secondary sources, such as the breakdown of larger plastic debris. Microplastics can have harmful effects on aquatic and terrestrial organisms and can also have implications for human health (Thompson, 2015). They can act as vectors for toxic chemicals and pathogens, and can also accumulate in the food chain, potentially leading to the ingestion of microplastics by humans. Research efforts are in particular devoted to understand the extent and impacts of microplastic contamination in the environmental compartments, as well as to develop strategies for mitigating its effects; these efforts include the development of new methodologies for detecting and quantifying microplastics.

In this regard, within this work, we comprehensively investigated the MP contamination in several natural compartments, i.e. natural waters, marine sediments, soils, as well as in selcted biota, i.e. oysters. For each of the above mentioned matrices, specific anlytical protocols were optimized, all of them based on a similar combined approach. Firstly, an oxidation of the interfering organic matter was performed testing several solutions such as KOH, NaClO, H_2O_2, avoiding the degradation of MPs, followed by a density separation, to isolate MPs from residual species. For each matrix, five types of micropolymers were investigated, namely PE-HD and PE-LD, PET, PA, PS (both as particles and fibers). All the protocols were fully validated in terms of extraction yields from fortified samples, obtaining recoveries no lower than 80% for all the MPs in all the matrices. In addition, the optimized methods were shown not to alter the polymer lattice of plastics, making them recognizable at identification through FT-IR.

The developed methods were successfully applied for the analysis of MP contamination in selected water basins and in agricultural and urban soils belonging from the Piedmont Region (Italy), as well as in ocean sediments and oysters from the Atlantic Ocean (Portugal). Contaminations from 30 to 90 MPs/L were detected in the water basins, with a prevalence of PP and PE partcles, rather than fibers. From 1800 to 3500 MPs/kg were detected in soils, with higher concentrations (in particular of LDPE fibers) detected in acrigultural soils, in agreement with the intensive use of mulching. From 10 to 700 MPs/g of MPs were detected in the ocean sediments, the majority of which were fibers, as expected from the thorough use of fishing nets, recognized as possble input sources of PA microplastics. Finally, from 10 to 50 MPs/g were detected in oysters.

The above mentioned detected concentrations were similar to those already reported in previous literature studies (when available).

References

Thompson, R. C. (2015). Microplastics in the marine environment: sources, consequences and solutions. Marine anthropogenic litter, 185-200

Interaction of Nanoplastics with Fresh Water and *Pseudomonas Aeruginosa* Biofilm

Y. Zhang[1]*, P. Westerhoff[2], and J.P. Croué[1]

[1]Université de Poitiers, Institut de Chimie des Milieux et des Matériaux, France
[2]Arizona State University, School of Sustainable Engineering and the Built Environment, Tempe, USA

yutong.zhang@univ-poitiers.fr

Plastic debris, recognized as the global environmental problem, comes in various sizes, ranging from micro to nano scales, which are defined as 1 µm-5 mm and below 1 µm, respectively (Hartman et al., 2019; Yu et al., 2019; Rahman et al., 2019). Many research studies focused on understanding the factors governing the transport and fate of nanoplastics (NPls) into aquatic environments, i.e., particle size, solution pH, ionic strength, valence of the electrolyte, dissolved organic matter (DOM). Biofilms are the prevalent form of bacteria and can grow everywhere in nature. Extracellular polymeric substances(EPS) as the major constituent substance of biofilm, mainly consist of polysaccharides, lipids and proteins. It is recognized that EPS can provide a suitable surface for the attachment and accumulation of nanoplarticles (NPs), which can then be incorporated into the biofilm matrix. Previous focus of research is looking at how nanoplastics affect the growth and function of fresh water or Staphylococcus aureus biofilm. However the study about the interaction of plastic NPs and biofilm are still at the beginning, especially under the existing of physical and chemical heterogeneous DOM (e.g., humic substances, biopolymers) and various electrolytes which also play a crucial role in altering the colloidal stability. In water treatment unit, biofilm may trap and accumulate NPls, as these particles may return to the aquatic environment liquid waste resulting from the cleaning procedure of filters/membranes, more attention would be focused on the capture and release of NPls in the biofilm system.

In this study, 200 nm negatively charged Palladium doped Polystyrene (PS) particles (0.36% Pd/PS weight ratio) were selected to investigate the interaction of NPls with dissolved organic matter (DOM) and biofilm. ICP-MS was used to quantify the amount of NPls, based on the Pd concentration detected and the Pd/PS ratio. In the first phase, the objective of our study was to investigate and compare the interaction (aggregation) of NPls with solution of biopolymers and humic substances isolated from surface waters by using the Dynamic Light Scattering(DLS). In the second phase, interactions of NPls with biofilms accumulated on surface was investigated with fouled reverse osmosis (RO) membranes harvested from modules operated at pilot scale with treated surface water. The third phase began with the *Pseudomonas Aeruginosa* (P.A) bacteria and its biofilm cultivation, studying the capture and release of the NPls on P.A biofilm in different growth stages. In-situ biofilm accumulation on the NF membrane coupons was measured daily using OCT focused through the quartz window (ATR206, Thorlabs, NJ). According to the results from the first phase, that Ca^{2+} can lead to the bigger aggregating size of NPls than Na+, and the 0.45 µm filtered colloidal biopolymers (20 to 40 KDa) would enlarge the hetero-aggregation of NPls-DOM compared to the humic substance. And both of biopolymer and humic substance could stabilize the NPls aggregation from Ca^{2+} and Na^{+} cations' effect. As for the accumulation of NPls on the biofilm, humic substance could contribute to the accumulation in the condition without electrolyte and in NaCl solution. And biopolymer only display the promotion of NPls deposit when in the CaCl2 solution. And becuase of the location of the RO membrane modules from the water plant, the inlet module makes contact with more untreated surface water than the outlet module, therefore the more biofilm mass was accumulated on the RO membrane of inlet and then more NPls aggregation was captured during the experiment. Currently, a more specific research is undertaken to investigate the interaction and mechanism of NPls with the P.A biofilm.

References

Nanna B Hartmann, Thorsten Huffer, Richard C Thompson, Martin Hassellov, Anja Verschoor, Anders E Daugaard, Sinja Rist, Therese Karlsson, Nicole Brennholt, Matthew Cole, et al. Are we speaking the same language? recommendations for a definition and categorization framework for plastic debris, 2019.

Fei Yu, Changfu Yang, Zhilin Zhu, Xueting Bai, and Jie Ma. Adsorption behavior of organic pollutants and metals on micro/nanoplastics in the aquatic environment. *Science of the Total Environment*, 694:133643, 2019.

Arifur Rahman, Atanu Sarkar, Om Prakash Yadav, Gopal Achari, and Jaroslav Slobodnik. Potential human health risks due to environmental exposure to nano-and microplastics and knowledge gaps: A scoping review. *Science of the Total Environment*, 757:143872, 2021.

The Disparity in Scientific Investigation: Microplastics are Ubiquitous but only when Accessible

H. Talasila[1], S. M. Kim[2], L. Y. Tseng[3]*

[1]Colgate University, Environmental Studies Program, 13 Oak Drive, Hamilton, NY 13346, USA
[2]Colgate University, Biology Department, 13 Oak Drive, Hamilton, NY 13346, USA
[3]Colgate University, Environmental Studies Program and Physics and Astronomy Department, 13 Oak Drive, Hamilton, NY 13346, USA

ltseng@colgate.edu

Science is said to be subjective, but despite that, there are inherent biases that may hinder research in certain regions. While microplastics (MPs) are thought to be pervasive worldwide, there are still geographic regions that lack tangible literature concerning this subject. This study aims to explore gaps in scientific studies in terms of regions because certain regions may not be included in collaborative studies at this time due to limited resources or other factors. Through the analysis of existing literature on MP, we compiled the location and what MPs were found. For this particular study, MP is defined as plastic pieces less than 5 mm. Currently, we have analyzed 70 research papers and have found varying concentrations of MPs located in soils, water, sewage, and animals. Depending on the research methods, core sample sizes, and other factors, concentrations have ranged from 0 to 2175 particles/kg dw (inter alia Piehl et al., 2018; Vianello et al., 2013). Additionally, the MPs we have currently recorded range from pellets to microfibers and a range of plastic materials including polyvinyl chloride, polyethylene, polypropylene, polyester, etc. We have found that Asia has the most literature with 41% of current literature being focused in this area, with a concentration in papers focused on China, while South America and Africa have the least, and the majority of the studies were focused on soils (55.3%). In contrast, a minority-focused on bodies of water (31.6%) and in animals (18.4%). We found an uneven distribution of studies on MP globally, and research collaborations may be needed in these areas to address the global MP issue.

References

Piehl et al. (2018) 'Identification and quantification of macro-and microplastics on an agricultural farmland', Scientific Reports, 8, p. 17950, doi: 10.1038/s41598-018-36172-y.

Vianello et al. (2013) 'Microplastic particles in sediments of Lagoon of Venice, Italy: First observations on occurrence, spatial patterns, and identification', Estuarine, Coastal and Shelf Science, 130, p. 54, doi: 10.1016/j.ecss.2013.03.022.

Validation of Analytical Chain for the Quantification of Microplastics in Sewage Sludge

G. Crosset-Perrotin[1*], M. Philipp[1], E. Morgenroth[1,2] and R. Kaegi[1]

[1]Swiss Federal Institute of Aquatic Science and Technology (Eawag), Process Engineering Department, Ueberlandstrasse 133, 8600, Duebendorf, Switzerland
[2]ETH Zürich, Institute of Environmental Engineering, John-von-Neumann-Weg 9, 8049, Zürich, Switzerland

guillaume.crosset@eawag.ch

The role of wastewater treatment plants (WWTPs) in controlling the release of microplastics into the environment is intensively debated. This debate is amongst others related to uncertainties associated with the employed analytical procedures, which are not validated. Furthermore, microplastic fluxes in and out of WWTPs are usually quantified by investigating the solids contained in influent or effluent water. Owing to the large volumes flowing through WWTPs and to the low and fluctuating concentration of solids in wastewater, representative sampling is challenging and laborious. Several reports suggest an efficient accumulation of microplastics in sewage sludge mainly caused the formation of microplastic – sludge floc heteroagglomerates. Due to the long residence time (tens of days) of sludge in the WWTPs, fluctuations observed in the incoming wastewater will be smoothed, making sewage sludge sampling a very promising approach to assess microplastics in WWTPs.

A pilot-scale WWTP composed of two biological tanks (oxic – 150L and anoxic – 90L) and sedimentation tank and fed with municipal wastewater (384 L d^{-1}) was used as study system. Blue polyvinyl chloride (PVC) fragments of a median equivalent circle diameter of 46 µm were spiked continuously in the pilot-scale WWTP to reach a concentration of 1 PVC fragment $mg(solids)^{-1}$. Sewage sludge and water effluent were regularly collected over one month. The microplastics were extracted with a Fenton reaction, an enzymatic digestion and a density separation (Philipp, Bucheli and Kaegi, 2022). Sample-specific recovery rates of red polyethylene (PE) spheres of 53-63 µm were determined to evaluate sample specific recovery rates. The spiked blue PVC particles were located with an optical microscope and analyzed with Focal Plane Array-Fourier Transform Infrared Spectroscopy (FPA-FTIR) to confirm the polymer type. Analyses with Pyrolysis-Gas Chromatography (Py-GC/MS) were carried as an orthogonal quantification approach.

The (spiked) microplastics are expected to attach to the solids, which will make the concentration of blue PVC per mass of solids similar in the effluent water and sewage sludge. This would demonstrate the advantage of sampling sewage sludge over effluent wastewater. The fluxes of the spiked microplastics in sludge and effluent water will be compared to assess the removal rate of microplastics during the activated sludge process. In conclusion, assessing the removal efficiency of microplastics in WWTPs using a robust analytical chain will reduce the uncertainty associated with the quantification of microplastics in full-scale WWTPs and the thereby enable an assessment of the relevance of WWTPs as sources for microplastic pollution of surface waters.

References

Philipp, M., Bucheli, T.D. and Kaegi, R. (2022) ‘The use of surrogate standards as a QA/QC tool for routine analysis of microplastics in sewage sludge’, Science of The Total Environment, 835, p. 155485. Available at: https://doi.org/10.1016/j.scitotenv.2022.155485.

The Influence of Polystyrene Nanoplastics on the Uptake and Distribution of Elements in Tomato Plants

P. Leban[1,2], J. Vidmar[1,2]*, K. Marković[1,2], S. Marković[1,2], R. Milačič[1,2], J. Ščančar[1,2], E. Heath[1,2], N. Kacjan Maršić[3] and M. Pintar[3]

[1]Jožef Stefan Institute, Department of Environmental Sciences, Jamova cesta 39, 1000, Ljubljana, Slovenia
[2]Jožef Stefan International Postgraduate School, Jamova cesta 39, 1000, Ljubljana, Slovenia
[3]Biotechnical Faculty, Department of Agronomy, University of Ljubljana, Jamnikarjeva 101, 1000, Ljubljana, Slovenia

janja.vidmar@ijs.si

Climate change, intensive agriculture and the increasing population are significantly contributing to the great pressure on water resources, leading to water scarcity. In agriculture, this problem can be overcome with the reuse of treated wastewater for plant cultivation. However, the potential health risks associated with human exposure to contaminants that may still be present in the reclaimed wastewater, and consequently taken up by edible plants, are still not well understood.

One of the potential pollutants is also nanoplastics (NPs), which are ubiquitous in all environmental compartments due to extremely large amounts of plastic waste generated and disposed of each year. Due to their small size, NPs may be more efficient at crossing biological membranes than microplastics, they serve as transfer carriers for the pollutants (e.g., heavy metals) adsorbed on them, thereby affecting their mobility and bioavailability in the environment. Understanding the risks posed by NPs in the human food chain is very scarce due to limited quantitative information on their potential uptake and translocation in edible plants.

In this study, the uptake of 200 nm polystyrene (PS) NPs by hydroponically grown tomato plants was investigated and their effects on the uptake and distribution of four elements (Cr, Zn, Cd and Pb) were studied. PS NPs were labelled with europium (Eu), which was used to quantify PS-Eu NPs in plants using inductively coupled plasma mass spectrometry (ICP-MS). Knowing the stability of the PS-Eu NPs during the exposure, we were able to correlate the Eu concentration with the PS-NPs concentration (Luo et al., 2022). The uptake of elements by tomato plants was followed by the use of isotopically enriched element tracers, which allowed studying the uptake of added elements without considering the contribution of the elements present in the nutrient solution. Tomato plants were exposed to standard Hoagland nutrient solution (pH around 7) prepared using potable water, that was spiked with a mixture of elements (100 ng/ml ^{53}Cr, 100 ng/ml ^{70}Zn, 50 ng/ml ^{106}Cd and 100 ng/ml ^{204}Pb), either in the absence or presence of PS-Eu NPs (1 mg/L). After five weeks of exposure, harvested plant samples (roots, stems, leaves, fruits) were digested and concentrations of Eu, Cr, Zn, Cd and Pb were determined by ICP-MS.

The results of the study showed that PS-Eu NPs were present in all parts of the tomato plant, with the highest accumulation found in the roots, from where they were transported, in low but not negligible amounts, to the edible parts of the plants. The presence of PS-Eu NPs in the nutrient solution had different effects on the uptake of elements in tomatoes. At pH around 7, Cd and Zn are present in the nutrient solution mainly as relatively small positively charged Cd^{2+} and Zn^{2+} ions, while Cr and Pb exist mostly in the form of larger neutral molecules $Cr(OH)_3^0$ and $PbCO_3^0$. For this reason, the presence of PS-Eu NPs accumulated in the root did not affect the uptake of small Cd^{2+} and Zn^{2+} ions, while the uptake of larger Cr and Pb molecules from the nutrient solution into the plant was significantly hindered, most likely due to steric effects.

References

Luo, Y. et al. (2022) Quantitative tracing of uptake and transport of submicrometre plastics in crop plants using lanthanide chelates as a dual-functional tracer, Nature Nanotechnology, 17, p. 424-431. doi:10.1038/s41565-021-01063-3

High-Mountain Lakes as Indicators of Microplastic Pollution: Insights From Cottian Alps

P. Pastorino[1]*, M. Renzi[2], S. Anselmi[3], M. Bertoli[2], G. Esposito[1], D. Barceló[4], A.C. Elia[5], E. Pizzul[2] and M. Prearo[1]

[1]Istituto Zooprofilattico Sperimentale del Piemonte, Liguria e Valle d'Aosta, Torino, Italy
[2]University of Trieste, Department of Life Science, Trieste, Italy; [3]Bioscience Research Center, Orbetello (GR), Italy
[4]Catalan Institute for Water Research (ICRA-CERCA), Girona, Spain
[5]University of Perugia, Department of Chemistry, Biology and Biotechnology, Perugia, Italy

paolo.pastorino@izsto.it

High-mountain lakes are, by definition, located above the tree line at an altitude above 1500 m a.s.l., generally between 1800 m and 2500 m a.s.l., and in the context of highly natural apparitions. By the virtue of their remote location, high-mountain lakes are believed to be less influenced by local anthropogenic impact such as direct pressure from agriculture and wastewater, which typically affect lakes at lower altitudes (Moser et al., 2019). However, despite their apparent inaccessibility, the influence of humans can be seen even in these environments, for example, signs of physicochemical, biological, and morphological change to these ecosystems (Moser et al., 2019). High-mountain lakes are indicators of problems of global concern. They are extremely sensitive to the deposition of acidic substances from the atmosphere, medium-long range transport of contaminants, and climate change (Moser et al., 2019). In their recent study, Pastorino et al. (2022a) proposed the use of high-mountain lakes as indicators of microplastic (MPs) pollution. With this study we wanted to determine whether MPs can be found only in abiotic compartments (water and sediment) or also in aquatic organisms typical to high-mountain lake, such as zooplankton, tadpoles, and fish. The study site was two high-mountain lakes (Upper and Lower Lake Balma) located in the western Alps (Italy); the lakes were selected because of their use as indicators of environmental changes in previous studies (i.e., Pastorino et al., 2022b). No MPs were found in water and zooplankton samples, whereas the mean MPs in sediment samples were 1.33±0.67 items/m3 and 1.75±0.62 items/m3 in Lower and Upper Lake Balma, respectively. The mean MPs in tadpoles was 0.33±0.58 items/individual and 0.66±0.58 items/individual in Lower and Upper Lake Balma, respectively. The mean number of MPs items found in the gastrointestinal tract (GIT) of fish (Salvelinus fontinalis) was considerably higher in specimens from the Lower (0.45 items/g GIT) than in those from the Upper Lake (0.20 items/g GIT). There was a negative relationship between fish size (weight and age) and MPs abundance in the GIT of fish, indicating that young fish accumulated more MP items probably due to the high prey ingestion rate compared to adults. The same MPs color (blue, white, black), shape (fibers and fragments), and chemical type (polypropylene and polyethylene) were found in the compartments of both lakes. Our findings suggest the use of S. fontinalis as an indicator of MP pollution in high-mountain lakes. Further studies are needed to better understand the sources and the effects of MPs in these remote ecosystems.

References

Moser, K.A. et al. (2019). Mountain lakes: Eyes on global environmental change. Global and Planetary Change, 178, 77-95.

Pastorino, P. et al. (2022a). High-mountain lakes as indicators of microplastic pollution: current and future perspectives. Water Emerging Contaminants & Nanoplastics, 1(1), 3.

Pastorino, P. et al., (2022b). Combined effect of temperature and a reference toxicant (KCl) on Daphnia middendorffiana (Crustacea, Daphniidae) in a high-mountain lake. Ecological Indicators, 145, 109588.

Fragmentation of Plastics in Shore Zones - Results of a Mesocosm Study

S. Meinecke[1]*, F. König[1], F. Liu[2], U. Scholz[1], R. Schmidt[1]

[1]German Environment Agency, IV 2.5 (Trace Analysis, Artificial Ponds and Streams),
Schichauweg 58, D-12307 Berlin
[2]Aalborg University, Department of the Built Environment, Thomas Manns Vej 23, 9220 Aalborg Øst, Denmark

stefan.meinecke@uba.de

The increased use of plastic materials in agriculture (agriplastics) and the predicted expanded use of plastics in consumer products and construction sectors (Lebreton et al., 2019), in combination with unwanted discharge into the environment, inevitably leads to the increased occurrence of plastics in terrestrial and semi-terrestrial systems. Lightweight plastic materials such as packaging, films, film fragments, or even plastic bottles, can be transported by wind and rain into streams, rivers, lakes and oceans. Along these shorelines, plastics are then subject to physicochemical-influences and mechanical stress.

The mechanical degradation behavior of typical plastic litter products was investigated on a pilot plant scale in flow channel mesocosms [Mohr et a. 2005] with different shore conditions (stone/fine gravel, gravel, sand) and a wave impact, similar to what would be expected in the environment, for up to 106 days. Changes in mass, thickness, surface roughness and surface texture of different plastic objects were regularly monitored. At the end of the experiment, water, sediment and pore water samples were analysed for microplastics by µFTIR imaging (Simon et al., 2018; Liu et al., 2019).

After only a few hours exposure, hollow objects (PET bottles, cups) already showed a rapid increase in surface roughness. After 106 days, up to 21 % mass reduction (PET bottles) was detected under the harsh conditions of the stone/fine gravel shore, whereas on the sand shore, mass reduction was only 1.5 %. Plastic films (PE) displayed a different behavior. There was hardly any loss of mass due to abrasion. Irrespective of the shore condition, microplastics (PE and PET) of different size classes were detected in all systems and compartments.

The results show that plastic fragmentation, particularly in the intertidal zone, is influenced by numerous factors including shape and polymer type, shoreline geometry, wave energy, water depth and other environmental conditions (e.g. temperature, UV light). For hollow objects, the modeled fragmentation kinetics indicate that the release of microplastics can already be expected after a short exposure time of only days, which, in contrast to long-term mechanical fragmentation as observed for plastic films, can be attributed to abrasion. Ultimately, the formation of microplastics cannot be counteracted; entry of plastic waste in general into the environment must be consistently prevented.

References

Lebreton, L., Andrady, A. 2019: 'A. Future scenarios of global plastic waste generation and disposal', Palgrave Commun 5, 6, doi: 10.1057/s41599-018-0212-7.

Mohr, S. et al., 2005: 'Enhanced Experimental Flexibility and Control in Ecotoxicological Mesocosm Experiments: A new outdoor and indoor pond and stream system', Env Sci Poll Res Int 12, 5–7, doi: 10.1065/espr2004.08.217.

Simon, M. et al., 2018: 'Quantification of Microplastic Mass and Removal Rates at Wastewater Treatment Plants Applying Focal Plane Array (FPA)-Based Fourier Transform Infrared (FT-IT) Imaging', Water Research, 142, 1-9.
doi: 10.1016/j.watres.2018.05.019.

Sorption Behavior of Antibiotics on Virgin and Aged PLA and PET Microplastics in Aqueous Matrices

D. Kalaronis[1]*, E. Evgenidou[1], G. Z. Kyzas[3], D. N. Bikiaris[1] and D. A. Lambropoulou[1,2]

[1]Aristotle University of Thessaloniki, Department of Chemistry, GR-541 24 Thessaloniki, Greece
[2]Center for Interdisciplinary Research and Innovation (CIRI-AUTH), GR-57001, Balkan Center, Thessaloniki, Greece
[3]International Hellenic University, Department of Chemistry, GR-65404, Kavala, Greece

dkalaron@chem.auth.gr

The release of microplastics (MPs) to environment is increasing dramatically by time, raising up the concerns in scientific community. MPs are able to interact with emerging contaminants and adsorb organic pollutants onto their surface, transferring them into ecosystems (Ainali et al., 2022). The main scope of this research was the study of interactions between four common antibiotics (Isoniazid, Metronidazole, Trimethoprim, Indomethacin) and two widely used polymers such as polylactic acid (PLA), and polyethylene terephthalate (PET). PLA, and PET particles were milled and sieved in size of 75 – 125 μm. Then, a quantity of MPs was aged under UV and simulated solar irradiation in order to study the effect of aging process to adsorption performance of MPs. The experiments were carried out into a bath with continuous stirring (200 rpm) and constant temperature at 25 °C. For monitoring the pharmaceuticals' adsorption onto MPs surface, four different types of experiments were carried out: (i) selection of optimal pH (values used 4 – 8), (ii) kinetics of reaction, (iii) isotherms, and (iv) adsorption using natural waters: (a) seawater, (b) wastewater effluent. According to the results, polymeric particles showed greater adsorption capacity in lower values of pH, while Indomethacin was adsorbed more than other target compounds. Regarding MPs, PLA showed better adsorption capacity than PET, while aged MPs adsorbed larger quantity of pharmaceuticals in comparison with virgin ones. Regarding wastewater effluent and seawater matrices, a removal of 5 – 10 % was observed in most of cases. Moreover, PLA and PET increased their adsorption capacity in wastewater matrix than seawater one. To sum up, MPs are able to adsorb common pharmaceuticals compounds onto their surface and especially, aged-MPs can increase their adsorption ability, posing a threat for ecosystems.

Acknowledgments
This work has been done after financial support received from the Greek Ministry of Development and Investments (General Secretariat for Research and Technology) through the research project "Intergovernmental International Scientific and Technological Innovation-Cooperation. Joint declaration of Science and Technology Cooperation between China and Greece" with the topic "Development of monitoring and removal strategies of emerging micro-pollutants in wastewaters" (Grant no: T7ΔKI-00220) and it is gratefully acknowledged.

References

Ainali, N.M. et al. (2022) 'Do poly(lactic acid) microplastics instigate a threat? A perception for their dynamic towards environmental pollution and toxicity', Science of the Total Environment, 832(March), p. 155014. doi:10.1016/j.scitotenv.2022.155014.

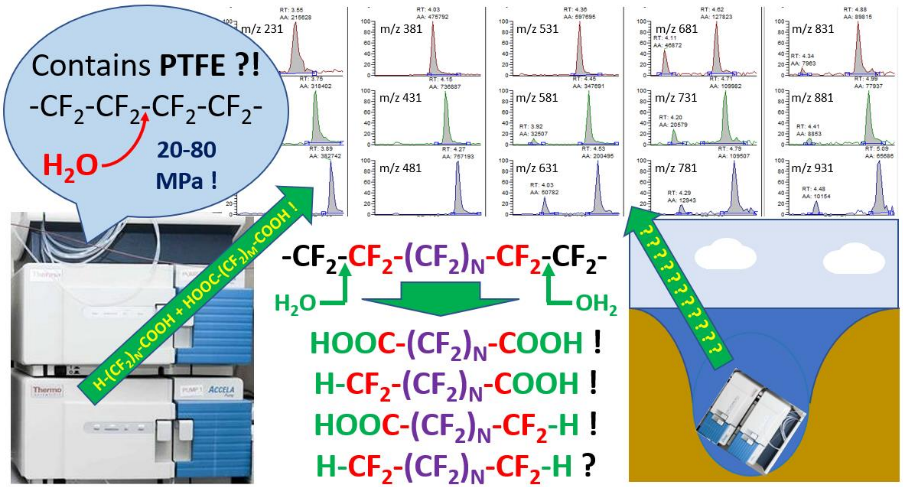
Does PTFE Degrade at High Pressure in the Deep Ocean? a Model Process Observed in a Common LC-Pump

V. Nikiforov[1]*

[1]The Climate and Environmental Research Institute NILU, Framsenteret, Hjalmar Johansens gate 14, 9007 Tromsø, Norway

van@nilu.no

One of the most stable polymers, PTFE is one of the least studied plastic pollutants - is it degradable at all?
A mysterious series of ESI (-) LC-MS peaks has been frequently observed, with m/z = 50n+31 (231, 281,…981) in our practice's series was identified as hydroperfluoroalcanoic acids $H-(CF_2)_n-COOH$, n = 5-20 with help of authentic standards. The observed ions are $M-H-HF-CO_2$.
Injection of fractions or standards yielded peaks with shorter retention times, pointing to the trap column as the source of mysterious peaks and to decomposition of PTFE parts inside the instrument as the origin.
In addition, a series of smaller, earlier eluting peaks with the same m/z was identified as perfluoroalcanedioic acids, $HOOC-(CF_2)_n-COOH$. For these congeners, the observed ions are $M-H-HF-CO_2-CO_2$.
A plausible explanation is cleavage of PTFE carbon-carbon bonds at high pressure (20-80 MPa). A perfluorinated fragment then adds a hydrogen atom or an oxygen atom, yielding $-CF_2H$ or $-COOH$ end group, respectively.
If so, the third product series will be dihydroperfluoroalcanes, $H-(CF_2)_n-H$; but detection of these would require a special experiment, since these neutral substances hardly produce ions in LC-MS.
We hypothesize the process is an environmental degradation pathway for PTFE items, micro- and nanoparticles in the ocean. Indeed, pressure at mean ocean depth (3.7km 1) is ca 37 MPa and in the lowest part ca 110 MPa, well in the range or exceeding the pressure inside the LC pumps. Possibly, the same pathway could cleave perfluorinated chain in smaller PFAS molecules like PFOS or PFOA.



Mysterious peaks with m/z 50n+31; confirmed formation in LC at hgh pressure; hypothetical degradation of PTFE in the deep ocean; hydrolysis pathway.

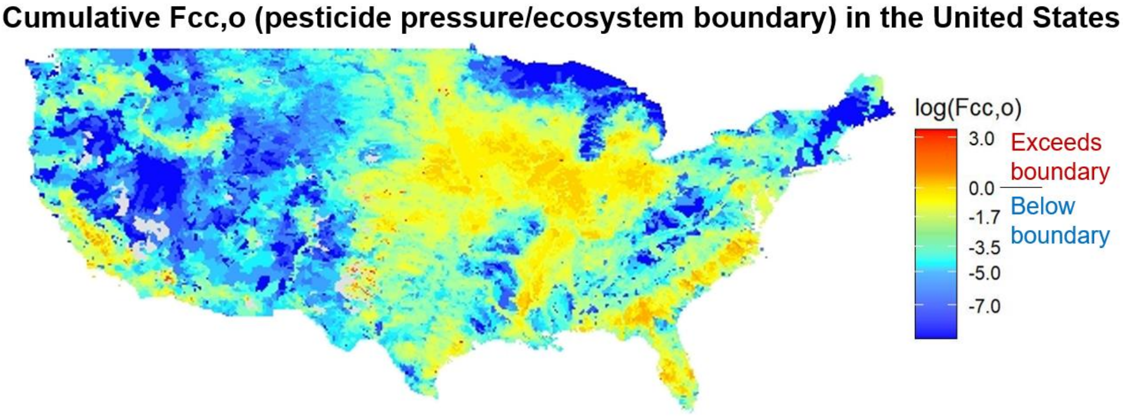
Identifying Global Regions with Pesticide Pressure Exceeding Protective Freshwater Ecosystem Boundaries

M. B. Kosnik[1*], M. Hauschild[1], O. Jolliet[1], F. Soheilifard[1], P. Fantke[1]

[1]Technical University of Denmark, Department of Environmental and Resource Engineering, Quantitative Sustainability Assessment, Produktionstorvet 424, 2800 Kgs. Lyngby, Denmark

markos@dtu.dk

Pesticide use nearly doubled from 1990 to 2018, and is projected to increase further with population growth. To determine whether current pesticide use is sustainable, pesticide pressure (based on use) must be related to protective ecological boundaries at relevant spatial scales (Kosnik MB, et al., 2022). We introduce a spatially explicit framework to relate pesticide pressure to freshwater ecosystem boundaries and identify regions of exceedance to guide sustainable chemicals management, following the life cycle impact assessment framework. Pesticide application data for 865 chemicals were translated into emissions and integrated into the Pangea spatial multi-scale model to determine the concentration of each chemical in 87,063 freshwater catchments globally. Pesticide pressure and ecosystem boundaries developed from species sensitivity distributions were combined, so the output for each chemical in a region is the fraction of the freshwater ecosystem capacity occupied by that pesticide, the Fcc,o. For each region, the Fcc,o was also analysed cumulatively across pesticides. We found that most pesticides do not exceed any boundaries individually, but some frequently used pesticides do in a subset of catchments (e.g., atrazine in the United States, US). Further, up to 15% of global freshwater ecosystems have cumulative pesticide pressure exceeding their boundaries (e.g., 13% of catchments in the US, Figure 1). This framework can identify chemicals dominating freshwater ecosystem boundaries to guide the design of safer and more sustainable pesticides and inform more sustainable pesticide use.



The cumulative fraction of occupied carrying capacity (Fcc,o) for 276 pesticides applied in the United States. 13% of regions exceed their boundary.

References

Kosnik MB, et al., (2022) Toward assessing absolute environmental sustainability of chemical pollution. Environmental Science & Technology 56:8, 4776-87. https://doi.org/10.1021/acs.est.1c06098.

Waste to Energy: Food Waste Valorisation toward Biofuel Production

G. R. Ivaniš[1]*, Z. V. Simić[2], S. P. Miškov Panić[1], M. Lj. Kijevčanin[1] and I. R. Radović[1]

[1]University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia
[2]University of Belgrade, Innovation Center of the Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia

givanis@tmf.bg.ac.rs

The uncontrolled and excessive use of fossil fuels is one of the main culprits for global warming due to the emission of greenhouse gases. Therefore, intensive work has been done to reduce the use of such fuels by replacing/adding biodiesel in transport sector since the use of biodiesel decreases the net emission of greenhouse gases by about 76 % than when using petroleum diesel (Ivaniš et al., 2016). On the other hand, the modern consumer lifestyle has led to the accumulation of large amounts of waste that additionally pollutes the soil and water, which indicates the necessity of a global transition from a linear to a circular economy where waste represents raw material.

The disposal of used cooking oil is a huge problem because it is usually poured down drains, which leads to clogging of kitchen pipes and local sewage. Consequently, waste cooking oil drastically reduces the efficiency of wastewater treatment plants and is extremely harmful to the aquatic ecosystem. The reuse of used cooking oil in food is not recommended so other forms of recycling such as biodiesel production are preferred. Biodiesel is obtained by the transesterification reaction of vegetable oils with short-chain alcohol in the presence of a catalyst, and glycerine is produced as a side product. By applying heterogeneously catalysed transesterification reaction, such as the use of CaO as catalyst, the generation of waste during the purification of products is avoided. Eggshells are solid organic waste that is generally discarded without prior treatment, making it a hazardous waste. It is considered that the eggshell mainly (about 96 %) consists of $CaCO_3$, which offers the possibility of its revalorisation through CaO production (Waheed et al., 2020).

As part of our research, waste hen’s eggshell was collected and annealed at 830 ° C producing CaO, which was used as a catalyst in the biodiesel synthesis from used cooking oil. The thermodynamic and transport properties of the obtained biodiesel and crude glycerine were determined at wide ranges of temperature and pressure, which is relevant for their further use [1]. The measured properties of the obtained biodiesel meet the limits prescribed by the standard for biodiesel EN14214 which confirms that it can be used in diesel engines and heating applications. The obtained raw glycerine can be mixed with biomass residues and used in the production of pellets. In this way, the problem of accumulation of waste in the form of eggshells, used cooking oil and crude glycerine is solved and their revalorisation is carried out, which is fully in accordance with the postulates of the circular economy. Furthermore, biodiesel, as an environmentally friendly alternative to petroleum diesel, was obtained.

Acknowledgements: This work was supported by United Nations Development Programme and Global Environment Fund (CIRCULAR VOUCHERS – Ref: 00123168/01-01) and by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contracts No. 451-03-47/2023-01/200135 and 451-03-47/2023-01/200287).

References

Ivaniš, G. et al. (2016) ‘Biodiesel density and derived thermodynamic properties at high pressures and moderate temperatures’, Fuel, 165, p. 244. doi: 10.1016/j.fuel.2015.10.050.

Waheed, M. et al. (2020) “Channelling eggshell waste to valuable and utilizable products: A comprehensive review”, Trends in Food Science & Technology, 106, p. 78, doi: 10.1016/j.tifs.2020.10.009.

Single and Combined Effect of Soil Amendment With Biochar and Wood Distillate in Young Vine Plants

S. Celletti[1*], R. Fedeli[1], M. Ghorbani[1], M. Grattacaso[1], B. Giannetta[2], C. Zaccone[2] and S. Loppi[1 3]

[1]University of Siena, Department of Life Sciences, Via P. A. Mattioli 4, 53100, Siena, Italy
[2]University of Verona, Department of Biotechnology, Strada Le Grazie 15, 37134, Verona, Italy
[3]Interuniversity Center for Studies on Bioinspired Agro-Environmental Technology (BAT Center), 80138, Napoli, Italy

silvia.celletti@unisi.it

Recycling plant biomass into bioproducts for agricultural practices, including biochar and wood distillate (WD), plays a key role in facing climate change and supporting global food security and circular economy (Tuck et al., 2012). However, the potential effect of biochar and WD, when co-applied as a soil amendment to maximize plant performance, needs to be further investigated (Becagli et al., 2022; Yuan et al., 2022). Pot experiments were performed in a climate chamber with the aim of evaluating the growth pattern of young vine plants (Vitis vinifera L. var. Sangiovese) in response to three soil amendments: 20% (w/w) woody biochar and 0.5% (v/v) WD weekly fertigation, alone (B and WD, respectively) and in combination (B+WD). At the end of the growth period (45 days), chlorophyll and primary metabolites (i.e., glucose, fructose and proteinogenic amino acids) were determined at shoot level, while the area and length at root level; fresh biomass, secondary metabolites as antioxidants (total polyphenols), and micro- and macronutrients (Ca, K, Mg, P, S, Cu, Fe, Mn, Mo, Zn, and Na) were determined in both shoots and roots. Finally, pH, electrical conductivity, cation exchange capacity (CEC), organic carbon and total nitrogen were determined in bulk soils, before and after the amendments. Results showed that plants fertigated with WD, irrespective of the combination with biochar, produced less leaf biomass, but more root biomass; in contrast, root expansion and length were positively affected by biochar application. Although the shoot glucose content was reduced by the application of both biochar and WD alone, their combination resulted in a glucose content similar to the control. The amino acid content, including that of phenylalanine (Phe) and tyrosine (Tyr), which are precursors of phenolic compounds, increased following WD application. In particular, WD reduced the content of Phe and Tyr only in the roots, whereas biochar, alone or combined with WD, lowered their concentration only in the shoots. The single or combined effect of biochar with WD strongly increased K content, but reduced Ca, Mg and P concentration in both shoots and roots. On the other hand, WD promoted an increase of P content in the roots. Although the Na content in soil amended with biochar was high, plants accumulated it mainly in the roots, whereas the root system of WD-treated plants showed a Na content even lower than the control. WD also increased the soil CEC, regardless of the biochar addition, while in the soil amended with biochar, the content of total nutrients (i.e., Ca, K, Mg, Fe, and Mo) was much higher than in the control. As expected, the organic C content increased in both the biochar-amended soil and in the WD-fertigated one. In conclusion, the synergic effect between biochar and WD was evident on plant physiology with a positive response especially in terms of root growth, suggesting that the combination of these bioproducts is a potentially feasible and eco-sustainable strategy for crop cultivation.

References

Becagli, M., Santin, M., Cardelli, R. (2022) ‘Co-application of wood distillate and biochar improves soil quality and plant growth in basil (Ocimum basilicum)#’, Journal of Plant Nutrition and Soil Science, 185, p. 120–131. doi: 10.1002/jpln.202100239.

Tuck, C.O. et al. (2012) ‘Valorization of Biomass: Deriving More Value from Waste’, Science, 337, p. 695–699. doi: 10.1126/science.1218930.

Yuan, Y. (2022) ‘Co-application of biochar and pyroligneous acid improved peanut production and nutritional quality in a coastal soil’, Environmental Technology & Innovation, 28, 102886. doi: 10.1016/j.eti.2022.102886.

A New Highly Active Hybrid Guanidine Zinc Catalyst for Lactide Polymerization and the Fast and Selective Chemical Recycling of (Bio)polyesters

M. Fuchs[1*], P. M. Schäfer[1], A. Hoffmann[1] and S. Herres-Pawlis[1]

[1] RWTH Aachen University, Institute for Inorganic Chemistry, Landoltweg 1A, 52072, Aachen, Germny

martin.fuchs@ac.rwth-aachen.de

To counteract the global environmental pollution, caused by non-degradable petroleum-based plastics, a circular plastics economy is needed to fulfill the needs that plastic materials offer to modern societies. Bioplastics, such as the polyester polylactide (PLA), use renewable resources, offer an insurance for unreclaimed materials at their end-of-life (eol) by being biodegradable, but show similar properties than common, petroleum-based plastics, such as polyethylene terephthalate (PET). Using chemical recycling strategies, polyester materials can be transformed to value added materials or new virgin-like monomer feedstocks, ensuring closed loop recycling, without a loss of product quality. PLA is therefore a highly promising candidate for future circular plastic value chains. However, current industrial production via metal catalyzed ring opening polymerization (ROP) relies on the toxic catalysts tin octanoate, which can harm the environment and needs to be replaced to make PLA a fully sustainable plastic (R. Auras et al 2022, McKeown P. et al. 2020). Herein, we present a new highly active catalyst for both, lactide ROP and the selective chemical recycling of (bio)plastics via alcoholysis, based on non-toxic Zn in combination with a new aliphatic hybrid-guanidine ligand, which is accessible in a fast one-pot procedure. Both, ligand and zinc complex were fully characterized using NMR spectroscopy, IR spectroscopy, mass spectrometry and crystal structure analysis. Fast catalytic activity towards lactide ROP was demonstrated under industrially preffered melt conditions, reaching a yield of >90% within 70 s. Even for the ROP in toluene the new catalyst outperforms the toxic industry standard tin octanoate by a factor of 10. Methanolysis of polylactide via transesterification to methyl lactate using mild reaction conditions, showed a high catalytic activity, achieving >90% PLA conversion within 6 h. The reaction rate constant was determined using ^{1}H-NMR spectroscopy to monitor the PLA degradation, which further emphasized the high catalytic activity of the catalyst by exceeding toxic tin octanoate by a factor of 4. Selective PLA methanolysis from different PLA-PET mixtures as well as from a polylactide-polycaprolactone (PCL) blend was demonstrated. Methanolysis at elevated temperatures in the polymer melt even further increased the activity of the catalyst, achieving full PLA conversion within 10 min, retaining catalytic activity even after catalyst recycling. Alcoholysis of PCL and for the first time alcoholysis of PET was achieved using a guanidine zinc catalyst, with good activities. Besides the reaction temperature, the use of additional solvent and the polymer structure were identified as the key factors for selective (bio)polyester alcoholysis, enabling the possibility for cascade polyester recycling. This makes the presented catalyst a highly attractive candidate for industry, to implement a circular (Bio)plastics economy (Fuchs M. et al. 2023).

References

R. Auras et al (2022) Poly(Lactic Acid): Synthesis, Structures, Properties, Processing, Applications, and End of Life, Second Edition, doi: 10.1002/9781119767480

McKeown, P. et al. (2020) The Chemical Recycling of PLA: a Review, sustainable chemistry, 1,1-22, doi:10.3390/suschem1010001

Fuchs, M. et al. (2023) Manuscript submitted to ChemPlusChem.

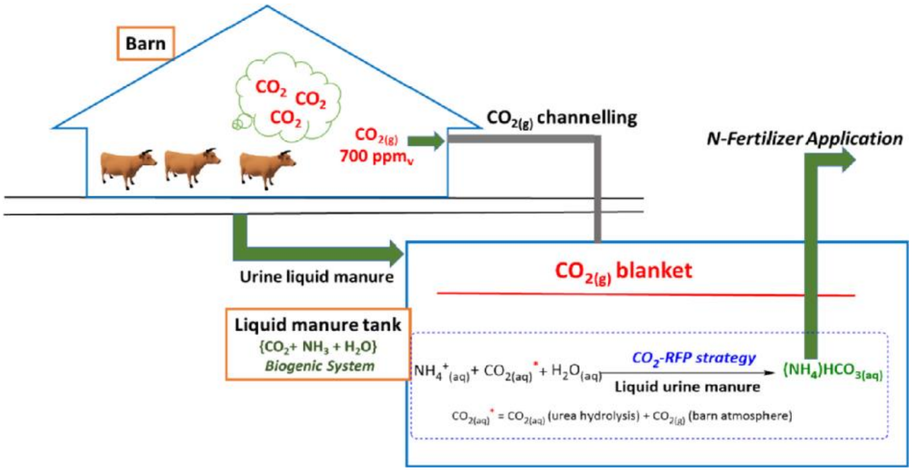
A Novel Approach for Environmentally Friendly Dairy Farms: The CO$_2$-RFP Strategy

A. Gueddari-Aourir[1*], C. Alonso-Moreno[1], J. Canales-Vázquez[2], J.E. Zafrilla[3], S. Garcia-Yuste[4]

[1]Castilla-La Mancha University, Department of Inorganic Chemistry, Paseo Estudiantes, 02071, Albacete
[2]Castilla-La Mancha University, Renewable Energy Research Institute, Paseo Investigación,1, 02071-Albacete
[3]Castilla-La Mancha University, Department of Economic Analysis, Plaza Universidad, 1, 02071, Albacete, Spain
[4]Castilla-La Mancha University, Department of Economic Analysis, Av. Camilo José Cela, 1013071, Ciudad Real, Spain

Abdessamad.Gueddari@uclm.es

A novel Carbon Dioxide Utilization (CDU) approach is proposed in the search for reducing emissions of carbon dioxide, CO2, and ammonia, NH3 in the husbandry industry. The idea relies on utilising these by-products released from minor biogenic emission sources, Rumen Fermentation Processes (RFP). This CO2-RFP Strategy represents an innovative route to treat the liquid dairy manure. The treatment is carried out with CO2-enriched air coming from cattle exhalation to produce one of the most demanded fertilizers such as NH4HCO3 (ABC, ammonium bicarbonate). In global terms, from a chemical point of view, this strategy would lead to the reduction of over 31.6 Million of tones, Mt, of ABC by using 18.0 Mt of CO2 and capturing over 6.9 Mt of NH3. Furthermore, the process involved would consume less energy than the traditional synthetic ABC fertilizer process. Additionally, this strategy would not produce any by-products or other chemical compounds which can affect negatively the dairy sector. Considering a scenario of large-scale implementation of this strategy in the most important dairy countries, almost four times the ABC world production per year would be produced. This production entails around 1.8 Gt of CO2 equivalent negative emissions and a reduction of 82.8 Mt of NH3 from this year until 2030. This strategy has been analysed within different possible scenarios in order to provide a realistic perspective: The CO2-RFP Strategy (1) in a typical dairy farm, (2) in the most significant countries and (3) as a N-fertilizer supplier.



CO2-RFP Strategy framework

References

Alonso-Moreno, C. et al. (2018) ‘The Carbon Dioxide-Rumen Fermentation Processes-strategy, a proposal to sustain environmentally friendly dairy farms’, Journal of Cleaner Production, 204, pp. 735–743. doi:https://doi.org/10.1016/j.jclepro.2018.08.295.

Gueddari-Aourir, A. et al. (2022) ‘The carbon footprint balance of a real-case wine fermentation CO2 capture and utilization strategy’, Renewable and Sustainable Energy Reviews, 157, p. 112058. doi:https://doi.org/10.1016/j.rser.2021.112058.

Life Cycle Assessment (LCA) of a Bio-Fuel Cell Fed with Waste Biomass: Potential for Scale-Up and Process Optimization

E. Rossi[1,2*], D. Cespi[1,2], I. Maggiore[1], F. Passarini[1,2], L. Setti[1,2]

[1] University of Bologna, Dep. of Industrial Chemistry “Toso Montanari”, viale del Risorgimento 4, 40136, Bologna, Italy
[2] University of Bologna, Interdepartmental Centre of Industrial Research ‘Renewable Sources, Environment, Blue Growth, Energy’ (CIRI FRAME), Via Dario Campana, 71, 47922 Rimini, Italy

eleonora.rossi51@unibo.it

Turning waste into a valuable resource is globally mainstreamed by approaches and legislations including the circular economy and several SDG goals (UN General Assembly, 2015). However, effective implementation of virtuous waste management strategies often requires innovative and versatile technologies and proven environmental preference over traditional waste treatment and disposal routes. In particular, biowaste is a material stream under investigation because of its potential source for added-value chemicals and renewable energy.

In a past research, a team from the University of Bologna has developed a bio-fuel cell (b-FC) technology to serve as a treatment for discarded biomass originated from agriculture. This cell aims to valorize biomass by producing electricity and soil conditioner.

This study focused on the life cycle assessment (LCA) application to estimate the environmental performance of the b-FC developed, with emphasis to understand which stages of the process are the most impactful to the environment and where prioritizing efforts should be dedicated during the upscaling of the technology.

Various scenarios were modeled to achieve this goal, depending on the life span of the cell, the reagents used, the amount and type of energy used. Impact assessment stage was performed using ReCiPe 2016 (Huijbregts et al., 2017) and CED (Verein Deutscher Ingenieure (VDI), 1997) methods.

The results showed that the impacts related to the production of the cell (i.e., infrastructure) are negligible if it is used about 400 times. It was also observed that the greatest impact is due to energy consumption and the usage of phosphoric acid, used during the neutralization stage. Environmental benefits, instead, results from the phosphorus recovered as soil conditioner. Further benefits are related to energy recovery and soil conditioner production.

LCA was then used as a scientific methodology to support the b-FC optimization. For this purpose, different combinations of acids and bases, the latter for neutralization, were tested. Nitric acid and potassium hydroxide were used instead of phosphoric acid and sodium hydroxide. KOH use seems promising, thanks to the added value of K in the outlet stream used as fertilizer. Because of the large portion of impacts are due to energy consumption, scenarios based on renewable sources (e.g., 100% solar energy) have been also explored. A further model was also created to check the benefits of heat recovery during the hydrolysis reaction. Finally, all these scenarios were compared with traditional treatments for biomass wastes, such as composting and anaerobic digestion.

The LCA results demonstrate that the b-FC system is highly promising and competitive technology for recovery of food and organic waste. However, life cycle analysis by also revealing further improvements should be aimed at decreasing the energy consumption and enhancing the nutrient recovery.

References

Huijbregts, M.A.J. et al. (2017) ‘ReCiPe2016: a harmonised life cycle impact assessment method at midpoint and endpoint level’, International Journal of Life Cycle Assessment, 22(2), pp. 138–147. Available at: https://doi.org/10.1007/s11367-016-1246-y.

UN General Assembly (2015) ‘Transforming our world: the 2030 Agenda for Sustainable Development’. Available at: https://doi.org/10.1163/15718093-12341375.
Verein Deutscher Ingenieure (VDI) (1997): Cumulative Energy Demand, Terms, Definitions, Methods of Calculation, VDI-Richtlinie 4600.

A Legally Binding Framework for Sustainable Management of Chemicals and Materials – An Illusion or a Long-Term Goal?

K. G. Steinhäuser and M. G. Ophoff

Sustainable management of chemicals and materials deals not only with the assessment of hazards and risks of substances to health and the environment in accordance with classic chemicals policy, but also the management of material flows from the extraction of raw materials up to waste. The constant increase in material flows now threatens the Earth system. Persson et al. showed that the planetary boundaries for 'novel entities' have already been significantly exceeded. This makes it clear that the sustainable management of chemicals and materials must become the third pillar of an international sustainability policy. In this context, there exist close links between the increasing consumption of materials and the emission of climate gases as well as the losses of biodiversity. No challenge will be met without a determined policy on the other two threats. Sustainable chemistry can provide a significant contribution to the future management of substances and materials. For chemicals, this means that they should be inherently safe, that is, they should not have hazardous properties, even in the long run, except these properties are closely related to an essential function. In particular, they should no longer be persistent. 'Forever chemicals' such as numerous fluorochemicals and microplastics create problems that are ever increasing and irreversible. Material flows must be significantly reduced. Reuse and recycling of materials are crucial elements of a circular economy. The raw material feedstock of chemical production must also change: renewable resources must replace mineral oil and natural gas. Three complementary strategies are critical to reducing material flows: efficiency, consistency and sufficiency.

Unlike climate change and biodiversity, no comprehensive legally binding international agreement exists for the management of substances and materials. Individual topics are covered, for example, in the Stockholm and Basel Conventions, and international exchange forums exist in the form of the Strategic Approach to an International Chemicals Management (SAICM) and the World Resources Forum. However, these agreements and processes are fragmented and lack a comprehensive set of rules as an umbrella for consistent policies to restore planetary boundaries for substances, materials, and wastes. This is very urgent given the overloading of the Earth system. But on the other hand, it may be a long-term process for which the political will still needs to grow. Nonetheless, the necessity to develop such an instrument will grow, too. The current decision to develop an International Plastics Convention is an important step in the right direction.

Alginate Derivatives: a Green Alternative for Industrial Tanning

I.Quaratesi[1]*, V.Ferrara[2], P.Chipurici[3], I.Călinescu[3], M. Vînătoru[3], C.Carşote[1], C.Casas[4], A.Bacardit[4], E.Badea[1]

[1]National Research & Development Institute for Textiles and Leather, ICPI division, St. I. Minulescu 93, 031215, Bucharest, Romania
[2]Università di Salerno, DCB "A. Zambelli", Via Giovanni Paolo II 132, I-84084, Fisciano, Italy
[3]Politehnica University of Bucharest, BSP, St. Gheorghe Polizu 1-7, 011061, Bucharest, Romania
[4]University of Lleida, A3 Leather Innovation Center, Av. Pla de La Massa 8, 08700, Igualada, Spain

i.quaratesi@gmail.com

Leather tanning is a multi-risk industry due to the tanning and re-tanning agents, as metal (e.g. Cr,Ti, Zr) salts or synthetic tannins (e.g. aldehyde-, phenol-, naphtalene-, bisphenol-based), as well as to the chemical auxiliaries used in beamhouse and finishing processes. The large amount of waste generated (wastewater, solid waste) should be appropriately managed to not degrade the ecosystem and reduce the human's risk of exposure to these chemicals. These issues are a call for developing greener leather processing and for producing 100% biodegradable leather. In this context, oxidized sodium alginate from renewable sources was studied as a potential crosslinker for hide collagen by Ding et al., 2017.

In this work, 100% biodegradable sodium alginate derivatives (SADs) were obtained by different green methods based on ultrasound technology (Simonescu et al., 2020) and tested in tanning and re-tanning processes. Tests were firstly performed at laboratory level for selecting the SADs with best performances. The ability of SADs to bind to collagen was evaluated by micro-Differential Scanning Calorimetry (Carşote, C. et al., 2016), while the interaction mechanism was investigated by single side NMR. ATR-FTIR spectroscopy and SEM-EDS were useful for assessing how uniformly the SADs distributed in the leather structure. The production of best performing SADs as well as the tanning process were upscaled at the pilot scale level. The stability of collagen-SAD matrix in leather was tested by both analytical methods (micro-DSC and single-side NMR) as well as by physical-mechanical standard tests. The results confirmed the feasability of the tanning process for obtaining a 100% biodegradable product through the exclusive use of SADs. This is the first attempt of using ultrasound technology for converting sodium alginate into effective tanning agents. The next step in the exploitation of US technology consisted in conferring antimicrobial to the SADs through functionalization with nanoparticles of metal oxides such as ZnO. The antibacterial effects of both functionalized SADs and leather wa evaluated against gram positive and gram negative bacteria. The use of a renewable, biodegradable, and non-toxic resource, such as alginate, would significantly reduce the chemical and environmental footprint of leather production and could pave the way to obtaining completely biodegradable leather. Moreover, value-added leather can be obtained by US-assisted functionalization. These results represent a first step in the development of new tanning/re-tanning agents for value-added leather without requiring changing in the well established wet-white technology.

References

Ding, W. et al. (2017) 'Preparation of oxidized sodium alginate with different molecular weights and its application for crosslinking collagen fiber', Carbohydrate Polymers, 157, pp. 1650–1656. doi: 10.1016/j.carbpol.2016.11.045.

Simonescu C.M. et al. (2020) 'Ultrasound assisted preparation of calcium alginate beads to improve absorption of Pb^{+2} from water', Ultrason. Sonochem., 68, pp. 105191. doi: 10.1016/j.ultsonch.2020.105191.

Carşote, C. et al. (2016) 'Study of the effect of tannins and animal species on the thermal stability of vegetable leather by differential scanning calorimetry', J. Therm. Anal. Calorim., 124, pp. 1255–1266. doi: 10.1007/s10973-016-5344-7.

Effect of Biochar Addition on the Behavior of the Allelochemical S-Carvone in Agricultural Soils

J. A. Galán-Pérez[1]*, B. Gámiz[1] and R. Celis[1]

[1]Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC), Avenida Reina Mercedes 10, 41012 Seville, Spain.

jagalan@irnas.csic.es

Biochar (BC) has been proposed as a soil amendment due to its environmental and agronomic benefits once added to soils, playing an important role in sustainable waste management and circular economy. Additionally, the excellent sorbent properties of BC have led to intended use to enhance the persistence of allelochemicals in agricultural soils, in the context of their potential application as ecofriendly alternatives to synthetic pesticides. Allelochemicals have shown very short half lives in soils, which become the main constraint for their widespread use as green agrochemicals. Accordingly, sustainable strategies to enhance their soil persistence are encouraged (Galán-Pérez et al., 2022).

This study aimed to characterize the changes in sorption and persistence of the allelochemical monoterpene S-carvone in two agricultural soils, one acidic and one alkaline, after their amendment with BC produced from composted olive mill waste at a pyrolysis temperature of 400 ºC. S-carvone was selected for being a representative of one of the most important families of allelochemicals, monoterpenes, and it is currently registered as a plant growth regulator. An additional novel approach of this work was to assess how the soil microbial activity of the soils was affected by the addition of BC and S-carvone through dehydrogenase enzymatic activity (DHA) and soil respiration measurements. The conditions used in the experiments were: rate of BC of 4%, soil humidity of 30%, and S-carvone application doses of 2 and 50 mg kg^{-1}.

The sorption of S-carvone was greater in the acidic soil (31%) as compared to the alkaline soil (12%). After the addition of BC, the sorption of the allelochemical significantly increased in both soils, but the effect was more pronounced after its addition to the alkaline soil. The persistence of S-carvone in the BC-amended soils was also greater as compared to the unamended soils at the two application rates tested. The soil respiration and the DHA measurements demonstrated that BC had a positive effect on the microbial activity since higher values for the two parameters were measured for the BC-amended soils in comparison to the unamended soils.

The results from this study suggest the effectiveness of BC in increasing the sorption and persistence of S-carvone and demonstrate that BC could contribute to modulating the behavior of allelochemicals in agricultural soils. Further studies relative to the analysis of the biodiversity of the unamended and BC-amended soil by DNA techniques are ongoing, which will help to gain a better knowledge of the effect of BC and allelochemicals on the soil microbial diversity and vice versa.

Acknowledgment: Project PID2020-112563RB-I00 and Doctoral Grant PRE2018-083293 financed by the Spanish Ministry of Science and Innovation and Project ProyExcel_00295 financed by Junta de Andalucía.

References

Galán-Pérez, J. A. et al. (2022) Soil modification with organic amendments and organo-clays: Effects on sorption, degradation, and bioactivity of the allelochemical scopoletin, Journal of Environmental Management, 302, 114102. https://doi.org/10.1016/j.jenvman.2021.114102.

Integrating Risk Assessment and Life Cycle Assessment: Opportunities and Challenges

E. Abbate[1,2*], C. Caldeira[2], I. G. Aguirre[3], M. Huijbregts[1], A. M. J. Ragas[1], S. Sala[2]

[1]Radboud University, Department of Environmental Science, Radboud Institute for Biological and Environmental Sciences (RIBES), Heyendaalseweg 135, 6525 AJ, Nijmegen, the Netherlands
[2]European Commission, Joint Research Centre,Sustainable Resources Directorate, Ispra (VA), Italy
[3]European Commission, Joint Research Centre, Health and Food Directorate, Ispra (VA), Italy

elisabetta.abbate@ec.europa.eu

The European Commission's (EC) Recommendation for Safe and Sustainable by Design (SSbD) chemicals and materials addresses one of the EU chemical strategy for sustainability ambitions: to integrate safety and sustainability to reduce human and environmental impacts due to chemicals (European Commission, 2022).

The EC SSbD framework proposes to adopt risk assessment (RA)-based approaches for the safety and Life Cycle Assessment (LCA) for the environmental sustainability. Although progress has been made in the development of a holistic vision to integrate safety and environmental sustainability aspects, there is the need to explore to which extent the two approaches can be aligned in addressing aspects of fate, exposure, and impacts of chemicals.

Safety aspects (to human health or environment) are usually assessed starting from the chemical hazard, as result of chemicals intrinsic properties. By means of multimedia modelling, the fate and exposure of the chemical is estimated, and ultimately the likelihood of the risk on human or ecosystem due to the chemical exposure is assessed by determining whether the exposure exceed a certain threshold.

Environmental sustainability aspects are usually addressed by adopting the LCA methodology. LCA estimates the potential impacts that a chemical might generate along its entire life cycle, from the raw material extraction up to the end of its life. The EC SSbD framework proposes to refer to the EU environmental footprint method to assess the impacts due to chemicals, considering 16 impact categories. Among them, several impact categories are usually addressed in RA, such as ecotoxicity and human toxicity. The impact models underpinning the toxicity assessments in LCA are usually also applying multimedia box models and toxicity data, assessing fate, exposure and impacts of chemicals..

Given the existence of similarities in model equipment and input data, the integration of LCA and RA has been debated by scholars over time. Some aspects are considered challenging, mainly due to different assessment goals and scope, underpinning principles, site-specificity, type of assumptions etc. To pursue an integration, several viewpoints exist: the parallel integration of LCA and RA, the inclusion of the RA into LCA, or the inclusion of the LCA into RA (Muazu et al., 2021).

According to the SSbD framework, the design or re-design of chemicals needs to be supported by integrating safety and environmental sustainability aspects. This leads to the necessity of creating a new approach that integrates the two aspects to boost the evaluation of the chemical under development.Hence, the present study aims at contributing to the scientific debate on the integration of LCA and RA, by systematically assessing:

- Goal and scope of the two approaches when applied to the design or re-design of a chemical
- Data and models used for the assessment of fate, exposure and risk, highlighting convergence and divergence
- Type of endpoints and categories of risk addressed by RA and LCA, unveiling the ones not currently addressed in LCA and exploring the possibility of integrating them

The analysis aims at paving the way for a streamlined approach in support to the EC framework on SS

References

European Commission (2022). Commission recommendation of 8.12.2022 establishing a European assessment framework for 'safe and sustainable by design' chemicals and materials. Brussels, 8.12.2022 C(2022) 8854 final.

Muazu, R.I. et al (2021). Integrating life cycle assessment and environmental risk assessment: a critical review. J. Clean. Prod., Article 126120, 10.1016/j.jclepro.2021.126120.

Safe and Sustainable by Design Chemicals and Materials: JRC Framework, Case Studies and Lessons Learnt

I. G. Aguirre[1]*, D. Lipsa[2], J. R. Sintes[1]

[1]European Commission, Joint Research Centre (JRC), Directorate F – Health and Food, Unit F.2 – Technologies for Health, Via E. Fermi, 2749. I-21027 Ispra (VA), Italy
[2]European Commission, Joint Research Centre (JRC), Directorate A – Strategy and impact, Unit- A.5 Scientific Development, Via E. Fermi, 2749. I-21027 Ispra (VA), Italy

irantzu.garmendia-aguirre@ec.europa.eu

The European Green Deal, with its ambition of attaining climate neutrality, a circular economy and a zero pollution/toxic free environment, sets the vision of the European Commission to transform the European economy and society into a sustainable future.

Contributing to those objectives, the Chemical Strategy for Sustainability establishes a number of actions to address and reduce the possible risks posed by hazardous chemicals to human health and the environment. Indeed, driving innovation to design and develop safe and sustainable chemicals and materials is vital to support the green and the digital transitions. The development of green energy sources, sustainable food systems, improved and new solutions in the health sector are only a few examples where innovations are of paramount importance.

This work aims to raise awareness and promote the Safe and Sustainable by Design concept by presenting the framework developed by the JRC (Caldeira et al., 2022), the EC Recommendation to implement the framework (EC, 2022) as well as on-going and future activities in support of the EU's broader sustainability goals.

The SSbD framework developed by the JRC addresses the dimensions, aspects and indicators to be considered, the methods and tools that can be used, and how to define criteria in the different steps of the SSbD assessment.

To check that the proposed framework is fit for purpose, it is undergoing an in-house evaluation where chemicals used in the food packaging field have been selected as case studies. Gaps and lessons learned so far in such evaluation will be discussed.

The JRC’s framework provides a rational and integrative procedure that puts together safety, environmental sustainability and socio-economic dimensions for the first time. It requires that safety and sustainability are considered for the entire life cycle of chemicals, materials and products, and assessed, as far as possible, from the beginning and at all stages of the R&D process,. The framework will also be a key approach to support replacement of the most harmful chemicals, materials and products on the market.

References

Caldeira, C. et al (2022). Safe and Sustainable chemicals by design chemicals and materials - Framework for the definition of criteria and evaluation procedure for chemicals and materials. Publications Office of the European Union, Luxembourg. https://doi.org/http://dx.doi.org/10.2760/487955.

EC. (2022). Commission recommendation of 8.12.2022 establishing a European assessment framework for ‘safe and sustainable by design’ chemicals and materials. Brussels, 8.12.2022 C(2022) 8854 final

Practical Guidance to a Holistic Safe and Sustainable by Design (SSbD) Approach for Advanced Materials

L. Pizzol[1], A. Livieri[1,2], B. Salieri[3], L. Farcal[4], L. G. Soeteman-Hernández[5], A. Zabeo[1], M. Blosi[6], A. Luisa Costa[6], S. Devecchi[1], W. Peijnenburg[5,7], S. Stoycheva[8], N. Hunt[8], M. López-Tendero[9] and D. Hristozov[10]*

[1]GreenDecision srl, Via Torino 155, 30172 Mestre - Venezia (VE), Italy
[2]Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Venice, Italy
[3]TEMAS Solutions GmbH, Lätteweg 5, 5212 Hausen. Switzerland
[4]European Commission, Joint Research Centre (JRC), Ispra, Italy
[5]National Institute for Public Health and the Environment (RIVM), Center for Safety of Substances and Products, Bilthoven, the Netherlands
[6]National Research Council of Italy-Institute of Science, Technology and Sustainability for Ceramics, CNR - ISSMC (former ISTEC), Faenza, Italy
[7]Institute of Environmental Sciences (CML), Leiden University, P. O. Box 9518, 2300 RA Leiden, the Netherlands
[8]Yordas Group, Äußere Nürnberger Straße 62, 91301 Forchheim, Germany
[9]Laurentia Technologies SLL, Benjamin Franklin 12, 46980 Paterna, Valencia, Spain
[10]EMERGE Ltd, Sofia, Bulgaria

danail.hristozov@emerge.bg

The European Green Deal policy ambitions set out in the Chemicals Strategy for Sustainability and the Zero Pollution Action Plan, identify the necessity for a Safe and Sustainable by Design (SSbD) approach to novel materials (European Commission, 2019). This need is addressed by the H2020 SUNSHINE project, in which has been developed a SSbD approach for advanced materials and applied it to specific multi-component nanomaterials (MCNMs). The SUNSHINE approach enables assessment of safety and sustainability at each stage of product development from a lifecycle perspective (Figure 1). This is achieved via a tiered approach that uses screening-level qualitative (Tier 1), semi-quantitative (Tier 2) and quantitative (Tier 3) assessment methods for the later stages. The focus of this contribution is on the qualitative Tier 1 self-assessment methodology designed to evaluate the safety, functionality and sustainability in the early R&D stages of developing advanced materials. This approach was developed to be easily implementable by industries, especially SMEs, which often do not have sufficient time and/or expertise to engage in resource-intensive safety and sustainability evaluations. This early screening self-assessment approach was tested on a real industrial case study in the SUNSHINE project, i.e., nano-enabled PFAS (Polyfluoroalkyl substances)-free anti-sticking coating for bakery molds. The results have shown that the innovative coating material has superior performance in terms of safety, functionality and sustainability as compared to a benchmark material (Teflon).

Figure 1 Life cycle thinking applied to the SSbD approach with the safety, sustainability and functionality dimensions taken into consideration.

References

European Commission (2019) 'Green Deal'.

A Comparative Life Cycle Assessment of Two Tanning Processes: Innovative Green Organic vs Traditional Chrome-Based

M. Menegaldo[1]*, A. Carlesso[1], L. Pizzol[1], A. Zabeo[1], R. Pasquale[2], E. Semenzin[1], A. Marcomini[1]

[1]Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Scientific Campus,
via Torino 155, 30172 Mestre, VE, Italy
[2]GSC Group S.P.A. Via dell'industria, 5, 36054 Montebello Vic.no, Vicenza, Italy

martina.menegaldo@unive.it

In Valle del Chiampo area (Veneto, Italy), tanning companies are facing a challenge related to the conversion of the conventional chrome-based leather production throughout a more sustainable leather production based on vegetable and synthetic tannins. The proposed technology relies on the combination of polymer-based chemicals and protocols which allows to produce chrome-free high-quality leather, to reduce hazardous substances, environmental risks and to simplify the entire tanning process (Pasquale et al. 2019). The achievement of this goal was supported by the LIFE GOAST (Green Organic Agents for Sustainable Tanneries) project. As part of this project, a Life Cycle Assessment (LCA) (ISO 14040-44) was performed to compare the innovative tanning process GOAST with the traditional tanning process TCTP (Traditional Chrome Tanning Process) environmental performance. The LCA was performed, from a "gate to gate" perspective and taking 1 kg of tanned hides per year as the functional unit. The Impact Assessment (LCIA) has been performed using the Environmental Footprint (EF) method and database 2.0 and applying the Simapro 9.1 software. The overall results suggested that the innovative tanning process (GOAST) could reduce the environmental impacts related to the traditional, chrome-based, leather production. Indeed, the TCTP process is very impactful for the impact categories related to toxicity due to the use of chrome as tanning agent. The LCA analysis also indicates the need for future optimization for the innovative tanning process (e.g., CO_2 emissions, land use, water consu

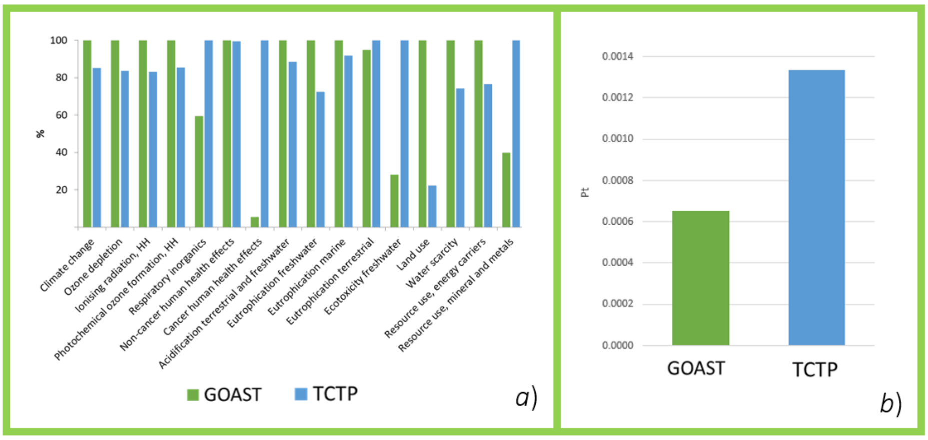


Figure 1: a) LCA characterized results at midpoint level; b) LCA single score results.

References

ISO 14040. 2021. "Environmental Management - Life Cycle Assessment - Principles and Framework ISO 14040:2021."

ISO 14044. 2021. "Environmental Management - Life Cycle Assessment - Requirements and Guidelines ISO 14044:2021."

Pasquale, R., C. Bortolati, F. Serafini, M. Signoretto, S. Tieuli, M. Silvestri, and L. Frighetto. 2019. "Life Goast Green Organic Agents for Sustainable Tanneries (LiFe16 Env/IT/000416)." in 35th IULTCS Congress 2019: "Benign by Design" Leather - The Future Through Science.

Waste to Energy: Agro-industrial Waste Valorisation Toward Enriched Pellet Production

Z. V. Simić[1]*, G. R. Ivaniš[2], S. P. Miškov Panić[2], M. Lj. Kijevčanin[2] and I. R. Radović[2]

[1]Innovation Center of the Faculty of Technology and Metallurgy, Belgrade, R. Serbia
[2]University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, R. Serbia

zsimic@tmf.bg.ac.rs

The negative impact of the use of fossil fuels on the environment has led to an increase in research in the field of renewable energy sources and intensified the production of biodiesel. The latter has caused the accumulation of a large amount of waste glycerol, since about 1 kg of crude glycerol is obtained for 10 kg of biodiesel. Crude glycerol is traditionally considered a low-value waste because of impurities and variable composition and its disposal was limited due to the harmful effects on the environment. To reuse this by-product of the transesterification reaction, in most cases it needs to be refined. However, crude glycerol purification requires additional costs while at the same time the glycerol market is already saturated and, consequently, the price of crude glycerol continues to decline. To avoid the accumulation of waste glycerol and pollution of the environment, it is necessary to find some applications for the raw glycerol obtained from the industrial production of biodiesel (Groesbeck et al., 2008).

Crude glycerol can be integrated with waste biomass, such as agricultural waste and wood residues, to improve its properties as a fuel. During the production of pellets, raw glycerol serves as a binder, which increases the yield and durability of pellets during storage and transportation. Additionally, it serves as a lubricant reducing the energy required for palletisation. It has been shown that when burning pellets with additional raw glycerol, a significantly lower amount of NOx is released than in the case of classic wood pellets (Zhang et al., 2022).

In this study, we investigated the possibility of adding waste crude glycerol to waste agro-industrial biomass in the production of enriched pellets. By applying the basic principles of the circular economy, the glycerol used for the purposes of this research was obtained from the transesterification reaction between used edible oil and short-chain alcohol, with the presence of a catalyst obtained from the waste shell of chicken egg. The characterization of the mixtures of different agricultural biomass and agro-industrial waste with different mass fraction of crude glycerol was performed. Standard analyses for determining the quality of pellets (such as calorific value, ash content, etc.) were performed to examine the possibility of using the enriched pellets obtained in this way in existing boilers designed for the use of commercial pellets.

Acknowledgements: This work was supported by United Nations Development Programme and Global Environment Fund (CIRCULAR VOUCHERS – Ref: 00123168/01-01) and by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contracts No. 451-03-47/2023-01/200135 and 451-03-47/2023-01/200287).

References

Groesbeck, C.N. et al. (2008) 'Effect of crude glycerol on pellet mill production and nursery pig growth performance', J. Anim. Sci., 86, p. 2228–2236 doi:10.2527/jas.2008-0880.

Zhang, J. et al. (2022) 'Crude glycerol and glycerol as fuels and fuel additives in combustion applications', Renew. Sust. Energ. Rev., 159 112206 doi: https://doi.org/10.1016/j.rser.2022.112206.

Hybridization of Pineapple Leaf Fiber with Natural Nanotube as Promising Sustainable Fillers for Improving Mechanical Properties of Epoxy Composite

N. Klinthoopthamrong[1], S. Thanawan[1], P. Sunintaboon[1], and T. Amornsakchai[1,2]*

[1]Mahidol University, Department of Chemistry, Polymer Science and Technology Program, Phuttamonthon 4, Salaya, Phuttamonthon, Nakhon Pathom, 73170, Thailand
[2]Mahidol University, Faculty of Science, Center of Sustainable Energy and Green Materials, Phuttamonthon 4, Salaya, Phuttamonthon, Nakhon Pathom, 73170, Thailand

taweechai.amo@mahidol.edu

Nowadays, several industries have been forced to reduce their carbon emission and non-sustainable products owing to the concern over climate crisis issue. To replace petroleum-based or synthetic materials, natural fiber composite receives tremendous attention due to its low carbon footprint and light weight. In this current work, pineapple leaf fiber (PALF) and halloysite nanotube (HNT) were combined as promising sustainable fillers for the reinforcement of epoxy composite. About 20 wt.% of PALF was unidirectionally arranged as fiber sheets and immersed in epoxy resin (EP) containing different HNT concentration levels (1-5 wt.%) via a hand layup method. The mixture of each formulation was left to cure under compression molding at room temperature for 48 hours and the hybrid epoxy composite was then obtained. We found that the incorporation of PALF highly promoted mechanical properties of EP composite. In contrast, impact strength of the composite reinforced with 5 wt.% HNT was slightly increased compared to that of neat EP (0HNT). For hybrid EP, HNT and PALF worked perfectly as effective reinforcing fillers. The incorporation of 3 wt.% HNT with PALF provided the highest strength and impact resistance over all EP samples. Compared with PALF composite (without HNT), its modulus was increased from 7080 to 7958 MPa and their flexural strength was increased from 145 to 154 MPa. Moreover, impact strength of the hybrid composite was improved by 108% compared with PALF composite and by 1355% compared with neat EP. Field Emission Scanning Electron Microscopy (FESEM) micrographs also confirmed an increase of surface roughness generated by many tiny crack paths, relating to more energy being dissipated when HNT was combined into the matrix. Dynamic Mechanical Thermal Analysis (DMTA) revealed that the addition of HNT did not affect glass transition temperature and increase thermal stability of the composite. The prepared hybrid composite could be beneficial for being used as structural materials and in automotive application (e.g., dashboard, door panels, and bumpers).

Catalysts for a Sustainable Future: from Synthetic Fuels to Water Treatment

J. L. Faria[1,2]*

[1]University of Porto, LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2]University of Porto, ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

jlfaria@fe.up.pt

Catalysts play a critical role in promoting chemical and biochemical reactions, and their use is essential in almost any industrial process. However, the paradigm of the XX Century based on activity performance led to the development of catalysts that can be environmentally harmful due to their high cost, toxicity, and limited availability. Green Chemistry and Green Engineering paradigms demand effective and environmentally sustainable catalysts.

Carbon-based catalysts have gained significant attention recently due to their low cost, abundance, and eco-friendliness. Typical examples of our previous works (Gomes, 2020; Machado, 2022) involve activated carbons, carbon nanotubes, graphene, and, more recently, carbon nitrides and graphyne. Due to limitations such as high cost, toxicity and limited availability, metal-free catalysts are preferred whenever possible. We address this challenge by using straightforward catalyst synthesis, starting from sustainable sources and chemicals, eliminating solvents other than water as much as possible, compromising the use of metals with atomic economy, and a workable ratio of selectivity-to-activity performance.

Carbon-nanotube-based catalysts modified with cobalt were synthesized by chemical vapor deposition. They will be used in a proprietary NETmix reactor aiming at high-performance Fischer-Tropsch synthesis of new fuels. Producing synthetic fuels of superior quality than those obtained by oil refining leads to a significant reduction in air emissions, substantially contributing to the carbon circular economy.

Mitigation of air pollution effects in big cities and industrial areas can be achieved through photocatalysis with solar activation. The need for UV activation severely limits the benchmark photocatalyst (titanium dioxide). In this study, we describe using carbon nitride as a photocatalyst to produce a visible light active multifunctional coating with photocatalytic and hydrophobic properties for integral protection of building materials.

Transfer of pollutants from different origins (air and surfaces) or incomplete degradation processes leads to critical water contamination in the hydrosphere, with an apparent negative impact on Earth’s climate and life support. Carbon nitride can be molded in different shapes by 3D-printing to produce effective photocatalyst frameworks adaptative to specific treatment needs. Some of the presented photocatalysts perform remarkably in removing psychoactive drug mixtures from water streams.

The three examples use carbon-based catalysts and photocatalysts to provide sustainable chemical solutions that immediately benefit society and the environment. Engineering systems for chemical applications in a sustainable future involve designing efficient, environmentally friendly, and economically feasible processes. That requires a new generation of catalysts and photocatalysts and novel approaches to their development.

Financial support by LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC); project Cat4GtL (POCI-01-0247-FEDER-069953), co-funded by ERDF through COMPETE 2020 under PORTUGAL 2020.

References

Gomes, H.T., Faria, J.L. (eds.) (2020) Catalysis for Global Development. Contributions Around the Iberoamerican Federation of Catalysis. Basel, Switzerland: MDPI.

Machado, B.F., Liu, L., Yu, Z.P., Faria, J.L. (2022), ‘Supported Metal Single-Atom Photocatalysis (Cap. 14)’. In: Serp, Ph., Minh, D.P. (eds), Supported Metal Single Atom Catalysis. Weinheim, Germany: Wiley-VCH GmbH.

Formulation of Synthetic Particulate Matter and Development of a Deposition Technique for Corrosion Studies

F. Bonfante[1], I. Vassura[1,2], C. Chiavari[3], C. Martini[4], E. Bernardi[1,2] *

[1]University of Bologna, Department of Industrial Chemistry "Toso Montanari", Viale del Risorgimento 4, 40136, Bologna, Italy
[2]University of Bologna, Center for Industrial Research - Fonti Rinnovabili, Ambiente, Mare e Energia (CIRI FRAME)
[3]University of Bologna, Department of Cultural Heritage, Via degli Ariani 1, 48121, Ravenna, Italy
[4]University of Bologna, Department of Industrial Engineering, Viale del Risorgimento 4, 40136, Bologna, Italy

elena.bernardi@unibo.it

Particulate matter (PM) is known to endanger not only human health and ecosystems, but also materials. In particular, PM can affect cultural heritage by processes of soiling and physical-chemical damage that deserve further investigations (Vidović K. et al. 2022). Tests in laboratory-controlled conditions can contribute to investigate the impact of different PM amounts and compositions on material decay, also in relation with different climate scenarios, as well as to assess the efficiency of new protective treatments with respect to this aggressive factor. Within this context, the aim of this work was to develop a reproducible and easily replicable methodology to create representative synthetic PM mixtures and to deposit them on specimens (by simulating dry deposition phenomena), in order to introduce PM in artificial ageing protocols. A quaternary bronze (Cu-5Sn-5Zn-5Pb) was chosen as a reference substrate for the development and validation of the methodology. On the basis of a wide literature survey, a general PM10 formulation was defined and, in this phase, water soluble and insoluble inorganic fractions, as well as elemental carbon were considered for formulating the PM mixture. The influence of each fraction in the formulation, deposition and ageing steps was evaluated by preparing and depositing mixture at different level of complexity. Each compound was ground to a particle size consistent with its environmental size distribution (fine or coarse PM fraction), then mixed with the others respecting the previously defined proportions. The dry deposition was simulated by blowing the synthetic PM on the specimens, with the aid of an airbrush. Operational conditions were standardized to obtain replicable results. The deposition process was validated by verifying that the ionic ratio of the deposits matched with the one of the starting mixture. Finally, to test and validate the whole methodology, bronze samples with PM mixtures were submitted to accelerated ageing simulating outdoor conditions. The ageing was conducted for three weeks in a climatic chamber by setting up a cycle simulating combined day-night and seasonal conditions. Morphological and chemical evolution of both PM and bronze surfaces was followed mainly by SEM-EDS and Raman analyses. Results obtained on the different replicates were consistent with each other. In general, synthetic PM was able to progressively corrode the surfaces by forming copper and lead corrosion products typical of outdoor bronzes. According to the Cl- and S- containing corrosion products found on the samples (Kratschmer A. et al. 2002), the chosen ageing conditions were able to accelerate the products formation in the order of months/years. Moreover, the presence of the water insoluble fractions favored both the deposition phase and the development of corrosion products. In conclusion, a replicable methodology to create and deposit synthetic PM mixtures was developed and validated on bronze substrates. This provides an interesting and innovative tool for assessing the impact of PM on materials, by allowing to include PM in accelerated ageing tests.

References

Vidović, K. et al. (2022), Impact of air pollution on outdoor cultural heritage objects and decoding the role of particulate matter: a critical review, Environmental Science and Pollution Research, 29, p. 46405–46437. doi: https://doi.org/10.1007/s11356-022-20309-8

Kratschmer, A. et al. (2002), The evolution of outdoor copper patina, Corrosion Science, 44, p. 425-450. doi: https://doi.org/10.1016/S0010-938X(01)00081-6.

Sustainable Conservation of Cultural Heritage through Alternative Solutions for Mitigating Biodeterioration Based on Plant Extracts or Silver Derived Nanoparticles

V.M. Corbu[1,2*], M. Cudălbeanu[3], A.Ș. Dumbravă[1], I.C. Marinaș[2], S.M. Avramescu[3], L. Marinescu[4], D. Ficai[4], A. Ficai[4], T.E. Șesan[1], I. Gheorghe-Barbu[1,2], I. Balotescu[2], M.C. Chifiriuc[1,2]

[1]University of Bucharest, Faculty of Biology, Intr. Portocalelor no 1-3, 060101, Bucharest, Romania
[2]Research Institute of the University of Bucharest, St. B.P. Hasdeu, no 7, 050107, Bucharest, Romania
[3]University of Bucharest, Faculty of Chemistry, Bd. Regina Elisabeta 4-12, 030018, Bucharest, Romania
[4]University Politechnica of Bucharest, Faculty of Applied Chemistry and Materials Science, St Polizu, no 1-7, 011061, Bucharest, Romania

viorica-maria.corbu@bio.unibuc.ro

The biodeterioration of cultural heritage objects is caused by the ability of different microorganisms, especially filamentous fungi, to form biofilm-type associations on different substrates (from stone to paper) and to produce organic acid-type metabolites, enzymes, pigments or mycotoxins) that could alter the respective objects. The deterioration could be also the result of the presence of environmental pollutants, of different climatic factors or applied chemical treatments. In this context, searching for new effective conservation strategies to prevent this process and preserve/restore the monuments' value is acutely needed (Liu et al., 2022). The present study aimed to investigate the effectiveness of silver nanoparticles (AgNPs) or plant extracts against a significant number of fungal strains isolated from XVII-XIXth centuries wooden and stone cultural heritage churches located in different Romanian regions.

The AgNPs were obtained using the solvo-thermal method and characterized using FT-IR, SEM, TEM, DLS and XRD analysis. The hydroalcoholic extracts (Vaccinium myrtillus, Equisetum arvense, Polygonum hydropiper, Taraxacum officinale, Artemisia abrotanum, Corylus avellana, Origanum vulgare, Artemisia absinthium, Xanthium spinosum, Hypericum perforatum, Salix alba, Plantago lanceolata and Ononis spinosa) were obtained using the microwave extraction method, their chemical composition was determined by HPLC analysis and antioxidant activity by DPPH and FRAP methods. Both NPs and natural extracts were tested against 75 fungal strains (Penicillium spp., Aspergillus spp. and Purpureocillium spp.) to demonstrate their antimicrobial activity spectrum against planktonic cells and inhibitory effect upon their deteriogenic machinery mediated by enzymes/organic acids production.

The tested AgNPs have a spherical shape and a size smaller than 10 nm and exhibit high efficiency against biodeteriogenic fungi, inhibiting the mycelial growth of more than 50% of the tested strains, the best results being obtained for Aspergillus strains (mean MIC values of 0.97-23.76 µg/mL). For the hydroalcoholic extracts, the best results were obtained for O. spinosa (MIC=15.03%), A. abrotanum (MIC=26.88%) and H. perforatum (MIC=28.07%) plant extracts. Their inhibitory activity could be correlated with the presence of polyphenolic compounds (phenolic acids and flavonoids) as main compounds, known for their antimicrobial and antioxidant properties. Furthermore, both nanoparticles and vegetal extracts inhibited to the production of enzymes such as esterase, amylase, and protease involved in biodeterioration, the best inhibitory effect being obtained for AgNPs.

Thus, the tested solutions might represent an ecological and economical alternative for the currently available chemical products used for heritage protection/ restoration treatments showing high antifungal efficiency against dominant etiological agents of Romanian heritage objects biodeterioration.

We acknowledge the financial support of the Research Projects PN-III-P2-2.1-PED-2021-2526 (736 PED/2022) and C1.2.PFE-CDI.2021-587, (41PFE/30.12.2021).

References

Liu, X., et al (2022). Innovative approaches for the processes involved in microbial biodeterioration of cultural heritage materials. Current Opinion in Biotechnology, 75, 102716.

Holistic Approach to the Examination of the Environment and Climate Influence on the Stone Façade of the XVIII Century

M. Valuh[1], B. Miljević[2], M. Mišljenović[2], S. Vučetić[1]*

[1]University of Novi Sad, Faculty of Technology, Laboratory of Materials in Culutural Heritage, Novi Sad, Serbia
[2]Institute for the protection of Cultural Monuments of the City of Novi Sad, Bul. Mihajla Pupina 22, 21000 Novi Sad, Serbia

heritagelab@uns.ac.rs

The Serbian Orthodox Church dedicated to the Saint Mary was built in the period from 1737 to 1758 in a baroque style and it is the last church built in the so-called Moravian style. The Church is located in Sremska Kamenica, near Novi Sad, the cultural and administrative centre of Vojvodina, the northern Serbian autonomous province. Since 1949, it has been protected as a cultural monument of great importance. Moreover, since the summer of 2002, part of the relics of Saint Petka have been in the church. Considering the importance of the Saint Mary church the aim of our research was to preform holistic characterization of the façade stone, detecting causes, mechanism and consequence of constitutive materials deterioration in order to propose adequate conservation methodology. To achieve this, in-situ investigation of the stone façade was done using HeritageLab mobile equipment: digital microscope (PRO10-3, Vitiny, USA), colorimeter/spectrophotometer (CM 700D, Konica Minolta, Japan), Fourier transformed infrared spectrometer (ALPHA, Bruker Optics, Germany), X-ray fluorescence spectroscopy (ARTAX, Bruker, Germany) salt content analysis (Quantofix strips, Macherey-Nagel, Germany), and thermal imaging camera (T440bx, FLIR, USA). The FTIR analysis was used to identify the mineral composition of the materials used in the construction of the church, which is a common method in the analysis of historic stone buildings and monuments (Ashurst and Dimes, 1990). The in-situ measurements of soluble salts were used to assess the degree of degradation of the materials, which is a critical factor in the conservation of historic structures (Semple, 2015). The digital microscopy of materials and IR camera were used to investigate the microstructure and moisture content of the materials, respectively, which are important factors in the long-term preservation of historical buildings and monuments (Sabbioni and Vos, 2000). The results of the study reveal that the materials used in the construction of the church are of good quality but highly degradated. Different types of degradation such as: patina, dirt deposits, eroding surfaces, yellow black crusts, large amounts of carbonaceous particles responsible for black shading of the stone surface, soluble salts, microbiological corrosion and stone powdering and exfoliation, were identified due to environmental and climate influences. Based on the gained results, combining several diagnostic techniques it was possible to determine the state of the original stone material, its degradation degree, and environmental impact on the identified degradation patterns which represented the basis for selecting adequate cleaning and protection strategy.

Acknowledgements
The investigation was supported by Serbian Ortodox church, The Ministry of Science of the Republic of Serbia, Technological Development and Innovation (451-03-47/2023-01/ 200134) and EUREKA PROGRAM, Advanced CleAning and Protection of TANgible culture heritage, CAPTAN E!13085.

References

Ashurst, J. and Dimes, F.G. (1990). Conservation of historic stone buildings and monuments. Butterworth-Heinemann.

Semple, J. (2015). Architectural and engineering methods in the analysis of historic structures. Routledge.

Sabbioni, C. and Vos, W.L. (2000). Environmental monitoring for cultural heritage. Kluwer Academic Publishers.

Evaluation and Monitoring of Climate Change Impacts on Architectural Surfaces in Venice

M. Gnemmi[1]*, L. Falchi[2] and E. Zendri[2]

[1]Ca'Foscari Univerzity of Venice, Department of Environmental Sciences, Via Torino 155, 30172, Venice Mestre, Italy and
Sapienza University of Rome, Department of Sciences of Antiquity, P.le Aldo Moro 5, 00186, Rome, Italy
[2]Ca'Foscari Univerzity of Venice, Department of Environmental Sciences, Via Torino 155, 30172, Venice Mestre, Italy

margherita.gnemmi@uniroma1.it

Considering the widespread presence of historical architectural limestone surfaces, Venice is a significant case study to assess the impact of climate change on cultural heritage. The present study focuses on the investigation of the effects of climate on Istrian stone surfaces, a limestone typical of venetian buildings, and proposes a non-invasive methodology to assess the physical, chemical, and morphological evaluation of environmental impacts. Open access data reported by the Regional Agency for Environmental Prevention and Protection -ARPAV- were processed, and the meteorological stations of the historical city center were considered to track temperature, precipitation and wind trends over the last twenty years. The data showed that the average temperature in Venice has increased over the previous twenty years, maintaining a relatively stable upward trend in recent years, and that rainfall phenomena have become increasingly intense. The relationship over time between the state of conservation of architectural surfaces and the considered environmental indicators was analysed through the surface analysis of three significant historic Venetian buildings (Ca' Foscari, Ca' Dolfin, Palazzo Garzoni) (Falchi et al., 2019). Roughness variation by surface profiling, associated with morphological observations by digital microscopy, and chemical analyses of the surfaces by infrared spectroscopy, allowed us to evaluate stone current surface textures and degradation patterns related to environmental factors and to quantify the decay trends. Results showed that morphological variations of the surfaces were closely related to the environmental impacts by considering the building position (nearby or far away from canals), façade location (overlooking canals or courtyards), and the specific exposure to rain. The morphology assessment of exposed areas pointed out smooth eroded areas and preferential runoff channels due to heavy water drain-off and wind-driven rains, with an average thickness loss of around 0,8 mm in five years (from 2015 to 2020). Future climate scenario and their possible impacts on stone surfaces were considered, too. Venice will face warmer and moister climates according to different future climate scenarios analysed by different climate models (European Commission, 2022). Seasonal precipitation will increase, with high intensity in winter and autumn rainfall, while a decrease in summer rainfall is expected. Rain is the most evident signal of climate change, with a possible increase in the surface degradation of historical buildings (Spano et al., 2021). To assess the future damage risk on architectural surfaces related to climate change, the proposed non-invasive methodology, easily reproducible in situ, can be a helpful tool to monitor the state of conservation and the transformations to which the city of Venice will be subjected due to climatic change. Moreover, non-invasive monitoring plays a crucial role in planning preventive maintenance of historical buildings by assessing the performances and suitability of the protective materials currently applied on the stone surfaces.

References

Falchi, L. et al. (2019) 'Investigation on the Relationship between the Environment and Istria Stone Surfaces in Venice.', Atmos.Environ.210,76-85. https://doi.org/10.1016/j.atmosenv.2019.04.044.

European Commission, Directorate-General for Education, Youth, Sport and Culture (2022), 'Strengthening cultural heritage resilience for cultural climate change: where the European Green Deal meets cultural heritage ', Publications Office of the European Union. https://data.europa.eu/doi/10.2766/44688.

Spano, D. et al. (2021) 'Analisi del rischio. I cambiamenti climatici in sei città italiane:Venice'.
doi: 10.25424/cmcc/analisi_del_rischio_2021.

Study on a Co-Benefit Legal and Policy Frameworks for Driving Toward Zero Emissions of Air Pollutants and Greenhouse Gases in Asia Region Using Policy Simulation with Cost-Benefit Analysis Models

E. Komotsu[1]*, D. Narita[2], T. Morikawa[3]

[1]Meiji University Centre for Environmental Law and Policy, 5-80 Aioi , Naka-ku, Yokohama, 231-0012, Japan
[2]The University of Tokyo Graduate School of Arts and Sciences, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan
[3]Japan Automobile Research Institute 2530 Karima, Tsukuba, Ibaraki, 305-0822, Japan

ccs2016@meiji.ac.jp

Asian high economic growth in recent decades has resulted in the region's equally high growth in carbon emissions. As a consequence, a significant part of global carbon emissions are now Asian developing economies. Correspondingly most of the world's most polluted cities are concentrated in Asia.

In this study, a cost-effectiveness analysis model (CEAM) for air pollutants reduction measures was developed using the marginal cost in order to study to achieve clean air in Asian urban areas. We fund that there is a 10-fold gap in reduction efficiency without considering cost-effectiveness.

Policy simulation results it is difficult to achieve the standard such as WHO guidelines (2021) even by applying reasonably available control technologies that optimized using CEAM and Community Multi-scale Air Quality (CMAQ), therefore policies to additional large-scale reduction using maximum technically feasible reduction measures (MTFR) and contributions of transboundary transfer from nearby countries are necessary.

MTFRs for air pollutants contribute to large GHG reductions, but are very high-cost, thus became very poor external economics. In this study, the analytical methodology that takes into account the relationship between policies to achieve GHG long-term targets and measures to clean air was developed, and by optimizing the each scenarios, a co-beneficial countermeasure scenario will be studied.

Finally conducting policy simulations for each Asian countries using the developed methodology, we address the co-beneficial policy frameworks in Asia region.

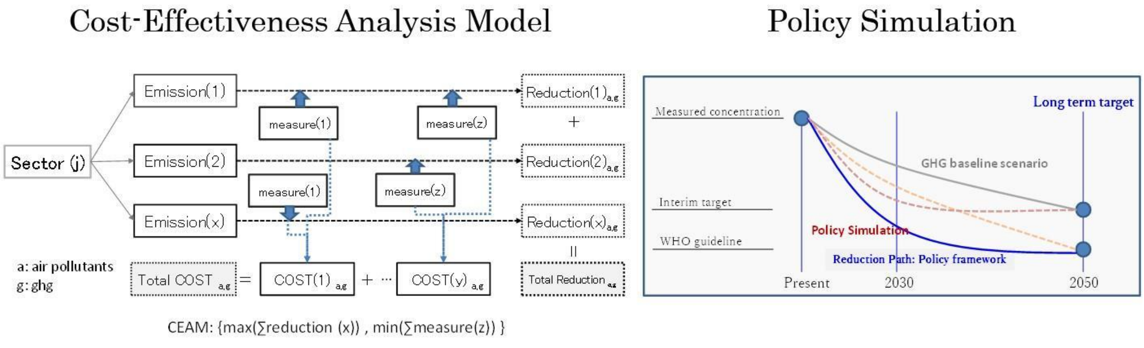


Figure 1 CEAM and Policy Simulation for co-benfit framwork

References

Komatsu, E. et al. (2022) 'Legal and political framework for CCUS with negative carbon emissions development in Asia', ISDRS 2022 Conference full paper.

Yanagi, K., et al. (2019) 'The importance of designing a comprehensive Strategic Environmental Assessment (SEA) & Environmental Impact Assessment (EIA) for carbon capture and storage in Japan', Int. J. Greenh. Gas Control. 91, 102823.
E. Komatsu, (2020) 'Open Innovation Model: Global Warming As a Challenge and Driver for Innovation', In book.

Availability of Data from Environmental Risk Assessments of Medicinal Products Status Quo and Proposed Monograph System for Environmental Data

S. Schwonbeck[1*,] S. Hahn[1], K. Teppe[2], C. Floeter[3]

[1]Fraunhofer ITEM, Department Chemical Safety and Toxicology, Nikolai-Fuchs-Str. 1, 30159 Hannover, Germany,
[2]Umweltbundesamt, Wörlitzer Platz 1, 06844 Dessau-Roßlau, Germany,
[3]Hamburg University of Applied Sciences, Faculty Life Sciences, Department Environmental Engineering, Ulmenliet 20
21033 Hamburg, Germany

susanne.schwonbeck@item.fraunhofer.de

For more than 15 years, medicinal products for human and veterinary use have had to undergo a marketing authorisation procedure before they can be launched on the European market. This procedure includes the assessment of the environmental risk (ERA) posed by the product after it has been used by the patient (or in the animal) and released into the environment. The environmental data collected are part of the marketing authorisation dossier, which is usually considered confidential and therefore not accessible to the general public, environmental agencies responsible for water management and scientists. Therefore, these data cannot be used for risk assessment and management, development of regulatory framework or scientific purposes. In addition, minor differences in data for the same active pharmaceutical ingredient (API) may lead to different conclusions in the authorisation procedure.

In order to address these shortcomings, the European Commission (EC) has commissioned an external feasibility study on potential alternatives to the existing authorisation system for veterinary medicinal products. The report of this study is available since October 2021 (Schwonbeck et al., 2021) and the EC has come forward with its recommendations to the European Parliament (COM(2023) 9 final) in January 2023.

The feasibility study analysed the recommendations and their implications in light of general EU goals stated in the EU Strategic Approach to Pharmaceuticals in the Environment (COM(2019)128) and in the Green Deal – zero emission – one substance, one risk assessment (OS-OA) approach (COM(2019)640). The EC states that it is appropriate to wait for the revision of the legal framework for human medicinal products before considering implementing the monograph system, because the new legislation would likely include new ERA requirements.

Thus, the results of a comparison of the data requirements for the ERA for human and veterinary medicinal products are presented. Special attention is given to newly required data categories of the draft version of the ERA guideline on human pharmaceuticals (EMEA/CHMP/SWP/4447/00 Rev 1), such as the assessment of persistent, toxic and bioaccumulative (PBT) properties of the active substance, to endocrine active substances (EAS), to the evaluation of the quality of studies and risk mitigation measures when a risk has been identified.

References

Schwonbeck, S., Breuer, F., Hahn, S., Brinkmann, C., Vosen, A., Radic, M., Vidaurre, R, Alt, J., Oelkers, K., Mezler, A., Floeter, C., (2021) 'Feasibility Study of an Active-substance-based Review System ('Monographs') and Other Potential Alternatives for the Environmental Risk Assessment of Veterinary Medicinal Products', EW-06-21-127-EN-N, European Union, Luxembourg, p 1-429. doi: 10.2875/94477.

Environmental Life Cycle Assessment Applied to Medical Devices

L. Pizzol[1], A. Livieri[1], A. Zabeo[1]*, S. Devecchi[1], M. Menegaldo[1], A. Sellitri[1], A. E. Luzuriaga[2], A. A. Izquierdo[2], T. Oroz[3], O. I. Moreno[4], D. Hristozov[1]

[1]GreenDecision srl, Via Torino 155, 30172 Mestre - Venezia (VE), Italy
[2]Fundacion Tecnalia Research & Innovation (TECNALIA), Parque cientifico y tecnologico de bizkaia, astondo bidea, edificio 700, derio bizkaia 48160, Spain
[3]Tecnologia Navarra de nanoproductos sl (TECNAN), Area industrial perguita c/a 1, los arcos 31210, Spain
[4] Biokeralty, C/Albert Einstein 25, Parque Tecnológico de Álava, Miñano ,01510 Vitoria-Gasteiz (Álava), Spain

alex.zabeo@greendecision.eu

The European Green Deal aim to transform the EU's economy into a more sustainable one with policies focusing on human health and environmental protection, climate, biodiversity and circularity, (European Commission, 2019). This includes an ambitious plan to tackle pollution from all sources and progress towards a zero-pollution economy for a toxic-free environment. With the European Green Deal, the EU commits both to reduce net greenhouse gas emissions by at least 55% by 2030, and to reach no net emissions by 2050. The health and care systems are not exempt from assessing, mitigating, and improving the environmental impacts across all the health and care value chain. Indeed, the healthcare sector is responsible for 4-5% of global total carbon emissions, and generates significant demands for energy and materials, as well as dangerous waste streams that can cause pollution on air, soil and water matrices.

These impacts can be assessed by applying widely established tools for quantitatively determining the environmental (e.g., Life Cycle Assessment, LCA), economic (e.g., Life Cycle Costing, LCC), and social (e.g., Social Life Cycle Assessment, s-LCA) impacts of products, processes, and services across the entire life cycle. The importance of employing a life cycle perspective in assessing sustainability of production and consumption systems has been increasingly acknowledged in the EU policies since the early 1990ies. The European Green Deal (European Commission, 2019) includes several policy initiatives which cite and mention LC thinking and methods. In the Chemical Strategy for Sustainability (European Commission, 2020) a life cycle perspective is required in the identification and minimization of potential negative impacts linked to chemicals and material.

These types of assessments are needed also for nanomaterials that are increasingly applied in many sectors such as construction, textile, food, cosmetics and medicine. Indeed, the application of nanomaterials in medicine has led to novel pharmaceuticals and medical devices that have demonstrated a strong potential for increasing the efficacy/performance, safety of therapeutic and diagnostic procedures to address a wide range of diseases.

To facilitate the fast transition to the market of new nanotechnology-based medical technologies, the European Commission funded SAFE-N-MEDTECH (https://safenmt.com) which is an Open Innovation Test Bed (OITB). It offers companies and reference laboratories the capabilities, knowhow, networks and services required for the development, testing, assessment, upscaling and market exploitation of nanotechnology-based Medical and Diagnosis Devices.

One of the objectives of the SAFE-N-MEDTECH is to assess the sustainability of nano-based medical technologies along the entire life cycle of the product through LCA techniques.

The topic of this contribution is to present a LCA study for a nanotechnology-based medical device which is a coating developed by TECNAN and evaluated within SAFE-N-MEDTECH. Thus, this study shows the results of life cycle environmental sustainability assessment of the innovative coating to prevent biological/microbial contamination to enhance MDs reprocessing.

References

European Commission (2019) ‘Green Deal’.

European Commission (2020) ‘Chemicals Strategy for Sustainability Towards a Toxic-Free Environment’.

Nitrogen Wars - Consequences of Failing Nitrogen Policy

W.T. de Lange[1,2]*

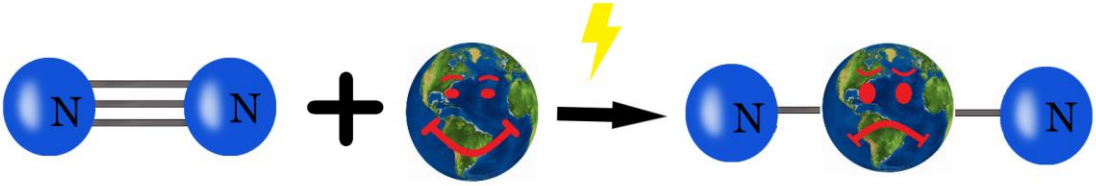
[1]Environment Agency Groningen, Lloydsweg 17, 9641 KJ Veendam, the Netherlands
[2]LaMilCo Consultancy, Groningen, the Netherlands

w@lamilco.nl

Ever since life emerged on planet Earth, nitrogen has been a key element due to its presence in main substances like DNA. In the early days of agriculture, it was the main limiting nutrient that was literally fought for, even leading to wars like the Guano Wars in South America. Since the 1800s, rapid population growth led to a large increase in demand for nitrogen around the world: guano, Chile saltpeter, and nitrogen compounds made out of air. Scientists like Birkeland[1], Ostwald, Haber and Bosch optimized[2] this process further: currently about 250 million metric tons ammonia per annum is produced, consuming 1 to 2% of the world's energy supply.

In the 21st century, the world is suffering from a surplus of nitrogen compounds. In many European countries, the amount of nitrogen compounds in the environment is one of the main causes of a dramatic biodiversity loss.
In the Netherlands, after decades of neglecting the problem by most actors involved, the highest administrative court ruled in May 2019 that the current strategy for reducing excess nitrogen in vulnerable natural areas is in breach of EU law. Since then, there is a lot of tension between all actors involved: lawmakers, scientists, farmers, industry and environmental movement, leading to an ongoing political crisis and stalemate.

This lecture puts the current situation in historical perspective and examines the possible political solutions, if any.



Planet Earth: from N deficiency to N abundance

References

Birkeland, K. (1906) 'On the oxidation of atmospheric nitrogen in electric arcs', Trans. Faraday Soc., 1906, 2, 98-116. doi: 10.1039/tf9060200098.

Smil, V. (2004) 'Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production', MIT Press, 2004

Can Master Students Experience and Learning Outcome be Improved?

Y. Stenstrøm[1,2]*, L. Jensen[3], L. Godager[4] and S. Antonsen[2]

[1]Dep. Chemistry, Biotechnology and Food Science, Norwegian University of Life Sciences
[2]Department of Mechanical, Electronics and Chemical Engineering, Oslomet - Oslo Metropolitan University
[3]Drammen sykehus, Vestre Viken Helseforetak.
[4]Dep. of Educational Science, Faculty of Science and Technology, Norwegian University of Life Sciences

yngve.stenstrom@nmbu.no

Most studies on the follow-up and supervision of students, are focused on PhD level, despite that most students complete their education with bachelor's or master's degrees. In previous studies on students working with their master's thesis in organic chemistry, our surveys revealed that many students feel that their own role and responsibilities are not well defined. This insecurity leads to decreased motivation and efficacy.

In some initial studies interviewing some students we suggested some measures to improve the situation. One of these was clarification of expectations. It seemed like a clear understanding of the student's expectation was important. But nearly equally important was their expectations of the supervisors, and an understanding on how they will be assessed during the master's thesis. This led to a targeted approach. The students worked more effectively on the different aspects of the project regarding theory, laboratory work, writing, data analysis etc., and thus had a better experience. The improvement was measured by questionnaires and interviews.

In this presentation, we will look more at the measures used, and results from qualitative study interviews done during the process. These interviews aimed to learn about students' experience of the whole process, in particular, what affected the motivation and how supervision affected how they approached learning outcomes.

These interviews also revealed that the students felt more confident with the assessment of the thesis after the measures were introduced. Even though the distribution of grades were not changed, students were more pleased with the given grade and the experience of doing a master's degree, compared to control group. In addition, we will focus on how the learning management system Canvas was used in combination with other digital resources and how the traditional group meetings were transformed into a learning forum. Students' feedback and experiences are reported.

Although the studies were done on organic chemistry students, the results are general and should easily be possible to implement in other disciplines as well.

Linking The Research and Education in an Intensive R&D and Innovation Process – A Model of the Jožef Stefan International Postgraduate School

M. Horvat, N. Ogrinc*

Jožef Stefan International Postgraduate School, Jamova 39, 1000 Ljubljana, Slovenia
Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

nives.ogrinc@ijs.si

The challenge of creating an environment where students can pursue excellent international comparative sciences while developing their creative and business skills is one of the major goals of Jožef Stefan International Postgraduate School (IPS). It was established in 2004 as an independent higher education institution and was strongly supported by larger Slovenian industry (Gorenje, Kolektor, Salonit) and an international network of cooperating universities and research institutes from the European Union, USA, Japan, and many other countries. The Jožef Stefan Institute provides the central research and educational basis, whereas other partners, such as invited research institutes, industrial and other enterprises also contribute their knowledge and innovation capacities for solving developmental problems.

Postgraduate studies for Master and Doctorate degrees are oriented towards solving research and development problems which require a multidisciplinary synthesis. The main research-educational strategy of IPS is therefore: (1) widening and deepening knowledge, and mastering and development of research methods and techniques, in natural sciences and high technologies, information and communication sciences and technologies, environmental sciences and ecotechnologies, and in management of technologies and innovations – with the aim of supporting excellence in basic research, strategic choice of priority developmental areas, systematic control and permanent innovation of processes and products, increasing economic efficiency and environmental acceptability; (2) development of an integral process of thinking which will support multidisciplinary communication, comprehensive definition of problems and their solving in group work, decision making in uncertain conditions, and long-term oriented strategic planning with emphasis on sustainable development. Realization of this strategy is presented more in detail in IPS study programs: Nanosciences and Nanotechnologies, Information and Communication Technologies, Ecotechnologies, and Sensor Technologies (www.mps.si).

Since 2004 a total of 442 PhDs, 40 masters of science and 86 professional masters are recorded at MPŠ. Given the very good qualifications, all students continue their careers in the academic sphere as postdoctoral fellows, mostly abroad, or continue their journey in the development departments of industry. The MPŠ model has proven to be very successful primarily due to its boutique nature, which places students at the center of the education process, both in terms of high-quality academic training, but also training in complimentary skills such as writing articles, work organization, leadership and effective communication at all levels.

References

www.mps.si

Higher Education Modernization-Pharmacist and Environmental Science

N. Milić1*, M. Milanović[1], S. Bijelović[2], J. Sudji[1], N. Milošević[1]

[1]University of Novi Sad, Faculty of Medicine, Department of Pharmacy, Hajduk Veljkova 3, 21000 Novi Sad, Serbia
[2]University of Novi Sad, Faculty of Medicine, Institute of Public Health of Vojvodina, Futoška 121, 21000 Novi Sad, Serbia

natasa.milic@mf.uns.ac.rs

There are numerous evidences about the negative effects of environmental contaminants on human health. However, many health-care professionals (i.e. medical doctors, dentists and pharmacists) are not able to comprehend the impact of environment on human health due to the lack of subject related to this topic during bachelor and master education. Therefore, it is of utmost importance to prepare future pharmacists for all the requirements of 21st century making environmental health and protection, a part of their standard curriculum. In Republic of Serbia, pharmacists are educated at four national universities. In spite of that, only at the Faculty of Medicine, University of Novi Sad, pharmacy students have possibility to choose as the elective subject "Water Quality in Pharmacy and Balneology”. Since 2014, this subject is included in the curriculum at the third year of integrated academic studies in pharmacy. The course aim is acquisition of knowledge in the field of quality, usage, importance and health safety of water for various purposes in the pharmacy and balneology. The course is organized through the combination of theoretical and practical lessons. In addition, students are obligate to wrote a report regarding the water supply system and the current status of wastewater treatment in their home town. Besides the important topics related to water as a raw material in the pharmaceutical industry and its application in hydrotherapy, water quality is studied from the wider perspective. Particularly, the current priority substances list under the Water Framework Directive and other substances of interest that can be present in raw water (in ng/L concentrations) together with the associated health issues are discussed. Visits to institutions such as Institute of Public Health, the public utility company "Water and Sewerage" and the special hospital for rheumatoid disease that deal with water quality issue from different angles are part of the practical education. Understanding the water quality for various purposes in the pharmacy, pharmaceutical industry and balneology and their importance in the health-care system realizing the close connection between health care and the environment are the expected outcomes of the course. There are numerous opportunities for pharmacy students and pharmacists to slow down ecosystem degradation and improve the status of the environment. The improvement of curriculum through making environmental health a part of the standard education could ensure acquisition of necessary competence for environmentally conscious pharmacy students.

Acknowledgement
This work was supported by the Provincial Secretariat for Higher Education and Scientific Research, AP Vojvodina, Republic of Serbia [Grant number 142-451- 3120/2022-01].

Research Guided Academic Teaching Concepts for Interdisciplinary Education in Arctic Environmental Sciences

R. Kallenborn[1], L. Yeung[2], H. Holbech[3]

[1]Norwegian University of Life Sciences (NMBU), Ås, Norway
[2] Örebro University (ÖU), Örebro, Sweden
[3]University of Southern Denmark (SDU), Odense, Denmark

The current observed changes in the circum-Arctic environment require new concepts for teaching the Arctic environmental experts of the future. These environmental changes are expected to result in dramatic changes in Arctic marine and terrestrial ecology as well as the cryosphere. These changes are both considered as economic and political opportunities as well as environmental disasters dependent on the intellectual angle. The current developments in the Arctic have, thus, the potential to provide a growing ground for potential conflicts both on a geopolitical, economic as well as environmental protection level. In many Arctic regions, already today the economic benefits of extracting and refining natural resources (i.e. minerals, petroleum, coal, etc) propagated by industrial enterprises are considered by conservation groups as in direct contrast to the urgent need for environmental protection. This situation is confirming the urgent need for balanced and sustainable international coordination in regional regulatory requirements for the Arctic region. The multifaceted requirements for inter-governmental-regional future regulations in the Arctic require comprehensive coverage and balancing all influencing factors. Therefore, a new generation of scientific academic experts must be educated with interdisciplinary expertise in environmental relevant sciences as well as in-depth understanding of geological, jurisdictive, and technological needs. Future Arctic environmental scientists need to approach environmental challenges with a strong interdisciplinary expertise and a solid understanding of the anthropogenic impact on the delicate Arctic ecosystem. Therefore, we established a new concept for the academic education of Arctic environmental scientists through the Nordic Master Program on Arctic environmental forensics. The Program will grant a double-degree master in chemistry (NMBU/ÖU) with a strong support of the ecotoxicology group at SDU. Some of the educational elements are also coming from the University Centre in Svalbard (UNIS).

The Nordic Master Program will be actively presented as an example for educational adjustments need for addressing future challenges in the region. During the presentation, general ideas and educational scenarios for possible University curricula for a study program in “Circum-Arctic regulation and environmental protection management” will be presented and discussed. The role of these educational and political developments as harbinger for other regions of the world will be highlighted.

Limits and Opportunities of Sorption Technology for the Removal of PMT and vPvM Substances from Water

B. M. Aumeier,[1] A. Georgi,[2] N. Saeidi,[2] G. Sigmund[3*]

[1]RWTH Aachen University, Institute of Environmental Engineering, Aachen, Germany
[2]Helmholtz Centre for Environmental Research – UFZ, Department of Environmental Engineering,Leipzig, Germany
[3]Environmental Technology, Wageningen University & Research, Wageningen, The Netherlands

gabriel.sigmund@wur.nl

Persistent, Mobile, and Toxic (PMT) and very persistent and very mobile (vPvM) substances are a growing threat to water security and safety. Many of these substances are distinctively different from other more traditional contaminants in terms of their charge, polarity, and aromaticity. This results in distinctively different sorption affinities towards traditional sorbents such as activated carbon (Sigmund G. et al. 2022, Sigmund G. et al. 2020). Additionally, an increasing awareness on the environmental impact and carbon footprint of sorption technologies puts some of the more energy-intensive practices in water treatment into question. We here critically review the interactions that drive removal of organic compounds via traditional sorbents like activated carbons, as well as next-generation sorbents such as cyclodextrins and zeolites. We also identify opportunities and limitations of tailoring sorbents for PMT and vPvM removal.

The current view that the combination of activated carbon sorption and its incineration or thermal regeneration can solve virtually all organic contaminant removal tasks may prove to be outdated. Increasing awareness about the risks of PMT and vPvM which challenges the global need to implement sustainability aspects in all areas of human activity are strong drivers for a diversification in water treatment technologies and materials. Sorption technologies will remain a valuable tool in future water treatment in view of the growing requirements for PMT and vPvM removal. However, commonly used approaches may need to be readjusted to become fit for purpose to safely and efficiently remove the large variety of PMT and vPvM substances while at the same time reducing the environmental footprint of these approaches. Traditional water treatment options may be complemented or replaced by novel on-site or in-situ regenerative approaches and next generation sorbent materials such as modified cyclodextrins, zeolites and metal-organic frameworks under certain conditions.

To achieve robust and environmentally sound water treatment options it will be necessary to phase out fossil fuels from all aspects of water treatment and transition towards technologies based on renewable materials and energy sources. This need creates strong advantages for biomass-based sorbents such as steam activated biochar and regeneration approaches driven by electricity that may be combined with other technologies. It is important to acknowledge that future water treatment trains will need account for demanding and complex contaminant mixtures which will increasingly be solved by multi-barrier approaches, which have the potential of integrating low-resource and low-energy demanding nature-based solutions. Finding the most efficient solutions and combinations of technologies for complying with strict water quality criteria and coping with the abovementioned sustainability issues in water treatment, will be a challenging but also stimulating task for research and fruitful developments in the water treatment sector in coming years.

References

Sigmund, G. et al. (2022) ‘Sorption and Mobility of Charged Organic Compounds: How to Confront and Overcome Limitations in Their Assessment’, Environmental Science & Technology, 56(8), pp. 4702–4710. Available at: https://doi.org/10.1021/acs.est.2c00570.

Sigmund, G. et al. (2020) ‘Deep Learning Neural Network Approach for Predicting the Sorption of Ionizable and Polar Organic Pollutants to a Wide Range of Carbonaceous Materials’, Environmental Science & Technology, 54(7), pp. 4583–4591. Available at: https://doi.org/10.1021/acs.est.9b06287.

Leachability as a Measure for Substance Mobility in the PMT/vPvM Framework

D. Skodras[1]*, J. Klein[1], M. Klein[1]

[1]Fraunhofer Institute for Molecular Biology and Applied Ecology IME, Auf dem Aberg 1, 57392 Schmallenberg, Germany

dimitrios.skodras@ime.fraunhofer.de

New hazard classification with regard to PMT/vPvM (persistent, mobile, toxic/very persistent, very mobile) will be introduced in the CLP and REACH regulation. This classification intends to encompass substances that pose a risk of reaching and accumulating in drinking water sources. While persistence (P) and toxicity (T) are already treated in guidances within the REACH legislation, mobility (M) of chemicals is not conclusively defined. In the CLP regulation the classification criterion for mobility is primarily the sorption constant logKoc which defines the adsorption of a substance to the organic carbon content of a soil or sediment. Substances with a logKoc below 3 are considered mobile, or very mobile (vM) if logKoc is below 2 (with Koc in units of mL/g). However, as shown in (Pawlowski S et al. 2022) and (Collard M et al. 2023) assessment of mobility solely based on the sorption constant is considered inaccurate, since (among other reasons) transport through soil and sediment also depends strongly on degradation in the transport matrix. Therefore, the amended regulation also foresees that other information from leaching, modelling and monitoring studies should be considered within a Weight-of-Evidence approach.

We propose an approach using the EU FOCUS framework which takes into account degradation, climate, soil and crop effects. Specifically, FOCUS-PELMO 6.6.4 (FOCUS Ground Water Work Group 2014) is used to provide a measure of mobility in terms of leachability. We define leachability as the percentage of substance leached at a soil depth of 1 m related to the exposure at the soil surface. Setting all substance properties to default except for Koc and the degradation half life (DegT50) in soil and sediment yields a two-dimensional grid of leaching predictions. We varied DegT50 between 1 day and 1 year while Koc values between 0 and 10,000 mL/g were used. Proposed thresholds for mobility are 1% and 10% leaching. Using this approach a substance of which more than 1% can be transported through a 1m soil or sediment layer is considered mobile. It would be considered very mobile in case of more than 10%. The proposed thresholds of 1% and 10% widely agree with the exposure thresholds of 0.1 µg/L and 10 µg/L in drinking water for plant protection products and their non-relevant metabolites. It is recommended that the leachability concept becomes part of a Weight-of-Evidence approach in cases where the initial screening based on logKoc indicates a risk of mobility.
The result of the simulations is implemented in a user-friendly tool that is publicly accessible [software.ime.fraunhofer.de] such that the user can easily predict the leachability of a substance based on Koc and DT50 in soil.

References

Pawlowski S, et al. (2022). Mobility in the context of exposure-based assessment of chemicals for drinking water resource protection. Integr. Environ. Assess. Manag. 00:1-17. doi:10.1002/ieam.4705

Collard M, et al. (2023). Persistence and Mobility (defined as organic carbon partitioning) do not correlate to the detection of substances found in surface and groundwater: Criticism of the regulatory concept of Persistent and mobile substances. Sci. Total Environ. 865:161228. doi:j.scitote

FOCUS Ground Water Work Group (2014) Assessing Potential for Movement of Active Substances and their Metabolites to Ground Water in the EU,. EC Document Reference Sanco/13144/2010 version 3.

Are Ozonation and Activated Carbon Filtration Effective Barriers Against Persistent and Mobile Chemicals? - A Monitoring and Screening Study on Wastewater Treatment

D. Zahn1[*], I. J. Neuwald[2], M. Muschket[1], A. H. Seelig[1], G. Gollong[2], D. Sauter[3], R. Gnirss[3], T. P. Knepper[2] and T. Reemtsma[1,4]

[1]Helmholtz Centre for Environmental Research - UFZ, Department of Analytical Chemistry, Permoserstraße 15, 04318 Leipzig, Germany
[2]Hochschule Fresenius gem. Trägergesellschaft mbH, Limburger Str. 2, 65510 Idstein, Germany
[3]Berliner Wasserbetriebe, Neue Juedenstr. 1, 10179 Berlin, Germany
[4]University of Leipzig, Institute for Analytical Chemistry, Linnéstraße 3, 04103 Leipzig, Germany

daniel.zahn@ufz.de

Persistent and mobile (PM) substances are recalcitrant during biological processes and sorb only poorly to natural materials like sludge or sediment (Reemtsma T. et al. 2016). Consequently, advanced wastewater treatment is essential in limiting their spread throughout the water cycle and negative impacts that may arise from it, yet corresponding data is still scarce.

In this study the occurrence and behavior of 111 suspected and known PM-substances was investigated in two wastewater treatment plants employing advanced treatment, either powdered activated carbon (PAC, full-scale) or ozonation with filtration (pilot-scale) with an additional granular activated carbon (GAC) filtration. For the 72 detected PM chemicals PAC reduced the total concentration from 103 µg/L to 87 µg/L while ozonation with subsequent sand/anthracite filtration led to a reduction from 40 µg/L to 19 µg/L. GAC filtration after ozonation resulted in a further reduction to 13 µg/L. Some high priority chemicals were identified, with effluent concentrations exceeding 1 µg/L and no removal by any of the treatment methods. In a complementary nontarget screening (Gollong G. et al. 2022) in the pilot plant samples were separated into a mobile and non-mobile fraction by sequential solid-phase extraction. This screening showed that chemicals in the mobile fraction are significantly less effectively removed during treatment (Figure 1; $p > 0.005$) and comprise a higher share of newly formed transformation products. Combined, these results indicate that advanced wastewater treatment may only be a partially effective barrier against PM chemicals.

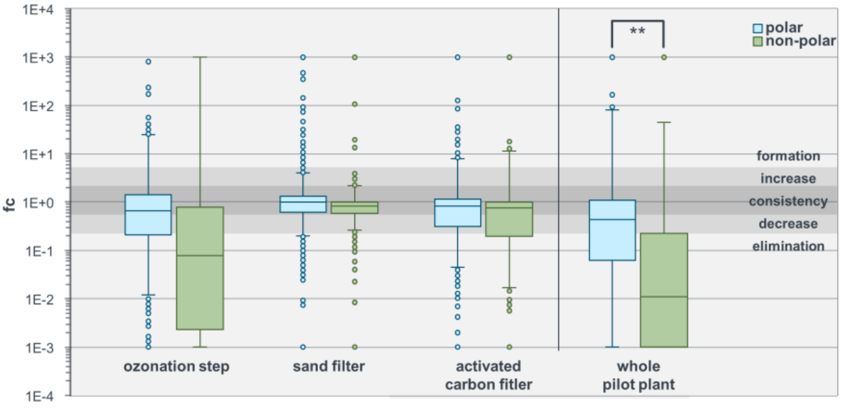


*Figure 1: Fold changes (fc; area after treatment step/area before treatment step) of almost 5000 features detected in the pilot plant. ** $p > 0.005$*

References

Reemtsma, T. et al. (2016) Mind the Gap: Persistent and Mobile Organic Compounds—Water Contaminants That Slip Through, Environ. Sci. Technol., 50, p. 10308–10315, https://doi.org/10.1021/acs.est.6b03338

Gollong, G. et al. (2022) Assessing the protection gap for mobile and persistent chemicals during advanced water treatment – A study in a drinking water production and wastewater treatment plant, Water Res.221, p.118847, https://doi.org/10.1016/j.watres.2022.118847.

Exploring Organic Carbon–Water Partition Ratio (K_{OC}) Data for Mobility Hazard and Exposure Assessments Using Big Data Approaches

S. Baskaran[1]*, R. Wolf[1] and H.P.H. Arp[1,2]

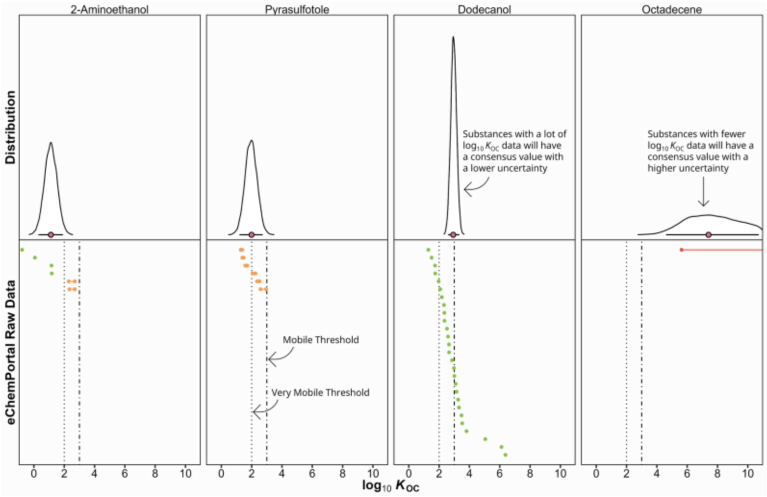
[1]Norwegian Geotechnical Institute (NGI), Sandakerveien 140, 0806 Oslo, Norway
[2]Norwegian University of Science and Technology (NTNU), Høgskoleringen 5, 7034 Trondheim, Norway

sivani.baskaran@ngi.no

Chemical hazard and risk assessments often use physical-chemical properties to categorize and identify chemicals of concern. Most recently, legislation regarding the classification, labelling and packaging (CLP) has introduced new categories for chemical hazard assessment including persistent, mobile, and toxic (PMT) and very persistent and very mobile (vPvM). Mobility is determined based on the logarithmic organic carbon–water partition ratio (log10 KOC) or logarithmic octanol–water partition ratio (log10 KOW) for neutral compounds and the logarithmic octanol–water distribution ratio (log10 DOW) for ionizable compounds, depending on the regulatory agency and the degree of mobility (Arp and Hale 2022).

In this work we use all available KOC data in a consensus approach that takes into account the variability, uncertainty, different sources and types of data. Data sources include the OECD's eChemPortal, experimental (log10) KOC datasets, and estimated values using poly-parameter linear free energy relationships (ppLFERs), OPERA, and EPI Suite. With Bayesian statistical inference approaches we aggregate values and their errors from these different sources to derive a probability distribution for the "true" log10 KOC value.

For risk assessments, the classification of mobility can then be done using the mode of the distribution with uncertainties using 95 % credibility interval (see figure). For a more risk adverse approach, the 5 % quantile of each log KOC distribution can be compared to the mobility thresholds.



4 examples of how data availability affects log10 KOC probability distributions which can be used in risk assessessments.

References

Arp, H.P. and Hale, S.E. (2022) “Assessing the persistence and mobility of organic substances to protect freshwater resources,” ACS Environmental Au, 2(6), pp. 482–509. Available at: https://doi.org/10.1021/acsenvironau.2c00024.

Seeking vPvM in Urban Groundwaters with a Method Combining Evaporation and HILIC-Orbitrap-MS

F. Labad[1], Sandra Pérez[1*]

[1]ONHEALTH, Dept. Environmental Chemistry, IDAEA-CSIC, Jordi-Girona 18-26, 08034, Barcelona, Spain

spsqam@idaea.csic.es

The amendment of the Directive 2006/118/EC on groundwater (GW) quality and protection was published in October 2022 (European Parliament and of the council, 2006). Although it includes persistent organic substances such as carbamazepine, sulfamethoxazole and 24 PFAS, very persistent and mobile compounds (vPvM) are not included yet (Directive of the European Parliament and of the council, 2022). Originating from different sources, vPvM may end up in urban GW which remains to be assessed. vPvM have been largely beyond the scope of typical analytical methodologies because of challenges related to their extraction and subsequent chromatographic separation. As far as sample enrichment is concerned, solid-phase extraction (SPE) is the standard method for the preconcentration of organic pollutants from aqueous samples but most commercially available SPE cartridges have demonstrated poor extraction efficiencies for vPvM. Besides the critical sample extraction step, poor analyte retention is commonly observed when using typical reversed-phase liquid chromatographic columns, which have been successfully employed in the past for multi-class organic contaminant separations. Here, urban GW from Barcelona was analysed using an evaporative enrichment methodology in combination with HILIC-Orbitrap-MS in search of polar organic compounds of a wide range of applications and use, including polar pharmaceuticals, industrial chemical, and tire wear substances. The outcomes highlighted a clear need for updating existing monitoring schemes to include very polar substances (sucralose, melamine, cyanoguanidine); which will allow to monitor GW quality in a more comprehensive way

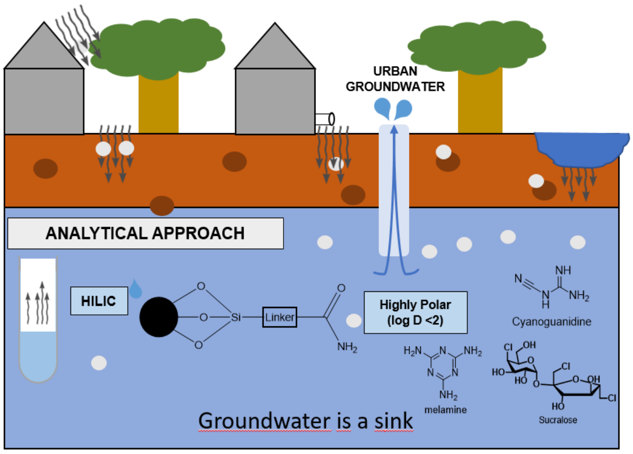


Figure 1: Pathways of vPvM into groundwater

References

European Parliament and of the council, 2006. DIRECTIVE 2006/118/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 December 2006 on the protection of groundwater against pollution and deterioration.

Directive of the European Parliament and of the council, 2022. DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL amending Directive 2000/60/EC establishing a framework for Community action in the field.

Where do PM Chemicals Come From: Searching for Sources in the Sewer System

A. H. Seelig[1*], D. Zahn[1], T. Reemtsma[1,2]

[1]Helmholtz Centre for Environmental Research - UFZ, Department of Analytical Chemistry, Permoserstrasse 15, 04318 Leipzig, Germany
[2]University of Leipzig, Institute of Analytical Chemistry, Linnéstrasse 3, 04103 Leipzig, Germany

alina.seelig@ufz.de

Persistent and mobile (PM) chemicals are poorly degraded by microbial processes and hardly sorb to natural surfaces. These potentially hazardous (PMT) substances can spread quickly in the water cycle and may eventually reach drinking water (S. Schulze et al. 2019). While some recent screening activities demonstrated the widespread occurrence of some PM chemicals (S. Schulze et al. 2019, I. J. Neuwald et al. 2022), their sources remain largely unknown. This limits the scope of targeted preventive actions.

In this study, we quantified 70 PM chemicals in 19 sewer samples by supercritical fluid chromatography coupled to tandem mass spectrometry. These samples were categorized in three source types (industrial, clinical, and domestic). 42 of the analytes (60%) could be detected in at least one wastewater sample. The maximum concentrations per analyte varied between 0.5 and 8,000 µg/L. While some substances seem to have specific sources (e.g. tetrafluoroborate), others show a broad distribution over all source types. In addition, we investigated the differences between industrial and domestic wastewater samples (Figure 1), demonstrating that industrial wastewater may show high concentrations of chemicals otherwise rarely detected. Some analytes could be attributed to specific industries, which also increases the risk of local hotspots.

This study shows that urban sewer systems can tell us about sources of PM chemicals. This is a basis for both, tailored monitoring activities fit to identify local PM hotspots and directed preventive measures that may help tackling the problem of PM contaminations directly at the source.

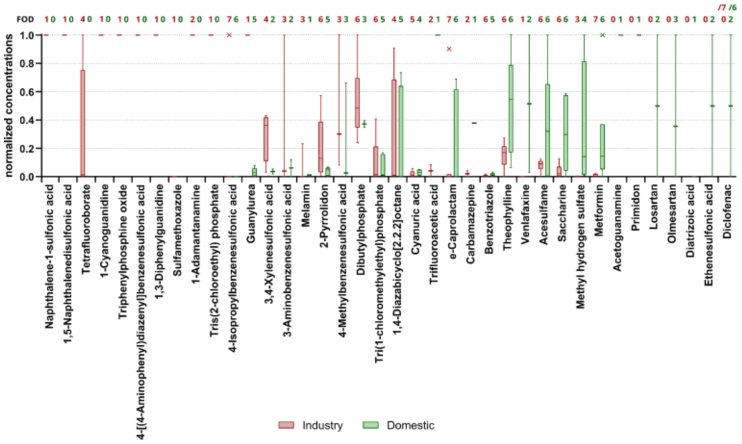


Figure 1: Normalized concentrations for PM chemicals in industrial (red) and domestic (green) wastewater. FOD - Frequency of detection.

References

S. Schulze et al. (2019) 'Occurrence of emerging persistent and mobile organic contaminants in European water samples', Water Res., 153, 80–90, doi: https://doi.org/10.1016/j.watres.2019.01.008

I. J. Neuwald et al. (2022) 'Occurrence, Distribution, and Environmental Behavior of Persistent, Mobile, and Toxic (PMT) and Very Persistent and Very Mobile (vPvM) Substances in the Sources of German Drinking Water', Environ. Sci. Technol., 56, 15, 10857–10867, https://doi.org/10.1021/acs.est.2c03659.

Usage of Tube Passive Sampler for Surveillance of Trace Parameters in Industrial Wastewater in Urban Industrial Sites

T. Hensel[1*], J.-H. Hein[2], R. Bloch[1], P. Simmons[1] and F. Zietzschmann[1]

[1]Berliner Wasserbetriebe, Wastewater Analytics, Motardstr. 35, 13629 Berlin, Germany
[2]GCI GmbH, Bahnhofstr. 19, 15711 Königs Wusterhausen, Germany

tobias.hensel@bwb.de

Many organic micro-pollutants are not or hardly retained by conventional wastewater treatment plants (WWTPs). Particularly in highly urbanzied areas with a semi-closed water cycle, there is a risk of contaminants being carried over from WWTP effluents into drinking water via surface and groundwater Jekel et al. (2013), Reemtsma et al. (2006). The emissions of such potentially harmful substances into WWTPs must be monitored in order to establish strategies for reducing the associated environmental burden. Monitoring by means of random sampling of industrial wastewater has major disadvantages, for example if the sampling period does not coincide with the disposal periods of the plants. Passive samplers are the best way to ensure longterm and continuous sampling Nguyen et al. (2021). Passive samplers, which are classically used in surface water, enrich the analytes while minimizing the influence of the matrix on the measurements. With the newly developed approach presented in our study, a constant controllable flow can be passed over the collection disks mounted into specially designed tube passive samplers. This allows precise and reproducible measurements. In addition, the passive collector can be used in pressurized lines, and can be installed permanently in sewer pipes. For calibration of the tube passive sampler, an autosampler was used to take continuous highly time-resolved mixing samples over the exposure time. We show that the uptake of different analytes by the disc material is linear to the flux as well as to the exposure time in the WWTP effluent. In our current research, the passive sampler will be tested in urban industrial plants. The goal is a time-integrative statement about whether and how much of an observed trace substance is emitted.

References

Jekel, M. et al. (2013) ‘Anthropogenic organic micro-pollutants and pathogens in the urban water cycle: Assessment, barriers and risk communication (ASKURIS)’, Environmental Sciences Europe, 25(1), p. 1072. doi: 10.1186/2190-4715-25-20

Nguyen, M.T. et al. (2021) ‘Comparative field study on bioassay responses and micropollutant upt-ake of POCIS, Speedisk and SorbiCell polar passive samplers’, Environmental Toxicology and Phar-macology, 82, p. 103549. doi: 10.1016/j.etap.2020.103549

Reemtsma, T. et al. (2006) ‘Polar pollutants entry into the water cycle by municipal wastewater: A European perspective’, Environmental Science & Technology, 40(17), pp. 5451–5458. doi: 10.1021/es060908a.

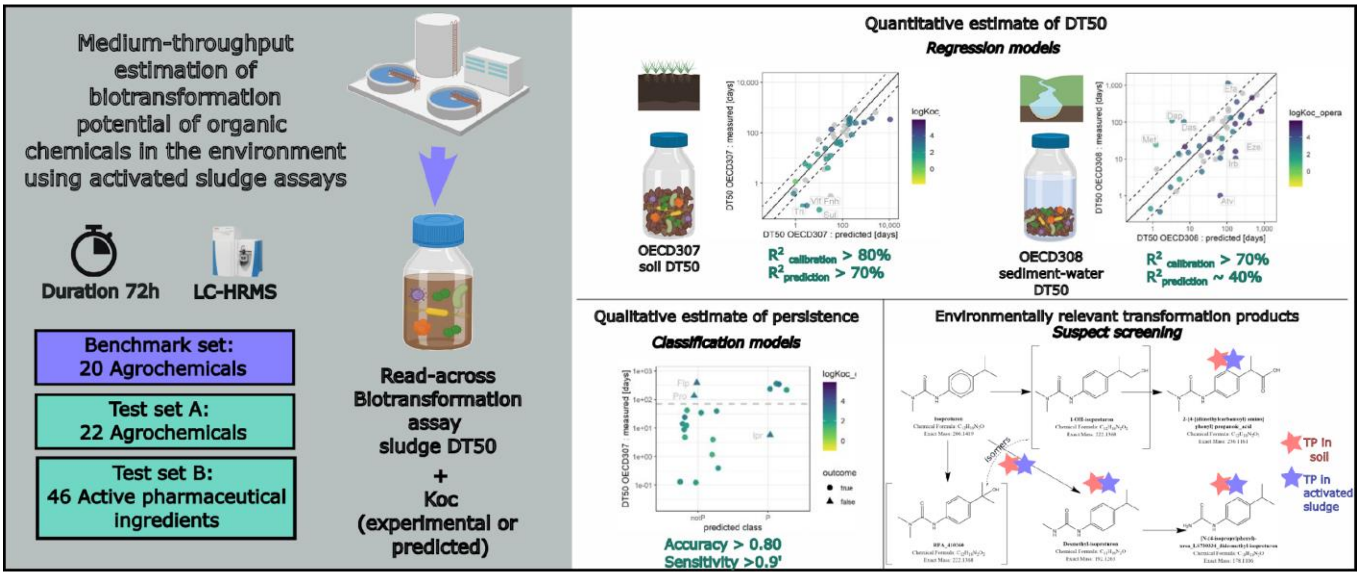
Read-Across in Practice: Biotransformation Potential Between Activated Sludge and the Environment

C. Coll[1,2]*, C. Screpanti[2], K. Fenner[1,3]

[1]Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland
[2]Soil Health Research Center, Syngenta Crop Protection AG, Chemical Research, Schaffhauserstrasse 101, CH-4332 Stein, Switzerland
[3]University of Zürich, Department of Chemistry, 8057 Zürich, Switzerland

claudia.coll@syngenta.com

Current green chemistry guidelines acknowledge that persistence (or biodegradability) of chemicals in the environment should be identified early in the product development process. However, evaluating persistence with the standard OECD tests 307 (soil) and 308 (water-sediment) would be inefficient. We have developed a medium-throughput assay to read-across biotransformation potential from 72h-assays in activated sludge to standard OECD 307 and 308 tests based on Fenner et al. (2020). In experiments performed between 2018 and 2021, a mix of 20 benchmark compounds was tested to calibrate regression and classification models using their half-life in sludge and their partition coefficient Koc as predictors. The regression models show good performance across experiments (R2>70%, RMSE ~0.4) and achieved satisfactory predictions of OECD 307 DT50 of a test set of 22 agrochemicals (R2>70%, RMSE ~ 0.7). Lower prediction performance for the OECD 308 DT50 of 46 pharmaceuticals (R2~40%, RMSE ~0.7) can partially be attributed to a lack of experimental Koc values. Classification models were able to segregate test compounds into persistent and non-persistent (according to a threshold of 70 d) with sensitivities between 0.75-0.92, indicating reliable predictions of non-persistence of agrochemicals and pharmaceuticals could be obtained. Finally, we screened for suspect transformation products of the benchmarks using LC-HRMS measurements, confirming many similarities in the degradation pathways in soil and activated sludge, especially in relevant oxidation and hydrolysis reactions.



Read-across biotransformation assay in activated sludge which are used to predict DT50s OECD307 and OECD308 test of agrochemicals and pharmaceuticals.

References

Fenner, K., et.al (2020) 'Comparison of Small Molecule Biotransformation Half-Lives between Activated Sludge and Soil: Opportunities for Read-Across?', Environ Sci Technol, 54(6), pp. 3148-3158. doi: 10.1021/acs.est.9b05104.

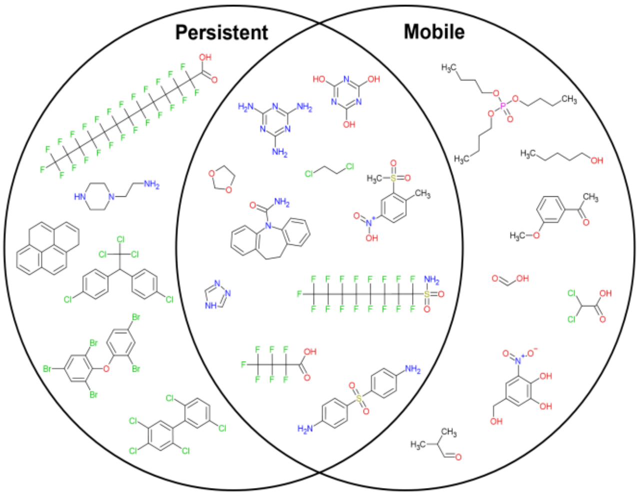
Grouping Persistent and Mobile Substances to Expedite Assessments and Avoid Regrettable Substitution

H. P. H. Arp[1,2]*, S. Baskaran[1], P. Chirsir[1], E. H. Palm[3], E. L. Schymanski[3], Z. Wang[4], R. Wolf[1] and S. E. Hale[1]

[1]Norwegian Geotechnical Institute, NO-0806 Oslo, Norway
[2]Norwegian University of Science and Technology (NTNU), Department of Chemistry, NO-7491 Trondheim, Norway
[3]University of Luxembourg, Luxembourg Centre for Systems Biomedicine (LCSB), 4367, Belvaux, Luxembourg
[4]Technology and Society Laboratory, Empa – Swiss Federal Laboratories for Materials Science and Technology, 9014 St. Gallen, Switzerland

hans.peter.arp@ngi.no

There is an interest by regulators and scientists working with chemical hazard assessment to transition from a one-substance-at-a-time approach to a substance-group approach based on based on structural similarity. Two main motivations for this are to expedite hazard assessments related to the large amounts of substances being introduced to the global chemical market, and avoiding regrettable substitution caused by drop-in substitution. The idea of substance grouping based on the relationship between chemical structure and hazard is not new. Many of the very first hazardous organic substances to be regulated as pollutants were groups sharing a similar structure, including DDT-derivatives, dioxins, PAHs, to name a few. This presentation will provide an overview of grouping hazardous substances based on chemical structure. In addition, we will also present our initial work on substance grouping in relation to persistent and mobile substances, as previously they have not received much attention. This work will be particularly relevant to identify groups substances with either a similar chemical structure, or common transformation products, that are considered persistent, mobile and toxic (PMT) or very persistent and very mobile (vPvM) (Arp and Hale, 2021). Tools are needed now to better assess and regulate them to protect drinking water sources. Grouping persistent and mobiles substances based on specific molecular substructures will support PMT/vPvM substance prioritization and directed risk assessment procedures.



Venn diagram showing the overlap between persistent and mobile substances; what are the common substance groups in this space?.

References

Arp, H.P.H. and Hale, S.E. (2022) "Assessing the Persistence and Mobility of Organic Substances to Protect Freshwater Resources", ACS Environ. Au 2022, 2, 6, 482–509. doi.org/10.1021/acsenvironau.2c00024.

Acknowledgment: This work is from the project ZeroPM, which has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 101036756.

Identifying Urban Pollutant Sources: Biocide Leaching from Paint and Render

M. Balda[1,2]*, R. Berg[2], A. Georgi[1], K. Mackenzie[1], U. Roland[1,2]

[1]Helmholtz-Centre for Environmental Research (UFZ), Department of Environmental Engineering, Permoserstraße 15, 04318 Leipzig, Germany
[2]Hochschule für Technik, Wirtschaft und Kultur (HTWK), Faculty of Civil Engineering, Karl-Liebknecht-Straße 132, 04277 Leipzig, Germany

maria.balda@ufz.de

The emerging water scarcity due to climate change calls for an increase of the re-use of rainwater. Especially in urban areas, it is important to identify the sources and types of potential pollution. One possible source is the runoff of building materials such as paint and render used for the coating of façades.

Within this work, the leaching of biocides from selected paint and render materials was investigated via irrigation of sample items and subsequent extraction and GC/MS analysis of the aqueous leachates. Different irrigation regimes were tested for up to 6 cycles. Based on product-specific information, targeted analysis was performed for 5 selected biocides: methylisothiazolinone, chloromethylisothiazolinone, octylisothiazolinone, diuron and terbutryn. The amount and type of leached biocide strongly depends on the material type and the manufacturer. A significant leaching was observed even after 6 irrigation cycles of 2 h continuous rain and 48-72 h of drying in between. This intensity of surface irrigation equates to approximately 6 months of average rainfall in Leipzig, Germany. These findings indicate that building materials such as façade coatings are a relevant long-term pollutant source in urban areas. As the amount of biocides in building materials as well as the tolerated leaching are not yet regulated by law, the present results highlight the need for the development of suitable remediation strategies. In order to achieve a greater knowledge about the adsorption mechanisms regarding the different classes of substances, various carbon-based adsorbents were tested regarding their adsorption performance in combination with material characterization. Based on this, recommendations for suitable filter materials and, if possible, remediation strategies can be given in order to successfully clean collected rainwater before re-use. In addition, suitable sorbents can be integrated in percolation zones for rainwater in order to mitigate the immission of persistent biocides into urban water cycles.

Comprehensive Investigation of Climbazole and its Transformation Products in Environmental Matrices: Assessing their Persistence, Mobility and Toxicity

K. Anagnostopoulou[1,2], C. Nannou[3] , E. Evgenidou[1,2], D. A. Lambropoulou[1,2]*

[1]Aristotle University of Thessaloniki, Department of Chemistry, GR 54124, Thessaloniki, Greece
[2]Centre for Interdisciplinary Research and Innovation (CIRI-AUTH), Balkan Center, Thessaloniki, 10th km Thessaloniki-Thermi Rd, GR 57001, Greece
[3]International Hellenic University, Department of Chemistry, Kavala, 65404, Greece

kyrianag@chem.auth.gr

Chemicals that are persistent and mobile (PM) can easily distribute through the water cycle and end up in drinking water resources(Schulze et al., 2019). In case that these compounds are also toxic (PMT), they can be considered as a jeopardy to the aquatic environment. Climbazole (CLB), a well-known PMT compound, is a member of the class of antimycotic imidazole drugs that are regularly used both in medicine and as cosmetic chemicals. As with most organic chemicals so with climbazole is slowly or rapidly transformed into numerous transformation products (TPs) (Castro et al., 2016). The ultimate goal of this study is to evaluate if the criteria suggested by the current REACH regulation are sufficient to evaluate CLB as a PMT, or if a more extensive study regarding the emission rates, detection frequency, and maximum concentration is required (Collard et al., 2023). Thereat, laboratory-scale degradation tests were performed under UV irradiation in ultrapure water. The kinetic profile of CLB and identification of arising TPs was executed by injecting different time aliquots in a liquid chromatography Orbitrap MS/MS System. In order to detect as many TPs as possible, the SPE was applied as an enrichment method, using different adsorbent materials. In summary, we identify 24 TPs from which, 14 are reported for the first time since CLB interacts with UV radiation through reductive dechlorination, hydroxylation, and cleavage of the ether bond imidazole and benzyl and imidazole ring opening. The strategy of suspect screening and semi-quantification was followed in order to evaluate the persistence of CLB and its TPs in wastewater treatment plants (WWTPs), surface, groundwater, and leachates of Greece. Results of the sampling campaigns reveal that CLB and some TPs pass through the barriers without significant reduction (maximum concentration of CLB in WWTPs influents and 1,065 ng/L effluents 1,014 ng/L), which is one of the primary justifications for adding PMT to the list of hazard chemicals in Europe. In vitro and in silico toxicity assessments have been also performed. To sum up, in comparison to non-PM chemicals, climbazole exhibits a higher tendency to exist in surface or groundwater. However, in order to conclusively determine whether the suggested criteria are appropriate for the situation, such a thorough examination is necessary for additional PMT compounds and their TPs. Concluding, there is probably demand for clarification or a general revision of the assumptions and criteria used to classify a molecule as a PM substance.

Funding
This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship, and Innovation, under the call RESEARCH – CREATE – INNOVATE (2nd Cycle) (Project acronym: PROMoTE; Project code: T2EDK-04066).

References

Schulze, S. et al. (2019) ‘Occurrence of emerging persistent and mobile organic contaminants in European water samples’, Water Research, 153, pp. 80–90. doi: 10.1016/j.watres.2019.01.008.

Castro, G. et al. (2016) ‘Time-of-flight mass spectrometry assessment of fluconazole and climbazole UV and UV/H2O2 degradability: Kinetics study and transformation products elucidation’, Water Research, 88, pp. 681–690. doi: 10.1016/j.watres.2015.10.053.

Collard, M. et al. (2023) ‘Persistence and Mobility (defined as organic-carbon partitioning) do not correlate to the detection of substances found in surface and groundwater: Criticism of the regulatory concept of Persistent and mobile substances’,

Science of the Total Environment. The Authors, 865(December 2022), p. 161228. doi: 10.1016/j.scitotenv.2022.

Stormwater PMT Substances: Removal and Transport in Columns Amended with Carbon-Based Materials

M. Teixidó[1]*, M. A. Cruz[1,2], J. Xu[1], J. W. Foppen[2,3], E. Vázquez-Suñé[1]

[1]Institute of Environmental Assessment and Water Research, Department of Geosciences,
(IDAEA-CSIC), Severo Ochoa Excellence, Jordi Girona 18–26, 08034 Barcelona, Spain
[2]Delft University of Technology, Department of Water Management, Faculty of Civil Engineering and Geosciences,
Stevinweg 1, 2628 CN Delft, Netherlands
[3]Department of Water Resources and Ecosystems, IHE-Delft Institute for Water Education,
Westvest 7, 2611 AX Delft, Netherlands

marc.teixido@idaea.csic.es

In the face of climate change and rapid urbanization, water-stressed urban environments are beginning to undertake initiatives aimed at replenishing local water aquifers using stormwater runoff. However, runoff represents one of the greatest sources of diffuse pollution in the urban water cycle. Stormwater can contain metals, nutrients, pathogens and also anthropogenic organic compounds of emerging concern (e.g., pesticides, plasticizers, flame retardants, corrosion inhibitors, personal care products, and pharmaceuticals). To become “sponge cities”, cities aim to augment their water supplies via blue-green infrastructures (BGIs) which were primarily designed to reduce flood risks. In fact, conventional blue-green infrastructures encounter difficulties in achieving a consistent removal of the most polar organic contaminants, e.g., the persistent, mobile, and toxic (PMT) organic pollutants. In order to address the current BGI treatment limitations, cost-effective and sustainable technologies should be developed to enable effective stormwater treatment in BGI units prior to aquifer recharge. Herein, we present the batch and column experiences to evaluate PMT removal by pyrogenic carbonaceous materials. We tested granulated activated carbon (GAC), regenerated activated carbon (RAC), and series of different biochars. Data obtained from single Kd experiments shows that GAC the best adsorbent. The RAC has been identified as the second most effective adsorbent, and followed by the biochars, which failed to remove many the polar organic contaminants. We also investigated the transport and removal of several PMTs, stormwater vehicle-related trace organic contaminants, such as 1H-benzotriazole, N'N-diphenylguanidine, and hexamethoxymethylmelamine (HMMM), in biochar/GAC-amended (0.5% w/w) and sand-only (control) columns operating under continuous-flow. GAC amendments attenuated the contaminants with faster adsorption kinetics and higher sorption capacity compared to biochar. The Langmuir sorption kinetics model described the breakthrough curves, suggesting the saturation of sorption sites might occur in infiltration systems with DOM fouling. In fact, the presence of NOM in the simulated stormwater matrix reduced contaminant removal. Results from column experiments corroborated preliminary batch experiments. Based on the estimated sorption parameters, we concluded that HMMM was the most mobile (i.e., least retained). Results from our case study determined that BGI amended with GAC and biochar could exhibit service life of over decade. Overall, these research results help to advance PMT removal technologies in environmental applications.

Closing the Gap: Ion Chromatography Coupled to High-Resolution Mass Spectrometry to Trace Highly Polar Anionic Substances in Groundwater

J. Schorr[1,2]*, S. Therampilly[1], L. Jiao[2], P. Longree[1], H. Singer[1], J. Hollender[1,2]

[1]Eawag: Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland
[2]Institute of Biogeochemistry and Pollutant Dynamics, Universitätstrasse 16, ETH Zürich, 8092 Zürich, Switzerland

johannes.schorr@eawag.ch

Persistent, mobile and toxic (PMT), and very polar and very mobile (vPvM) substances pose a threat to the water cycle but are often not covered in conventional environmental monitoring programs. Within this realm of substances, one compound class of concern are pesticides and their transformation products as they are deliberately introduced into the environment. To detect very polar anionic substances, including many pesticide transformation products with log DOW values ranging between -7.4 and 2.2, an ion chromatography high resolution mass spectrometry method was developed in this study. Since inorganic anions, such as chloride and sulfate, interfere with the analysis of organic species, their removal via precipitation with Ag/Ba/H cartridges was assessed. To improve LOQs, vacuum assisted evaporative concentration (VEC) was evaluated. By using VEC and removing inorganic salt ions, the median LOQ improved from 100 ng/L in evian® water without sample treatment to 10 ng/L after enrichment and 30 ng/L in karst groundwater. Using this method, twelve out of 64 substances covered by the final method were found in karst groundwater in concentrations of up to 5600 ng/L, and seven exceeded 100 ng/L. To the authors' knowledge, the dimethenamid TP M31 and chlorothalonil TP SYN548008 were detected for the first time in groundwater samples. The coupling to a high-resolution mass spectrometer also allows for non-target screening and hence, this method presents a powerful tool to tackle PMT/vPvM substances.

Limits and Opportunities of Sorption Technology for the Removal of PMT and vPvM Substances from Water

B. M. Aumeier,[1] A. Georgi,[2] N. Saeidi,[2] G. Sigmund[3*]

[1] RWTH Aachen University, Institute of Environmental Engineering, Aachen, Germany
[2] Helmholtz Centre for Environmental Research – UFZ, Department of Environmental Engineering,Leipzig, Germany
[3] Environmental Technology, Wageningen University & Research, Wageningen, The Netherlands

gabriel.sigmund@wur.nl

Persistent, Mobile, and Toxic (PMT) and very persistent and very mobile (vPvM) substances are a growing threat to water security and safety. Many of these substances are distinctively different from other more traditional contaminants in terms of their charge, polarity, and aromaticity. This results in distinctively different sorption affinities towards traditional sorbents such as activated carbon (Sigmund G. et al. 2022, Sigmund G. et al. 2020). Additionally, an increasing awareness on the environmental impact and carbon footprint of sorption technologies puts some of the more energy-intensive practices in water treatment into question. We here critically review the interactions that drive removal of organic compounds via traditional sorbents like activated carbons, as well as next-generation sorbents such as cyclodextrins and zeolites. We also identify opportunities and limitations of tailoring sorbents for PMT and vPvM removal.

The current view that the combination of activated carbon sorption and its incineration or thermal regeneration can solve virtually all organic contaminant removal tasks may prove to be outdated. Increasing awareness about the risks of PMT and vPvM which challenges the global need to implement sustainability aspects in all areas of human activity are strong drivers for a diversification in water treatment technologies and materials. Sorption technologies will remain a valuable tool in future water treatment in view of the growing requirements for PMT and vPvM removal. However, commonly used approaches may need to be readjusted to become fit for purpose to safely and efficiently remove the large variety of PMT and vPvM substances while at the same time reducing the environmental footprint of these approaches. Traditional water treatment options may be complemented or replaced by novel on-site or in-situ regenerative approaches and next generation sorbent materials such as modified cyclodextrins, zeolites and metal-organic frameworks under certain conditions.

To achieve robust and environmentally sound water treatment options it will be necessary to phase out fossil fuels from all aspects of water treatment and transition towards technologies based on renewable materials and energy sources. This need creates strong advantages for biomass-based sorbents such as steam activated biochar and regeneration approaches driven by electricity that may be combined with other technologies. It is important to acknowledge that future water treatment trains will need account for demanding and complex contaminant mixtures which will increasingly be solved by multi-barrier approaches, which have the potential of integrating low-resource and low-energy demanding nature-based solutions. Finding the most efficient solutions and combinations of technologies for complying with strict water quality criteria and coping with the abovementioned sustainability issues in water treatment, will be a challenging but also stimulating task for research and fruitful developments in the water treatment sector in coming years.

References

Sigmund, G. et al. (2022) ‘Sorption and Mobility of Charged Organic Compounds: How to Confront and Overcome Limitations in Their Assessment’, Environmental Science & Technology, 56(8), pp. 4702–4710. Available at: https://doi.org/10.1021/acs.est.2c00570.

Sigmund, G. et al. (2020) ‘Deep Learning Neural Network Approach for Predicting the Sorption of Ionizable and Polar Organic Pollutants to a Wide Range of Carbonaceous Materials’, Environmental Science & Technology, 54(7), pp. 4583–4591. Available at: https://doi.org/10.1021/acs.est.9b06287.

Sorption of Organic Xenobiotics on Soil Organic Matter Requires Attention to Electrolytes as Well as Organic Matter Itself: A Case Study of Acetamiprid

H. Murano[1*], A. Watanabe[2] And T. Isoi[1]

[1]Meijo University, Faculty of Agriculture, 1-501 Shiogamaguchi, Tempaku, Nagoya, Aichi 468-8502, Japan
[2]Nagoya University, Graduate School of Bioagricultural Sciences, Chikusa, Nagoya, Aichi 464-8601, Japan

murano@meijo-u.ac.jp

Organic matter in soils (SOM) and sediments and dissolved organic matter affect the behavior of organic xenobiotics, such as pesticides and pollutants. They have been classically extracted according to their solubility in acidic or alkaline solutions and classified as humic substances (HS), such as humic acids (HAs), fulvic acids (FAs), and humin (HM), for convenience. It has been debated whether studies using these fractions correctly reproduce organic matter in the environment (Kleber and Lehmann, 2019). Nevertheless, these fractionated HS still provide some insight into the dynamics of organic xenobiotics in the environment. It is also known that aluminum in volcanic ash soils and calcium in limestone soils interact with HS and play a role in the accumulation of organic matter in the soil. On the other hand, knowledge of the effects of these interactions on the sorption of organic xenobiotics is limited.

In this study, we report on the effects of humic substances and electrolytes, iron and aluminum, on the sorption of organic isomers into the soil in weakly acidic soil using acetamiprid (Murano et al., 2018). Some neonicotinoid insecticides have been reported to contribute to the Colony Collapse Disorder of the honey bee, and their use is regulated in Europe and the United States. On the other hand, they are still used in some countries.

To investigate the differences in isotherm values of acetamiprid sorption on soil due to different properties of HS fractions, batch experiments were conducted with a combination of the above three HS fractions prepared from the same field soil. The sorption of acetamiprid onto soil minerals associated with HM (MHM) decreased with the addition of HA or FA, despite the increased organic matter content in the test solids. Dissolved organic matter content when HA and FA were added was not significantly different from MHM. Therefore, this decrease was attributed to the hydrophobic interaction of HM with HA and FA, which directed dissociated carboxyl and phenolic groups toward the soil solution. The addition of aluminum ions increased the amount of acetamiprid adsorbed on (MHM + HA) or (MHM + FA), and the addition of iron ions also increased the amount of acetamiprid adsorbed. Acetamiprid was not sorbed on inorganic minerals in the soil, and the addition of aluminum or iron ions to MHM did not increase the sorption as much as the addition of HAs or FAs. In the presence of HA or FA, these electrolytes formed HS-metal complexes by cation cross-linking, thus directing the hydrophobic sites of HA or FA toward the soil solution, and this cross-linking could have formed a denser structure. This could have increased the amount of acetamiprid adsorbed on the structure.

It has been reported that soil organic matter is the primary sorption medium in the sorption of many organic xenobiotics to the soil. However, more attention needs to be paid to the influence of electrolytes on the state of the existence of soil organic matter in the natural environment. Our results highlight the importance of interactions between soil components in the fate of acetamiprid as well as various other xenobiotics in the pedosphere.

References

Kleber, M. and Lehmann, J. (2019) 'Humic Substances Extracted by Alkali Are Invalid Proxies for the Dynamics and Functions of Organic Matter in Terrestrial and Aquatic Ecosystems', Journal of Environmental Quality, 48, pp. 207-216. doi: 10.2134/jeq2019.01.0036

Murano, H. et al. (2018) 'Influence of humic substances and iron and aluminum ions on the sorption of acetamiprid to an arable soil', Science of the Total Environment, 615, pp. 1478-1848. doi: 10.1016/j.scitotenv.2017.09.120.

The Effect of Organic Matter on the Photolysis of Emerging Compounds (ECs): Mixture of Organic ECs, Microplastics and Nanoparticles

L. Ramadan[1]*, I. Ozturk[1], C. Yatmaz[1], E. Yuksel[1], E. Topuz[1]

[1] Gebze Technical University, Department of Environmental Engineering,
Kocaeli/TURKEY

l.ramadan2021@gtu.edu.tr

Emerging contaminants (ECs) are persistent substances, released in the environment for which no regulations are established. It is frequently detected in aquatic environment at a range of ng/L to µg/L which could pose detrimental effects on human health and biota. In recent years, studies have typically focused on the fate of ECs by studying the transformation of these compounds in distilled water and as individual or limited to a group of compounds (e.g. pesticides). However, ECs belong to different classes and chemical groups and coexist with various environmental components such as natural organic matter (NOM), microplastics and nanoparticles that could substantially alter the transportation and persistency of these contaminants in the environment due to their interactions (Wilkinson et al., 2017). Therefore, the findings obtained with single compounds and in the absence of natural organic matter are not sufficient for estimating the fate and behaviour of ECs in the natural environment, thus, there is an urgent need to support the environmental risk management with the data obtained from the studies done with more environmentally relevant conditions.Diclofenac, terbutryn, ciprofloxacin, 17α-ethynylestradiol (EE2) and diuron were selected for this study. These contaminants belongs to various ECs groups and are included in the EU watch list of substances that should be monitored (Council, 2020). The fate of these contaminants in mixture and as individual was investigated by testing their photolysis behaviour in distilled water (DW) and synthetic surface water (SSW) with two different concentrations of NOM (humic acid). Photochemical by solar light is a fundamental process for the environmental risk assessment of ECs (Guo et al., 2022). The experiments were also conducted in the presence of polypropylene microplastics (PP-MP) and silver sulphide nanoparticles (Ag2S-NP) to increase the variety of ECs'groups, in order to mimic more realistic environmental conditions.

Low and high amount of NOM has enhanced the photolysis rate of diuron from no degradation in DW to 0.0514 min-1 with low NOM and 0.0514 min-1 with high NOM. While the photolysis rate of EE2 and terbutryn were affected reversibly by the different NOM concentrations. EE2 photolysis rate was significantly enhanced from no degradation with DW to 0.024 min-1 with lower NOM while it decreased with the addition of higher NOM (0.024 min-1 to 0.022 min-1). Whereas the mixture had recorded a decreasing impact on the photolysis rate of all the tested ECs. These results demonstrate the variation in the aquatic fate of ECs in the environment when tested as a mixture and with the presence of multiple components of natural surface water (e.g. NOM) which provide insight for examining the accuracy of the data that are found for individual ECs in the simple water matrix and their properness for data driven environmental risk assessment.

References

Council, O.F.T.H.E. (2020) 'Directive 2013/11/EU of the European Parliament and of the Council', Fundamental Texts On European Private Law, 2013(July), pp. 1–17. Available at: https://doi.org/10.5040/9781782258674.0032.

Guo, Z. et al. (2022) 'Photodegradation of Organic Micropollutants in Aquatic Environment: Importance, Factors and Processes', Water Research, p. 118236. Available at: https://doi.org/10.1016/j.watres.2022.118236.

Wilkinson, J. et al. (2017) 'Occurrence, fate and transformation of emerging contaminants in water: An overarching review of the field', Environmental Pollution, 231, pp. 954–970. Available at: https://doi.org/10.1016/j.envpol.2017.08.032.

High-Frequency and in Situ Fluorescence Measurements of Organic Matter Quality and Quantity in Wastewater for Better Treatment Process Control

A.Goffin[1*], N. Musabimana[1], S.Guerin[2], V. Rocher[2], G. Varrault[1]

[1]University Paris Est-Creteil, LEESU, 64 avenue du Général de Gaulle, 94000, Creteil, France
[2]Greater Paris Sanitation Authority (SIAAP), Innovation Direction, 82 avenue Kleber, 92700, Colombes, France

angelique.goffin@u-pec.fr

To improve wastewater treatment plants (WWTP) efficiency and to better protect the receiving environment, it is essential to know quickly the quantities and qualities of Organic Matter (OM) throughout the treatment process. To date, the analytical methods available for obtaining this informations are time-consuming (Biochemical Oxygen Demand (BOD5): 5d ; Chemical Oxygen Demand (COD) : 2h), not available in situ and in real time. It is therefore necessary to develop alternative monitoring methods to meet these objectives. Previous work has shown that fluorescence spectroscopy is a good substitute as it is a fast measurement method (around one minute) that can be used in situ (Carstea et al., 2020). In addition to distinguishing different types of OM (i.e. protein substances and humic substances like compounds), some fluorophores related to wastewater OM show good relationships with BOD5 and COD standardized measurements (Goffin et al., 2018; 2019).

Having established these relationships on the scale of a benchtop spectrofluorometer, it was necessary to transpose them to the scale of an in-situ measurement probe. In absence of a commercial solution adapted to the monitoring of these WWTP fluorescence indicators, a high-frequency in situ measurement probe called "Fluocopée" allowing the measurement of several dozen (n=32) fluorophores was developed between 2018 and 2021 at LEESU and SIAAP (patent pending). In this study, we show probe qualification result and his deployment for the in situ high frequency monitoring of BOD5 and COD in the Seine-Aval WWTP settling effluent (1 500 000 m³/d, SIAAP, Achères, France).

The qualification of the "Fluocopée" probe gives very good results, whether in terms of response linearity, repeatability or accuracy. Its sensitivity (in Tyrosine, Tryptophan and Humic Acid equivalents) is largely sufficient for use in wastewater and aquatic environments. During his deployment, predictive models (n=41) of BOD5 and COD based on fluorescence measurement were established. The differences between the measured values and the predicted values are in the order of 5 to 10%. The validation r² is 0.86 and 0.89 respectively.

The "Fluocopée" probe will allow to better control WWTP treatment plants as well as savings in reagents and energy. Indeed, carbon neutrality and energy sustainability are at the heart of measures to limit the overall impact of WWTPs in the context of climate change (Delre et al., 2019). This tool will help to achieve the United Nations Sustainable Development Goals (SDGs) 6 and 12, by allowing an improvement in the quality of water returned to receiving environments while allowing responsible consumption of resources (SDG 12).

References

Carstea E.M. at al. (2020) 'In situ fluorescence measurements of dissolved organic matter: A review.', Science of The Total Environment, Vol 699, doi: 10.1016/j.scitotenv.2019.134361

Goffin A., et al. (2018). 'Towards a better control of the wastewater treatment process:EEM fluorescence spectroscopy of dissolved organic matter as a predictive tool of soluble BOD5 in influents of six Parisian wastewater treatment plants'. Environ. Sci. and Poll. Res. vol 25, 8765–8776. doi: 10.1007/s11356-018-1205-1

Goffin A., et al. (2019) 'An environmentally friendly surrogate method for measuring the soluble chemical oxygen demand in wastewater: use of three-dimensional excitation and emission matrix fluorescence spectroscopy in wastewater treatment monitoring.' Environ. Moni, doi:10.1007/s10661-019-75.

Arctic Shelf Molecular Study: Dissolved Organic Matter of the Methane Seep Regions

A.N. Khreptugova[1]*, V.R. Zakirov[1], S.F. Starr[2], R. G. Spencer[3], I.P.Semiletov[1,4] and I. V.Perminova[1]

[1]Lomonosov Moscow State University, Department of Chemistry, Leninskie Gory 1-3, 119991 Moscow, Russia
[2]The University of Alabama, Department of Biological Sciences, SEC, 300 Hackberry Lane, Tuscaloosa, AL 35487, U.S.A
[3]NHFML Geochemistry Group and Department of Earth, Ocean, and Atmospheric Science, FSU, Tallahassee, Florida 32306, U.S.A
[4]POI, Far Eastern Branch of the Russian Academy of Sciences, 43 Baltic Street, Vladivostok, Russia

khreptugova.anna@gmail.com

The East Siberian Arctic Shelf (ESAS) represents the broadest and shallowest shelf in the ocean with significant influence of subsea and terrestrial permafrost. Climate change has caused substantial mobilization of a huge pool of dissolved organic matter (DOM) and abyssal methane CH_4 from the permafrost thawing into the Arctic Ocean (Shakhova et al., 2007), which has led to systematic oversaturation of marine water with CH_4. The molecular composition of DOM is responsive to environmental changes, which reflects its role as an ecosystem metabolome. Determining the molecular composition of DOM by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) is examined in comparison to an evaluation of the methane source and assessing the environmental process of methane release in the remote regions of the Arctic shelf. The goal of the work was to study unique molecular signatures of DOM on the ESAS under presence of released subsea methane.

The sample collection was performed aboard vessel Ac. Mstislav Keldysh in October 2020 in the Laptev and East Siberian Sea regions. Marine water for solid phase extraction was filtrated through GF/F filters, acidified and passed through 500 mg Bond Elut PPL cartridges. The extraction procedure was conducted in the laboratory using methanol. The molecular-level assessment of DOM isolates was performed on a custom 9.4-T FT-ICR MS with a 22 cm diameter bore at the National High Magnetic Field Laboratory (Tallahassee, FL). The assignment of molecular formulae and data visualization was performed with in-house Nomhsms software. The relationship of H/C versus O/C values was represented by van Krevelen (VK) diagrams. The VK diagrams were binned into 20 cells, which are assigned to seven major classes of the biomolecular precursors of HS (Perminova, 2019).

Degradation of subsea permafrost, retreat of submerged ice complexes, an increase in the discharge of East Siberian Rivers are factors influencing the methane release in the ESAS region (Shakhova et al., 2007). The observed extreme CH_4 concentrations in the ESAS regions reached 700-800 nM/L. The examination of the relative abundance of molecular formulae in DOM mass-spectra and methane concentration revealed a positive correlation between CH_4 release and aromatic structures of DOM. Methane release was directly related to the condensed and hydrolysable tannin areas. The inverse correlation was observed between methane release and biogenic elements within aquatic system. Additional studies are required to shed light onto the source and fate of methane in the marine system.

Acknowledgements: This research was financially supported by the Russian Sceince Foundation grant no 21-77-30001 (experiment on DOM isolation). This research was conducted in the framework of the scientific educational school of the Lomonosov Moscow State University “Future of the planet and global environmental change”.

References

Shakhova N., Semiletov I. (2007) Methane release and coastal environment in the East Siberian Arctic shelf. Journal of Marine Systems. 66. №. 1-4. 227-243.

Perminova, I.V. (2019) From green chemistry and nature-like technologies towards ecoadaptive chemistry and technology. Pure Appl. Chem., 91, p. 851–864.

Mega Ports and Climate Change

F. Sakellariadou[1*], I.-M. Hassellöv[2], C.F. Wooldridge[3] and D. Kitsiou[4]

[1]University of Piraeus, Dept of Maritime Studies, Piraeus 18534, Greece.
[2]Dept of Mechanics and Maritime Sciences, Chalmers University of Technology, SE-412 96 Göteborg, Sweden.
[3]Science Coordinator, EcoPorts EcoSLC.
[4]Dept. of Marine Sciences, University of the Aegean, Greece.

fsakelar@unipi.gr

Projected climate change, potential impacts and associated risks strengthen the global response in the context of sustainable development. All industrial sectors, including shipping, are facing the sustainability challenge. Seaports play a crucial role for international trade and globalization as they are vital hubs of the global supply chain. They are located on the coastal area that supports various anthropogenic activities. The various coastal uses, including industry, tourism, fisheries, and human settlements, cause multiple environmental stressors to the fragile coastal ecosystem and have several socioeconomic impacts. Port activities create pressures on all environmental compartments; air, water, and soil. The most addressed pressures include various emissions from sources related to port operation that emit GHGs that contribute to the global climate change, and air and water pollutants that cause direct local and regional effects of acidification, eutrophication and degradation of the ecosystems. This degradation of the marine environment will indirectly impact climate change as the capacity of the ocean to withstand and hamper climate change will decrease. Ships are the single largest source of port-related air pollution and in some regions, like the Baltic Sea, shipping is also a significant contributor of contaminants to the marine environment. The IMO has set ambitious targets to achieve lower GHG emissions from shipping. However, to reduce contribution of shipping to climate change, both direct and indirect impacts need to be addressed. To guide shipping companies towards reduced contribution to climate change, port authorities should facilitate increased supply of alternative fuels, extend shore-side power supply, and apply environmentally differentiated port dues for ships. Relevant EMS Quality Standards require port authorities to set their own targets for GHG reduction, air emissions and to set low emission zones or berth standards. The sector recognizes that these issues require an integrated approach to monitoring, reporting and management because of cross-boundary considerations of multi-stakeholder involvement from quayside to port area, and on to hinterland connections including the logistics chain. The identification and application of related EPIs are vital if sustainability is to be achieved. Another incentive for ports to reduce contribution to climate change is their own susceptibility to climate change related effects. Coastal areas are particularly susceptible to sea level rise and intense storms while estuaries are at risk from flooding hazards. The severity of the potential impacts on seaports creates an urgent need to strengthening the climate resilience of seaports and their climate change adaptation. For this purpose, a collaboration of a broad range of experts and stakeholders is required, along with more systematic approaches, technological considerations, the construction of new resilient infrastructure and the use of soft and hard adaptation measures to increase the resilience of existing infrastructure.

This study is part of the #2021-026-3-600 project sponsored by IUPAC Division VI.

References

Winnes, H. et al. (2015) "Reducing GHG emissions from ships in port areas" Res. Transp. Bus. Manag. 17, 73–82, doi:10.1016/j.rtbm.2015.10.008

Styhre, L. et al. (2017). "GHG emissions from ships in ports – Case studies in four continents" Transp Res D Transp Environ . 54, 212-224., doi:10.1016/j.trd.2017.04.033

Alamoush, A.S. et al. (2022) "Ports' role in shipping decarbonisation: A common port incentive scheme for shipping GHG emissions reduction" CLSCN, 3, 100021, doi:10.1016/j.clscn.2021.100021.

Complex Assessment of the Pomorie Salt Lake Waters in the Nature 2000 Zone

D. Rabadjieva[1*], A. Kovacheva[1], S. Tepavitcharova[1], R. Gergulova[1], R. Ilieva[1]

[1]Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Acad. G. Bonchev Str., Bl. 11, 1113 Sofia, Bulgaria

didiarab@svr.igic.bas.bg

Pomorie salt lake, Bulgaria, is a natural lagoon located in the immediate proximity of the Black Sea and Pomorie city. Over it passes Via Pontica, the second-largest avian migratory route in Europe. It is a protected area of the European ecological network Nature 2000, Ramsar site (reg. N 1229) and national protected area.

Monitoring studies are insufficient for the ecological assessment of waters. In this work we applied a complex approach using field and laboratory studies of the waters and subsequent thermodynamic modeling for calculation of trace metals chemical species distribution. The research was carried out in three stages over a period of ten months - December 2014, June 2015 and October 2015. The period of December 2014 was characterized by high water and the salinity of the lake fell to about 14.4‰, i.e., nearly 3 times lower than the average annual salinity (36‰); in the period July - October 2015 there was shallow water and the salinity of the lake reached about 20‰. In December 2014, low levels of Al, Fe, Mn, Cu, Zn, Co, Ni, Cd and Pb were found in the water, in most cases below the limits of admissibility for this type of water. In June 2015, however, the contents of Zn, Cd and Pb exceeded the permissible limits, and Co was at the limit of admissibility. In October 2015 self-cleaning ability of the lake was observed in relation to most of the investigated heavy metals, with the exception of Pb and Al.

Thermodynamic equilibrium model that considers interactions between metal ions and ligands of different origin was applied to calculate chemical species distribution of the trace metals under study. Combined ion-association – ion-interaction model, proposed by us, was applied for inorganic chemical species calculation, while Stockholm Humic Model - for organic ones. Results showed a similar distribution of the forms of the studied transition metals, with the exception of Al, where only $Al(OH)n^{3-n}$ (n=4,3) dominated in June 2015 while organic AlOrgOH complexes were also registered in 2014. Fe, Cu and Pb existed mainly as organometallic complexes, and Mn, Co, Ni, and Cd - as free ions and inorganic (chloride, sulfate, and carbonate) complexes. Zn took an intermediate position - both inorganic and organic forms were present in close amounts in all the studied waters.

In conclusion, most harmful for the aquatic fauna are Co, Cd, Ni and Mn, not only because of the high levels of Co and Cd, but also because of the dominance of their more toxic free ions. Fe, Cu and Pb are more harmful for the aquatic vegetation because their organometallic complexes are a prerequisite for their assimilation. Al is the least harmful among them, since its dominant hydroxy complexes stimulate the precipitation of $Al(OH)3$ and thus, the self-purification of the waters.

Acknowledgement: This work has been carried out in the framework of the National Science Program "Environmental Protection and Reduction of Risks of Adverse Events and Natural Disasters", approved by the Resolution of the Council of Ministers № 577/17.08.2018 and supported by the Ministry of Education and Science (MES) of Bulgaria (Agreement № Д01-271/09.12.2022).

Holistic Environmental Impact Assessment from Shipping: a Decision Support Tool for Stakeholder Engagement

S. Guéret[1*], W. Winiwarter[1,2], E. Giubilato[3], L. Calgaro[3], A. Marcomini[3]

[1]International Institute for Applied Systems Analysis (IIASA), Schloßplatz 1, 2361, Laxenburg, Austria
[2]University of Zielona Góra,Institute of Environmental Engineering, Licealna 9, 65-417 Zielona Góra, Poland
[3]University Ca' Foscari Venice, Dept. of Environmental Sciences, Informatics and Statistics, Via Torino 155, 30172, Mestre - Venezia, Italy

gueret@iiasa.ac.at

The shipping industry is a major cause of environmental harm, affecting both atmosphere and hydrosphere, as well as climate. While the Global Sulphur Cap implemented in January 2020 focusses on removing Sulphur Dioxide, other compounds released into the air or sea and their environmental effects remain untouched. Environmental impact assessments are essential methodologies to evaluate the effects of operational shipping in comparison to other sources of pollution and to fill regulatory gaps. However, port authorities, policy makers, and other stakeholders require more readily accessible tools to develop science-based decisions to uphold environmental quality relevant to their specific situation.

In this study, we present a decision support tool that enables stakeholders to evaluate the impacts of Exhaust Gas Cleaning Systems (EGCS, known as scrubbers) and other emission control options in future shipping scenarios on very different media and targets, which allows identification of co-benefits or trade-offs connected to environmental management measures imposed on shipping. The tool is being codesigned between scientists and stakeholders and it translates scientific insights into results useful for decision makers.

We use an established air pollution assessment scheme in combination with a newly developed marine impact assessment approach presented by Guéret et al (this conference) to evaluate impacts leaning on the categories established as the U.N. Sustainable Development Goals:

- Human Health (SDG3): using Years of Life Lost and ozone related health damage as parameters, impacts are taken from the GAINS model (Amann et al., 2011)
- Life on land (SDG 15): ecosystem impacts of acidification and eutrophication are quantified via a critical load approach, and photochemically caused damage is parameterized as phytotoxic ozone dose (POD), again from GAINS
- Life below sea (SDG 14): differentiating between epipelagic and benthic marine ecosystems, critical loads of metals and Polycyclic Aromatic Hydrocarbons (PAHs) as well as the calcite saturation state are proposed as new impact indicators to characterize biota toxicity and acidification, respectively.

We use results from the ship emission model STEAM (Jalkanen et al., 2021), the atmospheric model SILAM (Sofiev et al., 2015), and the water model Chemical Drift to quantify ship emissions and their fate in air and water, respectively. Scenarios have been elaborated in the Horizon 2020 EMERGE project and reflect a general understanding of possible future shipping developments over Europe in 2030 and 2050.

The decision support tool allows users to understand the impact of different shipping scenarios on the respective local environment of any given grid cell (representing 20x20 km grids) in the European seas and adjacent shorelines. Adjustments to the scenarios allow to account for local conditions, to mimic change in ship movements as well as local restrictions regarding the release of certain compounds to air and sea and their respective altered impacts on environmental endpoints.

References

Amann, M. et al. (2011) 'Cost-effective control of air quality and greenhouse gases in Europe: modeling and policy applications.' Environmental Modelling and Software 26, p. 1489-1501. doi: https://doi.org/10.1016/j.envsoft.2011.07.012
Jalkanen, J. et al. (2020). 'Modelling of discharges from Baltic Sea shipping.' Ocean Science 17, p. 699-728. doi: https://doi.org/10.5194/os-17-699-2021.

Sofiev, M. et al. (2015). 'Construction of the SILAM Eulerian atmospheric dispersion model based on the advection algorithm of Michael Galperin.' Geoscientific Model Development 8, p. 3497-3522. doi: https://doi.org/10.5194/gmd-8-3497-2015.

Impact Assessment of Shipping Activities: Applying The Critical Load Concept to Both the Atmosphere and Marine Environment

S. Guéret[1]*, W. Winiwarter[1,2], A. Lunde Hermansson[3], E. Giubilato[4], L. Calgaro[4], J. Borken-Kleefeld[1,5], I.-M. Hassellöv[3], E. Ytreberg[3], and A. Marcomini[4]

[1]International Institute for Applied Systems Analysis (IIASA), Schloßplatz 1, 2361 Laxenburg, Austria
[2]University of Zielona Góra,Institute of Environmental Engineering, 65-417 Zielona Góra, Poland
[3]Chalmers University of Technology, Department of Mechanics and Maritime Sciences, Hörselgången 4, 41296 Göteborg, Sweden
[4]University Ca' Foscari Venice, Dept. of Environmental Sciences, Informatics and Statistics, Via Torino 155, 30172 Mestre-Venezia, Italy
[5]Technische Universität Dresden, Chair of Transportation Ecology, 01069 Dresden, Germany

gueret@iiasa.ac.at

The IMO global sulphur cap regulation permits the use of scrubbers to control atmospheric sulphur dioxide emissions while using cheaper heavy fuel oil with high sulphur content. Yet, scrubber discharge water contains high concentrations of harmful pollutants that threaten marine life and the ocean's buffering capacity. The Critical load approach, which is widely used to devise emission control policies (De Vries et al., 2015), is a relevant option to evaluate the trade-off between atmospheric and marine pollution. Here we propose the critical levels of metals and PAHs, as well as the calcite saturation state, as new marine indicators for marine biota toxicity and ocean acidification, respectively. Impacts are assessed in three steps: (i) deriving maximum permissible concentration per grid cell, (ii) estimating concentrations per grid cell, taken from the STEAM model (Jalkanen et al., 2021) and the water model Chemical Drift (Aghito et al., 2022) , and (iii) estimating exceedances of critical levels. We combine this approach with an established air pollution scheme to assess the impact on water and air, and biota, based on a set of shipping scenarios. In a first application to a shipping lane in the Baltic Sea, scrubbers are identified as contributing to local exceedance of benzo[a]pyrene critical levels (Figure 1) and increased calcite-under-saturated areas. Our research provides groundwork for cost-effectiveness analyses and a decision-support tool allowing stakeholders to identify trade-offs or co-benefits connected to shipping measures (Guéret et al., this conference).

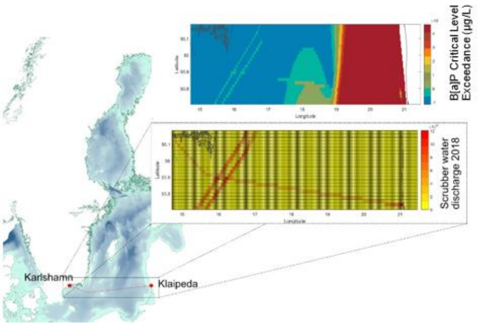


Figure 1 - Map of the Baltic Sea showing exceedance of critical levels of B[a]P (µg/L) and open-loop scrubber discharges (L) based on the STEAM model.

References

Jalkanen, J. et al. (2020). 'Modelling of discharges from Baltic Sea shipping.' Ocean Sci. 17, p. 699-728. doi:10.5194/os-17-699-2021

Aghito, M. et al. (2022) ChemicalDrift 1.0: an open-source Lagrangian chemical fate and transport model for organic aquatic pollutants. Geosci. Model Dev. [preprint]

De Vries, W. et al. (2015). 'Critical Loads and Dynamic Risk Assessments: Nitrogen, Acidity and Metals in Terrestrial and Aquatic Ecosystems.' Environ. Pollut. Ser. vol. 25. Dordrecht: Springer.

Environmental Fate Modelling of Organic Pollutants from Land-Based and Shipping Emissions in the Northern Adriatic Sea Coastal Areas

L. Calgaro[1]*, E. Giubilato[1], M. Aghito[2], J.P. Jalkanen[3], C. Ferrarin[4], E. Semenzin[1], A. Marcomini[1]

[1]University Ca' Foscari Venice, Dept. of Environmental Sciences, Informatics and Statistics, Via Torino 155, 30172 Mestre, Venice, Italy
[2]Norwegian Meteorological Institute, Allégaten 70, 5007 Bergen, Norway
[3]Finnish Meteorological Institute, Erik Palménin aukio 1, FI-00560 Helsinki, Finland
[4]CNR-ISMAR, Arsenale Castello, 2737/F, 30122 Venice, Italy

loris.calgaro@unive.i

Transitional, coastal, and marine ecosystems are highly complex and linked systems, subjected to a multitude of different anthropogenic stressors, both from land-based sources (e.g., industrial and agricultural activities) and direct discharges (e.g., shipping emissions). Recently, the adoption of the global limits on sulfur content for marine fuels is causing a drastic increase in the use of shipping emission abatement technologies like exhaust gas cleaning system (scrubbers) as an alternative to the use of cleaner but more expensive fuel types, whose acidic exhaust discharge water contain diverse chemical contaminants. For these reasons, the presence of shipping lanes and ports may significantly contribute to the exposure of chemical pollutants in coastal areas, potentially increasing risks posed to aquatic ecosystems and human health.

Fate and transport modelling offers an effective way to estimate the contribution of shipping emissions to the overall exposure to chemicals in transitional, coastal, and marine waters.

In this work an exposure assessment for benzo(a)pyrene and fluoranthene accounting for both land-based sources and shipping emissions was carried out for the Northern Adriatic Sea. The modelling effort, realized within the H2020 "EMERGE" project, focused on the integration of several high-resolution predictive models to help exploring the implications of different abatement emissions techniques in managing environmental risks under current and future scenarios.

In detail, shipping-related emissions of pollutants were simulated with the STEAM (Ship Traffic Emission Assessment Model) model, based on Automatic Identification System data, while land-based emissions were quantified by combining daily river flow measurements with water concentrations from routinely monitoring of each tributary. The newly-developed ChemicalDrift model, a chemical transport module part of the open-source Lagrangian framework OpenDrift, was applied for a baseline scenario using 2018 data. Forcing data for the case study area have been obtained from the SHYFEM model (ocean currents, temperature, and salinity) and Copernicus Marine Services (mixed layer depth and winds).

Preliminary results showed that shipping emissions can contribute significantly to the exposure to the selected contaminants, especially during the summer period when water flow from the tributaries reaches its minimum values and the number of cruise ships equipped with open-loop scrubbers increases.

Prioritization of Contaminants of Emerging Concern for a Screening Study in The Venice Lagoon (Italy) – a Methodological Approach

E. Giubilato[1]*, M. Cecchetto[1], L. Calgaro[1], E. Barbaro[1], M. Picone[1], A.Volpi Ghirardini[1], A. Gambaro[1], E. Semenzin[1], A. Marcomini[1]

[1]Ca' Foscari University Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino 155, 30172 Venezia-Mestre, Italy

giubilato@unive.it

Understanding the occurrence and behaviour of contaminants of emerging concern (CECs) in transitional environments is essential to complement the knowledge of "traditional" and regulated pollutants and achieve a thorough evaluation of the environmental quality status. Since the risk posed by CECs in the Venice lagoon (Italy) has been poorly investigated, in the framework of the Venezia2021 research programme a screening study was conducted to provide some preliminary knowledge and propose chemical candidates for a more comprehensive lagoon monitoring plan.

The inclusion of new chemical substances in local monitoring programmes asks for a robust prioritization approach, suitable to integrate diverse typologies of data and effective in supporting environmental management decisions in data-poor contexts. For this purpose, a risk-based methodology was developed to identify emerging contaminants that either are expected to pose a significant ecological risk or need to be further investigated due to the high uncertainty in the available data.

The proposed methodology is based on the integration of i) experimental exposure data from a field campaign in the Venice lagoon, addressing both water and sediment contamination (Measured Environmental Concentrations, MECs); ii) modelled exposure data simulated through a multi-media fate model (Predicted Environmental Concentrations, PECs); iii) ecological effect thresholds derived from literature ecotoxicological data on marine species, complemented with the results of additional bioassays performed on lagoon species for a sub-set of contaminants (Predicted No Effect Concentrations, PNECs).

With the aim of making the most of available exposure and effect data, a decision tree was built on a set of criteria to guide the assessment and prioritization of CECs, so that decisions could be made about the inclusion of considered chemicals into a "Watch List" for the Venice lagoon.

This decision tree was applied to a set of 29 CECs considered in the project, including plant protection products, pharmaceuticals, and industrial chemicals. Results proved it can differentiate chemicals that, based on the estimated risk, should be included in future monitoring plans from those contaminants with great data uncertainty requiring additional investigation efforts. In the latter case, the recommendation may concern new ecotoxicity tests on marine and estuarine species or refinement of analytical methods to reach lower quantification levels in environmental matrices. The proposed approach is eligible for iterated applications in case new exposure and effect data will become available in the future and can be used to evaluate extended/different sets of contaminants.

Poster presentations

Catalytic Combustion of Methane over Pd-Meox-CeO$_2$/Al$_2$O$_3$ (Me= Co Or Ni) Catalysts

S. Todorova[1]*, A. Naydenov[2] and R. Velinova[2]

[1]Institute of Catalysis, Bulgarian Academy of Sciences, Sofia 1113, Acad. G. Bonchev str., bl.11, Bulgaria
[2]Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Acad. G. Bonchev str., bl.11, Bulgaria

todorova@ic.bas.bg

Catalytic combustion of methane has been extensively investigated for emission control and power generation during the last decades. The alumina-supported palladium catalyst is widely accepted as the most active catalysts for catalytic combustion of methane. The activity of Pd/Al2O3 decreases during time on stream, especially under water vapor. The following order of activity in the reaction of complete oxidation of methane was established: Co3O4> CuO>NiO> Mn2O3> Cr2O3. It may be expected that the combination between Pd and these oxides could lead to the promising catalysts in reaction of complete methane.In the present work, we investigate the activity of Pd/Al2O3 catalysts promoted with other metal oxides (MOx; M= Ni, Co, Ce). The Pd-based catalysts modified by metal oxide were prepared by sequential impregnation of Al2O3 with aqueous solutions of Me(NO3)2.6H2O and Pd(NO3)2H2O. All samples were characterized by XRD (X-ray diffraction), TPR (temperature-programmed reduction) and XPS (X-ray photoelectron spectroscopy). An improvement of activity was observed after modification with different oxides. The results demonstrate that the Pd/Al2O3 catalysts modified with cobalt ar with boght Co and Ce by impregnation with common solution of respective salts, exhibit the most promising catalytic activity for methane oxidation. Most probably, the presence of Co3O4 and CeO2 on catalytic surface increases surface oxygen and therefore leads to the better reactivity in methane combustion.

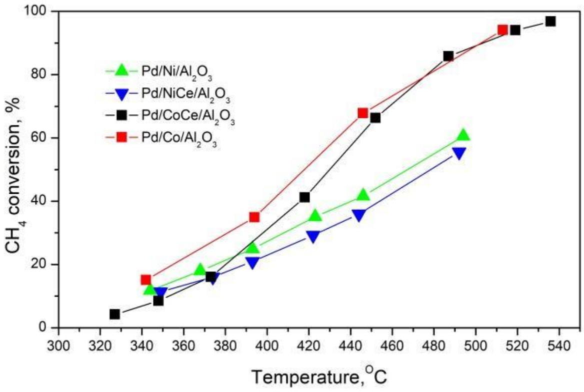


Figure 1. Temperature dependencies of the methane combustion over the different catalysts.)

References

McCarthy J. G. et al., Div. Petrol.Chem. 42 (1997) 158–162.

Acknowledgement: This work was supported by the European Regional Development Fund within the OP “Science and Education for Smart Growth 2014 - 2020”, Project CoE “National center for/of mechatronics and clean technologies“, № BG05M2OP001-1.001-0008-C01.

The Spatial and Temporal Variability of Odour Concentration in Intensive Farm Rearing of Poultry Pigs

O. Popa[1], M. A. Constantin[1]*, C. Constantin[1], S. Călinescu[1], G. Tănase[1]

[1]National Research and Development Institute for Industrial Ecology-ECOIND, Pollution Control Departament Air, Drumul Podu Dambovitei Street 57 -73, ZIP Code 060652, Bucharest, Romania

alina.constantin@incdecoind

At the global level, odors from various industrial and non-industrial activities represent a significant environmental issue. The main sources that require increased attention due to their negative impact on the environment and human health are intensive pig rearing farms. The present study follows the evolution of the odor concentration both inside the farms and in the surrounding air for three consecutive years using the dynamic olfactometer.For this purpose, annual sampling campaigns were organized at 200 meters, 500 meters in the wind direction and centrally from the rearing halls to determine the exposure of odors to the receivers. For indoor air, samples were taken from two halls: adult animals and youth animals. The methodology for this step considered the most appropriate and sustainable BAT options, considering several environmental, economic, and social requirements specified in the Industrial Emissions Directive. For example, the composition of the manure influences the emissions in the surrounding air and in the hall. The results obtained show overshoots of over 45% in the ambient air and a maximum of 5789 OUE/m3 in the indoor air of the halls. This leads to further measures to reduce odor concentration by modifying animal feeding strategies that decrease NH3 emissions from manure in both hall and surrounding air.Feeding strategies cause a decrease of about 10% when the average protein content decreases by 10 grams/kg in the feed. This is an efficient and economically attractive measure.

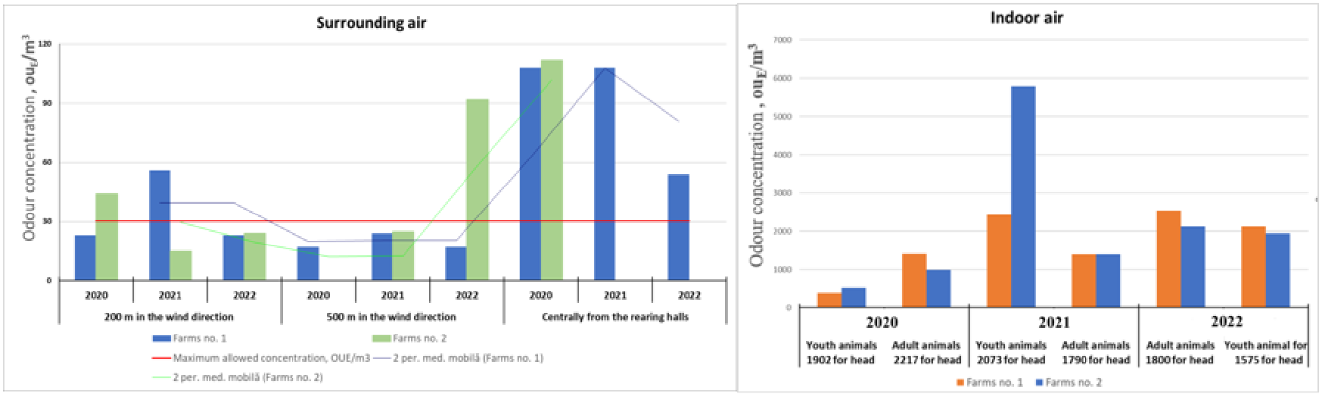


Diagram of the evolution over time of the odor concentration at the two intensive pig rearing farms in the period 2020-2022)

References

Yong-Chao, W. et al. (2021) 'Emissions, measurement, and control of odor in livestock farms: A review', Science of the Total Environment, 776, 145735, https://doi.org/10.1016/j.scitotenv.2021.145735

Blazy, V. et al. (2014) 'Odorous gaseous emissions as influence by process condition for the forced aeration composting of pig slaughterhouse sludge', Waste Management, 1125–1138,https://doi.org/10.1016/j.wasman.2014.03.012.

The Odor Reduction Effect of non-Thermal Plasma Technology in the Tire Industry

C. Constantin[1], M. A. Constantin[1]*, O. Popa[1], S. Călinescu1 and C. Dan[1]

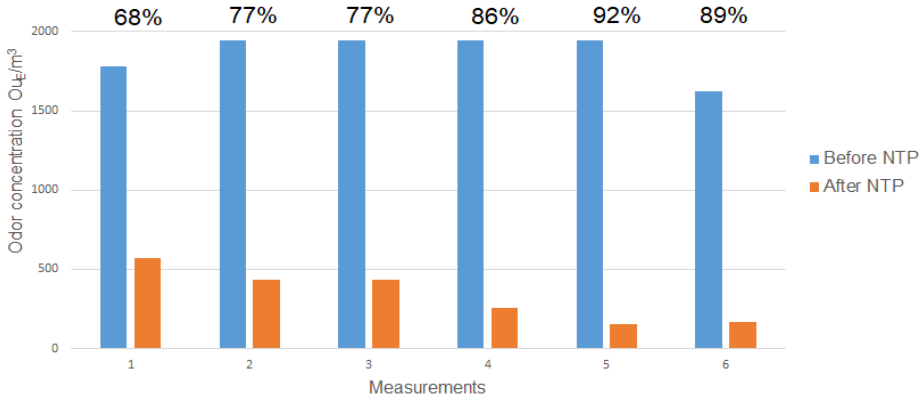
[1]National Research and Development Institute for Idustrial Ecology - ECOIND, Pollution Control Departament Air, Drumul Podu Dambovitei Street 57 - 73, ZIP code 060652, Bucharest, Romania

alina.constantin@incdecoind.ro

This study was conducted to estimate whether a low-energy non-thermal plasma (NTP) system can be a good odor reduction technology in the tire industry, which requires solutions that can treat large volumes of air at a reduced cost. Currently, non-thermal plasma technology is used in various applications, such as for the removal of volatile organic compounds, decontamination in the food industry, in the meat industry, in food packaging as well as in the reduction of odor emissions from various industrial activities.

A pilot NTP odor removal system was installed on a ventilation air stream in a sector of a tire factory. The odor concentration was determined through delayed dynamic olfactometry, in compliance with the provisions of the SR EN 13725:2022 standard - Stationary source emissions - Determination of odour concentration by dynamic olfactometry and odour emission rate. Sampling was carried out simultaneously before and after the treatment plant, in order to determine the efficiency of odor removal. In order to estimate the odor concentration in the ambient air in the vicinity of the factory, a mathematical modeling of the dispersion in the air of the emissions was carried out, using the Aermod View software platform.

In conclusion, we can say that in order to reduce the level of odor pollution on site and in its vicinity a low energy non-thermal plasma (NTP) system can be a good odor reduction technology in the tire industry with an efficiency of up to to 92%.



The odor reduction efficiency of non-thermal plasma technology in tire factory

References

Christine D., Bernd G., (2020) "Plasma Technology and Its Relevance in Waste Air and Waste Gas Treatment." Review MDPI Sustainability, 1-37, 21, doi:10.3390/su12218981

Firefighter's Exposure to PAHs in Prescribed Forest Fires

B. L. van Drooge[1]*, J. Gili[1], C. Jaén[1], M. Viana[1]

[1]Institute of Environmental Assessment and Water Research - Spanish National Research Council (IDAEA-CSIC)
c/Jordi Girona 18-26, 08034 Barcelona, Spain

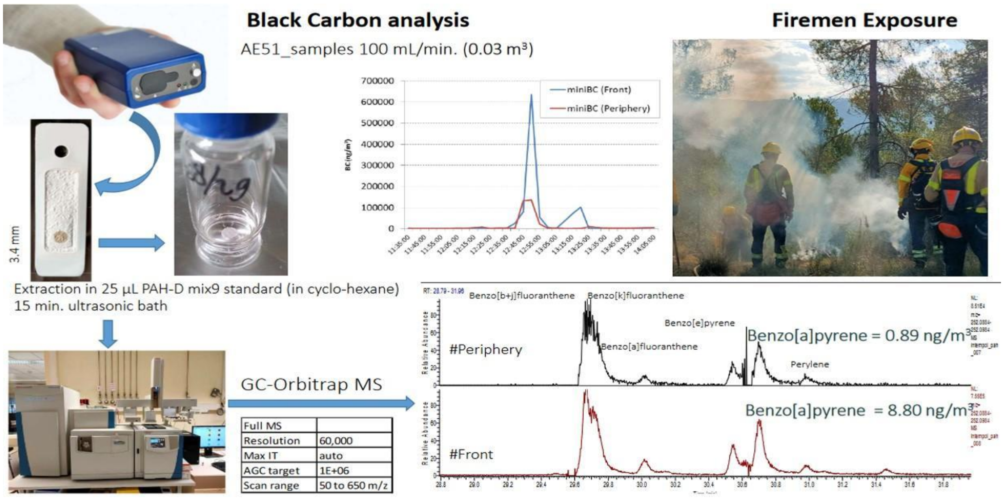
barend.vandrooge@idaea.csic.es

Presence of polycyclic aromatic hydrocarbons (PAHs) in wildfire smoke is one of the reasons that occupational exposure as a firefighter is classified as "carcinogenic to humans" (group 1). Forest firefighters don't wear respiratory equipment, which makes exposure to smoke very relevant.

Here we present a method for the for the analysis of PAHs in the 3 mm spot on filter strips from real-time Aethalometers AE51 (AETHLABS) equivalent black carbon (eBC) analyzers, used as personal exposure monitors for firefighters during a prescribed forest burns in Mediterranean forests (catalunya). The PM2.5 sample spot was taken from the filter strip, extracted and analyzed by Q-exactive GC Orbitrap mass spectrometry for particle-bound PAHs (benz[a]anthracene to benzo[ghi]perylene) (LOQ = 0.5 pg/μL).

Peak eBC concentrations were around several 100s of μg/m3, and 5-h mean eBC concentrations were higher than 1 μg/m3. Benzo[a]pyrene concentration were also higher than 1 ng/m3 and related to extinction tasks during fires. Based on the eBC peak concentrations at 5-min monitoring resolution, the direct exposure to high concentrations of smoke particles and PAHs was probably even less than 1.5 h.

These results show that firefighters are exposed to significant eBC and PAH concentrations during prescribed burns, which is related to the activities around wildfires extinction.



Full MS	
Resolution	60,000
Max IT	auto
AGC target	1E+06
Scan range	50 to 650 m/z

Scheme of analytical procedure to determine PAHs in Aethalometer AE51 PM2.5 samples for BC detection during a prescribed forest fire

References

B.L. van Drooge, R.M. Prats, C. Jaén, J.O. Grimalt. (2023). Determination of subpicogram levels of airborne polycyclic aromatic hydrocarbons for personal exposure monitoring assessment. Journal of Environmental Monitoring and Assessment, 195:368, https://doi.org/10.1007/s10661-023-10953-z.

Multicentric Study of Urban Air Quality in Vojvodina (Serbia) and Assessment of Associated Carcinogenic Risk

S. Bobić[1]*, Lj. Torović[1,2], D. Lukić[1], M. Jovanović[1], N. Stanojković[1] and S. Bijelović[1,2]

[1]Institute of Public Health of Vojvodina, Center for Hygiene and Human Ecology, Futoska 121, 21000, Novi Sad, Serbia
[2]University of Novi Sad, Faculty of Medicine, Hajduk Veljkova 3, 21000, Novi Sad, Serbia

stanka.bobic@izjzv.org.rs

Ambient air pollution in urban areas represents one of prime concerns regarding adverse health effects. The aim of this study was to assess air quality as well as carcinogenic risk due to inhalation exposure to lead, cadmium, nickel, arsenic and benzo(a)pyrene bound to PM10 in ambient air of four major cities in Province of Vojvodina, Republic of Serbia. The data applied were obtained by official air quality monitoring and include data from 2021 and 2022. Fixed measurements were conducted at the locations classified as urban traffic (Novi Sad and Zrenjanin), and urban background (Kikinda and Sombor) in accordance with Directive 2008/50/EC (European Commision, 2008). Obtained results showed that mean annual levels of PM10 were slightly higher on urban traffic (Novi Sad/Zrenjanin 30/39 µg/m³ in 2021, and 36/38 µg/m³ in 2022) compared to urban background locations (Kikinda/Sombor 30/27 µg/m³ in 2021, and 31/23 µg/m³ in 2022), but all remained under the limit value. Oppositely, daily PM10 limit value was exceeded more frequently than allowed, i.e., in 37, 65 and 37 days in Novi Sad, Zrenjanin and Kikinda, respectively, in 2021, and in 2022 in 49 and 54 days in Novi Sad and Zrenjanin, respectively. Mean annual levels of measured toxic metals did not exceed the limit value in any of the cities, whereas in case of benzo(a)pyrene the annual target value was surpassed in 2021 in all cities (max annual mean 2.4 ng/m³ in Sombor), and in 2022 only in Sombor (1.1 ng/m³). Although below the target value, the annual levels of benzo(a)pyrene on other locations in 2022, ranging from 0.9-1.0 ng/m³, should be consider as a warning. The obtained results were exploited for inhalation health risk assessment. The carcinogenic risk assessment carried out according to OEHHA (OEHHA, 2015) guidance, considered differences of daily breathing rate, body weight, age sensitivity and exposure duration. At all cities, increased carcinogenic risk (ICR) for children (<16 years) related to lead exposure was lower than $1x10^{-6}$, the level considered as the limit of acceptability according to US EPA guidelines (USEPA, 2005), while ICR related to cadmium, nickel, arsenic and benzo(a)pyrene exposure was higher than $1x10^{-6}$. For adults (16-70 years) exposed to arsenic and benzo(a)pyrene, ICR was between $1x10^{-6}$ and $1x10^{-4}$, till ICR derived from exposure to other toxic metals was below the acceptable level. The highest carcinogenic risk in all age groups was attributed to arsenic (children, up to $1x10^{-5}$; adults, up to $4.9x10^{-6}$) in each measuring site. Such results should prompt undertaking of appropriate management measures.

References

European Commission. (2008) Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. Official Journal of the European Union, L152, 1-154.

USA California Environmental Protection Agency, Office of Environmental Health Hazard Assessment, OEHHA. (2015) Air Toxics Hot Spots Program. Guidance Manual for Preparation of Health Risk Assessments. Retrieved from: https://oehha.ca.gov/media/downloads/crnr/2015guidancemanual.pdf.

United States Environmental Protection Agency (USEPA). (2005) Guidelines for Carcinogen Risk Assessment. EPA/60/P-03/001F. Retrieved from: https://www.epa.gov/risk/guidelines-carcinogen-risk-assessment.

Poly- and Perfluorinated Alkyl Substances in the Atmospheric Aerosol From a Rural Area of the Italian PFAS Hotspot (Veneto Region)

R. Zangrando[1]*, S. Pizzini[2],[3], E. Barbaro[1], M. Feltracco[3] and A. Gambaro[3]

[1]National Research Council, Institute of Polar Sciences (CNR-ISP), Via Torino, 155, 30172, Venice Mestre (VE), Italy
[2]National Research Council, Institute for Marine Biological Resources and Biotechnology (CNR-IRBIM), Largo Fiera della Pesca, 2, 60125, Ancona, Italy
[3]Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino, 155, 30172, Venice Mestre (VE), Italy

roberta.zangrando@cnr.it

Poly- and Perfluoroalkyl substances (PFASs) comprise a large group of more than 8.000 synthetic organic surfactants, of which only a limited number is known and analyzed. They have a wide range of industrial and commercial applications and are commonly found in a broad variety of industrial and consumer goods.

The physico-chemical properties of PFASs are not yet known in detail and are widely debated. Nevertheless, they show a high water solubility, which makes water resources the principal medium for their environmental transport. From the toxicological perspective, their environmental persistence and bioaccumulative properties make the PFASs a threat for the ecosystems and human health.

In 2013, a widespread PFAS contamination of surface, ground, and drinking waters was discovered in the Veneto Region (North-Eastern Italy), mainly caused by the RiMAr-Miteni S.p.A. industrial wastewaters. Active since the mid-'60s, this chemical factory contaminated one of the largest underground aquifers in Europe. The inhabitants of the provinces within the so-called "PFAS Red Zone" were exposed, unbeknownst to them, to a PFAS contamination through drinking water for a long time, which led to high concentrations of these chemicals in citizens' serum.

Given the high resonance and impact of this environmental and health emergency, the PFAS levels in the Veneto Region are continuously monitored in inland freshwaters by the Veneto Regional Environmental Prevention and Protection Agency. Nevertheless, limited information is available in literature on PFAS levels in the atmospheric aerosol, a matrix still little-investigated, even in this highly impacted area.

This work was conducted in order to overcome the lack of data relating to the occurrence of PFASs in the atmosphere of the Veneto Region.

Sampling was conducted in a rural area near the municipality of Roncade, in the Treviso province, using a using a low-volume aerosol sampler Skypost PM (TRC-Tecora S.r.l.), equipped with a sequential sampler that operates at a flow rate of 38.3 L min^{-1}. 76 aerosol samples were collected between 02/07/2021 and 12/01/2022.

Analysis of a broad spectrum of PFASs (target compounds, their precursors and substitutes) was carried out by High-Performance Liquid Chromatography coupled with tandem Mass Spectrometry (HPLC-MS/MS).

The compounds detected most frequently were the fluorotelomer 6:2 FTS and PFOS, while those with the highest concentration were 6:2 diPAP (802 ± 591 pg m^{-3}), Me-FOSAA (15 ± 10 pg m^{-3}), Et-FOSAA (9 ± 8 pg m^{-3}), and the new generation compound GenX (13 ± 12 pg m^{-3}).

It has been observed that the total monthly PFAS concentration in the particulate increases in the winter season, especially for the compounds that belong to the classes of Perfluorinated carboxylic acids (PFCAs) and Perfluorinated sulfonic acids (PFSAs). This evidence is related to the reduction of their volatility with the decrease in temperature. Furthermore, the total monthly PFAS concentration increases with increasing relative humidity during the sampling seasons.

Generally, the concentration levels detected in this study for PFOA and PFOS are comparable with those reported in literature.

Source Apportionment of Inorganic and Organic Aerosols in a High-Altitude Mountain Site in South Spain

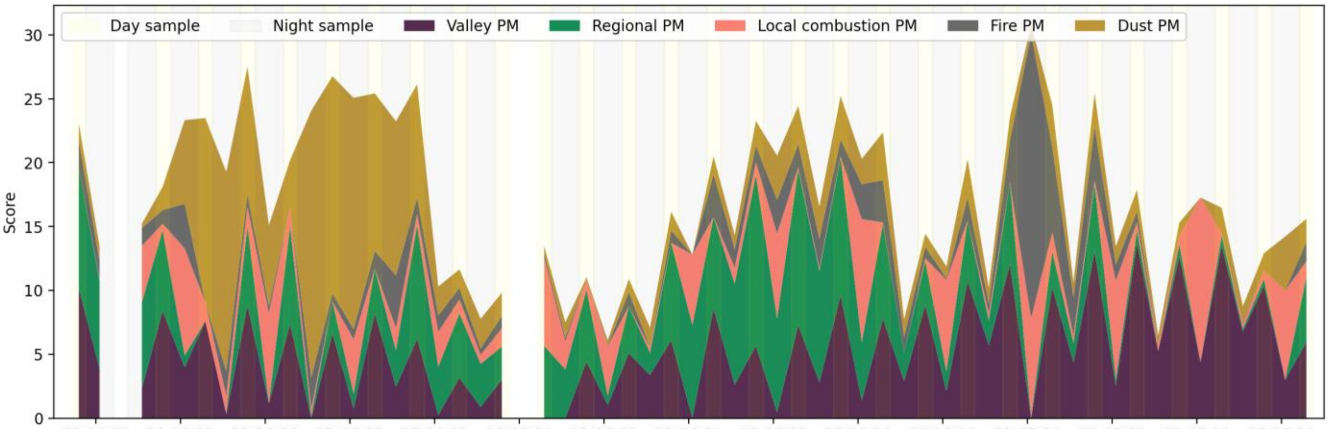
C. Jaén[1]*, G. Titos[2,3], S. Castillo[2,3], A. Casans[2,3], F. Rejano[2,3], A. Cazorla[2,3], J. Herrero[3], L. Alados-Arboledas[2,3], J. O. Grimalt[1], and B. L. van Drooge[1]

[1]Institute of Environmental Assessment and Water Research (IDAEA-CSIC), c/Jordi Girona 18-26, 08034 Barcelona, Spain
[2]Andalusian Institute for Earth System Research (IISTA), University of Granada, Avenida del Mediterráneo sn, 18071 Granada, Spain
[3]Department of Applied Physics, Sciences Faculty, University of Granada, Avenida Fuentenueva sn, 18071 Granada, Spain

clara.jaen@idaea.csic.es

High-altitude mountains can provide representative sampling sites of free troposphere conditions. However, regional and local transport by the mountain breezes may influence the composition of the particulate material in those remote sites. Many transformations and atmospheric processes can take place during transportation and result in complex mixtures of primary and secondary aerosols from both biogenic and anthropogenic activities which involve a challenge to determine the PM origin in those sites.

In this study, a one-month intensive campaign during summer 2021 was performed in Sierra Nevada National Park (southern Spain; 2500 m a.s.l.) by collecting PM_{10} filters during day and night periods. The concentrations of PM, OC, EC, 12 major inorganic compounds, 18 trace elements and 44 organic molecular tracer compounds were analyzed and used to perform a source apportionment study by bilinear decomposition with MCR-ALS method. It resolved 5 main PM_{10} sources: 1) Saharan dust, 2) advection from the urbanized valley, 3) local combustion, 4) smoke from a fire-event, and 5) regional PM. The contribution of each source was clearly linked with the meteorological conditions and the origins of the air masses. Specific day and night trends were observed for most of them. Moreover, the contribution of the sources to PM, OC and EC allows a differentiation between the minor contribution from the local sources and the major contributions from mid- and long-range sources during daytime favored by local circulations of air driven by the orography.



Stacked area of the scores for each source during the sampling period

References

Jaén, C. et al. (2023) 'Diurnal source apportionment of organic and inorganic atmospheric PM at a high-altitude mountain site under summer conditions (Sierra Nevada; Spain)' Atmospheric Chemistry and Physics. Manuscript submitted for publication.

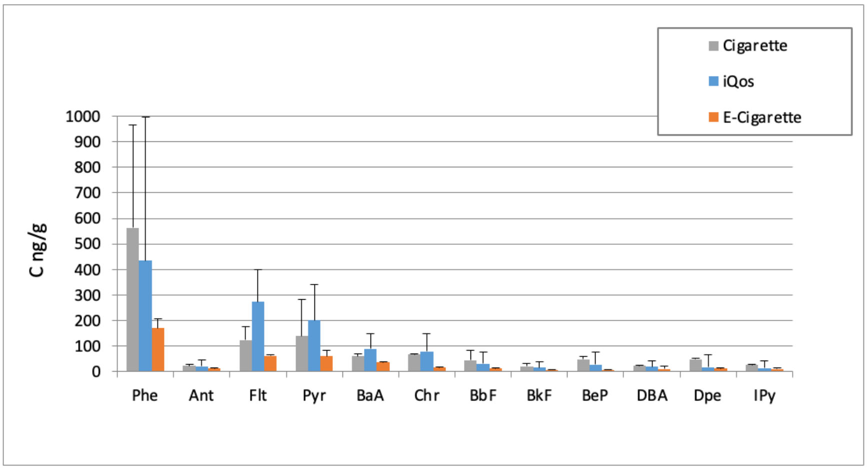
Risk Assessment of Household Dust-Bound PAHs in Relation to Residents' Smoking Habits

A. Avgenikou[1]*, E. Manoli,[2] A. Kouras[3] , G. Lammel[4] and C. Samara[5]

[1,2,3,5]AUTH, Department of Chemistry, Environmental Pollution Control Laboratory, Ethnikis Aminis 41,Thessaloniki, 54124
[4]Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany
[4]Masaryk University, Research Centre for Toxic Compounds in the Environment, Kamenice 5, 62500 Brno, Czech Republic

annaavge@chem.auth.gr

Indoor dust is an increasingly serious public health problem, encouraging various researchers to study exposure to dust-bound pollutants for different vulnerable groups, especially children and senior citizens (Besis et al., 2022). Among the hazardous pollutants bound to indoor dust, Polycyclic Aromatic Hydrocarbons (PAHs) are important due to their carcinogenicity and mutagenicity. Indoor sources of PAHs are smoking, cooking, fireplaces, and infiltration/transport from the outdoor environment. In this study, the exposure to household dust PAHs was studied in relation to smoking habits of residents. Dust sampling was carried out in typical residential from the floor (FD) and the air conditioning filter (ACFD). PAHs were extracted by a microextraction method using Whatman Mini™ UniPrep Filters and analyzed by HPLC/FLD. Fig. 1. shows the mean concentrations of PAHs found in floor dust of smokers' houses in relation to the smoking mode, i.e., conventional cigarette (N=8), heated tobacco products such as i-QOS (N=6), and electronic (e-)cigarette (N=6). The abundance of total PAHs (Σ12PAHs) in floor dust was similar with conventional cigarette and iQOS, but it was significantly lower with e-cigarette (Uguna and Snape, 2022). Inhalation cancer risk was assessed for children and adults. The ILCR of exposure to indoor dust PAHs was calculated on the basis of three routes (ingestion, dermal contact, and inhalation) for children and adults following standard models from the US EPA.



Concentrations of PAHs in floor dust from smokers' houses depending on the type of tobacco (Mean±SD)

References

Besis, A. et al. (2022) 'Hazardous organic pollutants in indoor dust from elementary schools and kindergartens in Greece: implications for children's health' Chemosphere 11, 136750. doi: 10.1016/j.chemosphere.2022.136750.

Uguna C.N. (2022) 'Should IQOS Emissions Be Considered as Smoke and Harmful to Health? A Review of the Chemical Evidence' ACS Omega 7, 22111−22124. http://pubs.acs.org/journal/acsodf.

Polycyclic Aromatic Compounds (PAH, NPAH And OPAH) and Aliphatic Hydrocarbons in Dwellings of an Urban Area: Levels, Sources and Health Risk Assessment

S. Lara[1,2], F. Villanueva[1,2], P.Martín[1,3]*, S. Salgado[1,3], B. Cabañas[1,3]

[1]Universidad de Castilla-La Mancha, Instituto de Combustión y Contaminación Atmosférica (ICCA), Camino de los Moledores s/n, 13071, Ciudad Real, Spain
[2]Parque Científico y Tecnológico de Castilla-La Mancha, Paseo de la Innovación 1, 02006 Albacete, Spain
[3]Universidad de Castilla-La Mancha, Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Avda. Camilo José Cela s/n 13071, Ciudad Real, Spain

mariapilar.martin@uclm.es

Clean air is a basic requirement of life. In the last several years, a growing body of scientific evidence has indicated that the indoor air can be more polluted than the outdoor air (WHO, 2010). Considering that human beings carry out their activities mainly inside buildings, it is necessary to increase the knowledge about air quality in these environments. In order to achieve this, pollutant measurement campaigns must be carried out. Among these pollutants is the particulate matter, PM10. It is well known that the effects on the environment and health are associated with the compounds present in the soluble organic fraction of this particulate matter such as Polycyclic aromatic compounds (PACs). In this work, an indoor air sampling campaign has been conducted in homes and bars in an urban area (Ciudad Real, Spain) with the aim of assessing the pollutant levels, their sources, the chemical and physical characteristics, and the health risk of the occupants of these environments regarding of PM10 and its adsorbed compounds. Eighteen polycyclic aromatic hydrocarbons (PAHs) were analyzed, among them, the 16 EPA priority PAHs and the nitrated and oxygenated derivatives (NPAHs and OPAHs). In addition, n-alkanes and branched alkanes, alkyl cycloalkanes, and n-alkanoic acids have been investigated.

The median daily concentration of Σ16PAHs and Σ7OPAHs in indoor air was lower than in outdoor air. No NPAH was detected indoor, and only 2Nflt was identified in the outdoor filters. The most abundant PACs at homes and outdoor air were BghiP, BbF, IndP, BaP and BA. In the bars, the range of daily concentrations for the Σ13PAHs was 2.61-1.23 ng m^{-3} and for the Σ5OPAHs was 0.97 - 0.46 ng m^{-3}. The concentration of BaP in seven houses and the two bars studied exceeded the guideline value established by WHO. The median concentration of Σ18alkanes in indoor air was 77.94 ng m^{-3}, for Σ3 branched alkanes 1.93 ng m^{-3}, for Σ5cycloalkanes 1.09 ng m^{-3} and for Σ8 n-alkanoic acids 221.59 ng m^{-3}.

The health risk associated to the concentrations of PACs found in the different indoor environments studied has been evaluated. A range between 8 and 95 cancer cases per million people has been estimated. However, it is worth highlighting the case of a home with a high potential risk, 309 cases per million inhabitants. This house is located in an area with high traffic density.

In conclusion, the origin of PM10 depends on the activities of the occupants, the PACs come from sources of external combustion processes that penetrate inside, while the main source of HA and n-alkanoic acids is inside.

References

WHO guidelines for indoor air quality: selected pollutants. Copenhagen: WHO Regional Office for Europe; 2010. https://apps.who.int/iris/bitstream/handle/ 10665/260127/9789289002134-eng.pdf?sequence=1&isAllowed=y. (Accessed 16 March 2023).

Environmental Implications of the Emission of Hydroxyethers into the Atmosphere

S.Salgado[1,2]*, I. Aranda[1,2], P. Martín[1,2], F. Villanueva[2,3], T. Pinés[1,2], B. Cabañas[1,2]

[1]Universidad de Castilla-La Mancha, Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Avda. Camilo José Cela s/n 13071, Ciudad Real, Spain.
[2]Universidad de Castilla-La Mancha, Instituto de Combustión y Contaminación Atmosférica (ICCA), Camino de los Moledores s/n, 13071, Ciudad Real, Spain.
[3]Parque Científico y Tecnológico de Castilla-La Mancha, Paseo de la Innovación1, 02006 Albacete, Spain.

sagrario.salgado@uclm.es

Hydroxyethers (HEs) are a type of oxygenated volatile organic compounds (OVOCs) that contains an alcohol group and an ether group in the structure. The use of these compounds as solvents and chemical intermediates has increased markedly in recent years (Cheremisinoff, 2003). Once released into the atmosphere, they can undergo degradation processes mainly by reactions with the atmospheric oxidants (OH and NO_3 radicals, Cl atoms and O_3 molecules) that can have significant effects on the environment. In this work, a compilation of the data obtained to date (by our research group and those of bibliographic references) regarding the reactivity of HEs with the main atmospheric oxidants is made. The influence of the structure on the reactivity is analyzed and conclusions are drawn regarding the mechanism by which these reactions take place. Briefly, for ·OH and Cl reactions, rate coefficients slightly increase with increasing the length of the chain to both sides of the oxygen of the ether group. There are insufficient data in the case of reactions with NO_3 or ozone to establish any trend.

Potential health and environmental effects of these compounds and by products of their reactions are evaluated. Toxicological studies (ECETOC Technical Report, 1995) have shown that ethylene glycol ethers are toxic to reproduction and are toxic to rapidly dividing cellular systems such as bone marrow. The short-chain ethylene glycol ethers are known to cause teratogenicity and foetotoxicity. Most of the products generated are carbonyls and multifunctional compounds, that could have a great impact in the atmosphere. HCHO generated in these processes is one of the substances considered as a human carcinogen (14th report on Carcinogens, 2016). Nitrated compounds are also formed in the presence of NOx and, in the atmosphere, organic nitrates and HCHO are known to be involved in processes such as the formation of photochemical smog or peroxyacylnitrates PANs.

Regarding the atmospheric implications have been established by estimating parameters such as lifetimes, global warming potential (GWP) and the photochemical ozone creation potential (POCPE). Briefly, the results of lifetimes obtained show that the dominant process of loss in the atmosphere of HEs is the reaction with OH radicals with lifetimes in the range of 7-23 hours. GWP calculated indicate that the contribution of these compounds to the greenhouse effect is negligible. In terms of ozone generation potential, compared to other volatile organic compounds, values of the amount of O_3 formed are higher than those of alkanes, in the same order as alcohols and ethers, and lower than unsaturated oxygenated and alkenes, therefore, we consider that hydroxyethers are important in tropospheric ozone generation processes.

References

Cheremisinoff, N.P., (2003) Industrial Solvent Handbook, second. ed. Marcel Dekker, New York.
ECETOC Technical Report 64 (1995). The Toxicology of Glycol Ethers and its Relevance to Man; ECETOC: Brussels.

Indoor Strains of *Aspergillus Calidoustus* and *Aspergillus Versicolor* Emit Mycotoxins in Guttation Droplets

R. Mikkola[1], M. Andersson[1], A. Varga[2], L. Kredics[2], and H. Salonen[1]

[1]Aalto University, Department of Civil Engineering, School of Engineering, Finland
[2]University of Szeged, Department of Microbiology, Faculty of Science and Informatics, Hungary

Active mold growth indoors is considered a health threat, and there is consensus that inhaling mold can cause health problems for people. However, why active mold growth is a more serious threat than the presence of dried, inactive mycelia (1) and how metabolically active molds release hazardous substances into indoor air is still a matter of debate. In other words, there is consensus that inhalation exposure to molds can cause human health problems (2), but the point at which indoor microbial contamination harms human health is not yet understood. In this study, we show that actively growing *Aspergillus* strains belonging to the species *A. calidoustus* and *A. versicolor* secrete mycotoxins in guttation droplets. Guttation enables the release of metabolic products into the environment and is associated with active fungal growth. The mycotoxins secreted by *A. calidoustus* were identified by LC-MS as ophiobolin H and G. *A. versicolor* strains secreted sterigmatocystin, 5-methoxysterigmatocystin and averufin. These metabolites have previously been detected in biomass extracts of indoor strains of *A. calidoustus* and *A. versicolor* (3). Toxic secondary metabolites in guttation droplets have previously also been detected in indoor *Penicillium Trichoderma* (4) and *Chaetomium* strains (5), but to our knowledge, this is the first time they have been found in guttation droplets secreted by indoor *Aspergillus* strains. We speculate that the guttation of these metabolites may contribute to the indoor air load of hazardous substances in polluted buildings. We suggest that the presence of mycotoxins, i.e., as sterigmatocystin produced by *A. versicolor*, a known indicator of indoor water damage, justifies this mold's bad reputation.

References

Cheremisinoff, N.P., (2003) Industrial Solvent Handbook, second. ed. Marcel Dekker, New York.
ECETOC Technical Report 64 (1995). The Toxicology of Glycol Ethers and its Relevance to Man; ECETOC: Brussels.

Chemical Characterization of Particulate Deposits on Electrical System Insulators

M. Borelli[1]*, G. Santucci de Magistris[3], Claudia Schianchi Betti[3], A. Bergomi[1], C. A. Lombardi[1], P. Fermo[1], V. Comite[1], A. M. Toppetti[2], L. Fialdini[2], P.Omodeo[2], E. Mannelli[2], A. Balzarini[2], G. Pirovano[2] and N. Luciano[2]

[1]University of Milan, Department of Chemistry, Via Golgi 19, 20133 Milan, Italy
[2]RSE S.p.A., Sustainable Development and Energy Sources Department, via Raffaele Rubattino, 20134 Milano, Italy
[3]RSE S.p.A., Power Generation Technologies and Materials Department, via Vittore Callegari, 29122 Piacenza, Italy

mattia.borelli@unimi.it

We are living in times of energetic transition, and we are increasingly relying on the electrical system. It is well documented (Mohammadnabi et al., 2021) that saline pollution of the insulators, arising from particulate matter deposition, in the presence of high relative humidity levels can lead to flashovers, with consequent possible service interruptions and high maintenance costs. Up to now, the majority of the studies, and even the technical standard (International Electrotechnical Commission, 2018), addressed the analytical problem of quantifying the risk of flashover only from the conductivity point of view, estimating the ESDD (Equivalent Salt Deposit Density) and NSDD (Non-Soluble Deposit Density) indicators. This doesn't allow an in-depth understanding of the phenomenon. In our project we focused the attention to the specific chemical composition of the deposit, in order to develop more robust and effective alert systems based on modelling tools.

The experimental set-up included the installation of tempered glass insulators chains within RSE, in Milan, and was put in place to study the influence, to the properties of the deposit, of: weather conditions, vertical profile, insulator surfaces. The deposit was sampled every two months for a year and a half, with the cleaning procedure described in the technical standard, distinguishing the top from the bottom.

The first characterizations were the ESDD and NSDD indicators; their respective mean values were 0.01 and 0.02 mg $\mathrm{cm^{-2}}$. These results proved the behavior of these chains to be comparable with the ones placed in the same area and belonging to the Italian transmission network We then evaluated the parameters contributing to the soluble and insoluble fractions. Ionic content was evaluated using Ion Chromatography. The main components were ammonium, calcium, sodium, potassium, chloride, nitrate and sulfate, respectively 36, 20, 14, 7, 9, 6 and 3% of the total equivalents, in average and excluding outliers. Metals and trace elements were evaluated using Optical Emission Spectroscopy (ICP-OES) technique. It is important to analyze both main and trace elements to obtain information on the sources. The insoluble carbonaceous content was measured using Thermal Optical analysis in Transmittance mode (TOT), to obtain Organic Carbon (OC) and Elemental Carbon (EC). The mean surface densities were found to be 7.1 and 0.2 μg $\mathrm{cm^{-2}}$, respectively. The OC/EC ratio was generally significantly higher than the typical value of atmospheric particles, thus indicating evolution phenomena of the deposit and of the sources. From this first dataset, the main factors influencing the concentrations were weather conditions and top vs bottom surface of the insulator.

This new information on chemical composition allow to describe the flashover phenomenon from the constituent point of view, thus linking it to the sources of pollution. In future works, this will allow us to create a prevention model, that can alert the network operator before the flashover happens. It is important to underline that this kind of chemical characterization is a novelty for Italy, and that also internationally there are few works on this topic (He et al., 2019).

References

Mohammadnabi, S. et al. (2021) 'Influence of humidity and contamination on the leakage current of 230-kV composite insulator', Electric Power Systems Research, Volume 194. doi: 10.1016/j.epsr.2021.107083.

International Electrotechnical Commission (2018) IEC 60815-1 'Selection and dimensioning of high-voltage insulators intended for use in polluted conditions'.

He, Z. et al. (2019) 'Analysis of natural contamination components and sources of insulators on ± 800 kV DC lines', Electric Power Systems Research, Volume 167, pp192-198. doi: 10.1016/j.epsr.2018.10.033.

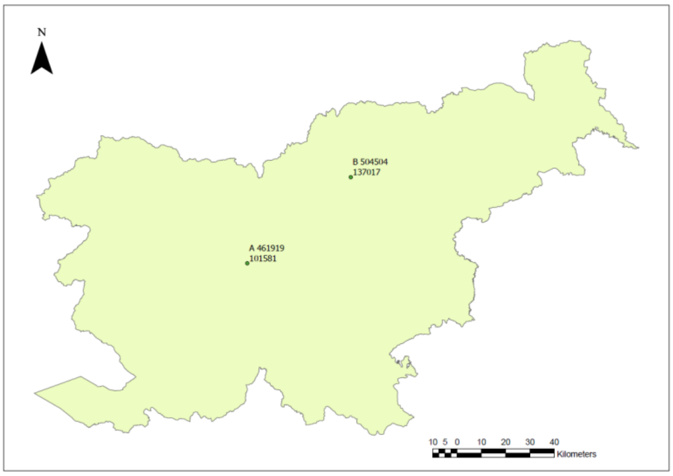
An Analysis of Air Pollutants (NO_2, NOX, PM_{10}, and $PM_{2.5}$) in the Republic of Slovenia Between Years 2019 and 2020

M. Ivanovski[1]*, R. Vončina[1]

[1]Elektroinštitut Milan Vidmar, Department for Environment, Hajdrihova 2, 1000 Ljubljana, Slovenia

maja.ivanovski@eimv.si

Air pollution can have a significant effect on human health (Kyung and Jeong, 2020). Currently, it represents a major global threat that is practically impossible to avoid, especially in the developing countries (Kyung and Jeong, 2020). Air pollution is defined as a contamination of the indoor or outdoor environment by any chemical, physical, or biological agent that modifies the natural characteristics of the atmosphere (WHO, 2021). Lately, there have been critically high concentrations of air pollutants measured in many large EU cities, affecting the quality of life and public health (European Commission, 2012). The potential sources of pollution are still traffic (mostly road and railway), agricultural residue burning, coal, biomass, and industry. The objective of this work is to analyse daily concentrations of four typical air pollutants (NO_2, NOX, PM_{10}, and $PM_{2.5}$) in the Republic of Slovenia. The study was conducted from January 2019 to December 2020 at two monitoring stations, so-called urban traffic and urban industrial. Obtained results showed a decline in average concentrations for all studied air pollutants through the years, respectively (< 12%). From the daily average data it can be observed that NO_2 and NOX daily average concentrations were higher in 2019 at urban traffic location. PM_{10}, and $PM_{2.5}$ daily average concentrations were higher in 2019 at urban traffic location. In total, obtained results showed a decline in average concentrations for all studied air pollutants through the years, respectively (< 12%).



Caption (max 150 characters - spaces included)

References

S. Y. Kyung and S. H. Jeong, "Particulate-Matter Related Respiratory Diseases," Tuberc. Respir. Dis. (Seoul)., vol. 83, no. 2, pp. 116–121, Apr. 2020, doi: 10.4046/trd.2019.0025.

WHO, "World Health Organization - Air Pollution," 2021.

European Commission, “Roadmap 2050,” Policy, no. April. 2012, pp. 1–9, 2012, doi: 10.2833/10759.

Inter-Comparison of Different Experimental Methods to Identify and Quantify the Uncertainties of Road Dust Resuspension Emissions

F. Ippolito[1]*, M. Bedogni[2], V. Vecchi[1], A. Rodrigue Luque[1] and F. Amato[1]

[1]Institute of Environmental Assessment and Water Research, IDAEA, Spanish Research Council (CSIC), 08034 Barcelona, Spain. 2 AMAT, Milano, Italy

federica.ippolito@idaea.csic.es

Road dust resuspension (RD) emissions are affected by a high uncertainty and consequently the resuspension contribution is usually not included in the emission inventories. This heavily affects the results of the air quality models, particularly when they are compared with the air quality data measured by monitoring stations. According to the EEA (EEA, 2022), road dust resuspension source is a key source of air pollution and important source of exceedances.

In this study we inter-compare different methods for estimating emission factors (EF) for road dust in two European cities Barcelona (Spain) and Milan (Italy), with the purpose to quantify their uncertainties. The measuring campaigns took place from June to November 2022 Figure 1. The estimations of RD EF were carried out using the following methods:

1) The NOx dilution method, described by Amato et al. (2010), in Barcelona, using two monitoring stations, more specifically the “Eixample” traffic monitoring station and the “Palau Reial” urban background station. The method is based on air quality measurements performed at both stations simultaneously. PM10 and PM2.5 daily sampling and chemical characterization was carried out following the methodology described by Querol et al., (2001).

2) The Vertical profile (VP) method, described by Amato et al., (2017), in Barcelona and Milan, used to define a vertical concentration profile for particles below 10 µm, as a result of two transport processes: (i) deposition (ii) the opposite rising movement of the particles produced by the turbulence (i.e., resuspension). If the road dust emissions depend on the amount of deposited dust on the road surface, then necessarily this dust loading has to evolve with time, until it is replenished at the same rate that it is removed, thus the resuspension flux can be obtained by calculating the deposition flux.

3) The road dust loading method described and used by Amato et al. (2011) in Barcelona city. The sampler instrument method is allowing sampling directly from the road pavement in a 50x100 cm road surface area during 15 minutes the mobile fraction of RD below <10 µm in aerodynamic diameter, and estimating EFs.

4) The Road dust loading estimation by Padoan et al., (2018) model based on the combination of: (a) the Mean Texture Depth (MTD) using the sand patch method: a standard evaluation of the surface macro-structure by careful application of a known volume of standard material (ASTM E 965,2015) on the surface, and subsequent measurement of the total area covered. (b) photographic analysis of the pavement surfaces: the size distribution and mean horizontal size of aggregates is estimated by counting the total number and the size of each aggregate along the ruler.

Moreover, the spatial variability within an urban environment will be investigated using the approach proposed by Padoan et al., (2018), where EFs can be easily estimated at several roads using traffic count data, distance from braking zoneS and road dust porosity data, which will be obtained in Milan and Barcelona. This work was carried out in the framework of the LIFE REMY project (PRE/IT000004).

References

Amato, F. et al. (2010) ‘A comprehensive assessment of PM emissions from paved roads: Real-world Emission Factors and intense street cleaning trials’, Science of the Total Environment, 408(20), pp. 4309–4318. Available at: https://doi.org/10.1016/j.scitotenv.2010.06.008.

Amato, F. et al. (2017) ‘Characterization of road dust emissions in milan: Impact of vehicle fleet speed’, Aerosol and Air Quality Research, 17(10), pp. 2438–2449. Available at: https://doi.org/10.4209/aaqr.2017.01.0017.

Padoan, E. et al. (2018) ‘An empirical model to predict road dust emissions based on pavement and traffic characteristics’, Environmental Pollution, 237, pp. 713–720. Available at: https://doi.org/10.1016/J.ENVPOL.2017.10.115.

INQUIRE - Improving Indoor Air Quality and Health: Identification of Chemical and Biological Determinants, their Sources, and Strategies to Promote Healthier Homes in Europe

M. Nipen[1]*, P. Bohlin-Nizzetto[1], L. Melymuk[2], P. Leonards[3], E. Wincent[4], C. Giorio[5], L. Schenk[4], J. Theunis[6], P. Rostkowski[1]

[1]NILU-Norwegian Institute for Air Research, Kjeller, Norway
[2]Masaryk University, RECETOX, Brno, Czech Republic
[3]Vrije University Amsterdam, the Netherlands
[4]Karolinska Institute, Stockholm, Sweden
[5]University of Cambridge, Cambridge, United Kingdom
[6]VITO, Mol, Belgium

mni@nilu.no

Air pollution has been identified as a main determinant of early death risk, and air quality standards for a range of pollutants in outdoor air have therefore been established. However, the indoor environment may be more relevant for exposure as European citizens spend up to 90% of their time indoors, and concentrations of many air pollutants are higher indoors than in urban outdoor environments. This is particularly relevant for young children. Existing indoor air quality (IAQ) guidelines are mainly focused on humidity, microbes, and a small number of volatile chemicals. There is, however, an evidence-based consensus that the chemical and biological determinants of IAQ are more numerous and complex than the existing guidelines account for.

To address this challenge, we are deploying a comprehensive research and innovation program, including a nonintrusive monitoring approach for residential indoor environments. We are in the process of gathering personal data, IAQ sensor data, air samples for volatile and semi-volatile organic compounds from indoors and outdoors, settled dust samples, and urine samples. Two countries have been selected from each region of Europe (North, South, East, West) to encompass regional, socioeconomic, and cultural variability in living conditions. Within each country, 25 families and homes are selected, prioritizing homes with young children. This will on completion yield a total of 200 family/home pairs across Europe. To provide a global context, parallel sampling will be conducted in 25 homes in Australia. The study will also carry out supplemental sampling to enable identification of sources of the chemical and biological determinants by screening three source categories: i) The outdoor environment. ii) The built structure (covering building age, primary building material, dwelling type), including a specific assessment of “green” buildings; and iii) Furnishings, consumer products, and personal behaviours. The collected samples will be subject to suspect and nontarget screening for volatile and semi-volatile organic chemicals and microbiome, and target analysis of chemicals and allergens. Also, comprehensive arrays of toxicological effect-studies will be carried out. This includes in-vitro based effect screening and detailed assessment of respiratory toxicity, endocrine disruption, and impaired immunity; and in-vivo validation of effects of local and systemic toxicity. Adverse outcome pathways (AOPs) and virtual effect-directed analysis (vEDA) will be applied for apportioning risk to its main determinants. Following up on the findings from the initial phase of the study, we will revisit some homes to implement strategies for improving IAQ based on e.g., air purifier and ventilation systems, behavioural changes, renovations, and introduction/removal of consumer products.

With the findings from this study, we will resolve knowledge gaps on the identity, sources, exposure and health risks of hazardous chemical and biological determinants in residential indoor environments and provide effective strategies to reduce the risk for residents. All data generated in the study will be made available as FAIR data.

Experimental Investigation on Coal Dust Suppression Efficiency of Environmentally Friendly Solution by Using Wind Tunnel

S. Petkovic[1]*, M. Pavlovic[1], A. Radojicic[2]

[1]Mining Institute, Laboratory of environmental protection and occupational safety, Batajnicki put 2, 11080 Belgrade, R.Serbia
[2]Mining Institute, Laboratory of solid fuels, Batajnicki put 2, 11080 Belgrade, R.Serbia

sandra.petkovic@ribeograd.ac.rs

In the aim to solve the problem of a complex environment and severe dust pollution in large surface coal mines, product based on alginate was developed to suppress coal dust. The dust suppression effectiveness tests were carried out in a constructed laboratory rectilinear pressure wind tunnel at air flow rate of 5 m/s. Before testing the product influence, the wind profile in the wind tunnel was determined by simulation of real conditions in surface coal mines. The investigation also included three sample conditioning regimes (room temperature 20°C, elevated temperature 40°C and low temperature -18°C to examine the impact under all climatic conditions during the year. The experiments showed that the mass concentrations of suspended particulate matters PM10 of the treated coal samples did not exceed the limit value recording the Regulation on monitoring conditions and air quality requirements (Official Gazette of the RS No. 75/10, 11 /10 and 63/13). By comparing the results for a moisture free coal sample, it was confirmed that there was no influence on the physical and chemical characteristics and quality parameters of the coal. The product adhesion testing showed that it was equally effective both at the test temperature of 40°C and when freezing at a temperature of -18° C. This research provides a new theoretical idea for coal dust control in a complex environment different from the so far used water curtain technology that requires continuous application and therefore irrational consumption of the most precious natural resource.

References

Chen, Yinping, et al. "Characterization of coal particles wettability in surfactant solution by using four laboratory static tests." Colloids and Surfaces A: Physicochemical and Engineering Aspects 567 (2019): 304-312.

Wang, Liang, et al. "A novel biomass thermoresponsive konjac glucomannan composite gel developed to control the coal spontaneous combustion: Fire prevention and extinguishing properties." Fuel 306 (2021): 121757.

Chen, Zhihui, et al. "Coking behavior and mechanism of direct coal liquefaction residue in coking of coal blending." Fuel 280 (2020): 118488.

Methane Abatement by Catalytic Oxidation over Zr Modified Pd/ La-Ce-Al Catalyst

R. Velinova[1]*, S. Todorova[2], D. Kovacheva[1], G. Ivanov[1], M. Shipochka[1], P. Markov[1], D. Nihtianova[3] and A. Naydenov[1]

[1]Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Acad. G. Bonchev Str., bl. 11, 1113 Sofia, Bulgaria
[2]Bulgarian Academy of Sciences, Institute of Catalysis, Acad. G. Bonchev Str., bl. 11, 1113 Sofia, Bulgaria
[3]Bulgarian Academy of Sciences, Institute of Mineralogy and Crystallography, Acad. G. Bonchev Str., bl. 107, 1113 Sofia, Bulgaria

raligeorgieva@svr.igic.bas.bg

Nowadays, air pollution is a very serious problem. There are different types of air pollutants, such as gases (ammonia, carbon monoxide, sulfur dioxide, nitrous oxides, methane, carbon dioxide and chlorofluorocarbons), particulates, and biological molecules. It can cause diseases, allergies, and even death to humans. Pollution can be caused by both human activities (Howell et al., 2016), and natural phenomena (Dimitriou et al., 2011). It is well known that the greenhouse gases are main contributor to climate change. Among them is methane which has an even greater global greenhouse previously considered (Howarth et al., 2011). One of the most promising technology for reducing methane emission is catalytic oxidation. Usually the Pd supported on γ-Al_2O_3 catalysts wetechnologiesut they are not enough stable at high temperatures. In order to improve the properties of palladium catalysts different additives have been used.

New results for methane abatement in the presence of H_2O and SO_2 by catalytic oxidation over Zr modified Pd/La-Ce-Al catalyst have been obtained. The catalyst characterization has been made by N_2- physisorption, XRD, SEM/EDX, HRTEM, XPS, EPR, O_2-TPD, CH_4/TPR and FTIR methods. Nitrogen adsorption-desorption isotherms show typical mesoporous materials. Investigation with XRD analysis shows that deposition of palladium on the supports lead to the appearance of peaks, that are characteristic of PdO and after the catalytic tests a new, highly crystalline cubic metal-Pd phase appears. The XPS analysis show that the palladium is homogeneously dispersed, and it is present on the surface of the catalyst in three oxidation states: Pd^0, Pd^{2+} and Pd^{4+}. The reaction of complete oxidation of methane proceeds at temperatures above 220ºC. T_{50} in dry gas feed is 350 ºC, while in the presence of 1.2 % water vapor T_{50} is 389 ºC (oxygen content of 5 vol. %, GHSV = 60 000 h^{-1}).

Therefore, the Zr modified Pd/ La-Ce-Al catalyst can be considered as perspective material for use as an active phase in preparation of environmental catalysts for reduction of emission of methane.

Acknowledgements: This research was funded by the Ministry of Education and Science under the National Program "European Scientific Networks" grant number Д01-272/02.10.2020 "European Network on Materials for Clean Technologies" and by the Operational Program "Science and Education for Smart Growth" 2014-2020, co-funded by the EU from the European Regional Development Fund, grant number No BG05M2OP001-1.001-0008.

References

Howell, R. et al. (2016) "The Environment and Environmentalism" In Daniels, P.; Bradshaw, M.; Shaw, D.; Sidaway, J.; Hall, T. (eds.). An Introduction To Human Geography (5th ed.). Pearson. p.134. ISBN 978-1-292-12939-6.

Dimitriou, A. et al. (2011), Khallaf, M. (ed.), "Causes and Consequences of Air Pollution and Environmental Injustice as Critical Issues for Science and Environmental Education", The Impact of Air Pollution on Health, Economy, Environment and Agricultural Sources, InTech, doi:10.5772/17654.

Howarth, R. et al. (2011) "Methane and the greenhouse-gas footprint of natural gas from shale formations" Climatic Change 106, 679-690 doi 10.1007/s10584-011-0061-5.

An Innovative Monitoring Approach for the Chemical Characterization of Particulate Matter (PM) in an Industrial Site in Southern Italy

A. Di Gilio[1]*, J. Palmisan[1] and G. de Gennaro[1]

[1]University of Bari, Department of Bioscience, Biotecnologies and Environment, via Orabona, 4, 70126, Bari

alessia.digilio@uniba.it

The temporal variability of emissive processes as well as the reactivity and transport of pollutants in the atmosphere drastically affect the chemical composition of PM during the day. The conventional approaches for air pollutants monitoring and control do not often allow the identification and characterization of occasional emissions and of short-term events of high PM. Consequently, especially in heavily polluted industrial areas, the real impacts of pollutant sources on the air quality and on health of the exposed populations become difficult to assess. Therefore, in order to overcome the limits of the conventional approaches and characterize fugitive emissions impacting in heavily polluted industrial areas as Taranto (South of Italy), in this study an high time-resolution monitoring campaign of particles, Total Polycyclic Aromatic Hydrocarbons (TPAHs) and heavy metals were conducted from 18th October to 19th December 2018 at a residential site a few kilometers from the industrial area of Taranto (Tamburi). Taranto is included in the list of high priority polluted sites of national interest due to the presence of an extended and complex industrial area near the urban settlement (Chiari et al., 2006; Palmisani et al., 2020). During the monitoring campaign, the number concentrations of particles with diameter between 0.28 and 10 um were continuously monitored by an optical particle counter (OPC) while the hourly concentrations of heavy metals and TPAHs were measured using a reel to reel X-ray analyzer (XACT 625) and a photoionization analyzer (EcoChemPas 2000), respectively.

Considering the complexity of the investigated area and the great diversification of pollutant sources, the hourly chemical characterization of particles has proved to be a useful tool to study the temporal evolution of industrial emissions and the meteorological factors affecting the PM composition. In fact, the integration of whole collected data with meteorological information allowed to localize and characterize industrial fugitive emissions, identify the number and features of sources and/or industrial processes significantly impacting in residential area of Tamburi district. In fact, the highest hourly concentrations of metals and TPAHs were registered in the hours when gusts of wind blew from the North-West allowing pollutants transport from industrial area on receptor site. An exception is made only for iron showing meanly high concentrations in correspondence of weak winds probably due to the 'dusting' and/or movement of materials in mineral park. Therefore, this study highlighted that the high time-resolution monitoring and chemical characterization of particles provide prompt feedback on the pollutant concentrations and a more accurately understanding of the real population exposure.

References

Chiari, M. et al.,(2006). "Hourly elemental composition and source identification of fine and coarse PM10 in an Italian urban area stressed by many industrial activities". Nucl. Instrum. Methods Phys. Res. B, 249, 584–587.https://doi.org/10.1016/j.nimb.2006.03.060.

Palmisani J. et al. (2020). "Particle-Bound PAHs and Elements in a Highly Industrialized City in Southern Italy: PM2.5 Chemical Characterization and Source Apportionment after the Implementation of Governmental Measures for Air Pollution Mitigation and Control". International Journal of Environmental Research and Public Health, 17,4843. https://doi.org/10.3390/ijerph17134843.

Biomonitoring for a Sanitary Landfill Air Quality Using Honeybees and Other Hive Products

S. Breda[1]*, A. Brunelli[1,2], G. Giovane[3], G. Bonacina[3] P.Scanferla[1], A. Marcomini[2]

[1]Fondazione Università Ca' Foscari, Dorsoduro 3859, 30123 Venezia, VE, Italy
[2]DAIS - Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Via Torino 155, 30170, Venice, Italy
[3]Progeco Ambiente S.p.A., via Ca' Vecchia 12/A, 37036 San Martino Buon Albergo VR, Italy

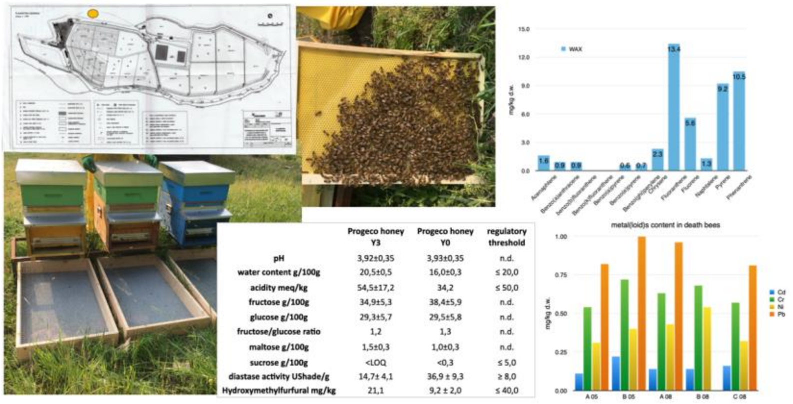
silvia.breda@unive.it

The use of bioindication techniques for assessing environmental contaminants has largely increased during last decades. Bee and beehive products have been used both for bioindication (qualitative information about contaminants presence) and biomonitoring (quantitative determination of contaminants) activities.

Landfill areas and their surroundings are considered in the same ways as contaminated sites and consequently are located into industrial or other non-urbanised portion of territories. The more hazardous or contaminated are the waste they host, the most the air quality of the surroundings is perceived as polluted and dangerous.

The method developed within this study allowed to obtain information on both air and environmental quality of a sanitary landfill area, located in the central part of the Padana plain hosting non-putrescible hazardous stabilized and non-hazardous industrial waste. Honey, death bees, wax, pollen, other environmental samples (leaves, stream water) and landfill leachate were collected to monitor the presence of landfill peculiar contaminants, including both organic compounds and metal(oid)s. The biomonitoring investigation was carried out over a three-year period, and the quality grade of honey was also assessed in order to evaluate the productive performance of bees within this peculiar area.

Air quality was always free from landfill-target contaminants, but several agricultural residues were founded as persistent ubiquitarians pollutants.



	Progeco honey Y3	Progeco honey Y0	regulatory threshold
pH	3,92±0,35	3,93±0,35	n.d.
water content g/100g	20,5±0,5	16,0±0,3	≤ 20,0
acidity meq/kg	54,5±17,2	34,2	≤ 50,0
fructose g/100g	34,9±5,3	38,4±5,9	n.d.
glucose g/100g	29,3±5,7	29,5±5,8	n.d.
fructose/glucose ratio	1,2	1,3	n.d.
maltose g/100g	1,5±0,3	1,0±0,3	n.d.
sucrose g/100g	<LOQ	<0,3	≤ 5,0
diastase activity UShade/g	14,7± 4,1	36,9 ± 9,3	≥ 8,0
Hydroxymethylfurfural mg/kg	21,1	9,2 ± 2,0	≤ 40,0

Figure 1: Site size, hive equipment and an example of results of organic compounds and inorganic elements concentrations in wax and death bees samples

References

Enrique Conti, M., Luisa, M., Mele, G., Ristorini, M., Vitiello, G., Massimi, L., Canepari, S., & Grazia, M. (2022). Performance of bees and beehive products as indicators of elemental tracers of atmospheric pollution in sites of the Rome province (Italy). *Ecological Indicators*, *140*, 109061–109061. https://doi.org/10.1016/j.ecolind.2022.109061

Zarić, N. M., Brodschneider, R., & Goessler, W. (2022). Honey bees as biomonitors – Variability in the elemental composition of individual bees. *Environmental Research*, *204*, 1–8. https://doi.org/10.1016/j.envres.2021.112237.

Validation Of a Voltammetric Approach for Determination of Mercury in Airborne Particulate Matter Using Screen-Printed Electrodes

F. Tsopelas[1]*, Th. Lymperopoulou[1], L.A. Tsakanika[1], K.M. Ochsenkuehn[1] and M. Ochsenkuehn-Petropoulou[1]

[1]School of Chemical Engineering, National Technical University of Athens, Athens, Greece

ftsop@central.ntua.gr

Mercury is a highly toxic and persistent contaminant found in all parts of the environment. It is mainly emitted as a result of combustion of fuels and during industrial processes, but unlike many industrial pollutants, it has the ability to spread globally through atmospheric transport. Over the years, there is an increasing awareness about the harmful effects of mercury on human health, occupational safety, and environmental sustainability. Mercury in the atmosphere is partitioned into gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate-bound mercury (TPM) [Yang et al., 2020, Raju et al., 2022]. As mercury concentrations are very low, appropriate analysis methods and their validation constitutes an important topic. For reasons of mercury quantification, inductively- coupled plasma (ICP-MS) and cold vapor atomic absorption spectrometry (CVAAS) have usually been proposed. However, electrochemical techniques are very attractive owing to their high sensitivity, inherent simplicity, miniaturization, low cost and their ability to be adapted for field analysis.
The aim of the present study is to evaluate Square Wave Anodic Stripping Voltammetry for purposes of TPM quantification. Voltammetric measurements were carried out using Boron Doped Diamond (BDD) screen-printed electrodes (Dropsens) in presence of 40 μg/L Bi3+, using pre-electrolysis potential of -1.0 V for 120 s. Two certified reference materials (CRMs) of different mercury content were employed. Microwave assisted sample digestion in presence of HNO3 and H2O2 was carried out, according to the EN14902:2005. Limit of Detection was found to be 3.0 μg/L (3.3*SD/slope) and Limit of Quantification (10*SD/slope) was 9.0 μg/L, corresponding to 40 ng•m-3 and 120 ng•m-3 for 1 h sampling (2.2 m3 air). Interference test carried out included Cu2+, Cd2+, Zn2+, Ni2+, Co2+ and Fe3+. Recoveries for CRMs were 95.5%, 104.3% and 106.7% for concentrations of 12.0, 20.0 and 50.0 μg/L, respectively. The methods were applied for mercury determination in five PM10 cellulose filters, collected by CMI (Cesky Metrologicky Institut) from the 4th to 13th of April 2022, at the building of Czech Metrology Institute, in Pardubice, Czech Republic using DEKATI PM10 impactor [Lymperopoulou et al., 2022]. The sampling time and the respective air volumes varied from 2.2 m3 for 1 hour sampling to 220 m3 for 4 days (96 hours). The total net deposited mass varied from 0.9 to 3 mg. No mercury was detected at any sample. Taking into account the method detection limit atmospheric mercury levels in the area of Pardubice, Czech Republic were found below 3 ng•m-3 for a sampling period of 4 days. Results are in agreement with ambient particulate Hg analysis during the same period using cascade impactor sampling and TXRF.

This work is supported by the EMPIR EURAMETAEROMET II project (19ENV08) http://www.aerometprojectii.com.

References

Raju, V.O. et al. (2020), "Impacts of Mercury on human health, safety and environment: Literature Review and Bibliometric Analysis (1995 to 2021)", International Journal of Occupational Safety and Health 12(4) pp. 336-352. doi: 10.3126/ijosh.v12i4.43125

L. Yang, Y. Zhang, F. Wang, Z. Luo, S. Guo, U. Stahle, "Toxicity of mercury: Molecular evidence", Chemosphere 245 (2020) 125586. doi: 10.1016/j.chemosphere.2019.125586

Lymperopoulou, T. et al. (2022), "Method validation for mercury determination in airborne particulate matter and implementation in Pardubice area (Czech Republic)" International Aerosol Conference IAC 2022, 4-9 September 2022, Proceedings 2022, p.1177.

Microplastics Detection Using Chemical Ionization MS With Multi-Scheme Chemical Ionization Inlet (MION)

J. Mikkilä[1], J. Mikkilä[1], J. Kontro[1], F. Partovi[1,2], H.J. Jost[1], E. Lattouf[1]*

[1]Karsa Ltd., A. I. Virtasen aukio 1, 00560 Helsinki, Finland
[2]Tampere University, Aerosol Physics Laboratory, Physics Unit, Faculty of Engineering and Natural Sciences, 33720 Tampere, Finland

elie.lattouf@karsa.fi

The process of Chemical Ionization (CI) involves using a chemical reagent to create ions that will charge a gaseous sample through ion-molecule reactions. This method is considered to be gentle and specific, but traditional CI and Electrospray Ionization have some drawbacks such as neutral reagent vapors/droplets that can negatively affect the sample chemistry and result in adverse matrix effects. However, the MION approach overcomes these limitations by using ion injection to allow only charged reagents to enter the sample flow and providing the ability to rapidly sample ions in both polarities. The system combines filters thermal desorption (TD), a MION source, and an orbitrap mass spectrometer (LTQ Velos pro) for substance identification. The aim of this work is to demonstrate that plastic compounds can be desorbed, ionized, and detected with Karsa TD-MION-Orbitrap setup without chromatographic separation.

Two methods were used for sample introduction to the system: polystyrene was in suspension in water and polypropylene in the form of solid beads. The first was introduced to the filters by injecting 2 µl of the solution and the second by rubbing the solid beads against the filters. The MION source was used with dibromomethane reagent gas leading to the formation of Br-reagents ions (Rissanen et al., 2019).

Results show that polystyrene and polypropylene containing samples are being desorbed, ionized and detected with TD-MION-Orbitrap setup. The filters have the potential to be used for collection of airborne plastic nanoparticles, and other applications.

References

M. P. Rissanen, et al., https://doi.org/10.5194/amt-12-6635-2019

Degradation of Imidazolium-Based Ionic Liquids by UV Photolysis and Pulsed Corona Discharge Combined with Persulfate

D. Nikitin[1], S. Preis[1] and N. Dulova[1]*

[1]Tallinn University of Technology, Department of Materials and Environmental Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

niina.dulova@taltech.ee

Ionic liquids (ILs) consist only of ions and are considered green solvents due to their unique physical and chemical properties such as low melting points (<100 °C), low vapor pressure, good solubility, electrochemical stability and recyclability (Bado-Nilles et al., 2015). However, the ever-increasing use of ILs will eventually lead to their accumulation in the environment as a result of process wastewater discharges, landfill leaching, accidental spills and irrigation. In turn, a number of studies have already confirmed the toxic effect of ILs on organisms of different trophic levels (Mena et al., 2022). The development of (energy-)efficient methods for the removal of ILs is crucial in avoiding their possible entry from industrial wastewater into aquatic environments. Advanced oxidation processes based on the production of hydroxyl radicals proved to be effective in the degradation of ILs in water (Mena et al., 2022). This study was aimed at evaluating and comparing the efficiency of combined UV/persulfate (UV/PS) and non-thermal gas phase pulsed corona discharge/persulfate (PCD/PS) oxidation for the degradation of imidazolium-based ionic liquids: 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) and 1-methyl-3-octylimidazolium chloride ([Omim]Cl). The effects of the cation alkyl chain length, persulfate doses, and aqueous solution pH on the efficiency of ILs degradation were examined. To assess the energy efficiency of the studied processes, energy yields were calculated at 90% IL conversion (E_{90}) considering the energies applied by UV or PCD treatment together with the cost of PS. Photochemical experiments were performed in batch mode in a water-jacketed cylindrical glass reactor. A low-pressure mercury germicidal lamp (11 W) placed in a quartz sleeve inside the reactor was used as a UVC source. The PCD experiments were conducted in a reactor containing an electrode system consisting of high voltage wire electrodes, positioned horizontally between two grounded vertical parallel plates. The pulse-generator was used to apply high voltage pulses to the wire electrodes. The PCD-based experiments for ILs oxidation were performed at the pulse repetition frequency of 50-880 pulses per second with the power input of 9-123 W, respectively. Direct UV photolysis proved ineffective in the degradation of ILs, while PCD oxidation showed the ability to decompose ≥95% of the studied ILs in a 2-h treatment. The addition of PS into the UV system substantially improved the efficacy of [Emim]Cl and [Omim]Cl degradation, and an increase in the dose of added PS led to faster degradation of ILs. For PCD/PS combinations, the addition of low PS doses resulted in little (if any) improvement in the rate of ILs degradation. The use of high PS concentrations provoked radicals self-scavenging reactions reducing the overall efficiency of treatment. Regardless of the studied IL, the calculated values of E_{90} were as follows: PCD oxidation ≈ optimized UV/PS combination > PCD/PS combinations. The findings of the study strongly suggest that the UV/PS combination and PCD oxidation are promising treatment technologies for deep purification of ILs contaminated water.

References

Bado-Nilles, A. et al. (2015) 'Coupling of OECD standardized test and immunomarkers to select the most environmentally benign ionic liquids option—Towards an innovative “safety by design” approach', Journal of Hazardous Materials, 283, pp. 202–210. doi: 10.1016/j.jhazmat.2014.09.023.

Mena, I.F. et al. (2022) 'An overview of ionic liquid degradation by advanced oxidation processes', Critical Reviews in Environmental Science and Technology, 52, pp. 2844-2887, doi: 10.1080/10643389.2021.18962732.

The Influence of Carbon Nanotube and GO on the Photocatalytic Activity of $WO_3/Bi_2S_3/Cu_2S$ Toward Pharmaceutical Active Compounds from Wastewater

L. Isac[1*], A. Enesca[1]

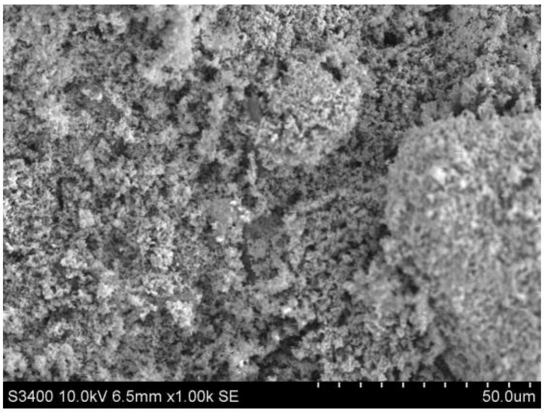
[1]Transilvania University of Brasov, Department of Product Design, Mechatronics and Environment, Eroilor 29 Street, 500036, Brasov, Romania

isac.luminita@unitbv.ro

The diversification of pollutants type and concentration in Wastewater has underlined the importance of finding new alternatives to traditional treatment methods. Advanced oxidation processes (AOPs), among others, are considered as promising candidate to efficiently remove organic pollutants such as pharmaceutical active compounds (PhACs) from wastewater (Hader D.P. et al 2020, Kaplan A. et al. 2020)

The present work focus on the development of WO3/Bi2S3/Cu2S heterostructure using carbon nanotubes (CNs)and graphene oxide (GO) as nucleation sites for the metallic semiconductors. The photocatalytic activity was testes toward ampicillin and amoxycillin from wastewater. The diffraction analysis indicates the presence of crystalline structure corresponding to the heterostructure components. The samples have a porous morphology and the specific surface varies from 38.2 m2/g for WO3 to 247 m2/g for WO3/Bi2S3/Cu2S@GO.

The photocatalytic experiment were made in the presence of UV-Vis irradiation and the results indicate that WO3/Bi2S3/Cu2S@GO is able to remove 92.4% ampicillin in 10h, comparing with WO3/Bi2S3/Cu2S@CNs and WO3/Bi2S3/Cu2S which exhibit 86.3%, and 73.5% respectively. A similar behavior was observed for amoxycillin removal were the photocatalytic efficiencies attempt 94.1% for WO3/Bi2S3/Cu2S@GO, 88.4% for WO3/Bi2S3/Cu2S@CNs and 71.8% for WO3/Bi2S3/Cu2S. The results indicate that the use of GO and CNs as nucleation sites serve as triple benefits: (1) homogenous surface distribution, (2) higher active surface area and (3) energy network for the charge carriers involved in oxidative species generation.



Porous morphology corresponding to $WO_3/Bi_2S_3/Cu_2S$@GO sample.

References

Hader, D.P. et al (2020) 'Anthropogenic pollution of aquatic ecosystems: Emerging problems with global implications.', Sci. Total Environ., 713, 136586. doi:10.1016/j.scitotenv.2020.136586.

Kaplan, A. et al. (2020) 'Trace organic compound removal from Wastewater reverse-osmosis concentrate by advanced oxidation processes with UV/O3 /H2O2.' Materials, 13, 2785. doi:10.3390/ma13122785.

The Precipitation of Secondary Minerals as a Suitable Tool for the Remediation of Contaminated Mine Waters

V. Krajanová[1]*, B. Lalinská-Voleková[2], T. Faragó[1], D. Szabóová[2], J. Brčeková[3], P. Šottník[4]

[1]Comenius University in Bratislava, Faculty of Natural Sciences, Department of Geochemistry, Ilkovičova 6, 84215, Bratislava, Slovakia
[2]Slovak National Museum - Natural History Museum, Vajanského nábrežie. 2, P.O. Box 13, 81006, Bratislava, Slovakia
[3]Comenius University in Bratislava, Faculty of Natural Sciences, Department of Mineralogy, Petrology and Economic Geology, Ilkovičova 6, 84215, Bratislava, Slovakia
[4]State Geological Institute of Dionýz Štúr, Division of Geology, Mlynská dolina 1, 81704, Bratislava, Slovakia

viktoria.krajanova@uniba.sk

Potentially toxic elements such as arsenic and antimony are dangerous contaminants for the ground and surface water in vicinity of abandoned Sb deposits. Numerous abandoned ore deposits in Slovakia represent a unique opportunity to study processes of migration and distribution of potentially toxic elements in the natural environment at different conditions. The process of sorption of these components onto the secondary mineral phases in an environment of tailings and mining discharges provides guidance on the design of appropriate remediation measures.

Our study indicates that in the supergene environment of tailing impoundments and soils rich in Fe, at pH values from 3.26 to 8.76, Sb is mainly incorporated into tripuhyite, pyrochlore-group minerals, and possibly goethite. Arsenic, on the other hand, associates with the iron oxides, either crystalline or amorphous, but rarely forms crystalline phases of its own.

Iron oxides were formed mainly by poorly crystallized 2-line ferrihydrite, with the content of arsenic in samples ranging from 0.7 wt.% to 13 wt.% and content of antimony ranging from 0.025 wt.% up to 1.2 wt.%.

Based on the results of the natural attenuation functioning in the environment of mine waters contaminated with arsenic and antimony, we performed sorption experiments in laboratory conditions. The first experiment confirmed the high efficiency of As sorption on laboratory-prepared Fe oxides; 99,96 % of As was removed from the solution. In the second experiment, we have focused on the controlled crystallization of tripuhyite from the solutions rich in Sb. Experimental studies have confirmed the ability of tripuhyite crystallization from the solution of variable chemical compositions. Both of our sorption experiments demonstrated the effectiveness of controlled crystallization of mineral phases, therefore these processes were included in the proposal of contaminated sites remediation.

Acknowledgements: This work was supported by the Grant Agency for Research and Development with project numbers: APVV-21-0212; APVV-17-0317 and the Operational Program of Integrated Infrastructure: “DNA barcoding of Slovakia (SK-BOL), as a part of international initiative International Barcode of Life (iBOL)” (ITMS2014+313021W683).

Evaluation of Antimony Bioremediation Potential of Certain Fungal Species Isolated from Natural Iron Ochres

B. Lalinská-Voleková[1]*, I. Kautmanová[1], J. Červenka[1], D. Szabóová[1], T. Faragó[2], V. Krajanová[2], J. Brčeková[3], O. Brachtýr[4]

[1]Slovak National Museum - Natural History Museum, Vajanského nábrežie. 2, P.O. Box 13, 81006, Bratislava, Slovakia
[2]Comenius University in Bratislava, Faculty of Natural Sciences, Department of Geochemistry, Ilkovičova 6, 84104, Bratislava, Slovakia
[3]Comenius University in Bratislava, Faculty of Natural Sciences, Department of Mineralogy, Petrology and Economic Geology, Ilkovičova 6, 842 15, Bratislava, Slovakia
[4]GEOtest Bratislava, s.r.o., Stavbárska 27, P. O. Box 4, 820 08 Bratislava

bronislava.volekova@snm.sk

Antimony (Sb) as a potentially toxic element represent dangerous contaminant for ground and surface waters around abandoned ore deposits worldwide. Here we report on the ability of certain fungal species isolated from natural iron ochres and cultivated in vitro not just to survive on medium with high concentrations of Sb but also to adsorb it. Dip slides were used to detect the presence of those types of fungi that were able to survive in water contaminated with high concentrations of antimony. The formed colonies were inoculated into in vitro culture on PDA agar in Petri dishes and isolates were molecularly identified. Altogether 17 samples were isolated and sequenced and identified as belonging to the species *Valsa sordida*, *Plectosphaerella cucumerina*, *Apiospora arundinis*, *Aspergillus fumigatus*, *Bjerkandera adusta*, *Mucor hiemalis*, *Trichoderma* spp., *Acremonium* sp., *Cosmospora* sp. and *Paraphaeosphaeria neglecta*. These were tested for Sb tolerance (from 0.01, 0.05, 0.1, 1, 2.5 and 4 g/kg Sb). Only six strains were able to grow at the concentration 1000 mg/kg and only one of them survived the concentration of 2500 mg/kg. Concentration of 4000 mg/kg was lethal to all studied fungal strains. Growth rates of these six species has been evaluated for the period of 30 days and the best performing strains were selected for further study of Sb removal in vitro.

Acknowledgements: This work was supported by the Grant Agency for Research and Development with project numbers: APVV-21-0212; APVV-17-0317 and the Operational Program of Integrated Infrastructure: "DNA barcoding of Slovakia (SK-BOL), as a part of international initiative International Barcode of Life (iBOL)" (ITMS2014+313021W683).

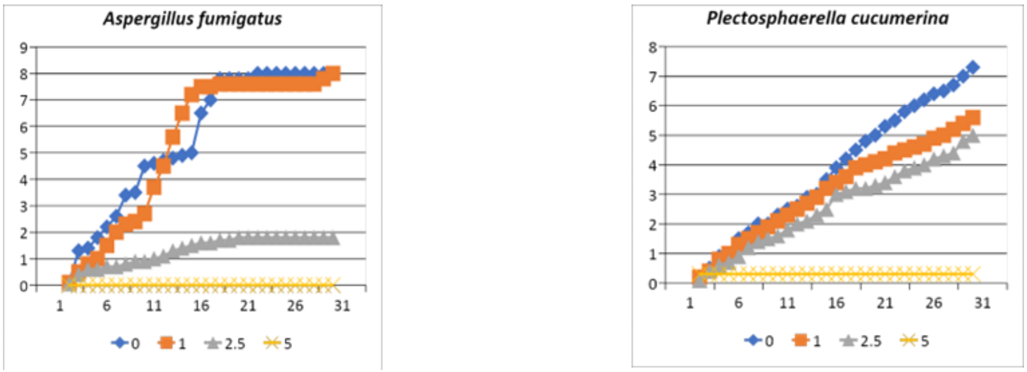


***Fig. 1** – Growth rate of selected fungal strains according to Sb concertation in agar medium (g/kg)*

Treatment of Olive Mill Wastewater by Combined Processes

A. Afonso[1,2]*, I. Gomes[2], A. Fernandes[2], A. Almeida[1], F. Carvalho[1], A. Lopes[2]

[1]FibEnTech-UBI, DTCA, Instituto Politécnico de Beja, 7800-295 Beja, Portugal
[2]Universidade da Beira Interior, FibEnTech-UBI, Rua Marquês D'Ávila e Bolama, 6201-001, Covilhã, Portugal

alexandra.afonso@ipbeja.pt

Water and food scarcity is a growing problem. The reuse of treated agro-industrial effluents can be the solution for an integrated management of sustainable effluents and the implementation of circular economy, in accordance with UN Sustainable Development Goals. This work intends to develop a viable, sustainable, and eco-innovative solution to treat olive mill wastewater (OMW), while obtaining a treated effluent that can be reused in irrigation systems in agriculture or for cleaning the olive mill facility, in a circular economy perspective.

The work consisted of comparing a one-step electro-oxidation (EO) with a combined treatment, involving immediate one-step lime precipitation (IOSLP) (Prazeres et al., 2021) followed by natural carbonation, with atmospheric CO_2 mitigation, and a final EO step (Barbosa et al., 2016). The EO was performed with BDD and MMO anodes and the applied current density was 70 mA/cm². No electrolyte was added. The best results were obtained with the BDD anode (Fig 1).

In the combined treatment, IOSLP promoted a partial clarification of the effluent, with a decrease in the organic load (20% COD removal) and an increase in pH up to 13. In the natural carbonation process, the pH decreased to 8 and only sligth changes were observed in the organic load. The posterior EO with the BDD anode removed almost completely the remaining COD, given a total COD removal in the combined process of 98%. In the one-step EO, COD removal from the raw effluent was 96%.

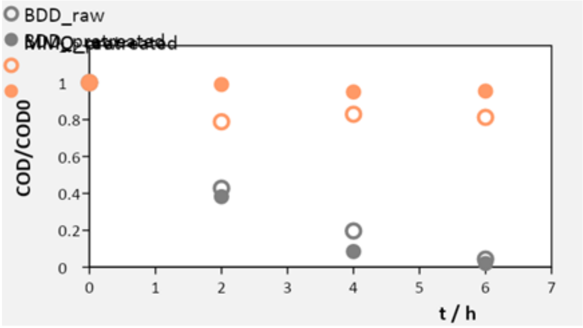


Fig. 1 - Removal of organic load at two different electrode materials, BDD and MMO, from the raw and pretreated OMW

References

Prazeres, A. R. et al. (2021). Contamination reduction of real olive oil mill wastewater using innovative acid and basic chemical precipitation processes, Intern J of Environment Sc. and Technol., 18, 799-808. doi.org/10.1007/s13762-020-02924-5.

Barbosa, J. et al (2016). Electrochemical treatment of olive processing wastewater using a boron-doped diamond anode. Clean Soil Air Water, 44 (2016) DOI:10.1002/clen.201500158.

Sb Resistant Bacteria Identified and Isolated from Antimony Mine in Western Slovakia - Potential Application for Mine Water Remediation

D. Szabóová[1*], H. Majerová[1], Z. Konyariková[1], B. Lalinská-Voleková[1], T. Faragó[2], V. Krajanová[2], J. Brčeková[3]

[1]Slovak National Museum - Natural History Museum, Vajanského nábrežie. 2, P.O. Box 13, 81006, Bratislava, Slovakia
[2]Comenius University in Bratislava, Faculty of Natural Sciences, Department of Geochemistry, Ilkovičova 6, 84215, Bratislava, Slovakia
[3]Comenius University in Bratislava, Faculty of Natural Sciences, Department of Mineralogy, Petrology and Economic Geology, Ilkovičova 6, 84215, Bratislava, Slovakia

dana.szaboova@snm.sk

Potentially toxic elements, such as antimony (Sb), are dangerous putative contaminants for ground and surface waters around abandoned mines and ore deposits in Slovakia. Nearby mines they are commonly coprecipitated in ochre sediments precipitated from Fe rich drainage waters and, therefore, these sites function as natural scavengers of the metalloids. Bacteria play a crucial part in regulating the precipitation and release of metalloids from the complexes. In the context of iron ochres microbiome characterization, the purpose of this work was to study the extremophilic bacterial community of ochreous precipitates at the efflux of Buducnost mine (abandoned Sb deposit). This site possesses well developed, sun exposed, circumneutral ochreous sediments polluted with high, but fluctuating, concentrations of antimony and represents a putative site for future bioremediation experiments. As a part of the current project, we determined bacterial taxonomic affiliations and their relative abundances at this site by the means of 16S RNA next generation sequencing, and we isolated As and Sb resistant bacterial strains as stable bacterial cultures. Here we compare the bacterial taxonomic affiliations of 529 independent zOTUs generated by MR DNA pipeline and 829 independent ASVs (alternative to zOTUs) generated by QIIME2 based pipeline from our metadata with the taxonomic affiliations of 48 isolated Sb resistant bacterial strains.

Acknowledgements: This work was supported by the Grant Agency for Research and Development with project numbers: APVV-21-0212; APVV-17-0317 and the Operational Program of Integrated Infrastructure: "DNA barcoding of Slovakia (SK-BOL), as a part of international initiative International Barcode of Life (iBOL)" (ITMS2014+313021W683).

Volatile Methylsiloxanes in Wastewater – a Comprehensive Sampling Scheme Combined with Risk Assessment

F. Bernardo[1,2], N. Ratola[1,2]*, F. Sánchez-Soberón[1], A. Alves[1,2], V. Homem[1,2]

[1]University of Porto, LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2] University of Porto, ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

nrneto@fe.up.pt

Volatile methylsiloxanes (VMSs) are high-production-volume anthropogenic chemicals included in personal care products and cosmetics used throughout the world (Rücker et al., 2014). Literature reviews indicate that industrial wastewater, municipal sewage and natural water present high concentrations of VMSs (Xiang et al., 2021) and may cause negative toxicological effects and environmental risks in the receptor media (Cantu et al., 2021). Most published studies focused on the analysis of influent and effluent, in addition to including few samples collected from specific seasons. Thus, in this work, seven VMSs (L3, L4, L5, D3, D4, D5, D6) were analysed in 327 wastewater samples collected along the treatment stages of a Portuguese WWTP, in four locationa including the influent entrance (SA1) and after preliminary, primary and secondary treatments (SA2, SA3 and SA4, respectively). Of the 327 samples, 107 SA1 samples were collected every 6 h and the other 220 were composite (24 h) from SA1, SA2, SA3 and SA4. The approach of contemplating 1 year of sampling, that included daily and weekly surveillance, was to assess the impact of different seasons. This was conducted in order to discern concentration patterns, that might occur along the day and also compare between weekdays. It also enabled the assesment of different climate conditions on VMS levels. The environmental risk was estimated considering three scenarios: the current treated effluent, the effluent if secondary treatment was not available, and finally, the discharge without treatment (the worst-case-scenario). Since PCPs formulations contain higher cVMSs content, when compared with lVMSs, the results showed that cyclic congeners (especially D5) were dominant. Total VMSs concentrations were higher in the influent (SA1), with a mean value of 5.07 µg L^{-1} (reaching up to 22.47 µg L^{-1}), decreasing along each treatment stage to 6.75 µg L^{-1} in SA2, followed by 1.80 µg L^{-1} in SA3 and finally 0.07 µg L^{-1}). The night period (6:00 PM to 12:00 AM) presented the highest concentrations, possibly due taking showers when arriving from work and before bed in the case of children. Daily concentrations varied in a way that it did not present a concentration pattern. In the effluent, minimal risk was detected for 18 samples (32%), while the rest was negligible. However, WWTPs that only contemplate primary treatment or in sporadic cases of direct discharge, environmental risk may be considerable. This work showed that future studies should include the aquatic medium in their assessments and study VMSs possible bioaccumulation in food webs.

This work was financially supported by: (i) LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), funded by national funds through FCT/MCTES (PIDDAC); (ii) Projects PTDC/ASP-PLA/29425/2017 and PTDC/CTA-AMB/32084/2017 - funded by FEDER funds through COMPETE2020 (POCI) and through FCT/MCTES (PIDDAC); (iv) Project “HealthyWaters" (NORTE-01-0145-FEDER-000069), supported by NORTE2020-PORTUGAL2020, through ERDF; (v) FCT is thanked for grant PD/BD/137758/2018 (F. Bernardo) and contract CEECIND/00676/2017 (V. Homem).

References

Cantu, M. A. et al. (2021) 'Bioaccumulation of dodecamethylcyclohexasiloxane (D6) in fish', Chemosphere, 281, p. 130948. doi: 10.1016/j.chemosphere.2021.130948.

Rücker, C. et al. (2014) 'Environmental Chemistry of Organosiloxanes', Chemical Reviews, 115(1), p. 466−524. doi: 10.1021/cr500319v.

Xiang, X. et al. (2021) 'Review of recent findings on occurrence and fates of siloxanes in environmental compartments'. Ecotoxicology and Environmental Safety, 224, p. 112631. doi: 10.1016/j.ecoenv.2021.112631.

Fouling Behaviors in Submerged Anaerobic Ceramic Membrane Bioreactor for High Concentration Food Wastewater Treatment: Measurements, Modeling and Influential Factors

C. Jung[1], Y. Lee1, H. Kim[1], and S. Lee[1]*

[1]Sungkyunkwan University, Department of Water Resources, Graduate School of Water Resources, Suwon 16419, Korea

sangyouplee@skku.edu

This study aims to investigate the fouling behaviors and factors affecting fouling in a submerged anaerobic ceramic membrane bioreactor (SACMBR) for treating high concentration food wastewater. Blocking filtration models, including complete blocking, standard blocking, intermediate blocking, and cake filtration, were used to model the fouling behavior. Various physical, chemical, and biological factors were examined, including initial flux, hydraulic retention time (HRT), backwash time and cycle, mixed liquor suspended solids (MLSS) concentration, influent chemical oxygen demand (COD), solids retention time (SRT), and the presence of extracellular polymeric substances (EPS) and soluble microbial products (SMP). At a constant flux filtration mode, increasing trans-membrane pressure patterns were used to apply the models. The results showed that the dominant fouling mechanism among the four blocking filtration models varied depending on the operating conditions of the SACMBR system. Moreover, there was a shift from one model to another as filtration progressed.

Removal of Reactive Blue 13 Using Modified Cellulosic Material Based on Rice Husks

P. Novachka[1]*, I. Uzunov[1], D. Voykova[1]

[1]Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Acad. Georgi Bonchev Str., Bl. 11, 1113, Sofia, Bulgaria

pnovachka@svr.igic.bas.bg

Textile wastewater is one of the most polluted wastewaters and has become an important and challenging issue because of its adverse effects on human beings and the environment. The main problem with reactive dyes is that generally 60-70% of them remained unutilized, leaving a large amount of colored sewage produced during the dyeing process. Wastewaters containing reactive dyes are toxic, mutagenic, and carcinogenic to mankind as well as animals. Adsorption techniques have been used widely due to their efficiency in the removal of dyes due to economical and environmentally friendly reasons.

The aim of the present study was the synthesis of cationic modified cellulose and its use for the adsorptive removal of Reactive blue 13 (RB 13) from aqueous solutions. Rice husks have been used as raw material for the extraction and separation of cellulose by alkaline and bleaching treatment. The cellulose was modified with N,N-dimethyl-1- octadecylamine to prepare a cationized adsorbent. Instrumental methods such as XRD, DTA, FTIR, SEM, as well as low-temperature nitrogen adsorption were used for its characterization. The removal of lignin and hemicellulose from the plant matrix leads to a change in the surface morphology of the sample; its phase composition; surface functional groups and porous structure. Characterization of amino-functionalized material showed that the quaternary ammonium group was successfully grafted onto a cellulose structure.

The effect of contact time, solution acidity, temperature, and initial RB 13 concentration on dye removal was studied by means of the batch method. The adsorption equilibrium was attained within 30 minutes. Equilibrium data were fitted to pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models and linear Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models. The adsorption process was well described by pseudo-second-order and Langmuir models predicting chemically rate-controlled monolayer adsorption. Thermodynamic studies show that the adsorption of RB 13 is spontaneous and exothermic. A suitable eluent for regeneration of the adsorbent is a 0.1 M NaOH solution. It was established that the new cationized cellulosic material could be used as a potential adsorbent for the effective removal of RB 13 from aqueous media. The obtained results reveal that renewable agriculture wastes can be successfully processed into products with added value and applicability in protecting the environment from hazardous pollutants.

Acknowledgements This work was supported by the European Regional Development Fund within the Operational Programme ‘‘Science and Education for Smart Growth 2014–2020” under the Project CoE ‘‘National Center of Mechatronics and Clean Technologies” (BG05M2OP001-1.001-0008-C01) and the Project D01-272/02.10.2020 - "European Network on Materials for Clean Technologies",

Health-Environmental Sustainability and Valorisation of Ecocenters. Removal of Pollutants and Recycling of Wastewater

V. Canaletti[1]*, A.Bonetto[1], L. Tessari[1], A. Brunelli[1], A. Marcomini[1], E.Semenzin[1], E. Badetti[1]

[1]Ca'Foscary University of Venice, Department of Environmental Sciences Informatic and Statistics, Via Torino 155, 30172, Venice Mestre, Italy

vanessa.canaletti@unive.it

The different categories of waste delivered to the eco-centers are collected into containers according to the material type, waiting for the subsequent recovery or disposal steps. One of the main critical issues relating to the storage phase, concerns the potential release of contaminants from the containers in which they are stored. In fact, the storage method for non-hazardous waste does not require watertight containers that, when placed outdoor, are subject to various atmospheric phenomena, including rain (Fig. 1). Rainwater could potentially produce leachate from the deposited waste that will consequently accumulate in various receptor bodies (i.e., surface waters, sewage systems, soils), specific for each eco-center. These runoffs, before being discharged into the eco-center's receiving body, are conveyed via drains towards an oil separator for the removal of sludge, oil and fat, and then they are disposed as wastewater according to legislative decree 152/2006. However, these measures allowed to manage only specific classes of substances potentially released from the stored waste, while others could be discharged into the environment. In this context, this work aims at identifying the most critical types of waste by investigating hazardous substances potentially released by them, and the corresponding physical-chemical characterization, in order to improve i) the sustainable management of the investigated eco-centers, and ii) the quality of the water leaving the plants. Emerging pollutants will also be considered.

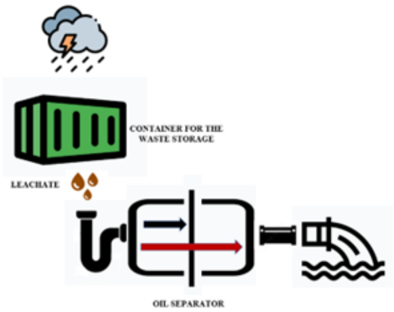


Figure 1 Schematic representation of the pollutant leaching process

References

Italian Council of Ministers, National Decree 152/2006 (in Italian), (2006).
https://www.gazzettaufficiale.it/dettaglio/codici/materiaAmbientale

Evaluation of Chemical Compatibility between two Mixed Produced Waters and Identification of Mineral Scale Sample in a Southern Tunisian Oilfield

S. BARBOUCHI[1]*

[1]Tunisian National Oil Company “ETAP”, Petroleum Srvices Department-Laboratories, Tunisia

sonia.barbouchi.etap@gmail.com

At global level, every barrel of produced oil is associated with the production of 3 to 5 barrels of water. One of the major problems related to this coproduction of water is scale formation. Mineral scale formation is a serious flow assurance issue experienced in the oil and gas sector. It can cause not only flow reduction but also inefficiency and failure of production equipment. One of the primary causes of scale deposition is mixing two waters which are incompatible (Nabzar and Duplan, 2010; Franco et al., 2009). In this case, predictive studies may help to evaluate the compatibility of the mixed waters and to prevent the scale formation, which usually occurs on rods, tubing or flow lines (Franco et al., 2009).

The purpose of this study is to evaluate the compatibility between two produced waters in a southern Tunisian oilfield, in order to identify the causes of scale deposition within the flowline of a comingled production.

Two water samples, “W1” and “W2”, collected from the involved wells were analysed using inductively coupled plasma atomic emission spectroscopy (ICP-AES), ion chromatography and other standard laboratory techniques.

The results of complete waters analysis were the typical input parameters, to determine scaling tendency. Saturation indices values related to CaCO3, CaSO4, BaSO4 and SrSO4 scales were calculated for the water mixtures at different share, under various conditions of temperature, using a computerized scale prediction model.

The mineralogical characterisation of the scale samples collected from the flowline of the commingled production has been realized using X ray diffraction (XRD) and scanning electron microscope (SEM).

The compatibility study results showed that mixing the waters tends to increase the probability of barite deposition. XRD and SEM analyses confirmed the compatibility study results, since they proved that the analysed deposit predominantly consisted of barite.

At the studied temperatures conditions, the tendency for barite scale is significantly increasing with the increase of “W2” water share in the mixture.

The future scale inhibition and removal strategies to be implemented in the concerned oilfield are being derived in a large part from the results of the present study.

References

L. Nabzar ; JL. Duplan., L’eau dans la production des carburants:Production pétrolière et raffinage IFP, 2010.

A.Franco, J.R.Solares, H.M.Almari, “Analysis of Deposition Mechanism of Mineral Scales Precipitating in the Sand Face and production Strings of Gas Condensate Wells”, J.Saud.Arab.Techno,(2009) 47-60.

UV-Vis Activated CuO/CuS/WO_3@PANI Heterostructure for Photocatalytic Removal of Pharmaceutical Active Compounds from Wastewater

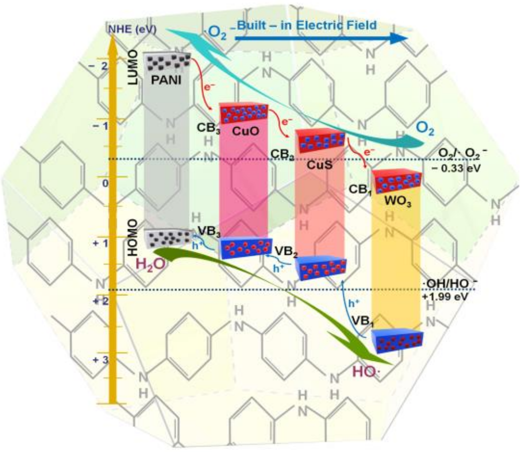
A. Enesca[1*], L. Isac[1]

[1]Transilvania University of Brasov, Department of Product Design, Mechatronics and Environment, Eroilor 29 Street, 500036, Brasov, Romania

aenesca@unitbv.ro

Pharmaceutically active compounds, such as tetracycline, ciprofloxacin, triclosan, carbamazepine, salicylic acid, ibuprofen and sulfamethazine, etc., are helpful to cure human diseases but the pollution from metabolized or partially metabolized pharmaceutical wastes is already recognized as a hazard. With the rapid development of industrialization, the presence of organic pollutants in Water and environment is now an important problem, creating hazardous threats to the ecological system (Tahreen et al., 2020; Guo et al., 2020).
The present work describes the development of CuO/CuS/WO3@PANI heterostructure and his application on penicillin G and amoxycillin photocatalytic removal from wastewater. The heterostructure was developed based on a three-step sol-gel method using PANI as initial substrate. The XRD analysis indicates that the semiconductor exhibits crystalline structure after the thermal treatment. The crystallite sizes vary from 69.2 A for CuS up to 94.7 A for CuO. The morphology consists mostly on granular structures and the EDS indicates a uniform surface dispersion of the elements.

The photocatalytic experiments in the presence of UV-VIS light indicate that the CuO/CuS/WO3@PANI exhibits superior photocatalytic abilities to remove both penicillin G and amoxycillin, comparing with bare semiconductors. CuO/CuS/WO3@PANI sample is able to remove 75% of penicillin G and 80% of amoxycillin in the first 10h of exposure to light irradiance. The photocatalytic reaction rate of CuO/CuS/WO3@PANI is 1.4x faster than that of CuO/CuS/WO3 and almost 4x faster than that of CuS/WO3.



Photocatalytic mechanism of the CuO/CuS/WO3@PANI heterostructure.

References

Tahreen, A. et al. (2020) 'Role of electrocoagulation in Wastewater treatment: A developmental review.', J. Water Proc. Eng., 37, 101440. doi:10.1016/j.jwpe.2020.101440.

Guo, W. et al. (2020) 'Surface Modification of Bentonite With Polymer Brushes and Its Application as an Efficient Adsorbent for the Removal of Hazardous Dye Orange I.' Nanomaterials, 10, 1112. doi:10.3390/nano10061112.

Combination of Fenton's Process and Membrane Distillation for the Treatment of Olive Mill Wastewater

A.R.T. Fernandes[1,2,3], C.S.D. Rodrigues[1,3*], A. M.T. Silva[2,3], L.M. Madeira[1,3]

[1]University of Porto, LEPABE, Faculty of Engineering, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.
[2]University of Porto, LSRE-LCM, Faculty of Engineering, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.
[3]University of Porto, ALiCE, Faculty of Engineering, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.

csdr@fe.up.pt

Olive oil extraction produces a significant volume of highly polluted wastewater. This wastewater is characterized by a dark color and high concentrations of organic matter (Davies, L.C. et al. 2004, Adhoum, N. et al. 2004) particularly various phenolic substances (Erguder, T.H. et al. 2000), resulting in high chemical and biological oxygen demand levels. Therefore, it is crucial to treat such effluents properly to minimize their environmental impacts. This study proposes the treatment of olive mill wastewater (OMWW) through the combined application of two processes: Fenton and membrane distillation. The goal of this combined treatment is to minimize the pollutant load and generate water streams with physicochemical characteristics that allow to reuse them (e.g. in olive oil extraction processes or irrigation of olive groves), resulting in the adoption of a circular economy model in this agro-industrial sector.

Fenton's process is a promising advanced oxidation technology for the treatment of OMWW that operates at room temperature and atmospheric pressure without requiring complex systems. This process is based on the formation of hydroxyl radicals with a very high oxidation potential through the catalytic decomposition of H_2O_2 in the presence of ferrous ions. Membrane distillation (MD) is a separation process in which the difference in vapor pressure between the two sides (hot side - retentate and cold side - permeate) of a hydrophobic and microporous membrane allows the transport of the produced vapor through the membrane.

In this work, the effluent was first submitted to the Fenton process, in which a systematic parametric study was carried out to evaluate the effect of process variables (hydrogen peroxide concentration, ferrous concentration, pH and temperature) and select the best ones that maximize the removal of polyphenols and total organic carbon (TOC) and increase the OMWW biodegradability (quantified by the ratio between biological oxygen demand - BOD - and chemical oxygen demand - COD). Then, MD was performed with the effluent resulting from the Fenton process. The influence of different parameters (such as flow rate, temperature, and operation time) on permeate flux, water recovery, and quality of recovered water were evaluated. Moreover, the physicochemical characteristics (pH, turbidity, total suspended solids, total nitrogen, ammonia nitrogen, total phosphate, BOD, COD, TOC, and polyphenols) of the permeate were determined to verify compliance with legislation for the reuse of wastewater, namely for irrigation or reuse in the olive oil extraction process.

Acknowledgments. This work was financially supported by: UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM) and LA/P/0045/2020 (ALiCE) funded by national funds through FCT/MCTES (PIDDAC); Projects: NORTE-01-0247-FEDER-39789 funded by ERDF through N2020. A.R.T.F. is grateful for her PhD research grant (022.12141.BD) from FCT, funded by national funds and by the EU through the ESF. C.S.D.R. thanks the FCT or the financial support of her work contract through the Scientific Employment Support Program (Norma Transitória DL 57/2017).

References

Davies, L.C. et al. (2004), Olive mil wastewater characteristics: modelling and statistical analysis. Grasas y Aceites, 55, pp. 233-241. DOI: 10.3989/gya.2004.v55.i3.171.

Adhoum, N. et al. (2004) Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation. Chemical Engineering and Processing, 43, pp. 1281-1287. DOI: 10.3390/w12123471.

Erguder, T.H. et al. (2000) Anaerobic treatment of olive mill wastes in batch reactors, Process Biochemistry, 36, pp. 243-248. DOI:https://doi.org/10.1016/S0032-9592(00)00205-3.

Using Lignocellulosic Vegetal Wastes as Adsorbents for Transition Metals from Wastewaters

A. Tirsoaga[1*], R. Zavoianu[1], O.D. Pavel[1], A. Cruceanu[1], O.T. Apreutesei[2], C. Tebrencu[2]

[1]University of Bucharest, Faculty of Chemistry, Bd. Regina Elisabeta, 4-12, 030018, Bucharest, ROMANIA
[2]Research Centre for Medicinal Plants Processing Plantavorel S.A., Str. Cuza Voda, 46, 610019, Piatra Neamt, ROMANIA)

tirsoaga@yahoo.com

Water pollution with transition metals such as Ni, Cr and Fe occurs frequently due to wastewaters discarded from electroplating industry (He Y. et al. 2022, Li T. et al. 2022) or mining (Guo X. et al. 2022). The removal of metallic pollutants by adsorption processes using vegetal wastes can bring some economic advantages since the adsorbents are cheap, and they could be further valorized by their conversion into Metal/biochar catalysts. This contribution presents the results of Ni, Cr and Fe removal from wastewaters using as adsorbent the vegetal wastes recovered after the microwave assisted extraction (MAE) of active phytoingredients from Rhamnus frangula L bark (RfL).

RfL bark was characterized before and after being submitted to MAE using physico-chemical analysis, infrared spectroscopy and thermogravimetric analysis (TGA). The recovered RfL vegetal waste had a humidity of 10 wt. %, and contained 1.1 wt.% oxymethylantraquinones (OMA), 2.6 wt.% polyfenols expressed as gallic acid, 0.51 wt.% tanins (expressed as tannic acid). The infrared spectra and TGA confirmed the presence of both cellulose and lignin in the vegetal waste. Synthetic waste water samples were prepared using $CrCl_3x6H_2O$, $K_2Cr_2O_7$, $Fe(NO_3)_3x9H_2O$ and $NiCl_2x6H_2O$ as Cr, Fe and Ni sources. The initial concentration of metallic polutants in the simulated wastewaters were chosen to be in a similar range as in the industrial wastewaters coming from electroplating (e.g. 1.8 mgCr(III+VI)/L, 0.9mgCr(VI)/L, 1.8mgNi/L He Y. et al. 2022, Li T. et al. 2022) or mining (e.g. 8.4 mgFe/L Guo X. et al. 2022). The RfL vegetal waste used as adsorbent was grinded before being used in the adsorption tests and the fraction with 0.25-0.315 mm grain size was employed in all adsorption tests. The concentration of adsorbant was 1g/L of wastewater. The tests were performed in triplicate in batch systems at room temperature, under magnetic stirring (150 rpm). Wastewater samples were analyzed by Visible spectrometry, using the specific colour reagents, at different time intervals (10 min, 20 min, 30 minutes and each 30 minutes after up to 5 hours).

The results of the experiments showed that Cr ad Ni are fastly adsorbed, and the concentration of metallic pollutant in the wastewater reaches the admissible level according to european legislation (91/271/EEC) for the discharge of the treated water in natural receptors according to in less than 1 hour, while for Fe this limit is reached in 5 hours. The kinetic studies showed that the adsorption of Ni and Cr fits a pseudo-second order kinetic model with the apparent rate constants k_2 of 8.8 h^{-1} for Cr and 10.5 h^{-1} for Ni, and correlation coefficients R^2 of 0.9998, and 0.9999 respectively. Meanwhile, in the case of Fe, the value of R^2 was 0.9772 and the calculated value of k_2 was sensibly lower (0.2 h^{-1}), which suggested a competition between two types of adsorption active sites.

The obtained results showed that vegetal wastes recovered after the microwave assistred extraction of active phytoingredients from RfL are selective adsorbents for Cr and Ni from electroplating wastewaters while the solid is less efficient for Fe removal from mining wastewaters.

References

He, Y. et al. (2022) 'Separable amino-functionalized biochar/alginate beads for efficient removal of Cr(VI) from original electroplating wastewater at room temperature', J. Cleaner Production, 373, 133790; doi: 10.1016/j.jclepro.2022.133790

Li, T. et al. (2022) 'Removal of low-concentration nickel in electroplating wastewater via incomplete decomplexation by ozonation and subsequent resin adsorption', Chemical Engineering Journal, 435, 134923 doi; 10.1016/j.cej.2022.134923

Guo, X. et al. (2022) 'Experimental study of the remediation of acid mine drainage by Maifan stones combined with SRB', PloS One, 17 e0261823, doi: 10.1371/journal.pone.0261823

Radiochemical Synthesized Hydrogel/Metal Nanoparticles for Catalytic Removal of Dyes From Wastewater

N.O. Nicula[1 2], E.M. Lungulescu[1], E. Radoi[1], O. Csutak[2*]

[1]National R&D Institute for Electrical Engineering (ICPE-CA) 313 Splaiul Unirii, Sector 3, 030138, Bucharest, Romania
[2]University of Bucharest, Faculty of Biology, Department of Genetics, 1-3 Intr. Portocalelor no. 1-3, 060101 Bucharest, Romania;

ortansa.csutak@bio.unibuc.ro

Industrial effluents, include various pollutants such as heavy metal ions, dyes, and organic materials, causing severe effects on human beings and other terrestrial and aquatic animals. Numerous studies have been focused on the design and development of new materials based on polymer matrices for the adsorption of contaminants from wastewater with particular attention being paid to polymer hydrogels (Sinha and Chakma, 2019). In this work, radiochemical synthesis was used to obtain hydrogels with Ag (AgNPs) and Pt (PtNPs) nanoparticles, starting from aqueous solutions of polyvinylpyrrolidone (PVP) as the base polymer matrix. The obtained nanocomposite hydrogels were characterized from a physico-chemical point of view (swelling, degree of gelation, UV-Vis) and in terms of catalytic activity for the reduction of dyes in the presence of sodium borohydride (NaBH4) from wastewater. The obtained materials show high water absorption capacity (up to 2000%), and a gel content up to 97%. Also, due to the presence of Ag and Pt nanoparticles, these materials show a high capacity to reduce dye-type organic compounds (methylene blue - MB or methyl orange - MO), in a relatively short time interval (40-60 min) (Fig. 1). The regenerative and reusable capacity of the hydrogels was also studied. These results are promising for the development of materials for the treatment of wastewater contaminated with organic compounds such as dyes.

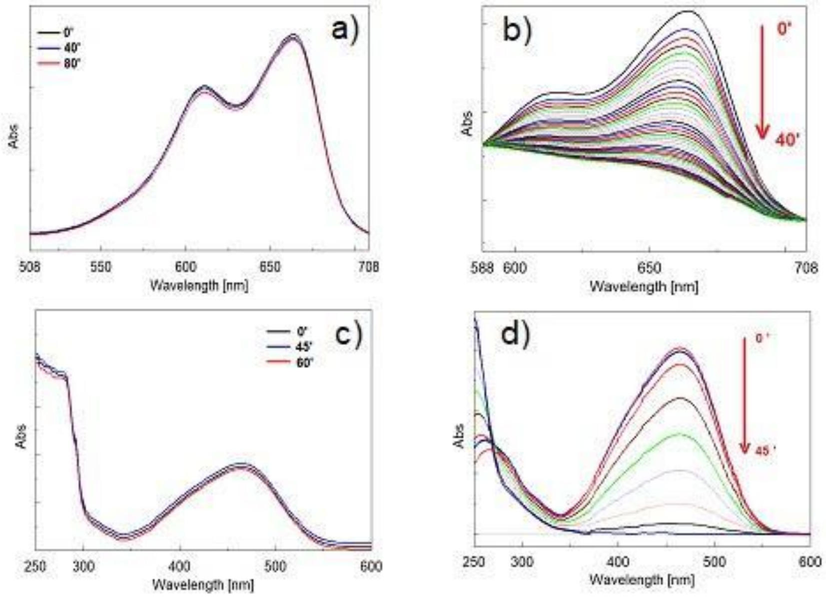


Figure 1. Removal efficiency of: MB – a) Hydrogel without NPs, b) Hydrogel with AgNPs; MO: c) hydrogels without NPs, d) Hydrogel with PtNPs

References

Sinha, V. et al. (2019). „Advances in the preparation of hydrogel for wastewater treatment: A concise review". Journal of Environmental Chemical Engineering, 7(5), 103295. https://doi.org/10.1016/j.jece.2019.103295s)

Biocatalytic Platforms of Immobilized Peroxidases for Micropollutants Conversion

J. Zdarta[1*], M. Bilal[1], K. Bachosz[1], A. Zdarta[1], T. Jesionowski[1]

[1]Poznan University of Technology, Institute of Chemical Technology and Engineering, Faculty of Chemical Technology,
Berdychowo 4, 60965 Poznan, Poland

jakub.zdarta@put.poznan.pl

Long-term exposure to harmful compounds such as phenolic substances and oestrogens can lead to health problems, including cancer, reproductive disorders and other dysfunctions of human internal systems. Hence, the need for efficient and environmentally friendly techniques for the removal of harmful substances. Enzymes of the oxidoreductase group, including laccase, tyrosinase, horseradish lignin peroxidase and manganese peroxidase, are biocatalysts capable of converting phenolic compounds and their derivatives, including environmental micropollutants (Zdarta J. et al. 2021). Increasing their stability through immobilisation can ensure their rapid separation from the reaction mixture, and also allows multiple uses of the immobilised enzyme (Zdarta, J. et al. 2018). However, carrier selection plays an important role in the immobilisation process. Recently, particular attention has been paid to electrospun materials as enzyme carriers due to the possibility of producing a material with a significant amount of reactive functional groups, defined diameter of fibers, significant porosity, increased stability and resistance (Jankowska, K. et al. 2021).

Within the framework of the presented research, the aforementioned electrospun materials were used and immobilisation of two enzymes from the peroxidase group: lignin peroxidase and manganese peroxidase was carried out , and then the produced biocatalytic systems were applied to remove selected contaminants from aqueous solutions.

Based on the results obtained, the effective immobilisation of both enzymes on the surface of the electrospun material was confirmed. Moreover, it was shown that the efficiency of the immobilisation processes of both enzymes exceeds 80%, but it was important to select the most favourable initial immobilisation parameters, making it possible to produce systems that retain more than 75% of the free enzyme activity. Data obtained by gas chromatography-mass spectrometry coupled to mass spectrometry confirmed the efficiency of EE2 removal by lignin peroxidase and manganese peroxidase at over 90%. In addition, it was shown that the most favourable conditions for the EE2 remediation process were 24 h, in a solution at pH 5, temperature 25 °C with the addition of 1 mM H_2O_2. Furthermore, it was shown that a significant increase in temperature and an excessive addition of H_2O_2 resulted in a decrease in EE2 removal efficiency. The results obtained demonstrate the great application potential of electrospun materials as carriers in the immobilisation of enzymes of environmental interest. In addition, the proposed catalytic systems can be easily separated from the reaction environment and replaced by a new one. The study also confirms that the fabricated systems are effective for more than one bioconversion cycle, which speaks in favour of the estrogen removal method using immobilised enzymes.

Acknowledgements:
The research leading to these results has received funding from the Norwegian Financial Mechanism 2014-2021 under Project number 2020/37/K/ST8/03805.

References

Zdarta, J. et al. (2021) ‘A contemporary review of enzymatic applications in the remediation of emerging estrogenic compounds’, Critical Reviews in Environmental Science and Technology, 52, p. 2661–2690. doi: 10.1080/10643389.2021.1889283

Zdarta, J. et al. (2018) ‘A general overview of support materials for enzyme immobilization characteristics, properties, practical utility’, Catalysts, 8, p. 92. doi: 10.3390/catal8020092

Jankowska, K. et al. (2021) ‘Electrospun biosystems made of nylon 6 and laccase and its application in dyes removal’, Environmental Technology & Innovation, 21, 101332. doi: 10.1016/j.eti.2020.101332

Estrogens Removal by HRP - Nanomaterials Biocatalytic System

A. Zdarta[1*], A. Rybarczyk[1], E. Kaczorek[1], J. Zdarta[1], M. Bilal[1]

[1]Institute of Chemical Technology and Engineering, Faculty of Chemical Technology,
Poznan University of Technology, Berdychowo 4, 60965 Poznan, Poland

agata.zdarta@put.poznan.pl

From the point of view of environmental applications, the use of immobilized peroxidases, which are capable of catalyzing the oxidation and reduction of phenolic compounds, including most environmental micropollutants, seems particularly interesting (Zdarta, J. et al. 2019). Moreover, the immobilization significantly improves the stability of the enzyme and facilitates its recycling in subsequent catalytic cycles. However, the search for effective, biocompatible, and environmentally friendly carriers, as well as the development of effective immobilization techniques that do not have a negative impact on the biocatalytic properties of enzymes, is a constant challenge. It should also be added that although there is more and more information about the use of biocatalysts in pollutant removal processes, data on their use on a larger scale is still limited (Zdarta, J. et al. 2018).

Based on the presented information, it seems important to start work whose main goal is to develop a method of immobilization of selected peroxidases, including horseradish peroxidase (HRP), on carriers of high porosity and stability. In this respect, the use of inorganic materials seems to be promising, due to the possibility of producing carriers with the desired characteristics but also containing many reactive functional groups, which significantly affects the possibility of stable enzyme binding. The key stage of the work, however, was the assessment of the catalytic and kinetic parameters of the produced systems, as well as testing them as potential catalytic tools in the processes of conversion of selected environmental pollutants, including antibiotics, from aqueous solutions, and analyzing the impact of process variables on the removal efficiency.

The analysis of the obtained data unequivocally confirmed the effective immobilization of horseradish peroxidase, and also made it possible to calculate the efficiency of immobilization, which oscillated at 85%. The obtained systems were also characterized by maintaining a relatively high catalytic activity, at the level of 80-90%, in relation to the free enzyme, and the analysis of kinetic parameters - the Michaelis-Menten constant and the maximum reaction rate - confirmed that the immobilized protein maintains a high affinity for the substrate (only a slight increase in the Michaelis-Menten constant was noticed). It was also shown that the immobilized HRP has a high, over 70%, activity over a wide range of pH, from 5 to 8, and temperature, from 15 to 45 °C, which indicates a significant increase in the stability of the enzyme after immobilization, since the free enzyme shows more than 70% activity only at pH 7 and 25 °C. The key results, however, relate to tests of the enzymatic removal of the antibiotic, sulfamethoxazole (SMX), from aqueous solutions under varying process conditions. It has been proven that using the manufactured HRP-based systems, it is possible to remove over 80% of the SMX.

Acknowledgements:

The research leading to these results has received funding from the Norwegian Financial Mechanism 2014-2021 under Project number 2020/37/K/ST8/03805.

References

Zdarta, J. et al. (2019) ‘Multi-faceted strategy based on enzyme immobilization with reactant adsorption and membrane technology for biocatalytic removal of pollutants: A critical review’, Biotechnology Advances, 7, 107401. doi: 10.1016/j.biotechadv.2019.05.007

Zdarta, J. et al. (2018) ’Developments in support materials for immobilization of oxidoreductases: A comprehensive review’, Advances in Colloid and Interface Science, 258, p. 1-20. doi: 10.1016/j.cis.2018.07.004

Graphene Based Materials for Water Treatment

S. Khaliha[1*], F. Tunioli[1], S.Mantovani[1], A. Bianchi[1], L. Bocchi[2], M.L. Navacchia[1], and M. Melucci[1]

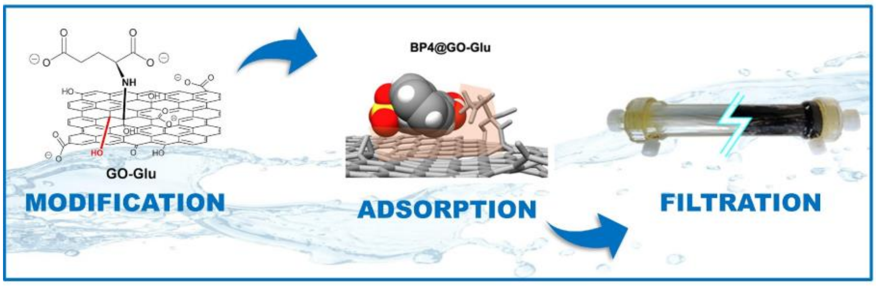
[1]Institute for Organic Synthesis and Photoreactivity (CNR-ISOF), Consiglio Nazionale delle Ricerche, via Piero Gobetti 101, 40129 Bologna (BO), Italy,
[2]Medica Spa, via degli Artigiani 7, 41036 Medolla (MO), Italy

sara.khaliha@isof.cnr.it

Academic and industrial interest is increasingly focusing on water treatments, especially on the removal of the Emerging contaminants, identified as potential environmental threats. The current water treatment technologies are not efficient in the removal of most of these contaminants from waters and new materials and technologies are required. Graphene based nanomaterials have shown great potential for water purification due to their high surface area and their adsorption properties, promoted by multiple interaction pathways with organic molecules and metal ions.

Here we report on the use of graphene oxide (GO) as sorbent for the removal of wide range of contaminants, including pharmaceuticals, additives, and dyes in drinking water.We also describe covalent chemical modification approaches, aimed at enhancing adsorption selectivity and capacities (i.e. aminoacids grafting for pharmaceuticals and PFAS removal) (Khaliha, S. et al. 2023).

Molecular Dynamic simulations and adsorption isothersm were exploited to unreval the adsorption mechanisms, investigating the role of surface chemistry. Finally, in order to overcome secondary contamination, we also describe a scalable and automatized procedure for water purification based on tandem adsorption on GO nanosheets and microfiltration (Khaliha, S. et al. 2022).



Modified graphene oxide used as sorbent for drinking water purification

References

Khaliha, S. et al. (2023) Amino acid-driven adsorption of emerging contaminants in water by modified graphene oxide nanosheets, Environ. Sci.: Water Res. Technol.,https://doi.org/10.1039/D2EW00871H

Khaliha, S. et al. (2022) 'Graphene oxide nanosheets for drinking water purification by tandem adsorption and microfiltration', Sep. Purif. Technol., 300, 121826. https://doi.org/10.1016/j.seppur.2022.121826

Influence of Dissolved Organic Carbon Nature on Adsorption of Ibuprofen, Caffeine and Diclofenac onto Powdered Activated Carbon–Does the Natural Coagulant Matter

T. Marjanović[1]*, M. Bogunović[1], I. Ivančev-Tumbas[1]

[1]University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg D. Obradovića 3, Novi Sad, Serbia

tijanam@dh.uns.ac.rs

Influence of different types of dissolved organic carbon (DOC) onto the removal of ibuprofen, caffeine and diclofenac from water by powdered activated carbon (PAC) was tested. As a representative of low molecular weight (LMW) DOC mixture of L-serine, L-leucine and resorcinol was used. Humic acid (HA) was applied as a high molecular weight (HMW) surrogate. Initial concentration of each pharmaceutical was 2-3 µg/L, while DOC content was near 3 mg C/L. Water matrices containing LMW DOC, HMW DOC and their mixtures were compared to laboratory synthetic water without DOC surrogate addition and real municipal wastewater treatment plant (WWTP) effluent. Positive effects of DOC surrogates on adsorption onto powdered activated carbon (PAC contact time 30 minutes, dose 5 mg/L) were observed in the matrix containing LMW surrogates (the efficiency of ibuprofen removal was 82% and 93% for two duplicate experiments, compared to the matrix without DOC surrogates, where it was 5% and 28%, and for caffeine 78% and 80%, compared to 48% and 50%). The addition of natural coagulant isolated from bean seeds (Prodanović, 2015) in dose of 37.5 µl/L also positively affected the adsorption of ibuprofen in synthetic matrix without DOC surrogates 25-45% while in matrix which contained LMW surrogates addition of natural coagulant did not have any effect. Less increase was observed (10-15%) in the synthetic matrix with the addition of HA for both ibuprofen and caffeine. In WWTP effluent only caffeine adsorption was 12% increased with addition of natural coagulant. Adsorption kinetics tests showed that the equilibrium is established the fastest in the synthetic matrix without the DOC surrogates and in matrices with the addition of the LMW DOC for all pharmaceuticals (after 2 h). A rough estimation of the film mass transfer coefficients (Worch, 2012) indicated that small DOC molecules accelerate the transport of pharmaceuticals compared to the synthetic matrix without the addition of the DOC surrogates. This was the most pronounced with caffeine. The addition of HA lowered the mass transfer coefficients of ibuprofen and diclofenac, but accelerated the transport of caffeine compared to the synthetic matrix. Similar effects were found when LMW and HMW surrogates were mixed and in the WWTP effluent. Freundlich equilibrium coefficients were only possible to calculate for caffeine and diclofenac in a synthetic matrix with HMW addition (Kf =8.162 (mg/g)/(mg/l)^n, n=0.5647 for caffeine, Kf =1.9201 (mg/g)/(mg/l)^n, n=0.2592 for diclofenac), while for ibuprofen Freundlich model was not possible to apply under given experimental conditions (PAC dose 1.5-8.0 mg/L, contact time 48h). In the synthetic matrix without DOC surrogates, the concentrations after the adsorption were below the practical quantification limit.

References

Prodanović, J. (2015) Natural coagulants from common bean (Phaseolus vulgaris) in water treatment. Dissertation, Faculty of Technology Novi Sad, University of Novi Sad.

Worch, E. (2012) Adsorption technology in water treatment– fundamentals, processes and modeling, DE Gruyter, ISBN 978-3-11-024022-1.2019, 176 p.

Photocatalytic Degradation of Ofloxacine Antibiotic Using Sphere-Shaped and Peanut-Like Zink Oxide and UV Light Irradiation

O. Makota[1,2]*, I. Melnyk[1]

[1]Academy of Sciences, Institute of Geotechnics of the Slovak Watsonova 45, 04001 Košice, Slovak Republic
[2]Lviv Polytechnic National University, Institute of Chemistry and Chemical Technologies, Stepana Bandery 12, 79013 Lviv, Ukraine

makota@saske.sk

Quinolone antibiotics are a popular class of antibiotics used to treat respiratory and urinary tract infections as well as multidrug resistant tuberculosis. Among them, ofloxacin, ciprofloxacin, norfloxacine, delafloxacin, and enrofloxacin have found wide applications due to their high antibacterial property and low cost (Moghaddam A.A. et al. 2023). However, antibiotics have caused serious pollution of water resources, easily toxified both surface and groundwater, and become typical organic chemical contaminants in wastewater, causing chronic diseases in humans and animals due to the growth of antibacterial resistant strains within their bodies. Therefore, antibiotic contaminant treatment methods have received much attention. Photocatalysis, as a “green chemistry” technology, has been regarded as an effective method of removing antibiotics from wastewater because of its simple construction, high mineralization rate, absence of secondary pollution, and low cost. Semiconductor zinc oxide (ZnO) with band gap energy 3.2 eV is one of the most promising photocatalysts for antibiotic degradation due to its non-toxic nature, inexpensive, simple preparation, and high photosensitivity (Moghaddam A.A. et al. 2023, Essawy A.A. et al. 2020).

In this work, sphere-shaped and peanut-like ZnO samples were prepared by the homogeneous precipitation method using zinc acetate as a zinc precursor and ammonium hydroxide as a precipitation agent. These samples were then applied as photocatalysts in the photodegradation reaction of ofloxacin under UV irradiation (9 W, $\lambda = 369$ nm). The structure of the prepared ZnO photocatalysts was studied using XRD, SEM, FTIR, z-potential measurements, and low-temperature nitrogen adsorption/desorption isotherms.

It was shown that ofloxacin demonstrated high stability under UV irradiation, and self-degradation did not occur. Furthermore, after stirring the antibiotic with ZnO samples in the dark, its concentration did not change, indicating that the adsorption process could be excluded. Sphere-shaped ZnO exhibited catalytic ability in the photodegradation reaction of ofloxacin, and the antibiotic removal percentage reached 99% after 3 hours, while for peanut-like ZnO, it took 4 hours. Therefore, sphere-shaped zinc oxide demonstrated higher photocatalytic performance.

Additionally, the influence of heavy metal ions, namely Ni^{2+}, Cd^{2+}, and Bi^{3+}, on the photodegradation process of ofloxacin catalyzed by the more active sphere-shaped ZnO was studied. It was established that Bi^{3+}ions enhanced the photodegradation efficiency, while Ni^{2+} and Cd^{2+} ions reduced it.

The photodegradation of the ofloxacin antibiotic using zinc oxide catalysts under UV irradiation in the absence and presence of the above-mentioned heavy metal ions followed pseudo-first-order kinetics, and the reaction rate constants were obtained accordingly.

Thus, the obtained results demonstrate the excellent photocatalytic performance of the prepared sphere-shaped and peanut-like zinc oxide in the photodegradation of ofloxacin under UV irradiation and their suitability for environmental protection.

This work was supported by the Office of the Government of the Slovak Republic (09I03-03-V01-00108 project).

References

Moghaddam, A.A. et al. (2023) ‘Antibiotics sequestration using metal nanoparticles: An updated systematic review and meta-analysis’, Inorganica Chimica Acta, 550, p. 121448. doi: 10.1016/j.ica.2023.121448.

Essawy, A.A. et al. (2020) ‘Green synthesis of spongy Nano-ZnO productive of hydroxyl radicals for unconventional solar-driven photocatalytic remediation of antibiotic enriched wastewater’, Journal of Environmental Management, 271, p. 110961. doi: 10.1016/j.jenvman.2020.110961.

Biotransformation Capacity for Trace Contaminants - from Wastewater to Natural Surface Water

M. Kalt[1,2*], E. Ceppi[1], A. Bösel[1], Y. Yu[1], K. Fenner[1,2]

[1]Swiss Federal Institute of Aquatic Science and Technology (Eawag), Departement of Environmental Chemistry,
Überlandstr. 133, CH-8600 Dübendorf
[2]University of Zurich, Institute for Chemistry, Winterthurerstr. 190, CH-8057 Zurich

martina.kalt@eawag.ch

Complex mixtures of trace organic contaminants (TrOCs) resulting from human activity and released into the environment are a major threat for ecosystems. Microbial biotransformation has the potential to remove them from the environment, but there is limited mechanistic understanding of the drivers of contaminant biotransformation. Activated sludge treatment in wastewater treatment plants (WWTPs), for instance, acts as partial barrier to prevent trace organic contaminants from entering the environment, but treatment efficiency varies among compounds and treatment facilities. Furthermore, treated effluents have been shown to affect the ecological functioning of downstream river biofilm communities, including their potential to biotransform TrOCs. In this project, the overall goal is to better understand and ultimately predict the level of TrOCs biotransformation during wastewater treatment and in downstream natural environments at the level of microbial communities and to evaluate the relevance and practical implications of these findings for contaminant transformation in wastewater-impacted freshwater microbiomes. We have, in a first step, explored the biotransformation capacity of river biofilm communities grown up- and downstream of six WWTP, as well as of the associated activated sludge, for a diverse selection of 200 test substances covering different classes of TrOCs. We aim to deepen our knowledge on the previously shown increased biotransformation capacity in downstream microbiomes, particularly with respect to whether it is indeed a result of concentration-dependent adaptation in the WWTP, and, if so, how it depends on the WWTP treatment technology employed (i.e., carbon eliminating, de-/nitrifying, de-/nitrifying with moving bed). The biotransformation kinetic data, which we have gathered for the altogether 36 microbial communities, will further allow us to answer to what extent increased downstream biotransformation of certain substances is related to their specific molecular structure, and how consistent patterns of variability among substances with similar potentially enzymatically transformed moieties, as predicted by enviPath (envipath.org), are.

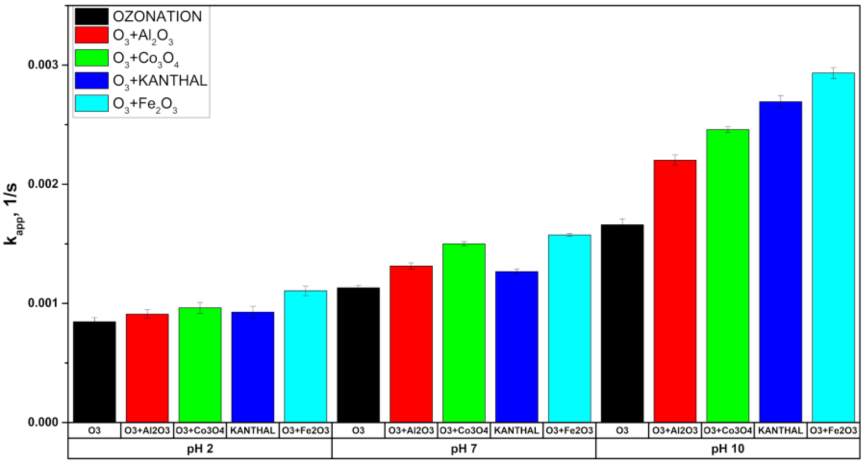
A Thin Layer Plasma Catalyst Used as a Structural Medium in Catalytic Ozonation of Textile Wastewater

M. Bilińska[1,2*], L. Bilińska[1,2], M, Gmurek[1]

[1]Lodz University of Technology, Department of Molecular Engineering, Wolczanska 213, 90-924 Lodz, Poland
[2]Bilinski Factory of Colour, Mickiewicza 29, 95-050 Konstantynow Lodzki, Poland)

magdalena.bilinska@dokt.p.lodz.pl

More than ten thous. m^3 of highly polluted textile wastewater is being emitted into the environment every day worldwide. The only chance to reduce this alarming number is through wastewater treatment (Dihom H.R. et al. 2022). New technologies give opportunities for more effective action against pollution. This study presents a newly developed plasma-prepared catalyst for textile wastewater ozone treatment. A thin layer of metal oxide was deposited on the surface of the structural material (knitted mesh made of kanthal alloy) with plasma-enhanced chemical vapor deposition (PECVD). This way, a three-dimensional stable catalytic material for heterogeneous catalysis was prepared. The activity of three types of metal oxide layers, cobalt, aluminum, and iron-based, were investigated in the study. The kinetic analysis of textile dye, Reactive Black 5, showed that cobalt and iron oxides were effective catalysts in dye removal. The kinetic constants were equal to $(2.46\pm0.03)\cdot10^{-3}$ 1/s and $(2.93\pm0.05)\cdot10^{-3}$ 1/s for cobalt and iron oxide, respectively. In contrast, the kinetic constant of classical ozonation was as low as $(1.66\pm0.05)\cdot10^{-3}$ 1/s. These data showed superactivity in alkaline pH, but the catalysts were also active in acidic and neutral pH. The XPS and SEM EDX analysis helped determine the catalytic layers' structure and composition. The cobalt oxide was found as Co_3O_4 spinel form and iron as Fe_2O_3.



Bar graph showing the difference between the reaction rate constants for processes at different pH.

References

Dihom, H.R. et al. (2022) ‘Photocatalytic degradation of disperse azo dyes in textile wastewater using green zinc oxide nanoparticles synthesized in plant extract: A critical review’, Journal of Water Process Engineering, 47, p. 102705. doi:https://doi.org/10.1016/j.jwpe.2022.102705.

Retinoid-Like Activities and their Drivers in Effluents of European Wastewater Treatment Plants

Smutná, M., Toušová, Z., Bláhová, L., Finckh, S., Brack, W., Hilscherová, K.

Biological effects of retinoids have been observed in samples of freshwaters affected by cyanobacterial blooms or sewage, however, current research is limited to a few studies mainly addressing the situation in Asian countries. Retinoids are biologically active compounds which are crucial for a variety of physiological processes in vertebrates including embryonic development, growth, reproduction, vision, cell differentiation and immune response. Retinoids and “retinoid-like” compounds may come from both natural and anthropogenic sources and excessive amounts of these compounds were shown to cause teratogenic effects in fish and frog embryos, which may adversely impact aquatic ecosystems.

The effluents of 20 wastewater treatment plants (WWTPs) with different capacities and treatment technologies from 15 European countries were subject to a sampling campaign using on-site large volume solid phase extraction. The extracts were tested in an *in vitro* bioassay based on retinoic acid receptor (RARα) reporter cell line. The potencies of samples relative to the potency of all-trans retinoic acid (ATRA), used as a standard reference, were expressed as retinoid equivalent concentrations (REQs). Targeted analysis of nine retinoid compounds was performed using liquid chromatography mass spectrometry.

Retinoid-like effects were detected at 8 out of 20 wastewater effluents with REQs of 4.5-37 ng/L (LOQ=2.5 ng/L), exceeding the proposed PNEC (predicted no effect concentration) for retinoid compounds of 3.93 ng/L. The targeted retinoids were detected at 9 out of 20 sites within the range of 4-359 ng/L (LOQ=1 ng/L), with 4-OH-atRA (all-trans-4-hydroxy retinoic acid) reaching the highest concentrations. The mass balance calculations revealed that the concentrations of detected retinoids could fully explain the biological activity at 2 sites, partially explain at 3 sites, while the activity at 3 other sites remained largely unexplained.

Our study brings a new insight into the effect assessment of European WWTP effluents and focuses on a yet understudied endpoint. Our results clearly show that biological effects of retinoids contained in treated effluents is a relevant endpoint, which should be included in the future effect-based monitoring of European surface waters under the umbrella of the Water Framework Directive (WFD) in order to protect aquatic biota. The project has received funding from the Czech Science Foundation (GACR) under grant agreement GX20-04676X.

Photocatalytic Degradation of Contaminants of Emerging Concern by N-Doped TiO_2 Using Simulated Sunlight in Real Water Matrices

P. Calza[1], E. Gaggero[1*], A. Giovagnoni[1], M.C. Paganini[1], D. Fabbri[1]

[1]University of Turin, Department of Chemistry, Via Pietro Giuria 5, 10125, Torino, Italy

elisa.gaggero@unito.it

Global water demand is increasing in accordance with population growth and economic development and overexploitation of water resources, pollution, anthropogenic activities, and related climate change have negative impacts on the quantity and quality of water resources. Contaminants of emerging concern (CECs) received increasing attention in recent years. The major concern is related to the number and variety of compounds that can be inscribed in this category (pharmaceuticals, hormones, pesticides, flame retardants, fragrances and more), and to the established hazardousness at low concentrations of many molecules. The latter aspect results in the difficult removal of molecules with conventional techniques and makes the development of innovative, environmentally friendly and low-cost systems for their removal essential (Ahmad, A. et al. 2022). In the present work we aimed of exploiting the photodegradation performances of N-doped TiO_2 photocatalysts with enhanced absorption of visible light for the abatement of some representative CECs. Pristine TiO_2 and N-TiO_2 were synthesized by hydrothermal (HT) and sol-gel (SG) routes and they were fully characterized. Their photodegradation efficiency was tested on a mixture of recalcitrant organic pollutants, namely benzotriazole, diclofenac, sulfamethoxazole and bisphenol A using a solar simulator lamp with two different cut-off filters (λ>340 nm and λ>400 nm). The evaluation of the photocatalytic performances was initially carried out in spiked ultrapure water and subsequently in aqueous matrices of increasing complexity such as Po River water and water coming from an aquaculture plant. The results obtained show that in the case of hydrothermally obtained materials, complete abatement is achieved for all matrices. Using irradiation with λ>340 nm, in the case of N-TiO_2-HT, a removal greater than 75% is achieved for all contaminants after the first hour and complete degradation is obtained within two hours. The employment of N-TiO_2-SG allows to achieve contaminants 'abatement more rapidly than the pristine TiO_2-SG, particularly when real matrices were used. In general, considering pristine materials we observe a decrease in kinetic constants values when moving from studying the system in Milli-Q water to real water matrices, however the diminution is less pronounced for doped materials, especially for N-TiO_2-SG, for which, in some cases, an increase in the abatement efficiency of contaminants is registered, especially in Po Water matrix. The use of visible light only (λ>400 nm) further highlights the advantage of introducing the dopant inside the TiO_2 photocatalyst, which without modification works mainly with UV-A (Guo Q. et al. 2019) and the better performances obtained for real water. In fact, for aquaculture water the abatement rates achieved with N-TiO_2-SG were 70% or greater within 2 hours, with kinetic constants even an order of magnitude higher than the corresponding pristine material as in the case of Benzotriazole and Diclofenac, thus making the material attractive for future field applications.

References

Ahmad, A. et al. (2022) 'Contaminants of emerging concern (CECs) in aquaculture effluent: Insight into breeding and rearing activities, alarming impacts, regulations, performance of wastewater treatment unit and future approaches', Chemosphere, 290, pp. 133319.

Guo, Q. et al. (2019) 'Fundamentals of TiO(2) Photocatalysis: Concepts, Mechanisms, and Challenges', Adv Mater, 31(50), pp. e1901997.

Waste Water Microbial Community Dynamics in MFCs Systems Using Anode Modification with Nanocomposites of Polyaniline/Nano-Oxides

A. M. Tanase[1]*, I. Lascu[1], C. Bradu[1], S. Toader[2], A. Dinu[2], A. Dumitru[2]

[1]Faculty of Biology, University of Bucharest, Bucharest, ROMANIA
[2]Faculty of Physics, University of Bucharest, Magurele, ROMANIA

ana-maria.tanase@bio.unibuc.ro

Water pollution, water depletion and energy crises are current problems of modern society with visible implications in our everyday life. Microbial fuel cells (MFCs) represent a promising technology that can overcome the challenges associated with wastewater treatment and bioenergy production in a single step based on the microbial metabolism of the biofilm developed at the anode. In this regard, an improved performance could be achieved using advanced materials for anode modification capable of high electron mediation. Our aim was to investigate the wastewater microbial community dynamics and wastewater treatment capability of MFC systems using anode modification with nanocomposites based on polyaniline (PANI) and nano-oxides such as TiO_2, WO_3, ZnO. The experimental set up consisted in dual chamber MFC systems with anodes consisting of carbon cloth (CC) modified with PANI-TiO_2, PANI-WO_3 and PANI-ZnO nanocomposites and 40% Pt/C ink-coated cathodes. Throughout operation 1 kΩ external resistance was used. Municipal wastewater supplemented with acetate and phosphate buffer were used as anolyte and catholyte, respectively. MFC systems with unmodified CC anodes were used as controls. MFC water treatment performance was evaluated by the reduction of Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC). The microbial communities from the initial wastewater and, following operation, of the anode biofilms were analyzed through 16S rRNA gene V3-V4 metabarcoding. Data analysis was performed in-house using the QIIME2 toolkit (Bolyen et al., 2019), a reference tree based on the SILVA 128 database was used for the phylogenetic placement of ASVs. A classifier based on the SILVA 138 99% database was used for the taxonomical annotation of ASVs. Polarization results showed that the maximum power density reached a value of 48.9 mW/m2 for anodes modified with PANI-ZnO nanocomposites, followed by PANI-TiO_2, PANI-WO_3, and much higher than unmodified CC. Preliminary wastewater treatment evaluation highlighted that the efficiency in the degradation of organic matter increases in the following order: carbon cloth < PANI-WO_3 < PANI-ZnO < PANI-TiO_2. Microbial communities from the initial wastewater had reduced diversity, the number of features was lower than those retrieved from MFC biofilms. Metabarcoding results showed that, for the wastewater samples, the most abundant taxonomic class was Gammaproteobacteria, followed by Bacteroidia and Campylobacteria, which resulted in an enriched anode biofilm community dominated by Chlorobia and Desulfuromonadia. Genus-level analysis revealed the presence of the Geobacter group in high abundance for all three modified anode biofilms, and a high abundance of Chlorobium in PANI-ZnO and PANI- TiO_2 indicate a synergistic effect on exoelectrogenic activity (Badalamenti, Torres and Krajmalnik-Brown, 2014). In conclusion, wastewater microbial community determined a drastically different biofilm composition in MFC systems, having observable taxonomic abundance differences between anode types, all of which highight microbial taxonomic groups involved in bioremediation, water treatment, and extracellular electron transfer.

References

Badalamenti, J.P., Torres, C.I. and Krajmalnik-Brown, R. (2014) “Coupling dark metabolism to electricity generation using photosynthetic cocultures,” Biotechnology and bioengineering, 111(2), pp. 223–231.

Bolyen, E. et al. (2019) “Reproducible, interactive, scalable and extensible microbiome data science using QIIME 2,” Nature biotechnology, 37(8), pp. 852–857.

Removal of Clozapine from Polluted Waters via C_3N_4 Based Materials

L. Ingaramo[1], V. Sakkas[2], C. Chrimatopoulos[2], MC Paganini[1], P. Calza[1]*

[1]University of Ioannina, Department of Chemistry, Laboratory of Analytical Chemistry, Ioannina 45 110, Greece,
[2]University of Turin, Department of Chemistry, Via P. Giuria 5/7, 10125, Torino, Italy

paola.calza@unito.it

A critical challenge for the 21st century is the water crisis resolution. Rapid growth in human population, urbanization, the increase in areas allocated to agriculture and climate change are some of the main causes of the shortage of clean water supplies, making this issue of primary concern. Nowadays, contaminants of emerging concern (CECs) are conveyed to the environment by multiple routes and targeted actions to treat contaminated water are required. CECs include a wide range of organic molecules, all sharing a poor removal in the conventional wastewater treatment plants, which results in their introduction in the environment with their detection at traces level in the aquatic system (Golovko O., et al. 2021). In particular, focusing on the class of drugs, it includes compounds exhibiting an extremely heterogeneous behavior once released in the water sector; many drugs are water-soluble and non-volatile, while others have high polarity and poor absorbability, or are lipophilic with a tendency to bioaccumulate or adsorb on sediments.

Since the conventional treatment processes generally used for water treatment are unable to guarantee the complete removal of CECs, the exploitation of Advanced Oxidation Processes is among the possible ways for increasing the treatment efficiency. In particular, the use of photocatalysis could be a powerful solution for environmental remediation due to its ability to generate highly reactive oxidizing species capable to remove a wide range of contaminants. However, the photocatalytic efficiency of the most frequently used semiconductors is limited by very poor response to visible light. In order to efficiently utilize solar energy, different strategies have been explored, such as anion and cation doping, surface deposition and instauration of heterojunctions. Within this scenario, we developed new materials characterized by a g-C_3N_4-ZnO heterojunction starting from different precursors; eight photocatalysts where produced, fully characterized and tested toward the abatement of clozapine, an antipsychotic drug widely used in the treatment of acute cases of schizophrenia and Parkinson's. All the experiments are conducted using a sun simulator and the evaluation of clozapine removal was assessed both in some environmental matrices (Pamvotis Lake, Ioannina, Greece and Po River waters, Turin, Italy) and on the drug tablet (commercialized as Leponex) in order to assess the role played by natural organic matter and by the excipients on the drug removal efficiency, respectively. In all cases, the tested materials allowed to easily achieve the complete abatement of the target molecule. Mechanicistic studies performed in the presence of selected radical scavengers evidenced that OH radicals are the key reactive species involved in the pollutant removal, while other species such as superoxide radical anion ($O_2^{\bullet -}$) and expecially singlet oxygen (O_2^1) played a marginal role in the degradation process.

References

Golovko O., et al. (2021) Occurrence and removal of chemicals of emerging concern in wastewater treatment plants and their impact on receiving water systems, Sci. Total Environ. 754 p. 142122. doi.org/10.1016/j.scitotenv.2020.142122

Treatment of Fish Canning Wastewater by Electrochemical Oxidation

I. Souli[1], C. Afonso[2], A. Lopes[2], M.J. Pacheco[2], L. Ciríaco[2], L. Labiadh[3], S. Ammar[1] and A. Fernandes[2]*

[1]Université de Gabès, UREME (UR17ES45), Faculté des Sciences de Gabès, Cité Erriadh, 6072 Gabès, Tunisia
[2]Universidade da Beira Interior, FibEnTech-UBI, Department of Chemistry, Rua Marquês D'Ávila e Bolama,6201-001 Covilhã, Portugal
[3]Huaqiao University, Xiamen Key Laboratory of Municipal and Industrial Solid Waste Utilization and Pollution Control, College of Civil Engineering, Xiamen, Fujian 361021, P.R. China

annabelf@ubi.pt

Fish canning industry generates large volume of wastewater containing high organic load and salinity, being the discharge in waterbodies of great environmental concern (Zufia, J. et al. 2002). Biological processes are often proposed to treat fish canning wastewater, but its application is hindered by the high salinity presented by this effluent (Zufia, J. et al. 2002). Conversily, electrochemical oxidation process is favoured by the high salinity of the wastewaters and, although its application to treat fish canning wastewater has never been reported, this technology is known by its high efficiency in the degradation of high polluted effluents (Fernandes A. et al. 2019). In the present study, fish canning wastewater was treated by electrochemical oxidation, using a boron-doped diamond (BDD) anode, and the influence of applied current density was investigated. The performance of the treatment process regarding organic load removal, biodegradability increment, toxicity reduction, and specific energy consumption, was evaluated. Experimental results obtained showed an increase in organic load removal rate with applied current density. However, the increase in current density substantially raised the energy consumption. At the lowest applied current density studied, 500 A/m², and without requiring the addition of chemicals, electrochemical oxidation, using a BDD anode, successfully treats fish canning wastewater, promoting the degradation of the organic load and ammonia nitrogen, the augment of the biodegradability index and the reduction in toxicity towards Daphnia magna (Figure 1).

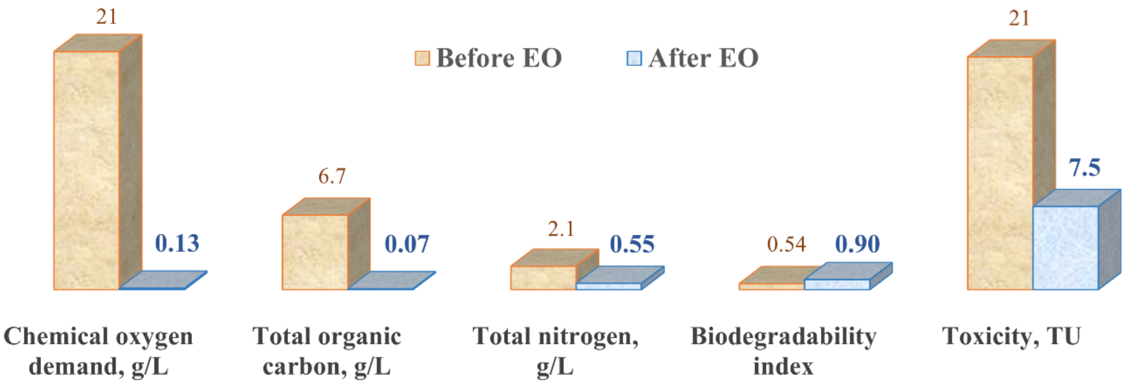


Figure 1 - Characterization of the FCW sample, before and after the EO treatment at 500 A/m² during 33.6 h.

References

Zufia, J. et al. (2002) ‘Integrated processing of fish canning industry wastewater: the EFLUCON project’, Journal of Aquatic Food Product Technology, 11, p. 303. doi: 10.1300/J030v11n03_22.

Fernandes, A. et al. (2019) ‘Ecotoxicological evaluation of electrochemical oxidation for the treatment of sanitary landfill leachates’, Environmental Science and Pollution Research, 26, p. 24. doi: 10.1007/s11356-018-2650-6.

An Interdisciplinary Study of Quality of Water from Long Island's Aquifer Impacted by Septic Systems

S. Sambasivan[1*], C.J. Foley[1], A. Migues[2], and N. Leonhardt[3]

[1]Suffolk County Community College, Physical Sciences Department, 533 College Road, Selden, NY 11784, USA
[2]Stony Brook University, Simmerling Lab, Laufer Center for Physical and Quantitative Biology, Stony Brook, NY, 11794, USA
[3]Suffolk County Community College, 533 College Road, Selden, NY 11784, USA

sambass@sunysuffolk.edu

This project in collaboration with the Physical Sciences, English and Engineering Departments focuses on water quality, a critical citizen science issue on Long Island (NY). Students enrolled in courses from four different disciplines - chemistry, journalism, engineering science, and construction technology- have explored this issue as a common theme and have identified and proposed solutions to the problem of water quality degradation, mainly due to increased Nitrogen loading. This topic is of particular interest since Long Island's drinking water is drawn from a sole-source aquifer and the primary means of waste disposal is through individual cesspools/septic tanks, particularly in Suffolk County, the easternmost county on Long Island, NY, USA.

An important component of the project highlights of civic engagements and responsibilities approach that features the teaching of course content through the lens of student identified civic issues and proposed solutions. The societal effects of the implementation of proposed solutions are also considered. An interdisciplinary college's learning management system (LMS) complemented the coursework and provided a central communication link for students from above mentioned disciplines, and professors to share resources, research and insights. In addition, collaboration extended to experts in local groundwater, professors, a Chemistry post-doctoral fellow with experience studying water quality issues, and community leaders that led online discussions. The chemical studies involved measurement of nitrate, nitrite, and pH of water samples from different parts of Long Island. The sources include tap water, local ponds/lakes, and run off from garden sprinkler systems. The measured nitrate levels were compared with publicly available data from the local water authority databases and Environmental Protection Agency (EPA) allowed ion concentrations (Database of nitrate levels, 2022). Student lab data indicate high levels of N in certain regions of Long Island. Student discussions included an examination of a new septic system currently being piloted in Suffolk County which reduces Nitrogen loading. This presentation will highlight lessons learned from this Citizen Science project including insights from student research, societal and renewable energy implications to arrive at a recommendation.

References

Database of nitrate levels. http://water.epa.gov/drink/contaminants/index.cfm and http://www.scwa.com/about/wq_reports/

Removal of Iron Water Pollution through Adsorption onto Chitosan Bound in Biodegradable Polyurethane Foams

R. Zeumer[1*], I. Tsetsila[1], K. Harre[1]

[1]University of Applied Sciences Dresden, Faculty of Agriculture/Environment/Chemistry, Friedrich-List-Platz 1, 01069 Dresden, Germany

richard.zeumer@htw-dresden.de

Emerging pollutants from industrial, urban and natural sources pose a risk for aquatic environments around the world. Hence, the development of sustainable and cost-effective solutions for the removal of those pollutants is still a challenging task. Although many promising bio-based adsorbents exist, which have been shown to effectively bind organic and inorganic pollutants, most of them have unfavourable mechanical properties in terms of surface area, binding capacity, morphology etc. Chitosan has shown to be to be capable of removing organic and inorganic pollutants from aqueous media taking into account, that modifications of chitosan (crosslinking, grafting, etc.) increased its adsorption capacity (Saheed et al., 2021). Likewise, modifications of polyurethane foams through incorporation of additives are able to increase their absorption capacity of a wide range of pollutants by influencing properties like hydrophobicity, surface area, selectivity (Selvasembian et al., 2021).

In this study, biodegradable chitosan polyurethane foams (BCPF) with up to 30 w/w% chitosan (particle size 63 – 2000 µm) were synthesized. BCPF samples (cuboids, 0.3 g) were incubated in Iron(II) sulfate solution (15 mg L-1) for 90 min or 7 days on a rotary shaker at 20 °C. After incubation, BCPF samples were removed, ammonium chloride, hydrochloric acid and sulfosalicylic acid were added to the solution and the iron content of the solution was measured photometrically at 424 nm. Control samples with pristine chitosan were treated identically. Biodegradability of polyurethane foams was assessed monometrically according to OECD TG 301F for 28 days while acute toxicity of eluates of polyurethane foams (8 weeks incubation in water) was investigated by performing bioassays with larvae of the fairy shrimp Thamnocephalus platyurus.

Incorporation of chitosan increased iron adsorption capacity of polyurethane foams by up to 400 % after 7 days incubation compared to pristine BCPF. Here, chitosan with smaller particle sizes showed higher adsorption capacities, whereas the influence of the mass percentage of chitosan on the adsorption capacity of polyurethane foams was strongly dependent on the formula of the foams. Biodegradation studies exposed degradation rates of more than 10 % while no toxic effects were observed for eluates diluted 1:2 with test media.

The presented results underline the potential of incorporation promising adsorbents for water pollutants into polyurethane foams. Modifications of the polyurethane foams as well as the use of mixtures of several additives allow adapting BCPF adsorbents for application to remove a wide range of pollutants. Since water can flow through BCPF and due to their pore-like structure, they could also eventually be used to remove particular substances like microplastic and could therefore be combined with existing techniques (Kurzweg et al., 2022).

References

Saheed, I. O. et al. (2021) "Chitosan modifications for adsorption of pollutants – A review", Journal of hazardous materials 408, 124889. doi:https://doi.org/10.1016/j.jhazmat.2020.124889.

Selvasembian, R. et al. (2021) "Recent advances in the polyurethane-based adsorbents for the decontamination of hazardous wastewater pollutants", Journal of hazardous materials 417, 125960. doi:https://doi.org/10.1016/j.jhazmat.2021.125960.

Kurzweg, L. et al., (2022) "Application of electrostatic separation and differential scanning calorimetry for microplastic analysis in river sediments", Frontiers in Environmental Science 10, 1032005. https://doi.org/10.3389/fenvs.2022.1032005.

Composite TiO_2-gC_3N_4 Thin Film Beads for Advanced Wastewater Treatment

M. Covei[1]*, C. Bogatu[1], D. Perniu[1], S. Gheorghita[1], A. Duta[1], H. Stroescu[2], M. Nicolescu[2], J.M. Calderon-Moreno[2], I. Atkinson[2], V. Bratan[2], M. Gartner[2]

[1]Transilvania University of Brasov, Department of Product Design, Mechatronics and Environment, 29 Eroilor Bd., 500036, Brasov, Romania
[2]"Ilie Murgulescu" Institute of Physical Chemistry, 202 Splaiul Independentei st., 060021, Bucharest, Romania

maria.covei@unitbv.ro

Advanced treatment methods are applied to wastewater in order to eliminate traces of pollutants (in the ppm range). One of the most versatile methods is photocatalysis which leads to the decomposition of organic pollutants from wastewater, under VIS or solar radiation (ideally) in the presence of a metal oxide semiconductor. The best known photocatalyst is TiO_2 which is chemically stable, low-cost and highly efficient. To extend the activation domain of TiO_2 from the UV to the VIS spectral range, the metal oxide can be coupled with carbon derivates, such as gC_3N_4. The composite materials can be used either as (nano)powders (wherein the higher surface area leads to higher photocatalytic efficiency, but the removal costs are also increased) or as planar thin films (with decreased removal efficiency but lower costs). A novel alternative is proposed in the frame of the current work, by depositing thin composite films using the sol-gel method on glass beads in order to maintain the high surface area but also to make sample retrieval, regeneration and reuse easier.

The thin films are obtained in two steps. The first step includes the deposition of a pure TiO_2 layer starting from titanium isopropoxide, ethanol, acetylacetone, acetic acid and water (20:16:0.89:0.18:2.4 vol) mixed to form a sol that is ultrasonated for 90 min. The bead substrate (d=2mm) is cleaned and treated in 98% sulfuric acid for 2h to increase the surface area and promote homogeneous film growth. One gram of beads is immersed in 5 mL of sol, under constant stirring (30 min). Drying is done at 110^{o}C for 1h, followed by annealing at 450^{o}C for 3h. Similarly, a second, TiO_2-gC_3N_4 layer is deposited from a sol, to which a gC_3N_4 ethanolic dispersion is added in order to obtain a 5% carbon derivate filler in the thin film. All other deposition parameters are maintained from the first deposition. For comparison, thin films without the first layer are also obtained.

The influence of the sol dilution ratio (sol: ethanol = 1 :1 or 1: 0) on the sample structure (XRD), morphology (SEM, AFM), chemical composition (EDX, Raman), optical (UV-VIS spectroscopy and ellipsometry) and photocatalical properties was investigated. Photocatalytic tests against methylene blue (MB) and imidacloprid (IMD) with the initial concentration 10 ppm, under UV+VIS (G=35 W/m^2) and UV (G=5W/m^2) radiation showed that all samples were VIS-active and suffer no clogging even after 9h of testing. Adsorbtion plays only a small role in the MB degradation (<5% compared to the overall ~70%), whereas it is much more significant in the case of IMD (10% adsorption to 40% overall removal efficiency). The sol dilution leads to more unstable thin films, that are partially washed off after three consecutive photocatalytic cycles. The addition of the intermediate TiO_2 layer proves beneficial not only for the uniform growth of the thin film on the beaded substrate, but also for their stability and improved photocatalytic efficiency. This is due to their higher crystallinity degree, higher surface area and thickness. Therefore, the TiO_2/TiO_2-gC_3N_4 samples obtained from undiluted sol are recommended for further upscaling.

Acknowledgements. This work was supported by a grant of Ministry of Research and Innovation, CNCS-UEFISCDI, project number PN-III-P2-2.1-PED-2021-2928, within PNCDI III, Contract no. 598PED/2022.

Modified Polymeric Films for the Enrichment of Steroid Hormones from Water Samples

F.Merlo[1], A. Profumo[1], A.Speltini[1], A. Cabrera[2], M. Martin[2], C. Fontàs[2], E. Anticó[3]*

[1]Università di Pavia, Department of Chemistry, Via Taramelli 12, 27100 Pavia, Italy
[2]Universitat de Girona, Department of Chemical Engineering, C/ Maria Aurèlia Capmany 69, 17003 Girona, Spain
[3]Universitat de Girona, Department of Chemistry, C/ Maria Aurèlia Capmany 69, 17003 Girona, Spain

enriqueta.antico@udg.edu

The presence of steroid hormones (both natural and synthetic) can be found in the environment at very low concentration levels. Recent research has demonstrated that co-presence of different steroid hormones can inhibit reproduction even when each hormone is present at a concentration below the one that would not invoke a measurable effect on its own. Then, the need to develop very sensitive methodologies to get a realistic picture of the presence of these emerging pollutants is evidenced. Powerful techniques like HPLC-MS/MS are used, but a preconcentration step prior to the detection is needed (Speltini, 2021).

In the present study, we have explored the use of self-prepared polymeric films for the enrichment of steroid hormones, e.g., estrogens, progestins, androgens and glucocorticoids, bearing log P values lower than 4. The films are prepared using cellulose triacetate as the polymer and different compounds as modifiers (Quintanilla, 2023). These include plasticizers (nitrophenyl octyl ether and dibutyl sebacate), the ionic liquid Aliquot 336, and a wood-derived biochar (NUCHAR), assayed alone or in combination.

Preliminary tests were undertaken in tap water (40 mL, native pH) enriched with 50 μg L^{-1} of each analyte (n=3), evaluating the extraction efficiency and kinetics at different extraction times (30 min- 24h) of each film composition. A different behavior in the extraction efficiency was observed, ascribable to the changes in the hydrophilicity of the films and to the wide polarity range of these compounds, from 1.46 of Cortisone to 4.02 of 17β-Estradiol. Films containing plasticizer and/or ionic liquid showed a good affinity for female sex hormones, but not for glucocorticoids and androgens. In details, the films with 60% CTA: 30% Aliquot 336: 10% NPOE gave the best results for estrogens, while the 70% CTA: 30% NPOE film allowed improved extraction of progestins. Ultrasound-assisted elution with methanol provided good recoveries for estrogens, progestins and testosterone.

NUCHAR-modified films efficiently extract all the families of steroid hormones. Studies on the elution conditions, due to the presence of biochar in the film, are ongoing to improve recovery.

To conclude, these films seem promising for thin-film microextraction of such kind of emerging pollutants, before their quantification in HPLC-MS/MS.

The financial support of the Spanish Government (research project PID2019-107033GB-C22) is acknowledged. Authors are grateful to Rachele Merli and Valentina Quarta for laboratory tasks.

References

Speltini, A. (2021) 'HA-C@silica sorbent for simultaneous extraction and clean-up of steroids in human plasma followed by HPLC-MS/MS multiclass determination', Talanta, 221, p. 121496. doi:10.1016/j.talanta.2020.121496.

Quintanilla, I. et al. (2023) 'Multiwalled Carbon Nanotubes Embedded in a Polymeric Matrix as a New Material for Thin Film Microextraction (TFME) in Organic Pollutant Monitoring', Polymers 15, p. 314. doi:10.3390/polym15020314.

Thermally Activated ZnCr Layered Double Hydroxide Based Photocatalysts: Photocatalytic and Antibacterial Efficiency

Dj. Karanovic[1]*, M.Hadnadjev-Kostic[1], T. Vulic[1], O. Govedarica[2], V. Rajakovic-Ognjanovic[2]

[1]University of Novi Sad, Faculty of Technology Novi Sad, Bulevar cara Lazara 1, 21000, Novi Sad, Serbia
[2]University of Belgrade, Faculty of Civil Engineering, Bulevar kralja Aleksandra 73, 11000, Belgrade, Serbia

djurdjicakaranovic@uns.ac.rs

Rapid industrial growth over the past few decades has had an immense negative influence on water eco-systems due to the presence of organic and inorganic contaminants in wastewater. Organic dyes, such as Methylene Blue (MB) and Brilliant Cresyl Blue (BCB), frequent wastewater contaminants, raised concerns regarding their toxicity and carcinogenic properties because of their excessive use in various industries and their presence in wastewater. Various wastewater purification processes have been researched, such as adsorption, ion-exchange and heterogeneous photocatalysis. Among them, photocatalytic wastewater purification has the greatest potential due to possible total degradation of pollutants and use of abundant and free solar radiation. Layered double hydroxides (LDHs) and their derived mixed oxides, have shown both, substantial efficiency in the photodegradation of various dyes and significant antibacterial activity. In this study, ZnCr LDH based photocatalysts have been synthesized and the influence of thermal treatment/activation temperature on their photocatalytic and antibacterial behaviour has been researched. ZnCr LDH photocatalyst was synthesized via low supersaturation coprecipitation method, dried at 100°C and thermally treated in air (5 h) at 300, 500, 700 and 900°C (denoted as: ZnCr LDH, ZnCr 300, ZnCr 500, ZnCr 700 and ZnCr 900). Structural and textural characterization, MB and BCB photodegradation efficiency, as well as photo induced antibacterial effect on gram-negative (E. coli) and gram-positive (S. aureus) bacteria was studied. Significant difference in photodegradation efficiency among photocatalysts treated at different temperatures was observed: ZnCr LDH had negligible photocatalytic and antibacterial efficiency, whereas thermally activated samples showed partial or complete degradation of pollutants, depending on the temperature of the thermal treatment. The best photocatalytic and antibacterial behaviour was observed for the photocatalyst treated at the highest temperature, ZnCr 900 (complete MB decomposition, 75% of BCB decomposition and 4 log units reduction of E. coli and S. aureus cell number i.e. 99.99% reduction). Thermal treatment triggered the formation of two photocatalytic active phases, ZnO and $ZnCr_2O_4$, initiating heterojunctions and synergistic effects, responsible for exceptional photocatalytic and antibacterial behaviour. The study showed that thermally treated ZnCr LDH based photocatalysts have great potential for use in wastewater treatment.

Acknowledgements: This work was supported by the Science Fund of the Republic of Serbia, project no. 7737365, Zero-Waste Concept for Flood Resilient Cities – Ø-Waste-Water

References

Hadnadjev-Kostic, M. et al. (2017) 'Photo-induced properties of photocatalysts: A study on the modified structural, optical and textural properties of TiO2-ZnAl layered double hydroxide based materials', Journal of Cleaner Production, 164, p. 1. doi: 10.1016/j.jclepro.2017.06.091.

Bencherif, S.D. et al. (2021) 'Synthesis, Characterization and Photocatalytic Performance of Calcined ZnCr-Layered Double Hydroxides', Nanomaterials, 11, p. 3051. doi: 10.3390/ nano11113051.

Landfill Leachate Degradation Using UV/Fe^{2+}/H_2O_2 and UV/Fe^{2+}/$S_2O_8^{2-}$ Processes

P. Parhtenidis[1]*, E. Evgenidou[1,2] ,D. A. Lambropoulou[1,2]

[1]Aristotle University of Thessaloniki, Department of Chemistry, GR 54124, Thessaloniki, Greece
[2]Centre for Interdisciplinary Research and Innovation (CIRI-AUTH), Balkan Center, Thessaloniki, 10th km Thessaloniki-Thermi Rd, GR 57001, Greece

pperiklis@chem.auth.gr

The formation of landfill leachate, as a consequence of landfilling, is a major social and environmental problem due to their complex composition (Kumar et al., 2023). Given the ecological risk, especially for aquatic ecosystems, treatment processes must be applied, in order to degrade these highly contaminated fluids. Advanced Oxidation Processes (AOPs) are a particularly attractive choice in leachate treatment as one can see by looking at relevant studies and reviews (Gautam, Kumar and Lokhandwala, 2019). This study evaluates the efficiency of two different processes (UV/Fe^{2+}/H_2O_2 and UV/Fe^{2+}/$S_2O_8^{2-}$) for the degradation of landfill leachate samples and examines the influence of various parameters like UV light, dosing mode and mixing of oxidants. The performance evaluation was done by measuring basic pollution indicators like chemical oxygen demand (COD), total organic carbon (TOC) and color index (CI). Regarding UV-Fenton, best removal efficacies (49.85-65.58% for COD, 48.12-61.17% for TOC and 86.65-93.78% for color index) were achieved under operating conditions as CODo:H2O2 mass ratio = 1:1, $[Fe^{2+}]/[H_2O_2]$ = 1:10, pH = 3.5 and treatment time = 60 minutes. UV/Fe^{2+}/$S_2O_8^{2-}$ process exhibited good performance in terms of degradation (76.34% COD, 71.44% TOC, 88.94% Color Index) in the respective conditions, albeit its efficacy was significantly affected by leachate composition. Additionally, other experiments proved that UV light didn't have a significant effect on dark Fenton's ability to degrade landfill leachate, as a result of the dark color of the sample and the solids generated in the beginning of the processes.

Funding
This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship, and Innovation, under the call RESEARCH – CREATE – INNOVATE (2nd Cycle) (Project acronym: UV-LEACH; Project code: T2EDK-00137).

References

Gautam, P., Kumar, S. and Lokhandwala, S. (2019) 'Advanced oxidation processes for treatment of leachate from hazardous waste landfill: A critical review', Journal of Cleaner Production, 237, p. 117639. doi:10.1016/j.jclepro.2019.117639.

Kumar, V. et al. (2023) 'Micropollutants characteristics, fate, and sustainable removal technologies for landfill leachate: A technical perspective', Journal of Water Process Engineering, 53(February), p. 103649. doi:10.1016/j.jwpe.2023.103649.

Analysis of Pesticides, Pharmaceuticals and Personal Care Products in Drinking and Environmental Water by Direct Injection Using UHPLC-MS/MS

H. Willmer[1], J.D Alwis[1] and C. Pinto[1]

[1]*Waters Corporation*

Monitoring for harmful substances in drinking and environmental water is essential for protecting human health and maintaining good environmental quality standards. Making accurate measurements at ultra- low levels is an essential part of any monitoring program. As more and more pesticides, pharmaceuticals and personal care products (PPPCP) are released into the environment, there is a growing demand for analytical methods with multiple compound groups.

The purpose of this work was to demonstrate a direct injection UHPLC-MS/MS method for the ultra-low level determination pesticides, pharmaceuticals and personal care products in drinking and environmental waters. The method performance study was completed on an ACQUITY™ Premier LC System with a Xevo™ TQ Absolute Mass Spectrometry System.

A method validation study was carried out on drinking water and environmental water matrices. The method performance was assessed using 3 spike levels at 10, 20, and 100 ng/L where applicable with 6 replicates at each level. Average method performance for trueness, repeatability, linearity, and sensitivity was assessed.

Study of Pesticide Residues in Polish River Basins in 2020 and 2021

D. Drożdżyński[1]*, A. Perczak[1], A. Hołodyńska-Kulas[1], R. Motała[1], D. Petlińska[1], M. Szczepański[1], A. Nowacka[1]

[1]Institute of Plant Protection - NRI, Department of Pesticide Residues Research, Władysława Węgorka St. 20, Poznań, Poland

d.drozdzynski@iorpib.poznan.pl

National authorities are responsible for enforcement of pesticide legislation following Regulation 1107/2009 and Directive 2009/128/EC while establishing a framework for Community action to achieve the sustainable use of pesticides. Professional users are responsible for proper application of plant protection products, thus ensuring that treated crops and environment will be free of excessive pesticide residues. According to the provisions of Directive establishing a framework for Community action to achieve the sustainable use of pesticides the EU Member States are obliged to establish national action plans to reduce risks associated with the use of plant protection products. The measures adopted also include those related to the monitoring of pesticide residues in water intended for human consumption and the monitoring of surface waters, groundwater and bottom sediments.

A total 483 in 2020 and 531 water samples in 2021 originating from different sampling points of Polish river basins were collected for pesticide residue analysis. The samples were taken from April to October, at monthly intervals. 317 pesticides and their metabolites were selected for testing in surface water samples. Respectively, 55 in 2020 and 56 substances in 2021 from various groups of pesticidal activity were detected in the samples, usually in low concentrations. In both years, the frequency of detected compounds was similar. The most popular group of pesticide activity determined in collected samples were herbicides (26 substances in 2020 and 30 in 2021), then fungicides (22 and 18, respectively) and six insecticide compounds in both years. The highest overall frequency of detection in 2020 was obtained for popular herbicides – metazachlor and nicosulfuron and widely used fungicide – tebuconazole, substances currently used in intensive chemical plant protection. While in 2021, two herbicides used in the protection of maize crops, i.e. bentazon and terbuthylazine, were most often determined in Polish river basins. During the entire sampling season, in 259 water samples out of 483 collected (53.6%) in 2020 and 300 out of 531 (56,5%) in 2021, no pesticide residues above level of determination were detected. Taking into account the requirements to be met by surface waters used as drinking water, which are set out in the Polish Regulation of the Minister of Maritime Economy and Inland Navigation of August 29, 2019 (Journal of Laws of 2019, item 1747), where for the highest category A1 the sum of residues pesticides must not exceed 1µg/dm^3, 95.9% in 2020 and 95.5% in 2021 met these requirements.

In summary, environmental monitoring and control activities are an important element of the risk analysis related to the use of plant protection products, and ultimately contribute to the dissemination of knowledge about their safe use for water environment in plant production.

In Vitro Evaluation of Silver Nanoparticles Activity Against 132 Multidrug Resistant Acinetobacter Baumannii Strains Isolated from Romanian Hospitals and Aquatic Environments During 2019-2022

I. Gheorghe-Barbu[1], I. Czobor Barbu[1], V.M. Corbu[1], A.Ș. Dumbravă[1], M. Surleac[2], S. Paraschiv[2], D. Oțelea[2], L. Marinescu[3], D. Ficai[3], A. Ficai[3], M.C. Chifiriuc[1,4]

[1] Faculty of Biology, University of Bucharest, Intr. Portocalelor no. 1-3, 060101, Bucharest, Romania,
[2]National Institute of Infectiosus Diseases "Matei Bals", Dr. Calistrat Grozovici no. 1, 021105, Bucharest, Romania,
[3]Faculty of Applied Chemistry and Materials Science, University Politechnica of Bucharest, Gh. Polizu, no. 1-7, 011061, Bucharest, Romania,
[4]Romanian Academy, 13 Septembrie, no. 1-55, 50711, Bucharest, Romania

irina.gheorghe@bio.unibuc.ro

Background: An increased incidence of multidrug resistant (MDR) Acinetobacter baumannii (AB) nosocomial strains is reported recently, harboring a high number of resistance determinants to antibiotics, including carbapenems and colistin, biocides as well as virulence markers (VMs). The study aims to demonstrate the in vitro efficiency of silver nanoparticles (AgNPs) against MDR AB strains isolated during 2019-2022 from intra-hospital infections (IHI) and different aquatic environments.

Methods: Three types of AgNPs encoded 1, 2, 3 synthesized by classical, solvo-thermal and Turkevich methods and characterized by FTIR, SEM, TEM, DLS and XRD were investigated for their antimicrobial and antibiofilm activity through qualitative and quantitative methods, on a total number of 132 AB strains isolated in the same temporal sequence from IHI, wastewater (WWs) and surface water samples (SWs) between march 2019 and august 2022 from different Romanian regions and characterized at phenotypic and genotypic level through disc diffusion, chromogenic methods, PCR and whole genome sequencing (WGS, Illumina).

Results: The comparative analysis of the antimicrobial resitance (AR) profiles according to the isolation source and the geographical location demonstrated the decrease of MDR level in AB recovered from WWs samples in 2022 from North Eastern/ Central/ Southern region (NE/C/S), in comparison to previous years. The AB strains belonged to eight phylogenetic groups: ST2-blaOXA-23 (IHI/WW/SWs AB from S/NE/C); ST636-blaOXA-72 (IHI/WWs AB from S/NE/C); ST1-blaOXA-72 (WW/SWs AB from S); ST79-blaOXA-23 (SWs AB from S); ST2-blaOXA-72 (IHI/WWs AB from NE); ST492-blaOXA-72 (WWs AB from NE); ST2-blaOXA23-blaOXA-72 (IHI/WWs AB from S/NE); ST1-blaOXA-23 (WWs NE) associated with the presence of VMs (ompA, epsA, csuE and bfmS). The qualitative screening of the antimicrobial activity of AgNPs showed that AgNP 3 inhibited the growth of all tested AB strains. The quantitative evaluation of the antimicrobial efficiency of Ag3 NPs against AB strains by isolation sources and year revealed that the highest efficiency corresponded to AB strains isolated from S and C regions (19.41 µg/mL respectively 31.46 µg/mL). The most susceptible were AB isolated in 2021 and respectively 2020 from WW (17.57 µg/mL / 9.75 µg/mL) and SW samples (15.62 µg/mL / 20.83 µg/mL). AB isolated from S and NE regions showed high potential for biofilm development. Ag3 NPs used in sub-inhibitory concentrations (minimum inhibitory concentration, MIC/2 and MIC/4) inhibit AB adherence to inert substratum. Best results were obtained for AB strains isolated from WW and SW from NE region at MIC/2 value (34,78% / 39,43%) and from IHI from S region.

Conclusions: We provide here the first report regarding the potential of Ag NPs to fight MDR AB high risk and virulent clones, demonstrated in vitro, on a significant number of strains isolated from clinical and aquatic environments.

We acknowledge the financial support of PN-III-P4-ID-PCCF-2016-0114, PN-III-P1-1.1-TE-2021-1515 (TE112/2022), PN-III-P2-2.1-PED-2021-2526 (736 PED/2022) and PN-III-P1-1.1-PD-2021-0540 (PD102/2022) research projects awarded by UEFISCDI.

Phenotypic and Genotypic Antibiotic Resistance of Lactococcus Garvieae and Petauri Isolated from Rainbow Trout in the Mediterranean Region

P. Pastorino[1]*, R.C. Ozturk[2], M. Ture[3], D. Ustaoglu[2], A.I. Vela[4], J.F. Fernandez-Garayzabal[4], M. Prearo[1], L. Fariano[5], D. Volpatti[6], K. Bitchava[7], C. Kotzamanidis[7], P.L. Acutis[1] and S. Colussi[1]

[1]Istituto Zooprofilattico Sperimentale del Piemonte, Liguria e Valle d'Aosta, Italy
[2]Karadeniz Technical University, Fisheries Technology Engineering, Turkey
[3]Fish Health Department, Central Fisheries Research Institute, Turkey
[4]Department of Animal Health and VISAVET Health Surveillance Centre, Spain
[5]Azienda Agricola Canali Cavour, Italy
[6]University of Udine, Italy
[7]Elgo-Demeter Thessaloniki, Greece

paolo.pastorino@izsto.it

Infectious diseases represent one of the main issue for sustainable and profitable aquaculture productions. The rapid emergence of antibiotic resistant bacteria endangers the efficacy of antibiotic and leads to the spread of resistance genes.
In the present study, phenotypic antibiotic resistance against 12 antibiotics (kanamycin 30 µg; ampicillin 10 µg or 25 µg; gentamycin 10 µg or 30 µg, florphenicol 30 µg; streptomycin 10 µg; erythromycin 15 µg; oxolinic acid 2 µg or 10 µg; flumequine 30 µg; penicillin 10 µg; amoxicillin 20 µg or 25 µg; neomycin 30 µg and oxytetracycline 30 µg) and the presence of 14 antibiotic resistance genes (florfenicol (floR), tetracycline (tetA, tetB, tetC, tetG), erythromycin (ermA, ermB, ermC), streptomycin (strB), β-lactamase ampicillin (blaSHV, blaOXA, blaTEM), quinolones oxalinic acid (gnrA), and quinolones flumequine (gyrA) were evaluated in archival Lactococcus garvieae and Lactococcus petauri strains isolated from small-scale rainbow trout farms in Turkey, Italy, Greece, and Spain.
Overall, antimicrobial susceptibility tests indicated that 93.8% of the isolates were resistant to oxolinic acid, followed by flumequine (91.3%), streptomycin (88.8%), kanamycin (72.5%), and neomycin (66.3%). Whereas, the highest susceptibilities were seen toward gentamycin (100%), oxytetracycline (97.5%), florfenicol (75%), ampicillin (73.8%), and amoxicillin (72.5%). Among all strains (n=80), 96.3% (n=77) had at least one resistance gene and 57.5% (n=46) had 2 or more antibiotic resistance genes. Among the screened tetracycline genes, tetC (57.5%) was the most prevalent gene followed by tetG (33.8%), ermC (23.8%) and tetB (21.3%), whereas floR (2.5%), ermA (2.5%), tetA (3.8%), and blaSHV (6.3%) were among the least detected genes.
Prevalence of resistance to commonly used antibiotics in aquaculture and detection of resistance genes in strains may lead to prolonged treatments and to the increase L. garvieae/L. petauri related mortalities. This study provides a starting point for comprehensive monitoring of antimicrobial resistance of L. garvieae/L. petauri strains in rainbow trout aquaculture in the Mediterranean Region.

References

Ture, M. et al. (2018) "Effects of Cage Farming on Antimicrobial and Heavy Metal Resistance of Escherichia coli, Enterococcus faecium, and Lactococcus garvieae", Microb Drug Resist, 24(9):1422-1430. doi: 10.1089/mdr.2018.0040.

Clonal Transmission of Colistin Resistant Klebsiella Pneumoniae Strains Harboring Endemic Mutations in mgrB Gene in Clinical Settings and Wastewaters from Romania

I. C. Barbu[1,2]*, I. Gheorghe-Barbu[1,2], M. Surleac[2,3], O. Vlaicu[3], S. Paraschiv[3], A. Rațiu[4], M. C. Chifiriuc[1,2]

[1]University of Bucharest, Faculty of Biology, Microbiology Dept.
[2]Research Institute of the University of Bucharest
[3]National Institute of Infectious Diseases "Matei Balş"
[4]University of Bucharest, Faculty of Biology, Genetics Dept.

ilda.barbu@bio.unibuc.ro

Resistance to colistin (Col), a last resort revived antibiotic, is a growing concern amongst clinically relevant Gram-negative bacilli. Besides the plasmid mediated mcr resistance mechanism, mutations in certain genes encoding lipopolysaccharide synthesis were described in Klebsiella pneumoniae (Kp) (Janssen et al., 2020). In this study, we have investigated the genetic background of Col resistance in Kp strains isolated from clinical and wastewater sources in different geographical urban locations in Romania.

Methods. A total of 46 Col resistant Kp (ColRKp) were selected from a collection of > 200 well characterised Kp strains isolated from six major Romanian cities during 2016-2021 from hospital settings and wastewater samples. Col resistance was tested/confirmed by the MIC method. All ColRKp strains were submitted to whole genome sequencing and subsequent bioinformatic analyses and for some of the clinical isolates, the mgrB gene variants were characterised by Sanger sequencing. The involvement of a novel mgrB mutation in col resistance was confirmed using complementation tests.

Results. The ColRKp strains (n=15) isolated in 2016 from a clinical institute in Bucharest exhibited multidrug-resistance phenotype, including Col resistance. The targeted sequencing of mgrB gene and WGS revealed the presence of two novel mutations in mgrB. The MLST analysis indicates the linkage of the novel mutation Leu18Stop with ST101 (n=7) and the Leu4Stop mutation with ST15 (n=2). The mgrB wild-type allele inserted in ColRKp strains harboring these novel mutations restored the susceptibility to Col. The same mutations were encountered in Kp strains isolated during 2018-2022 (5 clinical strains, 1 strain isolated from wastewater treatment plant effluent and 5 from hospital sewage). The Leu18Stop mutation was associated with Kp ST101 (3 clinical strains and 6 wastewater strains), while the Leu4Stop mutation was associated with ST2010 in two clinical strains. The NCBI database search indicates that the Leu18Stop mgrB mutation is also present in one ST11 Kp strain isolated from Spain, suggesting a different mutation event, not related to the ColRKP strains isolated from Romania.

Conclusions. The local dissemination of ColRKp is linked with the ST101 clone and endemic mutations of mgrB gene. The presence of these mutations both in clinical and WWTP effluent samples suggests the possible dissemination of ColRKp from clinical settings to surface waters in Romania, a country with high rates of antibiotic resistance, according to ECDC surveillance studies (Atlas of infectious diseases, 2023).

Acknowledgements. We acknowledge the financial support of PN-III-P4-ID-PCCF-2016-0114, PN-III-P1-1.1-TE-2021-1515 (TE112/2022), PN-III-P1-1.1-PD-2021-0540 (PD102/2022) and ERANET 243/2021 research projects awarded by UEFISCDI

References

Janssen, A. B., Doorduijn, D. J., Mills, G., Rogers, M. R. C., Bonten, M. J. M., Rooijakkers, S. H. M., Willems, R. J. L., Bengoechea, J. A., & van Schaik, W. (2020). 'Evolution of Colistin Resistance in the Klebsiella pneumoniae Complex Follows Multiple Evolutionary Trajectories with Variable Effects on Fitness and Virulence Characteristics'. Antimicrobial agents and chemotherapy, 65(1), e01958-20. https://doi.org/10.1128/AAC.01958-20.

https://atlas.ecdc.europa.eu/public/index.aspx?Dataset=27&HealthTopic=4.

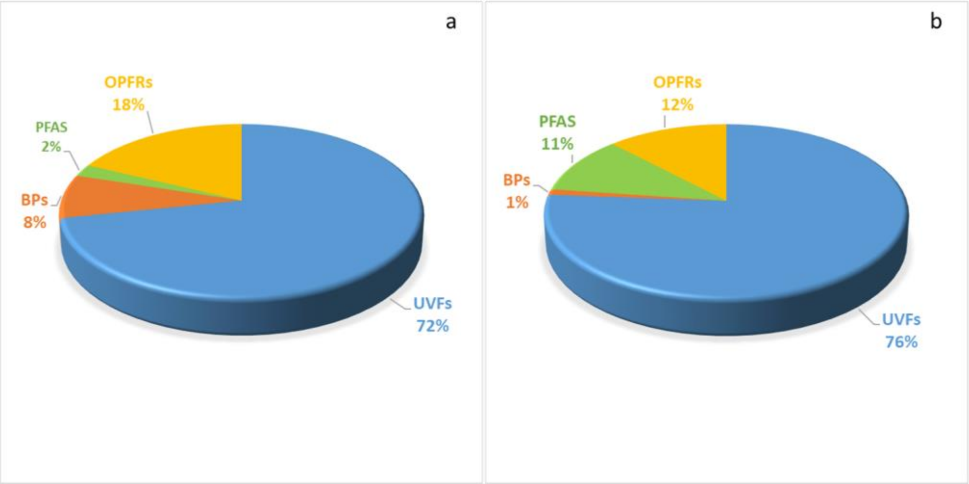
Occurrence of Endocrine Disruptors and Related Compounds Along the Romanian Marine Environment

F.L. Chiriac[1], V.I. Iancu[1], I. Paun[1], F. Pirvu[1], V.A. Petre[1], I.N. Cristea[1], N. Vasilache[1], M. Niculescu[1], G.G. Vasile[1]* and V. Cojocaru[1]

[1]National Research and Development Institute for Industrial Ecology-ECOIND, Pollution Control Department, Drumul Podu Dambovitei Street 57 -73, 060652, Bucharest, Romania

gabriela.vasile@incdecoind.ro

The risk of environmental exposure to various anthropogenic substances, which can modify the normal functioning of the endocrine system, represents a major health and safety concern for aquatic species and human life (Jasrotia, R. et al. 2021). In the present study, concentration levels of several endocrine disruptor compounds (ECDs) and related substances beloging to organic UV-Filters (UVFs), Bisphenols (BPs), Perfluorinated substances (PFAS) and Organophosphate flame retardants (OPFRs) familys were determined in seawater and sediment samples collected from the Romanian Black Sea coast. From theese four classes, the well-known ECDs are benzophenone-3 (BP-3), homosalate (HS), benzyl-salycilate (BS), bisphenol A (BPA), perorooctanoic acid (PFOA) and perflorooctansulfonate acid (PFOS), Tris(chloroethyl)phosphate (TCEP), Tris(2-chloroisopropyl)phosphate (TCPP) and Tris(1,3-dichloro-2-propyl)phosphate (TDCPP). From each class of compounds, in seawater, the maximum concentration was determined for BP-3 (5607 ng/L) and HS (1826 ng/L), BPA (416 ng/L) and Bisphenol E (194 ng/L) (Chiriac, F.L. et al. 2021). PFOA (112 ng/L), Triphenyl phosphate (1417 ng/L) and TCEP (575 ng/L). In sediment samples, the major compound were BP-3 (up to 975 ng/g d.w.), BS (749 ng/g d.w.) and HS (964 ng/g d.w.), BPC (16.2 ng/g d.w.) (Chiriac et al., 2021), PFOS (613 ng/g d.w.) and PFOA (130 ng/g d.w.), TPP (1823 ng/g d.w.) and TCPP (190 ng/g d.w.). The percentage distribution of these classes of ECDs and related compounds in seawater and sediment, showed that UVFs are by far the dominant compounds.



Percentage distribution of selected ECDs and related compounds in seawater (a) and sediment (b) samples

References

Jasrotia, R. et al. (2021) 'Endocrine disrupting chemicals in aquatic ecosystem: an emerging threat to wildlife and human health', Proceedings of the Zoological Society, 634. doi: 10.1007/s12595-021-00410-5.

Chiriac, F.L. et al. (2021) 'Investigation of endocrine disruptor pollutants and their metabolites along the Romanian Black Sea Coast: occurrence, distribution and risk assessment', Environmental Toxicology and Pharmacology, 103673. doi: 10.1016/j.etap.2021.103673.

Determination of Perfluoroalkylated Substances in Drinking Water from Spain and other European Countries According to Directive 2020/2184/Eu

J. López-Vázquez[1], R. Montes[1], R. Rodil[1], J.A. Martínez-Pontevedra[2], M.T. Pena[2], J.B. Quintana[1]*

[1]Universidade de Santiago de Compostela, Department of Analytical Chemistry, Institute of Research on Chemical and Biological Analysis (IAQBUS), 15782 Santiago de Compostela, Galicia, Spain.
[2]Applus Norcontrol S.L.U., Carretera NVI Km.582, 15168 Sada, Galicia, Spain.

jb.quintana@usc.es

Per- and poly-fluoroalkyled substances (PFAS) comprise a large family of synthetic chemicals manufactured for more than 80 years with unique properties, among which their amphiphilic character and persistence made them very attractive for several applications (OECD, 2018). As a result, however, they have spread in the environment, where they have become an important problem because of the difficulties for their removal. Therefore, PFAS may also constitute a threat to human health, because of contamination of drinking water.

Thus, recently, Directive 2020/2184/EU (EC, 2020) regulated the presence of 20 PFAS (C4-C13, both carboxylates and sulfonates) in drinking water, concerning the quality of water intended for human consumption. This regulation limited the sum of the concentrations of these 20 PFAS to less than 100 ng/L.

Therefore, in this work we pursued two main objectives. The first one was to develop and validate a methodology capable of achieving limits of quantification (LOQs) that are 30% of the value indicated in the directive as a sum (i.e. 30 ng/L). Considering that this limit is the sum of 20 congeners, the LOQ to be achieved for each compound should be ≤ 1.5 ng/L. The second objective was to apply the method to a series of samples collected across Spain and Europe to investigate the presence of those 20 PFAS in tap and bottled mineral water and compare the concentrations obtained to the limit established in the recent EU directive (EC, 2020).

The method developed consisted on a solid-phase extraction (SPE) with Oasis Weak Anion Exchange (WAX) cartridges and subsequent analysis by liquid chromatography tandem mass spectrometry (LC-MS/MS) on an Agilent 1290 Infinity II LC coupled to an Agilent 6495 triple quadrupole, equipped with a Zorbax Extend C18 RRHT column and an Agilent delay column. This combination provided sub-ng/L LOQs (≤ 0.3 ng/L for all congeners) with good trueness (Recovery 70-120%) and precision (RSD ≤ 19%) determined at 3 concentration levels. Finally, 46 water samples (11 bottled water from Spain, 23 Spanish and 12 European tap water samples) were subject to the analytical method. Up to 10 different PFAS were detected in the samples with a detection frequency between 2 and 91% and concentrations ranging from 0.1 to 20.1 ng/L for each PFAS. The concentration sum was below 100 ng/L in all cases, therefore meeting the standards of Directive 2020/2184/EU.

Acknowledgements: Agilent for the kind let of LC-MS/MS instrumentation. Several colleagues for the supply of samples. Xunta de Galicia (ED431C 2021/06) and the Spanish Agencia Estatal de Investigación –MCIN/AEI/10.13039/501100011033 (ref. PID2020-117686RB-C32) for funding.

References

EC. (2020). Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption. Official Journal of the European Union, 435, 1-62.

OECD. (2018). Towards a new comprehensive global database of per-and polyfluoroalkyl substances (PFASs): Summary report on updating the OECD 2007 list of per-and polyfluoroalkyl substances (PFASs). Series on Risk Management, 39, 1-24.

UHPLC-Q-TOF Methodology for the Comprehensive Characterization of PFASs in Larus Michahellis Eggs and Blood from the Ebro Delta

B. Oró-Nolla[1]*, M. Dulsat-Masvidal[1], A. Bertolero[2], A. López-Antía[1], S. Lacorte[1]

[1]IDAEA-CSIC, Department of Environmental Chemistry, Jordi Girona 18-26, 08034, Barcelona, Spain
[2] Associació Picampall de les Terres de l'Ebre, Amposta, Spain

bonqam@idaea.csic.es

Gull eggs have been used as bioindicators of Perfluoroalkyl Substances (PFASs) due to their high biomagnification potential (Verboven et al., 2009). PFASs comprise an extended family of chemicals such as PFOS, PFUdA, PFTrDA, PFDoA, PFDA or PFNA which can potentially affect wild birds. Gull (Larus michahellis) eggs from the Ebro Delta have been analyzed for over 10 years and PFASs have been systematically detected at concentrations of total PFASs from 13.7 ± 5.9 to 164 ± 17 ng/g wet weight (Colomer-Vidal et al., 2022). The aim of the present study is to extend the number of PFASs detected in gull eggs by developing a targeted/untargeted methodology based in ultra-high liquid-chromatography coupled to high-resolution mass spectrometry using a Q-TOF with negative electrospray ionization by data-independent acquisition (DIA) mode through a full-scan obtaining MS1 at 6 eV and MS2 at 30 eV. The database Per- and perfluoroalkyl substances (NORMAN, 2023) was selected being the second most extensive (with 5,676 PFASs to March 2023), easy to access (a .csv file could be downloaded) and containing IUPAC names, monoisotopic exact masses, molecular formulas, analytical techniques, and other relevant compound parameters. A first screening of PFASs was based on filtering by analytical technique and by type of ionization source (LC-MS and ESI-) reducing the database to 561 compounds. Then, identification criteria were based on (i) searching the molecular ion in the MS1 spectra with a mass tolerance < 5 ppm, abundance of the base peak > 1000, and minimum 5 scans per peak and (ii) assuring the presence of at least one qualifier fragment ion or a diagnostic fragment in the MS2 spectra, except for substances that do not yield more fragments because of their chemical structure. Based on that identification protocol, 62 compounds were detected in samples with their molecular ion in the MS1 spectra. PFASs appearing in the blanks were discarded which led to a 31 PFASs present in gull eggs and blood. A final list with 12 potential compounds was used to go through identification with MS1 and MS2 in detail. Results showed the full identification of 2-(Perfluorohexyl)ethanol (6:2FTOH, CAS number 647-42-7) and perfluoro-p-ethylcyclohexylsulfonic acid (PFECHS, CAS number 646-83-3) and other 10 suspect PFASs in Larus michahellis eggs and blood from the Ebro Delta. The developed method aims helps in enlarging the identification capacity of PFASs in biota matrices. More research is needed to assess the complexity to fully-resolve PFASs and evaluate the risks in birds breeding in vulnerable areas.

Acknowledgments

This work was supported by the Spanish Ministry of Science and Innovation Project TED2021-131552B-C21, Excelencia Severo Ochoa Project CEX2018-000794-S and project PID2019-105732GB-C21.

References

Colomer-Vidal, P., et al. (2022) 'Distribution and ten-year temporal trends (2009–2018) of perfluoroalkyl substances in gull eggs from Spanish breeding colonies' Environ. Pollut. 293. https://doi.org/10.1016/j.envpol.2021

Verboven, N., et al. (2009) 'Differential investment in eggs by arctic-breeding Glaucous Gulls (Larus hyperboreus) exposed to persistent organic pollutants' Auk 126, 123–133. https://doi.org/10.1525/auk.2009.08039

NORMAN, Per- and perfluoroalkyl substances - NORMAN SusDat [21 March 2023], available from www.norman-network.com/nds/susdat/

Adaptation of Large Panels of Per- and Polyfluoronated Alkyl Substances (PFAS) for Routine Analysis in Drinking and Environmental Waters by Direct Injection Using UHPLC-MS/MS

J. Davies, JD[1]. Alwis[1] and C. Pinto[1]

[1]Waters Corporation

Per- and Polyfluoroalkyl Substances (PFAS), are extremely persistent in the environment. Their production and use have resulted in severe contamination of soil, water and food. To protect public health, advisory and regulatory limits continue to be created and updated. Consequently, routine PFAS analysis has become challenging as not only low detection limits are required, but extensive compound coverage is a prerequisite nowadays.
The purpose of this work was to demonstrate a direct injection UHPLC-MS/MS method for the ultra-low-level determination of multiple PFAS compounds in drinking and environmental waters. The method performance study was completed on an ACQUITY^{TM} Premier System with a Xevo^{TM} TQ Absolute Mass Spectrometer and UniSpray^{TM} Ion Source. Samples were prepared by dilution with an acidified organic solution.

A method validation study was carried out on 2 common drinking water and 2 surface water matrices. The method performance was assessed using 3 spike levels at 1, 5, and 10 ng/L for all analytes, with 6 replicates at each level. Average method performance for trueness, repeatability, linearity, and sensitivity was assessed.

.

Improvements in both the analytical and isolator column technologies demonstrated in this work, as well as enhancements in negative ion sensitivity from the Xevo TQ Absolute Mass Spectrometer are helping to support ongoing efforts in PFAS analysis. This allows for easier, more robust, and accurate options as PFAS analysis continues into the future.

Detection and Quantitation of Volatile PFAS with Gas Chromatography Atmospheric Pressure Chemical Ionization (GC-APCI)

S. Dowd[1], K. Organtini[1], D. Stevens[1], C. Pinto[2]*

[1]Waters Corporation, Milford, MA United States, 01757
[2]Waters Corporation

Cecile_Pinto@waters.com

Perfluoroalkyl substances (PFAS) are a group of compounds with unique chemistry that are widely used in industrial and consumer goods. As a result of their widespread use, these compounds have been found in all types of environmental samples. As the global concern for the prevalence of these compounds and their potential adverse health effects has escalated, the demand for their detection and characterization has also escalated. Current regulatory methods are limited to looking for certain target PFAS compounds with part per trillion (ppt) detection levels using LC-MS/MS. An outstanding challenge in the study of the fate of PFAS in the environment will be the detection and quantitation of certain volatile or neutral PFAS compounds that are not amenable to LC analysis. Volatile PFAS, such as fluorotelomer alcohols, are of interest as potential precursors to the problematic perfluorocarboxylic acids like perfluorooctanoic acid (PFOA) (Morales-McDevitt et al., 2021). Trace level detection of volatile and neutral PFAS compounds is not easily done with the standard LC-MS/MS methodology and requires separation with GC. In this work, we looked at the detection and quantitation of volatile/neutral PFAS compounds with atmospheric pressure chemical ionization (APCI) from a commercial atmospheric pressure GC source. The softer ionization of the APCI source coupled to the GC outlet leads to the formation of intact molecular ions with very little fragmentation. The propensity to create an intact molecular ion allows for highly selective MRM methods on an MS/MS instrument and increased sensitivity compared to traditional vacuum source electron ionization (EI) instruments (Portoles et al., 2015). Limits of detection were determined to be <50 fg on column for a set of standards that included fluorotelomer alcohols, fluorotelomer acrylates, and N-alkylfluorooctane sulfonamides/-ethanols. Calibration curves with neat standards of were prepared in ethyl acetate in the range of 0.02 – 50 pg/µL and had R2 > 0.99 for the compounds analyzed. The results indicate that this analytical methodology is well suited for qualitative and quantitative analysis of volatile/neutral PFAS at low levels.

References

Morales-McDevitt et al (2021) 'The Air That We Breathe: Neutral and Volatile PFAS in Indoor Air', Environmental Science & Technology Letters, 8, 10, 897-902. DOI: 10.1021/acs.estlett.1c00481.

Portoles et al (2015) 'Gas chromatography-tandem mass spectrometry with atmospheric pressure chemical ionization for fluorotelomer alcohols and perfluorinated sulfonamides determination', Journal of Chromatography A¬, 1413, p 107-116. DOI: 10.1016/j.chroma.2015.08.016.

Legacy and Emerging Per- and Polyfluoroalkyl Substances in Leachate from MSW Landfill and in Municipal Sludge from WWTP: a Routine Analytical Method in LC-MS/MS

S. Marangoni[1], A. Perissi[2], A. Pivato[3], M. C. Lavagnolo[3], G. Beggio[3], R. Piazza[4], T. Bonato[1,4]

[1]Società Estense Servizi Ambientali (S.E.S.A. S.p.A.), Este, PD, Italy
[2]Waters S.p.a. - Sesto San Giovanni, MI, Italy
[3]University of Padova, Dept. of Civil, Environmental and Architectural Engineering, Italy
[4]University Ca' Foscari of Venice, Dept. Environmental Sciences, Informatics and Statistics, Italy

Per- and polyfuoroalkyl substances (PFAS) are a class of man-made synthetic compounds used in many industrial applications because of their high thermal and chemical stability. Legacy PFAS were phased out of production due to their adverse health effects, however they were substituted by emerging PFAS. Due to their widespread use, environmental persistence and chemical stability, PFAS can be ubiquitously detected in numerous matrices. The aim of the present study was to develop a method for detecting PFAS (both legacy and emerging PFAS) in the sludge from municipal wastewater treatment plants (WWTP) of large population centers and the leachate from MSW landfills. LC-MS/MS quantification of PFAS was performed using a Waters Xevo TQ-S Micro triple quadrupole MS (ESI-). Chromatographic separation was achieved using an ACQUITY Premier BEH Shield RP 18 1.7 µm, 2.1 x 100 mm Column, at flow rate of 0.35 mL min-1 using a linear gradient with (A) NH4Ac in 95%/5% H2O/MeOH and (B) NH4Ac 2 mM in MeOH on an ACQUITY HCLASS PLUS UPLC. The results showed that: (a) it is possible to quantify 12 legacy and 17 emerging PFASs by a routine LC-MS/MS method, with direct injection of the extract, without a purification step, for both leachate (LOQ=0.05 µg L-1) and sludge (LOQ=0.05 µg kg-1); (b) emerging PFASs are more abundant in the sludge than in landfill leachates (25% and 6%, respectively); (c) in leachate, the most abundant PFAS is PFBS (13.6±1.1 µg L-1), while in sludge it is PFOS (7.6±0.8 µg kg-1). In conclusion, it was developed a simple and fast multi-residual routine LC-MS/MS method in sludge and leachate matrixes for the analysis of both old and new generation PFAS.

Evaluation of the Impact of Surface Properties on the Adsorption of PFAS Using Quartz Crystal Microbalance

O. Beyioku[1]* and A. Ronen[1]

[1]Ben Gurion university of The Negev, Department of Desalination & Water Treatment (DWT), The Zuckerberg institute for Water Research (ZIWR), The Jacob Blaustein Institutes for Desert Research, Sde Boker Campus, 8499000, Israel

beyiokuo@post.bgu.ac.il

Per- and polyfluoroalkyl substances (PFAS) are anthropogenic organofluoride micropollutants of increasing global health concern. Adsorption of PFAS to surfaces is critical for their fate and transport in the environment (Lei et al., 2023). For example, PFAS partitioning to biosolids during wastewater treatment controls their fate and distribution and is influenced by the physicochemical properties of the organic material (Ebrahimi et al., 2021). Although the adsorption kinetics and capacity of PFAS to various adsorbents has been reported, there is limited studies focusing the interaction between PFAS and surfaces at fundamental nanogram scale. We aim to evaluate how surface properties impact PFAS adsorption using highly sensitive quartz crystal microbalance for direct measurement of adsorption of long chain Perfluorooctanoic acid (PFOA), and short chain Perfluorobutanoic acid (PFBA).

The hydrophobicity, surface charge and surface area of commercial QCM sensors were modified using 3-Aminopropyl Triethoxysilane (APTES), Polyethersulfone (PES), Polyethylene imine (PEI), 3-Glycidyloxypropyl) trimethoxy silane (GPTMS), PVDF, Carboxylated Carbon nanotubes (CNTs-COOH) and Fluorinated carbon nanotubes (CNTs-F). The sensors were evaluated for adsorption with PFOA and PFBA. Our result showed that hydrophobicity and higher surface area increased the adsorption of PFOA, compared to PFBA. Fluorinated CNTs showed the highest absorption for PFOA and PFBA attributed to higher surface area, hydrophobicity, and fluorine groups (Fig.1).

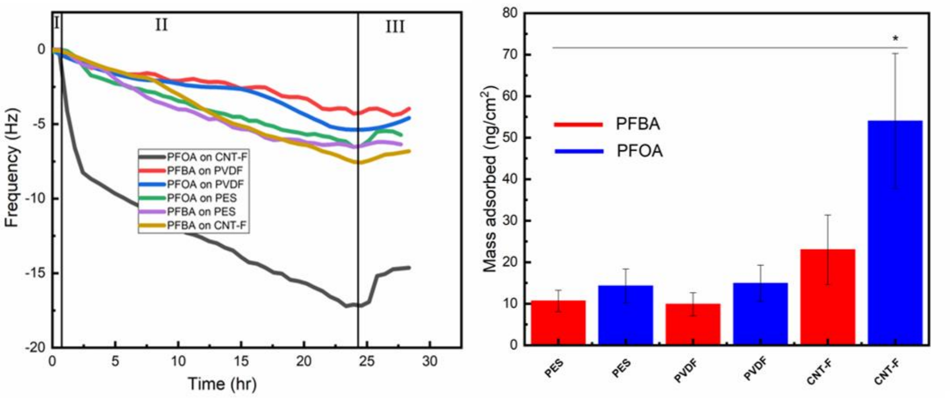


Figure 1. (a) Frequency change on sensors, with section I: baseline, II: PFAS and III: water (b) The final mass adsorbed on the sensors' surface.

References

Ebrahimi, F. et al. (2021) 'Linking PFAS partitioning behavior in sewage solids to the solid characteristics, solution chemistry, and treatment processes', Chemosphere, 271, p. 129530. doi: 10.1016/j.chemosphere.2020.129530.

Lei, X. et al. (2023) 'A review of PFAS adsorption from aqueous solutions: Current approaches, engineering applications, challenges, and opportunities', Environmental Pollution, 321(January), p. 121138. doi: 10.1016/j.envpol.2023.121138.

Levels of Per- and Polyfluoroalkyl Substances in Ski Wax Products and Snow from the Czech Republic

D. Parizkova[1], O. Parizek[1], V. Svobodova[1], L. Libenska[1], D. Dvorakova[1], J. Pulkrabova[1]*

[1]University of Chemistry and Technology Prague, Department of Food Analysis and Nutrition, Czech Republic, 166 28,

turnerod@vscht.cz

Per- and polyfluoroalkylated substances (PFAS) are a group of organohalogenated pollutants that are currently receiving a lot of attention due to their ubiquity and a proven negative effect on human health. In recent years, ski waxes have been identified as a potential source of PFAS in the environment. Commission Regulation 2020/784 came into force on July 4, 2020, which regulates the presence of pefluorooctanoic acid (PFOA) in selected products sold in the European Union, including ski waxes. The concentration of PFOA and their precursors should not exceed a concentration of 25 ng/g of the product. Based on this regulation, the use of hydrofluorocarbon-based sliding waxes in international ski competitions was banned by the International Ski Federation in starting winter season 2020-2021. However, recreational athletes use this type of wax without any restrictions. Although some ski wax manufacturers have stated that they have changed the chemical composition of their products, it was not confirmed by the chemical analysis performed in current study (Fang et al., 2020). Possible contamination of snow with ski wax can lead to secondary contamination of the surrounding soil and groundwater (Carlson and Tupper, 2020).

The aim of this study was (i) to develop analytical procedures for the isolation of 24 PFAS (C4–C18 perfluoroalkyl carboxylic acids; C3–C13 perfluoroalkyl sulfonic acids) from cross-country ski wax and snow samples and (ii) to apply the new procedures to a total of 20 cross-country skiing waxes from local cross-country clubs and a total of 15 snow samples from national competitions in cross-country skiing and biathlon in the Czech Republic. Extraction of PFAS from waxes was performed with a methanol solution in an ultrasonic bath. The snow processing procedure is based on the method for determination of PFAS in water (Jurikova et al., 2022), using solid phase extraction. All samples were subsequently analyzed using ultra-performance liquid chromatography in reverse phase coupled with tandem mass spectrometry (UHPLC-MS/MS) using electrospray ionization in negative mode. Limits of quantification (LOQs) were determined between 0.025-0.25 ng/liter for snow and 0.1-0.5 ng/g for wax samples. Recoveries of all analytes were in the acceptable range of 70–120%, with RSDs of up to 20%. This study will help to clarify the composition of currently used ski waxes and to what extent they may affect the contamination of snow through which PFAS can potentially enter the aquatic ecosystem. The potential profiles of PFAS found will then be discussed with the current literature on the occurrence of PFAS in the environment.

References

Carlson, G. L. et al. (2020) Ski wax use contributes to environmental contamination by per- and polyfluoroalkyl substances. Chemosphere, 261.

Fang, S. H. et al. (2020) Levels of per- and polyfluoroalkyl substances (PFAS) in ski wax products on the market in 2019 indicate no changes in formulation. Environmental Science-Processes & Impacts, 22, 2142-2146.

Jurikova, M. et al. (2022) The occurrence of perfluoroalkyl substances (PFAS) in drinking water in the Czech Republic: a pilot study. Environmental Science and Pollution Research, 29, 60341-60353.

Kinetics and Proposed Mechanisms of Hexafluoropropylene Oxide Dimer Acid Degradation via Vacuum-UV (VUV) Photolysis and VUV/Sulfite Processes

J. Kim[1], T. Kim[1], H. Park[1], M.K. Kim[1], S. Eom[1], K.D. Zoh[1]*

[1]Seoul National University, Department of Environmental Health Sciences, School of Public Health, Seoul, South Korea
[2]Seoul National University, Institute of Health and Environment, Seoul, South Korea

zohkd@snu.ac.kr

We investigated the degradation of GenX in water via VUV photolysis and VUV/sulfite reactions under nitrogen-saturated conditions. Approximately 35% and 90% of GenX were degraded in 3 h in the VUV photolysis and VUV/sulfite reaction. While GenX removal rate was highest at pH 6 in VUV photolysis, it increased under alkaline pHs in VUV/sulfite reaction. While both eaq- and •H contributed to VUV photolysis, eaq- played a significant role, and •OH had a negative effect during VUV/sulfite reaction. Two transformation products (TPs) (TFA and PFPrA) were identified in VUV photolysis, whereas five TPs (TFA, PFPrA, TP182, TP348, and TP366) were identified in VUV/sulfite reaction by LC–MS/MS and LC–QTOF/MS. Defluorination of GenX was observed, with the defluorination efficiency after 6 h reaching 17% and 67% in the VUV photolysis and VUV/sulfite reactions, respectively. Degradation mechanism for GenX based on the identified TPs and the theoretical calculations confirmed the susceptibility of GenX to nucleophilic attack. The initial reactions for GenX decomposition were C–C and C–O bond cleavage in both reactions, whereas sulfonation followed by decarboxylation was observed only in the VUV/sulfite reaction. ECOSAR ecotoxicity simulation showed that the toxicities of the TPs were not as harmful as those of GenX.

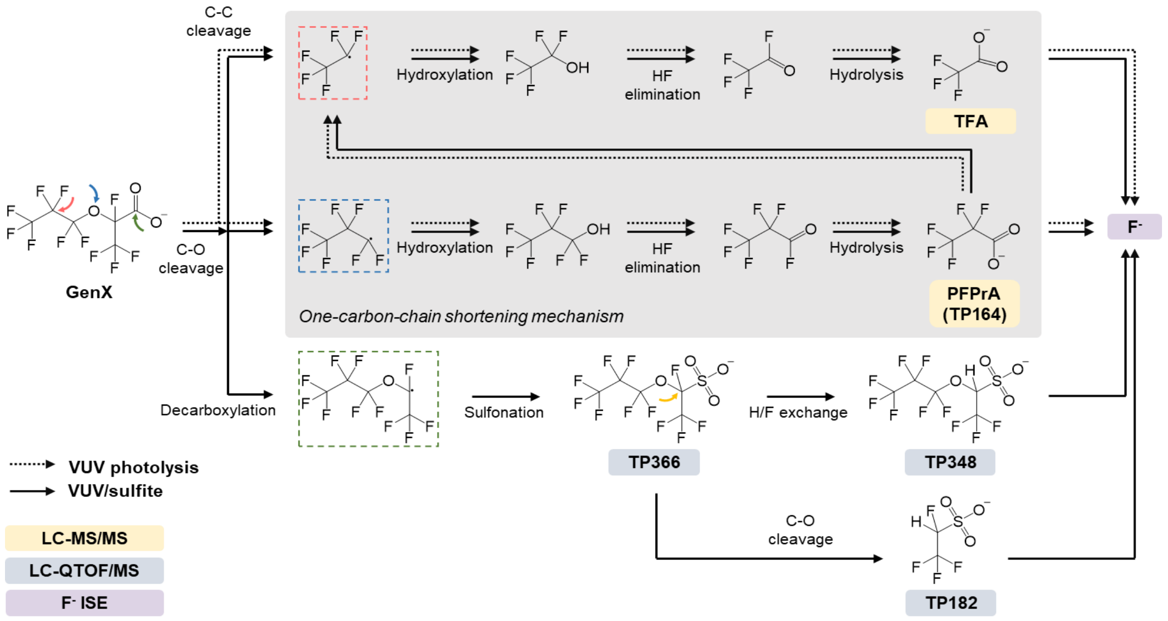


Fig. Proposed degradation pathways of GenX in VUV photolysis and VUV/sulfite reactions.aption

References

Gu, Y, Liu T, Wang H, Han H, Dong W., 2017. Hydrated electron based decomposition of perfluorooctane sulfonate (PFOS) in the VUV/sulfite system. Science of The Total Environment 607-608, 541-548. doi.org/https://doi.org/10.1016/j.scitotenv.2017.06.197.

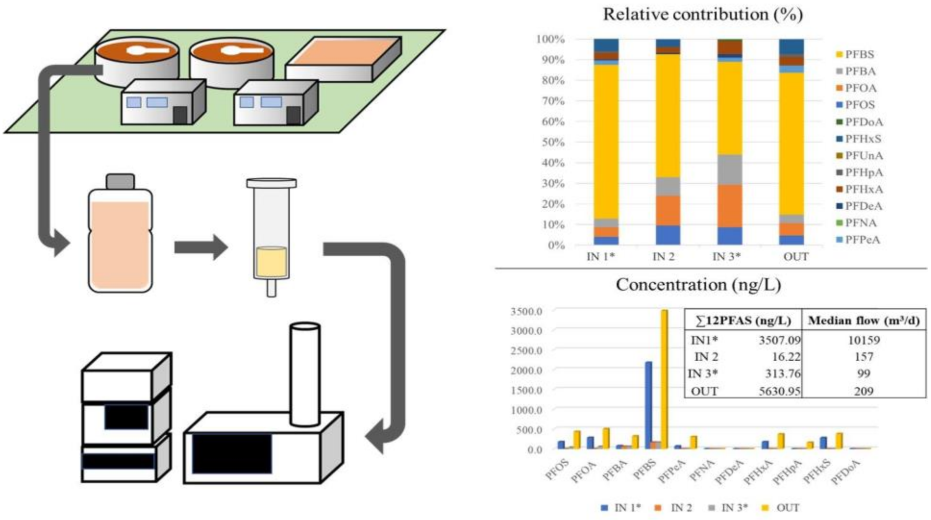
Long-Chain vs Short-Chain PFAS in an Industry-Serving Wastewater Treatment Plant

F. Calore[1], A. Bonetto[1], A. Marcomini[1]*

[1]University Ca' Foscari of Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino 155, Mestre Venice, 30172, Italy

francesco.calore@unive.it

Per- and polyfluoroalkyl substances (PFAS) are a class of persistent, bioaccumulative xenobiotics that are widespread in the environment and pose a risk to human and environmental health. The monitoring of secondary sources of PFAS such as industrial wastewater treatment plants (WWTP) is pivotal to characterize their overall occurrence, changes in the chemical profile and composition, and, ultimately, production trends. In particular, perfluoroalkyl acids (PFAA) with a longer fluoroalkylated chain were progressively substituted by the shorter, more hydrophilic, less bioaccumulative PFAA. However, the latter are more difficult to remove from natural and drinking waters by means of adsorbent materials such as activated carbons. The purpose of this work is to evaluate the occurrence of PFAS in a WWTP serving an industrial district in Northern Italy. Wastewater and sludge samples underwent solid phase extraction and extracts were analyzed by means of LC-TOF-MS (Fig.1, left). Two years monitoring of the industrial influents (IN 1*, IN 3*), the civil influent (IN 2) and the final effluent (OUT) of the wastewater line of the WWTP have shown the predominant occurrence of short-chain PFAS, especially PFBS (Fig.1, right). Median concentration of the 12 monitored PFAS (Fig. 1) reflect those typically reported in the literature for civil and industrial WWTPs. The higher overall concentration in the effluent likely indicates the conversion of polyfluoroalkyl precursors in PFAA upon the treatment operations.



	∑12PFAS (ng/L)	Median flow (m³/d)
IN1*	3507.09	10159
IN 2	16.22	157
IN 3*	313.76	99
OUT	5630.95	209

Figure 1- Workflow of the sample processing (left) and PFAS profile and concentration (right) in the influents and final effluent of the WWTP (2020).

Biochemical Effects of Polycyclic Aromatic Hydrocarbons (PAHs) on Black Alder Seedlings: Secondary Metabolites, Photosynthetic Pigments, MDA, and Sugars

G. Striganaviciute[1]*, V. Sirgedaite-Seziene[1]

[1]Lithuanian Research Centre for Agriculture and Forestry, Institute of Forestry, Liepu St. 1, Girionys, LT-53101 Kaunas distr., Lithuania

Greta.striganaviciute@lammc.lt

Polycyclic aromatic hydrocarbons (PAHs) are environmental contaminants that can be emitted through various combustion processes. They have the potential to accumulate in tree tissues and have been associated with adverse effects such as reduced tree growth, alterations in leaf structure, and impaired photosynthesis efficiency. Although alder trees are tolerant to pollution, the effects of PAHs on their seedlings have not been extensively investigated.

The aim of this study was to assess the influence of specific PAHs on secondary metabolism, photosynthesis pigments, lipid peroxidation, and sugars of different black alder (Alnus glutinosa) half-sib families. Four different black alder half-sib families (genetic groups) were grown with one of four specific polycyclic aromatic hydrocarbons (pyrene, fluoranthene, naphthalene, or phenanthrene) hydroponically at varying concentrations (0, 10, 100, or 200 μg L^{-1}). The plants were then cultivated for a duration of 4 weeks, after which samples were collected for subsequent biochemical analyses (lipid peroxidation (MDA), total phenol content (TPC), carotenoids, chlorophylls a and b, and sugars). All biochemical analyses were done using a SpectroStar Nano microplate reader (BMG Labtech, Offenburg, Germany).

MDA, TPC, and carotenoids are biochemical markers used to assess plant stress response. MDA indicates membrane damage and oxidative stress, while TPC and carotenoids are associated with antioxidant defense. The 41-65-7K half-sib family showed significant differences when exposed to phenanthrene. MDA and TPC levels were lowest in this family, while carotenoid content was exceptionally high, indicating elevated photosynthetic pigment levels. In general, half-sib families with higher MDA and TPC had lower carotenoid levels, and vice versa.

During stress, sugars, and the ratio of chlorophylls a/b in plants are interrelated. Sugars influence photosynthesis and can regulate it via negative feedback. Stress can affect sugar production, which, in turn, impacts photosynthetic efficiency. Similarly, stress affects the chlorophyll a/b ratio, and a decrease in this ratio suggests reduced overall photosynthetic performance. In this study changes in the chlorophyll a/b ratio are usually accompanied by similar shifts in sugar levels compared to control groups. In the presence of PAHs, two half-sib families showed lower sugar levels, while two other families exhibited higher sugar levels. In summary, plants with higher chlorophyll a/b ratios synthesize more sugars.

Overall, each half-sib family responds differently to varying PAHs and their concentrations, exhibiting distinct changes in secondary metabolites, photosynthetic pigments, and sugar levels.

Application of Micellar Mobile Phase for Quantification of Sulfonamides in Medicated Feeds by HPLC-DAD

E. Patyra[1*], K. Kwiatek[1]

[1]National Veterinary Research Institute, Department of Hygiene of Animal Feedingstuffs, Partyzantow 57 Avenue,
24 – 100 Pulawy, Poland

ewelina.patyra@piwet.pulawy.pl

In recent years, a technique known as micellar liquid chromatography (MLC) has been used as an alternative method to conventional liquid chromatography. Micellar liquid chromatography is one of the modes of reversed phase liquid chromatography (RPLC) in which the mobile phases are aqueous solutios of a surfactant at a concentration above the critical micelle concentration.

The aim of this work was to optimize the isocratic mobile phase based on MLC along with using SDS as the modifier agent for simultaneous isolation and quantification of sulfonamides: sulfaguanidine, sulfadiazine, sulfamerazine, sulfametazine, and sulfamthoxazole in medicated feeds. To our knowledge, the stability indicating green reverse phase HPLC (RP-HPLC) method using environmentally benign eluents (propan-2-ol) has not been reported in the literature for the analysis of sulfonamides in medicated feed.

Satisfactory separation of sulfonamides from medicated feeds was achieved using a Zorbax Eclipse XDB C18 column (4.6 x 150 mm, 5 µm particle size) with a micellar mobile phase consisting of 0.05 M sodium dodecyl sulphate, 0.02 M phosphate buffer, and 6% propan-2-ol (pH 3). UV quantitation was set at 260 nm. Application of the proposed method to the analysis of five pharmaceuticals gave recoveries between 72.7% to 94.7% and coefficients of variations for repeatability and reproducibility between 2.9% to 9.8% respectively, in the range of 200 to 2000 mg/kg sulfonamides in feeds. Limit of detection and limit of quantification were 32.7–56.3 and 54.8–98.4 mg/kg, respectively, depending on the analyte.

The proposed procedure for the quantification of sulfonamides is simple, rapid, sensitive, free from interferences and suitable for the routine control of feeds. In the world literature, we did not find the described method of quantitative determination of sulfonamides in medicated feeds with the use of micellar liquid chromatography. the use of micellar liquid chromatography technique is advantageous because it protects analysts from the exposure to volatile organic solvents during chromatographic analysis In addition, the selected mobile phase is cheaper and less toxic than those used in conventional RPLC. The proposed chromatographic procedure is useful for routine quantification analysis of the sulfonamides in medicated feeds for pigs and poultry.

References

Martinez-Algaba C.,et al. (2006) Analysis of pharmaceutical preparations containing antihistamine drugs by micellar liquid chromatography. J. Pharm. Biomed. Anal. 40, 312–321

Kawczak P., et al. (2012). Recent theoretical and practical applications of micellar liquid chromatography (MLC) in pharmaceutical and biomedical analysis. Cent. Eur. J. Chem. 10, 570–584.

Feasibility of Residue Analysis of Biopesticides by Prototyping Using MALDI-TOF MS

H. Tamura[1*]

[1]Meijo University, Graduate school of agriculture

hiroto@meijo-u.ac.jp

As the SDGs become widely accepted around the world, the establishment, promotion, and expansion of next-generation Integrated Pest Management will become even more important for achieving the establishment of a sustainable food production system. In EU countries, biopesticides have become popular as one of the key technologies for sustainable and environmentally friendly agriculture, both for reducing environmental impact and for controlling pest resistance developed to chemical pesticides.

For chemical pesticides, analytical methods for pesticide residues in crops and the environment have been established for risk management. Then, is it necessary to establish analytical techniques for biopesticides in crops and the environment?

Especially in food processing, the types of microorganisms originating from raw materials and the number of adhering bacteria are important indicators for quality control of potential hazards such as food poisoning and spoilage, and may also have a significant impact on determining the shelf life of food products. In other words, if the types and number of bacteria adhering to food at the time of shipment from a company can be determined, it will can not only provide safer and more secure food, but it can also reduce food loss and contribute to the SDGs.

<Methods and Results> Among biopesticides, B. thuringiensis, which is widely used as a bioinsecticide, is phylogenetically closely related to B. cereus, a food poisoning bacteria, making it difficult to distinguish these species by 16S rRNA gene homology. Therefore, we applied our S10-GERMS method1) for rapid and simple proteotyping using MALDI-TOF MS to the identification of the B. cereus group.

As results, the four biomarkers (L30, S10, S16, S20) combing the two ribosomal proteins encoded outside the S10-spc-alpha operon (S16 and S20) and two ribosomal proteins encoded in this operon (L30, S10) clearly distinguished B. thuringiensis and B. cereus in the B. cereus group and further enabled proteotyping the spoilage bacteria B. mycoides and B. weihenstephanensis. Furthermore, the B. cereus group contains a toxin (cereulide) producer that causes nausea and vomiting. The four biomarkers, L30, S20, S10, and cereulide (m/z: 1191.8), could simultaneously identify the presence or absence of cereulide production and B. cereus group strains2). That cereulide production by PCR could be misjudged by false positives indicated the importance of reliable detection of the substance by mass spectrometry2).

<Conclusion> The combination of bacterial quantification by the general viable bacterial count method and strain-level identification of each colony by proteotyping using the S10-GERMS method is a promising method for identifying and quantifying bacterial residues as chemical pesticide residues.

<Significance> The development of innovative crop protection technologies is an urgent issue, but it will also bring with new challenges. It will become even more important to consider countermeasures (solutions) to these problems before they become apparent, in order to promote and expand the use of new technologi

References

Hotta, Y., et al., Classification of Genus Bacillus based on MALDI-TOF MS analysis of ribosomal protein coded in S10 and spc operons, J. Agric. Food. Chem., 59, 5222-5230, 2011

Takahashi, N., et al. Simultaneous Discrimination of Cereulide-Producing Bacillus cereus and Psychrotolerant Bacillus cereus group by MALDI-TOF MS, J. Food Protect., 85, 1192–1202, 2022.

Detection of Antacid Pharmaceutical Compounds and their Metabolites from Wastewater and Surface Water Samples by SPE-LC-MS/MS

V. I. Iancu[1], L.F. Chiriac[1], C. Dinu[1], F. Pirvu[1], I. Paun[1], G.G. Vasile[1]*, M. Niculescu[1], I. Cristea[1], G. Serban[1], N. Vasilache[1]

[1]National Research and Development Institute for Industrial Ecology ECOIND, Pollution Control Department, 57-73
Drumul Podul Dambovitei Street 57-73, 060652, Bucharest, Romania

gabriela.vasile@incdecoind.ro

The intense use of antacid pharmaceutical compounds, for the treatment of digestive tract disorders and their incomplete metabolism in the human body, in addition to their incomplete degradation in sewage treatment plants, led to the discharge of high concentrations of these substances into the aquatic environment (Kristofco L. A. et al. 2017, AKosma, C. I. et al., 2016). In this work, a method based on liquid chromatography coupled with mass spectrometry (LC-MS/MS) was developed, optimized and validated for the quantitative determination of four proton pump inhibitors (omeprazole, pantoprazole, lansoprazole and rabeprazole) and four antihistamines (famotidine, ranitidine, nizatidine, cimetidine) and three degradation metabolites (5-hydroxy omeprazole, 4-hydroxy omeprazole, 5- hydroxy lansoprazole) from surface water and wastewater samples. The contaminants were isolated from surface water (0.5 L) and wastewater (0.25 L) samples by automated solid phase extraction (SPE), using C18 cartridges (500mg, 6mL), and a preconcentration factor of 500 for river water and 250 for waste water. The compounds were separated chromatographically in 8.4 minutes, on a Luna Omega Polar C18 column, at a temperature of 40 C, using a mobile phase composed of (A) 10mM ammonium acetate and (B) acetonitrile, at a flow rate of 0.2 mL/min and an injection volume of 5 µl. The identification and detection of the analytes was achieved through the positive ionization mode using the Multiple Reaction Monitoring (MRM) transition between the precursor ion and the most abundant product ion. The quantification limits (LOQ's) determined for real water samples varied between 0.10 ng/L (omeprazole) and 2.86 ng/L (ranitidine), and for surface water samples, the limits ranged between 0.05 ng/L (omeperazole) and 1.43 ng/L (ranitidine). Correlation coefficients (R2) ≥ 0.9959 were obtained for all contaminants within the linearity range of 1–100 ng/L. The mean recoveries for all compounds ranged from 71.0 – 102.8 % for wastewater and 74.7- 98.5 % for river water, respectively. For intra-day analysis, precision of the method, calculated as relative standard deviation (RSD), ranged from 2.8 to 5.2 % (river water) and from 5.4 to 7.6 % (wastewater), respectively. For inter-day analysis, relative standard deviation was in the range of 5.9-10.1 % (river water) and 9.7-14.5 % (wastewater), respectively. The developed method was successfully applied for the detection of antacids in wastewater samples and receiving surface waters. High concentrations of antacid compounds were detected in the Wastewater Treatement Plants, from Galati and Rm-Valcea cities, as follows: ranitidine (8.2-374 ng/L), the metabolite 4-hydroxy-omeprazole (52.8-216 ng/L), famotidine (10.1 -189.6 ng/L), pantoprazole (4.2-102 ng/L), nizatidine (10-55.2 ng/L), omeprazole (3.1-51.6 ng/L). The following compounds were observed in the Bahlui and Olt rivers: nizatidine (6.6-197 ng/L), 4-hydroxy-omeprazole (5.2-19.8 ng/L), famotidine (2.6-5.6 ng/L), Ranitidine (4.8-2.9 ng/L).

Acknowledgment:
The authors acknowledge the financial support offered by the Ministry of Research, Innovation and Digitization of Romania through the Romanian National Research Program “Nucleu” through contract no. 20N/2019, Project code PN 19 04 01 01.

References

Kristofco, L. A. et al., (2017), 'Global scanning of antihistamines in the environment: Analysis of occurrence and hazards in aquatic systems', Sci. Total Environ. 592, p. 477, doi: 10.1016/j.scitotenv.2017.03.120.

AKosma, C. I. et al., (2016) 'Analysis, occurrence, fate and risks of proton pump inhibitors, their metabolites and transformation products in aquatic environment: A review, Sci. Total Environ, 569–570, p. 732, doi 10.1016/j.scitotenv.2016.06.160.

OCPs, PCBs and PAHs in Seabird Plasma, Liver and Stomach Oil Analysed by GC–Orbitrap–MS

L. Michel[1]*, G. Dell'Omo[2], B. Oró-Nolla[3], P. Quillfeldt[1], S. Lacorte[3]

[1]University of Giessen, Animal Ecology and Systematics, Heinrich-Buff-Ring 26-32, 35392 Giessen, Germany
[2]Ornis Italica, Piazza Crati 15, 00199 Roma, Italy
[3]IDAEA-CSIC, Department of Environmental Chemistry, Jordi Girona 18-26, 08034 Barcelona, Spain

lucie.michel@bio.uni-giessen.de

To understand the impact and interaction of different types of pollutants on seabirds it is necessary to have insight into different exposure routes and accumulation stages (Lewis et al. 2022). In bird biomonitoring, different matrices can reflect different body burdens (Waszak et al. 2021), and thus, minimally invasive sampling procedures are useful as can be used in routine basis to reflect the quality of the environment. The analysis of biological samples poses analytical challenges (Gkotsis et al. 2023), as generally little sample volumes can be collected. Thus, methods have to be highly sensitive and specific. In this study, we developed a method to analyze 32 polychlorinated biphenyls (PCBs), 27 organochlorine pesticides (OCPs) and 15 polycyclic aromatic hydrocarbons (PAHs) in three different seabird matrices: (i) stomach oil representing pollutant uptake; (ii) plasma representing the current body burden and (iii) liver representing longer-term exposure and elimination. Samples were collected during the chick-rearing season in 2020 in Scopoli's shearwaters (Calonectris diomedea) from Linosa Island (Sicily Chanel). Small sample amounts from plasma (100 µL), liver (50 mg) and stomach oil (100 µL) were spiked with internal standards (9 PCBs, 5 labelled PAHs and 2 labelled OCPs) and extracted in an ultrasonic bath and extracts were purified with Florisil cartridges (5 g, 20 mL). Five quality controls were produced for each matrix. Analysis was performed by GC–Orbitrap–MS using a TRACE 130 GC (60 m, 0.25 mm, 0.25 µm) coupled to a Hybrid Quadrupole-Orbitrap™ Mass Spectrometer from Thermo Fisher Scientific (Waltham, MA, USA). All of the OCPs and most of the PCBs and PAHs with some exceptions were well resolved in 41.6 minutes and could be quantified in all matrices. Recoveries in spiked samples at 5 ng/g ranged between 80-120%. Stomach oil, being a high lipid matrix, showed some interferences and recoveries were lower than in the other matrices. The methodology was applied to determine the presence of PCBs, OCPs and PAHs in shearwaters and it was found that some of them were systematically detected. This study proposes a relatively straightforward method to analyze an array of different pollutants in different biological matrices that can be used in ecotoxicological studies from biomonitoring to exposure/effect studies. Our method is especially advantageous in terms of the comparability of pollutant profiles and concentrations between the matrices.

References

Gkotsis, G. et al. (2023). Advanced throughput analytical strategies for the comprehensive HRMS screening of organic micropollutants in eggs of different bird species. Chemosphere, 312, 137092.

Lewis, P. et al. (2022). New and legacy persistent organic pollutants (POPs) in breeding seabirds from the East Antarctic. Environmental Pollution, 309, 119734.

Waszak, I. et al. (2021). Estimation of native and alkylated polycyclic aromatic hydrocarbons (PAHs) in seabirds from the south coast of the Baltic Sea. Environmental Science and Pollution Research, 28, 4366-4376.

Multiresidue Analysis of Emerging (PAEs, OPEs, Alternative HFRs) and Legacy Persistent Organic Pollutants (PBDEs, PCBs, OCPs) in Marine Sediments Using GC-MS/MS

B. Carr[1], D. Huertas[1], P. Bersuder[1], I. Tolosa[1]*

[1]IAEA Marine Environment Laboratories, 4a Quai Antoine 1er, 98000 Monaco, Principality of Monaco

I.Tolosa@iaea.org

With the need to monitor an ever-increasing number of new emerging organic contaminants in the environment, analytical methodologies are evolving to allow the simultaneous determination of multiclass contaminant groups while using the same sample preparation procedure (Tolosa et al., 2020). The aim of this work was to develop and validate a multiresidue analytical procedure for sediment samples, combining the measurement of legacy contaminants regulated under the UN Stockholm Convention on Persistent Organic Pollutants (POPs) with new emerging contaminants that are of growing concern to the health of marine ecosystems. A special focus was devoted to emerging plastic additives and flame retardants, e.g. phthalate esters (PAEs) and organophosphate esters (OPEs), for which limited data is available concerning their global presence or fate in the marine environment (Hidalgo-Serrano et al., 2022; Xie et al., 2022).
The legacy POPs targeted by this methodology include 14 PBDES, the 6 marker PCBs, and 22 organochlorinated pesticides (OCPs). In order to incorporate new emerging plastic additives and flame retardants, this methodology also targets 17 alternative halogenated flame retardants (aHFR), 19 phthalates esters (PAEs) and 17 organophosphate esters (OPEs). The optimized methodology utilizes microwave extraction with hexane and dichloromethane, sulphur clean-up with copper, and silica SPE fractionation to separate the legacy POPs and aHFRs from the PAEs and OPES. Gas chromatography coupled to triple quadrupole mass spectrometry was used to measure the target analytes within two isolated fractions. Method validation including recovery yields in matrix spiked sediments, reproducibility, repeatability, and important considerations for blank optimization have been taken into account. Method detection limits for the PAEs and OPES ranged from to 0.03 ng/g to 12 ng/g dw, driven mainly by the presence and variability of background contamination in the blanks. The validated method was applied to marine sediment samples, including IAEA reference materials, to provide preliminary data on the occurrence of these compounds in the marine environment. Integrating the analysis of PAEs and OPEs into the existing analytical procedures for legacy contaminants is a cost-effective way to increase the data available for this rapidly growing field of emerging organic pollutants.

References

Hidalgo-Serrano, M. et al. (2022) ‘Phthalate esters in marine ecosystems: Analytical methods, occurrence and distribution’, TrAC Trends in Analytical Chemistry, 151, p. 116598. doi.org/10.1016/j.trac.2022.116598.

Tolosa, I. et al. (2021) ‘A comprehensive evaluation of two sample treatment procedures for the determination of emerging and historical halogenated flame retardants in biota’, Environmental Science and Pollution Research, 28(42), pp. 59345–59357. doi.org/10.1007/s11356-020-10966-y.

Xie, Z. et al. (2022) ‘Organophosphate ester pollution in the oceans’, Nature Reviews Earth and Environment, 3(5), pp. 309–322. doi.org/10.1038/s43017-022-00277-w.

Transcriptomic Analysis to Determine Mode of Action and Effects of Three Emerging Contaminants in the Japanese Clam Ruditapes Philippinarum

Nieves R. Colás-Ruiz[1]*, Pablo A. Lara-Martín[1], Miriam Hampel[2], M.L. Tovar-Salvador[1], Ruben Rios Quintero[1], Marina G. Pintado-Herrera[1].

[1]University of Cadiz, Faculty of Marine and Environmental Sciences (CASEM), 11510, Puerto Real, Cádiz, Spain
[2]Institute of Marine Research (INMAR), University of Cadiz, 11510 Puerto Real, Spain

rocio.colas@uca.es

Personal Care Products (PCPs) are one of the largest classes/categories within the emerging contaminants group. PCPs are widely used in modern human life and contribute to improve its quality. Many of these compounds are not efficiently removed by conventional sewage treatment plants and thereby they are discharged into the environment making these chemicals ubiquitous in many aquatic ecosystems, including oceanic and coastal settings (Lara-Martín et al., 2020). This, together with their physicochemical properties, could suppose a risk for wild organism exposed to them.

Three PCPs were considered for this study: triclosan (TCS), a preservative and broad-spectrum antimicrobial agent extensively used in household and personal care products; N,N-diethyl-meta-toluamide (DEET), one of the most commonly used active ingredients in insect repellents topical lotions and Sulisobenzone (BP-4), the benzophenone type UV filters most used in cosmetics, sunscreens, and PCPs formulations. These three pollutants are commonly detected in aquatic ecosystems. In the present work, the Japanese clam (Ruditapes philippinarum), which is the second most produced and consumed mollusc worldwide (FAO, 2022), was exposed to a nominal concentration of 10 µg L-1 of TCS, BP-4 and DEET in separate tanks using a continuous flow-through seawater system under controlled laboratory conditions for 22 days followed by a depuration period of 7 days. Concentration of pollutants in the water was monitored during the whole experiment as well as in organism tissue.

After exposure and depuration periods, digestive glands of organism were dissected for transcriptomic analysis. This organ was chosen for its key role as target tissue for the xenobiotics incorporated by the organism (Faggio, Tsarpali and Dailianis, 2018).

After applying data processing and statistical analysis, it was observed that 834, 430 and 993 genes were significantly expressed in the digestive gland of clams exposed for 22 days to BP-4, DEET and TCS, respectively. Furthermore, after the depuration period (7 days) 157 and 311 genes were observed differentially expressed in clams exposed to BP-4 and TCS, whereas no genes were observed differentially expressed in clams after the depuration phase of DEET exposure assays. Several functions were commonly impacted by the exposure to the three contaminants, such as ribosome, lysosome, and phagosome as well as certain pathways related to lipid metabolism. On the other hand, some key processes, such as oxidoreductase activity, chaperone binding and kinase activity were only impacted by BP-4, DEET and TCS exposure, respectively.

References

Faggio, C., Tsarpali, V. and Dailianis, S. (2018) ‘Mussel digestive gland as a model tissue for assessing xenobiotics: An overview’, Science of The Total Environment, 636, pp. 220–229. doi:10.1016/J.SCITOTENV.2018.04.264.

FAO (2022) The State of World Fisheries and Aquaculture 2022. Towards Blue Transformation. FAO. doi:10.4060/cc0461en.

Lara-Martín, P.A. et al. (2020) ‘Tracing Urban Wastewater Contaminants into the Atlantic Ocean by Nontarget Screening’, Environmental Science and Technology, 54(7), pp. 3996–4005. doi:10.1021/acs.est.9b06114.

NOT Lost and Found but Applied and Found - Pesticides Residues in Soil Over Three Consecutive Years Compared with Application Data in Potato Production

A. Escobar[1]*, B. Peña[1], D. Sosa[1], N. Pérez[3], I. Hilber[2] and T.D. Bucheli[2]

[1]Centro Nacional de Sanidad Agropecuaria (CENSA), Departamento Salud Animal; Apartado 10, CP 32700, San José de las Lajas, Cuba
[2]Agroscope, Methods Development and Analytics, Reckenholzstrasse 191, CH-8046, Zurich, Switzerland
[3]Universidad Agraria de La Habana, Departamento Sanidad Vegetal, Autopista Nacional km 22, CP 32700, San José de Las Lajas, Cuba

arturo.escobar60@gmail

The pressure of pests on cash crops as for instance potato (Solanum Tuberosum L.), is higher in tropical than in temperate regions due to the warm and humid climate (Kroschel et al. 2020). Synthetic pesticide use impairs the environment as for instance soil because active ingredients (ai), after application, can enter and reside in this matrix. The aim of this study was to (i) determine ai in soil of potato fields of six farms over three consecutive years, (ii) to compare the concentrations with application records, and (iii) explain relations between applied and detected incidences (applied and found) of selected farms and ai. Soil samples, in total 54, were taken from 2018-2021 at three times per year (in October before planting (s1), between December and February when pesticides are mostly applied (s2) and between March and April at harvest (s3) from 0 – 20 cm depth in Mayabeque province, the potato belt in Cuba. Thirty-one ai and seven transformation products (TPs) were extracted by the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method and quantified by gas chromatography tandem mass spectrometry. Of the 30 ai half were fungicides (F), nine herbicides (H) and six insecticides (I). Twenty-one ai and three TPs were detected in soil samples. S-metolachlor (H) was most frequently found, 91% of all samples, which is why we focus on this ai in the following. It is effective on weeds when applied before germination. Of a theoretic maximum of 18 applications (yes/no of 6 farms * 3 years) it was applied 11 times but detected 16 times (y/n of 6 farms * 3 years). Hence, residues of s-metolachlor must have originated from previous crop applications. Mean concentrations (± standard deviation) of s2 were 131.8±40.4 µg/kgsoil > s3 of 32.6±7.2 µg/kgsoil > s1 of 6.3±1.3 µg/kgsoil. This concentration gradient corresponds well with the sampling time because it was always applied between s1 and s2. The pesticides properties database (PPDB) indicates a half-life (DT50) of s-metolachlor of 23 days in field soil and Fernandez et al. (2020) of values between 12 and 24 days in a sugarcane field in Florida, USA, which corresponds to the same climate as the present study. Half-lives calculated by first order kinetics from our field data, no losses due to runoff presumed, resulted in values ranging from 13 to 34 days with a mean of 23 days. The hypothesis that a DT50 in tropical soils is lower than in temperate climate does not seem to hold, although the span of DT50 is a factor of three. Although small, this insight is promising when it comes to the behavior of pesticides in tropical soils. Soil monitoring of pesticide residues in Cuba is advancing and will help to optimize the application amounts of ai.

References

Kroschel, J et al. (2020) "Insect pests affecting potatoes in tropical, subtropical, and temperate regions." The potato crop: Its agricultural, nutritional and social contribution to humankind: 251-306.

Pesticide properties database (PPDB) http://sitem.herts.ac.uk/aeru/ppdb/en/docs/5_1.pdf, accessed 03/17/2023).

Fernandez, J. V., et al. (2020). "Field dissipation of S-metolachlor in organic and mineral soils used for sugarcane production in Florida." Weed Technology 34(3): 362-37.

Application of Micro-Volume Detection Setup for Cloud Point Extraction of Cadmium

K. Terebesiová[1], A. Gajdošová[1], J. Šandrejová[1*] and V. Andruch[1]

[1]P. J. Šafárik University in Košice, Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science,
Moyzesova 11, SK-041 54 Košice, Slovakia

jana.sandrejova@upjs.sk

Introduction the green analytical chemistry procedures into laboratory practice constantly holds the important place in number of scientific articles. The scientific community dedicates time mainly to development of greener approaches, mostly for sample treatment. The second possible way to increase the 'green' potential of the analytical methods is the detection step. For instance, detection systems that can use micro-volumes of samples. The objective of our study is to create new approaches comparable or better than thus far traditional methods and will be universally usable in analytical labs (Zaruba et al., 2016, 2017).

We present the cloud point extraction (CPE) coupled with a spectral pipette as the detection device for determination of cadmium in water samples. The reaction mechanism is based on the reaction of Cd(II) with 6-hexyl-4-(2-thiazolylazo)resorcinol at pH 9.5. With the reaction occurs a formation of a complex with the absorption maximum of 550 nm. For the CPE, 5 mL of 10% Triton X-114 solution was used for Cd extraction of a 50 mL sample. The optimum extraction conditions were found to be incubation time of 20 min at ca. 65°C and cooling time of 30 min at ca. −20°C for easy removal of the supernatant. The linear range from 10 to 200 µg/L Cd was achieved and the limit of detection was obtained at 3.5 µg/L Cd. The proposed method was applied to real river water samples.

Acknowledgement: This work was the result of the research project No. 1/0124/20 financed by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences.

References

Zaruba, S. et al. (2017) A two-in-one device for online monitoring of direct immersion single-drop microextraction: An optical probe as both microdrop holder and measuring cell RSC Advances, 7 (47), p. 29421-29427. doi: 10.1039/c7ra02326j.

Zaruba, S et al. (2016) Using an optical probe as the microdrop holder in headspace single drop microextraction: Determination of sulfite in food Samples Analytical Chemistry, 88 (20), pp. 10296-10300. doi: 10.1021/acs.analchem.6b03129.

Application of Natural Deep Eutectic Solvents for Analysis of Herbal Samples

A. Kalyniukova[1], A. Várfalvyová[2], V. Andruch[2*]

[1]Czech University of Life Sciences Prague, Faculty of Forestry and Wood Sciences, CZ-165 21 Prague 6 - Suchdol, Czech Republic
[2]Institute of Chemistry, Department of Analytical Chemistry, Faculty of Science, P. J. Šafárik University, SK-041 80 Košice, Slovakia

vasil.andruch@upjs.sk

Herbal preparations are often used as a complementary treatment for various diseases. For the analysis of biological active ingredients in plants, it is necessary to separate, pre-concentrate, and quantify them by appropriate analytical technique. For this purpose, conventional sample pretreatment procedures, such as liquid-liquid and solid-liquid extraction, ultrasound or microwave assisted extraction are utilized. Recently, natural deep eutectic solvents (NADESs) were introduced into analytical practice as an alternative to the hazardous extraction solvents (Shishov et al., 2017). In general, these solvents can be considered as more environmentally friendly due to their natural origin. Despite the fact that application of DES in analytical chemistry is still in its early stage, several NADES-based microextraction procedures were developed and applied for the determination of the bioactive components of plant materials (Diuzheva et al., 2018). The procedures provide high extraction efficiency in a short extraction time along with reduced solvent consumption. The aim of this study was developing a DES-based solid-liquid extraction procedure of polyphenolic compounds from botanical samples and their quantification by LC-MS technique. Choline chloride-based DESs were tested. The effect of several experimental variables were investigated and optimized using one-variable-at-a-time method. The developed procedure was applied for extraction of bioactive compounds in Alnus glutinosa L. Gaertn roots and Populus tremula. The changes in structure of plant material were studied by scanning electron microscopy.

Acknowledgements: The authors thank the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic (VEGA 1/0220/21). A. K. thanks to "Advanced research supporting the forestry and wood-processing sector´s adaptation to global change and the 4th industrial revolution", No. CZ.02.1.01/0.0/0.0/16_019/0000803 financed by OP RDE".

References

Shishov, A. et al. (2017) Application of deep eutectic solvents in analytical chemistry. A review. Microchemical Journal, 135, 33-38. doi: 10.1016/j.microc.2017.07.015.

Diuzheva, A. et. al. (2018) Use of Innovative (Micro)Extraction Techniques to Characterise Harpagophytum procumbens Root and its Commercial Food Supplements, Phytochem. Anal., 29 233-241. doi: 10.1002/pca.2737.

Sampling Air and Water in a Wastewater Treatment Plant: 16S rRNA Gene Metabarcoding for the Identification of the Bacterial Communities

A.S. Gateano[1]*, S. Semeraro[1], A. Pallvicini[2], M.G. Perrone[3], M. Zonca[3], A. Cain[4], P. Barbieri[1]

[1]University of Trieste, Department of Chemical and Pharmaceutical Sciences, Via Giorgieri 1, 34127, Trieste, Italy
[2]University of Trieste, Department of Life Sciences, Via Giorgieri 5, 34127, Trieste, Italy
[3]TCR-Tecora Srl, via delle Primule 16, 20815, Cogliate (MB), Italy
[4]ACEGASAPS AMGA, via degli Alti Forni 11, 34121, Trieste, Italy

anastasiaserena.gaetano@phd.units.it

The present study is focused on the analysis of the bioaerosol formed in the aeration tank of the wastewater treatment plant (WWTP) in Trieste (Italy) managed by AcegasApsAmga (Gruppo Hera). Wastewaters represent the whole enteric pathogen load from a local catchment region and capture the community disease burden, therefore provide an ideal matrix for disease monitoring and surveillance of human activity. The study of the microorganisms present in wastewaters can be performed thanks to environmental DNA (eDNA) metabarcoding of the 16S rRNA gene, which is a technique that allows the simultaneous identification of many taxa of bacteria in the same environmental sample (Barnes et al., 2016; Deiner et al., 2017). Currently, no standardized methods for bioaerosol sampling and analysis for molecular ecology research exist.

One of the aims of this study is to develop a procedure for the characterization of microorganisms in the environmental bioaerosol by comparing different sampling devices and defining both a sampling strategy and laboratory protocols for the identification of the species in the WWTP.

Here, we focus on describing bacterial abundances and community composition in the water and in the near-surface of the aeration tank of the WWTP in Trieste.

The bacterial populations were analyzed using a 16S rRNA gene-based barcoded sequencing procedure. Bioaerosol samples were collected as close as possible to the aeration tank emissions with three different sampling devices: AirPort MD8, BioSampler, BioSpot-VIVAS. In addition to bioaerosol samples, water samples were collected directly from the sewage in order to obtain a true representation of the microbiological community present in the plant.

Samples were transported to laboratory where total DNA was isolated. A quantitative real-time PCR (Polymerase Chain Reaction) was performed using three primers that together target the V3 and V4 subregions of the 16S rRNA gene in order to cover the entire bacterial community. The PCR step allowed to obtain libraries of sequences representative of the microbial diversity, which were sequenced on an NGS (Next Generation Sequencing) platform. This technology permitted to generate millions of reads from the samples, which were then compared to a reference database for the taxonomic assignment and determination of the relative abundance of the various components of the microbiome.

Our results regarding the bacterial community composition are consistent with previous studies, confirming that airborne microbial communities do not entirely resemble those in aquatic environment but rather are composed of taxa from a variety of source environments, with composition depending on various factors (Bowers et al. 2011).

A consistent pattern with comparable biodiversity may be found among all the wastewater samples. On the other hand, each air sample present different characteristics in terms of biodiversity, and this suggests that even when the sampling site is the same, the results obtained may vary depending on the sampling system.

References

Barnes, M.A. et al. (2016). The ecology of environmental DNA and implications for conservation genetics. Conserv. Genet. 17, p. 1-17. doi: 10.1007/s10592-015-0775-4.

Bowers, R.M. et al. (2011). Spatial variability in airborne bacterial communities across land-use types and their relationship to the bacterial communities of potential source environments. ISME J., 5, pp. 601–612. doi: 10.1038/ismej.2010.167.

Deiner, K. et al. (2017). Environmental DNA metabarcoding: Transforming how we survey animal and plant communities. Mol. Ecol., 26(21), pp.5872-5895. doi: 10.1038/ismej.2010.167.

OCPs, PCBs and PAHs in Seabird Plasma, Liver and Stomach Oil Analysed by GC–Orbitrap–MS

L. Michel[1]*, G. Dell'Omo[2], B. Oró-Nolla[3], P. Quillfeldt[1], S. Lacorte[3]

[1]University of Giessen, Animal Ecology and Systematics, Heinrich-Buff-Ring 26-32, 35392 Giessen, Germany
[2]Ornis Italica, Piazza Crati 15, 00199 Roma, Italy
[3]IDAEA-CSIC, Department of Environmental Chemistry, Jordi Girona 18-26, 08034 Barcelona, Spain

lucie.michel@bio.uni-giessen.de

To understand the impact and interaction of different types of pollutants on seabirds it is necessary to have insight into different exposure routes and accumulation stages (Lewis et al. 2022). In bird biomonitoring, different matrices can reflect different body burdens (Waszak et al. 2021), and thus, minimally invasive sampling procedures are useful as can be used in routine basis to reflect the quality of the environment. The analysis of biological samples poses analytical challenges (Gkotsis et al. 2023), as generally little sample volumes can be collected. Thus, methods have to be highly sensitive and specific. In this study, we developed a method to analyze 32 polychlorinated biphenyls (PCBs), 27 organochlorine pesticides (OCPs) and 15 polycyclic aromatic hydrocarbons (PAHs) in three different seabird matrices: (i) stomach oil representing pollutant uptake; (ii) plasma representing the current body burden and (iii) liver representing longer-term exposure and elimination. Samples were collected during the chick-rearing season in 2020 in Scopoli's shearwaters (Calonectris diomedea) from Linosa Island (Sicily Chanel). Small sample amounts from plasma (100 µL), liver (50 mg) and stomach oil (100 µL) were spiked with internal standards (9 PCBs, 5 labelled PAHs and 2 labelled OCPs) and extracted in an ultrasonic bath and extracts were purified with Florisil cartridges (5 g, 20 mL). Five quality controls were produced for each matrix. Analysis was performed by GC–Orbitrap–MS using a TRACE 130 GC (60 m, 0.25 mm, 0.25 µm) coupled to a Hybrid Quadrupole-Orbitrap™ Mass Spectrometer from Thermo Fisher Scientific (Waltham, MA, USA). All of the OCPs and most of the PCBs and PAHs with some exceptions were well resolved in 41.6 minutes and could be quantified in all matrices. Recoveries in spiked samples at 5 ng/g ranged between 80-120%. Stomach oil, being a high lipid matrix, showed some interferences and recoveries were lower than in the other matrices. The methodology was applied to determine the presence of PCBs, OCPs and PAHs in shearwaters and it was found that some of them were systematically detected. This study proposes a relatively straightforward method to analyze an array of different pollutants in different biological matrices that can be used in ecotoxicological studies from biomonitoring to exposure/effect studies. Our method is especially advantageous in terms of the comparability of pollutant profiles and concentrations between the matrices.

References

Gkotsis, G. et al. (2023). Advanced throughput analytical strategies for the comprehensive HRMS screening of organic micropollutants in eggs of different bird species. Chemosphere, 312, 137092.

Lewis, P. et al. (2022). New and legacy persistent organic pollutants (POPs) in breeding seabirds from the East Antarctic. Environmental Pollution, 309, 119734.

Waszak, I. et al. (2021). Estimation of native and alkylated polycyclic aromatic hydrocarbons (PAHs) in seabirds from the south coast of the Baltic Sea. Environmental Science and Pollution Research, 28, 4366-4376.

Analysis of Pesticide Residues in Agricultural Soils in Poland

K. Pszczolińska[1], D. Lalek[1], A. Krzyżanowska[1], B. Kociołek[1], D. Drozdzynski[2]*

[1]Institute of Plant Protection – National Research Institute Sosnicowice Branch (Gliwicka 29, 44-153 Sosnicowice, Poland)
[2]Institute of Plant Protection – National Research Institute Poznan (Wladyslawa Wegorka 20, 60-318 Poznan, Poland)

k.pszczolinska@iorpib.poznan.pl

Pesticides are used in the agriculture sector because they are beneficial in enhancing both the quality and yield of crops. Soil may be exposed to pesticides through direct application, accidental spillage, runoff from plant surfaces or from pesticide contaminated plant materials. Soil properties play an important role in the fate, behavior and dispersion of chemical pesticides and has become the repository of pesticides. Soil is an important agricultural resource which has the ability to retain pesticides, so it is crucial to study pesticide residues in soil, because they might negatively affect succeeding crops.

Complex matrices such as soil, require proper extraction and clean-up techniques to separate the analytes with matrix interference, which can cause signal response of the instrument in detecting the target compound. The analysis of multi-class pesticides in environmental matrices remains a challenge due to the low concentration of these compounds in complex matrices.

The aim of this work was to develop and validate a selective and reliable method for the determination of pesticide residues in soil. The extraction and cleanup steps of the QuEChERS method were modified and extracts were analysed by GC-MS/MS and LC-MS/MS. The second stage of research was to evaluate the presence of pesticide residues in soil under agricultural production.

Moreover, soil samples from spring barley and sugar beet fields, collected before, during and after the growing season, were analysed. In the soil samples from the spring barley field, only pesticide residues didn't use were detected. On the other hand, in the soils from sugar beet cultivation, both residues of applied pesticides and not applied were detected.

Ceramic Passive Samplers for the Analysis of Contaminants in Groundwater

S. Lacorte[1]*, F. Labad[1], E. Vazquez[1], S.Pérez[1]

[1]IDAEA-CSIC, Department of Environmental Chemistry, c/Jordi Girona 18, 08034 Barcelona, Catalonia, Spain

silvia.lacorte@idaea.csic.es

In order to preserve a healthy environment and provide safe water services to the population, millions of water samples are collected each year worldwide, following EU and US-EPA water regulations, as well as WHO guidelines. All over the world, millions of samples are analysed annually to determine hazardous substances and meet Environmental Quality Standards (EQS) as requirement for protecting water bodies. At present, there is a growing concern in the water sector about the economic sustainability of the traditional grab sampling methods in a context of a more stringent water quality monitoring requisites that require more samples for an increased number of contaminants, including priority and emerging.
Current water quality monitoring methods are based on time-consuming grab sampling or costly autosampler devices. Both methods fail in providing a time representative sample and require a laborious pre-concentration step in the laboratory. The objective of this study is to develop and apply customized Ceramic Passive Samplers (CPS) for the time integrated monitoring of multiple organic pollutants in groundwaters. CPS are porous ceramic cylinders where a sorbent is placed in the inner cavity of the sampler to allow sorption of contaminants of different physico-chemical properties (Orera et al., 2018). The ceramic wall is designed in a customized size and pore structure to optimize the uptake capacity of contaminants in different types of water without the problem of clogging and fouling (Orera et al., 2018; Lacorte et al., 2022). CPS are deployed just by dropping them in the water inside a container net. They are retrieved after days, weeks or months and transported to the laboratory, where analysis is performed by liquid chromatography coupled to high resolution mass spectrometry to identify multiple contaminants (regulated and non-regulated) at trace levels: pesticides, drugs, pharmaceuticals, plasticisers, perfluorinated compounds, polycyclic aromatic hydrocarbons, flame retardants, etc. By using sampling rate libraries, detected contaminants are reported in terms of concentrations. This study demonstrates the usability of CPS for groundwater monitoring and reveals severe contamination of urban aquifers from the area of Barcelona.

Acknowledgements
This work was supported by the Spanish Ministry of Science and Innovation Projects TED2021-131552B-C21, Excelencia Severo Ochoa Project CEX2018-000794-S and project PID2019-105732GB-C21.

References

Orera, V.M., et al. (2018). Design and characterization of macroporous alumina membranes for passive samplers of water contaminants. Journal of the European Ceramic Society, 38(4), 1853-1859. https://doi.org/10.1016/j.jeurceramsoc.2017.12.012.

Lacorte, S, et al. (2022). Experience and lessons learnt in the design, fabrication and deployment of ceramic passive samplers for contaminant monitoring in water, Boletín de la Sociedad Española de Cerámica y Vidrio, 61, S50-S59, 2022. https://doi.org/10.1016/j.bsecv.2021.09.010.

Ceramic Passive Samplers Using a Mixed Mode Strong Cation-Exchange Sorbent to Efficiently Monitor Pharmaceuticals and Drugs in River Water

S. Lacorte[1]*, P. Clivillé-Cabré[2], F. Borrull[2], N. Fontanals[2], R. M. Marcé[2]

[1]IDAEA-CSIC, Department of Environmental Chemistry, Jordi Girona 18, 08034 Barcelona
[2]Univesitat Rovira i Virgili, Department of Analytical Chemistry and Organic Chemistry, Sescelades Campus, Marcel·lí Domingo 1, 43007 Tarragona

silvia.lacorte@idaea.csic.es

The prevalence of pharmaceuticals and drugs in water requires the implementation of efficient monitoring strategies to preserve the quality of water resources. Although most of the analytical methods developed for the monitoring of contaminants in environmental waters are based on discrete grab sampling, an alternative of increasing interest is the use of passive sampling. Passive sampling allows sampling and pre-concentration of contaminants in-situ, thus sample treatment is less time consuming and costly than using discrete grab samples (Franquet-Griell et al., 2017). In this study, ceramic passive samplers (CPSs) using mixed-mode strong cation-exchange sorbent (Oasis MCX) as retention phase were evaluated for the determination of 21 therapeutic and illicit drugs and some of their metabolites in river waters. Analysis was performed by liquid chromatography-tandem mass spectrometry (LC-MS/MS). After assessing the stability of the analytes, the CPSs were calibrated for 9 days with bottled water and river water, obtaining, for the stable compounds, sample rates (Rs) ranging between 0.18 and 1.76 mL/day and diffusion coefficients (De) between 2.02E-8 and 2.81E-7 cm2/s, respectively. Once calibrated, CPSs were deployed in the Ebre river (south Catalonia, Figure 1) allowing the detection of gabapentin at 76 ng/L, caffeine at 203 ng/L or ketamine at 95 ng/L, among others, with good reproducibility (n=4). This study opens the possibility to use other mixed-mode sorbents or other types of sorbents as retaining phase in CPSs for the time-integrated analysis of contaminants of varying polarities in water.

Acknowledgements
Acknowledgement to Ministerio de Ciencia e Innovación, the Agencia Estatal de Investigación (CIN/AEI/10.13039/501100011033) and the European Regional Development Fund (ERDF) under project PID2020-114587GB-I and Excelencia Severo Ochoa Project CEX2018-000794-S.

Figure 1. Set up for sampling with CPSs in Ebre River; Before sampling (A) and after 9 days of sampling (B).

References

H. Franquet-Griell, et al. (2017). Development of a macroporous ceramic passive sampler for the monitoring of cytostatic drugs in water, Chemosphere. 182, 681–690. https://doi.org/10.1016/j.chemosphere.2017.05.051.

Bisphenol Analogues and Alkylphenols in Soil, Terrestrial Biota, and House Dust from an Urban Environment

M. Nipen¹*, J. S. Skar¹, P. Rostkowski¹, E. S. Heimstad², L. Hansen²

¹NILU-Norwegian Institute for Air Research, Department of Environmental Chemistry, Kjeller, Norway
²NILU-Norwegina Institute for Air Research, Department of Environmental Chemistry, Tromsø, Norway

mni@nilu.no

Bisphenols and alkylphenols may have harmful effects in humans or other animals at very low concentrations, and their environmental levels are therefore of interest. A number of studies have investigated the presence of these substances in the aquatic environment, but for the terrestrial environment knowledge remains more limited. The multitude of potential sources present in urban areas for bisphenols and alkylphenols may make the urban terrestrial environment particularly prone to contamination by these substances. For bisphenols, studies have often focused exclusively on BPA, however, given increasing regulatory attention, production has shifted to alternative bisphenols. There is therefore increasing importance of analysing a wider range of bisphenol analogues.

The analysis of bisphenols and alkylphenols in environmental samples is challenging given the similarity of their physicochemical properties with those of many natural substances present in samples. In this work, we have analysed 21 bisphenols and 8 alkylphenols in soils and terrestrial biota (earthworms, fieldfare eggs, and rats). In addition, settled dust from residents was analysed to provide an indication of use and sources for bisphenols and alkylphenols. The wide range of products in use in homes, makes house dust an excellent matrix for monitoring organic contaminants. Sample preparation for soil and biota was done using supramolecular solvent extraction (SUPRAS) (Ballesteros-Gómez et al., 2019), while filters with dust were subject to accelerated solvent extraction. Instrumental analysis was done using LC/HRMS.

Ten of the bisphenols (4,4-BPA, 2,4-BPA, 4,4-BPF, 2,4-BPF, 2,2-BPF, 4,4-BPS, 2,4-BPS, BPAF, BPB, and BPC) were detected in one or more samples, while BPAP, BPBP, BPE, BPFL, BPG, BPM, BPP, BPPH, BPTMC, BPZ, and TBBPA were not detected in any sample. House dust had the highest number of detected bisphenols, and the highest concentrations. 4,4-BPA was found at the highest concentration in dust (range 650 – 3970 ng/g) followed by 4,4-BPS (range 70 – 2040 ng/g). In terrestrial biota, 4,4-BPA, 4,4-BPS, 4,4-BPF, 2,4-BPF, and 2,2-BPF were detected. 2,4-BPF had the highest detection frequency and concentrations (range <LOD – 22 ng/g ww), followed by 4,4-BPF (range <LOD – 6,6 ng/g ww) and 4,4-BPS (range <LOD-5,2 ng/g ww). In soil only 4,4-BPA, 4,4-BPF, and 2,4-BPF were detected. Seven of the alkylphenols (branched and n-heptylphenol, branched and n-nonylphenol, branched dodecylphenol, n-octylphenol, and t-octylphenol) were detected in one or more sample. n-dodecylphenol was not detected. As for bisphenols, dust showed the highest number of detected alkylphenols, and the highest concentrations. Of the alkylphenols, branched nonylphenol showed the highest concentrations in dust (range <LOD – 2270 ng/g). Branched nonylphenol was also detected in considerable levels in rat liver and earthworm. The results from this study shows that alternative bisphenol analogues are found in higher levels that BPA in urban terestrial biota. The multiple bisphenols and alkylphenols present in the urban terrestrial environment indicate that monitoring of such environments is merited.

References

Ballesteros-Gómez, A., Lunar, L., Sicilia, M. D. and Rubio, S. (2019) 'Hyphenating supramolecular solvents and liquid chromatography: tips for efficient extraction and reliable determination of organics', Chromatographia, 82(1), pp. 111-124.

Sampling Air and Water in a Wastewater Treatment Plant: 16S Rrna Gene Metabarcoding for the Identification of the Bacterial Communities

A.S. Gateano[1]*, S. Semeraro[1], A. Pallvicini[2], M.G. Perrone[3], M. Zonca[3], A. Cain[4], P. Barbieri[1]

[1]University of Trieste, Department of Chemical and Pharmaceutical Sciences, Via Giorgieri 1, 34127, Trieste, Italy
[2]University of Trieste, Department of Life Sciences, Via Giorgieri 5, 34127, Trieste, Italy
[3]TCR-Tecora Srl, via delle Primule 16, 20815, Cogliate (MB), Italy
[4]ACEGASAPS AMGA, via degli Alti Forni 11, 34121, Trieste, Italy

anastasiaserena.gaetano@phd.units.it

The present study is focused on the analysis of the bioaerosol formed in the aeration tank of the wastewater treatment plant (WWTP) in Trieste (Italy) managed by AcegasApsAmga (Gruppo Hera). Wastewaters represent the whole enteric pathogen load from a local catchment region and capture the community disease burden, therefore provide an ideal matrix for disease monitoring and surveillance of human activity. The study of the microorganisms present in wastewaters can be performed thanks to environmental DNA (eDNA) metabarcoding of the 16S rRNA gene, which is a technique that allows the simultaneous identification of many taxa of bacteria in the same environmental sample (Barnes et al., 2016; Deiner et al., 2017). Currently, no standardized methods for bioaerosol sampling and analysis for molecular ecology research exist.
One of the aims of this study is to develop a procedure for the characterization of microorganisms in the environmental bioaerosol by comparing different sampling devices and defining both a sampling strategy and laboratory protocols for the identification of the species in the WWTP.
Here, we focus on describing bacterial abundances and community composition in the water and in the near-surface of the aeration tank of the WWTP in Trieste.

The bacterial populations were analyzed using a 16S rRNA gene-based barcoded sequencing procedure. Bioaerosol samples were collected as close as possible to the aeration tank emissions with three different sampling devices: AirPort MD8, BioSampler, BioSpot-VIVAS. In addition to bioaerosol samples, water samples were collected directly from the sewage in order to obtain a true representation of the microbiological community present in the plant.
Samples were transported to laboratory where total DNA was isolated. A quantitative real-time PCR (Polymerase Chain Reaction) was performed using three primers that together target the V3 and V4 subregions of the 16S rRNA gene in order to cover the entire bacterial community. The PCR step allowed to obtain libraries of sequences representative of the microbial diversity, which were sequenced on an NGS (Next Generation Sequencing) platform. This technology permitted to generate millions of reads from the samples, which were then compared to a reference database for the taxonomic assignment and determination of the relative abundance of the various components of the microbiome.
Our results regarding the bacterial community composition are consistent with previous studies, confirming that airborne microbial communities do not entirely resemble those in aquatic environment but rather are composed of taxa from a variety of source environments, with composition depending on various factors (Bowers et al. 2011).
A consistent pattern with comparable biodiversity may be found among all the wastewater samples. On the other hand, each air sample present different characteristics in terms of biodiversity, and this suggests that even when the sampling site is the same, the results obtained may vary depending on the sampling system.

References

Barnes, M.A. et al. (2016). The ecology of environmental DNA and implications for conservation genetics. Conserv. Genet. 17, p. 1-17. doi: 10.1007/s10592-015-0775-4.

Bowers, R.M. et al. (2011). Spatial variability in airborne bacterial communities across land-use types and their relationship to the bacterial communities of potential source environments. ISME J., 5, pp. 601–612. doi: 10.1038/ismej.2010.167.

Deiner, K. et al. (2017). Environmental DNA metabarcoding: Transforming how we survey animal and plant communities. Mol. Ecol., 26(21), pp.5872-5895. doi: 10.1038/ismej.2010.16

Unveiling the Chemical Universe of PFAS in Biota Using a Combined Targeted and Untargeted Workflow, Utilizing LC-VIP HESI(-)-TIMS-QTOF MS

G. Gkotsis[1]*, D. E. Damalas[1], C. Baessmann[2], B. Galvin[2], N. S. Thomaidis[1]

[1]National and Kapodistrian University of Athens, Department of Chemistry, Panepistimiopolis,
157 84, Athens, Greece
[2]Bruker Daltonik GmbH, Bremen, Fahrenheitstraße 4, 28359 Bremen, Germany

geogkotsis@chem.uoa.gr

Per- and Polyfluoroalkyl Substances (PFAS), also known as “forever chemicals”, are a large and diverse group of anthropogenic fluorinated chemicals, daily used due to their unique properties. PFAS are a prominent group of organic micropollutants, due to their ubiquitous occurrence in the environment and the organisms and their persistent, bioaccumulative and toxic (PBT) properties. The large number of commercially available PFAS along with their transformation products make their systematic monitoring in the enviromental compartments a challenging task. The integration of trapped ion mobility spectrometry (TIMS) to LC-HRMS workflows, allows a more extensive monitoring of organic micropollutants (PFAS, pharmaceuticals, pesticides, etc.) in complex environmental matrices, such as biota, through targeted and untargeted workflows.

The focal point of the present study was the establishment of a combined CCS-aware targeted and untargeted workflow for the comprehensive PFAS characterization in complex environmental matrices, such as biota. More broadly, the overall analytical performance of RPLC-VIP HESI(-)-TIMS-QTOF MS in environmental applications was demonstrated.

Biota extracts suitable for untargeted screening were generated through a generic sample preparation protocol developed for the simultaneous extraction of 56 PFAS from different sub-groups. The analysis of the extracts was performed using RPLC-VIP HESI(-)-TIMS-QTOF MS. Two different acquisition modes, broadband collision-induced dissociation (bbCID), a data independent acquisition and PASEF, an efficient data-dependent mode, were used for targeted and untargeted workflow, respectively.

The CCS aware target analysis was utilized using a target list of 60 PFAS, including information regarding precursor ion formula, retention time, MS1 and MS2 qualifier ions as well as ion mobility-derived collision cross section (CCS) values. The target screening results indicate higher sensitivity and, thus, lower PFAS detection limits. Moreover, full-scan MS and bbCID MS/MS spectra of significantly higher quality were obtained, due to mobility filtrating. Finally, the use of collisional cross sections (CCS), as additional identification criterion, enhanced the identification confidence.

In the untargeted data processing workflow, after the transformation of the raw data into a comprehensive feature table, the detected features were prioritized using Kendrick mass analysis and further annotated using a PFAS suspect list with approximately 5,000 compounds. In-silico prediction of MS/MS spectra and CCS values for the suspected compounds was performed to facilitate their identification. Examples highlighting the prioritization and annotation of suspected features as PFAS-related compounds were revealed. The extensive MS2 coverage provided by PASEF facilitated the identification process.

The comprehensive PFAS monitoring is performed through the proposed workflow, combining LC-TIMS-HRMS with target, suspect and non-target screening. Therefore, it will assist understanding the chemical universe of PFAS in the environment and protecting environment, wildlife, and human health.

Non-Target Screening of Organic Aerosol Tracers to Elucidate Atmospheric Composition with Ice Cores

C. J. Huber[1,2,3*], D. Salionov[4], F. Burgay[1,3], A. Eichler[1,3], T. M. Jenk[1,3], S. Bjelic[4] and M. Schwikowski[1,2,3]

[1]Paul Scherrer Institut, Laboratory of Environmental Chemistry, Forschungsstrasse 111, 5232, PSI Villigen, Switzerland
[2]University of Berne, Department of Chemistry, Biochemistry and Pharmaceutical Sciences, Freiestrasse 3, 3012, Berne, Switzerland
[3]University of Berne, Oeschger Centre for Climate Change Research, Hochschulstrasse 4, 3012, Berne, Switzerland
[4]Paul Scherrer Institut, Bioenergy and Catalysis Laboratory, Forschungstrasse 111, 5232,

carla.huber@psi.ch

Atmospheric aerosols influence the Earth's radiative balance by absorbing or scattering solar radiation as well as affecting cloud properties. The overall radiative forcing caused by aerosols is a large source of uncertainty in global climate models. A large part of this is attributed to organic aerosols, which contribute 20 to 70% of today's particulate matter mass in the lower troposphere. Characterising sources as well as understanding the pathways of these organic aerosols is a major challenge due to the large variety of organic molecules contained.

A way to narrow the knowledge gap is to use natural archives, e.g., high-alpine glaciers, for reconstructing past composition and concentration trends of organic aerosols. Here, we show data from a firn core collected on the Corbassière glacier (Grand Combin, Swiss Alps) in 2020. The firn core was dated by annual layer counting using the stable oxygen isotope ratio ($\delta^{18}O$). We analysed organic tracers with a hybrid target/non-target screening approach optimised for determining oxidation products of volatile organic compounds. As these tracers are usually present at low concentrations, we performed solid phase extraction as a pre-concentration step. The samples were analysed with high-performance liquid chromatography coupled with high-resolution mass spectrometry, using ESI and Orbitrap technology. This approach allowed the identification of a wide range of compounds at low concentrations through the comparison of their MS/MS spectra with spectral libraries (e.g., mzCloud) and reference standards.

We present a unique record of the molecular composition of organic aerosols in the Corbassière firn core and discuss seasonal trends as well as concentration evolution over 6 years from 2020 to 2014. With this approach, we can detect previously unknown species and identify biogenic or anthropogenic sources. In addition, we may be able to identify new proxies for climate reconstruction.

Optimization and Application of a Pyrolysis – GC-Orbitrap Method for the Identification and Quantification of Microplastics in Air

A. Torres-Agulló[1]*, A. Karanasiou[1], S. Lacorte[1]

[1]Institute of Environmental Assessment and Water Research of the Spanish Research Council (IDAEA-CSIC), Jordi Girona 18-26, 08034, Barcelona, Spain.

ana.torres@idaea.csic.es

Microplastics (MP) are globally spread throughout the environment. Airborne MP can be inhaled and, once in the organism, they release not only their own harmful additives (Verla et al., 2019) but also different contaminants such as organic pollutants and heavy metals (Wang et al., 2021) which had been adsorbed onto their surface. Most of these chemicals are linked with cytotoxicity, carcinogenic and endocrine disrupting effects (Prata, 2018). In this study, a pyrolyzer coupled to a gas chromatography-orbitrap mass spectrometer (Pyr-GC-Orbitrap) was used as a reliable system to unravel in a target-untargeted approach the complex mixture of MP, plastic additives, and associated contaminants in air samples. The challenge was to quantitatively determine the different MP polymers with certainty, as well as to simultaneously identify other contaminants present in the samples. In the present study, we have developed and optimized a Pyr-GC-Orbitrap method with a triple objective: (i) to determine the presence of ten different polymers (polyethylene terephthalate (PET), polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS), polycarbonate (PC), acrylonitrile butadiene styrene (ABS), poly(methyl methacrylate) (PMMA), nitrile rubber (NBR), and polyamide (PA)) in air samples; (ii) to evaluate the performance of the method to enable identification and quantification in a precise and accurate way and (iii) to process and resolve the samples into pure mass spectrums through a comprehensive use of the Deconvolution Plugin of TraceFinder 5.1 (ThermoFisher Scientific, USA) software to identify plasticizers and associated contaminants. The sampling filter and clean-up, pyrolysis temperature and filter-polymer interaction during pyrolysis were evaluated and optimized. Instrumental limit of detection (LOD) and quantification (LOQ) ranged between 0.3 – 0.8 and 0.9 – 1.9 µg, respectively, depending on the polymer. Linearity was evaluated from 5 to 50 µg and all polymers presented a coefficient of determination (r^2) > 0.995 and the accuracy (RSD, %) ranged between 6.5 – 12.3%. The optimum method conditions were determined as 600 °C during 30s for pyrolyzing the polymers. Moreover, using quartz filters during sampling minimized potential interferences during the analysis. Finally, the optimized method was applied to different indoor air samples, where six polymers were properly identified and quantified, and phthalates and organophosphate esters were detected using the non-targeted approach.

This work was supported by the Spanish Ministry of Science and Innovation Project TED2021-131552B-C21, Excelencia Severo Ochoa Project CEX2018-000794-S and project PID2019-105732GB-C21. A. Torres-Agullo also acknowledges this Ministry for its financial support (predoctoral grant PRE2021-097960).

References

Prata, J.C. (2018) ‘Airborne microplastics: consequences to human health?’ Environ. Pollut. 234, 115–126. doi: https://doi.org/10.1016/j.envpol.2017.11.043.

Verla, A. W. et al. (2019) ‘Microplastic toxic chemical interaction: a review study on quantified levels, mechanism and implication’ SN Appl. Sci. 1 (11), 1–30. doi: https://doi.org/10.1007/s42452-019-1352-0.

Wang, Y. et al. (2021) ‘Effects of exposure of polyethylene microplastics to air, water and soil on their adsorption behaviours for copper and tetracycline’ Chem. Eng. J. 404, 126412. doi: https://doi.org/10.1016/j.cej.2020.126412.

Effluent Wastewater as Local Source of Contamination at The Mario Zucchelli Station (Antarctica)

R. Zangrando[1]*, E. Scalabrin[1], N. Ceolotto[2], M. Vecchiato[1], E. Magi[3], A. Gambaro[4]

[1] Institute of Polar Sciences, National Research Council (CNR-ISP), Via Torino, 155, 30172, Venice Mestre (VE), Italy
[2] University of Bath, Department of Chemistry, Claverton Down, Bath, BA2 7AY, United Kingdom
[3] University of Genoa, Department of Chemistry and Industrial Chemistry, Via Dodecaneso 31, 16146 Genoa, Italy
[4] Ca’ Foscari University of Venice, Department of Environmental Sciences, Via Torino 155, 30170, Mestre (VE), Italy

roberta.zangrando@cnr.it

The levels of pollutants in Antarctica are generally lower than somewhere else in the world. Since there isn’t any industrial activity, but only a limited presence of human settlements, pollutants present in the Antarctic are mainly transported for long distances by atmospheric transport (atmospheric aerosols) and ocean currents. Furthermore, research stations contribute as local pollution sources due to emissions and discharges of domestic waste, effluents, and incineration. For many years, organic micropollutants such as personal care products and hormones have been disregarded as an environmental risk by classical toxicology, since their environmental concentrations are below the toxic thresholds obtained from standardized dose-response curves. However, toxicants can exert biological activity well below their toxic threshold concentration. These sublethal effects are not directly associated with adverse events, but they may lead to the disruption of cell communication or endocrine regulation systems. Therefore, the study of new compounds used in everyday life, the so-called “emerging contaminants”, have recently become more and more relevant; nevertheless, at present, only few data are available regarding Antarctica, especially in the Terra Nova Bay area.

The aim of this work was the qualitative screening of effluents of Mario Zucchelli Station wastewater treatment plant, by suspects screening and untargeted analysis using high resolution mass spectrometry, in order to verify the presence of a wide range of emerging contaminants and/or metabolites. The integration of the two methods permit to obtain a complete profiling of water samples, including both known and unknown compounds. Among the tentative compounds detected there are personal care products (such as fragrances, detergents, sunscreen agents), pharmaceutical and drugs molecules, pesticide metabolites, surfactants. Other detected compounds, such as plasticizers, compounds used in construction and building materials, flame retardants, PFAS etc, have probably different sources. The obtained results could help in the evaluation of the impact of the scientific Station on the Ross Sea environment.

Nontarget HRMS Analysis as a Tool for Revealing True Water Treatment Efficiency

P. Nováková[1*], H. Švecová[1], R. Grabic[1]

[1]University of South Bohemia in České Budějovice, Faculty of Fisheries and Protection of Waters, South Bohemian Research Centre of Aquaculture and Biodiversity of Hydrocenoses, Zátiší 728/II, CZ-389 25, Vodňany, Czech Republic

novakovapetra@frov.jcu.cz

Threats from organic micropollutants (MPs) remaining in drinking water become more urgent with their increasing environmental concentrations. A conventional drinking water treatment plants (DWTPs) assurance approach is anchored in the legislature and is based on targeted analytical methods. However, targeted methods for the qualitative and quantitative determination of micropollutants cannot reach all potential risk substances. An approach combining monitoring known and unknown/new substances and their changes during treatment with different analytical approaches could reveal comprehensive treatment effects. High-resolution mass spectrometry coupled with liquid chromatography (LC-HRMS) is crucial for evaluating all detectable compounds' presence and change.

We applied nontargeted screening (NTS) to assess the drinking water treatment effect without compound identification. We deployed passive polar compound integrative samplers (POCIS) in four DWTPs in spring and autumn. Sampling sites were at the inlet and outlet before granular active carbon filters (GAC). Nontarget data were acquired by combining full scan HRMS with data-independent MS2 experiments (DIA) at hybrid quadrupole orbital trap mass spectrometer Q Exactive. The data was processed by Compound Discoverer 3.1. to achieve compound detection and grouping by m/z, retention time, and predicted molecular formula. In the next step, we compared sampling sites against each other based on Log2FoldChange of individual signals. This procedure provided a list of detected compounds eliminated or decreased by treatment and, more importantly, the compounds formed or increased by GAC/ozonation. Determined treatment effect (TE) from numbers of nontarget compounds without formed compounds allowed comparison with removal efficiency for concentration and numbers of target analytes. In the last step, we attempted to identify four suspect chemicals based on database searches and confirmation with MS/MS fragments.

Evaluation of the treatment efficiency based on a nontarget approach and detected compounds numbers and areas has several issues to improve, like inconsistency in peak detection, ion signals intensity affected by matrix, and recently unconventional and software-limited data processing. Nevertheless, the outcome of this study on real DWTPs showed the capability of a nontarget approach combined with routine target analysis. Additionally, new MPs can be identified from full scan data by searching databases.

Critical Evaluation of LDTD-APCI for Investigation of Pharmaceutical Transformation Products Formed by Soil Bacteria

A. Bořík[1], P. Novákova[1], R. Grabic[1], A. Chroňaková[2], R. Kodešová[3]

[1]University of South Bohemia in České Budějovice, Faculty of Fisheries and Protection of Waters, South Bohemian Research Centre of Aquaculture and Biodiversity of Hydrocenoses, Zátiší 728/II, CZ-38925 Vodňany, Czech Republic
[2]Biology Centre of the Czech Academy of Sciences, Institute of Soil Biology, Na Sádkách 7, 37005, České Budějovice, Czech Republic
[3]Czech University of Life Sciences Prague, Faculty of Agrobiology, Food and Natural Resources, Dept. of Soil Science and Soil Protection, Kamýcká 129, CZ-16500 Prague 6, Czech Republic

The environmental impact of active pharmaceutical ingredient transformation products (TPs) is a recently emerging research subject. TPs formation pathways and fate are typically studied under controlled laboratory conditions such as *in vitro and in vivo* experiments. The primary analytical approaches for investigating TPs and their parent compound are gas or liquid chromatography (LC) with mass spectrometry techniques. The most relevant disadvantages of these techniques are extensive time requirements for sample preparation and sample analysis (at least single minutes per sample), which could be critical, especially for large sample sets. Also, the high consumption of organic solvents for LC and sample preparation do not align with green chemistry principles.

LDTD-APCI represents an ambient ionization technique omitting chromatographic separation, which enables high-speed sample analysis (low tens of seconds) and reducing sample treatment (e.g., filtration). Coupling LDTD-APCI with advanced high-resolution mass spectrometers (orbitrap) helps increase method selectivity critical for complex biological sample matrix analysis and can help overcome difficulties such as interfering compounds.

This combination of advanced analytical instrumentation has been evaluated under complex requirements of TPs investigation in bacteria biological culture sample matrix. Quantitative and qualitative data have been obtained and mutually compared with LC-HRMS. Results obtained with LDTD-APCI show equal quantitative performance and summarize partial limitations for structural identification of the formed TPs.

Acknowledgment:

The authors acknowledge the financial support of the Ministry of Agriculture of the Czech Republic, project “The fate of selected micropollutants, which occur in treated water and sludge from wastewater treatment plants, in soil” (No. QK21020080).

Validation of Multi-Residue LC-MS/MS and GC-MS/MS Method for the Determination of Pesticide Residues in Water

A. Perczak[1], A. Hołodyńska-Kulas[1], A. Nowacka[1], F. Stachowiak[1], R. Motała[1], D. Drożdżyński[1]*

[1]Institute of Plant Protection – National Research Institute, Department of Pesticide Residue Research
Władysława Węgorka St. 20, Poznań, Poland

d.drozdzynski@iorpib.poznan.pl

Modern multi-residue methods based on liquid and gas chromatography coupled to tandem mass spectrometry (LC-MS/MS, GC-MS/MS) can be used for determination of hundreds of pesticides from different chemical classes as well as their metabolites in many matrices, including environmental samples. The aim of the research was to develop and validate a multiresidue method for monitoring surface and groundwater at the lowest possible levels, covering active substances of plant protection products currently used in agriculture as well as withdrawn from use.

In the study, development and validation of a multi-residue method for pesticide residues determination in water were performed using LC-MS/MS Eksigent ekspert ultraLC 100-XL system interfaced with a mass spectrometer equipped with an electrospray ionization source operated in the positive and negative mode (AB Sciex, Qtrap 6500), chromatographic separation - Kinetex C18 (100 x 2.1mm x 2.6µm) column, water/methanol gradient and GC-MS/MS Agilent Intuvo 9000GC system combined with a triple quadrupole mass spectrometer equipped with an EI ionization source (Agilent, Triple Quad 7010B), chromatographic separation - Agilent HP-5MS column (15m x 0.25mm x 0.25µm). The quantitative analysis was based on the multiple reaction monitoring (MRM) technique.

The method validation was carried out according to the SANTE/11312/2021 guideline (SANTE, 2021). The recovery tests were performed by spiking blank samples of water with a solution of 342 pesticides at 0.025, 0.1 and 0.5 µg/dm^3 levels. QuEChERS extraction (Foods of plant origin, 2018), was used to isolate the analytes and remove the impurities. The aliquot of extract was evaporated to dryness and diluted in mobile phase (in case of LC-MS/MS) or acetonitrile (in case of GC-MS/MS) prior to the instrumental determination. The method is very simply, complicated and time-consuming analytical steps are avoided.

Recoveries of the majority of compounds tested were in the 70–120% range and were characterised by precision lower than 20%. The high sensitivity of the method allowed the successful determination of 281 compounds at the level of 0.025 µg/dm^3. The validation and PTs results (Aquacheck - AQ576) demonstrate the applicability of this method in the routine analysis.

In 2022, a total of 445 water samples from 78 sampling points in Polish river basins were tested using the optimized and validated method. Overall, 74 different pesticides in various concentrations were detected in the analyzed surface water samples. The most popular group of pesticidal activity determined in the collected samples were herbicides (32 substances), followed by fungicides (26 substances) and insecticides (12 substances). Four pesticide metabolites have also been detected.

References

Guidance document on analytical quality control and method validation procedures for pesticides residues analysis in food and feed. SANTE/11312/2021.

Foods of plant origin - Multimethod for the determination of pesticide residues using GC- and LC-based analysis following acetonitrile extraction/partitioning and clean-up by dispersive SPE - Modular QuEChERS-method. EN 15662:2018.

Tris(2,4-Ditert-Butylphenyl)Tiophosphate - A New Plastic Additive or a Transformation Product of a Common Plastic Additive? Report on the First Time Detection, Structure Elucidation and Synthesis of an Authentic Sample

V. Nikiforov[1]*, M. Huiser[1,2], D. Herzke[1]

[1]The Climate and Environmental Research Institute NILU, Framsenteret, Hjalmar Johansens gate 14, 9007 Tromsø, Norway
[2]The Arctic University of Norway, Department of Pharmacy, Faculty of Health Sciences, UiT –Tromsø

van@nilu.no

Tris(2,4-ditert-butylphenyl) phosphite (central structure on the figure), known as Irgafos 168, is one of the major anti-oxidants in plastic products (Wolf et al., 2000). It is well-known, that in the environment it forms an oxide, tris(2,4-ditert-butylphenyl) phosphate (structure to the left on the figure). We have detected, first in the sample of plastic feeding pipe from aquaculture facility, then in a number of other samples a new congener, which was provisionally identified as previously unknown sulfur derivative, tris(2,4-ditert-butylphenyl) tiophosphate (structure to the right on the figure). HRAM spectra (GC Q Exactive) were rather similar to those of the mentioned oxygen derivative, and analysis of the isotope clusters was in good agreement with the proposed chemical structure. A critical evidence was obtained from the fine structure of the m+2 isotopomer of the double-charged M-30 ion (loss of two methyl groups), with 34S and 13C2-isotopomers sufficiently resolved.
Finally, the authentic sample was prepared by reaction of the phosphite with sulfur in presence of ethylenediamine. The obtained specimen had both retention time and mass-spectrum identical with those of the substance detected in the pipe.
The oxide and the sulfide have close retention times, however on TG-5MS column they were partially resolved, the sulfide coming first.
We have no information to suggest whether this new substance is a transformation product or was introduced on purpose in the original material.

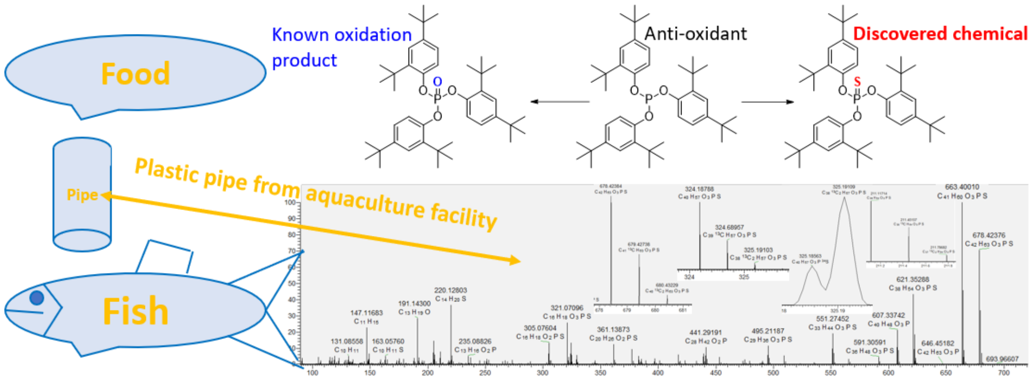


Figure. Formation/synthesis pathways for addition of oxygen or sulfur to tris(2,4-ditert-butylphenyl) phosphite; HRAM spectra of the title compound.

References

Rainer Wolf; Bansi Lal Kaul (2000). "Plastics, Additives". Ullmann's Encyclopedia Of Industrial Chemistry. doi:10.1002/14356007.a20_459. ISBN 3527306730.

An Automated Toxicity Based Prioritization Framework for Fast Chemical Characterization in Non-Targeted Analysis and its Validation in Sludge Water

C. Rathmann[1], Y. Xiao[2], A. Ong[2], J. Yang[3], M. Fang[3*]

[1]Waters GmbH, Helfmann-Park 10, 65760 Eschborn, Germany
[2]International Food and Water Research Centre, Waters Pacific Pte Ltd, Science Park II, 117528 Singapore
[3] Nanyang Technological University, School of Civil and Environmental Engineering, 639798, Singapore

The identification of environmental pollutants with harmful effects is usually performed by non-targeted analysis (NTA) using liquid chromatography coupled with high resolution mass spectrometry. However, the prioritization of possible candidates is challenging due to the large number of candidates from MS acquisitions. Therefore, we have developed an R package application, "NTAprioritization.R", for fast prioritization of suspect lists, where candidates with potential exposure are prioritized based on their toxicity and identification evidence in the matrix. In this workflow, candidates were first rated for their identification levels based on spectral matching and retention time prediction. The level of toxicity levels was rated according to candidates' toxicity of different endpoints or ToxPi score. Finally, the candidates' level of exposure was ranked from Tier 1-5, in order of priority from highest to lowest. For validation of this workflow, it has been used to identify pollutants in a sludge water sample spiked with 28 environmental pollutants. The workflow reduced the number of potential candidates from 6,982 candidates to a final list of 2,779 compounds with 21 out of 28 spiked standards ranked in 5 tiers (Tier 1 to 5). Overall, this study shows the added value of an automated prioritization R package based on the NTA method for the fast screening of environmental pollutants.

Air Pollution in the Context of Mitigation of Environmental Climate Change

A. Cozea[1], M. A. Constantin[1*], S. Calinescu[1] , G.Tanase[1]

[1]National Research and Development Institute for Industrial Ecology, Laboratory of Air Pollution Control, Drumul Podu Dambovitei No. 57-73, ZIP code 060652, Bucharest, Romania

alina.constantin@incdecoind.rr

Climate change, environmental degradation, and air pollution are issues we are now facing at the national and international levels. Air pollution in the context of climate change is an important global issue, having significant impacts on human health and economic development.

This paper aims to contribute to the existing knowledge on reducing pollution by investigating how we can contribute to reducing pollution effects.

We used data to investigate the extent of global differences in air pollution indicators correlated with socioeconomic development. Therefore, we first sought to identify possible relationships between air pollution and a set of socioeconomic metrics. The primary air pollutants are carbon monoxide (CO), particulate matter (PM), nitrogen oxides (NOx), volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), ozone (O_3) and sulphur dioxide (SO_2). In general, the increase in these pollutants' emissions is due to the rapid industrialization and urbanization of countries. Countries were categorized based on CO_2 emissions and of outdoor PM 2.5.

Correlations between gas emissions and air pollution levels and socioeconomic development indicators and population health, were evaluated on a national and global scale. The study concluded that socioeconomic development at the country level is correlated with emissions per capita.

The results of the studies suggested that the annual estimated CO_2 and PM 2.5 could be reduced, eliminating the percentage risk of illness and death associated with air pollution and mitigation of Environmental Climate Change

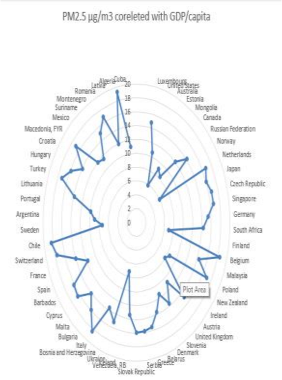


Fig 1- PM2.5 concentration corelation with GDP/capita

References

Liu, Q. et al. (2019) “A global perspective on national climate mitigation priorities in the context of air pollution and sustainable development”, City and Environment Interactions, Volume 1, doi:10.1016/j.cacint.2019.100003.

Ru M. et al., (2018), “The long-term relationship between emissions and economic growth for SO2, CO2 and BC”, Environmental Research Letters, 13, doi:10.1088/1748-9326/aaece2.

Active Pharmaceutical Ingredients (APIs) and Personal Care Products (PCPs) in the Kongsfjorden Ecosystem (Svalbard, Norway)

F.Spataro[1]*, J. Rauseo[1], T. Pescatore[1], I. B. Øverjordet[2] and L. Patrolecco[1]

[1]National Research Council – Institute of Polar Sciences, Rome, Italy
[2]SINTEF Ocean, Department of Climate and Environment, Trondheim, Norway

francesca.spataro@cnr.it

Polar regions are subject to environmental, economic, political, and societal changes, which impact not only on a regional scale but also the entire planet. While climate change (CC) is more evident in the Poles compared to other parts of the world, other aspects such as pollution dynamics, need to be investigated. The conclusions reported by the most recent intergovernmental and scientific panels on CC indicate that the Artic is warming with impacts on sea ice retreat, melting glaciers, thawing permafrost, weather events and alterations of atmospheric and oceanic circulations and biogeochemical cycles (AMAP. Arctic Monitoring and Assessment Programme. 2017). These changes have also favoured the development of anthropogenic activities (e.g., fisheries, cruise tourism and mineral exploitation), which are additive contamination sources. This causes particular concern, especially considering the low technologies of wastewater treatment plants (WWTPs) currently used in Arctic regions (AMAP. Arctic Monitoring and Assessment Programme. 2017, Hung H, et al.2022).

In this context, active pharmaceutical ingredients (APIs) and personal care products (PCPs) have recently attracted considerable interest, due to their bioactive nature and potential detrimental effects on wildlife and humans. These chemicals are considered "pseudo-persistent" because they are continuously released into the environment being components of daily-use products. Depending on their chemical-physical properties, some of them have a relatively high lifetime, and thus can be long-range transported from mid-latitudes. Specifically, antibiotics cause particular concern due to their role in the spread of antibiotic-resistant genes (ARGs) and bacteria (ARBs), which can reduce their therapeutic efficacy for the treated organisms (Hung H, et al.2022).

In the framework of SED-POPs ("Sedimentation processes of legacy and emerging organic micropollutants in the Kongsfjord-Krossfjord systems in a climate change scenario" RiS ID: 11451) and PHARMASVALBARD ("Harmonization and monitoring of pharmaceuticals and personal care product –PPCPs- pollution in Svalbard" RiS ID: 12001) projects, the occurrence, distribution, and sources of selected APIs and PCPs in seawater and sediment samples collected on board MS Teisten vessel (Kings Bay, Ny-Ålesund) along a transect of Kongsfjorden were evaluated during summer season from 2018 to 2022. An ecological risk assessment for the pelagic and benthic communities based on measured concentrations was also carried out.

Target APIs and PCPs were detected in seawater and sediment samples, suggesting their ubiquitous occurrence. In particular, significant concentrations were detected in seawater samples ranging between 20 and 100 ng/L. Higher concentrations were found in the sampling points close to the Ny-Ålesund village (hosting several scientific bases), suggesting an important role of local sources of contamination, even if a contribution from atmospheric and sea current transport can not be excluded. Similar trends were identified for sediment samples with concentrations ranging from below the limit of quantification to 300 ng/g d.w.The risk analysis, performed by calculating the Risk Quotients, indicated that target APIs and PCPs can pose a high risk for the pelagic and benthic communities.

References

AMAP. Arctic Monitoring and Assessment Programme. (2017). Assessment 2016: chemicals of emerging Arctic concern (www.amap.no).

Hung H, et al.(2022). Climate change influence on the levels and trends of persistent organic pollutants (POPs) and chemicals of emerging Arctic concern (CEACs) in the Arctic physical environment – a review. Environ. Sci.: Processes Impacts 24: 1577.

Assessment of Legacy and Emerging Persistent Organic Micropollutants in Arctic Ice and Snow

T.Pescatore[1*], F. Spataro[1], J. Rauseo[1], A. Spolaor[2], F. Scoto[3] and L. Patrolecco[1]

[1]Institute of Polar Sciences, National Research Council (CNR-ISP), via Salaria km 29.300, 00100 Montelibretti, Roma, Italy
[2]Institute of Polar Sciences, National Research Council (CNR-ISP), c/o Cà Foscari University of Venice, via Torino 155, 30172, Venice Mestre, Italy
[3]Cà Foscari University of Venice, via Torino 155, 30172, Venice Mestre, Italy

tanita.pescatore@isp.cnr.it

The Arctic has been traditionally considered free from local contamination sources due to its distance from more anthropogenic areas. However, the occurrence of several legacy and emerging persistent organic pollutants (POPs) in Polar areas have been reported. In fact, the Arctic region represents the final receptor of pollutants, which are transported by atmospheric circulation from lower latitudes and deposited to the ground through dry deposition, rain and snowfall events. Snow pack and later glaciers can act as "cold condensers" of contamination, accumulating organic and inorganic contaminants (Pawlak et al., 2021). For example, PCBs deposition to glacier surfaces can occur through their condensation to falling snowflakes, trapping of particles by snowflakes, and freezing of aqueous aerosols (moisture) to ice crystals (dry snow) containing gases or particles. In this context, glacier can preserve several years of snow accumulation and the ice cores that can be retrive from them, are excellent archives of natural and anthropogenic emissions (e.g., industry, mining, transport). From the ice core archive we can extract precious information about the past atmospheric characteristics, climatic (e.g., carbon dioxide) evolution of our planet and the history of atmospheric pollutant transport (Gabrielli and Vallelonga, 2013). Most studies on ice have been focused on the determination of inorganic components, such as major ions and trace elements, and their isotopic fingerprint, while monitoring of organic pollutants trapped in the cryosphere has only marginally explored, mainly due to high sample volume request for this analysis (Giorio et al., 2018).

The present study investigates the occurrence of "old" and "new" organic pollutants, including pesticides (p,p'-dichlorodiphenyltrichloroethane, dichlorodiphenyldichloroethene, alpha-beta-gamma and delta hexachloro-cyclohexanes, endosulfan, clorpyrifos, dacthal), polychlorobyphenyls (PCBs), bisphenol A (BPA) and nonylphenols (NPs) in shallow ice cores (about 1 m) collected during April 2022 in Austre Brøggerbreen and Kongsvegen glaciers (Svalbard Islands, Norway). In these sites, each year snow melts completely, exposing the older glacier ice underneath and potentially reintroducing pollution from old emissions into Arctic systems. This may alter the fate and distribution of organic contaminants both seasonally and over the long term. Surface snow samples were also collected to compare the budget of target contaminants in the seasonal snow.

Preliminary results show that target contaminants occurred in both compartments. On average, the pesticides and BPA were detected at higher concentrations in the ice cores (from <LOD to 1.07 ng/L and <LOD to 5.60 ng/L for pesticides and BPA, respectively) than in snow samples. On the contrary, PCBs and NPs were more concentrated in snow (mean of 0.09 and 46 ng/L, respectively), suggesting a more recent deposition of these substances.

References

Pawlak, F. et al.(2021)"Chemical hazard in glacial melt?The glacial system as a secondary source of POPs (in the Northern Hemisphere).A systematic review", Science of the Total Environment, 778, 145244. 10.1016/j.scitotenv.2021.145244

Gabrielli, P. et al.(2015)"Contaminant records in ice cores".Environmental Contaminants:Using natural archives to track sources and long-term trends of pollution,393-430. 10.1007/978-94-017-9541-8_14

Giorio, C. et al.(2018)"Prospects for reconstructing paleoenvironmental conditions from organic compounds in polar snow and ice",Quaternary Science Reviews,183,1-22.10.1016/j.quascirev.2018.01.007.

Temporal Dynamics of Anthropogenic Pollutants in the Sediment of Kongsfjorden-Krossfjorden System (Svalbard, Norway)

S. Giansiracusa[1]*, L. Patrolecco[3], F. Spataro[3], J. Rauseo[3], T. Pescatore[3], S. Miserocchi[2], F. Giglio[2], R. Guerra[4], T. Tesi[2], G. Ingrosso[2], L. Langone[2], G. Capodaglio[1]

[1]University Ca' Foscari of Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino 155, 30172 Venice-Mestre, Italy
[2]Institute of Polar Sciences (ISP), National Research Council (CNR), Via P. Gobetti 101, 40129, Bologna, Italy
[3]Institute of Polar Sciences (ISP), National Research Council (CNR); Str. Prov. 35d km 0.7, 00010, Montelibretti, Italy
[4]Department of Physics and Astronomy, V.le Pichat 6/2, 40127 Bologna, Italy

sara.giansiracusa@unive.it

Pollution research in the Arctic has usually focused on the long-range transport (LRT) of pollutants (atmospheric and oceanic currents, sea ice drift, and rivers). In the last decades, several studies on Persistent organic pollutants (POPs) in Arctic environmental matrices have been carried out. POPs are organic compounds produced by human activities, with common characteristics of persistence, toxicity, bioaccumulation potential and the tendency of LRT. Polybrominated diphenyl ethers (PBDEs) are mainly used as flame retardants in a wide range of products, including plastics, furniture, upholstery, electrical equipment, electronic devices, textiles and other household products. Primary sources of release of these contaminants in the environment occur during production, use or disposal, or as a by-product of other activities (de Wit et al., 2010). Once released, POPs partition into air, water, soil, snow/ice and sediment according to their physical–chemical properties. These properties are influenced by temperature; thus, climate change will affect their fate and concentrations in the environment. In this regard, soils, sediment and oceans as environmental reservoirs, become secondary sources of POPs after they are no longer used, reemitting previously deposited chemicals (Ma et al., 2011). Depth profiles of these contaminants in sediment cores represent valuable natural archives of environmental contamination. However, in literature only a few studies conducted on sediment cores in the Arctic show a temporal trend of these contaminants. Therefore, the aim of this study is to evaluate the occurrence and concentration of PBDEs in a sediment core to better understand the temporal variability and contaminant fluxes in the Arctic marine ecosystem. Sediments from core were analysed. Sediment core NYA21-03 (78°56.940' N, 012°09.115' E), 117cm long, was collected in 2021 at 190 m depth in the Kongsfjorden (Svalbard). Along this fjord is located the research village of Ny-Ålesund which can be considered a source of local contamination vs LRT. The sediment core was stored at +4°C; then, subsamples, with 0.5 cm resolution, were freeze-dried. Pressurized Liquid Extraction (PLE) was performed using the Speed Extractor E-916 system (Buchi Italia). The separation, identification and quantification of target compounds were performed using gas chromatography-mass spectrometry (GC-MS) (Thermo Fisher Trace 3000-ISQ7000; Chromeleon Software). The ΣPBDE concentrations measured in sediment core ranged from below the detection limit (LOD) to 5.0 ng g-1 dry weight. The highest concentration was found at first 0.5 cm depth suggesting a recent release of these contaminants. Specifically, Σpenta-BDEs resulted to be in highest amounts than Σepta-BDEs > Σhexa-BDEs > Σtetra-BDEs > Σtri-BDEs. In particular, the BDE47 and 99 prevailed in accordance with their strong cyclical pattern, due to their re-volatilization occurring mainly in summer. The overall results suggest that the observed distribution pattern may be the combined effect of multiple factors, such as atmospheric transport, local input of technical PBDEs and mixing in sediment.

References

DE WIT, C. A., HERZKE, D. & VORKAMP, K. 2010. Brominated flame retardants in the Arctic environment — trends and new candidates. Science of The Total Environment, 408, 2885-2918.

MA, J., HUNG, H., TIAN, C. & KALLENBORN, R. 2011. Revolatilization of persistent organic pollutants in the Arctic induced by climate change. Nature Climate Change, 1, 255-260.

Modeling Nature-Based Solutions Suitability in Marine Coastal Areas Under Climate Change Scenarios

O. Ozkiper[1,2]*, E. Allegri[1,2], A. Bianconi[1,2], H.V. Pham[1,2], E. Furlan[1,2], R. Simide[3] and A. Critto[1,2]

[1]Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino 155, 30172, Venice, Italy
[2]Centro Euro-Mediterraneo sui Cambiamenti Climatici, Risk Assessment and Adaptation Strategies Division, via Marco Biagi 5, 73100 Lecce, Italy;
[3]Oceanographic Institute Paul Ricard, Embiez Island 83140 Six-Fours-Les-Plages, France

ozan.ozkiper@cmcc.it

Climate change (CC) impacts and anthropogenic stressors threaten the survival and growth of aquatic ecosystems by changing ocean and marine dynamics. In addition to the acceleration of geophysical hazards (e.g., storm surges, coastal erosions), the increase in water quality (WQ) alteration (e.g., eutrophication) linked to marine pollution due to excessive human-based emissions, as well as changes in sea surface temperature (SST) are causing in concert irreversible biodiversity loss in aquatic ecosystems. Against this interplay, the capacity of marine and coastal ecosystems to provide services (e.g., water purification) is reduced, and the quality of marine life is further negatively affected, resulting in positive feedback (Van et al., 2007).

Nature-based solutions (NbS), an umbrella concept including various ecosystem-based approaches, are emerging as key climate adaptation and mitigation tools to contrast biodiversity loss and respond to societal challenges (including CC), while improving human well-being (Cohen-Shacham et al., 2016). Within H2020 MaCoBioS project, a GIS-based Multiple Criteria Decision Analysis (MCDA) model was developed for NbS suitability mapping in the marine coastal areas of the Mediterranean eco-region. In particular, the developed model allows to rank and select areas for NbS design and implementation, specifically focusing on seagrass meadows. Environmental suitability indicators (e.g., dissolved inorganic nitrogen (DIN), SST), underpinning the survival and growth of seagrass meadows, were selected based on literature review, and then classified in different sub-groups (i.e., geomorphology, WQ, and climate). Integration of heterogeneous data and prioritization of selected indicators (i.e., weighting) were achieved via the Analytic Hierarchy Process (AHP) based on expert judgments. Suitability maps of each sub-group were obtained by combining suitability scores of each indicator with their weights. The results indicated that geomorphological variables, especially depth, are the most limiting factor of suitable areas for seagrass growth. In particular, the Northern Adriatic and Gulf of Gabés showed wide suitable regions geomorphologically. On the other hand, even though the case study area has large suitable areas in terms of WQ, very shallow parts of the Veneto region showed the lowest WQ scores due to excessively high DIN concentration and light attenuation coefficient, which is the most dominant WQ variable. The southern Mediterranean (e.g., Egyptian coasts) resulted with lower climate suitability scores due to thermal stress on seagrasses. Moreover, it was observed that climatic indicators will be the limiting factor for seagrass growth due to accelerating emissions in future CC scenarios (e.g., RCP8.5 under 2050 and 2100 timeframes).

Environmental suitability results pave the way for the implementation of NbS in the frame of wider transformative adaptation pathways, allowing to increase the resilience of ecosystems against changing environmental conditions, while providing a basis for the integration of socio-economic and governance-related variables for a complete NbS suitability assessment in further studies.

References

Cohen-Shacham, E. et al. (2016) 'Nature-based Solutions to address global societal challenges', IUCN, pp. xiii + 97. Available at: https://doi.org/10.2305/iucn.ch.2016.13.en.

Van, T. et al. (2007) 'Positive Feedbacks in Seagrass Ecosystems: Implications for Success in Conservation and Restoration', Ecosystems, 10, pp. 1311–1322. Available at: https://doi.org/10.1007/s10021-007-9099-7.

Mercury Concentration and Its Trophic Dynamic in a Dominant Antarctic Zooplankton Species with a Focus on the Krill Euphausia Superba

E. Korejwo[1]*, A. Panasiuk[2], J. Wawrzynek-Borejko[3], A. Jędruch[1], J. Bełdowski[1], A.Paturej[4], M. Bełdowska[4]

[1]Polish Academy of Sciences, Institute of Oceanology, ul. Powstańców Warszawy 55, 81-712 Sopot, Poland
[2]University of Gdansk, Faculty of Oceanography and Geography, Al. Piłsudskiego 46, 81-378 Gdynia, Poland
[3]University of Gdansk, Faculty of Oceanography and Geography, Al. Piłsudskiego 45, 81-378 Gdynia, Poland
[4]University of Gdansk, Faculty of Oceanography and Geography, Piłsudskiego 45, 81-378 Gdynia, Poland

ewakorejwo@iopan.pl

The Antarctic is the most isolated region in the world, nevertheless, it has not avoided the negative impact of human activity, including inflow of toxic mercury (Hg). Hg deposited in the Antarctic marine environment can be bioavailable and accumulate in the food web, reaching elevated concentrations in the high-trophic-level biota, especially if methylated. Zooplankton, together with phytoplankton, is critical for the transport of pollutants, including Hg to higher trophic levels. For the Southern Ocean ecosystem, one of the key zooplankton components is the Antarctic krill Euphausia superba, smaller euphausiid Thysanoessa macrura, and amphipod Themisto qaudichaudii - crucial food source for most predatory fish, birds, and mammals. The main goal of this study was to determine the Hg burden, as well as the distribution of different Hg forms, in those dominant Antarctic planktonic crustaceans.

The results showed that the highest concentrations of Hg were found in T. gaudichaudii, a typically predatory taxon. Most of the Hg in the crustaceans tested was labile and potentially bioavailable for planktivorous organisms, with the most dangerous methylmercury (MeHg), which accounted for an average of 16% of total mercury. Elevated Hg concentrations were observed close to the land, which is influenced by the proximity to penguin and pinnipeds colonies. In areas near the shore, volcanic activity might be a possible cause in the increase of the content of mercury sulfide (HgS). The total Hg concentration increased with the trophic position and ontogenetic stage of predation, specific to adult organisms. In contrast, the proportion of MeHg decreased with age, indicating more efficient demethylation or elimination. The Hg magnification kinetics in the study area were relatively high, which may be related to the climate-change-influenced alteration of the Antarctic ecosystem: additional food sources and reshaped trophic structure.

References

Cabrita, M. T. et al. (2017) 'Evaluating trace element bioavailability and potential transfer into marine food chains using immobilised diatom model species Phaeodactylum tricornutum, on King George Island, Antarctica.', Marine Pollution Bulletin 121:192-200. https://doi.org/10.1016/j.marpolbul.2017.05.059.

Cossa D. et al. (2011) 'Mercury in the Southern Ocean.', Geochimica et Cosmochimica Acta 75:4037-4052. https://doi.org/10.1016/j.gca.2011.05.001.

Sedimentary Records of POPs and Heavy Metals in Concepción Bay, Central Chile

K. Pozo[1,2]*, V. Gómez[3], C. Galbán-Malagón[3], A. Rudolph[4], R. Ahumada[4], P. Přibylová[1],
J. Kuta[1], O. Audy[1], R. Urrutia[5], M. Salamanca[6], G. Lammel[7], B. Vrana[1], J. Klánová[1]

[1]Masaryk University, Faculty of Science, RECETOX, Kamenice 5, 62500 Brno, Czech Republic
[2]Universidad San Sebastián, Facultad de Ingeniería, Arquitectura y Diseño, Concepción 4080871, Chile.
[3]Universidad Mayor, GEMA Center for Genomics, Ecology & Environment, Santiago 8580745, Chile
[4]Universidad Católica Santísima Concepción, Facultad de Ciencias, Concepción 4090541, Chile
[5]Universidad de Concepción, Facultad de Ciencias Ambientales/Centro EULA, Concepción, Chile
[6]Universidad de Concepción, Laboratorio de Oceanografía Química, Concepción, Chile
[7]Max Planck Institute for Chemistry, Multiphase Chemistry Dept., Mainz, Germany

karla.pozo@recetox.muni.cz

In this study we assess the environmental health status of Concepción Bay (36°40'S, 73°01'W), Chile, using sedimentary records. In the early 1980s the bay underwent rapid industrial development because hosted the main fishing industrial development and the biggest shipyard construction/repair activities of the country (since 1970). Furthermore, the bay received the wastewater of Concepción and Talcahuano commune. This enhanced the degradation of the marine environment. A sediment core was taken within the bay, cut in slices (1-25 cm) and analyzed for persistent organic pollutants (DDX, HCHs, PBDEs, PFAS) (using GC-MS/MS), heavy metals (As, V, Cr, Mo, Co, Ni, Cu, Zn, Cd, Pb, Hg) (ICP-MS) and for radioisotopes (^{210}Pb, constant rate supply dating). The core encompasses the years 1930-2014. Results showed the following decreasing concentrations (ng (g dw)$^{-1}$) pattern: Σ_{21}PFASs (1.8±0.5), Σ_{10}PBDEs (0.46±1.1) (BDE209 accounting for >95%), Σ_{16}PAHs (78±13), retene (5.5±2), Σ_7PCBs (3.1±3.4), Σ_6DDX (0.6±0.4), and Σ_4HCH (0.4±0.3). For inorganic chemicals, levels (mg kg^{-1}) were As (19±2), V (130±10), Cr (49±1), Mo (9.3±1), Co (9±0.5), Ni (19±0.6), Cu (37±4.3), Zn (81±6.3), Cd (3.6±0.6), Pb (24±3), Hg (0.12±0.05): Total organic carbon (TOC) was also measured (2±0.1%). The sedimentation rates, based on ^{210}Pb activities, were rather constant in the last 40 years (0.51±0.87 µg m^{-2} yr^{-1}). In general, the estimated fluxes showed two high values at the top of the sediment core (at 1 and 4 cm depth, corresponding to 1995). Except for some of the inorganic contaminants, these concentrations are low in comparison with historical organic contamination patterns of highly industrialized coastal environments in the northern hemisphere. Further research is needed to assess the implementation of national or international regulations i.e., the implementation of the Stockholm Convention.

Assessment of Mechanisms of Behavioral Toxicity of Tire Rubber-Derived Chemicals Using Zebrafish as Model Species

N. Alvarez-Vigata[1], M. Faria[2], N. Montemurro[2]*

[1]Department of Chemical Engineering and Analytical Chemistry, University of Barcelona, Barcelona, Spain
[2]ONHEALTH Group, Department of Environmental Chemistry, IDEA-CSIC, Jordi Girona 18-24, Barcelona, Spain

nmoqam@cid.csic.es

Stormwater runoff is generated from rain and snowmelt that flows over land or impervious surfaces, such as paved streets, parking lots, and building rooftops carrying different anthropogenic pollutants directly into streams and rivers which are harmful to the health and reproduction of aquatic life. Chemical composition of these waters also includes tire ware particles (TWPs), which have very recently become a hot topic of scientific and public interest. TWPs are generated by abrasion due to the interaction between the tire tread and the road surface. Although TWPs have been produced since the 1960s, they are increasingly recognized as important sources of contamination to air, soil, water and biota. Associated with the TWPs are numerous tire rubber additives (TRAs) and TPs, such as several N,N'-substituted p-phenylenediamines (PPDs), which are currently manufactured and widely used as antioxidants and antiozonants in the rubber industry. Specifically, 6-PPD –one of the main TRAs– is used almost universally in tire manufacturing and also in other products. Recently, a TP of this compound, 6-PPD-Quinone, has been found to be the cause of the acute mortality of coho salmon in Canada. In fact, the process of tire degradation by atmospheric agents or aging can lead to the breaking of the polymer-additive bonds with the consequent release of more toxic additives with more significant ecological risks. However, as it is an emerging concern, still toxicological information is lacking, and the existing data is largely based on acute toxicity studies. As behaviour is a much more sensitive indicator of toxicity than mortality, the aim of this project would be to investigate the behavioural toxic effects of five TRAs (N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine (6PPD) and its degradation product 6PPD-Q; hexa(methoxymethyl)melamine (HMMM), 1,3-Diphenylguanidine (DPG) and 1,3-Di-o-tolylguanidine), using the vertebrate model species, the zebrafish (Danio rerio). Surface water samples will be also investigated during rain events to evaluate the presence and environmental concentration of several TWPs using suspect and non-target screening approaches.

References

Ricarte, M. et al. (2023) Environmental concentrations of the tire rubber derived 6-PPD quinone alter CNS function in zebrafish larvae, Science of the Total Environment (STOTEN-D-23-07369, under revision)

In Vitro Effects of Low-Density Polyethylene Micro(Nano)Plastics on Human Airway Epithelium

A. Vailionytė[1,2], T. Jelinskas[2], I. Uogintė[3], S. Byčenkienė[3], R. Aldonytė[1]

[1]Department of Regenerative Medicine, State Research Institute Centre for Innovative Medicine, Lithuania
[2]Department of Nanoengineering, State research institute Center for Physical Sciences and Technology, Lithuania
[3]Department of Environmental Research, State research institute Center for Physical Sciences and Technology, Lithuania

Micro(nano)plastics (MNPs) are defined as plastic particles with a diameter of <5 mm for microplastics, and <1 µm for nanoplastics. MNP pollution has become a major concern worldwide, with the potential to cause adverse health effects. Airborne MNPs have been found in various environmental matrices, including the air we breathe. Recent studies have shown that micro(nano)plastics can penetrate deep into the human lungs reaching the alveolar regions (Jenner et al., 2022). The limited data available on the effects of airborne MNP on pulmonary toxicity highlights the urgent need for more research in this field. Low-density polyethylene (LDPE) is a commonly used plastic material that can degrade into micro(nano)plastic particles. It is among the most common polymers detected in atmospheric dust (Lwanga et al., 2023). However, current in vitro research on micro(nano)plastics' cellular effects is mostly focused on polystyrene beads. Therefore, in this study, we aimed to investigate the biological impact of less explored LDPE MNPs of various shapes and sizes on human airway epithelium.

LDPE MNP was produced via the degradation of LDPE granules (laboratory standard), producing MNPs of different sizes and shapes similar to native atmospheric plastic particles. Human bronchial epithelial cells BEAS-2B were exposed to different concentrations of LDPE MnP for 24 and 48 hours. After exposure, intracellular particle distribution, cell viability, morphology, and metabolic response were evaluated using various assays. Our results showed that exposure to LDPE micro(nano)plastic particles resulted in a significant decrease in cell viability and proliferation at higher concentrations. Furthermore, exposure to LDPE MNP altered cell morphology causing epithelial cell elongation and significant change in cell shape index. Atomic force microscopy was employed to observe the intracellular distribution of MNP. Moreover, the altered energy metabolism induced by LDPE MNP was confirmed by a Seahorse Real-Time Cell Metabolic analysis.

In conclusion, these findings suggest that exposure to LDPE micro(nano)plastic particles may adversely affect human airway epithelium by interacting with the cellular membrane, inducing phenotype change, reducing viability, and changing the regular cell metabolism. Further studies are needed to determine the long-term effects of exposure to LDPE MNP on human health and the environment. This study highlights the importance of reducing plastic waste and implementing sustainable practices to protect public health and the environment.

References

Jenner, L.C., Rotchell, J.M., Bennett, R.T., Cowen, M., Tentzeris, V., Sadofsky, L.R. Detection of microplastics in human lung tissue using µFTIR spectroscopy. Sci Total Environ. 2022 Jul 20;831:154907.

Lwanga, E.H., van Roshum, I., Munhoz, D.R., Meng, K., Rezaei, M., Goossens, D., Bijsterbosch, J., Alexandre, N., Oosterwijk, J., Krol, M., Peters, P., Geissen, V., Ritsema, C. Microplastic appraisal of soil, water, ditch sediment and airborne dust: The case of agricultural systems. Environ Pollut. 2023 Jan 1;316(Pt 1):120513.

The Use of Zebrafish as an Ever-Expanding Model in Ecotoxicology, Drug Research and Human Diseases Treatment

E. Santos[1], O. Ribeiro[1,2,3], A. R. Lado Ribeiro[4,5]*, C. Ribeiro[3,6], and J. S. Carrola[1,2]

[1]University of Trás-os-Montes and Alto Douro, Vila Real, Portugal
[2]CITAB/Inov4Agro, University of Trás-os-Montes and Alto Douro, Vila Real, Portugal
[3]TOXRUN, University Institute of Health Sciences, CESPU, CRL, Gandra, Portugal
[4]LSRE-LCM, FEUP, Faculty of Engineering, University of Porto, Portugal
[5]ALiCE, Faculty of Engineering, University of Porto, Porto, Portugal
[6]CIIMAR, University of Porto, Matosinhos, Portugal

ritalado@fe.up.pt

Currently, the zebrafish (*Danio rerio*) is a widely used model in ecotoxicology to study several toxic compounds, including psychoactive substances and illicit drugs. Lots of pollutants reach the environment and thus, it is important to assess accurate risk assessment, zebrafish being a useful model (Stegeman et al., 2010).

Additionally, it is an organism widely used in the research and development of drugs against numerous human diseases, since it has high genetic and physiological homologies with humans (70%), transparent embryos, reduced size and costs, short generation time (fast development). It is also used for large-scale genetic mutant and therapeutic compound screenings, and other biomedical research applications. Also, zebrafish has a high degree of genetic, anatomical, and physiological similarities to humans, with over 80% of disease-causing human proteins have an orthologue in zebrafish (Teame et al., 2019) Zebrafish is being increasingly used as disease model for biomedical research, mainly in developmental disorders (bone, cardiovascular, renal, blood and cancer) (Adhish et al., 2023), mental disorders, and metabolic diseases (nonalcoholic fatty liver disease, type 2 diabetes mellitus, dyslipidemia, and other hepatic diseases) [4]. The use of CRISPR/cas 9-based approaches and the various technological developments in zebrafish are expanding and improving their numerous applications like knockouts, introduce specific changes in the genome and repair mutant alleles, transcriptional regulation, in vivo chromatin imaging, epigenome modulation, genome-wide knockout screens, etc.

The objective of this study was to carry out a mini-bibliographic review related to the increasing use of zebrafish model to assess aquatic ecotoxicity, and also as an expanding model to understand human diseases and improve their treatment.

An online scientific literature search was performed using the PubMed and ScienceDirect search engines by searching for: “zebrafish”, “human diseases” and “treatments”.

This model is widely used and each year more research in done with embryo, juveniles and also adults as a useful tool to better understand environmental toxic effects, drugs development understanding, the progression of diverse diseases and mechanisms, and also to be used for more precise and personalize disease treatment.

Acknowledgments: This work was financially supported by project PTDC/CTA-AMB/6686/2020 (ENANTIOTOX) and also supported by: UIDB/04033/2020 (CITAB/Inov4Agro), LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), all funded by national funds through FCT/MCTES (PIDDAC), and 2022.00184.CEECIND funded by FCT. Ondina Ribeiro thanks FCT for the PhD Grant 2022.12242.BD.

References

Teame, T. et al. (2019) The use of zebrafish (Danio rerio) as biomedical models. Animal Frontiers 9(3): 68-77. doi: https://doi.org/10.1093/af/vfz020.

Stegeman, J. J. et al. (2010) Perspectives on zebrafish as a model in environmental toxicology. In Fish Physiology, Vol. 29, 367-439: Elsevier. doi: https://doi.org/10.1016/S1546-5098(10)02910-9.

Adhish, M. et al. (2023) Effectiveness of zebrafish models in understanding human diseases—A review of models. Heliyon 9(3): e14557. doi: https://doi.org/10.1016/j.heliyon.2023.e14557.

Enantiotoxicity of Butylone on Zebrafish Larvae Behaviour - Preliminary Data

O. Ribeiro[1,2], L. Félix[1], C. Ribeiro[2,3], M.E. Tiritan[2,3,4] A.R. Lado Ribeiro[5,6]*, and J.S. Carrola[1]

[1]CITAB/Inov4Agro, University of Trás-os-Montes and Alto Douro, Vila Real, Portugal
[2]TOXRUN, University Institute of Health Sciences, CESPU, CRL, Gandra, Portugal
[3]CIIMAR, University of Porto, Matosinhos, Portugal
[4]LOPC, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Portugal
[5]LSRE-LCM, FEUP, Faculty of Engineering, University of Porto, Portugal
[6]ALiCE, Faculty of Engineering, University of Porto, Porto, Portugal

ritalado@fe.up.pt

Each year, new psychoactive substances (NPS) are identified and their consumption cause indirectly their detection in aquatic environments (Shafi et al., 2020). Butylone (BTL) is a chiral synthetic cathinone present in water bodies (concentration of 0.01 µg/L), and this NPS and its enantiomers may exhibit different biological activities (Spálovská et al., 2018) and adverse effects in non-target organisms, such as fish. However, until now, no research study has been found regarding its enantiotoxic effects in fish, like *Danio rerio*. This small vertebrate is a valorous animal model in aquatic toxicology, used to investigate the potential adverse effects of different toxins during early-life stages (Ribeiro et al., 2023). The main objective of this work was to evaluate the possible toxic effects of BTL on zebrafish larvae behaviour, as well as to assess the potential enantiotoxicity. *D. rerio* embryos with approximately 3 hours post-fertilization (hpf) were exposed until 96 hpf (in triplicate) to different concentrations of (*R*,*S*)-BTL, (*R*)-BTL and (*S*)-BTL (0.01, 0.1, 1, 10 and 100 µg/L). At 120 hpf, the following behavioural parameters were assessed in larvae: speed, distance to the centre of the well, absolute turn angle, total distance moved, and active time. No significant effects were observed on the behavioural parameters evaluated for racemate and both enantiomers. Additionally, no enantioselective effects were observed. These findings suggest that the exposure to environmentally relevant concentrations of BTL during early life stages of zebrafish does not affect the behaviour of this species at later stages. Further research is necessary to study the effects of BTL on fish under chronic exposure to estimate the potential impacts on wild fish populations and improve risk assessment considering simultaneous multiple exposure to diverse NPS.

Acknowledgments: This work was financially supported by project PTDC/CTA-AMB/6686/2020 (ENANTIOTOX) and also supported by: UIDB/04033/2020 (CITAB/Inov4Agro), LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), UIDB/04423/2020 and UIDP/04423/2020 (Group of Marine Natural Products and Medicinal Chemistry, CIIMAR), all funded by national funds through FCT/MCTES (PIDDAC), and 2022.00184.CEECIND funded by FCT. Ondina Ribeiro thanks FCT for the PhD Grant 2022.12242.BD.

References

Shafi, A. et al. (2020). New psychoactive substances: a review and updates. Therapeutic advances in psychopharmacology 10: 2045125320967197. doi: https://doi.org/10.1177/2045125320967197.

Spálovská, D. et al. (2018). Structure determination of butylone as a new psychoactive substance using chiroptical and vibrational spectroscopies. Chirality 30(5): 548-559. doi: https://doi.org/10.1002/chir.22825.

Ribeiro, O. et al. (2023). Effects of acute metaphedrone exposure on the development, behaviour, and DNA integrity of zebrafish (Danio rerio). Environmental Science and Pollution Research: 1-10. doi: https://doi.org/10.1007/s11356-023-25233-z.

Zebrafish Embryos (*Danio rerio*) as a Model for the Evaluation of Teratogenicity Caused by Toxics and Psychoactive Substances

O. Ribeiro[1,2], L. Félix[1], S.M. Monteiro[1], C. Ribeiro[2,3], A. Fonteínhas-Fernandes[1], M.E. Tiritan[2,3,4], A.R. Lado Ribeiro[5,6]* ,
and J.S. Carrola[1]

[1]CITAB/Inov4Agro, University of Trás-os-Montes and Alto Douro, Vila Real, Portugal
[2]TOXRUN, University Institute of Health Sciences, CESPU, CRL, Gandra, Portugal
[3]CIIMAR, University of Porto, Matosinhos, Portugal
[4]LOPC, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Portugal
[5]LSRE-LCM, FEUP, Faculty of Engineering, University of Porto, Portugal
[6]ALiCE, Faculty of Engineering, University of Porto, Porto, Portugal

ritalado@fe.up.pt

The use of vertebrate animal models in research has contributed greatly to the understanding of human physiological processes and human diseases, namely teratogenesis effects, which has led to their increased use to this day (Franco, 2013). In the last two decades, there has been a growing interest in the use of alternative vertebrate models, considering the principle of the 3 R's proposed by William Russell and Rex Burch in 1959 (Russel et al., 1959). In this way, zebrafish (*Danio rerio*) is an alternative vertebrate model to rodents (and other vertebrate models) in research. The easy observation of embryonic development (semitransparent chorion and embryo) and the fact that the early stages of life are not classified as experimental animals according to European Union guidelines 2010/63/EU, highlights the ethical advantages in assessing the teratogenic potential of chemical compounds (Raghunath et al., 2018). Despite the increase in the use of early-life stages of *D. rerio* for teratogenic assessment, there is a high variation between the endpoints evaluated and the nomenclature used in the numerous studies analyzed. This heterogeneity reflects the importance for a better standardization of the classification system to compare data. Additionally, there is a lack in the assessment of the final severity of different teratogenic effects evaluated in several studies, making it necessary to implement a methodology to assign a severity score to the different zebrafish endpoints to define whether a compound can be considered teratogenic or not, through a teratogenic index. Thus, we review some of the methodologies used to assess malformations in *D. rerio*, the different endpoints that can be used and the different systems of classifying the severity of malformations.

Acknowledgments: This work was financially supported by project PTDC/CTA-AMB/6686/2020 (ENANTIOTOX) and also supported by: UIDB/04033/2020 (CITAB/Inov4Agro), LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), UIDB/04423/2020 and UIDP/04423/2020 (Group of Marine Natural Products and Medicinal Chemistry, CIIMAR), all funded by national funds through FCT/MCTES (PIDDAC), and 2022.00184.CEECIND funded by FCT. Ondina Ribeiro thanks FCT for the PhD Grant 2022.12242.BD.

References

Franco, N. H. (2013). Animal experiments in biomedical research: a historical perspective. Animals 3 (1): 238-273. doi: https://doi.org/10.3390/ani3010238.

Russel, W. M. S et al. (1959). The principles of humane experimental technique. The Principles of Humane Experimental Technique. London: Methuen & Co. Special edition published by Universities Federation for Animal Welfare (UFAW), 1992.

Raghunath, A. et al. (2018). Analysis of lethality and malformations during zebrafish (*Danio rerio*) development. Teratogenicity testing: methods and protocols: 337-363. doi: https://doi.org/10.1007/978-1-4939-7883-0_18.

Prevalence of Veterinary Antibiotics in Fertilizers from Animal Food Production and Assessment of Their Potential Ecological Risk

E. Patyra[1*], C. Nebot[2], R. Elvira Gavilán[2], K. Kwiatek[1], A. Cepeda[2]

[1]National Veterinary Research Institute, Department of Hygiene of Animal Feedingstuffs,
24 – 100 Pulawy, Poland
[2]Department of Analytical Chemistry, Nutrition and Bromatology, Faculty of Veterinary Medicine, University of Santiago de Compostela, Lugo 27002, Spain

ewelina.patyra@piwet.pulawy.pl

Livestock feces and liquid manure are used as land fertilizer for its high levels of phosphorus, nitrogen and organic matter that can improve the physical and chemical properties of soil and provide essential nutrients to plants [7]. Application of manure as fertilizer is a common practice in many countries including those of the European Union countries. Residues of antibiotics excreted and present in the animal manures/feces enter into the environment either by spreading of livestock wastes onto agricultural fields as fertilizer or in form of sludge after manure collection and storage. Antibiotics present in manures/feces can be a risk for humans and the environment. Therefore, work was undertaken on the occurrence of antibiotics in fertilizers. for this purpose, in the first stage of the research, an analytical method was developed using LC-MS for the analysis of selected antibiotics tiamulin (TIAM), tetracycline (TC), oxytetracycline (OXT), doxycycline (DC), chlortetracycline (CTC), ciprofloxacin (CIP), tylosine (TYL), lincomycin (LINCO), enrofloxacin (ENR), trimethoprim (TRIM) in the concentration range from 25 to 1500 ug/kg depending on the analyzed substance. The second stage of the work was the analysis of natural and organic fertilizers from Poland and Spain. In total, 70 samples were analyzed, of which 49 were pig feces, 3 poultry manure, 4 pig liquid manure and 14 digestate from the biogas factory. The presence of antibiotics was detected in 18 fertilizer samples. The most often antibacterial substance detected in the analyzed samples was doxycycline but also we found oxytetracycline, tetracycline, chlortetracycline, enrofloxacin, tiamulin and lincomycin. The concentration range for the detected antibiotics was from 0.05 to 175.4 mg/kg The next step of the work was to conduct an environmental risk analysis and determine the Risk Quotient value for fertilizer samples in which antibiotics were found.

Our research has shown that The presence of OXT, TC, LINCO, and ENR was seen to not pose serious ecological risks as predicted by the lower RQ value (<0.1); however, TIAM and DC RQ values showed medium to high ecological risk. Possible medium risk due to DC and TIAM was in the range of 24% as shown by the RQ value of 0.1 – 1.0. Therefore, possible adverse effects on TIAM and DC can be expected after the application of manure in soil and long-term application of manure containing doxycycline should be avoided. Our results suggest that regular monitoring of antibiotics in fertilizers is needed to prevent the risk from excessive use of antibiotics in the livestock and proper management of their discharges to the environment.

References

Patyra E., Kwiatek K., Nebot C., Gavilán R.E. (2020) Quantification of Veterinary Antibiotics in Pig and Poultry Feces and Liquid Manure as a Non-Invasive Method to Monitor Antibiotic Usage in Livestock by Liquid Chromatography Mass Spectrometry Molecules. 25, 3265; doi:10.3390/molecules25143265.

HPLC-FLD Method for the Detection of Sulfonamides in Natural and Organic Fertilizers Collected from Poland

Z. Osiński[1], E. Patyra[1*], K. Kwiatek[1]

[1]Department of Hygiene of Animal Feedingstuffs, National Veterinary Research Institute, Partyzantow 57, 24 – 100 Pulawy, Poland

ewelina.patyra@piwet.pulawy.pl

Antibacterial substances such as sulfonamides are used all around the world for treatment in human therapy and veterinary medicine. After the administration of antibiotics, between 30% and 90% of the initial dose given is excreted. Thus, poultry droppings, pig feces and liquid manure, used as fertilizer for agricultural land, are often contaminated with antibiotics. Little is known about concentrations and the fate of antibiotics in manure and soil. These parameters are of great importance when evaluating the role of contaminated manure in the spread of antibiotic agents into the environment and assessing the risk of water and food contamination through this pathway. Nevertheless, manure is the source of a significant part of veterinary drug pollution in the environment and is currently not actively monitored. Therefore, a chromatographic method with a fluorescence detector was developed for the determination of sulfonamides (sulfaguanidine, sulfadiazine, sulfamerazine, sulfamethazine and sulfamethoxazole) in natural and organic fertilizers in order to determine the frequency of these antibacterial substances and their quantification in poultry and pig feces, slurry and digestates. The method was validated according to EU requirements. Using the HPLC-FLD method for all analyzed matrices, recoveries were satisfactory (77.00–121.16%). The limit of detection and limit of quantification were 13.53–23.30 and 26.02 –40.38 µg/kg, respectively, depending on the analyte. The forty-four samples of natural and organic fertilizers were analyzed, in four samples showed sulfamethoxazole in the amount from range 158 to 11070 µg/kg. Our results showed that sulfonamides in animal feces samples were not detected frequently, but the concentrations are comparable to published research results by other scientists around the world. The results may also indicate that other antibiotics are used more often than sulfonamides in Poland, e.g., tetracycline antibiotics. The results of the research indicate that the presence of antimicrobial substances in natural and organic fertilizers should be monitored before introducing them to farmland. The amounts of sulfamethoxazole found in the present study could have an ecotoxic effect on the microbiota inhabiting land and surface waters and could be absorbed by crops.

References

Berendsen B.J.A. et al., (2015). The analysis of animal faeces as a tool to monitor antibiotic usage. Talanta, 132, 258–268.

Osiński Z. et al., (2022).HPLC-FLD-Based Method for the Detection of Sulfonamides in Organic Fertilizers Collected from Poland. Molecules, 2022, 27, 2031. https://doi.org/10.3390/molecules27062031.

Benzo[*C*]Fluorene - A Highly Toxic but not Systematically Analyzed Polycyclic Aromatic Hydrocarbon

Jan T. Andersson[1]

[1]Institute of Inorganic and Analytical Chemistry, University of Münster, Münster, Germany

Polycyclic aromatic hydrocarbons (PAHs) are routinely analyzed in environmental samples of the most various kinds because of the well-known adverse properties, including carcinogenicity, of several PAHs. However, even in studies devoted to human health issues, very often benzo[*c*]fluorene (BcF) is not included, even though it is one of the most carcinogenic PAHs known. It has been assigned a toxic equivalence factor of 20, meaning it has a toxic potential 20 times that of benzo[*a*]pyrene (BaP). Its concentration is often similar to that of BaP, meaning that it has a major effect on the toxicological profile of such a sample. This omission obviously leads to an irresponsible underestimate of the toxic properties of the sample.

This contribution will look at the occurrence of BcF in different kinds of environmental matrixes, published in the literature, and review its contribution to the carcinogenic potential of samples, In some of them BcF accounts for 90% of the toxic equivalence concentration of the total PAH load. It will thus become clear that without consideration of this compound, any conclusions as to possible health hazards will be quite erroneous. The compound is included in the European Union’s set of 15+1 PAHs to be analyzed in food but it is not on the EPA list of priority PAHs.

The conclusion of this overview is obvious: To rectify this situation and to obtain more realistic risk assessments, this compound should be routinely included in all environmental PAH analyses, especially when an estimate of health hazards is the goal of such a study. At the same time, a review of the toxic equivalence factor of 20 through more experimental work is called for.

Growth and Development of Satureja Hortensis on as and Cd Contaminated Soils. Accumulation of Toxic Metals in Different Organs of the Plant

C. Dinu[1], A.G.Tenea[1], G.G.Vasile[1*], V.I.Iancu[1], L.E.Barbulescu[1]

[1]National Research and Development Institute for Industrial Ecology ECOIND, Pollution Control Department, 57-73 Drumul Podul Dambovitei Street 57-73, 060652, Bucharest, Romania

gabriela.vasile@incdecoind.ro

Metal toxicity is one of the main environmental risk that block the normal development and metabolic processes of plants.This has become a significant threat to the natural bio-geo-chemical cycle and the food chain (Haider F.U., et al. 2021). In plants, arsenic behaves similarly to phosphorus. The content of cadmium in medicinal plants is very important due to the very high degree of toxicity as well as the effects on human health (Anjitha K.S. et al, 2021). Thyme is an aromatic plant from the Satureja genus, Laminaceae family, very often used both as a spice and for medicinal purposes. This study was carried out in order to evaluate the bioaccumulation of As and Cd in the root, stem, leaves and flowers of thyme grown on a soil that was enriched with the elements of interest. In order to carry out the experiments, thyme seeds were planted in the mini greenhouse, in universal soil and watered with tap water. A physical-chemical characterization was carried out for the seeds that were planted, to the soil and the tap water that was used to water the plants. After the seedlings appeared, they were planted in pots containing As and Cd polluted soil. The experiments carried out were: As (15 mg/kg), Cd (3 mg/kg) and AsCd (As 15 mg/kg, Cd 3 mg/kg). The concentrations of metals added to the soil were chosen so as to exceed the alert threshold in Romanian Order 756/1997. In addition to the experiments carried out on the polluted soil, control experiments were also carried out. All the experiments were realized in three different pots in which 15-20 seedlings were planted. After the plants bloomed (3 months after cultivation), the concentration of As and Cd was determined by optical emission spectrometry with inductively coupled plasma (ICP-OES).To evaluate the plant's ability to accumulate metals from the soil and translocate them from the root to the aerial parts (stem, leaves, flowers) the following coefficients were calculated:the bioaccumulation factor (BCF) and transfer factors (TF). BCF is calculated as a ratio of metal concentration in the root and metal concentration in the soil. TF represents the ratio between metal concentration in the aerial parts of the plant and metal concentration in the root of the plant. To ensure the quality and validity of the results, a certified reference material containing traces of the elements in lichen powder was used (BCR-482, IRMM Geel, Belgium). The obtained results show that arsenic accumulates only in the root of the plant unlike cadmium which exceeds the phytotoxic concentration (10 mg/kg) in all experiments, both in the root and in the edible parts of the plant (stem, leaves, fores), the highest concentration being in the AsCd experiment (14.28 mg/kg). For the experiment in which only Cd was added, the maximum concentration was found in the leaves (11.09 mg/kg). The bioaccumulation (BCF) and transfer indices from the root to the aerial parts of the plant indicate bioaccumulation (BCF>1) only for cadmium and a transfer of this element (TF>1) from the root to the leaves only in the experiment in to which cadmium was added in combination with arsenic.

References

Haider, F.U., et al., (2021) 'Cadmium toxicity in plants: impacts and remediation strategies', Ecotoxicol. Environ. Saf. 211, 111887. doi.org/10.1016/j.ecoenv.2020.111887.

Anjitha, K.S. et al, (2021) 'Functional aspects of plant secondary metabolites in metal stress tolerance and their importance in pharmacology', Plant Stress, 2, 100038. doi.org/10.1016/j.stress.2021.100038.

Acknowledgment:
The authors acknowledge the financial support offered by the Ministry of Research, Innovation and Digitization of Romania through the Romanian National Research Program “Nucleu” through contract no. 20N/2019, Project code PN 19 04 01 01.

The Case of Ponce-Enríquez ASGM District in Ecuador: Trace Metal Distribution and Movement in a Mixed Land Use Landscape

J.L. Rivera-Parra[1]*, P. Vargas [2], C. Ramos [2], Masayuki Sakakibara [3] [4] and X. Diaz [5]

[1]Escuela Politécnica Nacional, Departamento de Petróleos, Quito 170525, Ecuador
[2]Escuela Politécnica Nacional, Departamento de Ciencias Nucleares, Quito 170525, Ecuador
[3]Ehime University, Faculty of Collaborative Regional Innovation, Matsuyama 790-8577, Japan
[4]Research Institute for Humanity and Nature, Kyoto 603-8047, Japan
[5]Escuela Politécnica Nacional, Departamento de Metalurgia Extractiva, Quito 170525, Ecuador

jose.riverap@epn.edu.ec

Understanding contaminants distribution and movement is critical in the case of mixed-land use landscapes, where different, and sometimes competing, activities co-exist. Such is the case of the Ponce-Enríquez mining district in south-western Ecuador; where artisanal and small gold mining (ASGM) occurs in the headwaters of a river basin that irrigates cocoa and banana plantations. ASGM practices encompass several stages where contaminants may enter the ecosystem, mainly trace metals (i.e. Hg, Cd, Cr, Pb, As, Mn) and organic compounds used in gold processing (i.e. xanthates).

Our main objective is to understand the distribution and movement of ASGM related contamination. So far, we have: 1) analyzed the concentration of trace metals in different environmental partitions (i.e. water, sediment, soil, crops, human hair), 2) conducted specific experiments to analyze native plants as potential trace metal hyperaccumulators to be used for phytoremediation projects, in collaboration with the local miners, 3) analyzed the sustainability of cocoa-bean production in the area, in relation to trace metal pollution. The samples were collected and analyzed following standard protocols and methods, including ICP-MS (protocols in Ramos *et al*., 2022).

Our results show widespread Hg, As, Cd and Pb distribution in the different environmental partitions, including evidence of high concentrations oh Hg in the hair from the local population. The distribution of Hg follows a pattern related to ASGM activities and Hg-Au amalgam burning. Moreover, water from shallow wells, used for human consumption, showed an elevated Mn content.

In the case of cocoa, it shows high Cd affinity, with a differential accumulation across different tissues. Cocoa trees do not absorb Hg or As, which are present in high concentration in the soil the plants are growing in. We tested removing the inner-most husk of the cocoa-bean to lower the final Cd content, with negligible results. Thus, production of cocoa in contaminated soils will end up with concentrations that may exceed the export and safety Cd standards. Bananas, did not show increased trace metal content, independent on the concentrations of the plant growing substrate.

We tested 6 different native plant species to test their potential as trace metal hypperaccumulators. Two of them, umbrella papyrus (*Cyperus alternifolius*) and rushes (*Juncus* sp), showed positive accumulation rates for Hg, Cd, Mn and Cr. The peak accumulation and mass increase was at about 3 months. These results are being implemented by the local miners as part of an artificial-wetland water treatment system, which will reduce the trace metal load of the local hydric system.

The collaboration with the local stakeholders has opened interesting research opportunities, which include: ecotoxicology of xanthates, ecosystem services and crop productivity, low cost Mn treatment for water for human consumption, and land use planning with the local authorities. Our project highlights the importance of interdisciplinary research conducted in collaboration with the local stakeholders to mitigate environmental impacts and contribute to a more sustainable development.

References

Ramos, C. et al. (2022). Sustainability of Cocoa (Theobroma cacao) Cultivation in the Mining District of Ponce Enríquez: A Trace Metal Approach. International Journal of Environmental Research and Public Health, 19(21), 14369. https://doi.org/10.3390/ijerph192114369.

Hazard Characterization of Tire Particles with Combined Calux and HPTLC-Bioassay Analysis

A.J. Bergmann[1*], T. Masset[2], F. Breider[2], W. Dudefoi[3], K. Schirmer[2,3,4], B.J.D. Ferrari[2,5], E. Vermeirssen[1]

[1]Ecotox Centre, Überlandstrasse 133, 8600 Dübendorf, Switzerland
[2]EPFL, School of Architecture, Civil and Environmental Engineering, Lausanne, 1015, Switzerland
[3]Eawag, Department Environmental Toxicology, Überlandstrasse 133, 8600 Dübendorf, Switzerland
[4]ETHZ, Institute of Biogeochemistry and Pollutant Dynamics, Zurich, 8092, Switzerland
[5] Ecotox Centre - EPFL ENAC IIE, GE, Station 2, CH-1015 Lausanne, Switzerland

alanjames.bergmann@oekotoxzentrum.ch

Tire and road wear particles (TRWP) are generated during normal use of cars and trucks. Subsequently, there is potential for chemicals to leach from TRWP into environmental media such as surface water and sediment. Organisms that ingest TRWP may thus be exposed to desorbing chemicals. The chemistry of TRWP is complicated by potential transformation of reactive additives into unknown toxic chemicals. If chemicals originating from TRWP can be characterized, potential toxic effects could be anticipated, and eventually identified toxicants could be monitored and evaluated for risk. Bioanalytical detection can help prioritize chemicals from among many unknowns for subsequent, resource intensive, toxicant identification. Here, we investigate chemical toxicity extracted from TRWP, and leaching into water and simulated fish gut.

Cryogenically milled tire tread (CMTT) as a model for TRWP were extracted into methanol and dichloromethane at 100 g/L. We prepared leachates with 100 g/L CMTT in simulated fish digestive fluid (Masset et al., 2022), and in contact with water/sediment. These aqueous scenarios represent media that are more realistic than extraction but are still well above environmental concentrations of TRWP to help detect and characterize potential hazards. We applied a panel of in vitro bioassays to the extracts and leachates. The target endpoints were aryl hydrocarbon (AhR) and estrogen receptor (ER) activation in CALUX® assays in microtiter plates, and ER activation, DNA damage, and bacterial luminescence inhibition (cytotoxicity) coupled to high performance thin layer chromatography (HPTLC).

Both CALUX endpoints were active in CMTT extracts. Levels of activity were down to 0.03 and 0.001 mg CMTT equivalent for ER and AhR, respectively, corresponding to approximately 0.6 ng/L bioassay medium for positive controls, 17b-estradiol and 2,3,7,8-tetrachlorodibenzodioxin. The extracts also indicated activity for two to four bands per ER activity, DNA damage, and cytotoxicity on HPTLC. This range of effects from CMTT corroborates previous reports for comprehensive extractions of TRWP (Eriksson et al., 2022). Further, despite high CMTT concentrations in aqueous leachates, we detected only ER activity and cytotoxicity in all CMTT leachate samples and, in one leachate, AhR activity. ER activity of digestates was confounded by estrogenicity of simulated digestive fluid itself. However, HPTLC analysis suggested that estrogenic and cytotoxic components of CMTT extracts were also found in aqueous leachates. These specific effects and the unknown responsible chemicals may be prioritized for further analysis.

These results compare CALUX and HPTLC-bioassays for chemicals leaching from TRWP. HPTLC provides more information through chromatography of samples and detection of multiple chemicals, but may be less suited to generating quantitative effect data. More biological endpoints are available in the CALUX format, although the suite of HPTLC-bioassays is growing. Therefore CALUX and HPTLC bioassays complement each other and can be used more broadly in combined or tiered strategies for evaluating materials such as TRWP.

References

Eriksson, U. et al., (2022) 'Examination of aryl hydrocarbon receptor (AhR), estrogenic and anti-androgenic activities, and levels of polyaromatic compounds (PACs) in tire granulates using in vitro bioassays and chemical analysis', Chemosphere, 298, pp. 134362.

Masset, T. et al., (2022) 'Bioaccessibility of Organic Compounds Associated with Tire Particles Using a Fish In Vitro Digestive Model: Solubilization Kinetics and Effects of Food Coingestion', Environmental Science & Technology.

Exposure of Marine Phytoplankton (Isochrysis galbana) to a Mixture of Organophosphate Esters: Impacts on Physiology, Metabolism, and Potential for Bioaccumulation

B. Carr[1], H. B. Gharbia[1], J. L. Rolland[2], M. Metian[1], P. Bersuder[1], I. Tolosa[1]*

[1]IAEA Marine Environment Laboratories, 4a Quai Antoine 1er, 98000 Monaco, Principality of Monaco
[2]MARBEC, Université Montpellier, CNRS, Ifremer, IRD, Sète, France

I.Tolosa@iaea.org

Organophosphate esters (OPEs) are commonly used as flame retardants or plasticizer additives in plastics as well as in other consumer and industrial products. These contaminants of emerging concern have recently come under scrutiny for their potential ecotoxicological effects. Despite their widespread presence in the marine environment, little is known about the effects of OPE exposure on phytoplankton, or the potential for accumulation of OPEs at the base of the marine food web (Amaneesh et al., 2023). This study addressed these questions by exposing the phytoplankton species Isochrysis galbana to a mixture of 11 organophosphate triesters over an 11-day period, using 3 different concentration levels ranging from environmental relevant concentrations (500 ng/l for each OPE) to much higher levels (5000 and 10000 ng/L for each OPE). Non-axenic I. galbana monoclonal cultures were grown in enriched natural seawater culture medium (F/2) at stable conditions (salinity: 40; temperature: 20°C; irradiance: 120 µmol photons $m^{-2}s^{-1}$ in a 12:12 light:dark cycle). Much attention has been paid to I. galbana due to its important nutritional value and application as feed in aquaculture. This species also produces relatively high levels of lipids (Sani et al., 2021), which may increase its capacity to accumulate organic contaminants such as OPEs.

The effects of OPEs on cell growth and production of reactive oxygen species (ROS) were assessed at the 3 different concentrations levels. Concentrations of OPEs were measured in the seawater at the beginning and end to examine how exposure changed over time. Phytoplankton cells were collected at the end of the experiment to observe OPE accumulation in the exposed group relative to the unexposed control. Chemical analysis of OPEs was conducted using gas chromatography – triple quadrupole mass spectrometry. Our results revealed that OPEs have inhibitory effects on the physiology and metabolism of I. galbana, and that the algae bioconcentrates OPEs from the seawater. Among the OPEs, higher bioconcenration factors were achieved for triphenyl phosphate, ethylhexyldiphenyl phosphate, tris(2-ethylhexyl) phosphate, and tritolyl phosphate. This study represents an initial step towards assessing the impacts that these chemicals of emerging concern may have to the health of marine ecosystems, as well as potential hazards to aquaculture and marine food webs.

References

Amaneesh, C. et al. (2023) 'Gross Negligence: Impacts of Microplastics and Plastic Leachates on Phytoplankton Community and Ecosystem Dynamics', Environmental Science & Technology, 57(1), pp. 5–24. Available at: https://doi.org/10.1021/acs.est.2c05817

Sani, E.R.A. et al. (2021) 'Growth and Lipid Production of Isochrysis galbana in an Upscale Cultivation System', Transactions on Science and Technology, 8(3–2), pp. 203–209

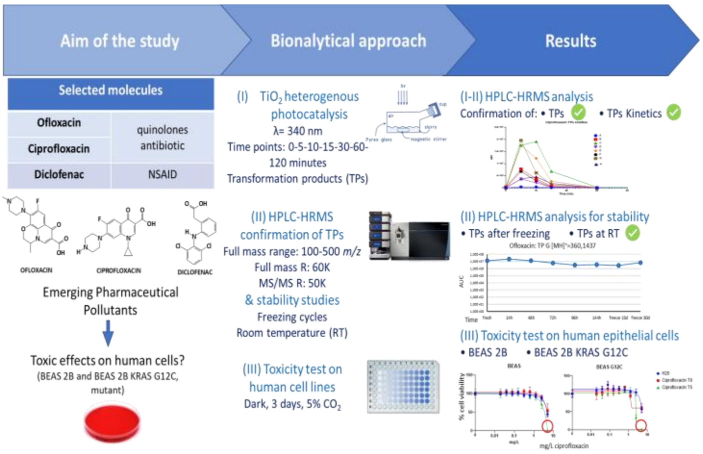
Emergent Water Pollutants: A New Challenge for Human Health

S. Vietti Michelina[1], E. Mecarelli[1], C. Medana[1], C. Ambrogio[1], P. Calza[2], F. Dal Bello[1*]

[1]University of Turin, Department of Molecular Biotechnology and Health Science, Via P. Giuria 5, 10125, Torino, Italy
[2] University of Turin, Department of Chemistry, Via P. Giuria 5, 10125, Torino, Italy

federica.dalbello@unito.it

Over the last decades, the worldwide environmental pollution had an abrupt growth. Numerous studies attempted to establish a connection between water pollution and environmental damage (Altenburger R. et al 2019), but only a few of them focused on human health. The aim of this study was to develop an analytical and a biomolecular approach to assess the human health risk connected to the presence of emerging pharmaceutical pollutants in aqueous environment. We selected three drugs: ofloxacin, ciprofloxacin and diclofenac. Despite the metabolism of these drugs is known, and their transformations in the environment were previously studied (Calza P. et al. 2008, Rodríguez-Chueca J. et al. 2009) the human toxicity of their transformation products (TPs) remains an open question. After the confirmation of the described TPs using heterogeneous photocatalysis, we assessed their stability after freezing and at room temperature (RT) with the developed HPLC-HRMS method. The results showed that freezing did not increase the stability of TPs. Once assessed the stability of the TPs, we were able to evaluate the toxicity of parent compounds and TPs incubating for three days at RT on selected human pulmonary epithelial cell lines (both normal and oncogenic, i.e. BEAS 2B and BEAS 2B KRAS G12C) and molecules. The data showed that the TPs formed after 5 minutes of irradiation were more toxic than the parent compounds. The viability of the cells decreased to reach <5% at the higher concentration (5 mg/L). In conclusion, preliminary results indicated an accumulation in human lung cells leading to toxicity of the selected molecules.



Bioanalytical method workflow for studying human toxicity of selected molecules and of their TPs.

References

Altenburger, R. et al (2019) Environmental Sciences Europe, 31(12). DOI:10.1186/s12302-019-0193-1.

Calza, P. et al. (2008) Rapid Communications in Mass Spectrometry, 22(10), p. 1533. DOI:10.1002/rcm.3537.

Rodríguez-Chueca, J. et al. (2009) Chemosphere, 226, p. 509 DOI: 10.1016/j.chemosphere.2019.03.152.

Exposure to Mercury as Environmental Pollutant Among Lung Adenocarcinoma Patients in Vojvodina

N. Milošević[1*], M. Milanović[1], J. Drljača[1], D. Sazdanić-Velikić[2], S. Bijelović[3], J. Sudji[4], M. Španović[4], N. Milić[1]

[1]University of Novi Sad, Faculty of Medicine, Department of Pharmacy, Novi Sad, Serbia
[2]University of Novi Sad, Faculty of Medicine, Institute for pulmonary diseases of Vojvodina, Clinic for pulmonary oncology, S. Kamenica, Serbia
[3]University of Novi Sad, Faculty of Medicine, Institute of Public Health of Vojvodina, Novi Sad, Serbia
[4]University of Novi Sad, Faculty of Medicine, Institute of Occupational Health, Novi Sad, Serbia

natasa.milosevic@mf.uns.ac.rs

The exponential increase of industrial, agricultural and technological development lead to continuous chronical environmental and occupational exposure to mercury (Hg). The association between mercury and lung cancer is not completely understood, although Hg exposure has been correlated with skin, prostate and renal cancer. In this study, 36 male patients (39-84 y) with IIIB and IV stage inoperable lung adenocarcinoma from the Institute for Lung disease of Vojvodina, Sremska Kamenica were enrolled. The mercury content was determined by ICP-MS in their morning urine samples. None of the patients was professional exposed to Hg.Mercury was detected in 91.67% (33/36) urine samples among which only one had value below the median urinary value (0.140 µg/L) for healthy adults given by the Tox Guide of the US Agency for Toxic Substances and Disease Registry. Furthermore, 63.89% (23/36) lung cancer patients exceeded the 95th percentile urinary Hg value (1.8 µg/L) for US. Taking in account the reference value when no adverse effects could be expected, 47.22% (17/36) of the observed patients surpassed 5 µg Hg/gCr or 27.78% (10/36) exceeded 7 µg Hg/L urinary level. There were no statistical differences in Hg urinary levels between patients with amalgam dental fillings (7.310±13.184 µg Hg/gCr) in comparison to those without (8.405±11.594 µg Hg/gCr). Almost 50% of lung adenocarcinoma patients (with inoperable IIIB-IV stage) from Vojvodina are exposed to mercury above levels when no adverse effects could be expected. Environmental pollution should be presumed as the main source of exposure to mercury.

Acknowledgement
This work was supported by the Provincial Secretariat for Higher Education and Scientific Research, AP Vojvodina, Republic of Serbia [Grant number 142-451- 3120/2022-01].

Legacy DDT Pollution in a River Ecosystem: Sediment Contamination and Bioaccumulation in Benthic Invertebrates

S. Tasselli[1]*, L. Marziali[1], C. Roscioli[1] and L. Guzzella[1]

[1]National Research Council - Water Research Institute (CNR-IRSA), Via del Mulino 19, 20861, Brugherio (MB) Italy

stefano.tasselli@irsa.cnr.it

DDT was employed in the past as insecticide for agricultural purposes and to control mosquitoes that spread malaria (Jaga and Dharmani, 2003). However, due to its persistence, toxicity and high bioaccumulation potential, the use of DDT was banned in the 1970s and the chemical was classified as persistent organic pollutant under the Stockholm Convention in 2001, and as priority substance under the European Directive 2013/39/UE. DDT can reach freshwater ecosystems through many pathways, as runoff from contaminated soils, sewage effluents or atmospheric deposition and tends to be absorbed onto suspended solids and particulate organic matter and to accumulates in bottom sediments, where it can be stored for decades (Karickhoff, Brown and Scott, 1979). From sediments, stored DDT can be released again in the water column and can bioaccumulate in benthic organisms living in contact with sediments, with potential biomagnification in the aquatic food web (Nfon, Cousins and Broman, 2008). For these reasons, even if environmental concentrations may be residual, the ecological risk to DDT contamination may be significant and needs to be assessed. In this study DDT contamination in the Toce River (North Italy) was studied by collecting data from 2016 to 2021 upstream and downstream a production factory which in the past discharged technical DDT. Analysis of sediments and of bioaccumulation in different benthic invertebrate taxa (Gammaridae, Diptera, Ephemeroptera Baetidae and Heptageniidae) was carried out to assess the transfer of DDT from sediments to benthic invertebrates and the environmental risk of this legacy pollutant for the river ecosystem. DDT and its metabolites dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD), here called DDx, were analysed by isotope dilution gas chromatography-mass spectrometry (GC-MS/MS). DDx values in sediments in upstream stations (1.14-2.25 ng/g 1% Organic Carbon) were lower than downstream the industrial site (5.60-7.60 ng/g 1%Organic Carbon), often exceeding Sediment Quality Guidelines for total DDx. Peak levels derived from new inputs of parental DDT, as confirmed by fingerprint analysis. Bioaccumulation was higher at downstream sites, up to 5107 ng/g lipid weight, confirming the bioavailability of residual DDT and active metabolism, with formation of DDD and DDE. The Biota-Sediment Accumulation Factor evidenced highest values (over 4.2) for Diptera and Gammaridae, highlighting that invertebrates can transfer contamination from sediments to the trophic chain. Linear regression models were developed to estimate DDx concentrations in benthic invertebrates from DDx concentrations in sediments. However, determination coefficients R^2 remained in the range of 0.36-0.51, highlighting that bioaccumulation analysis is needed to fully estimate the environmental risk. Results highlight that DDT contamination, even if residual, may still represent a risk due to effective transfer to trophic chains.

References

Jaga, K. and Dharmani, C. (2003) ‘Global surveillance of DDT and DDE levels in human tissues’, International Journal of Occupational Medicine and Environmental Health, 16(1), pp. 7–20.

Karickhoff, S.W., Brown, D.S. and Scott, T.A. (1979) ‘Sorption of hydrophobic pollutants on natural sediments’, Water Research, 13(3), pp. 241–248. doi:10.1016/0043-1354(79)90201-X.

Nfon, E., Cousins, I.T. and Broman, D. (2008) ‘Biomagnification of organic pollutants in benthic and pelagic marine food chains from the Baltic Sea’, Science of The Total Environment, 397(1), pp. 190–204. doi:10.1016/j.scitotenv.2008.02.029.

Pharmaceuticals in Surface Waters – Comparing Half-Lives in Lab and Field – Regulatory Consequences and Ways Forward

S. Berkner, J. Wöltjen, C. Seller, M. Honti, K. Fenner

Pharmaceuticals are detected in rivers all around the world. This poses risks for aquatic organisms and contributes to contamination of groundwater and raw water for drinking water production. One desired property of pharmaceutical active ingredients (ai) is stability against metabolic processes. Consequently, it is to be expected that ai tend to be persistent in the environment. Therefore, it is important to study the environmental fate of pharmaceuticals in the regulatory environmental assessment for pharmaceuticals. Tests according to OECD TG 308 in water/sediment-systems are used to derive information on transformation and persistence of ai in surface waters. Up to now, it has not been possible to compare kinetic data derived from laboratory experiments to data derived from field measurements.

Here, experiments similar to the OECD 308 study design were conducted in the laboratory with water/sediment sampled from river Rhine for 24 pharmaceutical ai. D(iss)T_{50w} values were derived by fitting SFO kinetics to the measured concentration over time in the water phase. Alternatively, the data were evaluated by a method that allows to disentangle transformation and sorption processes and thus to derive DegT_{50w} values for the water phase (lab values). Concentration data from a monitoring program in the Rhine were then used to model DegT_{50w} values for the water compartment in the Rhine (field values).

Comparing the lab and field values shows that D(iss)T_{50w} values underestimate persistence, whereas DegT_{50w} values seem to be protective concerning a regulatory environmental assessment. However, D(iss)T_{50w} values are presently the only values used in the environmental assessment for pharmaceuticals for the aquatic compartment. Therefore, additionally reporting DegT_{50w} values would give a more complete picture with regard to persistence in surface waters.

Deriving DegT_{50w} values requires measuring and reporting some additional parameters in OECD 308 studies, i.e.

- Koc for same sediment as used in OECD 308 (L/kg)
- TOC_w (mg/L) (is mostly already measured and reported)
- fraction of organic carbon in sediment (f_{ocsed} ,%) (is already measured and reported)
- test vessel geometry (shape (e.g. cylindric, etc.; diameter in cm, etc.)
- thickness of water layer (cm)
- thickness of sediment layer (cm)
- sediment porosity (%).

These additional data requirements are already partially implemented in REACH Guidance R.11. It would be helpful to include these data requirements across regulatory frameworks for conducting and evaluating OECD 308 studies. This could also help to further standardize the study design. A software is being developed to derive DegT_{50w} in a user-friendly manner. It should be considered that the results presented here stem from one river catchment and are not necessarily generalizable to other river catchments.

Assessment of Atmospheric Pollution by Toxic Elements from Artisanal and Small-scale Gold Mining (ASGM) Activity: A Case of Myanmar

Win Thiri Kyaw[1]*, Xiaoxu Kuang[1], Sakakibara Masayuki[1,2]

[1]Research Institute for Humanity and Nature, Kyoto 603-8047, Japan
[2]Ehime University, Faculty of Collaborative Regional Innovation, Matsuyama 790-8577, Japan

thiri@chikyu.ac.jp

Artisanal and small-scale gold mining (ASGM) has been undertaken in developing countries for socioeconomic reasons; however, it accounts for the largest anthropogenic source of mercury (Hg) emission, releasing over 700 metric tons into the atmosphere annually, in addition to approximately 800 metric tons into land and water, exposing both ASGM miners and nearby communities to the mercury. Furthermore, toxic elements other than Hg have been discharged into the environment as a consequence of the ASGM process. Myanmar, a Southeast Asian country, has been known to have numerous ASGM activities and high Hg usage due to inadequate management of the national ASGM industry as well (Kuang et al., 2022) as a lack of study into environmental and health issues. Our previous preliminary studies found environmental Hg pollution and community health issues in an ASGM area in Myanmar (Kyaw et al., 2020), however, there is still a need to assess the atmospheric pollution in larger area with increasing sample numbers.

Therefore, in our study, we assessed the status of atmospheric pollution of an ASGM area, Yamethin Township of Mandalay Region in Myanmar in 2021 by analyzing a large number of house dusts and tree barks collected from the different locations from ASGM activities to evaluate the content of Hg and other possible toxic elements. House dusts were analyzed with Particle Induced X-Ray Emission (PIXE), and tree barks were analyzed with inductively coupled plasma mass spectrometry (ICP-MS).

On evaluation, house dusts showed the content of toxic elements, including Hg, at various distances from the source of ASGM activity. Therefore, it can be concluded that the analysis of house dusts for toxic elements with PIXE method conducted in this study can be applied as a reference in detecting the atmospheric pollution caused by ASGM activity.

Finally, since the ASGM issue is complex and based on socioeconomic reasons, in addition to the current interdisciplinary research, the authors recommend an approach to solving it with transdisciplinary research by working with various stakeholders such as governments, companies, and citizen groups, and a platform to link the bottom-level research findings to the top-level decision-making parties.

References

Kuang, X. et al. (2022) 'A Preliminary Study on Mercury Contamination in Artisanal and Small-Scale Gold Mining Area in Mandalay Region, Myanmar by using Plant Samples', Pollution, 8(1), pp. 225-238. doi: 10.22059/poll.2021.327548.1147.

Kyaw, W.T. et al. (2020) ‘Health Impact Assessment of Artisanal and Small-Scale Gold Mining Area in Myanmar, Mandalay Region: Preliminary Research’, International Journal of Environmental Research and Public Health, 17(18), 6757, http:/doi.org/10.3390/ijerph17186757.

Contamination Patterns of Soils and Sediments from Important Bird and Biodiversity Areas

M. Dulsat-Masvidal[1]*, C. Ciudad[2], O. Infante[2], R. Mateo[3], S. Lacorte[1]

[1]IDAEA-CSIC, Department of Environmental Chemistry, Jordi Girona 18-26, 08034, Barcelona, Spain.
[2]SEO/BirdLife, Melquiades Biencinto, 34, 28053 Madrid, Spain.
[3]Instituto de Investigación en Recursos Cinegéticos (IREC), CSIC-UCLM-JCCM, 13005 Ciudad Real, Spain

mdmqam@cid.csic.es

Persistent Organic Pollutants (POPs) are recalcitrant compounds representing a global environmental problem due to their persistence, bioaccumulation capacity, toxicity and potential for long-range transport. Soils and sediments are important reservoirs of legacy compounds such as organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) or polycyclic aromatic hydrocarbons (PAHs), but also emerging contaminants such as phthalates and flame retardants. Soil and sediments act as reservoirs of POPs and can cause habitat degradation and biodiversity loss being of particular concern in biodiversity hotspot areas. Important Bird and Biodiversity Areas (IBAs) are sites designated by the non-profit organisation Birdlife International to preserve natural areas with high value for biodiversity conservation (Donald et al., 2019). In the present study, we have assessed the presence and distribution of 52 organic contaminants in soils and sediments from140 IBAs in Spain to identify contamination patterns in highly valuable ecological sites. A total of 280 samples of soils and sediments have been analysed using ultrasonic extraction, Florisil clean-up and gas chromatography coupled with tandem mass spectrometry (GC-MS/MS). Land-use information of each area was used to identify the geographical distribution of compounds and main pollution sources. A Tier I Environmental Risk Assessment (ERA) was performed to identify the most impacted natural areas and the most concerning compounds.

Soils were found to be impacted by OCPs found at 87% of the IBAs (0.03 to 626 ng/g), followed by PAHs detected in 69% (2.57 to 1909 ng/g). Plasticizers were quantified at 50% of the samples and were the chemical group detected at the highest levels from 5.50 to 7026 ng/g. PCBs were detected in 44% of IBAs but at background levels, their presence has been found to be related to artificial surface land use. From the 50 target compounds detected, 24 were found at levels considered at risk (RQ>1) for soil organisms in at least one area. Benzo[b]fluoranthene was the most frequently detected compound above the security thresholds in 71 IBAs, followed by the organophosphate insecticide chlorpyrifos found at high risk levels in 38 IBAs.

In sediments, PAHs were the most ubiquitous compounds present in 87% (from 1.24 to 2193 ng/g) of the samples followed by OCPs found in 68% (from 0.07 to 37.6 ng/g). Plasticizers were also the chemical group found at higher levels from 18.5 to 30278 ng/g and quantified at 43% of the samples. PCBs were detected in 31% of the IBAs also at low concentrations from 0.08 to 69.9 ng/g, the highest values were found at IBAs near large urban areas. 25 out of the 50 compounds detected were found at RQ>1. The compounds detected at high-risk levels were Benzo[b]fluoranthene and Benzo[k]fluoranthene found at 97 and 73 IBAs above the PNEC values for sediment organisms, followed by the plasticizer nonylphenol present in 52 IBAs at high-risk levels.

Overall, the study highlights the widespread use of organic contaminants in natural reservoirs and the importance to implement monitoring studies to identify potential contamination sites that need remediation actions.

Aknowlagments
This work was supported by the Spanish Ministry of Science and Innovation Project PID2019-105732GB-C21 and Excelencia Severo Ochoa Project CEX2018-000794-S

References

Donald, P.F. et al., (2019). Important Bird and Biodiversity Areas (IBAs): the development and characteristics of a global inventory of key sites for biodiversity. Bird Conserv. Int. 29, 177–198. https://doi.org/10.1017/S0959270918000102.

PAHs in Agricultural Soils with Related Ecological and Health Risk: Polish Case Study

A. Wódkowska[1*], T. Czech[2], A. Gruszecka-Kosowska[1]

[1]AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Department of Environmental Protection, Al. A. Mickiewicza 30, 30-059 Krakow, Poland
[2]University of Agriculture in Krakow, Faculty of Agriculture and Economics, Department of Agricultural and Environmental Chemistry, Al. A. Mickiewicza 21, 31-120 Kraków, Poland

awodkows@agh.edu.pl

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment and are of great concern due to their toxic and carcinogenic effects. They are released into the environment during a diverse range of anthropogenic activities and their emissions are increasing due to rapid industrialization and urbanization. Due to their semi-volatility, PAHs have a long-range atmospheric transport potential and therefore they might contaminate other environmental compartments. Presence of PAHs in soils might pose adverse health effects through direct contact with receptors as well as through PAHs migration in the food chain.

The aim of our study was to investigate the potential ecological and health risk related with the presence of PAHs in agricultural soils. Results of PAHs concentrations in soils of Lesser Poland region were obtained from the State Environmental Monitoring Programme performed each 5 years by Polish Chief Inspectorate of Environmental Protection (CIEP, 2023) and the values were taken for years 2015 and 2020. Also, our own results from research performed in 2017 (unpublished) on agricultural soils in the same investigation regions were used in this study.

Concentrations of PAHs were subjected to statistical analysis involving determination of mean, standard deviation, minimum and maximum values and the software package STATISTICA (TIBCO Software Inc., PaloAlto, CA, USA) was used for this purpose. Risk values together with variability and sensitivity analysis with 10,000 iterations were performed with Monte Carlo simulation method using the DecisionTools Suite (Lumivero). Risk values were calculated using following indices: risk quotient (RQ), mutagenic equivalency factor (MEQ), carcinogenic equivalency factor (TEQ), and human health risk assessment (HHRA). The maximum permissible concentration of PAHs needed for RQ values calculations were obtained from the Polish regulation (RME, 2016) as permissible concentrations values of individual PAHs in soils. In the HHRA assessment, based on the land use pattern according to the USEPA method (USEP, 1989), we have considered the residential exposure scenario as well as the occupational scenario of the farmers exposure.

The detailed characterization of calculated ecological and health risk alowed for detailed characterization of the risk values otained, also in terms of risk values variability and uncertinity. Apart detemining the total ecological and health risk values, we have also identified the key factors having the highest contribution in the total risk value. Based on the descriptive risk characterization the adequate actions of mitigation strategies were proposed in order to achieve and maintain the acceptable level of risk arising form PAHs presence in soils.

References

CIEP (2023) Chemical monitoring of arable soils. Available at: https://www.gios.gov.pl/chemizm_gleb (Accessed: 22 March 2023).

RME (2016) Regulation of the Minister of Environment of 1 September 2016 on how to conduct pollution assessment the surface of the earth (OJ 2016, item 1395).

USEPA (1989) Risk Assessment Guidance for Superfund, Vol. 1: Human Health Evaluation Manual, Part A.; Interim Final; Office of Emergency and Remedial Response. US EPA: Washington, DC, USA.

Relationship between Forms of Mercury and the Speciation of Iron in Sediments of the Southern Baltic Sea

U. Kwasigroch[1], K. Łukawska-Matuszewska[1], A. Jędruch[1,2]*, O. Brocławik[1], M. Bełdowska[1]

[1]University of Gdańsk, Institute of Oceanography, Department of Marine Chemistry and Marine Environment Protection, Marszałka Józefa Piłsudskiego 46, 81-378, Gdynia, Poland
[2]Polish Academy of Sciences, Institute of Oceanology, Department of Marine Chemistry and Biochemistry, Powstańców Warszawy 55, 81-712, Sopot, Poland

ajedruch@iopan.pl

Marine sediments are an important sink for mercury (Hg), a bioaccumulative toxic pollutant that impairs human and ecosystem health. Iron (Fe) is known to affect the complexation and bioavailability of Hg in sediments; however, the number of field studies investigating the forms of both elements is limited. The study was conducted in the Baltic Sea, known for its history of Hg pollution. Fractions of Hg were determined using themodesorption technique, while sequential extraction were applied to identify forms of Fe. The results obtained confirmed the important role of Fe speciation in the formation and horizontal and vertical distribution of labile and stable fractions of Hg in marine sediments. The main factors that positively influenced the content of most labile Hg fractions and thus possibly also the bioavailability of Hg were the contribution of the organic matter, reactive form of Fe and Fe-containing clay minerals (Kwasigroch et al., 2023).

This work was supported by the National Science Centre grants (2013/11/B/ST10/00322, 2014/13/B/ST10/02807 and 2018/31/N/ST10/00214) carried out at the University of Gdańsk.

References

Kwasigroch, U. et al. (2023) 'Form and bioavailability of mercury in sediments of the southern Baltic Sea in relation to the speciation of iron: spatial and temporal patterns', Marine Environmental Research (under review).

Influence of Environmental Factors on the Leaching of Phthalates from Polyvinyl Chloride Microplastics into Aqueous Systems - Insights from Laboratory Experiments and Modeling

C. Henkel[1,2,3]*, T. Hüffer[1,3] and T. Hofmann[1,3]

[1]University of Vienna, Centre for Microbiology and Environmental Systems Science, Department for Environmental Geosciences, Josef-Holaubek-Platz 2, 1090 Vienna, Austria
[2]University of Vienna, Doctoral School in Microbiology and Environmental Science, Djerassiplatz 1, 1030 Vienna, Austria
[3]University of Vienna, Research Platform Plastics in the Environment and Society (Plenty), Josef-Holaubek-Platz 2, 1090 Vienna, Austria

charlotte.henkel@univie.ac.at

Plastics are widespread pollutants in the environment which can accumulate due to low degradation rates. They are a source of organic contaminants including non-intentionally and intentionally added substances (additives). Since additives are in most case not chemically bound to the polymer, they can transfer to the surrounding environment within the life span of the plastics. Phthalic acid esters (phthalates) are commonly used plasticizers, especially to improve the stability and flexibility of polyvinyl chloride (PVC). However, phthalates like bis(2-ethylhexyl) phthalate (DEHP) are harmful for aquatic organisms due to their endocrine disrupting effects and toxicity. For the assessment of exposure concentrations of plastics and additives a thorough understanding of leaching kinetics of additives from (micro-) plastics into aqueous environments is required. The release of additives and non-additives from microplastics is controlled by internal and external diffusion, i.e., intraparticle diffusion (IPD) and aqueous boundary layer diffusion (ABLD), respectively. The leaching of phthalates from PVC microplastics into aqueous media is limited by ABLD (Henkel et al., 2022). In the aquatic environment, microplastics are exposed to abiotic and biotic weathering. Leaching can be affected by environmental factors such as the water temperature, the dissolved organic carbon (DOC) content, salinity and flow conditions. Photoaging changes the polymer properties and leads to the transformation of phthalates to smaller molecules such as monoesters. However, the influence of environmental factors on the leaching process of phthalates and transformation products is not yet known.

In this work, we applied an infinite sink method, using activated carbon powder as sorbate, to investigate the leaching of phthalates from PVC microplastics under different experimental conditions (Henkel et al., 2019). Batch leaching experiments were conducted over a time span of 120 days with PVC microplastics containing DEHP as a model phthalate. The effect of salinity and flow conditions on leaching was determined from the obtained leaching data. By additionally accounting for the effects of the water temperature and the concentration of dissolved organic carbon (DOC) on the leaching process, specific desorption times, i.e., desorption half-lives, for the leaching of DEHP from PVC microplastics in different aquatic systems were calculated. Leaching data from experiments conducted with pristine and photoaged PVC microplastics were used to elucidate the interaction of aging and leaching and to identify the governing leaching process of transformation products. Our calculations enable the assessment of the time frame of leaching processes and clearly show that even in environments where leaching is accelerated, leaching half-lives of phthalates from PVC microplastics remain rather long, in the order of decades. Therefore, we can demonstrate that PVC microplastics are a long-term source for xenobiotics in the environment.

References

Henkel, C. et al. (2022) Polyvinyl Chloride Microplastics leach Phthalates into the Aquatic Environment over Decades, Environ. Sci. Technol., 56, 20, p. 14507- 14516 . https://doi.org/10.1021/acs.est.2c05108.

Henkel, C. et al. (2019) The Leaching of Phthalates from PVC can be determined with an Infinite Sink Approach. MethodsX, 6, p. 2729–2734. https://doi.org/10.1016/j

Automated Rapid (Sub)Micron Scale Microplastics Analysis with Simultaneous IR and Raman Microscopy with Optional Co-Located Fluorescence Pre-Screening

M. Kansiz and C. Prater

Photothermal Spectroscopy Corp, 325 Chapala St, Santa Barbara, CA, 93101, USA

mkansiz@photothermal.com

Microplastic (MP) contamination have been recognized as a global environmental problem. MP particles are found globally in water, air, soil and regularly ingested by marine life. MPs can enter the human body by via contaminated water, beverages, and food, and by breathing airborne particles. The MP research community has grown quickly to address questions related to environmental/health risks. Spectroscopic analysis is frequently used to characterize populations of MPs, but most IR microspectroscopic analyses have been limited to >20 µm particles due to issues associated with spatial resolution with better spatial resolution techniques such as Raman microscopy often suffering from limited sensitivity and/or autofluorescence issues. This has left a critical unmet need in the analysis of micron scale MP particles, which are of particular concern for human and animal health, because these particles are able to pass through the gut wall to accumulate in tissue with potential impact to organ function.

We have developed an optical microscopy based platform with automated capability for the measurement and analysis of micron scale MP particles based on Optical Photothermal Infrared Spectroscopy (O-PTIR) and complementary Raman spectroscopy. Preparations of microplastic particles can be automatically screened via optical microscopy (or Fluorescence imaging) to identify particles of interest and then automatically measured by O-PTIR and/or Raman. While conventional infrared spectroscopy (and even Raman) can struggle to spectroscopically identify micron scale MP particles, the O-PTIR approach overcomes the spatial resolution limits of conventional infrared spectroscopy by using a photothermal detection mechanism that employs a separate visible probe beam to detect infrared absorption. Because of the smaller wavelength or the probe beam, O-PTIR can achieve spatial resolution 10-30X smaller than infrared diffraction limits, while also avoiding size and shape dependent scattering artifacts that often limit the repeatability of traditional FTIR/QCL based techniques.. Using O-PTIR, MP identification has been achieved on polymeric particles small as 0.5 µm with no upper size limit, with typical measurement times being in the order of seconds. Because O-PTIR can operate with very low probe beam power, it can analyze dark/colored MP particles without photodamage. O-PTIR is also insensitive to autofluorescence which can be problematic with Raman. That said, O-PTIR and Raman measurements can be performed simultaneously on the same MP particles to provide enhanced discrimination/confirmatory analysis. As an optional enhancement, fluorescently labelled MPs (e.g., with Nile Red) can also be measured on the same platform to assist with pre-screening out any non-plastics particles with the fluorescent image providing the location of particles of interest, thus speeding up the overall measurement by targeting only plastic particles.

This presentation will review O-PTIR technology and operating principles and then discuss the automated measurement and analysis of arrays of MP particles whilst providing key measurement performance metrics

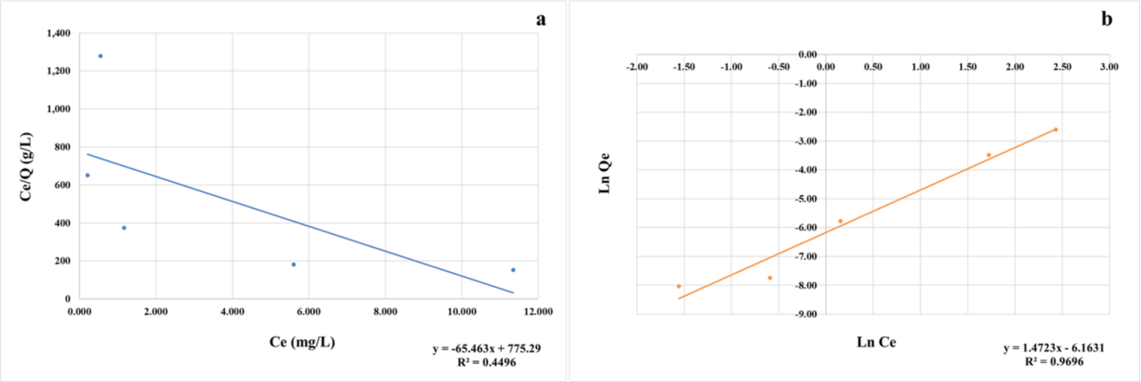
Adsorption Mechanism of Cadmium on Polypropylene Microplastics in Synthetic Solutions

A.G. Tenea[1], C. Dinu[1], F.L. Chiriac[1], G.G. Vasile[1*], S. Gheorghe[1], G.V. Serban[1], L.E. Barbulescu[1]

[1]National Research and Development Institute for Industrial Ecology-ECOIND, Pollution Control Departament, Drumul Podu Dambovitei Street 57 -73, 060652, Bucharest, Romania

gabriela.vasile@incdecoind.ro

Toxic metals and microplastics represent two classes of pollutants often found together in aquatic ecosystems (Oz N. et al. 2019). Their combined toxic effects represent potential hazards to both aquatic fauna and human health. This study investigated the adsorption of Cadmium-Cd(II) on polypropylene (PP) microplastic beads. For this purpose, the effects of parameters such as the pH of the solution and the duration of contact were studied. The experimental results were applied to the adsorption models of the Langmuir and Freundlich isotherms. The correlation coefficient was 0.9696 in the case of the Freunlich adsorption isotherm, indicating that the Freundlich model best describes the adsorption process of Cd(II) on the PP microplastic, highlighting the fact that the adsorption of the toxic metal on the PP surface takes place in a multilayer. Moreover, it was observed that the pseudo-order kinetic model better describes the studied adsorption process, compared to the pseudo-order kinetic model. This model assumes that the adsorption of heavy metals by microplastics is mainly controlled by the chemisorption mechanism, which involves the sharing or transfer of electron pairs between the active centers of the adsorbent material (microplastic, PP) and the retained pollutant (metal ion, Cd(II)) (Guo X. et al. 2020).



Linearized Langmuir (a) and Freundlich (b) isotherms for the Cd adsorption process on PP

References

Oz, N. et al. (2019) 'Investigation of Heavy Metal Adsorption On Microplastics', Applied Ecology and Environmental Research, 4, 7301.

Guo, X. et al. (2020) 'Sorption properties of cadmium on microplastics: the common practice experiment and a two-dimensional correlation spectroscopic study', Ecotoxicology and Environmental Safety, 110118.

Acknowledgment: Project PN-III-P1-1.1-TE-2021-0073, TE 61: Microplastics. Ecotoxicological effects and mechanisms of action in Cyprinus carpio fish.

Determination of Nickel Adsorption on Soil in the Presence of Chemically Aged Polypropylene Microplastics

D. b. Bartan[1*], D. A. çinar[1]

[1]Gebze Teknik Üniversitesi, Environmental Engineering Department, 41400, Gebze/KOCAELİ

dilara.bartan2016@gtu.edu.tr

Plastic particles smaller than 5 mm are defined as microplastics (MP). They are produced for various uses or are formed by the decomposition of plastics under various environmental conditions. One of the main risks of MP is that they may pose environmental risks as they can facilitate the transport of the pollutants in environment by adsorbing various organic and inorganic pollutants. Moreover, aging of MP can change the plastic’s surface characteristics ad affect adsorptive properties. It has been observed that agricultural soils may contain MP due to plastic mulches, and it has been found that especially Polypropylene (PP) type microplastics are common in the soil environment. Additionally, application of biosolids to agricultural soils may introduce heavy metal to soil. It has been reported that the concentration of Nickel heavy metal in the biosolid can be higher than the amount declared in the regulation. Therefore, agricultural soils have been determined as environments where MP and heavy metals can coexist and MPs can affect the fate of heavy metals. The aim of the study is to examine the effect of PP, one of the common MP species in the soil environment, on the adsorption of Ni heavy metal, which can be transferred to the soil environment by biosolid applications, in soil. Moreover, how chemical aging of PP affects Nickel adsorption on soil was investigated. For this purpose, soil samples containing 150 mg/kg Nickel at moisture content of 45% were prepared. Then, 10% by weight of chemically aged PP MP was added to the soil samples and the prepared mixtures were shaken mechanically. Supernatant was obtained at different times by centrifuging the soil mixtures. The nickel concentration in the filtrate was measured by ICP. For all cases. The amount of Nickel adsorbed was calculated using the difference between the initial dissolved Nickel and the amount of Nickel in the filtrate. Nickel adsorption capacity of the soil was calculated i the case PP MP was fresh and aged. Also, adsorption rate constants were determined according to pseudo first order, pseudo second order and intraparticle diffusion models. Among the kinetic models, the second order pseudo model was found to represent the adsorption kinetics best. It is found that at 10% MP concentration Nickel adsorption capacity increased if PP MP was aged. This showed that aging of MPs may affect adsorption and the fate of Nickel in the soil environment.

Acknowledgement:

This study was supported by the TUBITAK project number 2209-A.

Contamination with PAHs Adsorbed on Microplastics Collected from Prahova and Ialomita Surface Water

F. Pirvu[1], L.F. Chiriac[1], I. Paun[1], V. I. Iancu[1], M. Niculescu[1], I. Cristea[1], N. Vasilache[1], G.G. Vasile[1*]

[1]National Research and Development Institute for Industrial Ecology ECOIND, Pollution Control Department, 57-73
Drumul Podul Dambovitei Street 57-73, 060652, Bucharest, Romania

gabriela.vasile@incdecoind.ro

Synthetic organic polymers have become indispensable in modern life due to their special properties as well as the low production cost. Water resistance, adaptability, high strength-to-weight ratio and high thermal resistance, as well as electrical insulation properties have determined their use in various fields such as: clothing, storage, transport, packaging, construction and in consumer goods (Alam F.C.et al. 2019). Currently, plastic gloves and single-use face masks are being discussed in detail, which can impose different levels of problems in the environment. In addition to the compounds used in the manufacture of plastic, there is the potential of exposure of aquatic biota to other contaminants that adsorb on microplastic particles. Microplastics are usually hydrophobic and have large surfaces, allowing the accumulation of organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) (Barnes D.K.A. et al. 2009). The higher is the molecular mass and the hydrophobic character of the PAHs, the equilibrium is reached in a longer time, implying the greater adsorption of the PAHs. Exposure of microplastics for a long time to the weather can lead to their fractionation as well as to an increase in the sorption capacity of PAHs due to the increase of the specific surface.

100 liters of surface water sampled from Prahova River (upstream and downstream Predeal, Azuga, Busteni, Sinaia, Comarnic localities) were filtered in order to extract microplastics particles. Then, microplastics were treated for estimation the adsorbed compounds (PAHs and PCBs) on the microplastics surface. The analytical methods for detection and quantification of the pollutants adsorbed on the microplastics were HPLC-FLD technique for PAHs and GC-µECD technique for PCBs. The obtained data indicated than only naphthalene and phenanthrene were determined in the Busteni upstream sample and pyrene in all samples. For the other compounds, the determined values were lower than the quantification limit of the analytical method (less than 0.0006 µg/L). Other study was performed on surface water collected from Ialomita River in the vicinity of Maia, Urziceni, Slobozia, Tandarei, Giurgeni localities. Naphthalene, chrysene, benz k fluoranthene, benz a pyrene and phenanthrene were identified and quantified in all samples collected from Ialomita River.

PCBs were not founded in the analyzed samples.

Regarding Prahova River, the sum of the PAH concentrations adsorbed on microplastics decrease in the order: ∑PAHs Azuga > ∑PAHs Sinaia > ∑PAHs Predeal > ∑PAHs Comarnic > ∑HAP Busteni. In Ialomita River the order of the PAH concentrations adsorbed on microplastics were: ∑HAP Maia < ∑HAP Tandarei < ∑HAP Giurgeni < ∑HAP Slobozia. In conclusion, was observed a strong interaction between PAHs and microplastics in the environment.

Acknowledgment:
The authors acknowledge the financial support offered by the Ministry of Research, Innovation and Digitization of Romania through the Romanian National Research Program “Nucleu” through contract no. 20N/2019, Project code PN 19 04 01 01.

References

Alam F.C.et al. (2019), Microplastic distribution in surface water and sediment river around slum and industrial area (case study: Ciwalengke River, Majalaya district, Indonesia). Chemosphere 224, 637–645, 2, doi: 10.1016/j.chemosphere.2019.02.188

Barnes D.K.A. et al. (2009), Accumulation and fragmentation of plastic debris in global environments. Philos Trans R Soc Lond Ser B Biol Sci 364, 1985–1998. doi: 10.1098/rstb.2008.0205.

Total-Organic-Carbon-based Method for Quantification of Microplastics in River Sediments

N.K. Kim[1]*, I. Lee[1], and H. Kim[1]

[1]University of Seoul, Dept. of Environmental Engineering, Seoul 02504, Korea

h_kim@uos.ac.kr

Microplastics (MPs) are defined as plastic particles with a diameter of 5 mm or less, and numerous studies are being carried out to address the mounting public concern about MP pollution. Currently, the primary focus of MP research lies in analytical methods and marine environments, with a growing interest in land-derived MPs. Nonetheless, this interest is largely skewed towards MPs in freshwater, with only a limited number of studies exploring the ones in subterranean environments such as sediments, soils, and groundwater.

Typically, Fourier-transform infrared (FT-IR) or Raman spectroscopic analysis is used to identify and quantify MPs smaller than 100 μm especially in an environmental sample; FT-IR is for MPs larger than 20 μm and Raman for MPs between 5 and 20 μm. Regardless of whichever spectrometric method utilized, a sample should be extensively pretreated before sample MPs are quantified. Especially, due to the broad MP-size distribution and existence of naturally occurring polymeric matters, pretreatment of soil or sediment samples is often challenging.

In this study, the total-organic-carbon (TOC)-based method is applied to investigate MPs in the sediments collected from the Nakdonggang River basin. Then, the results are compared with those from the spectroscopic approaches; a soil sample pretreatment process tailored for spectroscopic analysis is also proposed. Lastly, the advantages and drawbacks of spectroscopic approaches are assessed and the feasibility of the TOC-based method as an alternative to the spectroscopic ones is discussed.

Combined Effects of Microplastics and Chlorpyrifos on the Anecic Earthworm Lumbricus Terrestris

H. Ju[1]*, X. Yang[1,2], R. Osman[1] and V. Geissen[1]

[1]Soil Physics and Land Management, Wageningen University & Research, 6700AA, Wageningen, the Netherlands
[2]College of Natural Resources and Environment, Northwest A&F University, 712100 Yangling, China

ju.hui@wur.nl

Chlorpyrifos (CPF), a broad-spectrum organophosphorus insecticide and acaricide, has been used worldwide to control pests in agriculture (Lewis et al., 2016). In 2018, the annual use of CPF was 28,600 tons and mainly concentrated on rice, corn, wheat, and cotton (Yang, 2019). Increasing evidence has shown that CPF can pose risks to human and animal health which has led to a ban of CPF in the European Union in 2019 and United States in 2022 (Jia et al., 2021). Despite its ban CPF is still present in European soils and CPF use is still prevalent in developing countries like India and China (Foong et al., 2020). CPF, either alone or in combination with other contaminants, is toxic to many organisms (Zhou et al., 2011, John and Shaike, 2015). Zhou et al. (2007) revealed that CPF caused acute toxicity (LC50 at 91.87-118.5 mg kg-1) and adverse effects on the growth and reproduction of the earthworm Eisenia fetida. Karbalaei et al. (2021) found that CPF in combination with polystyrene microplastics (MPs)caused stronger toxicity in rainbow trout, especially in gill tissue, than CPF alone. Existing studies have proven that the ingestion of MPs or CPF alone affected the health of the earthworm Lumbricus terrestris (Martinez Morcillo et al., 2013, Huerta Lwanga et al., 2016). However, the ingestion of combinations of different MPs (especially biodegradable MPs) and CPF and the combined effects of these compounds on earthworms have rarely been studied.

References

EFSA 2014. Conclusion on the peer review of the pesticide human health risk assessment of the active substance chlorpyrifos. EFSA Journal, 12.

FOONG, S. Y., MA, N. L., LAM, S. S., PENG, W., LOW, F., LEE, B. H. K., ALSTRUP, A. K. O. & SONNE, C. 2020. A recent global review of hazardous chlorpyrifos pesticide in fruit and vegetables: Prevalence, remediation and actions needed. J Hazard Mater, 400, 123006.

HUERTA LWANGA, E., GERTSEN, H., GOOREN, H., PETERS, P., SALANKI, T., VAN DER PLOEG, M., BESSELING, E., KOELMANS, A. A. & GEISSEN, V. 2016. Microplastics in the Terrestrial Ecosystem: Implications for Lumbricus terrestris (Oligochaeta, Lumbricidae). Environ Sci Technol, 50, 2685-91.

Do Microplastics Enhance Toxicity of 4-MBC?

N. Milošević[1]*, J. Drljača[1], M. Milanović[1], S. Vasiljević[2], T. Simetić[2], N. Milić[1], A. Tubić[2]

[1]University of Novi Sad, Faculty of Medicine, Department of Pharmacy, Hajduk Veljkova 3, 21000 Novi Sad, Serbia
[2]University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia

natasa.milosevic@mf.uns.ac.rs

The 4-methylbenzylidene camphor (4-MBC) is one of the most commonly used organic UV filter in personal care products. Since 2022, it is identified as an endocrine disruptor with significant toxicological potential. Hence, 4-MBC related adverse effects are attracting growing concerns nowadays. Bearing in mind the physicochemical properties of 4-MBC, it could be expected to easily adsorb on microplastics surface due to their ubiquitously presence in the environment. Therefore, microplastics might act as carriers that alter 4-MBC toxicity. However, despite the widespread occurrence of these compounds within the aquatic environment, the possible human toxicity of adsorbed 4-MBC on different kinds of plastics has not been investigated yet. MRC-5 cell line, human embryonic lung fibroblasts, was used to examine the effects of 4-MBC, alone or adsorbed on polyvinyl chloride (PVC), on the cell viability using MTT assay. The tested samples (PVC, 4-MBC, as well as adsorbed samples) were used as extracts, according to ISO 19003-5 guidelines. The samples were resuspended in the cell medium (DMEM/F12) and left on a shaker for 24 hours at 37 °C to desorb. Afterwards, samples were centrifuged and the supernatant was used for treating the cells. Based on the obtained results 4-MBC showed non-linear cytotoxicity when cells were treated with alone UV filter in concentration 1 µM (68.04%), 5 µM (69.48%) and 10 µM (88.52%). The same concentrations of 4-MBC were used in adsorbed samples. Also, 4-MBC adsorbed on PVC expressed non-linear dose-response dynamics (68.44%, 61.54% and 104.30%, respectively). 4-MBC alone or in combination with PVC exerted U-shape nontraditional dose-response curve suggesting that 4-MBC might have more potent effects at low doses. Moreover, 4-MBC adsorbed on PVC showed the increased toxicity compared to 4-MBC alone. Hence, microplastics might act as carriers that adsorb, concentrate and increase 4-MBC toxicity. The study presents the first report on the cytotoxic effects of UV filters adsorbed on plastics on human fibroblast cell line.

Acknowledgement: This contribution is based upon work from COST Action CA20101 "Plastics monitoRIng detectiOn RemedIaTion recoverY"- PRIORITY, supported by COST (European Cooperation in Science and Technology), www.cost.eu, and by the Provincial Secretariat for Higher Education and Scientific Research, AP Vojvodina, Republic of Serbia [grant number 142-451- 3120/2022-01].

References

Tubić, A., et al. (2023). Sorption potential of microplastics for azo-and phthalocyanine printing dyes. Dyes and Pigments, 209, p. 110884. doi.:10.1016/j.dyepig.2022.110884.

The Fate of Egested Conventional and Bio/Biodegradable Microplastics During the Earthworm's Cast Ageing Process

K. Meng[1]*, E. Huerta Lwanga[1,2], Maarten van der Zee[3], Violette Geissen[1]

[1]Wageningen University & Research, Soil Physics and Land Management Group, Droevendaalsesteeg 3, 6708PB Wageningen, The Netherlands
[2]El Colegio de la Frontera Sur, Unidad Campeche, Agroecología, Av Polígono s/n, Cd. Industrial, Lerma, Campeche, Mexico
[3]Wageningen Food & Biobased Research, Bornse Weilanden 9, 6708WG Wageningen, The Netherlands

ke.meng@wur.nl

The accumulation of conventional plastics debris (e.g., LDPE) and the potential accumlation of plastic debris derived from emerging plastic polymers (bioplastics and biodegradable plastics) pose potential risks to soil health. Previous study has shown that microplatics of certain polymer types could be physically fragmented during the passage through the earthworm gut, mainly due to the grinding action in the gizzard. Some polymer types could even undergo depolymerization in the gut (Meng K. et al. 2023). Here, we try to explore the potential of earthworms and earthworm-related biological processes for reducing microplastic contamination in the soil, focusing on the cast ageing process after earthworm's microplastic ingestion and egestion. Three plastic types including LDPE, PLA and PBAT were used in the experiment. The concentrations of microplastics in the cast were monitored during a 180-day incubation, which simulates the cast ageing process on the soil surface under controlled conditions. Additional charaterization including H-NMR, ATR-FTIR, LDIR, GPC, etc. were conducted to profile the changes of microplatics. We expect that the concentration of PLA and PBAT microplastics might show a notable reduction by the end of the incubation, though with little observable difference in the remaining plastics from the original ones. A slight change in the microplastic size distribution is likely to happen for all three plastics. Findings of the current study could deepen the knowledge on the fate of different microplastics in the terrestrial ecosystem, as well as providing new insights into the bioremediation of plastic contamination with in-situ natural approaches.

References

Meng, K. et al. (2023) ‘Fragmentation and depolymerization of microplastics in the earthworm gut: A potential for microplastic bioremediation?’, Journal of Hazardous Materials, Volume 447, 130765. doi:10.1016/j.jhazmat.2023.130765.

Challenges Facing Pyrolysis GCMS in the Identification and Quantification of Multiple Micro- and Nano- Plastics in Environmental Samples

H.Carter[1]* and G. Pereira[1]

[1]UKCEH, Library Avenue, LA1 4AP, Lancaster, UK

herb@ceh.ac.uk

Plastics are ubiquitous in our environment because of their extensive use, due to their versatility. There has been a large amount of research into the analyses of plastics pollution to determine abundance and distribution in he environment. There is a multitude of studies reporting plastic analysis using optical approaches, however these methods have limitations in accurately identifying and quantifying small size plastics. Pyrolysis coupled to Gas Chromatography-Mass Spectrometry can be used to identify and quantify micro- and nano-plastics. Much of the work reported in the literature has been undertaken to assess a single polymer type within environmental samples, however the challenges come when assessing for more than one polymer simultaneously in the same sample. This work focused on analysing five common polymers together (Polyamide, Polyethylene, Polypropylene, Polyethylene Terephthalate and Polyvinyl Chloride), from tap water samples, in the micro and nano particle size range. Challenges were found within the sample extraction as well as the instrument analyses. Within extraction sample size, choice of solvent and physical transfer to the instrument were the main obstacles. The main difficulties with the instrument method included distinguishing unique identifiers for each polymer, attaining a reasonable LOD, QA controls and calibrations. Here we present our approach to overcoming these challenges, as well as some preliminary results.

Surface Sea Water Monitoring of Micro- and Mesoplastics in a Northern Adriatic Coastal Area

F. Barbieri[1]*, B. Zavattini[1], D. Marchetto[1], L. de Ferri[2], G. Pojana[1]

[1]Ca' Foscari University of Venice, Department of Philosophy and Cultural Heritage, Dorsoduro 3484/D, 30123, Venice, Italy
[2]Univesity of Oslo, Department of Collection Management-Museum of Cultural History, Kabelgaten 34, 0580, Oslo, Norway

francesca.barbieri@unive.it

One of the global issues widely debated in recent times are the presence and effects of microplastics in the marine environment. Their presence and abundance in every examined environment put all marine habitats at high risk, as the preeminent raw materials in present-day industrial manufacture are polymeric materials. The presented study describes the results acquired by the monitoring of surface sea water sampled from two transects in the coastal area near to the inlet of the Venice Lagoon (Italy). The purpose was to collect new data about the presence and relevance of plastics pollution in the area. Plastic particles collected with a 0.3-mm mesh size net (manta net) were rigorously chemically classified by using a multi-technique procedure (three different spectroscopic methods), differentiating them also by shape, dimension, colour, and spatial density. All collected data allowed the definition of specific subgroups of plastic micro-debris in this Northern Adriatic Area. The approach proposed in this study was effective for the management of massive data quantity gained from the characterization of microplastics collected and allowed to highlight existing differences among data obtained from diverse sampling campaigns. This protocol could be exploited for future studies in the Adriatic Sea and other marine areas.

References

Barnes, D.K.A. et al. (2009) 'Accumulation and fragmentation of palstic debris in global environments', Philosophical Transaction of the Royal Society B Biological Science, 364, p.1985-1998. doi: 10.1098/rstb.2008.0205

Brown, D. and Cheng, L. (1981) 'New Net for sampling the Ocean Surface', Marine Ecology Progress Series, 5, p.225-227. doi:10.3354/meps005225

Vianello, A. et al. (2018) 'First evaluation of foating microplastics in the Northwestern Adriatic Sea', Environmental Science and Pollution Research, 25, p.28546-28561. doi: 10.1007/s11356-018-2812-6

Microplastics and Leaf Litter Decomposition Dynamics: Insights from a Lotic Ecosystem

M. Bertoli[1], M. Renzi[1], S. Anselmi[2], D. Lesa[1], A. Mele[1], D. Barceló[3], M. Prearo[4], E. Pizzul[1] and P. Pastorino[4]*

[1]University of Trieste, Department of Life Science, Via Giorgieri 10, 34127, Trieste, Italy
[2]Bioscience Research Center, Via Aurelia Vecchia 32, 58015, Orbetello (GR), Italy
[3]Catalan Institute for Water Research (ICRA-CERCA), Emili Grahit 101, 17003, Girona, Spain
[4]Istituto Zooprofilattico Sperimentale del Piemonte, Liguria e Valle d'Aosta, Via Bologna 148, 10154, Torino, Italy

paolo.pastorino@izsto.it

Microplastics represent one of the main environmental concerns of our time and their presence is well known in all freshwater ecosystems. However, there is still a lack of knowledge about the interference with some environmental dynamics, such as the leaf litter decomposition, which represents a key process in freshwater ecosystems (Seena et al., 2022). Moreover, most of the studies regarding the relationship between leaf litter decomposition and microplastics were performed mainly in laboratory via microcosmos approaches and were not directly carried out on the field. Another point is that often these studies were carried out only considering target species and/or one trophic level. The work presented herein analyzed the leaf litter decomposition in a lotic ecosystem (Vipacco River, northest Italy), in relation to water physicochemical parameters, macrobenthic invertebrate functional feeding guilds (FFG) and, as a novelty, the microplastics as additional factor.

Vipacco River is the major left tributary of the Isonzo River. The springs of the Vipacco River are located in Slovenia, within the karstic area of Mount San Lorenzo (1019 m a.s.l.). The watercourse flows for 45 km and then crosses the State border between Slovenia and Italy. The Italian stretch is 4.5 km long high plain watercourse, and it flows within the Savogna d'Isonzo municipality (Friuli Venezia Giulia Region), where it joins the waters of the Isonzo River. Physicochemical features were monitored every 15 days for one year. Phragmites australis decomposition rates were investigated during four seasons (summer, autumn, winter, and spring) using the leaf bag technique. Microplastic items were also collected within the leaf bags (used as retaining tool) and within macrobenthic invertebrate colonizers. Shredders were the most contaminated FFG in summer and autumn, while scrapers showed high microplastics levels in autumn and winter. Decomposition rates significantly differed among seasons ($0.007 < k < 0.022$) and water temperature was the main driver of the decomposition dynamics (relative importance = 70.3 %), positively affecting the decay rates, followed by pH (9.7 %), which showed a negative contribution. Microplastics showed a negative effect (3.1 %), with a relative importance similar and opposite to that observed for the shredders (3.9 %), which value was similar to those recorded for scarpers (2.7 %). This study represents a field investigation regarding the microplastic effects on the organic matter decomposition rates in freshwater environments carried out directly on field. Our results provide new insights into the microplastic interference on environmental dynamics and could represent a starting point for further studies.

References

Seena, S. et al. (2022) Impacts of low concentrations of nanoplastics on leaf litter decomposition and food quality for detritivores in streams. Journal of Hazardous Materials, 429, 128320. https://doi.org/10.1016/j.jhazmat.2022.128320.

The Invasive Red Swamp Crayfish (Procambarus Clarkii) as a Bioindicator of Microplastic Pollution: Insights from Lake Candia (Northwestern Italy)

P. Pastorino[1*], M. Renzi[2], S. Anselmi[3], G. Esposito[1], A. Zanoli[1], T. Bezzo[1], F. Bondavalli[1], A. Dondo[1], D. Barceló[4] and M. Prearo[1]

[1]Istituto Zooprofilattico Sperimentale del Piemonte, Liguria e Valle d'Aosta, Via Bologna 148, 10154, Torino, Italy
[2]University of Trieste, Department of Life Science, Via Giorgieri 10, 34127 Trieste, Italy
[3]Bioscience Research Center, Via Aurelia Vecchia 32, 58015, Orbetello (GR), Italy
[4]Catalan Institute for Water Research (ICRA-CERCA), Emili Grahit 101, 17003, Girona, Spain

paolo.pastorino@izsto.it

Microplastic pollution has become pervasive. To date, most microplastics (MPs) research has focused on the marine environment, as the oceans are considered the main basin of contamination (Amelia et al., 2021). However, since most plastic is used and disposed of on land, both terrestrial and freshwater environments may be affected by MP pollution and serve as long-term reservoirs (Wang et al., 2021). Recent monitoring studies have established that MPs are ubiquitous in biotic and abiotic compartments of freshwater watercourses and lakes. Identifying a bioindicator species to track the occurrence and effects of MPs on ecosystems is crucial for determining their impact on the environment. Despite their ecological and economic importance, freshwater decapod crustaceans and their interaction with MPs have been understudied (Yin et al., 2022). The digestive tract of Procambarus clarkii was thought to be of interest for investigating MPs accumulation in freshwater organisms. Our hypothesis was that the same type of MPs found in abiotic compartments (water and sediment) could be found in P. clarkii, which would make it an ideal candidate for use as a bioindicator of MP pollution in freshwater ecosystems. Water, sediment, and P. clarkii specimens were collected from four sites in a protected area (Lake Candia; northwestern Italy) for two consecutive years (2021-2022). The mean MPs count was 1.75±0.95 items/m^3 in 2021 and 2±0.81 items/m^3 in 2022 in the water samples and 6.75±1.5 items/kg and 8±0.81 items/kg in the sediment samples in 2021 and 2022, respectively. In 2021, the average was 0.06±0.07 items/g in the males and 0.05±0.05 items/g in the females; in 2022, the average was 0.04±0.05 items/g and 0.05±0.06 items/g in the males and the females, respectively. MP fibers and fragments (black, white, blue, light blue) of polypropylene and polyethylene terephthalate were found in the biotic and the abiotic compartments. The generalized linear mixed model revealed that the number of items/g was predicted only by total weight: the lowest number of items/g was recorded for crayfish with the highest weight probably due to the feeding habits of P. clarkii. Our findings suggest that the invasive P. clarkii (smaller individuals, in particular) could be a good candidate bioindicator for MP pollution since the same type of MP items were recorded in the abiotic compartments. Further research is needed to better understand the feeding behavior of P. clarkii and the dynamics of MPs in aquatic ecosystems.

References

Amelia, T.S.M. et al. (2021) Marine microplastics as vectors of major ocean pollutants and its hazards to the marine ecosystem and humans. Progress in Earth and Planetary Science, 8(1), 1-26. https://doi.org/10.1186/s40645-020-00405-4.

Wang, C. et al. (2021) Environmental source, fate, and toxicity of microplastics. Journal of Hazardous Materials, 407, 124357. https://doi.org/10.1016/j.jhazmat.2020.124357.

Yin, J. et al. (2022) Microplastic pollution in wild populations of decapod crustaceans: A review. Chemosphere, 291, 132985. https://doi.org/10.1016/j.chemosphere.2021.132985.

Microplastics Detection Using Chemical Ionization MS With Multi-Scheme Chemical Ionization Inlet (MION)

J. Mikkilä[1], J. Mikkilä[1], J. Kontro[1], F. Partovi[1,2], H.J. Jost[1], E. Lattouf[1]*

[1]Karsa Ltd., A. I. Virtasen aukio 1, 00560 Helsinki, Finland
[2]Aerosol Physics Laboratory, Physics Unit, Faculty of Engineering and Natural Sciences, Tampere University, 33720 Tampere, Finland

elie.lattouf@karsa.fi

The process of Chemical Ionization (CI) involves using a chemical reagent to create ions that will charge a gaseous sample through ion-molecule reactions. This method is considered to be gentle and specific, but traditional CI and Electrospray Ionization have some drawbacks such as neutral reagent vapors/droplets that can negatively affect the sample chemistry and result in adverse matrix effects. However, the MION approach overcomes these limitations by using ion injection to allow only charged reagents to enter the sample flow and providing the ability to rapidly sample ions in both polarities. The system combines filters thermal desorption (TD), a MION source, and an orbitrap mass spectrometer (LTQ Velos pro) for substance identification. The aim of this work is to demonstrate that plastic compounds can be desorbed, ionized, and detected with Karsa TD-MION-Orbitrap setup without chromatographic separation.

Two methods were used for sample introduction to the system: polystyrene was in suspension in water and polypropylene in the form of solid beads. The first was introduced to the filters by injecting 2 µl of the solution and the second by rubbing the solid beads against the filters. The MION source was used with dibromomethane reagent gas leading to the formation of Br- reagents ions (Rissanen et al., 2019).

Results show that polystyrene and polypropylene containing samples are being desorbed, ionized and detected with TD-MION-Orbitrap setup. The filters have the potential to be used for collection of airborne plastic nanoparticles, and other applications.

References

M. P. Rissanen, et al., https://doi.org/10.5194/amt-12-6635-2019.

A Novel Approach for Sampling Microplastics in Rainwater

N. M. Ashta[1]*, R. Kaegi[2], D. Schoenenberger[1], C. Hueglin[1]

[1]Swiss Federal Laboratories for Materials Science and Technology (EMPA), Ueberlandstrasse 129, 8600 Duebendorf, Switzerland
[2]Swiss Federal Institute of Aquatic Science and Technology (Eawag), Ueberlandstrasse 133, 8600 Duebendorf, Switzerland

narain.ashta@empa.ch

The atmosphere may play an important role in the transport and distribution of microplastics in the environment. However, an understanding of the fate of atmospheric microplastics is still in its infancy. To understand how meteorological conditions affect the fate of atmospheric microplastics, some studies have sampled wet and dry atmospheric deposition separately and quantified their microplastics content (e.g., Brahney et al., 2020; Sun et al., 2022). The collection of wet deposition samples has typically been carried out by exposing a collection vessel such as a glass bottle to ambient air, allowing particles including microplastics to be collected together with the rainwater with which they are washed out. However, the collection of large volumes of rainwater can lead to practical challenges during sampling (e.g., overflow of collected water in case of heavy rain) as well as during pre-analysis sample treatment (e.g., via losses of particles during transfer of samples between glassware for different sample treatment steps). One of these treatment steps is typically a filtration of collected rainwater through a mesh or filter membrane that retains particles in a size class of interest.

We performed a feasibility study to see whether the filtration step could be directly incorporated during the passive sampling of wet deposition. To do so, we used a plastic-based filtration device fitted with a stainless-steel mesh that could be mounted onto the wet deposition sampler and connected to a vacuum pump, thereby serving as a built-in rainwater filtration unit. In doing so, particles present in rainwater could be collected without collecting large volumes of rainwater. A suspension containing known amounts of surrogate standards (red polyethylene spheres, 53-63 microns in diameter), as described by Philipp et al. (2022), was poured through this setup to test the recovery of particles from this setup. The setup performed comparably as with using a 2-liter glass bottle. The next step is to construct and test a metal-based counterpart filtration device to avoid contamination that could be expected from using a plastic-based filtration device in the field.

References

Brahney, J. et al. (2020) 'Plastic rain in protected areas of the United States', Science, 368(6496), pp. 1257-1260. doi:10.1126/science.aaz5819.

Philipp, M., Bucheli, T. D. and Kaegi, R. (2022) 'The use of surrogate standards as a QA/QC tool for routine analysis of microplastics in sewage sludge', Science of The Tota Environment, 835(155485). doi:10.1016/j.scitotenv.2022.155485.

Sun, J. et al. (2022) 'The atmospheric microplastics deposition contributes to microplastic pollution in urban waters', Water Research, 225(119116). doi:10.1016/j.watres.2022.119116.

When Microplastics Meet Aerobic Granular Sludge: Exploring the Consequences

P. Jachimowicz[1]*, A. Cydzik-Kwiatkowska[1]

[1]University of Warmia and Mazury in Olsztyn, Department of Environmental Biotechnology, Poland

piotr.jachimowicz@uwm.edu.pl

Microplastic pollution is a growing environmental concern worldwide, with potential impacts on ecosystems and human health. Aerobic granular sludge (AGS) technology is an efficient and sustainable method for wastewater treatment, but its potential to remove microplastics needs to be better understood. This study aimed to investigate the effect of different concentrations of microplastics on the protein and polysaccharide content of AGS. The experiment was conducted by exposing AGS to four different concentrations of microplastics (0, 10, 25, and 50 mg/L) for 60 days. AGS's protein and polysaccharide content were measured at the end of each 20 days using the Lowry and anthrone-sulfuric acid methods, respectively.

Results showed that the concentration of microplastics significantly affected the protein and polysaccharide content of AGS. The protein content decreased with increasing microplastic concentrations, while the polysaccharide content increased. At the highest microplastic concentration (50 mg/L), the protein content was reduced by 56% and the polysaccharide content increased by 194%, compared to the control group. These findings suggest that exposure to microplastics may affect AGS's microbial composition and activity, leading to changes in the sludge's extracellular polymeric substances (EPS) composition.

In conclusion, this study demonstrates that microplastic pollution can significantly impact the protein and polysaccharide content of AGS, which could ultimately affect the efficiency of the wastewater treatment process. The results emphasize the need for further research to understand the potential long-term effects of microplastic pollution on AGS and to develop strategies to mitigate its negative impacts. This study contributes to the growing body of research on microplastic pollution and its impact on the environment and highlights the importance of sustainable wastewater treatment practices.

This study was supported by project No. 2020/37/N/NZ9/02090 from the National Science Centre (Poland).

Influence of Carbon Nanotubes Surface Chemistry on the Production of Sustainable Fuels

D.F. Aguillar[1,2,3], C.M. Magalhães[1,2,3], T.S. Berberich[1,2,3], B.F. Machado[1,2], J.L. Faria[2,3*]

[1]CoLAB Net4CO2 - Network for a Sustainable CO_2 Economy, Porto, Portugal
[2]University of Porto, LSRE-LCM – Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials, Faculty of Engineering, Porto, Portugal
[3]University of Porto, ALiCE – Associate Laboratory in Chemical Engineering, Faculty of Engineering, Porto, Portugal

jlfaria@fe.up.pt

Our current lifestyle is highly dependent on dwindling non-renewable fossil resources, such as petroleum, natural gas, or coal. Extracting energy from these sources releases unwanted particulate matter and an abnormal increase of air pollutants, like CO_2, to the atmosphere, whose emission is responsible for increasing global climate change at an aggravating rate. This impact cannot be ignored, marking the immediate need for efficient answers.

One potential pathway to reducing the emissions from traditional fossil fuels involves the large-scale production and utilization of clean and sustainable synthetic fuels through, for example, Fischer-Tropsch synthesis (FTS), an essential part of Gas-to-Liquid (GtL) processes (Gholami et al., 2021). These synthetic fuels can be processed into fuels of superior quality compared to those obtained by oil refining, leading to significant reductions in the emission of particles, NO_x, SO_x, and aromatics to levels lower than those found in oil-based fuels (Jürgens et al., 2019). These synthetic fuels are considered environmentally friendlier than fossil alternatives, and their production contributes to the carbon circular economy.

This study aims to develop cobalt-based catalysts supported on carbon nanotubes (CNT) with tailored surface chemistry. To achieve this, pristine CNTs, synthesized through chemical vapour deposition, were modified with oxygen and nitrogen-containing species, which strongly influence the physicochemical properties of the material. CNTs with different doping levels were used to prepare catalysts with 10% cobalt loading using incipient wetness impregnation. The CNT-based supports and catalysts were thoroughly characterized before being tested in fixed-bed FTS using a fully automated Microactivity Effi unit at $T = 220$ °C, $P = 20$ bar, $GHSV = 4.0\ m^3 \cdot kgcat^{-1} \cdot h^{-1}$ and $H_2/CO = 2$ to test their performance.

The influence of the oxygen and nitrogen groups is analyzed regarding the stability and acidity/basicity of the CNTs, cobalt deposition, and catalytic performance, including CO conversion, specific yield, selectivity, and product distribution (paraffins/olefins/isomers).

This work was financially supported by LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC); project Cat4GtL (POCI-01-0247-FEDER-069953), co-funded by ERDF through COMPETE 2020 under PORTUGAL 2020.

References

Gholami, Z. et al., (2021) ‘Recent advances in Fischer-Tropsch synthesis using cobalt-based catalysts: a review on supports, promoters, and reactors’, Catalysis Reviews, 63:3, pp. 512-595, DOI:10.1080/01614940.2020.1762367.

Jürgens, S., et al., (2019) ‘Assessment of combustion properties of non-hydroprocessed Fischer-Tropsch fuels for aviation’, Fuel Processing Technology, 193, pp. 232-243, DOI:10.1016/j.fuproc.2019.05.015.

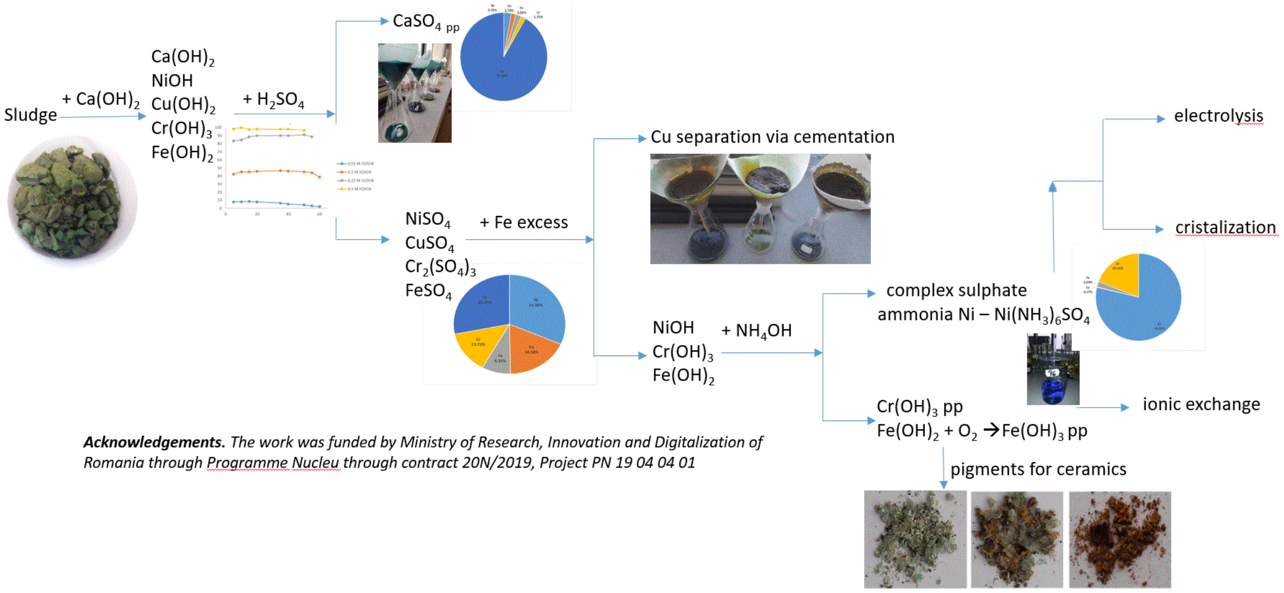
Recovery of Metals from Galvanic Sludges Using Hydrometallurgical Methods

M.A. Constantin[1*], L.A. Constantin[1], V. Achim[2]

[1]National Research and Development Institute for Industrial Ecology - ECOIND, Department for Evaluation, Monitoring Environmental Pollution, Department for Environmental Technologies and Technological Transfer , Drumul Podu Dambovitei Street, No.57-73 ZIP Code 060652,Bucharest, Romania
[2]SC TYRO PRODUCT SRL, Drumul Între Tarlale Street, No.45D, ZIP Code 032982, Bucharest, Romania

alina.constantin@incdecoind.ro

Experiments on metals' recovery from sludge generated by galvanising plants were investigated using hydrometallurgical methods. Sludges were homogenised and afterwards processed by leaching with H2SO4 solutions at various concentrations. In order to recover Cu from the obtained solutions cementation process of Cu with powder Fe was studied. Sollutions were stirred at 400 rpm for a period of 1 hour at 20 C, 40 C and 60 C. Maximum extraction efficiency for Cu was obtained after 2 minutes leaching using a H2SO4 solution with a concentration of 0.5 M. Optimum cementation temperature was found to be 40 C which led to a Cu recover efficiency of 97%. The resulted precipitates were treated by leaching with ammonium hydroxide in the sequential Cr and Fe extraction at the same three different temperatures: 20 C, 40 C and 60 C. Fe and Cr recovery from the precipitate mixture take place in various proportions: in the precipitate obtained at 20 C - Cr is predominant, at 40 C the proportions of Fe and Cr are aproximately the same, at 60 C - Fe prevails in composition. In all three situations Ni concentration is constant. Therefore a treatment scheme composed from the following steps was proposed: leaching with H2SO4, followed by cementation for Cu separation and precipitate treatment with ammonium hydroxide for separation of a sulphate ammonia complex of Ni that can be further processed by electrolysis or cristalization and a precipitate containing Cr and Fe that be further separated by ionic exchange or can be used for pigments production.



Acknowledgements. *The work was funded by Ministry of Research, Innovation and Digitalization of Romania through Programme Nucleu through contract 20N/2019, Project PN 19 04 04 01*

Experimental model for metals' recovery

References

Walawalkar, M., et al. (2016). Process investigation of the acid leaching of rare earth elements from phosphogypsum using HCl, HNO3, and H2SO4, Hydrometallurgy, 166, p. 195–204.
10.1016/j.hydromet.2016.06.008

Maleic Anhydride Production from Renewables: A Life Cycle Assessment at Pilot Scale

D. Cespi [1*], R. Cucciniello [2] , M. Riccardi[3], E. Neri[4], F. Passarini [1]
and F. M. Pulselli[3]

[1]University of Bologna, Dep. of Industrial Chemistry “Toso Montanari”, viale del Risorgimento 4, 40136, Bologna, Italy
[2]University of Salerno, Dep. of Chemistry and Biology “Adolfo Zambelli”, via Giovanni Paolo II 132, 84084, Fisciano, Salerno, Italy
[3]University of Siena, Ecodynamics Group, Department of Physical, Earth and Environmental Science Pian dei Mantellini 44, Siena, Italy
[4]INDACO2 Srl, Colle di Val d'Elsa, Siena, Italy

daniele.cespi2@unibo.it

The necessity to feed chemical industry with bio-based platform chemicals encourages the usage of a life cycle perspective in order to evaluate potentialities and drawbacks, before launching them at industrial scale. Maleic anhydride (MA) represents one of the most intersting and diffused commodities worldwide, with a potential market volume of 3.40Mt in 2029 (statista, 2023). In this study we proposed the application of the green metric E-factor (Ef, Sheldon, 1992) and the Life Cycle Assessment (LCA) methodology (ISO 14040) to two bio-based routes for the production of MA, by selecting 1000 kg as functional unit (FU). We investigated the production from bio-butanol (bio-ButOH MA) and from bio-furfural (bio-Furf MA). In both cases dedicated biomasses were used to feed the pilot plants, since it represents a more realistic scenario. In the bio-ButOH MA pathway the system was modelled by assuming the usage of maize, sugarcane and switchgrass (Panicum virgatum) in equal amount. On the contrary, in the case bio-Furf it is assumed the precursor derive 100% from switchgrass.

The study considers two levels of analysis for Ef and LCA. In the first case (Level I Ef) MA is considered the sole valuable output; during Level II Ef level other co-products are included within the mass allocation. In the case of LCA, first level (Level IEN) represents the simplest situation, in which no energy recovery is considered within the system boundaries. In second assessment level (Level IIEN) it is assumed that 100% of the heat released by the reaction (extremely exothermic) is recovered to feed the plant and co-produce steam (available for other commodities). In both cases the production of MA from bio-Furf results more competitive. Life cycle impact assessment phase, evaluated in terms of carbon footprint (IPCC), cumulative energy demand (CED) and following a multi-impact approach (ReCiPe method), confirms the scores achieved from the application of the Ef. In fact, the higher selectivity of the catalytic system used to convert bio-Furf into MA implies a lower amount of raw materials per FU with a consequent minor potential impacts on the several impact categories considered. Results, also confirmed by Monte Carlo analysis, could be used to set future improvements and supporting the design or the retrofit of innovative industrial plants able to enhance the whole efficiency.

References

statista.com, Market volume of maleic anhydride worldwide from 2015 to 2021, with a forecast for 2022 to 2029. Available at: https://www.statista.com/statistics/1245233/maleic-anhydride-market-volume-worldwide/#:~:text=In%202021%2C%20the%20global%20market,worldwide%20in%20the%20year%202029 (accessed 22 February 2023).

R. A. Sheldon, et al., (1992) Chem. Ind., , 23, 903–906. doi:10.1016/1381-1169(95)00229-4.
International Organization for Standardization (ISO) (2006a) 14040:2006, Environmental Management—Life Cycle Assessment—Principles and Framework. Geneva, Switzerland: ISO.

Development of Dye Removal Materials from Pineapple Leaf Fibers for Textile Wastewater Treatment

C. Rungrattanachai[1], T. Ratvijitvech[1] and T. Amornsakchai[1, 2, 3]*

[1]Mahidol University, Polymer Science and Technology Program, Department of Chemistry, Faculty of Science, Phuttamonthon 4 Road, Salaya, Phuttamonthon District, Nakhon Pathom, 73170, Thailand
[2] Mahidol University, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Phutthamonthon 4 Road, Salaya, Phutthamonthon Nakhon Pathom 73170 Thailand
[3] Mahidol University, Center of Sustainable Energy and Green Materials, Faculty of Science, Phuttamonthon 4 Road, Salaya, Phuttamonthon District, Nakhon Pathom, 73170, Thailand

taweechai.amo@mahidol.edu

At present, greater attention is paid to the pollution problem from chemicals released into water sources. Chemicals such as dyes have a huge impact on the environment. In this work, dye-containing wastewater was treated with dye adsorption materials derived from pineapple leaves, one of the abundant agricultural wastes in Thailand. Pineapple leaf microfiber (PALMF) was obtained by bringing pineapple leaf fibers through the process of washing with alkaline. It is a material that is easy to find, cheap, environmentally friendly, and biodegradable. To increase the efficiency of the adsorbent, various methods were used, such as increasing the surface area by homogenization-sonication technique or creating proper functional groups (chitosan, polyethylenimine (PEI), and 2,3-dialdehyde cellulose) on the adsorbent surface. In the experiment, methylene blue (MB) and methyl orange (MO) dyes were used as dye representatives. The dye adsorption efficiency was calculated by using UV-vis spectrophotometry. From the experiment, the adsorption capacity of PALMF for MB reached more than 80 mg/g at a concentration of 250 mg/L. When PALMF-PEI was used to adsorb MO, the adsorption capacity was approximately 100 mg/g at a concentration of 200 mg/L. Subsequently, the MB and MO adsorption efficiency of the PALMF was explored in various conditions, such as adsorption time and pH. It is expected that this research will be beneficial in wastewater disposal by using natural materials to remove dyes instead of synthetic materials that have a negative impact on the environment.

Alternative and Conventional Waste Management Methods for Leather Industry

A. M. N. Codreanu[1, 2], M.A. Constantin[1*] and D. S. Stefan[2]

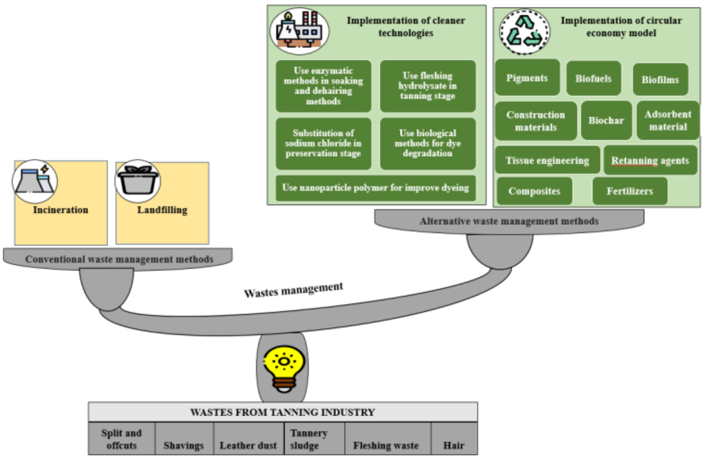
[1]National Research and Development Institute for Industrial Ecology, Department for Evaluation, Monitoring Environmental Pollution, Drumul Podu Dambovitei Street, No 57-73, ZIP Code 060652, Bucharest, Romania
[2]University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Department of Analytical Chemistry and Environmental Engineering, Polizu Street, No 1-7, ZIP Code 011061 Bucharest, Romania

alina.constantin@incdecoind.ro

The purpose of this study is to present the most current methods used to reduce the large amounts of solid wastes from leather industry which can provide the transfer from a polluting leather industry to a greener leather industry.

The leather industry is one of the most polluting industries from the world because it is based on the linear economy principle (take-make-waste) and produces large amounts of wastes. For the production of one ton of finished leather, 4 times more solid waste is generated. The use of toxic compounds in the production process and the ineficinet management of these solid leather wastes, such as incineration and storage, have a negative effect for the environment and human. For reduce all these problems, it is necessary to transfer to a cleaner industry. This can be done by implementing ecological methods in the production process and by adopting circular economy model. Ecological methods can be implemented in all production stages and consist in use of eco friendly reagents or use reagents which can reduce hazardous waste produced. Also, due to the high content of value substances (fat, protein, keratin, chromium) solid leather wastes generated can be extracted or valorized as secondary raw materials in many processes using different treatments (biological, chemical, thermal treatment) to obtain value added products.

Acknowledgements: The work was funded by Ministry of Research, Innovation and Digitalization of Romania through Programme Nucleu through contract 3N/2022, Project PN 23 22 04 01



The main methods used to reduce large amounts of leather industry wastes

References

Kanagaraj, J. et al. (2015) "Eco-friendly waste management strategies of greener environment towards sustainable development in leather industry: a comprehensive review", Journal of Cleaner Production, 89, p. 1. doi:10.1016/j.jclepro.2014.11.013.

Muralidharan, V. et al. (2022) "Turning problem into possibility: A comprehensive review on leather solid waste intra-valorization attempts for leather processing", Journal of Cleaner Production, 367, p. 133021, doi:10.1016/j.jclepro.2022.133021.

Application of the Life Cycle Assessment to A Vermicomposting Process: An Innovative Pathway to Produce High Quality Soil Conditioner

F. Arfelli[1]*, L. Ciacci[1], F. Passarini[1,2]

[1]University of Bologna, Department of Industrial Chemistry “Toso Montanari”, viale del Risorgimento 4, 40136 Bologna;
[2]CIRI Frame, University of Bologna, via Angherà 22, 47922 Rimini.

francesco.arfelli3@unibo.it

The large-scale industrialization resulted in a growth of solid waste generation and especially biowaste, which constitute about 46% of the total amount (Das, 2020; Kiyasudeen, 2020). The impressive growth of biowaste generation, is associated with an increasing need of soil conditioners and fertilizers, at date essential to supply the agricultural sector. The aim of the study is to apply the Life Cycle Assessment (LCA) to an innovative system which consists in an anaerobic digestion, a vermi-composting step and other complementary processes (Figure 1a), developed to convert biowaste into a high quality soil conditioner (HQ-SC). The system is entirely fed by self-produced renewable energy. The inventory data are collected as primary information, referring to a real system currently active in Piemonte region (Italy) and due to their very similar characteristics, peat is identified as HQ-SC commercial alternative. Results are reported as function of 1 ton of HQ-SC produced or 1 ton of peat extracted, following a "from cradle-to-gate" approach. Since the GHG emissions are considered a representative parameter to evaluate the environmental impacts of a system, the chosen LCIA method is IPCC 2021 GWP 100a.

Results presented in Figure 1b show that HQ-SC not only allows to valorize biowaste and to replace peat (fossil material), but it also showed better environmental performances (-24.9 kg CO2 eq/ ton against -20.2 kg CO2 eq/ ton). The carbon credit is due to the excess of electrcitiy produced by the renewable stations and accordingly sold to the national grid.

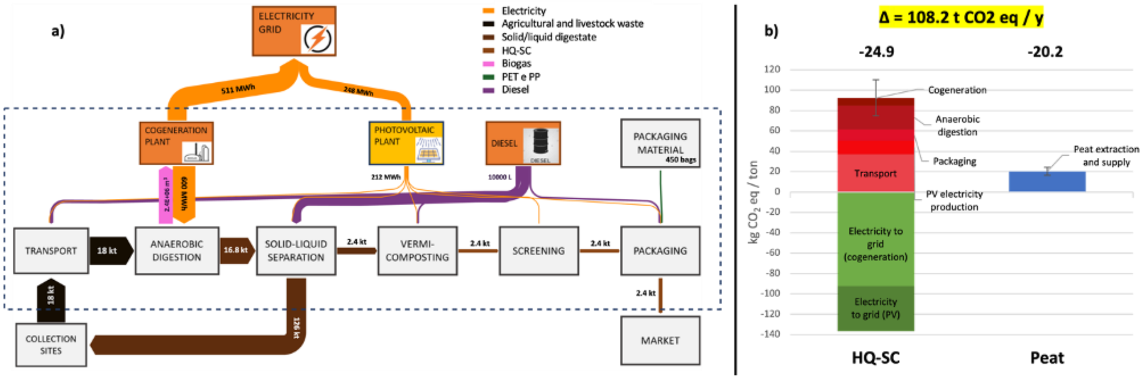


Figure 1: a) Scheme of the HQ-SC product system; b) Comparison between carbon emissions of HQ-SC and peat.

References

Das, S. et al. (2020) Vermicomposting, Current developments in biotechnology and bioengineering, pp. 79-102. https://doi.org/10.1016/B978-0-444-64309-4.00003-9

Kiyasudeen, K. et al. (2020), Vermicomposting of organic wastes and the production of vermicompost, Biovalorization of wastes to renewable chemicals and biofuels, https://doi.org/10.1016/B978-0-12-817951-2.00014-6.

New Environmental Strategies for the Capture and Transformation of CO_2 into Value-Add Products

J. Canales-Vázquez[1*], A. Muguruza-Blanco[1], B. Garcia-Rodríguez[2], J.E. Zafrilla-Rodríguez[3], S. Garcia-Yuste[4]

[1]Castilla-La Mancha University, Renewable Energy Research Institute, Paseo Investigación,1, 02071-Albacete
[2]Castilla-La Mancha University, Department of Inorganic Chemistry, Paseo Estudiantes, 02071, Albacete
[3]Castilla-La Mancha University, Department of Economic Analysis, Plaza Universidad, 1, 02071, Albacete, Spain
[4]Castilla-La Mancha University, Department of Economic Analysis, Av. Camilo José Cela, 1013071, Ciudad Real, Spain

Jesus.Canales@uclm.es

A novel sustainable production strategy is proposed aligned with the Carbon Dioxide Utilisation in industry. This strategy is based on the CO2 capture and, therefore, the non-emission of CO2 from the alcoholic fermentation process, as a residue, to obtain a high added value product such as sodium carbonate (Na2CO3). For this, the strategy requires another chemical reagent such as sodium hydroxide (NaOH), a very abundant alkali, obtained as a by-product of the chlor-alkali industry, so that with this "industrial symbiosis" aligned with circular economy, Na2CO3 of very high purity is obtained. Moreover, this is one of the most demanded chemical products by the industry at a global level. The demand for this product is mostly covered by the Solvay method, an energy-intensive and highly polluting method. Therefore, this research addressed the challenge of implementing an alternative route, technically, environmentally and economically viable and profitable, which takes advantage of alcoholic fermentation processes. This is a totally innovative and bold development, unprecedented in CO2 capture in fermentation industries. The CO2-AFP Strategy process was studied under experimental conditions in a progressive manner: (1) at laboratory scale, with a 3.0 L maximum capacity reactor; (2) at pre-pilot scale with a proof of concept run in plant with a reactor volume of 200 L; and (3) scaled up to pilot plant with a reactor volume of up to 800 L maximum volume. The pilot plant scale-up were executed in situ within the facilities of a medium production winery and distillery in Spain. This research, development and innovation (R&D&I) process allowed the generation and transfer of important know-how of great utility for the social structures.

References

Alonso-Moreno, C. and García-Yuste, S. (2016) 'Environmental potential of the use of CO2 from alcoholic fermentation processes. The CO2-AFP strategy', Science of The Total Environment, 568, pp. 319–326. doi:https://doi.org/10.1016/j.scitotenv.2016.05.220.

Alonso-Moreno, C. et al. (2018) 'The Carbon Dioxide-Rumen Fermentation Processes-strategy, a proposal to sustain environmentally friendly dairy farms', Journal of Cleaner Production, 204, pp. 735–743. doi:https://doi.org/10.1016/j.jclepro.2018.08.295.

Gueddari-Aourir, A. et al. (2022) 'The carbon footprint balance of a real-case wine fermentation CO2 capture and utilization strategy', Renewable and Sustainable Energy Reviews, 157, p. 112058. doi:https://doi.org/10.1016/j.rser.2021.112058.

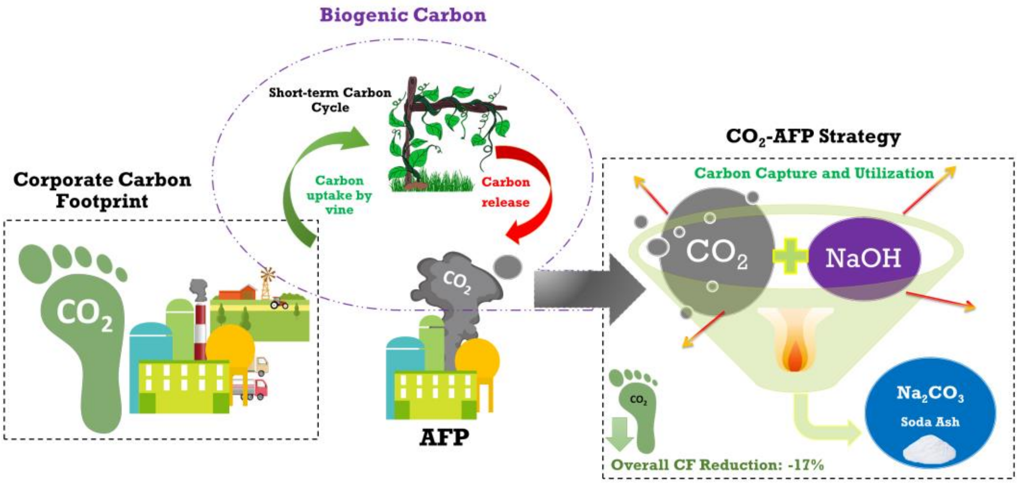
Balancing Corporate Carbon Footprint by CO_2 Capture and Utilization from Alcoholic Fermentation Processes

C. Alonso-Moreno[1*], S. Garcia-Yuste[2], A. Gueddari[1], A. Garcia-Alaminos[3], A. Muguruza-Blanco4, J.E. Zafrilla[3]

[1]Castilla-La Mancha University, Department of Inorganic Chemistry, Paseo Estudiantes, 02071, Albacete
[2]Castilla-La Mancha University, Department of Economic Analysis, Av. Camilo José Cela, 1013071, Ciudad Real, Spain
[3]Castilla-La Mancha University, Department of Economic Analysis, Plaza Universidad, 1, 02071, Albacete, Spain
[4]Alcoholes de Tomelloso S.A., Environment Department, C/Avila,4, 13710, Tomelloso, Ciudad Real, Spain

Carlos.AMoreno@uclm.es

The devastating social and economic consequences of the COVID-19 crisis and climate change mitigation and adaptation programs can be considered as the main global challenges humankind will face in the next few years. Industrial innovation is destined to play a major role in this greener and more resilient recovery. In this context, the development of circular economy disruptive strategies will be supported and promoted as the basis of an efficient and sustainable recovery toward a more decarbonized world. In this work, we propose the carbon footprint evaluation of a new circular strategy based on the capture and utilization of CO2 from alcoholic fermentation processes, the so-called “CO2-AFP Strategy”. The process results in the production of a green chemical marketable product, sodium carbonate. The analysis has been carried out estimating the global carbon footprint balance (carbon calculation, capture potential, and carbon balance) of a medium-sized fermentation process in Spain. We combine detailed information about the winery activity with a refined version of a tiered hybrid life-cycle assessment multi-regional input-output model proposed to calculate global emissions. To evaluate the potential of the “CO2-AFP Strategy”, we present a detailed and tested carbon capture and utilization scheme that allows us to deliver the carbon balance of the overall process.



CO2 capture and utilziation from alcoholic fermentation process

References

Gueddari-Aourir, A. et al. (2022) ‘The carbon footprint balance of a real-case wine fermentation CO2 capture and utilization strategy’, Renewable and Sustainable Energy Reviews, 157, p. 112058. doi:https://doi.org/10.1016/j.rser.2021.112058.

López, L.-A. et al. (2019) ‘The carbon footprint of the U.S. multinationals’ foreign affiliates’, Nature Communications, 10(1), p. 1672. doi:https://doi.org/10.1038/s41467-019-09473-7.

Bioconversion of Industrial Wastes into Compounds of Biotechnological Interest Using Genetically Improved Pichia Kudriavzevii Strains

V. Corbu[1*], O. Csutak[1]

[1]University of Bucharest, Faculty of Biology, Department of Genetics, Intr. Portocalelor no. 1-3, 060101 Bucharest, Romania;

viorica-maria.corbu@bio.unibuc.ro

The neutral intracellular lipids used for obtaining third generation secondary biofuels represent one of the main class of compounds of biotechnological interest produced by yeasts. Despite their immeasurable biotechnological applications, the oleaginous yeasts are still poorly used at industrial scale due to high production costs. A solution for reducing the financial deficit, might be the replacement of the substrate used for biomass accumulation with cheap alternatives available in large quantities (crude glycerol resulting from the production of biodiesel, alcoholic fermentation wastewater, lignocellulose biomass or sugar processing waste- molasses) (Robles-Iglesias et al., 2023). Another approach involves improvement of biotransformation efficiency using random mutagenesis techniques based on physical or chemical mutagenic agents.

The present study aims to genetically improve the ability of the strain P. kudriavzevii to assimilate and biotransform different types of wastes (lignocellulose waste, molasses) in intracellular lipids, possible precursors in biofuel production.

The non-specific mutagenesis protocol with N-methyl-N`-nitro-N-nitrosoguanidine was applied to a P. kudriavzevii M6 strain isolated from spontaneously fermented wine wort. Following the genetic improvement protocol, three mutants with improved phenotypes were selected. Their descent from the P. kudrivzevii M6 parental strain was confirmed by PCR-RFLP on the ITS1-5.8S-rDNA -ITS2 region. Since the mutagenic agent can affect the entire genome, the possibility of changing the virulence and pathogenicity profile was taken into account. Thus, we obtained three mutant strains that were tested for synthesis of hydrolytic enzymes involved in pathogenicity. Evaluation of the ability of mutant strains to convert industrial wastes into intracellular lipids was determined using the growth rate in the presence molasses and D-xylose as carbon sources, followed by qualitative (NileRed fluorescence stainning) and quantitative (quantification of fluorescence emission in presence of NileRed) determination of the intracellular lipid accumulation.

The results indicated that the mutagenic process did not influence the virulence and pathogenicity profile of the mutant strains. The dynamics of the growth rates was strain-dependent and was influenced by the carbon source used. Both mutant strains and the parental one assimilated molasses and xylose in high concentrations (up to 5%) in presence of organic, respectively, inorganic nitrogen substrate. However, the highest growth rates were recorded for two out of three mutant strains. The parental strain showed the highest potential to convert glucose into intracellular lipids, in contrast with the mutant strains which preferred xylose and molasses.

In conclusion, three new P. kudrivzevii strains with improved bioconvertion potential were obtained using random mutagenesis techniques. Moreover, one of the mutant strains showed an increased ability to assimilate and transform D-xylose into intracellular lipids with multiple applications in different industrial branches.

References

Robles-Iglesias, R., et al. (2023). Factors affecting the optimisation and scale-up of lipid accumulation in oleaginous yeasts for sustainable biofuels production. Renewable and Sustainable Energy Reviews, 171, 113043, https://doi.org/10.1016/j.rser.2022.113043.

Valorization of Agricultural Waste: Synthesis of Starch Nanoparticules (SNPs) for Food Packaging Application

Harrane[1], M. A. Beekhami[1], M. Belalia[1]

[1]University Abdelhamid Ibn Badis, Laboratoire Structure, Elaboration et Application des Matériaux Moléculaires, Department of Chemistry, Faculté de Sciences Exactes et de I'Informatique, 27000 Mostaganem, Algeria

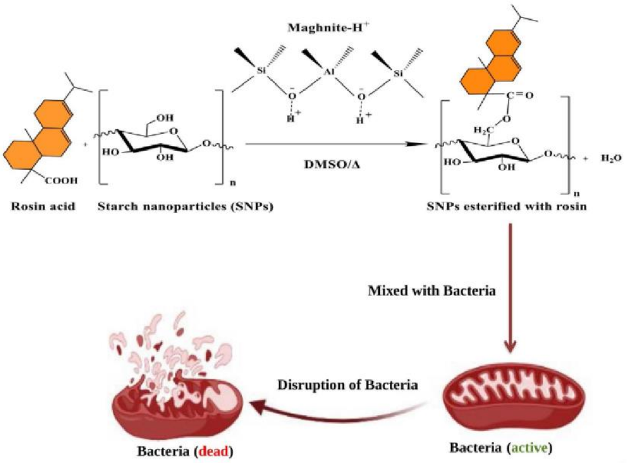
Since the role of food packaging is primarily to preserve the quality and safety of food, with, packaging materials must first meet the specific constraints of the application, namely to be economically competitive, mechanically resistant and with adequate barrier properties to water, water vapour and gases. The availability of materials that meet all of these criteria is limited. The majority of materials meeting these criteria are of fossil origin, and from the petrochemical industry they are far from biodegradable. In order to preserve the environment and develop sustainable materials, the packaging industries are increasingly moving towards the use of economically competitive biodegradable polymers, and renewable resources from biomass including, in particular, by-products and waste from the agricultural and forestry industries .

. In this general context, our goal is to develop the next generation of 100% bio-circular packaging from biodegradable materials and natural resources, by combining inexpensive and mechanically resistant ligno-cellulosic substrates from branches, agricultural waste, wood debris, biodegradable and bio polymers (starch, polycaprolactone, polyethylene glycole, polylactides.. etc.), and resins extracted from maritime pine trees or other coniferous species such as Rosin using economical and sustainable methods

In this regard, this research is concerned with the synthesis of new antibacterial nanomaterial based on starch nanoparticules (SNPs) and Rosin, a natural resin extracted from pine trees. We have used eco-friendly facile method to produce SNPs modified with natural antimicrobial rosin. In this research we have successfully, grafted rosin molecules on starch nanoparticles ((scheme 1).

This new Rosin-SNP nanoparticle showed good antibacterial properties and good thermic stability. Therefore it will be suitable candidate for antibacterial food packaging prepared by conventional manufacturing methods (extrusion and thermoforming).

Keywords *agricultural waste, starch nanoparticles · Maghnite-H+ · Rosin acid · Esterification ·*



Scheme1: The synthesis of starch nanoparticles (SNPs) esterified with rosin acid and its antibacterial mechanism

Green and Sustainable Solvent Extraction of Rare Earth Elements

M. Atanassova[1*], N. Todorova[1], V. Kurteva[2], D. Gerginova[2]

[1]University of Chemical Technology and Metallurgy, Department of General and Inorganic Chemistry,
8 Kliment Okhridski blvd., 1756 Sofia, Bulgaria
[2]Bulgarian Academy of Sciences, Institute of Organic Chemistry with Centre of Phytochemistry,
Acad. G. Bonchev street, Block 9, 1113, Sofia, Bulgaria

ma@uctm.edu

The investigation aims at a rational search for unfamiliar, high yield and eco-efficient processes to extract and separate valuable metals via sustainable extraction that embodied 4f-ion high-performance behaviours. Unfortunately, end-of-life recycling rates for all rare earth elements are below 1%. The global objective is to propose so far unexplored and versatile new strategies: the optimization of the aqueous-biphasic systems composed of water (or not) and organic phase incorporating “green” extracting moiety(s) dissolved in different adopted media. The choice of the right systems is a key factor for effective process focusing on the employment of more eco-friendly, “best” organic molecular or ionic liquid diluents. Study of the liquid-liquid extraction with a chelating compound, 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP) and determination of the process parameters are presented employing two ionic liquids ($[C_1Cnim^+][Tf_2N^-]$, n=4, 10) and $CHCl_3$, as diluents. By comparison to $CHCl_3$, the ionic liquid offers again increased distribution ratios in aqueous medium. A step forward, enhanced solvent extraction and improved separation upon addition of ethylene glycol (EtG) are demonstrated, i.e. boost of two immiscible organic phases, comparing to traditional aqueous solutions. The main goal is to develop a non-aqueous process for switchable separation of 4f-ions, that is to be competitive over conventional aqueous solvent extraction systems, and to test this process further with other switchable hydrophilicity diluents. However, this is noticeable when using $CHCl_3$, but unfortunately not with ionic liquid, $[C_1C_{10}im^+][Tf_2N^-]$. Several conclusions are given highlighting the role of the ionic diluent in complexation processes and selectivity with an employment of the chelating agent HP for various metal s-, p-, d- and f-cations. The competitive solvent extraction test of almost 25 metal ions by the chelating ligand HP diluted in two ILs and $CHCl_3$ has also been conducted in order to evaluate the switchable hydrophilic diluent, EtG as a more polar liquid phase. It is a known fact in coordination chemistry that different metal ions show a different affinity towards given specific extractant molecule, so, they will distribute, probably, differently over both immiscible liquid phases and metal separation can be easily achieved. Nevertheless, it is worthy to underline again, that the extraction ability and selectivity is a pair of contradictory elements almost always, videlicet frequently high extraction efficiency was not accompanied with marked selectivity with any change in the solvent system, i.e. the nature of the two liquid phases or extracting moiety. The impact will be game-changing on various areas of chemistry, chemical engineering technology, metallurgy and recycling pinpointed the green concept.

Acknowledgement
The research leading to those results received funding from the Bulgarian National Science Fund: Grant Agreement № КП-06-H69/5(2022), “Green twist to synergistic solvent extraction and separation of rare earth metals”.

References

Atanassova, M. (2022) 'Thenoyltrifluoroacetone: Preferable Molecule for Solvent Extraction of Metals—Ancient Twists to New Approaches', Separations 2022, 9, 154. https://doi.org/10.3390/separations9060154.

Atanassova, M. (2022) 'Assessment of the Equilibrium Constants of Mixed Complexes of Rare Earth Elements with Acidic (Chelating) and Organophosphorus Ligands', Separations 2022, 9, 371. https://doi.org/10.3390/separations9110371.

New Circular Bio-Economy Strategies in Biowaste Valorization- Anthropogenic Pollutants as Sustainability Factor

R. Kallenborn[1*]

[1]Norwegian University of Life Sciences (NMBU) - Faculty of Chemistry, Biotechnology and Food Sciences (KBM)

As an important societal measure for establishing sustainable future circular bioeconomy strategies, recycling and reuse of both non-renewable and renewable resources mainly derived from organic residues is considered an important prerequisite. Thus, applying, reusing and refining organic residues, previously considered as wastes, is an important research and societal focus on the national and international level. In many countries, biowastes are currently applied as preferred soil amendment and fertilizer for the effective recycling the nutrients incl. nitrogen and phosphorous in modern sustainable agricultural applications. However, such soil amendments may also lead to dispersal and accumulation of contaminants in agricultural soils if not properly monitored and treated. From soils, these contaminants may be absorbed and accumulated into food and fodder plants, ultimately resulting in animal and human exposure. The development of suitable production and refinement pathways for recycling and renewable energy production in recent years still do not take potential associated pollutant transfer sufficiently into account when commercialising their refined products. Various technologies have been promoted and applied with the potential of uncontrolled emission of anthropogenic pollution. For instance, the use of biological (waste) materials in anaerobic digestion processes, both as decentralized farm based as well as municipal biogas plants is currently marketed as new pathway for sustainable energy production. Hence, among others, organic household waste, as substrates for biogas production has increased significantly in Europe, Asia and the North Americas. This development leads not only to an increasing amount of bioenergy produced, but also to a considerable amount of production waste to be handled properly as starting material for new products. Also, recent development in large scale Urban Agriculture (UA) for greening of large cities is expected to develop into an important new pathway for bioeconomic production in an urban context. AS part of UA related urban sustainable strategies, agricultural substrate soil, fertiliser and infrastructures from the respective urban areas are utilised or reused. However, pollutant associated aspects of the soils and the potential for uptake in commercially available consumer products are not sufficiently implemented in the current international UA strategies. Possible consequences of organic pollutants in UA installations and commercially distributed products will be discussed as case studies in the presentation.

Recycling of Rare Earths Elements from Electric Motors of the E-mobility

T. Gianluca[1]*, F. Passarini[1]

[1]University of Bologna, Department of industrial chemistry "Toso Montanari", Viale del Risorgimento, 4, 40136, Bologna, Italy

Gianluca.torta2@unibo.it

NdFeB permanent magnets are the strongest magnets on the market. These magnets are made of rare earth elements (REEs) such as Nd, Pr and Dy which are listed in the EU's list of critical raw materials. The main reason why REEs are considered highly critical material for Europe is the geographical distribution of global production. The main producer globally is China. Europe has no internal production of rare earth elements, even though, some interesting mines are present in the European territory (e.g., Sweden). The situation becomes even worse if the global distribution of refined products is considered (European Commission, 2020). Almost the totality of the global production of rare earth metals and permanent magnets is in China with 91% and 94%, respectively. NdFeB permanent magnets have a key role in the ecological transition that will take place in the next decades, being a key component of the electric motors of e-mobility. So, the criticality of rare earth elements such as Nd, Pr and Dy is likely to increase in the next future. Other important applications are in consumer electronics such as HDDs and acoustic transducers, in wind turbines, in the compressors of air conditioners. The demand for almost all of these applications are destinated to grow (Shulze et al., 2016) Thus, it is of crucial importance for Europe to find a solution to become less dependent from China in the next few years. The possible solutions are to start exploiting the existing mines, finding new sources of rare earth elements, start recycling of rare earth bearing waste. Europe is one of the largest consumers of products containing NdFeB magnets, so recycling has high potential. More than 75% of the European demand of REEs could be satisfied by recycling in 2050 (Metals for Clean Energy, 2022). Nowadays, the global recycling rate of REEs is less than 1% because the current recycling processes applied to NdFeB magnets bearing waste valorize only the iron, aluminum and copper fraction and not the REEs content. For example, electric motors are shredded and mechanically processed to separate the ferrous metals from the non-ferrous fraction. During this process NdFeB magnets are diluted in the ferrous fraction and not recovered.

The aim of this project is to quantify and characterize the NdFeB magnets content in different types of electric vehicles such as electric cars, plug-in hybrid cars to evaluate the economic potential and the feasibility of recycling and develop a recycling process able to recover the rare earth content from electric motors of the e-mobility.

References

European Commission, Study on the EU's list of Critical Raw Materials (2020), Factsheets on Critical Raw Materials.

Rita Schulze et al (2016), Estimates of global REE recycling potentials from NdFeB magnet material, Resources, Conservation and Recycling,pp 12-27. doi:https://doi.org/10.1016/j.resconrec.2016.05.004.

Metals for Clean Energy - Pathways to solving Europe's raw materials challenge, (2022).

The Anthropogenic Elemental Cycle of Manganese, Nickel and Natural Graphite in the Eu

L. Ciacci[1,2]*, E. Bernardi[1,2], F. Passarini[1,2]

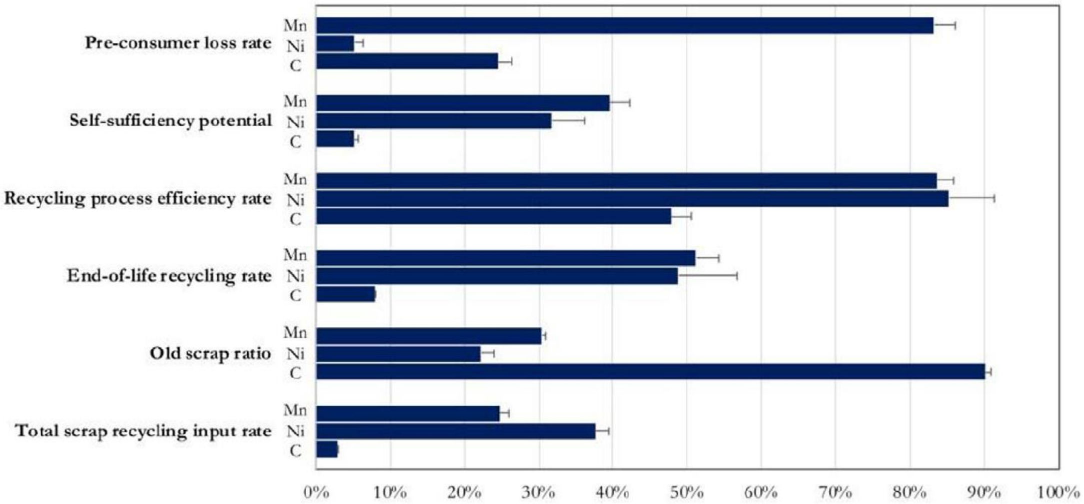
[1]Department of Industrial Chemistry "Toso Montanari", University of Bologna, 40136 - Bologna, Italy
[2]Interdepartmental Centre for Industrial Research "Renewable Resources, Environment, Sea and Energy", University of Bologna, 40136 - Bologna, Italy

luca.ciacci5@unibo.it

The characterization of elemental cycles has a long history in bio-geo-chemistry. Two main goals have driven this effort: to establish a firm scientific understanding and to do so with sufficient reliability and in enough detail that policy options related to human activities might be reasonably discussed. A growing effort in the recent years has been addressed to the cycles of materials dominated by human action such as manganese, nickel, and natural graphite, examples of materials having a consolidated supply chain with essential role in clean energy systems and e-mobility.

To this aim, the EU Material System Analysis (MSA) (BIO by Deloitte, 2015) is among the assessment tools for mapping materials flows though the economy and to achieve quantitative understanding of industrial development and potential environmental impact about the flows of resources, ultimately informing strategies for elemental circular economy.

In this study, we developed and applied MSA to analyze the anthropogenic cycle of manganese, nickel, and natural graphite from 2012 to 2016. We provide a detailed characterization of their material stocks, flows, and changes in selected performance indicators including end-of-life recycling rate, self-sufficiency potential, old scrap ratio, recycling input rate, recycling process efficiency rate, and pre-consumer losses rate. The achieved results may inform decision-makers engaged with raw materials recovery and recycling as well as the strategic security of a reliable material supply to the EU for resilient industrial ecosystems.



Performance indicators results for manganese (Mn), nickel (Ni), and natural graphite (C) in the EU. Averages and standard deviations for 2012–2016 [1]

References

Ciacci, L. et al. (2022) Journal of Industrial Ecology, 1-14. doi: 10.1111/jiec.13226.

BIO by Deloitte. (2015). Study on data for a raw material system analysis: roadmap and test of the fully operational MSA for raw materials. Final Report prepared for the European Commission, DG GROW.

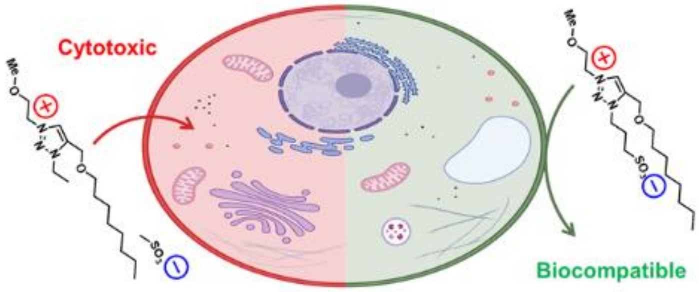
Developing Biocompatible Ionic Liquids Using Chemistry and Computation Tools

W. Min[1], J. Yan,[1] X. Pan[1], J. Jia[1], T. Yue,[2] Y. H. Chu[3], X. Yan[1], B. Yan[1*]

[1]Guangzhou University
[2]Ocean University of China, China
[3]National Cheung Cheng University, Taiwan

madayildiya@gmail.com

Due to their unique properties, ionic liquids (ILs) have been widely used as “green solvents” in diverse areas. Despite their very low vapor pressure and lack of air pollution, they pose a pollution threat to environmental waters and soil. Therefore, understanding their toxicity mechanisms and improving their biocompatibility are essential. We applied IL library design and synthesis, cellular investigations, and computation to discover more biocompatible ILs. By incorporating a triazolium cation ring to replace the imidazolium ring, the cytotoxicity was reduced by five folds. By connecting cation and anion in ILs, the zwitterionic liquids (ZILs) exhibited nearly thousands of fold reduction in cytotoxicity in human cells. In contrast to structurally related ILs, the molecular simulation revealed that these zwitterionic molecules evaded the cell by accelerated self-aggregation instead of perturbing cell membranes like ILs. These results established a design principle for the next generation of highly biocompatible ionic liquids.



Sustainable Synthesis of a Flavor Ester in a Continuous Solventless System

C. Vasilescu[1], I. Miloş[1] and C. Paul[1]*

[1]Politehnica University Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, Department of Applied Chemistry and Engineering of Organic and Natural Compounds, Carol Telbisz 6, 300001, Timisoara, Romania

cristina.paul@upt.ro

Increasing awareness of environmental and health concerns among the public has led to the development of greener, safer processes for the production of valuable industrial esters, such as flavor and fragrance esters. In this regard, the use of ecological catalysts (biocatalysts) in industrial processes was considered essential to meet the demands of sectors including the food, cosmetic, and personal care industries, which require high-quality products (Miguel Júnior et al., 2022). Enzyme-catalyzed processes take place under mild reaction conditions, ambient temperature, atmospheric pressure, and physiological pH, therefore being more environmentally friendly and cost-effective (Vasilescu et al., 2022).

The continuous flow esterification of caproic acid and n-amyl alcohol was carried out in a solventless system, using a packed-bed reactor with 1.5 g immobilized enzyme (20 mg of protein); the main parameters of the synthesis process were optimized using design of experiments. The biocatalyst used was lipase from Candida antarctica B (GenoFocus, South Korea) immobilized by entrapment in sol-gel hybrid matrices obtained with epoxy functionalized silane precursors.

The reaction parameters investigated were the alcohol to acid ratio, flow, and temperature, each at three distinct levels. The parameters were optimized using a face-centered CCD design, and the biocatalytic system was evaluated in terms of ester yield and productivity of the enzyme biocatalyst. Ester formation was determined by GC-FID analysis of samples collected within a set time frame, following the stabilization of the system. The optimal parameters were determined as: the alcohol to acid ratio of 1:1, the flow rate of 0.2 ml/min, and the temperature of 80 º C. This study demonstrates the applicability of sol-gel entrapped lipases in a packed-bed reactor for continuous aroma ester synthesis.

Acknowledgments
This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE-2019-1179, within PNCDI III, contract number TE 94.

References

Miguel Júnior, J. et al. (2022) ‘Improved Catalytic Performance of Lipase Eversa; Transform 2.0 via Immobilization for the Sustainable Production of Flavor Esters - Adsorption Process and Environmental Assessment Studies’, Catalysts, 12, doi:10.3390/catal12111412.

Vasilescu, C. et al. (2022) ’Development of a Tailored Sol-Gel Immobilized Biocatalyst for Sustainable Synthesis of the Food Aroma Ester n-Amyl Caproate in Continuous Solventless System’, Foods, 11, doi:10.3390/foods11162485.

Rich in Polyphenols Dry Extract from R.Damascena - a Way For Utilization the Waste from Industrial Rose Processing

D. Antonova[1]*, K. Gechovska[1], V. Deneva[1], S. Bozhanov[2], L. Antonov[3]

[1]Bulgarian Academy of Sciences, Institute of Organic Chemistry with Centre of Phytochemistry, 1113 Sofia, Bulgaria
[2]Medical University of Sofia, Faculty of Pharmacy, 1000 Sofia, Bulgaria
[3]Bulgarian Academy of Sciences, Institute of Electronics, 1784 Sofia, Bulgaria

daniela.nedeltcheva@gmail.com

The wastes and by-products of the industrial processing of various plant raw materials represent a serious problem due to the need for their disposal, but they can also be a promising source of useful compounds that can be used for their technological, pharmacological or nutritional properties. From an economic point of view, the significant costs of drying, storing and transporting waste products are also a limiting factor. For this reason, agro-industrial waste is most often used as feed or as fertilizers. That is why the efficient, cheap, and environmentally friendly utilization of these materials is becoming increasingly important.

In Bulgaria, annually the rose oil industry produces over 2 500 kg high quality rose oil and creates internationally recognizable image of the country (Bulgarian rose oil) and provides income for the local rural population (including minorities). At the same time the rose oil industry generates large amounts of waste due to the low content of essential oil in the fresh rose petals. Therefore, the reduction and valorisation of waste is one of the main challenges from an ecological point of view and also for the recovery of valuable biologically active substances (Slavov et al., 2017).

Therefore, the aim of this study was development of an extraction procedure of the by-product from the rose concrete production and exploring the content of the biologically active compounds in the extracts by means of HPLC/DAD.

According to the technological process in the production of rose concrete (solvent extraction with non-polar solvents of fresh rose flowers), it can be assumed that the resulting plant residue would be as rich of polyphenolics, as the plant itself, and could be used for development of novel products with promising health-promoting effect.

An optimisation of extraction procedure of the by-product from the rose concrete production was carried out. An assay of the extracts in respect of their total polyphenols and total flavonoids content was performed. HPLC analysis of quercetin and kaempferol, the two main flavonoids found in R. damascena, was also carried out. The results have shown that the flavonoid content in the rose extracts is comparable to that of the green tea or Gingko biloba and they could be used for development of various products (food supplements, natural cosmetic and phyto-pharmaceutical formulation, etc.).

Acknowledgements: The financial support of the project KP-06-OPR-01/5 “BG ROSEnsing: Traditional and e-sensing of Bulgarian Rose aromatic products: towards fast authenticity and quality control”, funded by the National Science Fund (Ministry of Education and Science) of Bulgaria is gratefully acknowledged.

References

Slavov, A. et al (2017) "Valorization of wastes from the rose oil industry", Rev Environ Sci Biotechnol,
doi: 10.1007/s11157-017-9430-5.

Identification of most Relevant Variables and Processes to Assess the Environmental Impacts of Remediation Technologies along their Life Cycles: Focus on the Waste Management Scenarios

M. Menegaldo[1,2]*, L . Pizzol[3], A. Tinello[2], P. Scanferla[2], A. Zabeo[3], S. Breda[2], A. Marcomini[1,2], E. Semenzin[1,3]

[1]Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Scientific Campus, via Torino 155, 30172 Mestre, VE, Italy
[2]Fondazione Università Ca' Foscari, Dorsoduro 3859, 30123 Venezia, VE, Italy
[3]GreenDecision s.r.l., Scientific Campus, via Torino 155, 30172 Mestre, VE, Italy

martina.menegaldo@unive.it

The application of Life Cycle Assessment (LCA) to remediation technologies is still not a consolidated practice and it is especially lacking in the assessment of the environmental impacts associated to the management of the remediation waste. This study aims at addressing these methodological gaps by addressing the following steps are: i) the identification of the classes and typologies of waste produced during the contaminated sites remediation and their classification according to European Waste Classification (EWC) Codes, ii) the identification of the waste management scenarios (WMSs) applicable to the identified waste typologies, iii) the selection of LCA processes that can be used to assess the impacts of the different WMSs and iv) the quantification and comparison of the environmental impacts caused by the different WMSs applied considering hazardousness levels to which the same waste may belong: inert, non-hazardous and hazardous waste (Waste Framework Directive 2008/98/EC).

As results, a matrix reporting the classes and typologies of waste, their EWC codes, their different WMSs and the suitable LCA processes from the Ecoinvent database that can be applied to each EWC within a specific WMS, has been developed. Additionally, this contribution will present the comparative assessment of the impacts caused by the LCA processes applicable to the same waste typology within the same WMS which has been performed to support the selection of the most appropriate WMS case by case.

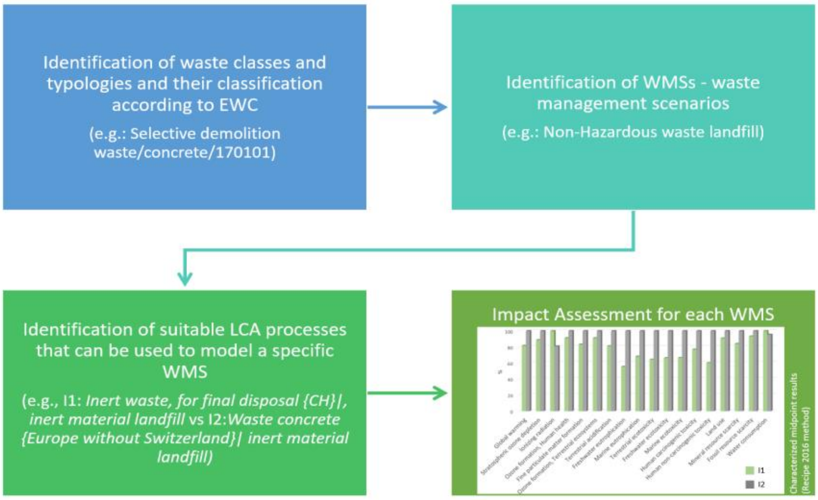


Figure 1: The developed approach.

References

European Union. 2008. Directive 2008/98/EC of the European Parliament and the Council of 19 November 2008 on Waste and Repealing Certain Directives. Official Journal of the European Union.

2002-2022: 20 Years of E-Waste Regulation in The EU And Evolution of World-Wide Recycling Technologies and Practices

A. Serpe[1]*, L. Bisschop[2], D. Chatterjee[3], G. De Gioannis[1], M. S. Ermolin[4], P. Fedotov[5], H. Garelick[6], B. Miller[7], V. M. I. Piro[1], O. E. Popoola[8], D. Purchase[6], Y. Shevah[9], S. Verbeek[2]

[1]University of Cagliari and IGAG-CNR, Cagliari, Italy
[2]Erasmus University Rotterdam, Rotterdam, Netherlands
[3]University of Kalyani, Kalyani, India
[4]National University of Science and Technology "MISiS", Moscow, Russia
[5]Russian Academy of Sciences, Kosyg, Russia
[6]Middlesex University, London, United Kingdom
[7]Littleton, CO, USA
[8]Yaba College of Technology, Lagos, Nigeria
[9]TAHAL Consulting Eng., Ltd., Tel Aviv, Israel

serpe@unica.it

Electrical and Electronic Equipment (EEE or simply "electronic devices") are integral to our daily life. In recent decades it has largely contributed to improving the quality of life, providing different benefits and opportunities in a variety of sectors: from energy, transport, health, security, to school/education. Population growth and consumer demand are driving manufacturing and fueling raw material consumption. On the other side, countries have to face an increasing accumulation of e-waste. A shift of paradigm to move away from the unsustainable linear economic model to a circular approach is therefore essential to reduce the pressure of our limited natural resources and limit the environmental impact of waste landfill. In this context, visionary regulations have been promulged world-wide addressed to change a concern into an opportunity. Among them, EU Directives have been playing a pivotal role in driving the "green" revolution in this field. The presentation reports the results of a multidisciplinary appraisal of 20 years (2003-2023) of the EU Directives *EUROPEAN COUNCIL DIRECTIVE, 2023), on WEEE management, carried out by an international team funded by the IUPAC Division VI - Chemistry and Environment. Specifically, the evolution of the sensitivity and responsibility of industrial and social communities around the world is discussed with specific reference to: i) the evolution over time of the e-waste concept, from an environmental issue to a valuable resource of secondary raw materials in the framework of circular economy; ii) regulations and policy developed in different countries, focusing on the responsibilities and on the request for innovation in products design (eco-design for an effective end-of-life management) and sustainability in treatments (green processes); iii) how new production and recycling processes have been developed to promote a more sustainable life-cycle of EEE; and iv) how countries have implemented the suggestions and encouragements of the regulations in recent decades through specific initiatives and achieving target goals. The work presented here aims to highlight the progress being made in e-waste recycling over the last 20 years, identifying key parameters to assess the progress towards more sustainable approaches to safeguard human health and the environment, and how to improve at the global level in this field to move towards the Sustainable Development Goals of United Nations - Agenda 2030 (UN, 2023).

References

DIRECTIVE 2002/96/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL, 27/01/2023 on waste electrical and electronic equipment (WEEE), https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32002L0096.

United Nations, Agenda 2030, https://sdgs.un.org/2030agenda.

Application-Oriented Zinc Oxide Nanocrystals Derived from Safe-By-Design Self-Supporting Organometallic Approach

J. Wielgórska[1,2*], M. Wolska-Pietkiewicz[1], J. Lewiński[1,3]

[1]Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
[2] Nanoxo, Kasprzaka 44/52, 01-224 Warsaw, Poland
[3] Institute of Physical Chemistry Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

julia.wielgorska.dokt@pw.edu.pl

The preparation of semiconducting nanocrystals including ZnO quantum dots (QDs) with specific size and shape as well as desired properties is one of the greatest interdisciplinary challenges for both chemists and materials engineering specialists. Moreover, the unique physicochemical properties of ZnO QDs as functional material offer a wide range of potential applications in many fields, such as electronics, optics, solar cells, anti-counterfeiting etc. The challenge is to obtain a material that is stable, monodisperse and soluble in protic and aprotic solvents, which determines its application.
In this work, we report on the preparation of ZnO QDs using organometallic self-supporting method (Wolska-Pietkiewicz M., et al., 2019, Lee D. et al., 2019) Our synthetic protocol for the preparation of ZnO QDs involves two steps conducted in a one-pot manner. In the first step, several reactions between Et2Zn and selected pro-ligands in THF were performed. Then the resulting solutions were exposed to air to initiate transformations leading to ZnO nanostructures with interesting features. The resulting ZnO QDs are highly monodispersed, non-toxic and few nanometers size. Moreover, optical, physical, and chemical properties of resulting ZnO QDs were systematically investigated and were confirmed by many different analytical techniques: HRTEM, DLS, PXRD, UV-VIS, PL, NMR, and IR.
Moreover the colloid of the obtained ZnO QDs using our novel method can be applied as an anti-counterfeiting ink owing to its solubility, colorlessness, and UV-excited luminescence. In a nutshell, the obtained luminescent inks based on ZnO QDs as transparent luminescent labels are stable over time, chemically inert and non-toxic, therefore they can be incorporated into a wide range of consumer products. The results demonstrate that self-supporting organometallic approach is a highly promising method to obtain high-quality ZnO QDs inks for anti-counterfeiting applications or sorting labels.

References

Wolska-Pietkiewicz M., et al., (2019) 'ZnO nanocrystals derived from organometallic approach: Delineating the role of organic ligand shell on physicochemical properties and nano-specific toxicity', Sci. Rep. 2019, 9, p.18071 doi: 10.1038/s41598-019-54509-z

Lee D. et al., (2019) 'Disclosing Interfaces of ZnO Nanocrystals Using Dynamic Nuclear Polarization: Sol-Gel versus Organometallic Approach', Angew. Chem. Int. Ed. 58, p. 17163-17168 doi: 10.1002/anie.201906726.

g-C_3N_4-Embedded Ormosil as Multifunctional Treatments with Photocatalytic and Hydrophobic Properties for the Protection of Building Materials

M. Luna[1,2,3], C.G. Silva[2,3], M.J. Mosquera[1] and J.L. Faria[2,3]*

[1]University of Cadiz, Department of Physical Chemistry, Campus Universitario Río San Pedro, 11510, Puerto Real, Spain
[2]University of Porto, LSRE–LCM – Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Rua Dr. Roberto Frias s/n, Porto, 4200-465, Portugal
[3]University of Porto, ALiCE – Associate Laboratory in Chemical Engineering, Rua Dr. Roberto Frias s/n, Porto, 4200-465, Portugal

jlfaria@fe.up.pt

Photocatalysis is an attractive method to mitigate the effects of air pollution in big cities and industrial areas since it can eliminate a wide range of pollutants to non-hazardous substances using sunlight. The use of TiO_2 for producing photoactive building materials is well-documented in the literature as a way to obtain buildings with depolluting and self-cleaning properties (Chen and Poon, 2009). On the other hand, several of the most common decay phenomena affecting cultural heritage buildings are related to the water ingress inside its pore structure. Pollutants can promote these degradation mechanisms accelerating the building's ageing. Therefore, employing hydrophobic treatments to reduce the water ingress in the material is one of the most effective methods for building protection (Zhao et al., 2022). In this way, combining TiO_2 with a hydrophobic agent can produce multifunctional coatings with photocatalytic and hydrophobic properties for the integral protection of building materials (Colangiuli, Calia and Bianco, 2015).

However, the use of TiO_2 on buildings presents a significant limitation because it is only activated by UV radiation, which is relatively scarce in sunlight. The choice of the hydrophobic agent is also an important issue since multiple factors should be considered. For example, the effectiveness and durability of the treatment can be limited if the hydrophobic action is restricted to the surface, and the hydrophobic component should be compatible with the photocatalyst and the substrate to ensure the suitable adhesion of the coating. With this in view, the present work investigates the use of graphitic carbon nitride (g-C_3N_4) as a photocatalyst to obtain visible light active building materials. A mixture of alkoxysilanes and alkylalkoxysilanes has been employed to obtain an organically modified silica (ormosil) that acts as a binder promoting the adhesion of photocatalyst to the building material and provides hydrophobic properties. The treatment consists of a g-C_3N_4 suspension in the ormosil sol applied on cement mortar samples by brush. The ormosil sol can partially penetrate the substrate pore structure and reacts spontaneously, producing the g-C_3N_4-ormosil coating on the material surface and a hydrophobic layer inside it.

The results confirmed the treatment's multifunctionality, exhibiting the treated samples photocatalytic and hydrophobic properties. Specifically, the treated samples degraded 75% of a Rhodamine B stain in 120 hours under visible light, an increase of 35% compared to the equivalent treatment containing TiO_2. The cement mortar's initially hydrophilic and absorbent surface turned hydrophobic. The change in capillary water absorption was also evaluated, determining that the treatment reduced the total water uptake of cement mortar by more than 97% and the water absorption coefficient by more than 99%. The substrate-treatment affinity was also evaluated by observing a high substrate-coating adhesion, which ensures durability.

Work financially supported by LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC).

References

Chen, J. et al. (2009) ‘Photocatalytic construction and building materials: From fundamentals to applications’, Building and Environment, 44(9), pp. 1899–1906. doi:10.1016/j.buildenv.2009.01.002.

Colangiuli, D., et al. (2015) ‘Novel multifunctional coatings with photocatalytic and hydrophobic properties for the preservation of the stone building heritage’, Construction and Building Materials, 93, pp. 189–196. doi:10.1016/j.conbuildmat.2015.05.100.

Zhao, J. et al. (2022) ‘Hydrophobic or superhydrophobic modification of cement-based materials: A systematic review’, Composites Part B: Engineering, 243(October 2021), p. 110104. doi:10.1016/j.compositesb.2022.110104.

PM-Induced Atmospheric Corrosion: Accelerated Ageing Tests by Using Ambient PM

E. Bernardi[1,2*], C. Velino[1], C. Chiavari[3], C. Martini[4], I. Vassura[1,2]

[1]University of Bologna, Dept. of Industrial Chemistry "Toso Montanari", Viale del Risorgimento 4, 40136, Bologna, Italy
[2] University of Bologna, Center for Industrial Research - Fonti Rinnovabili, Ambiente, Mare e Energia (CIRI FRAME)
[3]University of Bologna, Dept. of Cultural Heritage, Via degli Ariani 1, 48121, Ravenna, Italy
[4]University of Bologna, Dept. of Industrial Engineering, Viale del Risorgimento 4, 40136, Bologna, Italy

elena.bernardi@unibo.it

Field studies of the corrosion mechanisms induced by outdoor atmospheric particulate matter (PM) are particularly complex, due not only to the spatio-temporal variability of PM concentration, size and composition, but also to its different deposition and removal rates as a function of the nature, geometry and environmental exposure conditions of cultural heritage artefacts. Therefore, several strategies can be adopted to investigate PM-induced corrosion, from the analysis of specific artefacts (Aramendia J. et al. 2015), to the exposure of coupons (Saha D. et al. 2016), the adoption of outdoor exposure systems Ferrero, (L. et al. 2018) allowing PM deposition on coupons by avoiding particles removal, the use of single salts or simple mix of salts to simulate PM, the formulation of representative synthetic PM mixtures to be included in artificial ageing protocols (under study in our research group). A further interesting strategy can be the combination of ambient PM sampling on coupons and their artificial ageing in controlled conditions. To this aim, an ad hoc accelerated sampling system was first set up to collect PM on metallic substrates. This system allows both to retain all the compositional complexity of ambient PM and to collect a significant amount of PM in a few hours; thus, coupons with PM deposits representative of specific periods (e.g. of the day or of the year) can be obtained. Then, in order to define a methodology to correlate PM characteristics and corrosion effects from both a qualitative and quantitative point of view, 15 samplings (4 coupons per sampling) where performed on bronze specimens (Cu-5Sn-5Zn-5Pb) with different sampling time and in different seasons, so as to maximize PM variability in term of mass and composition. For each sampling, the amount of PM per surface unit was determined for all the 4 coupons. Subsequently, 2 coupons were extracted in ultrapure water to chemically analyze the PM soluble fraction, while the other 2 underwent 3 weeks of accelerated ageing, consisting in the repetition of a T, RH and UVA irradiation cycle simulating daily and seasonal variations. Coupon surfaces were characterized by optical microscopy, FEG-SEM/EDS, ATR-FTIR, Raman spectroscopy and Vis-spectrophotometry. Alloying metals in the water-soluble and insoluble fractions of the developed corrosion products were quantified. Finally, mass loss and changes in the surface profile were determined. Results showed that the accelerated sampling system is effective in simultaneously collecting PM on 4 metal coupons, providing homogeneous and reproducible deposits, representative of the atmospheric PM composition and concentration in the sampling period. The experimental protocol for PM sampling, PM analysis, accelerated ageing and aged coupons characterization proved to be suitable for obtaining appreciable corrosive effects and quantitative information, allowing a first evaluation of the correlations between PM composition and bronze corrosion. The proposed protocol can represent a "hybrid" solution between outdoor exposure and laboratory tests, allowing to analyze the effects of ambient atmospheric PM in controlled conditions and in a relatively short time.

References

Aramendia, J. et al. (2015), Structural and chemical analyzer system for the analysis of deposited airborne particles and degradation compounds present on the surface of outdoor weathering steel objects, Microchemical Journal, 123, p. 267–275.

Saha, D. et al. (2016), Role of environmental particulate matters on corrosion of copper, Atmospheric Pollution Research, 7, p. 1037-1042.

Ferrero, L. et al. (2018), Chemically and size-resolved particulate matter dry deposition on stone
and surrogate surfaces inside and outside the low emission zone of Milan: application of a newly developed "Deposition Box", Environmental Science and Pollution Research, 25, p. 9402–9415.

Green Materials for the Conservation and Restoration of Parchment and Leather Artefacts

I. Quaratesi[1*], C. Carsote[2], L. Miu[1], M. Niculescu[1], E. Badea[1,3]

[1]National Research and Development Institute for Textile and Leather - Research Institute for Leather and Footwear (INCDTP-ICPI), Ion Minulescu Str. 93, 031215 Bucharest, Romania.
[2]National Museum of Romanian History, Calea Victoriei Str. 12, 030026 Bucharest, Romania.
[3] University of Craiova, Department of Chemistry, Faculty of Sciences, Calea Bucuresti Str. 107 I, 200512 Craiova, Romania.

i.quaratesi@gmail.com

The concept of sustainability has an ever-growing presence in our society and green possibilities can significantly contribute to a sustainable conservation of cultural heritage. In fact, the research efforts to substitute hazardous chemicals used in the conservation made significant advancements: new eco-friendly materials and technologies for conservation have already been developed using green chemistry. In this study we will present the development of bio-based products, innovative green methods, products, and strategies which have been incorporated into environmentally sustainable conservation practices. Fully biodegradable parchment, leather and collagen-based adhesives were developed for conservation and restoration purposes such as patch loses, stitching, in-filling or mending. By combining the adhesive technique with the old sewing practice, functional and durable solutions can be created because the strength of the parchment allowed fine stitches to be used without risk of tearing (Miu L. et al., 2007). An effective consolidanting solution for red rot leather was developed based on haloysite nanotubes and nano-MgO for long-term pH buffering and antimicrobial activity (Badea et al., 2019). A green emmolient composition based on extracts from Tanacetum vulgare, showing both antifungal and insecticidal activity, was developed for the preventive care and maintenance of historical leather artefacts (Miu L. et al., 2020).
These bio-based products enables a green approach (methods, materials, strategies) in the preventive and active consercation that reduce the employ of the chemical, solvents and toxic products currently used to clean, consolidate, protect and restore cultural heritage artefacts. They represent a step towards a green conservation approach. Hoevery, every new proposed treatment needs to be deeply investigated in its efficiency in preserving the artefact, in its long- term effects eventually induced in the substrate as well as in its easiness of application, safety and environmental biocompatibility.

References

Miu L., et al. (2007) 'Documente medievale pe pergament – avaluare şi investigare' Certex edition, cap. 2, pp.41-42.

Badea E., et al. (2019) 'The effect of halloysite nanotubes dispersions on vegetable tanned leather thermal stability', Herit. Sci., 7, 68. doi: 10.1186/s40494-019-0310-x.

Miu L. et al. (2020) 'Aspects regarding the effectiveness of volatile oils of the tanacetuma vulgare kind in the conservation of heritage objects' ICAMS 2020 – 8th International Conference on Advanced Materials and Systems, Bucharest, Romania. doi: 10.24264/icams-2020.V.5.

The ARMID@Venezia: a Project Post-Acqua Granda

M. Baldan[1]*, A. Martignon[1], S. Eupani[2], P. Da Col[3], D. Manzini[4] and G. Pojana[1]

[1]Ca' Foscari University of Venice, Department of Philosophy and Cultural Heritage, Dorsoduro 3484/D, Calle Contarini, 30123, Venice, Italy
[2]Ca' Foscari University of Venice, Department of Molecular Sciences and Nanosystems, Via Torino 155, 30172, Venice Mestre, Italy
[3]Benedetto Marcello Conservatory of Venice, San Marco 2810, 30124, Venice, Italy
[4]MADATEC Srl, Via Monte Grappa 18, 20060, Pessano con Bornago (Milan), Italy

maela.baldan@unive.it

The ARMID@Venezia (ARchivio Musicale e Iconografico Digitale A Venezia) project aims to safeguard the extraordinary document collections preserved in the library of the Benedetto Marcello Conservatory of Venice, heavily damaged by the exceptionally high tide of November 2019 (named “Acqua Granda”). The project provides to digitalize, through high photographic reproduction, virtually restore and investigate in detail the materials (supports, inks, pigments and dyes, etc.) with a view to their future physical restoration. Only non-invasive and non-destructive techniques are being employed, such as Imaging Analysis in the Visible (including macro- and micro-photographic examination), near-infrared (NIR) and near-ultraviolet (UV-Induced Fluorescence, Reflected UV) range, on representative artefacts. Non-invasive spectroscopic techniques, such as Fiber Optic Reflectance Spectroscopy (FORS), Infrared Spectroscopy (FTIR, NIR, DRIFT), µ-Raman and X-Ray (XRF) are being applied as well for the chemical characterization of materials. The result of near-infrared, UV-Induced Fluorescence and X-Ray investigation to reveal the damage of brackish water caused by the “Acqua Granda” phenomenon on ancient materials (inks and papers) will be presented.

Some of Benedetto Marcello Conservatory of Venice's ancient musical documents damaged by the Acqua Granda phenomenon

References

Craig-McFeely J., Lock A. (2006), Digital Restoration Workbook, Oxford Select Specialist Catalogue Publications, Oxford.

Dyer J. et al. (2013), Multispectral imaging in reflectance and photo-induced luminescence modes: a user manual, British Museum, London.

Barrett, T. et al. (2012). XRF analysis of historical paper in open books. In A. N. Shugar (Ed.), Handheld XRF for Art and Archaeology, Leuven University Press, pp. 191–214.

Interplay between Bacterial Biofilm and Historical Outdoor Bronze Surfaces in the Climate Change Context

A. Timoncini[1], E. Bernardi[2], C. Martini[3], A. Balbo[4], Laura de Bellis[4], M. Bertoldo[5], E. Buratti[5], C. Chiavari[1]*, R. Turner[6]

[1]University of Bologna, Department of Cultural Heritage
[2]University of Bologna, Department of Industrial Chemistry "Toso Montanari"
[3]University of Bologna, Department of Industrial Engineering
[4]University of Ferrara, Corrosion and Metallurgy Study Centre "A. Daccò", Department of Engineering
[5]University of Ferrara, Department of Chemical, Pharmaceutical and Agricultural Sciences
[6]Calgary University, Department of Biological Sciences, Canada

cristina.chiavari@unibo.it

Compared to the past, climate and atmospheric changes are modifying the degradation processes of Cultural Heritage (CH) materials. This also results in an alteration in the composition of the microbial biofilm living on their surfaces, which in turn leads to colouration and biocorrosion processes. The influence of bacteria on the corrosion of outdoor bronze artefacts is still scarcely studied. Until now, the role of bacteria has been primarily studied in carbon steel corrosion with few evaluated bronze degradation (Moradi et al., 2022) with both investigated only in an anaerobic environment (underground). The aspect of the ability of bacteria biofilms to survive on such surfaces is confusing as metal alloys with antimicrobial properties due to freed metal cations. However, a recent study by Timoncini et al., (2022), characterizing the bacterial communities on outdoor bronze monuments, has been released, finding the dominance of Methilobacterium within the bacterial communities. Still, the biochemistry involved in biofilm formation on bonze in an aerobic environment is not entirely clear yet. In this changing environment, biological agents need to be considered, to predict the decay of CH materials. Therefore, the aim of this work is to deeply investigate the influence of bacterial species on bronze materials in outdoor conditions to fine-tune conservation and preservation strategies for bronze artefacts in the next years.

The study consists of two parts: in the first step, we aim to investigate the growth inhibitory effects of different substrates made of copper and bronze alloys (both pristine and coated with a cutin-based anti-corrosion polyester-urethane coating derived from tomato peel waste). The study will be systematic using strong environmental forming bacteria strains as well as metal-tolerant bacterial strains. In the second part, we aim to analyze the corrosion morphology and rate due to the growth of the most resistant and biofilm-forming bacterial strain able to sustain growth on the tested materials. During the first part, the adhesion and biofilm growth capacities will be investigated, which provides information regarding the selection and inhibitory effects of the different substrates. The selected substrates simulate both the pristine surfaces and the aged surfaces corroded by exposure to outdoor rainfall. The biological test on copper alloys coated with the cutin-based polymer will assess the antimicrobial capacity of this innovative protective film, which might represent an environmentally sustainable alternative to conventional fossil-oil coatings. Non-aged and aged bronze coupons will be compared to assess the biocidal effects of free-copper ions after ageing. This work will provide information on the most suitable material for bacterial growth/inhibition, and on the bacterial strain, which can grow more easily on copper and bronze surfaces. Our model system will also provide a tool to evaluate cleaning and sterilization methodologies. The results will improve the knowledge for safeguarding outdoor bronze artefacts under a climate change scenario, as well as for understanding bio-corrosion-inhibition processes.

References

Moradi, M. et al. (2022) 'Understanding biofilm impact on electrochemical impedance spectroscopy analyses in microbial corrosion and microbial corrosion inhibition phenomena', Electrochimica Acta, 426. doi:10.1016/j.electacta.2022.140803.

Timoncini, A. et al. (2022) 'Insight on bacteria communities in outdoor bronze and marble artefacts in a changing environment', Science of The Total Environment, 850, p. 157804. doi:10.1016/j.scitotenv.2022.157804.

Real-Time Estimation of Regulatory Parameters of Directive 91/271/CEE in WWTP Discharges Using Simple Parameters and Artificial Intelligence

M. Batlle[1], J. Cros [1], A. Queralto[2]

[1]Adasa sistemas, Innovation department. Ignasi Iglesias 217-219, 08820, El Prat de Llobregat, Barcelona, Spain
[2] Adasa sistemas, Technical Area. Ignasi Iglesias 217-219, 08820, El Prat de Llobregat, Barcelona, Spain

mbatlle@adasasistemas.com

One of the main sources of environmental contamination is the outlets from the wastewater treatment plants (WWTP). (Sousa, et al., 2021). However, the samples and controls carried out usually are punctual, losing visibility of what is happening in the plant for most of the time.

This is the case of Directive 91/271/EEC on the treatment of urban wastewater, which sets permitted quality limits based on specific parameters. These parameters (Chemical oxygen demand, Biochemical oxygen demand, Total suspended solids, Total phosphorus, and total nitrogen) have complex measurements, high cost of both acquisition and maintenance, and long measurement times that do not allow continuous monitoring.

In the executive summary of the evaluation of the Directive 91/271/CEE (European Commission, 2019), it is stated that, even though the monitoring under the Directive has been effective, the innovation outcomes enable advances in monitoring methods more efficient.

The challenge is to provide full-time coverage of the quality of the water discharged by the treatment plant expressed in the regulatory parameters to know the real impact in the environment.

The present study describes how, through the measurement of simple and continuous physicochemical parameters with low cost of acquisition and maintenance (pH, conductivity, dissolved oxygen, Redox, turbidity, SAC and microbial activity), the Artificial Intelligence system, trained with the laboratory values, estimates in real time the parameters required in regulations providing a full vision of the WWTP discharges.

The XG Boost machine learning model has been tested as the most appropriate, showing an error in the estimates of 13% in the Chemical Oxygen Demand, 4 % in the Total Nitrogen, and 11% in the Total phosphorus.

The system shows the possibility to improve these results feeding the system with new laboratory data.

Being able to have a continuous vision of the water quality that the WWTP is discharging into the environment can be very useful to induce an improvement in plant operators who, by constantly knowing the quality of this discharge, trigger greater efficiency in management of the WWTP process.

References

Council Directive 91/271/EEC concerning urban waste-water treatment (1991). Official Journal of the European Communities, L 135, 40-52.

European Commission, S., 2019. SWD(2019) 701 final: Commission staff working document: Executive summary of the evaluation of the Council Directive 91/271/EEC of 21 May 1991, concerning urban waste-water treatment. Brussels. {SEC(2019) 448 final}. s.l.:s.n.

Sousa, A. I., Azevedo, J., Ribeiro, A. R. & Lopes, A., 2021. Screening of emerging contaminants in wastewater treatment plants effluents and their ecotoxicological impact: A review.. Science of The Total Environment, 755, p. 142477.

A Review of the Occurrence of Persistent and Mobile Chemicals in Environmental Samples Relevant for Human Exposure

D.H. Kim[1], Y. A. Bamai[1], L. Belova[1], J. Bessems[2], G. Poma[1], A. Covaci[1]*

[1]Toxicological Centre, University of Antwerp, 2610 Wilrijk, Belgium
[2]VITO Health, Flemish Institute for Technological Research (VITO), 2400 Mol, Belgium

adrian.covaci@uantwerpen.be

Persistent and mobile chemicals (PMs) are highly polar organic chemicals of anthropogenic origin, which have been documented as an emerging issue of concern for environmental and human health. However, comprehensive scientific information regarding the occurrence of PMs in environmental samples relevant for human exposure are limited. The aim of this work was to review the recent knowledge on the occurrence of PMs in environmental matrices relevant for human exposure.

Eight groups of PMs: melamine (MEL), quaternary ammonium compounds (QACs), benzotriazoles (BTRs), benzothiazoles (BTHs), 1,4-dioxane (1,4-D), 1,3-di-o-tolylguanidine (DTG), 1,3-diphenylguanidine (DPG), and trifluoromethane sulfonic acid (TFMS), including their derivatives were searched for suitable examples of chemicals following the persistency and mobility criteria provided by the German Environment Agency (UBA). As a result, 28 PM chemicals that have logDow/Kow or logDoc/Koc ranging from -3.0 to 2.59 were included in this review. The environmental matrices were limited to those relevant to human exposure, such as drinking water, food, indoor dust, and consumer products.

Water, including drinking water, surface water, and ground water, was the most studied environmental matrix, followed by dust and food. Higher levels of MEL and its derivatives and 1,4-D have been reported in drinking water compared to other groups of PMs. Higher levels of BTHs were observed in indoor dust, followed by QACs and MELs. Clothing/textiles, cosmetics, and household products were commonly investigated and higher levels of MELs and 1,4-D were detected from infant clothing and cleaning products, respectively. BTH levels in food (seafood: mollusks) showed values 10-fold higher than other groups of PMs. MELs were detected in food packaging with 10-fold higher median levels than in foods, however, lower than animal feed.

Most of the PMs discussed in this review were detected in various environmental matrices relevant to human exposure, especially in water and dust, indicating the importance of human biomonitoring and risk assessment of PMs. However, there is still limited knowledge of QACs and TFMS, which may be caused by a lack of reliable analytical methods. Further research is needed to fill these gaps in both analytical and biomonitoring fields.

Agri-Food Waste as Soil Amendments to Control Leaching of Agrochemicals into the Subsoil

M. Granetto[1], R. Sethi[1], T. Tosco[1]*

[1]Politecnico di Torino, DIATI - Department of Environment, Land and Infrastructure Engineering, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

tiziana.tosco@polito.it

Ensuring a high quality and health of the environmental matrices, and in particular of soils and groundwater, is a crucial challenge for a sustainable agriculture. Among agrochemicals, highly soluble organic and inorganic pesticides represent a potential source of contamination for the environmental matrices, due to their high leaching potential, and therefore mobility in the subsoil (Carvalho F.P. 2017). Possible risks in this sense can be due to diffuse pollution which may be generated by routine application on crops, but also point sources associated to storage, preparation and handling of pesticides, runoff infiltration areas, etc. As a consequence, the development of low-impact strategies aimed at controlling the leaching of soluble agrochemicals con contribute to reduce the overall impact of agricultural production on the quality of environmental matrices (Boudh, S. et al. 2019).

In this work, the potential of agri-food waste to serve as soil amendments (Garbowski T. et al. 2023) for the immobilization of agrochemicals is assessed. In particular, biochar, milled corncob and coffee grounds have been studied for the adsorption and immobilization of copper sulfate, a well-known fungicide, and of dicamba, a post-emergence herbicide used for broad-leaf weed control, and characterized by a high solubility in the order of g/l. The efficacy of the three candidate amendments have been compared with a zeolite. The four pristine materials have been characterized in terms of grain size distribution, morphology and composition. Amendment-soil mixtures have then been prepared with amendment mass ratios in the range 1% to 20%, and characterized from bulk density, pH, electrical conductivity, water holding capacity. Batch adsorption tests have been performed putting in contact the amended soil with copper sulfate or dicamba solutions at concentrations representative of those typically employed for crop treatments. The results indicate that the addition of the amendments to the soil decreases its bulk density, significantly increases its electrical conductivity and water holding capacity and modifies its pH. Batch tests provided sorption isotherms and allowed to identify the order of affinity of the tested materials toward the copper sulfate and dicamba: biochar, coffee grounds and zeolite showed a higher affinity to copper sulfate compared to milled corncob; conversely, coffee ground and milled corncob exhibited a higher adsorption capacity toward dicamba compared to biochar and zeolites.

Finally, leaching tests in unsaturated columns packed with the soil-amendment mixtures have been performed to assess the adsorption capacity of the studied materials in dynamic conditions, thus mimicking the interactions that pesticide-containing water can have with the soil in the presence of irrigation or rain over treated crops, or pesticide unintentional releases. The results showed that the use of the amendments, and in particular of biochar, is effective in adsorbing both pesticides, retarding their infiltration and consequently leaching into deeper soil layers, thus reducing the potential of groundwater contamination.

References

Carvalho F.P. (2017), 'Pesticides, environment, and food safety', Food and Energy Security, Volume 6 (2), pp. 48 - 60, DOI: 10.1002/fes3.108

Boudh, S., et al. (2019). 'Pesticide Contamination: Environmental Problems and Remediation Strategies'. Emerging and Eco-Friendly Approaches for Waste Management. ISBN 978-981-10-8668-7. DOI: 10.1007/978-981-10-8669-4_12

Garbowski T. et al. (2023), 'An overview of natural soil amendments in agriculture', Soil and Tillage Research, Volume 225, 105462, ISSN 0167-1987, DOI: 10.1016/j.still.2022.105462.

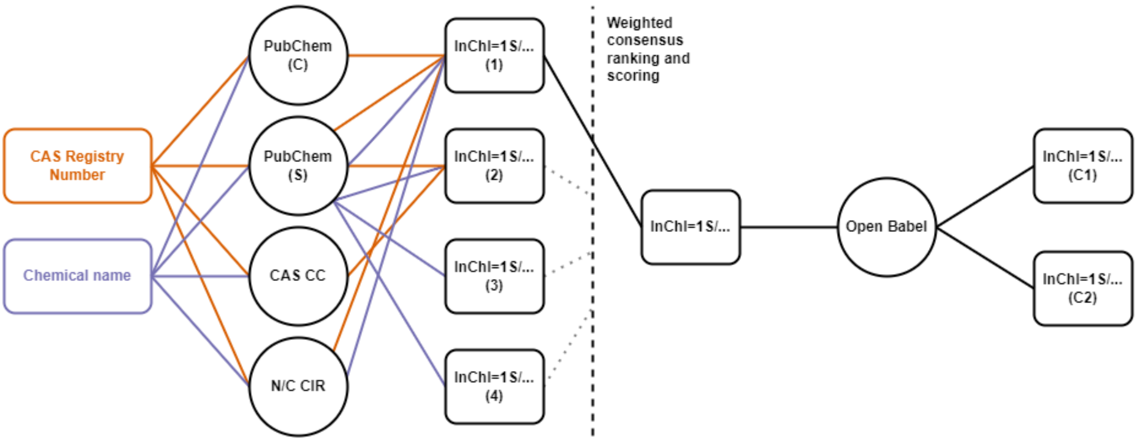
"Cleanventory": Identifying the Chemical Structures of Persistent and Mobile Substances on Global Trade Markets

R. Wolf[1], S. Baskaran[1]*, E. L. Schymanski[2], Z. Wang[3], H. P. Arp[1] and S. E. Hale[1]

[1]Norwegian Geotechnical Institute (NGI), Geotechnics and the Environment, Sandakerveien 140, 0484 Oslo, Norway
[2]University of Luxembourg, Environmental Chemoinformatics, 6 avenue du Swing, 4367 Belvaux, Luxembourg
[3]Swiss Federal Laboratories for Materials Science and Technology (EMPA), Environmental Risk Assessment and Management (ERAM), Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland

sivani.baskaran@ngi.no

To advance the ability to assess, manage and regulate the use of persistent and mobile substances, a sound overview of the chemical diversity regulated within global trade markets is needed. A pioneering effort to index the global chemical inventory, i.e., all chemicals registered on (super-)national economic trade markets, was first published by Wang et al. in 2020. As part of the H2020 project ZeroPM (https://zeropm.eu), a fully reproducible and open-source re-construction of the global chemical inventory – the "cleanventory" – is being developed to help identify, prioritize, and group persistent and mobile substances.
So far, 18 inventories in twelve trade markets have been considered. These contain over 960,000 inventory entries with over 215,000 unique CAS Registry Numbers and over 360,000 unique chemical names. To convert inventory identifiers to InChI strings (i.e., structural information), three freely available API services are used: PubChem (compound and substance domain), CAS Common Chemistry, and NCI/CADD Chemical Identifier Resolver.
So far, over 320,000 unique InChI strings have been retrieved by the API services. After a weighted consensus ranking approach, 160,000 unique InChI strings are identified as being the "most probable" chemical structure for the given inventory entries. The work on the "cleanventory" continues and new data sources will be incorporated. This will enable effective prioritization and substance grouping strategies to help regulators, industry and the water treatment sector achieve zero pollution of persistent and mobile substances.



The "cleanventory" workflow: both CAS and name information is used to identify the most probable chemical structure and its components.

References

Wang, Z. et al. (2020) "Towards a global understanding of chemical pollution: a comprehensive analysis of national and regional chemical inventories", Environmental Science & Technology, 54, p. 2575. doi:10.1021/acs.est.9b06379.

A Source Based Methodology for The Prioritization of Site-Specific Emerging Contaminants in Surface Water

P. Guolo[1]*, P. Ronco[2], L. Calgaro[1], A. Bonetto[1], A. Artuso[2], C. Giacon[2], F. Rosada[3], A. Marcomini[1]

[1]Ca' Foscari University of Venice, Department of Environmental Sciences, Via Torino 155, 30172, Venice Mestre, Italy
[2]Water Resources Research Center RIVE (VIACQUA spa)
[3]GreenDecision Srl., Venezia, Italy

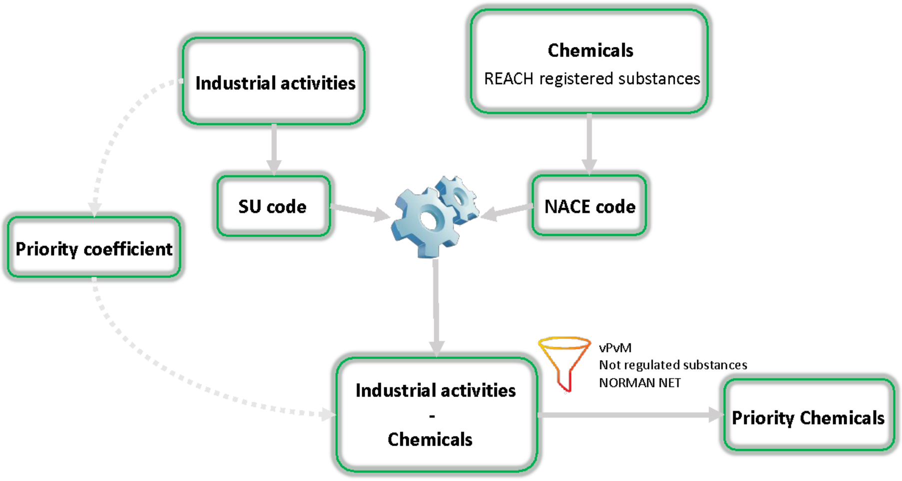
pierpaolo.guolo@unive.it

The implementation of Water Safety Plans (WSPs), promoted by World Health Organization (WHO), has introduced a novel approach to ensure the safety of drinking water supplies by carrying out a risk assessment that consider the entire supply chain in addition to the water quality controls already in place. This process involves the catchment area characterization to identify potential hazards specific to that region. One of the main challenges that authorities and utilities faced by is to identify and characterize compounds of concern, especially the ones not regulated and not monitored.

The aim of this study is to develop a methodology to implement a surface water monitoring plan tailored to the case study situation by correlating local industrial production patterns with classes of non-regulated chemicals of concern.

In detail, substances contained in the REACH database were associated with the industrial activities present in the case study area by linking each industry NACE code (Statistical classification of economic activities in the European Community) with each chemical's sector of use (SU) as reported in REACH dossier. Moreover only substances that i) are classified as vPvM (Arp, Hans Peter H. and Hale, Sarah E., 2019), ii) are not regulated and iii) have been already detected in the environment were considered. Finally, a priority ranking was proposed for the selected chemicals according to the type of discharge (i.e. surface water, sewer, unknown) associated to each identified source.

The database obtained was combined with information on the geographical position of each industrial activity to identify possible pollution hotspots. This information will be useful to plan further monitoring activities to ensure the safety of drinking water in the case study area.



Methodological flow used to obtain the list of prioritized substances.

References

Arp, H., Hale, E., 2019. REACH: Improvement of guidance and methods for the identification and assessment of PMT/vPvM substances, German Environment Agency.

Groundwater Mobility of Brake Wear Particles Modified with Humic Acid: Laboratory Tests

M. Acocella[1]*, M. Granetto[1], C. Bianco[1], R. Sethi[1] and T. Tosco[1]

[1]Politecnico di Torino, DIATI - Department of Environment, Land and Infrastructure Engineering, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

michela.acocella@polito.it

Road transport emissions have become one of the most important sources of atmospheric pollutants, especially in urban areas. The progressive reduction of emissions related to fuel combustion (exhaust emissions, EE) and the simultaneous increase in the number of vehicles in circulation do not lead to a proportional decrease in particulate matter (PM) linked to vehicular traffic, because of the considerable impact of non-exhaust emissions (NEE). They include particulate matter generated by the resuspension of road dust and wear of brakes and tires. Among others, the brake wear dust (BWD) is responsible for the 55% of PM10 road transport emissions and represents a dangerous source of heavy metals for different environmental matrices (Piscitello, A., et al. 2021). Actually, once emitted into the air, the BWD is subject to deposition phenomena, reaching the ground and, in case of rain events, to infiltration phenomena, reaching the deeper layers of subsoil, down to the aquifer system. The travel through the subsoil and the aquifer causes the interaction between BWD and humic acids (HA) which are naturally present in the porous matrix and natural waters, and are expected to adsorb on the particles once dispersed in groundwater. The reduced aggregation and the improved mobility of particles in porous media when coated with humic substances (Tiraferri, A., et al. 2017), the concerning results coming from the characterization of BWD particles (Sinha, A., et al. 2020) and the lack of extensive analysis on the BWD interaction with HA form the basis of the present study. Here, we investigated the physico-chemical mechanisms that govern the transport and deposition of BWD particles modified with humic acid in a saturated porous medium.

Column transport tests were performed injecting a stabilized solution of 2 g/L BWD, previously modified with a coating with humic acid at the ratio 1:50, through saturated sand-packed columns. The influence of hydraulic conditions was investigated by varying the flow rate (q1=0.56, q2=1.07, q3=1.93 mL/min). Measurements of outlet BWD concentration, as well as profiles along the column, were performed using magnetic susceptibility sensors, given the high percentage of magnetic metals in the chemical composition of the BWD. Test results confirm the infiltration capacity of surface-modified BWD particles in the porous medium, consistent with improvement of mobility and reduction of instability as a consequence of sample modification with HA. Moreover, we found that the flow rate significantly affects the mobilization and deposition of BWD in the porous medium. Actually, outlet concentrations from columns, cout/c0, were equal to 20.4%, 27.5% and 36.8%, for flow rates equal to q1, q2 and q3, respectively. Findings from this study add significant understanding to the transport mechanisms of BWD in aquifer system, and confirm its role as an emerging contaminant produced by NEEs, thanks to the interactions with HA in terms of mobility, posing a real threat to the quality of groundwater resources.

References

Piscitello, A., et al. (2021). 'Non-exhaust traffic emissions: Sources, characterization, and mitigation measures'. Science of The Total Environment, 766, 144440. DOI: 10.1016/J.SCITOTENV.2020.144440

Tiraferri, A., et al. (2017). 'Colloidal behavior of goethite nanoparticles modified with humic acid and implications for aquifer reclamation'. J Nanopart Res 19, 107. DOI: 10.1007/s11051-017-3814-x

Sinha, A., et al. (2020). 'Experimental Characterization Protocols for Wear Products from Disc Brake Materials'. Atmosphere 2020, 11, 1102. DOI: 10.3390/atmos11101102

Chemical Safety on Cruise Ships: Understanding Chemical Risks to Humans and the Environment

V. van der Schyff[1*], V. Meraldi[2], A.L. King[3], B. Vrana[1] & L. Melymuk[1]

[1]Masaryk University, RECETOX, Faculty of Science, Kotlarska 2, Brno, Czech Republic
[2]Hurtigruten Expeditions, London, UK
[3]Norwegian Institute for Water Research (NIVA), Økernveien 94, 0579, Oslo, Norway

veronica.vanderschyff@recetox.muni.cz

All modern indoor spaces contain many synthetic chemicals to give building materials and consumer products the properties we require – fire resistance, plasticity, stain- and water repellency, etc. These chemicals have a benefit, but some also pose a hazard to humans and the environment. Some of these chemicals disrupt hormonal processes or might even be carcinogenic (Sérafin et al. 2021). We are exposed to these chemicals by inhaling air indoors and through exposure to indoor dust (Zhu et al. 2020). Researchers have measured many of these synthetic chemicals in homes, workplaces, schools, and automobiles. The indoor spaces of cruise ships, with their luxurious, modern interiors, should be no different. However, these unique environments have received little attention in studies of indoor environmental quality.

As the EU transitions to a greener economy, the EU Action Plan “Towards Zero Pollution for Air, Water and Soil” aims to eliminate harmful chemical releases across all environments, including indoor spaces and the marine environment (European Commission, 2021). Cruise ships, with their size and amenities, are effectively mobile villages, containing a mixture of synthetic chemicals necessary for our modern lifestyle. To progress towards a zero-pollution future in the marine sector, it is crucial to understand what potential chemical pollutants are present on cruise ships, and how passengers, crew, and the marine environment can be exposed.

In this project, we investigate the levels of chemicals of concern (including flame retardants, surfactants, plasticizers and preservatives) in onboard dust, air, and water from cruise ships in the North Atlantic Ocean. Water samples from the onboard wastewater treatment plant allow us to evaluate chemical releases to the marine environment. The chemical measurements are supplemented by air quality sensors, measuring temperature, ventilation, and particle concentrations in the air from different areas onboard the ship. Indoor environmental quality of a ship built in 2002 and renovated in 2020 will be compared against a ship of similar capacity built in 2021. This will enable development of an optimized strategy to allow comprehensive characterization of indoor environmental quality on board cruise ships, and on a larger scale, estimate the scope of air and water emissions of hazardous chemicals from cruise ships to European coastal regions.

References

European Commission (2021) Pathway to a Healthy Planet for All. EU Action Plan: 'Towards Zero Pollution for Air, Water, and Soil'. Date accessed: 10/2/2023. https://ec.europa.eu/environment/pdf/zero-pollution-action-plan/communication_en.pdf.

Sérafin, G., Blondeau, P. and Mandin, C. (2021) Indoor air pollutant health prioritization in office buildings. Indoor Air, 31(3), pp.646-659. https://doi.org/10.1111/ina.12776

Zhu, Q., Wang, M., Jia, J., Hu, Y., Wang, X., Liao, C. and Jiang, G., 2020. Occurrence, distribution, and human exposure of several endocrine-disrupting chemicals in indoor dust: a nationwide study. Environmental Science & Technology, 54(18), pp.11333-11343. https://doi.org/10.1021/acs.est.0c04299

Dosage Concentration and Pulsing Frequency Affect the Degradation Efficiency in Simulated Bacterial Polycyclic Aromatic Hydrocarbon-Degrading Cultures

A. L. Vogel[1]*, K. J. Thompson[1], S. Kleindienst[1,2] and C. Zarfl[1]

[1]Eberhard Karls University of Tübingen, Department of Geosciences, Schnarrenbergstr. 94-96, 72076 Tübingen, Germany
[2]Department of Environmental Microbiology, Institute for Sanitary Engineering, Water Quality and Solid Waste Management (ISWA), University of Stuttgart, Germany

anjela.thon@uni-tuebingen.de

Repeated diffuse and – often low-dosage – anthropogenic polycyclic aromatic hydrocarbon (PAH) emissions account for up to 40% of the total amount emitted per year but are overlooked and underrepresented in research. Microbial PAH degradation is a crucial process for contaminant removal and well-studied for high-pollution events, but is unexplored for repeated low-dosage scenarios, because such highly variable events are hard to identify, quantify, and investigate *in-situ* or in the laboratory. To predict the fate of low-concentration PAH-contaminations, we developed a process-based numerical model to simulate marine batch cultures receiving repeated low-dosage naphthalene pulses compared to the conventionally used one-time high-dosage. We found that pulsing frequency as well as dosage concentration substantially impacted the degradation efficiency in the simulated experiments. Our results indicate that dissolution kinetics dominate biodegradation kinetics, making biomass concentration of PAH-degrading bacteria alone no sufficient indicator for quantification of active biodegradation. Further, a one-time input of a high naphthalene-dosage was degraded faster than repeated low-dosages, implying that repeated low-dosage input could lead to PAH accumulation in vulnerable pristine environments. Our study elucidates the interactions of coupled low-concentration pollutant degradation and microbial growth processes and may have important implications for future management and risk assessment of diffuse oil contamination in the marine environment.

Coastal Environmental Matrices to Assess the Potential Impact of Volatile Methylsiloxanes

S. Ferreira[1,2], F. Sánchez-Soberón[1], J. Castro-Jiménez[3], P. Jiménez-Guerrero[4], F. Cereceda-Balic[5], X. Fadic[5], J.P. Coelho[6], V. Homem[1,2], N. Ratola[1,2]*

[1]University of Porto, LEPABE - Faculty of Engineering, 4200-465 Porto, Portugal
[2]University of Porto, ALiCE - Faculty of Engineering, 4200-465 Porto, Portugal
[3]IFREMER, Rue de l'Ile d'Yeu, BP 21105, 44311, Nantes, Cedex 3, France
[4]University of Murcia, GMAR, Department of Physics, 30100 Murcia, Spain
[5]Universidad Técnica Federico Santa María, CETAM and Dep. Chemistry, Valparaíso, Chile
[6]University of Aveiro, CESAM, 3810-193 Aveiro, Portugal

nrneto@fe.up.pt

The emerging contaminants volatile methylsiloxanes (VMSs) have linear or cyclic structures of sequenced silicon and oxygen atoms (Si-O-Si) with organic side functional groups (Rucker et al., 2014). With numerous advantageous properties that make them extensively used in industrial processes and consumer and personal care products, their release into the environment reaches all environmental compartments, including coastal areas (Capela et al., 2019). Particularly in countries where beach tourism is established, the increased use of products such sunscreens and other cosmetics, particularly in summer can have an impact on coastal and marine ecosystems. In this work, sand and mussels were chosen as indicators of the presence and trends os VMSs in worldwide coastal sites. For that, dry beach sand samples were collected in 10 countries in Europe and South America and wet and dry sand was taken from 59 beaches in Catalonia (Spain). Moreover, 12 beaches in the north of Portugal were sampled from May to December and 30 beaches in 3 countries (France, Portugal, Spain) were taken in summer and winter to assess a possible temporal distribution. A daily trend was searched in one beach in the south of Portugal). Wild mussels were sampled from 8 beaches in the north of Portugal in August, September, and December, whereas depurated and non-depurated (wild) mussels were collected in 9 spots from Ria de Aveiro (Portugal), a 45 km long lagoon connected with the Atlantic. The analysis in the two matrices was performed by QuEChERS extraction, with subsequent GC-MS identification and quantification. VMSs were detected in all sand samples (from n.d. to 33±7 ng/g dw), with a predominance of the cyclic congeners, such as D5 and D6, likely due to a higher deposition proneness and permanence in the sand. VMS levels peaked in the Canary Islands (Spain), up to 115 ± 9 ng/g dw, likely reflection the intensive use of the beach by tourists at the time of the sample collection. But the spatial trends of VMSs in coastal areas are linked with climate, which attract a higher anthropogenic impact in summer months. In fact, the daily study suggested that the VMS presence is in line with the number of people at the beach. Mussels confirm the same trends in general and stressing the importance of the depuration process before consumption to lower the human exposure by ingestion. In fact, the depurated mussels showed a mean total VMS concentration of 15±5 ng/g ww while the wild ones went up to 52±6 ng/g ww, that is, 69±12% more.

This work was financially supported by: (i) LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), funded by national funds through FCT/MCTES (PIDDAC); (ii) Project "HealthyWaters" (NORTE-01-0145-FEDER-000069), supported by NORTE2020-PORTUGAL2020, through ERDF; (iii) ANID-FOVI210064 and CETAM-UTFSM (Chile); (iv) FCT is thanked for contract CEECIND/00676/2017 (V. Homem).

References

Capela, D. et al. (2019) 'Footprints in the sand – Assessing the seasonal trends of volatile methylsiloxanes and UV-filters', Marine Pollution Bulletin, 140, p. 9-16. doi: 10.1016/j.marpolbul.2019.01.021.

Rücker, C. et al. (2014) 'Environmental Chemistry of Organosiloxanes', Chemical Reviews, 115(1), p. 466−524. doi: 10.1021/cr500319v.