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Divisione di Chimica
Ambiente e Beni Culturali

XIX Congresso Nazionale della Divisione di Chimica dell'Ambiente e dei Beni Culturali

SFIDE ED OPPORTUNITA' EMERGENTI PER L'AMBIENTE E PER I BENI CULTURALI

TORINO, 20 - 23 GIUGNO 2022

XIX National Congress of the Environmental and Cultural Heritage Division of the Italian Chemical Society

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BOOK OF ABSTRACT

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Foreword

The XIX National Congress of the Environmental and Cultural Heritage Division (EHD) of the Italian Chemical Society (SCI) is held at the Department of Life Sciences and Systems Biology of the University of Turin, Italy, from 20 to 23 June 2022. The XIX National Congress is organized by the Department of Chemistry (University of Torino) under the auspices of University of Turin and the Municipality of Turin.

The XIX National Congress is organized for the first time in Torino, a city full of history which was and was the first Italian capital from 1861 to 1865.
Over 140 scientists from the main Italian universities and research centers are attending the XIX National Congress with about 120 total contributions.
In line with the national conferences organized by the Environmental and Cultural Heritage Division tradition, both oral and poster sessions feature many hot research topics, like: soil/air/water chemistry; climate change; circular economy, enhancement and recovery of resources; emerging contaminants; environmental processes and reactions; green chemistry/reduction of impacts on the environment and cultural heritage; sustainable methodologies and protocols; communication and sharing of data; characterization and knowledge of artistic materials; development of advanced diagnostic protocols for the characterization of objects of historical, artistic and archaeological interest; archaeometry; development and optimization of innovative and environmentally sustainable materials for conservation; evaluation of restoration and conservation methods; business and research in the environment and cultural heritage.

The opening of the XIX National Congress takes place under the auspices and the welcome of the Director of the Department of Chemistry of the University of Turin (Professor Lorenza Operti).
For the first time, the XIX National Congress is the occasion to present the three new divisional medals reserved to eminent scientists, namely, the "D.H. Meadows & R.L. Feller" Medal (for researchers who have distinguished at national and international level for their activity of research in the cultural identity areas of the Division of Chemistry of the Environment and Cultural Heritage); the "Mario Molina" Medal (reserved for young researchers under 40 who work in the field of Environmental Chemistry); the "Raffaella Rossi Manaresi" Medal (reserved for young researchers under 40 working in the field of Chemistry of Cultural Heritage).
For their outstanding research achievements, the three recipients of the medals are:
Antonio Marcomini (University Ca’ Foscari, Venice) for the "D.H. Meadows & R.L. Feller" Medal
Daniele Cespi (University of Bologna) for the "Mario Molina" Medal
Letizia Monico (National Research Council of Italy – CNR) for the "Raffaella Rossi Manaresi" Medal
Medals are presented by Luciano Celi (CNR) who reported on the genesis of the book “The limits to growth”, by D.H. Meadows, D.L. Meadows, J. Randers, that this year turns 50.

The meeting includes two invited plenary lectures by F. Bianchi (University of Helsinki, Finland), and by M. Malagodi, (University of Pavia).

To stimulate the participation of young researchers, many awards are also given by the Environmental and Cultural Heritage Division of the Italian Chemical Society (SCI). Hence, we congratulate with the following young researchers for: participation awards (Antonio Faggiano, Angelo Fenti, Zelan Li, Paola Lucini, Michele Molin, Francesca Porpora, Clarissa Barbara Raguso, Francesca Ramacciotti, Maria Ricciardi, Andrea Timoncini); master degree thesis awards (Andrea Campostrini, Prisco Prete) and PhD thesis awards (Luca Carena, Michele Castiglioni, Giacomo Fiocco).

Thanks are due to the members of the Scientific Committee (Antonio Proto, University of Salerno
Maria Concetta Bruzzoniti, University of Turin, Raffaele Cucciniello, University of Salerno, Nadia Marchettini, University of Siena, Giuseppe Mascolo, National Research Centre, CNR, Silvia Prati, University of Bologna, Luca Rivoira, University of Turin, Davide Vione, University of Turin, Elisabetta Zendri, University of Venice) and Antonio Marcomini, University of Venice, as past president of the EHD division; Organizing Committee (Maria Concetta Bruzzoniti, Angelo Agostino, Monica Gulmini, Marco Minella, Monica Passananti, Luca Rivoira, Dominique Scalarone and Davide Vione); and Local Organizing Committee (Michele Castiglioni and Luca Rivoira) for their valuable contributions.

We would like to thank our Sponsors (Shimadzu Co., Inspect In-Line Lab, SRA Instruments, XearPro, University of Ca’ Foscari Venice, Chemical Research 2000 and Department of Chemistry of the University of Turin) for the joint financial support.
Special thanks are given to the Logistic Services of the Natural Sciences Pole of the University of Turin and to Dr. Daniele Di Modugno and Giulio Oliva for their assistance with the preparation of the location.

We hope that XIX National Congress of the Environmental and Cultural Heritage Division stimulates fruitful discussions and the start of new scientific collaborations, thus providing an added value to the scientific endeavors of our esteemed participants.

Finally, we would like to encourage all of you to enjoy the friendly atmosphere of the XIX National Congress, the social program as well as the town, which you hopefully may have the opportunity to visit.
On behalf the Organizing Committee and of the Environmental and Cultural Heritage Division of the Italian Chemical Society, we welcome you in Torino and wish you a pleasant Congress!

Turin, Italy, June 2022

Antonio Proto
President of the Environmental and Cultural Heritage Division of the Italian Chemical Society

Maria Concetta Bruzzoniti
Chairwoman of the XIX National Congress of the Environmental and Cultural Heritage Division

IS01

THE INTERDISCIPLINARY CHEMISTRY OF CULTURAL HERITAGE: THE CASE OF ANCIENT MUSICAL INSTRUMENTS

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1. Introduction

Musical instruments, and bowed string ones in particular, are a peculiar class of artworks, with a central role both in the intangible (e.g. music, craftsmanship) and in the tangible cultural heritage. Made to be played, their acoustic properties must be preserved as long as possible over the years.

This presentation gives guidelines to obtain the maximum amount of information when investigating musical instruments and overviews the past Cremonese violin making art. The scientific study of these peculiar artworks and of their unique coating systems is intrinsically complex due to: i) the presence of many micrometric overlapping layers, ii) the large variety of organic materials applied, in most cases, as a mixture (e.g. linseed oil-colophony varnish), iii) the low concentrations of organic and inorganic phases, when present, dispersed in the layers, and iv) the scarce availability of samples.

Scientists shall therefore master the analytical approaches by exploiting and/or developing analytical procedures aimed at maximizing the information that can be retrieved from priceless historical musical instruments.

2. Results and Discussion

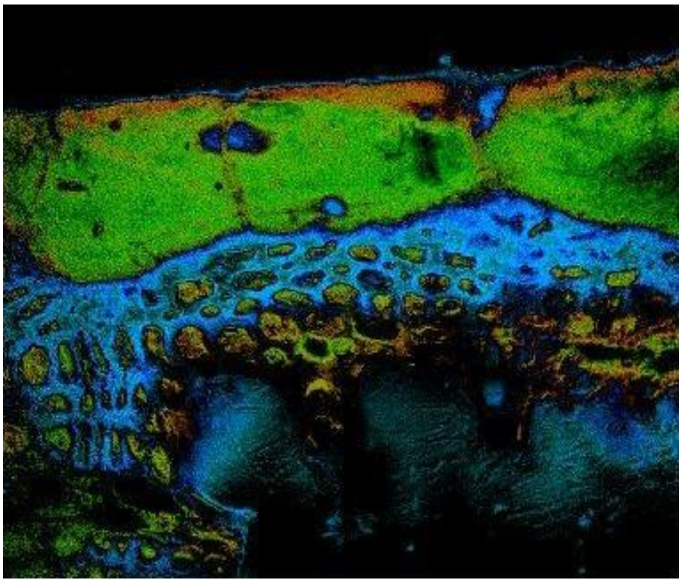
The main results obtained combining a suite of non-invasive, micro-invasive, and micro-destructive analytical techniques are reported and discussed to mark out the present horizon of the research on the finishing layers of bowed string instruments. Many case studies are presented, aimed at demostrating the different strategies that can be employed to obtain chemical evidence on the materials, to be integrated with those retrieved from information already available literature. The interdisciplinary and multi-technique strategy allows to obtain a precise characterization of the materials and their distribution in the stratigraphic sequence, as well as to recognize the presence of both original and conservation layers variously spread and overlapped on the surface. The possibility to take samples enables to develop the best sampling strategies and procedures, and to optimize the treatments for embedding and polishing the fragile micro-samples to be prepared as cross sections. and then to gain further information on the layers, their thickness and composition.

The non-invasive characterization of varnishing layers and other treatments carried out on wooden objects is accomplished combining XRF and reflection FTIR spectroscopies with highly informative and innovative techniques as NMR-MOUSE and OCT [1] to an in-depth investigation through the coating system from the wood – and the related pre-treatments – up to the external varnish or restoration layers. Micro-invasive and micro-destructive spectroscopic approaches are explored on real case studies with in-situ measurements and analysis on cross sectional samples detached from valuable historical violins. A promising approach for the study of the different thin layers of the cross sections is obtained by combining Hyperspectral Photoluminescence (PL), HyperSpectral Imaging (micro-HIS) micro-imaging with μFTIR-ATR mapping and SEM-EDX analysis [2].

3. Conclusions

An interdisciplinary approach, with non-invasive, micro-invasive and micro-destructive analytical techniques, is necessary understand the potential and limits of each phase in the study of varnishes and other organic and inorganic materials present in the coating systems of historical bowed string instruments. Laboratory mock-ups, fragments detached from historical violins and valuable musical instruments produced by the most representative masters of the Cremonese violin-making school, carefully selected to fulfil the aim of the research, have been examined to investigate the past art of violin making. As for other arworworks from the

Cultural Heritage, the overall effort allowed to focus on the various issues that are encountered in the investigation of such complex stratigraphies.



Lorenzo Storioni 1793 - SAM (Spectral Angle Map) + False colours reconstruction

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IS02

CHASING PRE-INDUSTRIAL AEROSOL AROUND THE GLOBE"

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Atmospheric aerosols affect the climate directly by absorbing or scattering incoming radiation and also indirectly by acting as cloud condensation nuclei (CCN) changing therefore the cloud albedo. A major fraction of these CCN comes from gas to particle conversion (nucleation). During the last decade, several nucleation studies have been published based on field observations, however most of them in the planetary boundary layer. Therefore, only little information is available about the free troposphere. The aim of this presentation is to elucidate the last founding about what species contribute to new particle formation (NPF) in remote places, especially at high altitude.

In the last years, we have used state-of-the-art instruments, first at the Swiss high alpine research station Jungfraujoch (3580 m asl, Bianchi et al., 2016), at the Himalayan Nepal Climate Observatory Pyramid (NCO-P) site on the southern slope of the Himalayas, not far from Everest base camp (5079 m asl)(Bianchi et al., 2021) and finally at the Chacaltaya stationin Bolivia (520 m asl)(Bianchi et al., 2022). Previous studies have already showed that at all these locations NPF takes place frequently. However, no chemical information of the vapours was retrieved.

In this presentation, in addition to present the results of these studies, I will also compare them with laboratory experiments (i.e. CLOUD experiment at CERN). I will present a detailed analysis of the particle evolution during nucleation and the chemical composition of the small clusters measured with advanced mass spectrometers. I will also show that these processes are potentially very interesting to understand the aerosol conditions in the pre-industrial era where information are really scares. Finally, I will give some insight regarding present project taking place on the Teide Volcano in Tenerife.

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SP01

AN LC-MS-MS APPROACH FOR THE ANALYSIS OF RED DYES IN HISTORICAL TAPESTRIES

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1. Introduction

The present study is aimed to unveiling the nature of natural dyes employed for the manufacture of an historical tapestry stored at the Quirinale Palace (Rome) and dating to the XXVII century. At this purpose high performance liquid chromatography coupled with mass spectrometry (HPLC-MS) have been employed for the analysis of both reference samples, obtained after dying of some natural textile fibres according to ancient recipes, and real some fragments taken from the back of some historical tapestries. In particular, the attention has been focused on the red colorants and at this purpose by means of an LC-MS-MS system the presence of molecular markers typical of the different natural substances employed to dye this precious work of art has been disclosed.

2. Results and Discussion

Some red yarns belonging to tapestries of different historical periods showing many hues, from pink to violet were collected and investigated to understand the type of dyes involved and their chemical nature. The use of LC-MS methods is well attested in scientific literature [1].

The analyses were performed using LC-MS 8045 instrument (Shimadzu Italia S.r.l.) thanks to the collaboration. The instrument was equipped with a UHPLC of NexeraTM series with photodiode array detector (PDA), electrospray ionization (ESI) and triple quadrupole, which operated both in Scan e Product Ion Scan mode. A preliminary screening was performed on some reference samples dyed accordingly to ancient recipes [2]. Subsequently some fibres coming from a tapestry dated to 17th century and stored at the Quirinale Palace (Rome) were investigated. In this case the use of madder as main dye was highlighted in all the analyzed samples. In particular, it has been demonstrated the presence of the anthraquinone compounds alizarin 239 m/z [M-H-] and purpurin 255 m/z [M-H-] together with other compounds. Finally the analysis performed on yarns collected from tapestries of the 19th century highlighted the use of a mixture of madder and cochineal in all the samples; the second one was identified thanks to the presence of carminic acid 491 m/z [M-H-], kermesic 329 m/z [M-H-] and flavokermesic acids 313 m/z [M-H-].

3. Conclusions

The HPLC-DAD-ESI-MS technique was suitable for the identification of various species of anthraquinones in different type of dyes, even in ancient artifacts where concentration of the colouring matter could have been lowered during time or where degradation processes could have been occurred. Furthermore, as observed for the samples of 19th century, it was possible to highlight the use of mixture of dyes. Particularly the possibility to collect the fragment ions spectra was fundamental to confirm the attributions.

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IN SILICO PREDICTION OF BIOACCUMULATION IN TERRESTRIAL AND AQUATIC ORGANISMS FROM THE MOLECULAR STRUCTURE

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1. Introduction

The assessment of Bioaccumulation (B) of chemicals is of great importance in chemical risk assessment procedures. In recent years different metrics have been proposed in the literature to assess the accumulation of chemicals in different organisms and media. Quantitative Structure Activity Relationships (QSAR) can be used as a valid approach to estimate Bioaccumulation related endpoints in silico, from the molecular structure. These models are useful to reduce the number of experimental tests necessary to quantify B parameters which are expensive, and time consuming.

In this study several datasets were collected from the literature to model the dietary biomagnification (BMF) [1] and the bioconcentration factor (BCF) in fish [2], in addition to the biota sediment bioaccumulation factor (BSAF) [3] in invertebrates of soil and sediment, and the bioaccumulation in plants [4]. Several regression and classification models were generated which can be used to predict B related properties of existing and new compounds. All these models will be included in the QSAR-ME Profiler software, which is under development by our research group at University of Insubria.

2. Results and Discussion

In this work, several B metrics have been modeled by QSAR starting from data collected and curated both from the literature and from online databases [1-4].

A first step of data curation was performed before the creation of QSAR models. The correctness and the consistency of the structural information encoded for each chemical into SMILES (Simplified Molecular Line Entry Systems) strings, reported in the literature, was verified. Furthermore, SMILES were harmonized (i.e. canonicalized) using the OpenBabel software (Open Babel v. 2.4.1) in order to identify isomeric structures and duplicates. All the data records associated with inconsistent molecular structures (i.e. conflicting CAS and SMILES), stereoisomers, salts and inorganics were excluded from the original dataset. Data curation was also performed to identify anomalous experimental records among multiple records reported for a chemical and a specific endpoint. The final curated datasets were modeled by QSAR using multiple linear regression (MLR) where values of the endpoints were available in the continuous scale, otherwise classification models were developed by linear discriminant analysis, for discrete categories endpoints. In particular, the cut off value BMF=1 [1,5,6] and BCF = 3.3 [6] were used to generate a priori groups to perform classification.

Theoretical molecular descriptors and binary fingerprints were calculated from SMILES using the software PaDEL Descriptor (PaDEL-Descriptor v2.21).

All the models were generated following the OECD guidelines for the validation of QSAR models [7] with particular focus to cross validation, external validation and evaluation of the applicability domain.

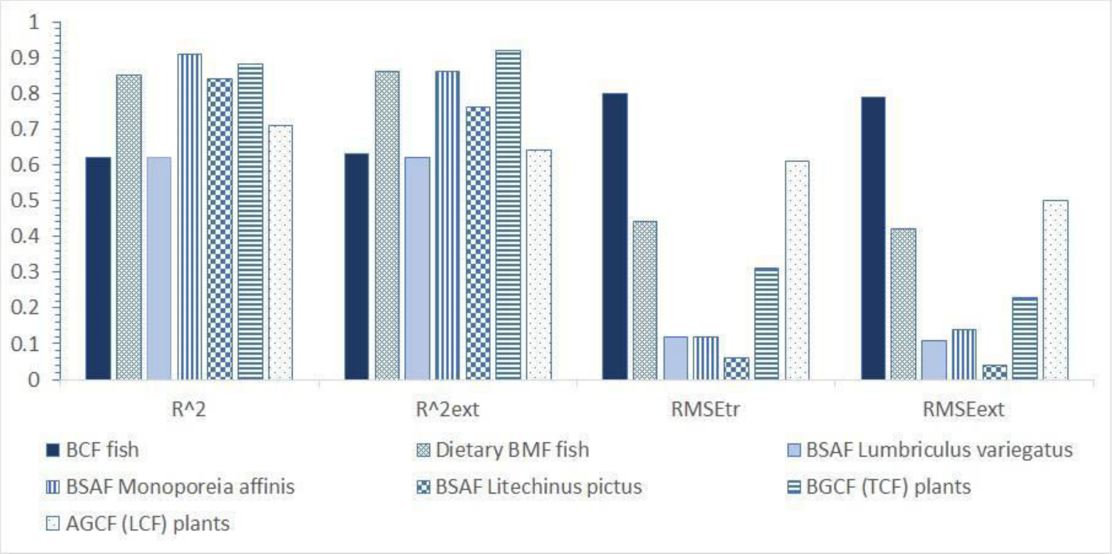
BCF and BMF models in fish were derived starting from two heterogeneous sets of about 1400 and 300 chemicals respectively. Classification and regression models have good statistical performances with MLR statistics for fitting between 0.6 and 0.9 and classification accuracy for BCF and BMF of about 0.9.

MLR QSARs developed to predict BSAF in soil or sediment invertebrates (i.e. Lumbriculus variegatus, Monoporeia affinis and Lytechinus pictus) had good statistics in fitting and prediction with R^2 and Q^2 values of these BSAF QSARs in the range 0.7-0.9 and 0.6-0.9, respectively.

The development of models for Bioconcentration factors in plants from below ground (BGCF) or above ground (AGCF) were developed on a limited number of available data but provided promising results.

3. Conclusions

The regression and classification models proposed in this study represent a novelty for the in silico prediction of Bioaccumulation, and offer the possibility to assess this property directly from the molecular structure for multiple exposure media and organisms. These models are useful to support risk assessment procedures for new and existing chemicals in the absence of experimental data.



Performances of MLR QSARs for B-related endpoints

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OP02

REMOVAL OF ATRAZINE FROM WATER USING AN ELECTRO-OXIDATION PROCESS

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1. Introduction

Atrazine (ATZ) is a selective herbicide extensively used in agriculture. ATZ, due to its stable ring structure, is high persistent and has been widely detected in water bodies in high concentrations. Traditional techniques are ineffective towards the removal of ATZ from impacted waters, hence the development of innovative methods is desirable. In the recent years, the electrochemical oxidation (EO) has been receiving more interest to remove ATZ from water [1]. In fact, previous studies have investigated the EO of ATZ under several operating conditions, and reported high removal treatment efficiences [2]. However, the formation of reaction by-products during the oxidation need to be closely examined. In the present study, experimental investigations on ATZ removal from water by means of EO using platinum-coated titanium anode on a lab-scale reactor were performed. In particular, the effects of operating parameters such as the electrolyte composition and applied current density were investigated. Moreover, the formation of potential ATZ by-products generated during the EO treatment was examined and a mechanism of degradation for ATZ was proposed.

2. Results and Discussion

As well-known, the EO process of organic compounds is typically affected by the composition of electrolyte. In order to evaluate the effect of the latter parameter, several EO of ATZ experiments were carried out using 3 types of salts, such as NaCl, $NaClO_4$, $NaNO_3$. In all of the experiments, the ATZ starting concentration was 5 mg/L, the initial pH was about 6.8, the salt concentration was 0.08 M and the applied current density was kept constant at 40 A/m^2. The results showed that the ATZ degradation efficiency is higher operating in presence of NaCl rather than $NaClO_4$, $NaNO_3$. Moreover, it is noteworthy that when $NaClO_4$, $NaNO_3$ were used, the same ATZ degradation efficiencies are basically achieved. In detail, 92.3, 75.5 and 74.9 % of ATZ removal efficiencies have been reported after 180 min of treatment for NaCl, $NaClO_4$, $NaNO_3$, respectively. In line with the literature, when NaCl is used, the enhancement rate of ATZ degradation is affected to the generation of strong oxidant chlorine species such as Cl_2 and ClO^-.

The applied current density is a key parameter in an EO process, impacting to both substrate degradation efficiency and operational cost. Hence, the applied current density was varied between 40 and 80 A/m^2 with the aim to determine the optimal operative condition having the highest atrazine degradation efficiency. A set of experiments has been built up operating with NaCl in a range of concentration between 0.02 - 0.08 M. The degradation efficiency increased with respect to a rise in the applied current density, for each of the investigated experimental conditions. These results are affordable since higher applied current leads to a larger generation of both hydroxyl radicals and electroactive chlorine species, either adsorbed on the anode surface or free in the bulk phase. In according to previous studies, Pt/Ti anodes are well known to be "active anodes" which promote chlorine evolution. Therefore an enhancement in the applied current density actually facilitates the consequently generation of electroactive chlorine species [3].

The production of ATZ by-products was monitored and quantified for an experimental run carried out in presence of $NaClO_4$ as electrolyte, at a current density of 40 A/m^2. The results, sketched in the Fig. 1.A, show that the formation of degradation products, such as desethyl-atrazine (DEA), desisopropyl-atrazine (DIA), 2-hydroxy atrazine (ATZ-OH), and desethyl-desisopropyl-atrazine (DEDIA) from ATZ was obtained. The EO pathway proposed was assumed to be a series – parallel reaction system, with a first step in which the ATZ generates DEA, DIA and ATZ-OH, followed by the production of DEDIA from DIA and DEA with a first-order parallel reactions of the ATZ, as sketched in Fig. 1.B. The comparison between ATZ and by-product concentrations from experimental results and ATZ and by-product concentration model findings as a function of time were reported in Figure 1. C. The series – parallel reaction equation system has been solved using a first-order finite difference forward approach. The reaction rate constants were statistically determined by the best fitting of the experimental findings reported in Fig. 1.A. The results shown in Fig. 1.C have highlighted a good fitting between the experimental results and the model findings.

3. Conclusions

The EO of ATZ is affected by electrolyte composition and applied current density. The results showed that the highest ATZ removal efficiency, of 92.3 %, was achieved operating in presence of NaCl, after 180 min of treatment. The rate of ATZ removal, with NaCl is not only addicted to the formation of hydroxyl radicals by water electrolysis at the anode surface, but also to the generation of electroactive chlorine species. Yet, the ATZ degradation efficiency increases with respect to a rise of the applied current density. During the treatment, the formation of ATZ by-products, named DIA, DEA, ATZ-OH and DEDIA was observed. An ATZ degradation model was proposed and the validity of the hypothesized reaction pathway is highlighted by the good fitting of the experimental data.

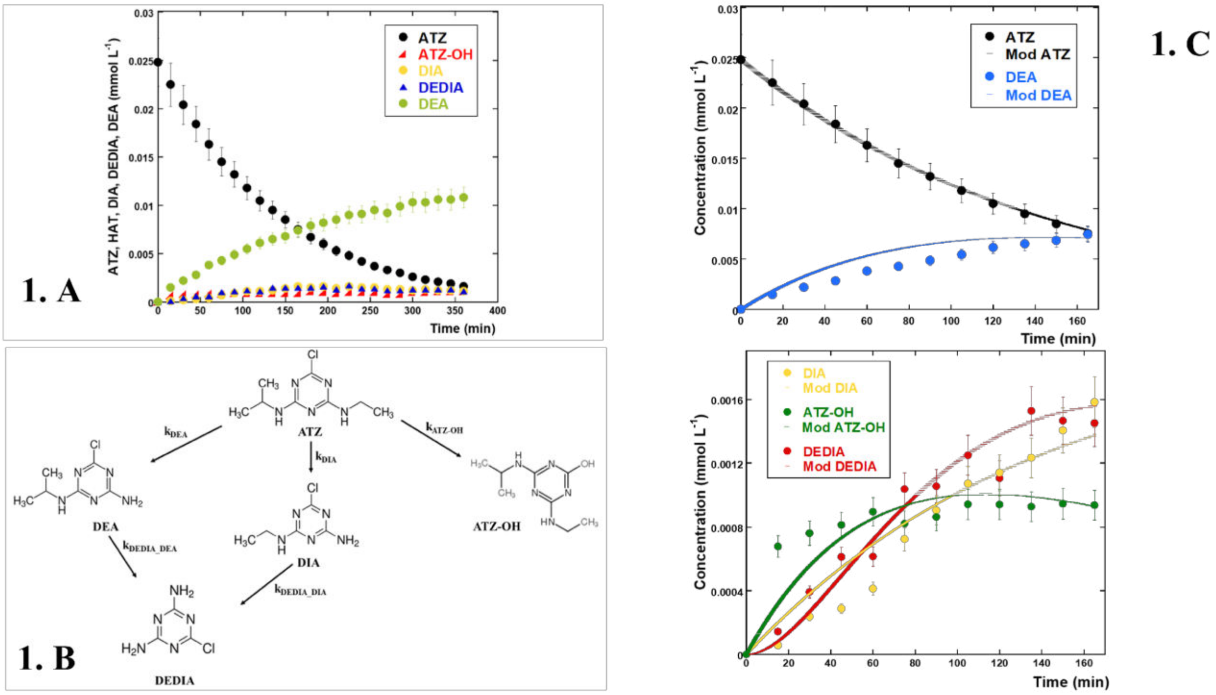

Figure 1. A)AZT and by-products evolution, B)ATZ degradation pathway; C)Time evolution model fitting.

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OP03

HIGH TIME-RESOLUTION MONITORING OF PAHS AND HEAVY METALS IN A HIGHLY INDUSTRIALIZED CITY IN SOUTHERN ITALY

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1. Introduction

To date, the chemical characterization of particulate matter (PM) samples provides daily data not allowing the identification of occasional sources and events of high PM and, thus, the evaluation of the real impacts of pollutant sources on the air quality and on health of the exposed populations. In fact, the temporal variability of emissive processes as well as dispersion, reactions and transport of pollutants in the atmosphere drastically affect the chemical composition of PM during the day. These findings are even more relevant in heavily polluted industrial areas as Taranto. Taranto, in fact, is included in the list of high priority polluted sites of national interest due to the presence of an extended and complex industrial area (characterized by the biggest European steel plant, a refinery, the most important harbor in southern Italy, a cement plant and a naval shipbuilding industry) nearby the urban settlement [1-2]. For this reason, the evaluation of air quality in Taranto and surrounding areas has been in the last two decades a priority for Italian competent authorities and till today, subject of in-depth investigation for scientists expert in air quality.

2. Results and Discussion

Therefore, in order to overcome the limits of the conventional approaches used for air quality monitoring that do not allow the identification and characterization of fugitive emissions and short-term events of high pollution, in this study an high time-resolution monitoring campaign of particles, Total Polycyclic Aromatic Hydrocarbons (TPAHs) and heavy metals has been conducted from 18th October to 19th December 2018 at a residential site a few kilometers from the industrial area of Taranto (Tamburi district). Tamburi district is positioned immediately outside the steel plant perimeter, in the closest urban settlement to the industrial area. During the monitoring campaign, the number concentrations of particles with an optical diameter between 0.28 and 10 um were continuously monitored by means of an optical particle counter (OPC) while the hourly concentrations of heavy metals and TOTAL PAHs were measured using a reel to reel X-ray analyzer (XACT 625) and a photoionization analyzer (EcoChemPas 2000), respectively.
Taking into account 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 on the quality and quantity of particulate matter in residential area of Tamburi district as well as deepen the factors increasing the concentration of metals and, especially, Iron in this area. In fact, the highest hourly concentrations of the most metals considered and PAHs were registered in the hours when gust of wind blew from the North-West allowing pollutants transport from industrial area on receptor site. Moreover, hourly concentrations of iron meanly high were also registered in correspondence of weak winds and unrelated to the concentrations of other pollutants probably due to the 'dusting' and / or movement of materials in mineral park.

3. Conclusions

Therefore, this study highlighted that the high time-resolution monitoring and chemical characterization of particles in the atmosphere provide prompt feedbacks on the pollutant concentrations and sources and allow to: 1) deepen and know the dynamics and temporal evolution of events of high PM, 2) evaluate the effectiveness of mitigation strategies and 3) more accurately understand the real population exposure.

OP03

Air quality laboratory for high time-resolution monitoring and chemical characterization of PM

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OP04

AIR QUALITY CHARACTERIZATION IN THE SANCTUARY OF THE BEATA VERGINE DEI MIRACOLI IN SARONNO, ITALY.

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1. Introduction

The sanctuary of the Beata Vergine dei Miracoli is a marian sanctuary located in the small town of Saronno, in the province of Varese, Italy. According to the inscription carved on the door that once represented the entrance to the sanctuary and that now connects the church to the cloister, the laying of the first stone took place on May 8th 1498. Construction was completed in 1525, when Bernardino Luini and Alberto da Lodi received the commission for the frescoes in the main chapel and the anti-presbytery. Finally, Andrea da Milano was commissioned to create two large wooden scultpures ("Cenacolo" and "Compianto sul Cristo morto") to be placed in the two main internal chapels [1]. Throughout the years these statues have been restored several times, the last one in 1995. In view of the artistic richness of the Sanctuary, environmental monitoring is essential for the preventive conservation of the works of art in order to limit the deterioration phenomena linked to poor air quality. Moreover, the lack of regulations regarding the concentration of air pollutants in indoor spaces such as sanctuaries further highlights the importance of the issue.

2. Results and Discussion

In order to achieve a complete characterization of the air quality, the presence of several air pollutants and the microclimatic conditions were monitored in different sites inside the Sanctuary (Figure 1). Data was also compared with outdoor values in order to evaluate potential sources and study accumulation phenomena. During the course of the different monitoring campaigns carried out throughout the year, temperature and relative humidity values were collected using data loggers (USB Mini TH, XS Instruments) and the results showed a large variability depending both on outdoor microclimatic conditions and indoor factors, such as the use of heating. Daily average values of the thermohygrometric variables were often outside the suggested ranges for the conservation of cultural heritage in museums [2], indicating poor microclimatic conditions in the Sanctuary.

Particulate matter was sampled using an optical particle counter (P-Dust Monit, conTec Engineering Srl) and indoor concentrations were consistently higher than outdoor values, indicating the presence of specific indoor sources in addition to the penetration of particles from outdoors. Indeed, a significant correlation was observed between the number of people attending religious ceremonies and the concentration of particulate matter. Moreover, several gaseous pollutants were detected inside the Sanctuary (CO, NO, NO_2, SO_2, O_3, and H_2S) thanks to the use of an air quality monitoring unit (MQA, conTec Engineering Srl). In particular, the nitrogen dioxide levels exceeded the 4.7 $\mu g/m^3$ limit suggested by the Italian Ministry for the conservation of cultural heritage [2]. These concentrations were mainly due to the proximity of the Sanctuary to a very busy road which resulted in the penetration of outdoor polluted air. The hypothesis of the vehicular traffic source was further supported by the presence of other pollutants belonging to the BTEX family, such as benzene and toluene, which were collected using diffusive passive samplers (Radiello®, Fondazione Salvatore Maugeri-IRCCS). In fact, these compounds are considered to be tracers of vehicular exhaust [3].

Finally, preliminary studies aimed at the evaluation of the damage induced by poor air quality on the works of art were conducted on some of the wooden sculptures. On-site analysis using X-Ray Fluorescence (XRF) was performed in order to obtain the elemental composition of the pictorial coating. The atmospheric dust deposited on the surface of these statues was also characerized using Scanning Electron Microscopy coupled with Energy-Dispersive X-ray spectroscopy (SEM-EDX) and revealed the presence of several elements that make up the pictorial coat, such as calcium, sulphur and iron. These results highlight the poor conditions of the work of art and possibly suggest the need for further restoration processes.

3. Conclusions

In this study a complete chemical characterization of the air quality inside the Sanctuary of the Beata Vergine dei Miracoli was carried out. The main air pollutants were monitored in different sites, along with temperature and relative humidity. The results obtained indicate poor indoor air quality, with many parameters falling outside the suggested ranges for the conservation of cultural heritage in museums. Also, the indoor concentration of pollutants often exceeded the outdoor values, indicating that both outdoor and indoor sources contribute to worsening air quality. Preliminary studies conducted on the recently restored wooden sculptures suggest the need for the application of mitigation strategies in order to better preserve the works of art.

Figure 1. a) Street view of the Sanctuary; b) P-Dust Monit and MQA; c) Diffusive passive samplers

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OP05

CHARACTERIZATION OF CARBONACEOUS FRACTIONS FROM THREE CULTURAL LAYERS OF DIFFERENT AGE FROM NORTH EAST ITALY

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1. Introduction

Cultural layers can be defined as soil deposits resulting from past settlements and human activities on natural soils. Materials from past domestic activities (i.e., waste, burned material, artifacts, etc.) buried into the soil matrix can be used to reconstruct human impact in a specific area in the past. Fire accompanied human development from its very beginning, and charcoal accumulation in soils and sediments is widely used as indirect evidence of human passage. In European towns, cultural layers with similar characteristics (dark, thick, and poorly stratified), have been recently defined as "Dark Earth" (DE) but their age, origin, and composition may differ significantly site-by-site.

This study examined three different sites in the North-Eastern Italy, where DE layers with similar characteristics were identified. The primary aim of this research was to understand the source and human impacts that led to the development of DE layers by evaluating and characterizing their geochemistry. A detailed characterization of these sites, evaluating both features and abundance of charred material from each layer, was performed.

2. Results and discussion

A specific focus was given to how cultural layers began to form with respect to the underlying substrates, in order to identify the 'roots' of the fine matrix making up these layers, including the micromorphology of 'black particles', i.e. the complex mixture of charcoal, coal, soot, partially charred plant matter, organic punctuations or organic fine substances, humified plant matter, etc, that can occur in these deposits.

Soil bioturbation is the main process observable in these Bronze Age cultural layers. This could be evidenced by a strongly expressed channel microstructure, by the presence of crescent-shaped complete infillings, loose discontinuous infillings of mineral fecal pellets, larger coalescing earthworm droppings, and by scattered earthworm granules. This was in contrast with the local substrate, which was a partially decalcified Cambisol formed on the Adige river sediments. A relatively high P content in all the sites agreed with the presence of an anthropogenic soil.

The occurrence of black particles probably derived instead from the admixture of combustion by-products (ash, charcoal, soot, etc.) to the cultural layer.

Stratigraphic correlations, material culture, and ^{14}C dating allowed to assume that they encompass the same period. The radiocarbon calibrated ages obtained from the humin fraction span a period between 75 and 380 CE. The differences in the dating between humin and charcoal suggested a possible initial anthropisation period resulting in an enrichment of organic matter (during 1st and 2nd century) before the cultural layer (during the 4th – early 6th) was deposited.

Both TOC and ROC resulted to be significantly correlated. The concentration profiles along all sites did not exhibit specific trends. The ROC could be related to the pyrogenic products detected. Found values were consistent with the concentrations found in other DE horizons all over Europe. The charcoal fingerprint distribution was similar within the profiles from the same site, confirming once again that in these horizons, neither trends nor internal differentiations could be highlighted, indicating that these soil had been likely mixed and reworked, in agreement with radiocarbon dates.

Raman analysis of collected charcoal fragments showed the typical features of carbon, with D and G bands located at ~1350 and ~1600 cm^{-1}, respectively. In all spectra, the D band showed an higher intensity with respect to the G band, suggesting a low level of crystallinity in the inner lattice of the material. Such hybrid graphitic-amorphous charcoal structure is in agreement with studies conducted on Amazonian soils.

The presence of slags and the droplets confirmed the presence of metallurgical production activities gathered from trace elements and from the detection of Fe microspheres, probably associated with local ironworking. To the best of our knowledge, these kinds of structures were never reported before in cultural layers.

3. Conclusions

Common features and different post-depositional phenomena of the three cultural layers sites were observed. Dumping of heterogeneous materials in sedimentary matrices highlighted how the reworking of older sediments seems to be at the base of cultural layers formation, as confirmed by the different radiocarbon dating of the humin fraction.

The information inferred from these cultural layers resulted as local and case-by-case method, even when the sites are close together, should be the best choice for understanding the activities underlying their formation. A statistical approach is necessary to connect the results of a multi-analytical and multidisciplinary research methodology, necessary to assess the human impact on the surrounding environment in the past.

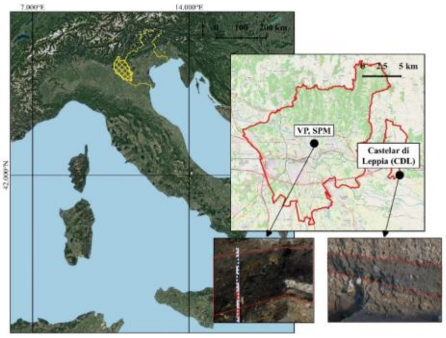

Fig. 1. Location of sampling sites in the Province of Verona and investigated soil profiles.

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OP06

A CUSTOM MADE LOW-COST MID-INFRARED HYPERSPECTRAL IMAGING DEVICE FOR NON-INVASIVE INVESTIGATION OF PAINTINGS

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1. Introduction

Mid-infrared spectroscopy (4000-400 cm-1) is a well-established technique for analyzing cultural heritage. In recent years, mid-infrared technology was adapted to perform hyperspectral acquisition.It consists of acquiring thousands or even hundred thousands of spectra in x and y spatial directions, allowing to obtain both spectral and spatial information from an investigated surface. The technology proved to be very informative in mapping artworks' pigments, binders, and deterioration products. However, the technique isn't progressing fast. To date, only a handful of studies reported the use of mid-infrared hyperspectral imaging, covering a limited spectral range for commercial devices[1-3]or a full range with custom-made portable devices but with a very long acquisition time[4-5].

To further the possibilities and applications of the promising mid-infrared hyperspectral devices, we developed a low-cost portable hyperspectral scanning system.The system acquired full range reflectance spectra in sequence along the x and y-axis and was used to investigate paintings.The idea follows the first custom-made portable mid-infrared scanner (MA-FTIR) developed by the University of Antwerp[4].

2. Results and Discussion

The research presented accounts for three main steps: (1) the construction and assembling of the imaging system, (2) the data acquisition from a painted surface, and (3) data pre-processing and processing to obtain meaningful chemical maps of the distribution of artists' materials.

Concerning the construction of the imaging device, a Cary 630 portable FTIR instrument from Agilent, operating in single point total reflection mode, was combined with a motorized translational stage (GMT Europe GmbH, Germany). The moving block was then incorporated into a custom-made rack, which allowed positioning the instrument to measure flat, vertical surfaces, such as paintings and wall paintings, but also retaining the possibility to perform analysis horizontally. The spectra were collected at 2.2 cm from the object, without contact between the art object and the sensor. The software for moving the motorized stage along the x and y dimensions was developed in the MATLAB environment (v. 2019b, The MathWorks, Inc., Natick,MA, USA) with an intuitive user interface. The interface makes it possible to set acquisition parameters, such as the dimension of the area to be imaged, the speed of travel from one point to the next one, and the step size in mm along the x and y-directions. Conversely, the FTIR instrument interface was kept as the one provided by the vendor. The communication between the instrument and motorized stage interface is performed by an interactive mouse move software, which iteratively acquires a spectrum and then moves the stage one step forward.

The scanned object is a mock-up reproduction of a 15th-century painting, prepared in the laboratory using ancient recipes. The spectra within the selected areas were acquired in the full mid-infrared range (4000-400 cm-1) with the possibility of enlarging the spectral window till the initial portion of the near-infrared (4000-5500 cm-1). In this way, we exploit not only the fundamental infrared bands, generally of difficult interpretation due to the specular reflection effects, but also the overtone and combination bands, which are of more straightforward interpretation. The spectra that are saved as single files were successively recombined in a hyperspectral data cube in MATLAB environment, using the information of the number of columns and rows reported by the custom motorized stage software.

Once the datacube was assembled, we applied pre-processing methods to reduce spectral noise. The data were then processed using either univariate (single band selection) or multivariate techniques such as Principal

Component Analysis (PCA). The chemical maps obtained allowed us to differentiate and spatially locate the areas painted with chemically different pigments.

The large infrared window provided by the instrument is very informative for recognizing pigments. On the other hand, point-by-point scanning (whiskbroom) resulted in a long acquisition time (hours).

3. Conclusions

The system presented here proved helpful and versatile to collect mid-infrared hyperspectral data. The low cost is a relevant factor that may contribute to further promoting the use of this technique in the cultural heritage field. Its compact dimensions and the option to disassemble it to a few easily transportable blocks make it suitable for analysis in situ inside museums. The data processing methods, tested on hyperspectral data cubes acquired on a painting mock-up, proved useful to extract the representative and meaningful chemical maps of painting components.

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OP07

SELECTED ION FLOW TUBE-MASS SPECTROMETRY (SIFT-MS) IN HERITAGE SCIENCE: ORGANIC MATERIALS IN ARCHAEOLOGICAL SAMPLES

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1. Introduction

The identification at molecular level of organic materials in heritage objects as paintings requires in most cases the collection of micro-samples followed by micro-destructive analysis. Non-invasive techniques mainly rely on spectroscopic investigation, which provides fundamental information but may lack specificity in case of complex mixtures of aged organic materials. In this context, in the last few years, we explored the possibility to characterize different types of organic materials by means of non-invasive analysis of released volatile organic compounds (VOCs) through selected ion flow tube-mass spectrometry (SIFT-MS). SIFT-MS is a transportable direct mass spectrometric technique that achieves the analysis of VOCs at trace levels in real time, by controlled ultra-soft chemical ionization using eight different chemical ionization agents.

2. Results and Discussion

We initially applied SIFT-MS analyses on different reference synthetic resins, natural resins, and paint binders to evaluate the possibility to obtain qualitative data for the identification of these materials in heritage objects avoiding any sampling. The application of principal components analysis to the interpretation of the data provided interesting insights, confirming the ability of the protocol to correctly identify complex mixtures of materials through the detection of the whole VOC profiles. The instrumentation was then tested in laboratory on small archaeological objects to evaluate the feasibility of applying this transportable approach directly in situ in museums. Finally, an in-situ analysis campaign was designed for the study of the burial assemblage of Kha and Merit, discovered in 1906, and now preserved at the Museo Egizio in Turin. The discoverer of the tomb and director of Museo Egizio, Ernesto Schiaparelli, limited investigations to a few non-unique items, leaving most of the assemblage untouched. His decision has enabled contemporary scholars to study such exceptional archaeological finding with non-invasive approaches that could not be foreseen at the time. The interpretation of the mass spectrometric data, supported by statistical data analysis, shed new light on the chemical nature of the organic materials preserved in 50 vessels of the Museo Egizio in a completely non-destructive way.

3. Conclusions

We successfully employed SIFT-MS to characterise reference materials, laboratory samples and finally archaeological objects in museum. Our findings pave the way to further applications in heritage science, as in characterising modern and contemporary synthetic materials and plastics in museums and in collections (including murals and street art), but also in monitoring restoration campaigns. SIFT-MS can thus be a useful tool to assess the safety of cleaning strategies for both works of art and professionals.

Figure 1. In museum SIFT measurement of the headspace of an amphora inside the nalophan bag (credit ME Torino).

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OP08

NON-INVASIVE ANALYTICAL COMPARISON OF TWO 18TH CENTURY VENETIAN VIOLINS BY GIORGIO AND SANTO SERAFINO

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1. Introduction

Modern violins originated in Italy as valuable products of the long-lasting tradition of musical instrument making that flourished in Cremona since the 16th century. Over the centuries, the stylistic and aesthetic influence of the renowned Cremonese manufacture reached other luthiers' workshops around Italy. Among them, the Venetian violin-making tradition represents one of the most appreciated expressions of Italian crafts thanks to the masterpieces made by Montagnana, Pietro Guarneri, Goffriller, and Santo Serafino, considered the finest Venetian luthier of the 18th century [1].

This project is aimed at the analytical investigation and comparison of two violins made by Santo Serafino in 1750 ca. and his nephew and pupil Giorgio Serafino in 1749. The two violins were non-invasively studied through XRF and contactless reflection FTIR, while the morphological manufacture features were highlighted with a 3D laser scanner in order to (i) non-invasively characterize the chemical composition of the coating systems, (ii) observe similarities and differences in the material and design features, and (iii) shed light on Venetian violin making, comparing it with historical Cremonese one.

2. Results and Discussion

XRF and reflection FTIR investigations were performed on the same analytical spots of the front and backplate of the two violins, selected on the basis of the VIS and UV images (figure below) to obtain a representative picture of the materials spread on the surfaces. Differently preserved areas (i.e. best conserved, worn-out, restored) were selected to obtain a complete non-invasive stratigraphic information, from the external varnish to the underlying wood. In particular, reflection FTIR provided for both violins information on varnishes, mainly composed of siccative linseed oil possibly mixed with natural resins [2] and, together XRF, on dispersed inorganic fractions. As for these inorganic particles, both violins revealed on some spots the characteristic reflection IR signals of silicate-based materials, possibly attributable to fillers under the varnish layer or pigments dispersed therein. It is worth noting that, on the same analytical spots, XRF revealed significative amounts of Si, Fe, and Mn, generally attributed to red earth pigments [3].

On the contrary, some differences were highlighted, through reflection FTIR, in the presence of proteinaceous material (e.g. animal or casein glue) on the backplate of Giorgio Serafino's violin. This could be attributed to a wood preparation spread before varnishing [4] as used in the renowned Cremonese manufacture in the same years.

On the front plate of the Santo Serafino's violin some contemporary restoration binders were identified: a possibly acrylic material used by restorers as adhesive, filler, or putty, was tentatively revealed by reflection FTIR in correspondence with some repaired cracks. On both violins, XRF highlighted small amounts of Pb, possibly attributed to a siccative agent used in the varnishes, and Br, as a consequence of the typical anti-wormwood fumigation processes used over the centuries [5].

As regards the study of the morphological features of the two violins, many differences in shapes, arching, and dimensions were highlighted by the 3D scan investigation. This can be surely attributable to the selection, by the two violin-makers, of different construction models representative of different historical references.

3. Conclusions

The non-invasive analytical approach with reflection FTIR, XRF, and 3D scan, allowed us to investigate both chemical and morphological features of two historical violins. The selection of differently worn areas allowed us to obtain a representative picture of the different original and restored areas, as well as obtain non-invasive stratigraphic information. As regards the obtained results, some similarities were highlighted in the materials of the varnishes and the particles. On the other hand, important differences were revealed in the wood preparation of Giorgio Serafino's violin, where a proteinaceous preparation could be present. These outcomes could play a key role for contemporary violin makers, who often attempt to reproduce the excellent features of the historical lutherie.

Figure 1. Front and backplates in vis and UV light of the Santo Serafino 1750 (a,b) and the Giorgio Serafino 1749 (c,d).

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OP09

ENVIRONMENTAL ANALYTICAL CHEMISTRY AND LCA

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1. Introduction

It has been proven that the method presently called LCA ("Life Cycle Assessment" or "Analysis") was firstly conceived in the industrial chemistry framework [1,2], even though in the following years this tool was developed much more by other scientific sectors. However, in recent times, a growing importance was recognised to LCA as a tool to assess the sustainability of the chemical product chain [3].

It could be debated if this method, usually associated to the environmental chemistry, could be more properly related to either an analytical or a physico-chemical approach. Here, the nexus between LCA and environmental analytical chemistry are investigated, looking for analogies and possible integrations, suggesting common and fruitful areas of interaction (see Figure 1).

2. Results and Discussion

LCA 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 (ISO 14044 [4]). 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 a 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 widely recognised as a powerful tool able 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 recognise 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 [5-8].

Another promising integration between these two methods has been suggested in the field of experimental design, for the optimisation of novel technologies in view of improving their environmental performances [9,10].

Last but not least, an increasing attention in recent years has been devoted to the sustainability of the analytical approach itself, to assess its impacts from an enviromental point of view. A first international conference on Green and Sustainable Analytical Chemistry has recently been launched by EuChemS (https://www.euchems.eu/events/1st-green-and-sustainable-analytical-chemistry/). The need of limiting waste generation, energy consumption, contaminant release, use of toxic reagents, and other adverse effects, lead to the setting of some principles of "green analytical chemistry" and to the quantification of environmental impacts by means of LCA application [11].

3. Conclusions

Life Cycle Assessment can integrate, from a systemic standpoint, data concerning the environmental effects of chemical substances monitored by the classical approach of environmental analytical chemistry. Furthermore, empolying similar data elaboration tools, a better insight can be gained from the processing of physico-chemical parameters describing environmental impacts, and prediction can be made by elaborating chemical information. Finally, the sustainability requirements recently introduced also into the analytical chemical practice involved the implementation of LCA to assess greener techniques and procedures.

This issue could hopefully be further discussed to better understand potentially profitable integration in chemical expertise, starting from our academic education courses.

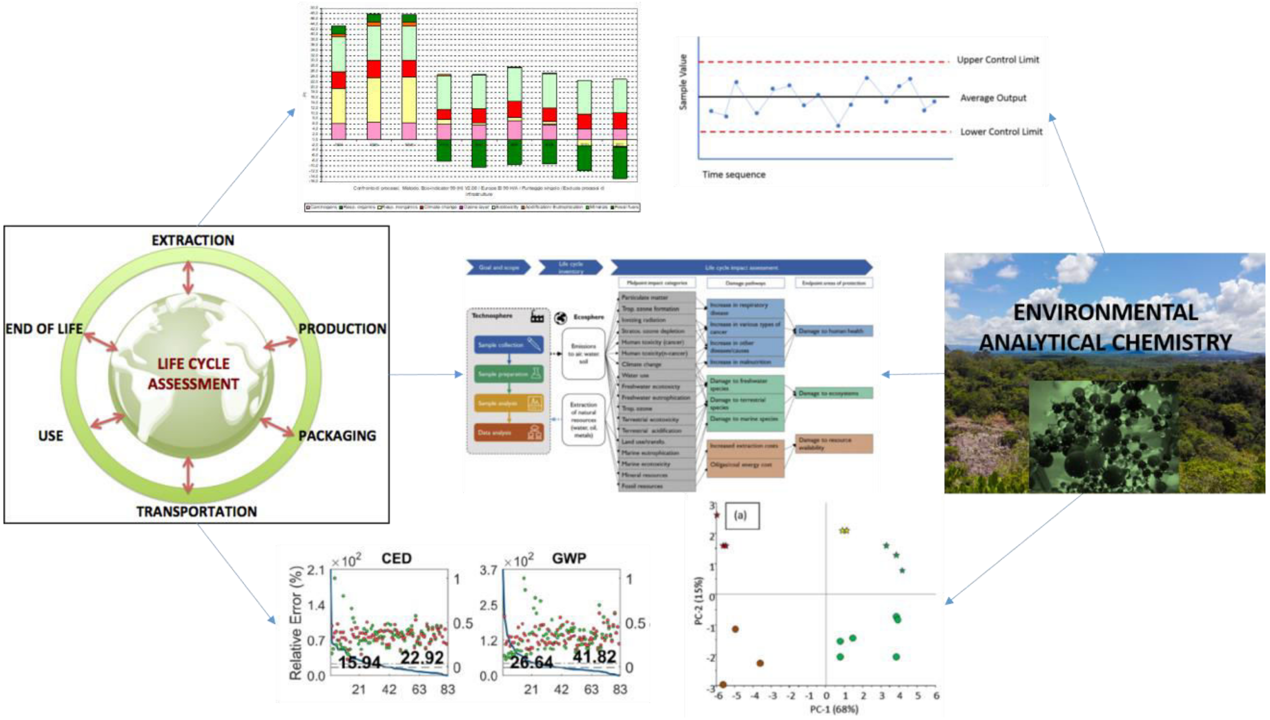

Figure 1: Possible areas of interaction between LCA and environmental analytical chemistry

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OP10

AMINO-MODIFIED SBA-15 ADSORBENTS FOR THE ABATEMENT OF SUGARS IN FOOD AND BEVERAGE WASTEWATERS

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1. Introduction

Sugars from food and beverage industrial wastewaters can impact the water quality with Biochemical Oxygen Demand (BOD5) as high as 5000–8000 mg/L. These BOD5 values are far higher than the limits imposed by regulations for discharging into natural waters and in sewage systems, thus exceeding the capabilities of the local sewage treatment plant.

Adsorption techniques, based on different kinds of substrates and silica, were identified as approaches alternative to biological methods for pre-treatments of food and beverages wastewaters and they deserve further insights. Based on the above-mentioned considerations, the aim of this work is to show the capabilities of ordered mesoporous silica of the SBA-15 family functionalized with primary and secondary amino groups, (3-aminopropyl)-triethoxysilane (S-APTES) and N-3-trimethoxypropylaniline (S-Aniline), to be used for the removal of sugars in wastewaters deriving from food/beverage industries.

Glucose, fructose and sucrose, the disaccharide derivative of glucose and fructose, were chosen since they are commonly used in the food and beverage industry processes and since they are naturally contained in fruit.

2. Results and Discussion

S-APTES and S-Aniline were characterized by nitrogen adsorption-desorption isotherms. For both samples, isotherms are of the type IV according to IUPAC classification, which are typical of mesoporous materials. Hysteresis loops are of the type H1, revealing well-defined cylindrical-like pores (SSA ranging from 298 to 323 m^2/g; Pore Volume ranging from 0.53 to 0.54 cm^3/g) . The pore size distributions appear narrow and unimodal for both materials, confirming their uniform porosity.

The adsorption performance of S-APTES and S-Aniline toward sugars were studied, through ion chromatography, investigating both the effect of the solution pH and the effect of solid:liquid (S:L) ratio.

For S-APTES and S-Aniline removal capabilities were governed by H-bonding and were inversely proportional to pH, and range from about 10-20% (pH 8.5) to about 90% (pH 2.1) for S-Aniline and from about 20% (pH 8.5) to about 70% (pH 2.1) for S-APTES. The decreasing of the removal capabilities upon increasing pH was observed to be larger for S-Aniline than for S-APTES, probably due to the weaker basicity of propylaniline. Since the highest removal yields were achieved at pH 2.1, further investigations were carried out at this pH value.

Subsequently, the choice of the most suitable S:L ratio was performed, to find the correct dosage of adsorbent that minimizes the mass of reagent required to achieve the desired performance, thus maximizing the cost-effectiveness of the approach. The use of higher S:L ratio 1:16 in respect to 1:40 was shown to improve removal performances which were as high as about 70% (S-APTES) and about 90% (S-Aniline) for all the tested sugars.

The functionalized adsorbents S-APTES and S-Aniline were finally tested for real case applications on a simulated soft-drink wastewater (SD-WW) in which 5000 mg/L BOD5 was simulated by adding sucrose (SD-WW-suc) or a cola-like beverage (SD-WW-cola). The performance of sugars by the adsorbents is shown in Figure 1. In the case of SD-WW-suc, the abatement of BOD5 is about 63% (relative standard deviations, RSD, below 2%) for both S-APTES and S-Aniline. For SD-WW-cola, the analysis allowed the detection of glucose, fructose and sucrose already present in the pristine cola-like drink. For this sample, the sugar removal capabilities for the two adsorbents were above 70% (RSD< 7%).

3. Conclusions

The ordered mesoporous SBA-15 modified with (3-aminopropyl)-triethoxysilane and N-[3-(trimethoxysilyl)propyl]aniline allows to obtain adsorbents suitable for the removal of high concentrations of glucose, fructose, sucrose from wastewater samples from food process industry.

The performance of S-APTES and S-Aniline adsorbents is pH dependent and is mainly ascribed to the formation of hydrogen bonds which provide strong interactions with sugars. The efficient removal of BOD5 by the modified SBA-15 adsorbents is achieved at an adsorbent dosage:solution ratio of $6 \cdot 10^{-5}$ g:L which is a far lower value than the ones usually reported in the literature [1] with advantages even for the disposal procedures at the end of the life of the materials.

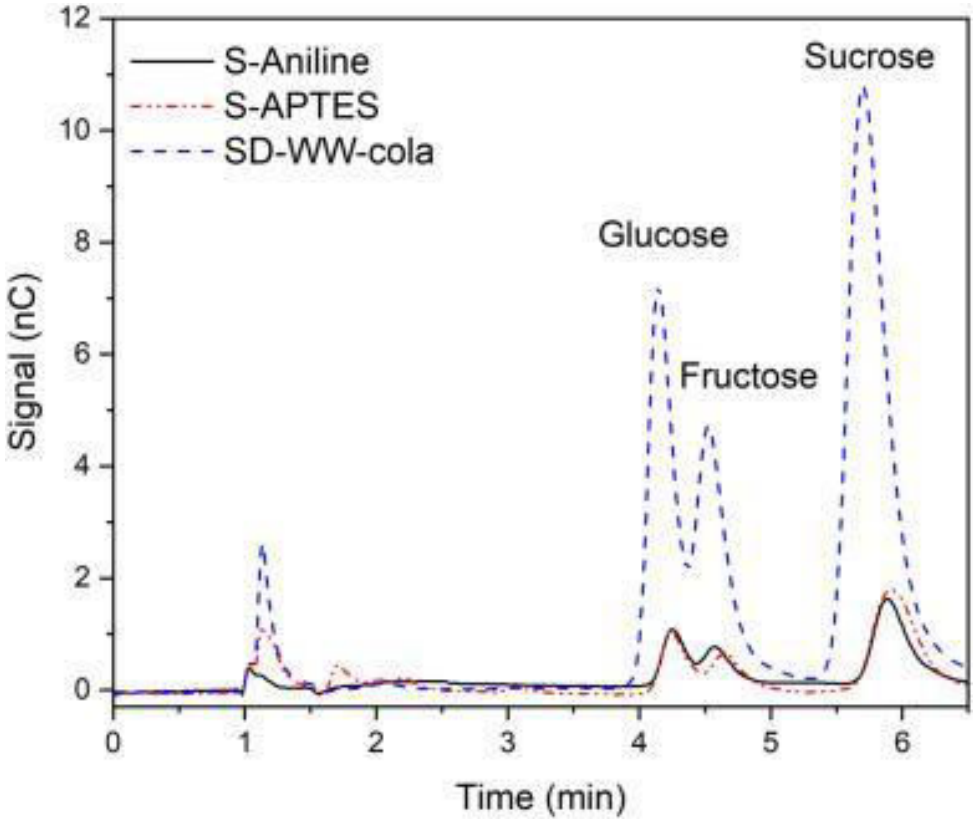

Figure 1. Chromatograms of simulated wastewaters BOD abatement through S-APTES and S-Aniline

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OP11

CLIMATIC CHAMBER TEST TO EVALUATE THE CATALYTIC ACTION OF HEAVY METALS IN THE SULPHATION PROCESS

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1. Introduction

Research conducted on the degradation of cultural and architectural heritage caused by the deposition of air pollutants indicates that both sulfur dioxide and particulate matter produced by the combustion of fossil fuels are the main agents responsible for the deterioration of carbonate materials (marble, limestone, etc.). The main chemical degradation process is the sulphation of the substrate and consists in the initial conversion of sulphur dioxide into sulphuric acid (H_2SO_4) and the subsequent reaction of sulphuric acid (SO_2) with calcium carbonate. This leads to the formation of dark heterogenous encrustations known as black crusts [1], which are composed of gypsum inside which particulate matter is embedded. Heavy metals adsorbed on the carbonaceous particles enable the sulphation of the substrate by acting as catalysts in both stages of the process. Despite the presence of numerous studies related to black crusts formation [2-3], a specific role of the single metals is still unclear. Aiming to unveil the catalytic action of different metals, a series of experimental tests was carried out in specific climatic chambers for accelerated aging.

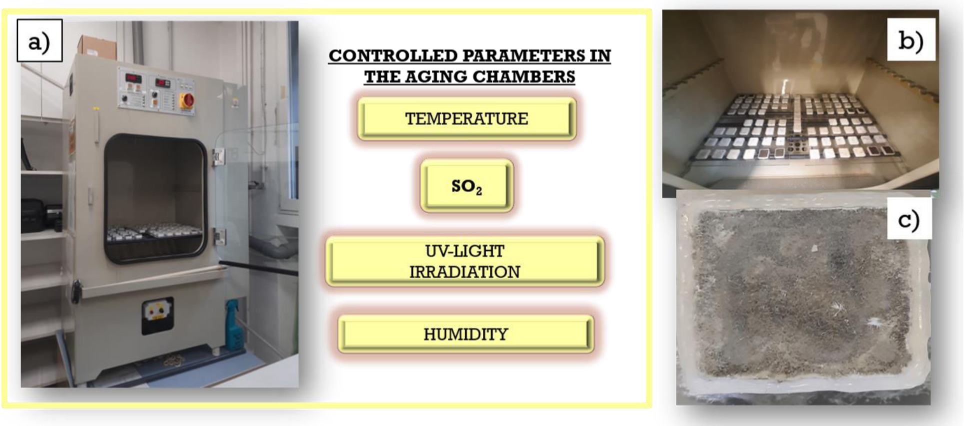
2. Results and Discussion

Accordingly, several Carrara marble specimens were prepared for exposure in the chambers by treatment with particulate matter, metal ion solutions, or mixtures of metal ion solutions. Graphitic carbon was also added into the samples (except for the ones covered with particulate matter) to simulate the behaviour of elemental carbon present in polluted outdoor environments. The simulation of the aging process was carried out with the use of a two climatic chambers for corrosion tests in a humid atmosphere with sulphur dioxide (fig.1a) and exposure cycles simulating solar irradiation (xenon arc climatic chamber) (fig.1b).The exposure of the specimens was performed for four consecutive weeks and, after each week, a portion of the samples was retrieved for analysis. The chemical characterisation was carried out before and after the accelerated aging tests by means of a multi-analytical approach involving different techniques. Colorimetric analysis was used to evaluate the variation of the chromatic coordinate L (brightness), which is related to the formation of gypsum on the surface. Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM-EDX) was employed to study the elemental composition and morphology of the surface and degradation products. Moreover, X-Ray Diffraction (XDR) was used to identify the mineralogical composition of the degradation layer and Ion Chromatography (IC) was performed to identify and quantify soluble salts, with particular focus on the sulphate ions. Finally, Thermogravimetric Analysis (TGA) was carried out to quantify the amount of gypsum formed, along with organic and elemental carbon present in the black crusts.

Some metal cations have been observed to activate the catalytic process faster than others, which appear to activate later. The different combinations of metal mixtures, with which some specimens have been treated, show a synergistic action that is greater in terms of gypsum formation (mainly in the subsequent weeks of experimentation). The samples treated with PM 2.5, after the fourth week of exposure, show gypsum concretions that resemble those of real black crusts (fig.1c). The formation of gypsum over time affects the degradation of the stone substrate and this is greater for some samples. Finally, from the analyses carried out on the untreated "blank" specimens it is possible to observe the development of a slowed down sulfation compared to the treated samples.

3. Conclusions

This first phase of experimentation has highlighted the complexity of the sulfation process. At the moment, there is no univocal evidence on the role of these catalysts in this process, but some considerations have been hypothesized. In fact, it will be essential to carry out further tests in climatimatche chambers as these results will be useful in the next stage of a project to create a predictive mathematical model. This will help predict the formation of black crusts on carbonate surfaces based on the outdoor pollution present in a given site. In fact, this research work is part of the interdepartmental SEED 2019 project of the University of Milan entitled SciCult.



a)climatic chambers for corrosion tests; b)exposure of the samples; c)sample PM exposed at 4 weeks

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OP12

BUILDING A DATASET FOR COPPER ALLOYS CORROSION PRODUCTS CHARACTERISATION BY NON-INVASIVE TECHNIQUES AND MACHINE LEARNING MODELS

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1. Introduction

This work reports the first achievements of a study dealing with the development of fast systems in characterisation of copper alloys corrosion products. In conservation assessment and documentation, the main problem is the identification of degradation typology in a timely manner, in order to plan the most suitable restoration work. In particular, it is crucial to distinguish the degradation by chlorides in order to diagnose and overcome the "bronze disease" [1]. Although there are several well-established analytical approaches, they imply considerable amounts of time and cost which, in most cases, are incompatible with conservation needs. Therefore, it's necessary the development of fast and non-invasive procedures able to give reliable results just using non-invasive analysis [2]. Additional recent studies provide useful tools to characterise corrosion products [3][4] but the main goal here is to combine information obtained from multi-techniques analysis in order to train machine learning classification models able to easily identify the degradation typology.

2. Results and Discussion

The adopted methodology includes colorimetry, UV-Vis-NIR Fiber optics diffuse reflectance spectroscopy (FORS) and X-ray fluorescence spectrometry (XRF) as non-invasive analyses, performed *in situ* by portable instrumentation. Further used techniques as X-ray diffraction (XRD) and Raman spectroscopy are, in this instance, micro-invasive and performed on a limited number of samples of corrosion products picked up from some degraded areas previously analysed by non-invasive approach in order to obtain additional information of the material and to validate the outcome. A large dataset including colorimetric, compositional and spectroscopic information was designed using analysis results of hundreds of points of measure on nearly 200 copper alloy artefacts requiring to be restored and belonging to different collections.

Colorimetric data are CIEL*a*b* coordinates and deltaE (dE) i.e. the colour variation in comparison with points of measure in the same item but without *patina* (whenever possible). The scientific definition of the colour allows an unequivocal determination of minerals with nuances difficult to define otherwise. Furthermore it provides a good distinction in the colour space of different corrosion products which can be grouped in patterns by clustering models according to their similarity.

Compositional information concerns the XRF results attributable to the presence of relevant detectable elements in corrosion products (Ca, K, Al, P, Si, Cl, S) allowed the possible presence of mineral phases including them and conversely, in absence of them, together with the dark matrix estimation suggested the occurrence of nitrates, carbonates or oxides.

Reflectance spectra are treated entirely or just considering the main features (minima, maxima, shoulder or point of inflection). In particular the observation of the reflectance minimum or minima of the absorption band at wavelengths ranging from about 640 nm to 920 nm provide a considerable diagnostic power. Taking in account that alteration products are often heterogeneous mixtures a few considerations can be possible in the light of the XRD or Raman characterisation of certain mineral phases in samples. Many copper corrosion products spectra present a single reflectance minimum whereas atacamite (copper hydroxychloride) shows a first reflectance minimum at about 715 nm and second one at about 850 nm with a weak shoulder between them. A similar trend is observed in antlerite (copper sulphate hydroxide) spectra but the first minimum at about 730 nm and a second one ranging from 750-920 nm.

The integration of the results, processing different data referred to the same area of measurement by machine learning models permits the distinction in macro groups among types of degradation.

3. Conclusions

This work represents a preliminary phase of a study still under development. This approach might be improved to be systematically applied in conservation assessment and restoration documentation. It allows the definition of an analytical protocol and in particular the suitable measurement condition and the main analytical variables to be considered. It is important considering that the presence of chlorides does not necessarily mean an active bronze disease corrosion, but it remains a relevant information for prioritising interventions or further analysis.

For this reason, the database provides a promising starting point for the development of a useful system to compare and distinguish different kinds of copper based alloy degradation analysed exclusively by fast, simple and non-invasive methodology.

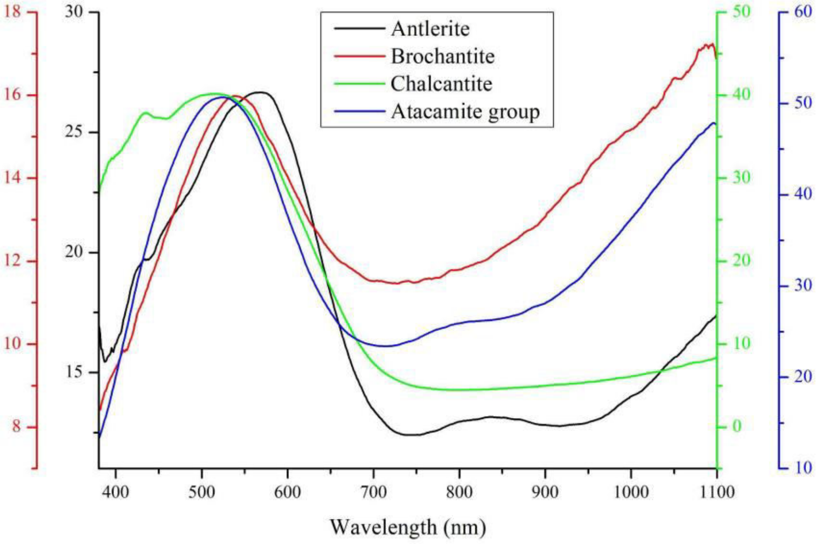

Fig.1 FORS spectra of some relevant copper alloy alteration products

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OP13

COMPREHENSIVE CHARACTERIZATION OF AGED LIPIDS BY USING CHROMATOGRAPHIC ANALYTICAL TECHNIQUES COUPLED TO MASS-SPECTROMETRY DETECTION

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1. Introduction

Analytical investigations of organic residues contained in ancient pottery can address a wide range of archaeological questions and provide important clues on diet, food storage and processing, ritual and medical practices, trade and use of commodities, domestication of animals, etc. To date, lipids are the main chemical class of substances investigated in archaeological pottery. This is due to their hydrophobicity that limits their percolation and allows their persistence in the archaeological site [1]. However, the lipids may undergo chemical or microbiological degradations in situ over time. This fact further complicates the interpretations on the origin of lipid matter [2]. Therefore, determining the nature and origin of lipids in ancient pottery is a difficult task since they reflect a range of complex transformations caused by a series of alteration processes (i.e. thermal decomposition, oxidation, hydrolysis). In this regard, accelerated ageing tests can provide key elements to study the formation of characteristic compounds that could indicate unambiguous origin for the organic archaeological remains.

2. Results and Discussion

Thermo-oxidative treatments were carried out in laboratory in order to simulate the natural degradation of lipid matter occurring in archaeological pottery. In detail, triglyceride standards of tristearin, triolein, trilinolein and trilinolenin were kept in an oven at 120°C for three weeks. In addition, the same ageing treatment was applied to Extra-Virgin Olive Oil (EVOO). The degradation of the aged samples was monitored weekly by using liquid and gas chromatographic techniques coupled to mass spectrometers (Figure 1). The sampling of highly volatile compounds was performed by using head-space solid-phase microextraction (HS-SPME) technique and the analyses were carried out using gas chromatography-mass spectrometry (GC-MS). Particular attention was also paid to the evaluation of oxidated fatty acid species, such as (α, ω)-dicarboxylic acid, analyzable by GC technique previous conversion to trimethyl silyl ether (TMS) derivatives. Intact lipids analysis was performed by Non-Aqueous Reversed Phase High Performance Liquid Chromatography coupled to Atmospheric Pressure Chemical Ionization Mass Spectrometry (NARP-HPLC-APCI-MS). Elution of the lipid species occurs according to increasing partition number (PN), derived from the equation $PN = CN - 2DB$, where CN and DB are the carbon number and double bond number of FAs in the structure. In both cases, a reliable identification was achieved combining the Linear Retention Index (LRI) system with the MS data.

3. Conclusions

Thermo-oxidation products were identified in univocal manner through the use of two different identification parameters: spectral similarity and linear retention index (LRI) correspondence, both by GC and LC methods coupled with MS detection. In addition, thermo-oxidation treatment produced several volatile compounds including short-chain fatty acids (SCFAs), aldehydes, ketones, lactones, esters.

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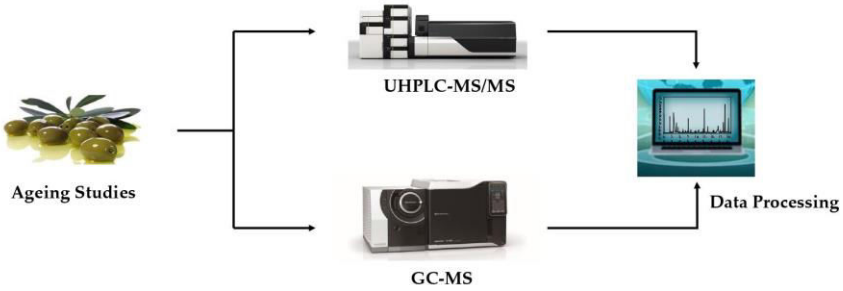

Figure 1. Schematic representation of the techniques employed to perform lipids ageing studies.

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OP14

A CUTTING-EDGE INTEGRATED XRF-VIS-NIR HYPERSPECTRAL IMAGING SYSTEM FOR A MULTIVARIATE AND MULTIBLOCK HIGH-THROUGHPUT CHARACTERISATION OF PAINTINGS

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1. Introduction

Hyperspectral imaging (HSI) systems that operate in different spectral ranges proved to be technologies highly potential for cultural heritage science, which usually facing heterogeneous and complex objects. However, due to the complexity of combined 3D imaging spectroscopy data, advanced data processing strategies are always required. This has often hindered the use of these technologies to non-research practitioners, and limited the utilization of information and results.

The present research aims to develop an integrated analytical protocol for the investigation of paintings based on the application of a new cutting-edge instrument developed by Bruker Nano Analytics, which permits to acquire simultaneously the co-registered spectral imaging data exploiting three different techniques: X-ray fluorescence (XRF, 1-40 keV), visible near infrared (VISNIR, 400–1100 nm) and short-wave infrared spectroscopy (SWIR, 1100–2500 nm).

Moreover, combining principal component analysis (PCA) and correlation diagrams, an multivariate chemometric strategy was developed, in order to extract the most useful information through visualization and inter-correlation assessment for the fused 3D datasets.

2. Results and Discussion

The highly innovate technology developed and the data processing strategy associated were applied on a painting mock-up representing a freely inspired version of "Sportsmen" by Kazimir Malevich. The mock-up holds a complex stratigraphy of two painting layers made of different pigments and binders.

The workflow can be describes as follows, divided in 6 steps:

After paint scanning (step 1) the datacubes in VNIR, SWIR and XRF were extracted (step 2) and pre-processed (step3) followed by data fusion (step 4). The chemometric approach was then applied to the fused data consisting in a preliminary analysis of PCA and brushing (step 5) which allowed to investigate score maps and clusters in the score plots, from which the related averaged spectrum can be extracted.

In detail, the score maps were visualized to identify the PCs yielding meaningful information (variance), useful to chemically characterize the different painted areas. The combination of the different spectroscopies applied simultaneously led to an efficient elemental and molecular characterization of the different areas.

Different painted areas identified by PCA were submitted to a further investigation by using correlation diagrams and maps (step 6) , which give an intuitive overview of the correlation within variables in the same range and between variables in different spectral ranges. At this stage, chemometric analysis was aimed at investigating more deeply the combined presence of components related to different types of pigments and/or present in different layers, exploiting the different penetration depth of the different spectroscopies employed.

Thanks to a relevant contribution of both the near-infrared and X-ray ranges, painting details, not visually detectable and localized below the first painting layer, were recognized. Indeed, although NIR spectroscopy might be considered as a surface analytical technique, it has been demonstrated that the radiation penetrates under sample surface to a significant extent depending on several factors, including the energy of the source, the incident angle and physical properties of the material analysed. Concerning the X-ray radiation, the high energy of the incident photons allows them to penetrate the inner layers of the paintings, collecting information from all the superimposed layers, down to the preparation one.

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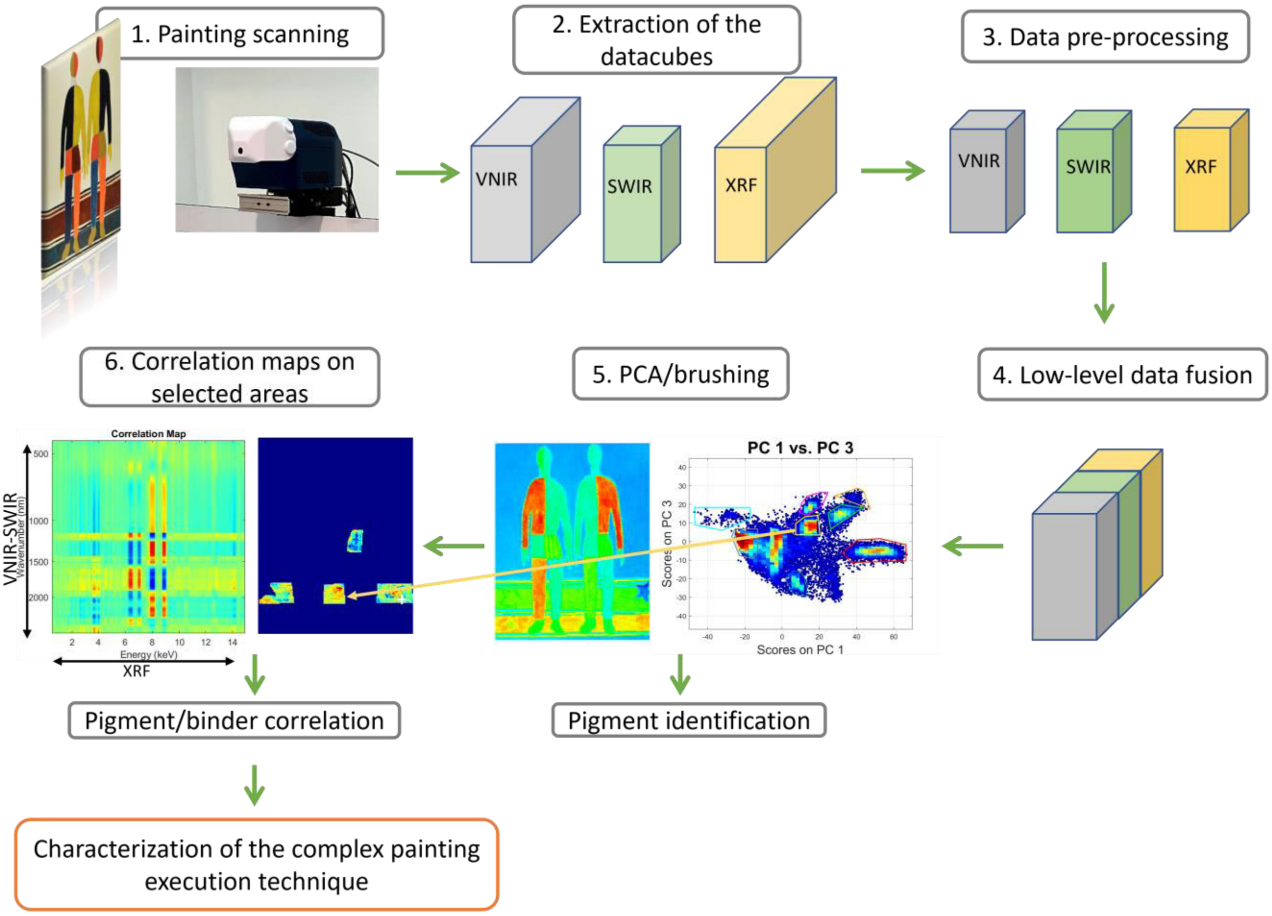
3. Conclusions

The XRF-VNIR- SWIR hyperspectral imaging system, combined three different spectroscopic techniques, showed great potential through the investigation of the mock-up painting with complex and heterogeneous stratigraphy.

The data from the three techniques are co-registered, thus inherently saved with high space coherence, reducing the time for post-processing and correlated analysis. A complementary elemental and molecular characterization is, therefore, provided simultaneously by this powerful analytical platform.

The chemometric strategy developed proved to be highly efficient in data reduction and for the extraction of the most useful information coming from the three different spectroscopies, through an effective data visualization and inter-correlation assessment.



Data collection, processing and visualization workflow

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OP15

APPLICATION OF THE LIFE CYCLE ASSESSMENT METHODOLOGY TO THE VERMICOMPOSTING PROCESS: AN INNOVATIVE PATHWAY TO PRODUCE HIGH QUALITY HUMUS

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1. Introduction

The large-scale urbanization and industrialization resulted in a growth of solid waste generation and especially biowaste, which constitute about 46% of the total solid waste produced worldwide [1]. The aim of this study, performed in cooperation with the company Paneco Ambiente S.r.l. [2], is to apply the Life Cycle Assessment (LCA) ISO 14040-14044 [3] to an innovative production pathway aimed to convert 18kt/y of agricultural and livestock waste into a high quality soil conditioner (HQ-SC) suitable to replace peat, a non-renewable material identified as commercial alternative. The production system consists in a series of processes, among which an anaerobic digestion and a vermi-composting step [4] that employs earthworms to obtain a peat-like material, meant as a resource with high carbon content, great porous property and water-holding capacity [5]. The presence of a photovoltaic plant (PV) and a cogenerator, fed with the biogas produced in the anaerobic digestion, allows the system to be completely independent from the national grid and to sold the excess of EE auto-produced.

2. Results and Discussion

The LCA analysis is performed using the software SimaPro 9.2. All the information related to the flows involved in the system (e.g. amount of input waste, electricity, diesel, packaging material, products and sub-products) are provided by the company, while the missing data needed to create the model are obtained by the Ecoinvent 3.7 database [6]. Results are reported as function of the equivalent organic carbon content of 1 ton of HQ-SC produced through the innovative way and include all the operation performed by the system, following a "from cradle-to-gate" approach. Since the CO_2 eq emissions are considered one of the most representative parameters to evaluate and determine the environmental impacts of a product, a system or a service, the chosen calculation method is IPCC 2013 GWP 100a (ISO 14067, [7]).

Being peat already available in nature, its supply consists only in the extraction, transportation and packaging of the resource. For this reason, the carbon emissions associated to the peat (20.2 kg CO_2 eq/FU) are lower with respect to the HQ-SC, which is instead obtained by a more complex and, accordingly, more impacting series of processes (Figure 1a). However, if the amount of EE auto-produced by the cogeneration and the PV plants (551MWh/y and 248 MWh, respectively) and sold to the national grid is considered as avoided product, the system resulted to be carbon negative (-24.9 kg CO_2 eq/FU), showing a difference between the HQ-SC and the peat of 45 kg CO_2 eq/FU, which is translated into a saving of 108.2 ton CO_2 eq/y (Figure 1b). The avoided impact is calculated assuming to not produce the amount of the sold EE from the resources that nowadays are used to generate the electricity of the national electricity mix (about 50% of fossil derivation), including the imported fraction, modeled using the last updated information available on IEA, 2020 [8]. The fraction of digestate obtained by the solid/liquid separation is assumed to be delivered to the input waste suppliers, since its chemical characteristics allows its employment for agricultural purposes, partially replacing the usage of commercial fertilizers [9-11]. Anyway, due to a lack of data and of the complexity to compare the nutrient intake of commercial fertilizers and liquid digestate, which has not been chemically characterized by the company yet, it has been chosen to exclude its employment from the system boundaries, in consistency with other studies [11].

From the contribution analysis it emerged that the higher direct impacts associated to the HQ-SC are due to the in-bound transportation of waste (33%) and to the anaerobic digestion emissions (21%), highlighting the influence of the supply chain.

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Then, a sensitivity analysis performed to test the robustness of the model created, confirmed that the sustainability of the innovative system is ensured mainly because of the presence of the renewable energy stations, since, assuming to not sold the excess of EE produced by the PV and to consume EE deriving by the national grid, again in substitution to the fraction produced by the PV, the total carbon emissions would be increased to 91.0 kg CO_2 eq/FU, corroborating the influence of the amount of electricity consumption and its derivation in a LCA [12].

3. Conclusions

The study demonstrates that it is possible to improve the exploitation of the energy and amending power contained in the organic waste in a sustainable way. The advantages of the proposed system do not derive only by its carbon emissions, which resulted to be significantly lower with respect to peat, but also to the benefits due to the stabilization of the input material, since it ensures a reduction of the organic waste spilled onto the agricultural fields and a consequent decrease of carbon losses associated to this practice [13]. Further studies will be performed extending the analysis to more environmental categories and assuming to introduce a biogas to biomethane raffination, in substitution to the cogenerator [14,15].

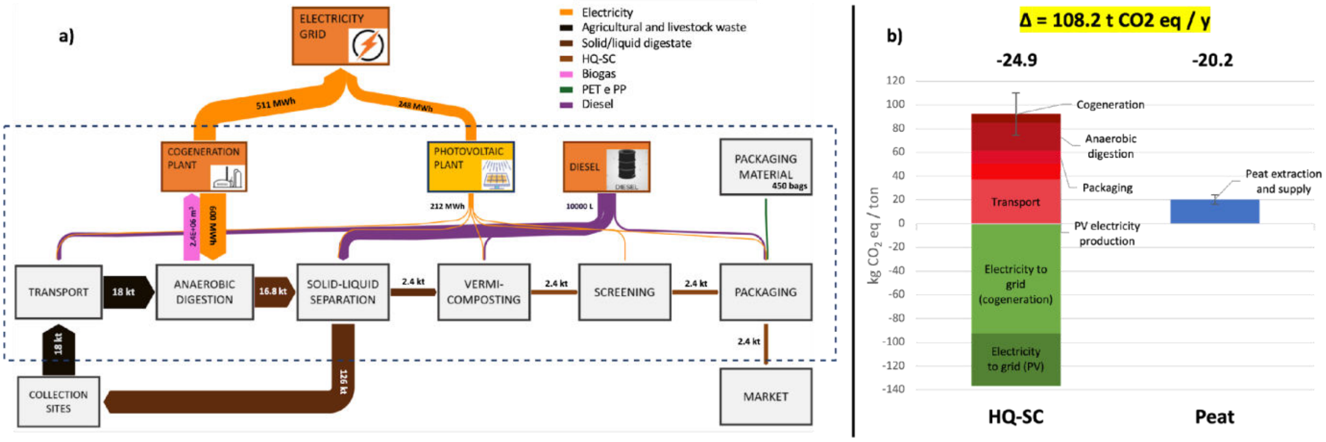

Figure 1a: Map of the system; Figure 1b: Comparison between the CF of HQ-SC and Peat

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OP16

THE CIRCULAR ECONOMY OF WASTE AND BIO-PRODUCTS FOR A NEW CONTROLLED RELEASE FERTILIZER SYSTEM

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1. Introduction

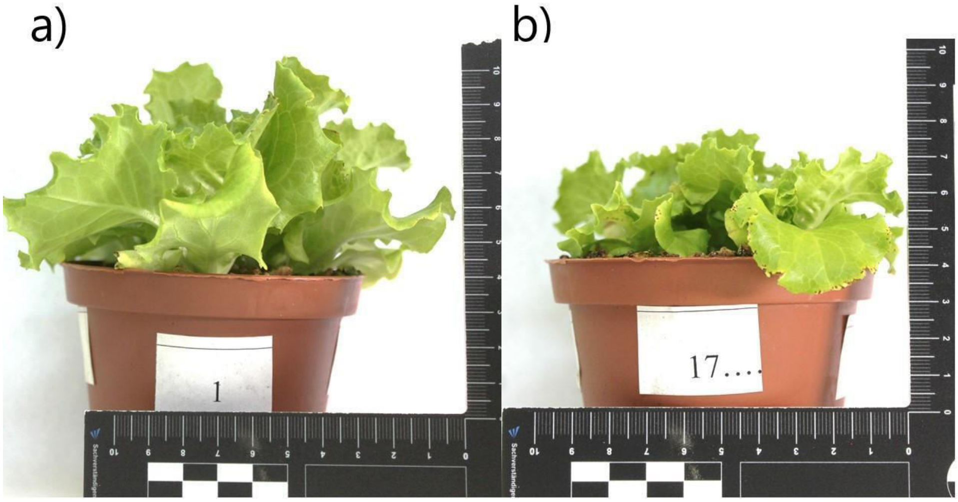
For facing up the consequences of climate change in agriculture, green roofs can be an eco-sustainable solution that involve the use of a drainage layer, usually made of porous inorganic materials, with high drainage capacity. These materials can be used also in indoor cultivations and integrated with nutrients to form controlled release fertilizers (CRF) for their high porosity and retention capacity. The slow release of nutrients prevents loss of ions and the consequent poisoning of the soil [1]. In a circular economy perspective, the porous materials were realized with local industrial wastes as pumice scraps, that partially replaced clay, as natural raw material, and by-products. The primary nutrients, phosphorous and potassium, were integrated in the core as they are (AP) or inside a fertilizer glass (APFG). An organic coating based on defatted black soldier fly (BSF) prepupae was used as nitrogen source. Aim of the study was to investigate the chemical and physical properties of the porous materials for their application in the soil, while the controlled release of nutrients was investigated through release tests simulated in citric acid and with grow test made on lettuce.

2. Results and Discussion

The porous materials had a spherical shape with a diameter of 1-2 cm. The core of samples was analyzed for physical properties such as porosity and water absorption capacity and chemical characteristics as pH and electrical conductivity (EC). From the analysis of the two formulations of fertilizers (AP and APFG) resulted a total porosity higher than 50% and an average water absorption capacity of 26%, higher for the not vitrified materials. These values appeared higher than those measured in previous studies that used porous materials of only clay [2], meaning that the use of pumice scraps as substituent of natural raw materials can improve the lightness and water retention of CRF [3]. Both core formulations, before the application of the organic coating showed a neutral pH and an EC on average of 0.2 dS/m, parameters indicated as optimal for the use of substrates as growth media. Covering the porous materials with the N-based coating the pH has been measured before and after the application in the soil for lettuce growth. The pH of the coated CRF resulted neutral, but it became alkaline after the application in the soil. The substrate used for lettuce growth made of peat and agri-perlite was therefore checked too for its final pH and resulted neutral both with and without the porous materials inside, meaning that the fertilizers didn't contaminate the soil for lettuce growth. The EC of the substrate at the end of the test was 2 dS/m due to the presence of free ions. The coated samples were also tested for their humidity, that decreased after the use in the soil, a parameter connected to the water drainage capacity of the materials, that helps the plants to grow for longer time without the need to add water. To investigate how nutrients can be released in the soil from the porous materials, release tests in citric acid were made on not coated samples after 7 and 21 days, to verify the controlled release of nutrients over time. In particular after 21 days, it was observed that K and P were released from the vitrified fertilizers respectively 12% and 17% more than from AP, and it was observed in general a higher release after 21 days for all the nutrients confirming a controlled and slow release over time. Finally, the coated samples were analyzed too, since the N-coating can influence the release of nutrients, slowing down the process. It was demonstrated that the main nutrients, nitrogen, phosphorous, potassium and magnesium passed almost completely in the soil in 21 days. Dangerous elements for the soil as aluminum and lead were present in low concentration and their concentration didn't change in the fertilizers, meaning they were not released in the soil. The absorption of nutrients from plants was confirmed through a grow test made on baby lettuce in a climate chamber integrated with a specific LED receipt. The fresh weight of the growth plants demonstrated an average increase of 50% using the CRF in the soil compared with a soil without fertilizer. An average leaf area (48% higher) was also seen in the tests that used fertilizers, compared with a not-fertilized soil.

3. Conclusions

The introduction of local wastes and by-products in porous materials had beneficial effects and confirmed the possibility to form a drainage layer in the soil for water retention. They showed high porosity and water absorption capacity, and a slow decrease of humidity, that helped to keep the soil wet. The pH and EC didn't compromise the soil and the growth of plants. The release of nutrients were confirmed for the core and in the coated samples without accumulation of any dangerous elements in the soil. The application for lettuce growth, showed improvement of the morphological characteristics if compared with a not fertilized soil, confirming that the CRF created, as an example of circular economy, can have a potential application for indoor cultivations and vertical forests.



Baby lettuce grown up with controlled release fertilizers (a) and in a non-fertilized substrate (b).

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OP17

POLYPHENOLIC COMPOUNDS IN OLIVE MILL WASTEWATERS AND THEIR POSSIBLE REPELLENT/INSECTICIDAL EFFECT TOWARDS BACTROCERA OLEAE

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1. Introduction

Bactrocera oleae, commonly called "olive fruit fly", is the most important adversity affecting olive tree cultivation. The pest management occurs mainly with the use of synthetic insecticides which, in recent years, have brought out important critical issues in the agronomic and environmental fields. Many attempts have been made to replace (and to eliminate) the common synthetic insecticides, but with unsatisfactory results so far. In this work, the presence of compounds with possible insecticidal/repellent effect against *Bactrocera oleae* in the wastewater from the mill processing has been investigated, in view of more sustainable approach to face this parasite. This approach could also lead to solve the problem of disposal of olive mill wastewaters (OMWWs): the possibility to obtain insecticide/repellent substances (produced by the plant itself) from a waste, is a way to give cyclicality to the production process. In fact, these wastewaters play an important role in the negative ecological footprint of olive oil production in view of their high ecotoxicity (they are one of the most harmful effluents produced by the agri-food industry) and the consequent cost of disposal.

2. Results and Discussion

Several studies have shown that some phenolic compounds are involved in the repellent action exerted by the aqueous fraction of the fresh olive juice and the olive oil wastewater toward the olive fruit fly. In this regard, we have developed and validated accurate analytical procedures for the quantification and extraction of the main polyphenols present in OMWWs in view of the future studies (*in-vivo*) on their effects toward the fly.

For the determination of the main polyphenols (oleuropein and its derivatives: hydroxytyrosol, pyrocatechol, tyrosol and caffeic acid) in OMWWs an UHPLC method with both UV-DAD and fluorescence (FLD) detection has been optimized. The method involves a simple liquid-liquid extraction/purification procedure before the RP-C18 chromatographic analysis. The method has been validated by ensuring that it allows an accurate quantification of the polyphenols of interest by the estimation of the recovery, uncertainty and LOD for each analyte. Moreover, analytical bias has been investigated by a statistical comparison of the result obtained by the two detection responses (DAD and FLD) and by a more selective detection procedure (ESI-HRMS). These measurements highlighted the satisfactory performances of the analytical method developed for the quantification of polyphenols in OMWWs: it is characterized by a very good level of precision, excellent detection limits and a negligible analytical bias.

We also developed a procedure for the isolation and collection of single phenolic compounds from OMWWs samples. This in view of the preparation of suitable standard solutions for both analytical use and the future *in vivo* experimentation. After liquid-liquid extraction from OMWWs, phenolic compounds were separated on a preparative RP-C18 column by a HPLC instrument equipped with a fraction collector. After several runs, appreciable quantities of each compound were collected and characterized by Nuclear Magnetic Resonance as regards the qualitative aspects and by HPLC-DAD-FLD analysis for their quantification. In particular, NMR spectra (one- and two-dimensional experiments) fully confirmed the structure of all analytes isolated from OMWWs samples, with results that totally coincide with the spectroscopic data reported in the literature.

3. Conclusions

A satisfactory analytical method for the accurate quantification of oleuropein and its derivatives in the olive mill wastewaters has been optimized and validated. Together with the excellent results obtained in the collection of the pure phenolic compounds, these procedures can be transferred and applied in the production processes for a better characterization of OMWWs and its possible use in the olive tree cultivation. In a more strictly scientific context, we are confident that the procedures here optimized can find immediate application in *in vivo* toxicological studies aimed at identifying the repellent and/or insecticidal properties of the individual phenols towards the olive fruit fly and thus representing a research line to be undertaken in the immediate future.

Figure 1. Bactrocera oleae and affected drupes.

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OP18

INVESTIGATING COATING APPLICATIONS FOR PROTECTION OF ROMAN FRESCOES

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1. Introduction

In the last decades, Climate Change has been having a significant impact on Built Heritage due to the degradation factors to which it is directly exposed. Current conservation practices consider mural paintings as an integral part of monuments and heritage sites, and advocate for their in-situ preservation whenever possible [1]. The application of protective coatings may thus play a crucial role in their conservation.

In this work, a new green protective coating for outdoor ancient frescoes surfaces is presented: its development is meant to fill a void in conservation products specially designed for wall paintings, both on the market and in the literature. The formulation is obtained by optimizing a one-pot synthesis, combining the stability and the reducing characteristics of the chitosan biopolymer [2] with the hydrophobic features of silver nanoparticles (Ag NPs) [3]. To validate the protective features of the proposed coating, its characteristics have been compared with those of two commercial products, i.e. Paraloid® B72 and Proconsol®. The analyses were carried out on both the coatings and the treated surfaces of fresco mock-ups.

2. Results and Discussion

For the formulation of the coating base, a gel with chitosan and Ag nanoparticles (NPs) was prepared. The main idea is to provide hydrophobic properties, by adding silver NPs, to a base made by a biopolymer that is green, has antimicrobial activity, and could help in surface protection in an outdoor environment. The chitosan has been solubilized in azelaic and lactic acid, in which Ag NPs were successfully developed by a one-pot synthesis, using calcium or sodium hydroxide as precipitating reagent. Finally, the obtained gel has been diluted with a mixture of glycerol and ethanol. For the determination of the adequate concentration of silver nitrate and of the best precipitation agent to use, the final formulation has been characterized by SEM, TEM, UV-Vis analyses. For the solvents choice, instead, rheological analyses were carried out to reach an adequate compromise between volatility and an adequate evaporation rate, also considering the nanoparticles' stability in the different environments.

Once the new coating was ready to be applied, the fresco mock-ups were treated with it and with the commercial products Proconsol® and Paraloid® B72 to compare and validate the protective features of the newly formulated coating (0.6 L/m2 applied by brush). Morphological, colorimetric (ΔE), and ATR analyses, along with hydrophobicity and water vapor permeability (δp) tests have been carried out for establishing the coatings' protective features and stability, before and after application, as well as after artificial ageing.

The results show that the formulation with chitosan and AgNPs is highly promising. Paraloid® B72 treated mock-ups presented good hydrophobicity and high stability over time, but the product determined a glossy effect on the samples and a change in the surface morphology after application. Proconsol® was not effective in terms of hydrophobicity, due to the absence of hydrophobic features. The hydrophobicity of the chitosan and Ag NPs-based coating did not result superior to that of the Paraloid® B72, but the coating has a higher water vapor permeability. Moreover, it displays good morphological and colorimetric features, without glossy effects, low color variations, and stability over artificial ageing. Thus, it can be said that the new formulation with chitosan and silver nanoparticles represents a valid alternative to the existing commercial products on the market today, proving to be effective and safe.

3. Conclusions

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In this study, a new green coating for frescoes has been successfully developed and tested. The results indicate that the new product represents a valid alternative to Paraloid B72® and Proconsol®. It was obtained by combining the stability and the reducing characteristic of the chitosan biopolymer with the hydrophobic and antibiotic features of silver nanoparticles.

The newly formulated coating is highly performing since it does not excessively alter the morphology nor the color of the materials, with no gloss, color variations lower than the human eye limit of the human eye, and chemical stability over artificial ageing. Therefore, the new green coating is promising for application on real frescoes exposed outdoors.

Green coating for protection of roman frescoes exposed outdoor

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OP19

COMPOSITE BIOFILMS BASED ON BYOPOLIMER AND WAX/HNT MICROSPHERES FOR COATING ARTWORK SURFACE

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1. Introduction

The surface treatment of artwork to prevent their aging process by natural and anthropogenic effects is an open issue in materials development for Cultural Heritage. The aim of this research is to design a new green coating based on biopolymers (chitosan (CHI) and pectin (PEC)) filled with wax/halloysite microspheres, which guarantee the hydrophobization of the surface artworks. The wax/halloysite composite microparticles were obtained by their corresponding Pickering emulsions (PE), which were prepared following the protocol reported in our previous works [1,2]. The addition of appropriate amounts of the ionic biomacromolecule (chitosan or pectin) to the Pickering emulsion drives the formation of a biopolymeric coating filled with hydrophobic microvax particles.

2. Results and Discussion

Both Pickering Emulsions systems (CHI/wax/halloysite and PEC/wax/halloysite) were analyzed on digital microscope to investigate the geometrical characteristics of the wax microparticles allowing us to determine their size distributions, which were correlated to their colloidal stability. As example, the optical image of PEC/wax/halloysite Pickering emulsion is presented in Fig. 1. We observed that the presence of both biopolymers affects the size of the wax droplets and their distribution due to electrostatic and steric effects. The fabrication of the corresponding biofilms were obtained by the solvent casting method of the emulsions. The physico-chemical properties of the biofilms were investigated to prove that the nanocomposite systems represent promising coating for surface protection and a comparison between different biopolymers were conducted. Transparency and colorimetric features of the nanocomposite films were studied to verify their suitability as modified biofilm filled with wax/HNT droplets in terms of attenuation linear coefficient of films and color alteration after the treatment of surface artwork.

Water contact angle experiments were carried out to investigate the contact angle values as a function of time and to obtain information on spreading and absorption phenomena, highlighting effects of the wax/halloysite microspheres on the hydrophobic/hydrophilicity character of biofilms. These results were also confirmed by vapor permeability analysis of the biofilms filled with wax/HNT microspheres, which can act as a vapor barrier.

Mechanical properties were evaluated on pure biofilms of CHI and PEC compared to CHI/wax/halloysite and PEC/wax/halloysite composite films. Specifically, tensile tests were carried out allowing us to determine the elastic modulus, the stress at breaking point and the ultimate elongation.

3. Conclusions

The proposed coating is environmentally friendly since water is the only solvent used and all the components (biopolymers, halloysite and wax) are biocompatible and non-toxic. The addition of microwax particles in both biopolymers (chitosan and pectin) induced a significant hydrophobization of the biofilm surface, which is viewed as protective coatings of cultural heritage materials. Accordingly, this work puts forward an easy and green strategy for the protection of artwork's surfaces.

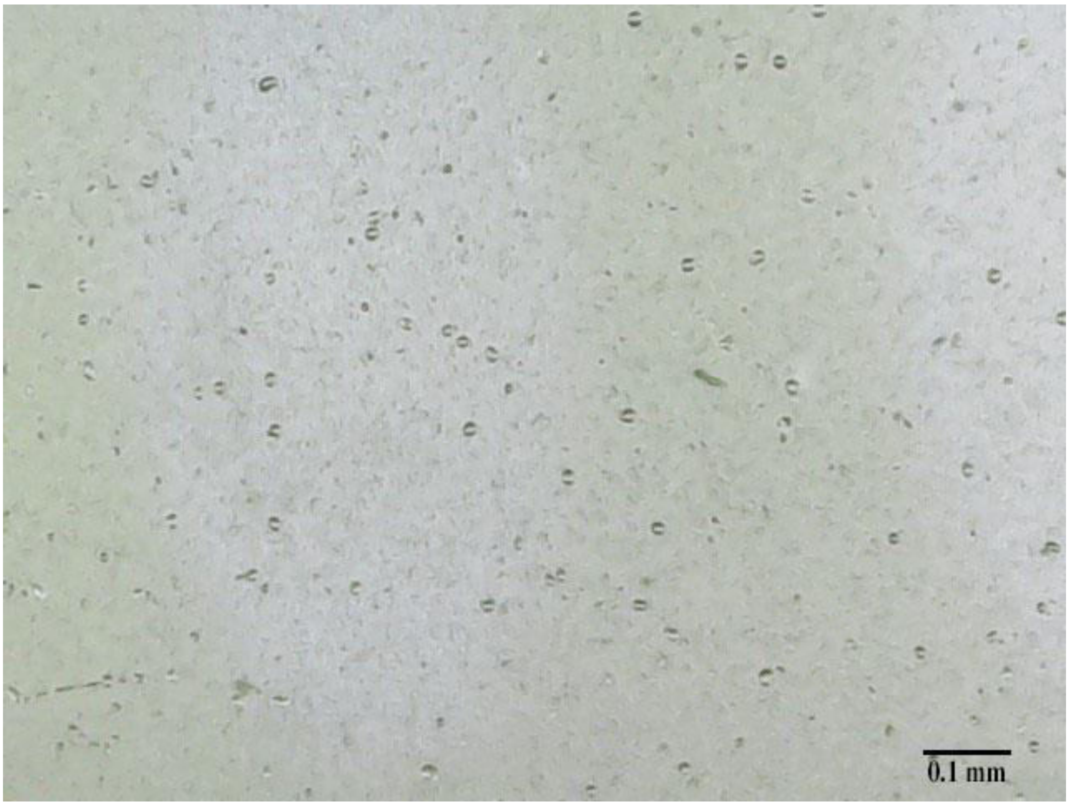

Fig. 1. Optical microscope image of wax/halloysite Pickering emulsion in the presence of pectin.

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OP20

JIN SHOFU STARCH NANO-SIZED HYDROGEL DISPERSIONS: A NEW AND ADVANCED APPROACH FOR THE CONSOLIDATION OF MODERN AND CONTEMPORARY ART

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1. Introduction

The preservation of brittle and fragile paint surfaces is undoubtedly one of the most significant issues in contemporary and modern art, both for their technical and optical properties, as well as their aesthetic values. Artists' unfettered experimentation with painting techniques and additive-rich paint formulations have led to artworks with weak powdering surfaces, exacerbated by severe climatic conditions and outdoor pollution. Furthermore, current conservation practice lacks suitable consolidation procedures, and traditional consolidants can result detrimental as optical properties and water permeability of the treated surfaces are dramatically altered [1].

Alternatively, to enhance penetration into porous paint layers, while avoiding optical modifications, we developed a novel starch-based nanostructured consolidant; the high surface area of the starch nanoparticles (SNPs) is rich with -OH groups, boosting pigment adhesion [2-3].

2. Results and Discussion

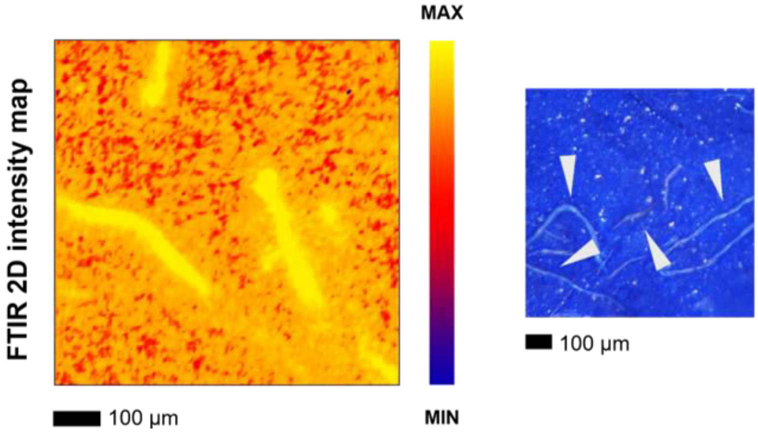
The SNPs were formulated through a bottom-up approach, where gluten-removed Jin Shofu wheat starch was gelatinized and then precipitated in a non-solvent [2-4].Wheat starch's low gelatinization temperature is most likely crucial in favoring disassembly in alkali and re-assembly in non-solvent. The synthesis conditions can be fine-tuned to produce amorphous SNPs with an adequate polydispersity and dimensions of around 50 nm. Once re-dispersed in an aqueous phase, SNPs form nano-sized gel-like fractal domains by the organization of smaller units in polymer-rich and deficient regions as observed with Cryogenic Electron Microscopy. Additionally, by means of infrared spectroscopy, X-ray diffraction, and calorimetric measurements, the amorphous nature of the SNPs was revealed. Short and mobile gluten-removed starch chains, obtained after gelatinization, assemble quickly by non-solvent precipitation, forming disordered, rather than crystalline, nano-structures.

Finally, aqueous and hydroalcoholic SNPs dispersions were satisfactorily tested as consolidant on artificially aged painted mock-ups that mimic degraded modern/contemporary painting surfaces. The efficacy of the consolidation was assessed using an in-house protocol: the SNPs disperse over the paint section and significantly boost pigment cohesiveness while maintaining the painted layer's original optical properties, despite bulk starch dispersions that merely accumulate on the paint surface generating superficial rigid and glossy films.

3. Conclusions

Overall, SNPs are an excellent example of how biopolymers and renewable sources can be used to create colloidal structures that can improve the resiliency of Cultural Heritage to degradation processes, favoring the transfer of works of art to future generations.

OP20



2D FTIR Imaging (false color) of starch distribution onto the treated paint mock-up' surface.

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OP21

PHYSICOCHEMICAL PROPERTIES AND SORPTION CAPACITIES OF SLUDGE-BASED BIOCHARS TOWARDS THE REMOVAL OF ORGANIC MICROPOLLUTANTS IN WASTEWATER

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1. Introduction

Biological sludge is a widely available waste material of high environmental concern, the disposal of which involves a high cost, whereas its reuse is in line with the modern approach to the waste management and the circular economy, thereby ensuring great savings. It should also be noted that thermal conversion of biological sludge for biochar production allows inhibiting the intrinsic toxicity related to the presence in this matrix of poorly biodegradable organic micropollutants (OMPs) and potentially pathogenic organisms. It is therefore evident that the conversion of biological sludge into biochar as a sorbent for wastewater treatment seems to be a ‘‘win–win’’ solution for both improving sludge management and protecting the environment. Based on the above-mentioned considerations, the objective of this research was the production of biochars from mixtures of biological sludge and waste woody biomass, their in-depth product characterization, the assessment of their environmental compatibility towards European Standards, and the evaluation of their applicability for the removal of selected OMPs and dyes.

2. Results and Discussion

The biochars were produced following the “design of experiment” approach, using a “reduced combinatorial design” that allowed to balance the number of experiments with the efforts required for the analysis of the multiple parameters necessary for achieving their in-depth characterization. The matrix of the experiments, which includes the production of nine biochars (plus three replicates) under different conditions of contact time, pyrolysis temperature, type of feedstock (two kinds of woody waste biomass and two kinds of sludge), and sludge percentage is shown in Table 1.

Table 1 – Matrix of the production experiments of biochars. The same superscript letter refer to different productions under the same experimental conditions. Woody waste was mainly oak (A) or poplar (B); n.a. = not available.

Biochar	**Woody waste**	**Sludge**	**Temperature (°C)**	**Contact time (min)**	**Sludge percentage**
B1	A	n.a.	450	120	0
B2	A	n.a.	650	60	0
B3(a)	B	n.a.	850	120	0
B4	B	Calice	450	60	15
B5	A	Vernio	650	120	15
B6	B	Vernio	850	60	15
B7	A	Vernio	450	60	30
B8(b)	B	Calice	650	120	30
B9(c)	A	Calice	850	60	30
B10(a)	B	n.a.	850	120	0
B11(c)	A	Calice	850	60	30
B12(b)	B	Calice	650	120	30

Moreover, this design allows to treat multilevel (i.e. pyrolysis temperature, contact time, sludge percentage) and qualitative (feedstock and sludge type) factors equally. Biochars were characterized for ash content, water leachable polycyclic aromatic hydrocarbons (PAHs) and trace metals, elemental composition, specific surface area (SSA) and porosity distribution, pH of the point of zero charge, and presence of crystalline phases, as elsewhere described1,2. None of the biochars produced met the European standards 12915-1 for materials suitable for water treatment3, most of them being characterized by ash percentage higher than 15% and/or release of some metals or PAHs higher than the corresponding limit. The materials most promising from the SSA viewpoint (i.e. B5, B6, B8, B10, and B11) were therefore subjected to a chemical activation using a by-product of the gasification of woody biomass, followed by washing with tap water, and final thermal activation. All the treated materials met the requisites requested by the EN 12915-1, and their SSA values were not negatively affected by the treatments, with the only exception of B10, the SSA of which dropped from about 700 to about 400 m^2/g. The material deriving from the highest percentage of sludge and providing the highest SSA (i.e. B11, with 30% of sludge, SSA=400 m^2/g) was tested for the removal of methylene blue and selected pharmaceutical compounds, in comparison with a commercial activated carbon, obtaining similar sorption efficiencies.

3. Conclusions

This research has shown, albeit on a laboratory scale, the possibility of producing carbonaceous materials from a feedstock containing high percentages of biological sludge (up to 30%) characterized by performances comparable to those of commercial activated carbon in terms of adsorption of organic compounds. In this way, it is possible to state that it has been set up a process for the recycling of biological sludge, capable of reaching the “end-of-waste” condition for this waste.

Graphical abstract.

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OP22

WASTE-DERIVED ZEOLITES AS ADSORBENT MATERIALS FOR HEAVY METALS REMOVAL FROM POLLUTED WATERS

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1. Introduction

Preserving water resources and water quality is one of the European Sustainable Development Goals, included in the 2030 Agenda. Over the last years, several technologies for water remediation have been proposed or studied. In particular, precipitation, membrane filtration, ultra-filtration, and electrochemical processes have been applied for heavy metals removal. However, some are expensive, not environmentally friendly, and do not match circular economy principles. On the contrary, the adsorption process has many pros: low cost, low energy, high efficiency, reusability, and easy integration in wastewater treatment plants (WWTPs). In addition, when adsorbent materials are secondary raw materials (RSM), the process well fits the circular economy principles.

Among various contaminants, heavy metals pose a serious threat. Risks due to heavy metal contamination are well known and involve bioaccumulation and biomagnification in living organisms and their non-biodegradability.

2. Results and Discussion

The present project investigates the removal efficiency of four waste-derived zeolites towards Pb^{2+}, Zn^{2+}, Ni^{2+}, and Cr^{3+}. Firstly, adsorption equilibrium and kinetic experiments were carried out for each adsorbent material with each metal. Finally, zeolite materials were tested for remediation of tap water and WWTP effluent spiked with Pb^{2+}, Zn^{2+}, Ni^{2+}, and Cr^{3+}.

The synthetic zeolites obtained through a low-temperature and sustainable hydrothermal process were described below: BA_Hy60 was synthesized starting from natural bauxite, PSA_Hy60 was prepared from pure sources of silicon, and aluminum combined with red mud, OS_Hy60 was made from rhyolitic obsidian, and OSRM_Hy60 was synthesized from rhyolitic obsidian and red mud. Red mud is a waste material obtained from the caustic leaching process to extract aluminum from bauxite, and it contains a high amount of iron oxy-hydroxides. Therefore, red mud also can provide ferromagnetic-like behavior to zeolites.

The synthesized materials were characterized by X-ray diffraction indicating the presence of more crystalline phases in PSA_Hy60 (sodalite and zeolite A) and OSRM_Hy60 (sodalite and zeolite X). BA_Hy60 and OS_Hy60 showed zeolite A and zeolite X, respectively.

Before the adsorption studies, preliminary tests were performed to evaluate the working pH and the experimental conditions to assure metal solubilization and adsorption. Subsequently, adsorption equilibrium experiments with different metal concentrations were conducted at room temperature to determine the maximum adsorption capacity of each sorbent material apiece for studied heavy metals. Langmuir and Freundlich isotherm models fitted the experimental data. Quantitative lead removal, in the concentration range of 6.4-64.2 mg L^{-1}, was reached by all tested materials. The Langmuir model best fitted the experimental data for zinc, nickel, and chromium, reaching maximum adsorption capacities values up to 30 mg g^{-1}. OSRM_Hy60 was the most efficient in heavy metals removal; on the contrary, BA_Hy60 gave the worst results.

Kinetic studies were carried out to assess the metals uptake rate on the zeolites. The experiments were done within 60 minutes for Pb, shaking suspensions by magnetic stirring. Zinc, nickel, and chromium adsorption was slower and required 24 hours of roller shaking. Experimental data were fitted both with pseudo-first-order and pseudo-second-order kinetic models. For all the considered metals, materials characterized by zeolite X (OS_Hy60 and OSRM_Hy60) showed faster adsorption, while samples with zeolite A (BA_Hy60 and PSA_Hy60) the slower.

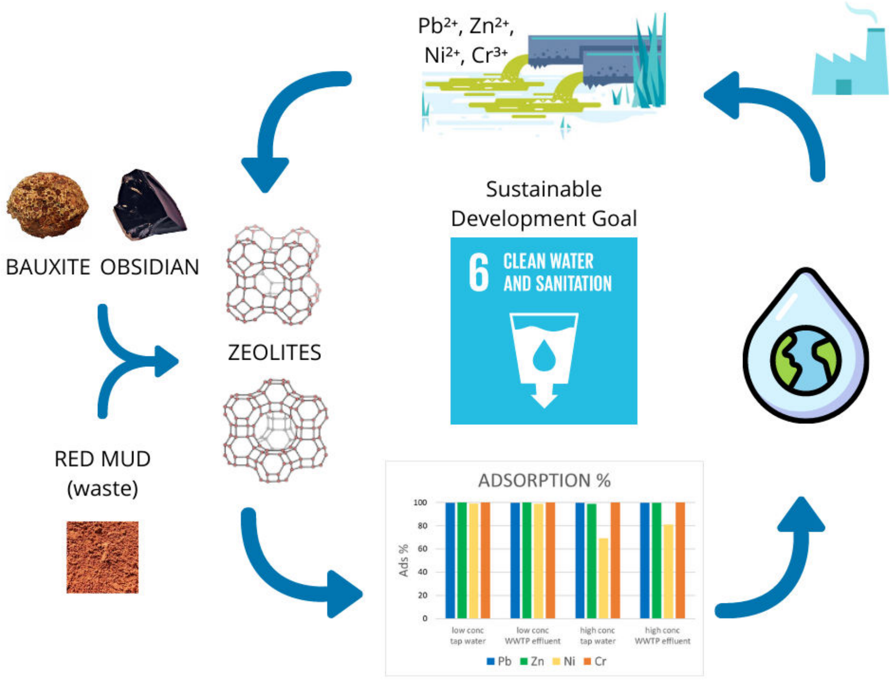
Finally, the adsorption experiments were carried out in tap water and WWTP effluent. Water samples (not containing the analytes) were spiked with metal ions concentrations close to river water levels and industrial wastewaters. Lead and chromium were quantitatively removed in tap water and WWTP effluent. OSRM_Hy60 was the most effective also in actual simulated conditions and with all four metals.

3. Conclusions

All the synthesized zeolites showed a good but quite different affinity towards the investigated pollutants. Adsorption experiments indicated monolayer adsorption for Zn^{2+}, Ni^{2+}, and Cr^{3+} and slow kinetic for all materials. On the contrary, Pb^{2+} removal occurred within 60 min.

The mechanisms controlling the heavy metal removal from polluted water can be attributable to both precipitation on the surface and immobilization inside the cavities of the newly formed zeolites, as demonstrated by X-ray diffraction and thermal analysis data.

The use of waste materials for water remediation provides a double step forward in the circular economy: saving a precious resource like water and exploiting waste for sorbent material synthesis.



Circular approach for polluted waters remediation by using waste-derived zeolites.

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OP23

CONVERSION OF SINGLE USE PLASTICS TO MULTI-USE ITEMS TO REDUCE THE ACCUMULATION OF WASTE IN THE NATURAL ENVIRONMENT

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1. Introduction

Plastics are the most common packaging materials for foods, pharmaceuticals, detergents etc due to the numerous advantages like safety, lightweight, easy of processing, storage and low cost [1]. However, there are several concerns about usage and disposal that include accumulation of waste in landfills and in natural habitats, physical problems for wildlife due to ingestion or entanglement (micro and macroplastics [2]), the migration of low molecular mass materials, such as residual monomers, oligomers or additives [3]. In order to reduce the drawbacks of plastic materials, the UE is promoting sustainable alternatives and approved the Directive on single-use plastics in 2019. From a waste management perspective, the three R's reduce, reuse and recycle can be advocated to reduce the amount of plastic generated. In this contribution, we consider the possibility to reuse at least 20 times polystyrene plates (PS) and evaluate the suitability of this product for microwave and dishwasher. The effects of the plastic reduction on the environment can be assessed through life cycle assessment (LCA) studies [4-5].

2. Results and Discussion

The polystyrene plates used have a three-layer structure with the middle layer containing a low amount of an inorganic filler. After the use with a microwave oven and dishwasher (schematic representation in Figure 1), polystyrene plates were characterized with analytical techniques like gas chromatography (GC-FID), mechanical dynamometer Instron and FTIR-ATR (Fourier transform infrared spectroscopy - Attenuated total reflection). Gas chromatography was employed to evaluate the concentration of styrene monomer in plates before and after the use. The analysis demonstrated that the concentration of the monomer doesn't change before and after 20 uses of microwave and 20 uses of dishwasher, therefore the polymer doesn't modify its chemical structure and molecular weight during the use. Moreover, the global migration was verified using acetic acid (3% w/v) as simulant, the overall migration was below the law limit. The properties of the plates were monitored through a digital camera to evaluate the presence of cuts, spots or other deformations. Microwave heating and washing were also performed separately to assess the optimal conditions of use. The plates can be washed 20 times with cycles of 55°C of 1 hour and 30 minutes, the microwave can be used in the range of powers 300-600 W. The stress-strain curves obtained with the mechanical dynamometer Instron showed that the mechanical properties of the washed dishes are more similar to the original plate compared to the microwave treatment. The FTIR-ATR analysis of the plates showed that the deformations obtained after higher powers of microwave (750 W) didn't lead to a shift of the inorganic filler from the middle to the upper layer.

3. Conclusions

In this study, polystyrene plates were characterized to establish their reusability after heating and washing. If plates possess a proper weight and thickness, they don't show dramatic changes in properties and can be reused at least 20 times decreasing the amount of raw material necessary for their production, the amount of CO_2 emitted and the amount of waste. Indicators such as non-renewable energy resources, greenhouse effect, solid waste production and water consumption should be used to compare single use items of polystyrene and reusable products of the same material.

OP23

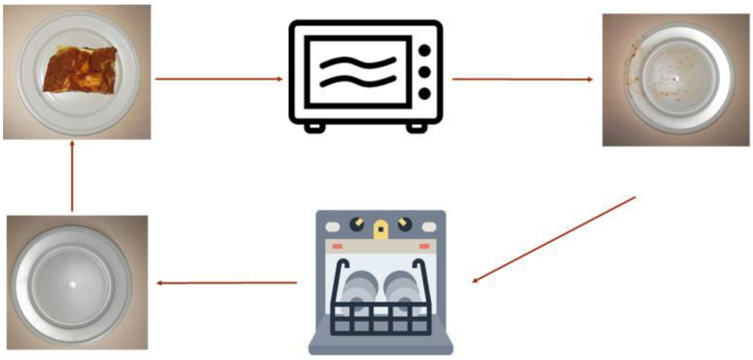

Figure 1. Schematic representation of the reuse of polystyrene plates reported in the present study.

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OP24

THE PRODUCTION OF METHANE AS AN ALTERNATIVE TO WHAT ARRIVES WITH GAS PIPELINES

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1. Introduction

This note will treat the production of methane in Italy as an alternative to that one that arrives with the gas pipelines with the following three technologies: by regassification of liquified methane that arrives by ship; by anaerobic digestion of biomass to produce a biogas and its purification to biomethane; by gasification of biomass to biogas and its subsequent hydrogenation to biomethane. Liquified natural gas (LNG) can arrive in large quantities by ship and then is unloaded in coastal locations on the sea, where regasification plants are installed, and then sent to the local gas pipelines[1,2]. Biomethane is produced by purification of biogas obtained from various types of agro-industrial, livestock and urban organic wastes by anaerobic digestion with coproduction of the digestate useful for agriculture and of CO_2 that is disposed of in atmosphere or used [3,4]. Biomethane can be produced also from wood wastes by gasification with small amount of oxygen and water to biogas and its subsequent hydrogenation [5], with the alternative of producing hydrogen by electrolysis of water and adding it to the biogas hydrogenation reactor in order to increase the biomethane yield [6].

2. Results and Discussion

LNG is essentially made of methane (>90%), with impurities of light paraffins (ethane, propane), and is present in the liquid phase at a temperature of -162^{o}C and 2bar.LNG can be used without further transformations as a fuel for marine navigation and for long distance heavy road transport (>1000km) or introduced after regasification in the national gas pipelines. LNG can arrive from countries thar are not connected with us by pipelines and therefore it is possible to have with a greater security of supply. Before liquefaction, LNG must undergo appropriate purification treatments and the high energy density makes it particularly suitable for long journeys, but the problem is that it is necessary to have ports where LNG can reach and can be unloaded and heated, returning it to its gaseous state. The Italian plants of regasification are on the coast of La Spezia, on a ship off the coast of Livorno and one an artificial island off the coast of Adria (Rovigo).

Biomethane is obtained through a pre-treatment of the biomass which consists of its shredding, homogenization and screening to remove the impurities and after is introduced in water and the obtained organic suspension is sent to the anaerobic digestion plant to obtain the biogas and the digestate. Biogas is currently mostly used to produce electrical and thermal energy and in a few plants it is also purified to obtain biomethane; the digestate in almost all plants is separated in a solid and in a liquid fraction to produce a solid soil conditioner for agricultural uses and a liquid fertilizer. The biogas is then send to the upgrading section, to eliminate CO_2 and other impurities in order to reach a methane concentration of 98-99,5% , and the biogas upgrading sector consists of the following phases: dehydration desulphurization, CO_2 elimination and removal other unwanted components to obtain the pure biomethane. The CO_2 separated from methane is in some cases recovered and purified to be used for industrial and food purposes, but the majority is now released into the atmosphere. A plant of production of biomethane has been realized at Bottrighe (Ro) by using as raw material the by -products of the production of biobutandiol obtained from biomass.

In Italy there are several pyrogasification plants using wood wastes and this technology is realized by treatment at temperature between 800-1200^{o}C, first in the absence of oxygen (pyrolysis) and the subsequently in lack of oxygen (gasification) of dried and ground wastes of wood biomass, to obtain a gas which is then sent to an internal combustion engine that produces electricity and heat. The biogas can be used after a very complex subsequent purification (elimination of aromatics, sulphur and chlorine compounds water and CO_2 because many of these impurities can deactivate the catalyst, based on nichel supported on Al_2O_3, used for the hydrogenation of the biogas to biomethane. In 2022 biomethane production takes pace in Europe only in pilot and demonstrative plants. At Casaccia (Roma) Enea built a experimental plant in 2017 for the production of biomethane by gasification of woody biomass, also creating an hydrogen production plant realized by electrolysis of water, using renewable energy and the hydrogen has been added to the reactor of hydrogenation of biogas to increase the amount of biomethane produced.

3. Conclusions

In order to import more LNG it is necessary to realize more regasification plants especially on a ship that can be more accepted by the local authorities. On 1 March 2022 the Prime Minister Mario Draghi in a speech to the Senate argued that “We must think about an increase in regasification capacity”. The Prime Minister Mario Draghi also recently declared that we must invest in the development of biomethane production with the objectives of the PNRR, as we have in Italy a lot of plants of biogas production and some of them can modified to produce biomethane. The production of biomethane by gasification of biomass has not been realized till now for the complexity of the plant, but the increase of the prize of methane will create surely in the future some plants.

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OP25

TUNING THE STRUCTURAL PROPERTIES OF PHEMA/PAA FOR APPLICATIONS IN CULTURAL HERITAGE CONSERVATION

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1. Introduction

The inclusion of polyacrylic acid (PAA) in poly(2-hydroxyethyl methacrylate) (pHEMA) hydrogels represents a significant improvement in the formulation restoration practice of bronze artworks.

pHEMA/PAA networks are capable of coordinating copper ions with carboxylate groups in alkaline conditions, boosting the removal of copper corrosion products, as confirmed by Cu(II) ion adsorption kinetics at different pH values [1].

The PAA moieties make the gel pH-responsive, as electrostatic repulsion between carboxylates increase the gel porosity at the nano- and micron-scale. In addition to providing ion-coordination sites, PAA also acts as a macro initiator in HEMA polymerisation, affecting chain reticulation and related physico-chemical properties [2].

2. Results and Discussion

We firstly focused our attention on the PAA features via Size Exclusion Chromatography (SEC, absolute molar mass determination) and Nuclear Magnetic Resonance (NMR). Content and molecular weight of PAA in the composite networks was tuned aiming to control and optimise the mechanical behavior, microstructure and porosity of the gels, as confirmed by rheological and mechanical measurements.

Structural differences of the pHEMA/PAA networks were investigated by Small Angle X-ray Scattering (SAXS) and Scanning Electron Microscopy (SEM) measurements. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were employed to evaluate the properties of the water entrapped in the polymeric network. The results obtained by thermal analysis were complemented by evaluating the diffusion coefficients in the systems by Fluorescence Recovery After Photobleaching (FRAP) measurements.

3. Conclusions

Overall, this approach allows the selection of the best formulations to be used on degraded bronze surfaces for the selective removal of corrosion patina, adding new tools to the metal restoration practice.

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OP26

INNOVATIVE NANOMATERIALS FOR BONE REMAINS CONSOLIDATION: PERFORMANCE EVALUATION AND IMPACT ON ^{14}C DATING AND ON PALAEOGENETIC ANALYSIS

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1. Introduction

Bone remains from historical and archaeological contexts represent peculiar and precious finds and offer an enormous source of information [1,2]. Skeletal remains are typically discovered in critical conservation conditions [3] and, in view of future studies, analyses and exhibitions, a consolidation treatment may be required. Since the twentieth century, the products typically used for this purpose are polymers [4], despite their low physical-chemical compatibility with the bone matrix and their poor chemical stability. In this study, an innovative, easy-applicable and compatible protocol for the consolidation of bone remains based on the use of nanometric HydroxyAPatite (HAP) was set up and tested through a multidisciplinary approach. A new protocol for the synthesis of HAP nanoparticles was developed and the consolidation performance of this new treatment was evaluated by applying it to degraded ancient bone findings. The new consolidation method was also tested to assess possible effects on two typical molecular analyses performed on ancient bones, named palaeogenetic analysis and radiocarbon dating.

2. Results and Discussion

The nanoparticles of HAP were synthesized by chemical precipitation from two aqueous solutions of calcium nitrate [($Ca(NO_3)_2{\cdot}4H_2O$)] and diammonium hydrogen phosphate [$(NH_4)_2HPO_4$, DAP] in an ultrasonic bath, maintaining the reaction environment at pH 9 and 25 °C [5]. Through Fourier Transform Infrared Spectroscopy and X-Ray Diffraction, we were able to confirm the formation of HAP. The size, shape and morphology of the synthesized particles were studied by Scanning Electron Microscopy (SEM): HAP particles appeared as pseudo-spherical crystals with dimensions centered at 65-75 nm and ranging in the order of few tens of nanometres. The HAP nanoparticles were applied as dispersion in 2-propanol. The stability of this system up to 2500 s was verified through turbidimetry measurements.

The proposed consolidation protocol is based on the consequential application by brush of the three following systems:

- a 1 g/L dispersion of HAP nanoparticles in 2-propanol;
- a 0.05 g/L dispersion of $Ca(OH)_2$ nanoparticles in 2-propanol [6];
- a 1M deionized water solution of DAP [7].

The consolidation performance of this new treatment was evaluated in terms of physico-chemical and mechanical properties and the possible effects on the palaeogenetic and radiocarbon analyses were also investigated. The aforementioned systems were applied to two sets of ancient long bones from the Longobard necropolis of Muŝov (Czech Republic) and from the medieval site of Porticus Octaviae (Rome, Italy).

SEM data indicated an increase in the homogeneity of the structure of the bone induced by the consolidation treatment. These data were confirmed by microtomography (Figure 1), which showed an increase in the density and a decrease in the total porosity (from 3.84% to 2.25%) and in the open porosity (from 3.48 to 1.31%) of the treated bones, not only on the surface of the samples but also in the bulk of the porous network of the bone, indicating a deep penetration of the treatment. In addition, an increase in the average value of the Vickers micro-hardness of about 64% was reported in the consolidated sample.

To investigate the impact of the consolidation protocol on the yield of human aDNA, the results of the palaeogenetic analysis from treated and untreated fragments were compared. Despite the high variability within the samples, the overall result may suggest that consolidation protocol does not significantly affect the quality of the genetic data in adequately well-preserved samples, where the same consensus sequences and, consequently, the same haplogroup, were obtained from both treated and untreated fragments. On the contrary, the consolidation treatment seems to potentially affect the yield of the palaeogenetic analysis when applied to specimens with particularly scarce DNA preservation. Additional bones with different conservation conditions need to be tested to confirm this hypothesis.

For what concerns the radiocarbon analysis, for each of the bones, the radiocarbon concentrations measured in the untreated and in the HAP treated fractions were compared. These data showed that no contamination due to the HAP treatment was detected.

3. Conclusions

In this study, we set up an innovative and easily applicable protocol for the consolidation of ancient bones based on the use of inorganic nanostructured materials with high physico-chemical compatibility with the bone matrix. From the physico-chemical and mechanical standpoint, several analytic tests proved the effectiveness of the proposed consolidation protocol, which was able to increase homogeneity and compactness and decrease the total porosity of treated samples. One of the key features of this work is the evaluation of the impact of the proposed protocol on the results of two analyses typically performed on ancient bone remains, namely palaeogenetic analysis and radiocarbon dating. In both cases, we obtained appreciable and promising results.

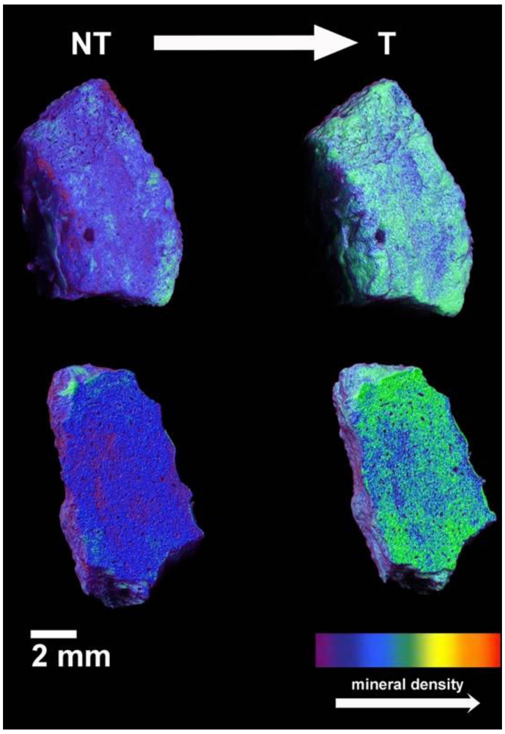

Figure 1. 3D reconstructions of a bone fragment before and after the consolidation treatment.

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OP27

ELECTROSPUN TISSUES COUPLED WITH GREEN SOLVENTS FOR THE SELECTIVE REMOVAL OF THIN COATINGS FROM PAINTINGS SURFACES

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1. Introduction

In recent decades, research efforts have been devoted to the development of new cleaning systems that allow the selective removal of coatings from painting surfaces and a controlled release of solvent to avoid interactions with the pictorial layers. To this aim, gels have been proposed as alternative retentive media to the traditional cleaning methods, such as cotton swabs, which display a lower control over solvent release.

To improve the cleaning performances and reduce gel residues on the painting surface, we have recently proposed new sandwich-like composites based on the combination of PHB-based green organogel and electrospun polymers.

Electrospinning (ES) is a technique that allows to obtain ultrathin fibers using an electrodynamic process. ES nanofibers are extensively studied for several applications, including sorbent materials.

In this work, we propose an ES-based cleaning system for the selective removal of varnishes from paintings, where the tissue acts at the same time as a retentive medium for the solvent and as an adsorbent toward the varnish. All the materials (tissues and mock-up) have been extensively characterized to assess cleaning performances and functioning.

2. Results and Discussion

Three solutions of Nylon 6,6 in hexafluoroisopropanol have been electrospun to obtain fibers with different diameters and pore sizes, which have been assessed by SEM image analysis and air permeability analysis. Precisely, the tissue obtained with the lowest concentration (10%) displays an average fiber diameter of 448 nm and pore size of 0,43 μm, while the one with the intermediate concentration (20%) has an average fiber diameter of 503 nm and pore size of 2,2 μm and last the one with the higher concentration (27%) has an average fiber diameter of 1,093 μm and pore size 5,06 μm.

The amount of polymer electrospun has been varied to obtain tissues whose thickness ranges between 200-600 μm.

The solvent selected is dimethyl carbonate (DMC) as it is volatile and green. It was adsorbed onto 0.7 x 0.7 cm sized tissues, and the volume was selected based on specific volume-to-mat weight ratios.

The cleaning tests have been performed on a mock-up with a red ochre-glue paint layer and a dammar varnish layer (average thickness of 50 μm), that have been characterized by μFTIR in ATR mode.

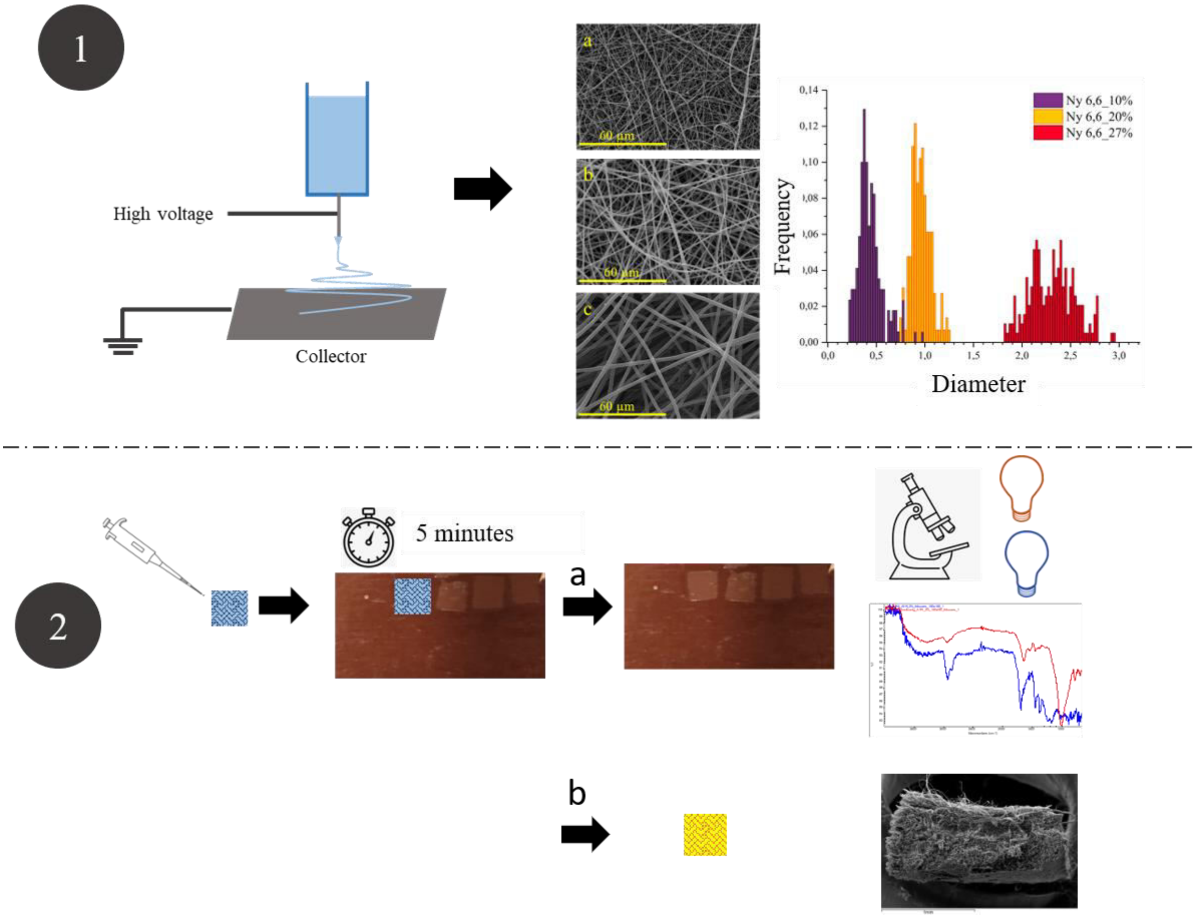
The systems have been applied on the mock-up for 5 minutes, then the treated surface has been documented with the optical microscope (visible and UV light) and analyzed with μATR-FTIR.

It has been observed that the tissues with small and intermediate fiber diameter had a positive outcome (no varnish residues) in all the tests, while the large diameter one had opposite results. In all three cases, after the application no damages to the paint layer have been observed neither, as expected, residues of DMC were detected.

Based on the results achieved, it has been possible to hypothesize that the ES pore size has a crucial role in the cleaning action Therefore, the cleaning mechanism and the differences in terms of cleaning performances among the ES tested may be tentatively attributed to the capillary absorption. Further evidence supporting this hypothesis was found thanks to SEM analysis made on the cross-sections of the tissues post-application. In fact, it was possible to observe that the varnish inside the mat is distributed in decreasing quantities starting from the side in contact. This suggests that the fibers do not act as gripping sites for the swelled varnish, but that the tissue behaves as an adsorbent medium.

3. Conclusions

This study proposes a system to remove thin layers from sensitive surfaces such as paintings without posing a risk to their integrity. The system is based on Nylon 6,6 ES tissues on which a highly volatile green solvent is absorbed. Several tests and thorough characterization of the materials have allowed us to assess the cleaning efficiency and the mechanism involved in the removal of the varnish: capillarity. The best performances are achieved when tissues with pore sizes in the range of 0,4 µm -2,2 µm are employed.
This research represents a first step towards sustainable approaches for sustainable cleaning. Nylon 6,6 can be replaced with more sustainable polymers and different solvents can be absorbed into the tissues adapting the method to different scenarios.



Workflow of the tissue production (1) and of the cleaning process (2): methods and characterization

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OP28

NANOSTRUCTURED EMULSIONS AS CLEANING MATERIALS FOR REMOVING POLYMER COATINGS

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1. Introduction

Cleaning is an essential operation which has to be handled by the conservators before applying new materials to any substrates [1]. The study have been focused on using nanostructured emulsions (NSE) as smart cleaning materials for removing polymer coatings (acrylic polymers). For this purpose, three different substrates (Lecce stone: LS, glass, and Arenaria stone: AS) were treated with Paraloid B-72, then cleaning was performed by using 3 nanostructured emulsions (NSE1, NSE2, and NSE3) which were prepared by using EcoSurf (surfactant) and different organic solvents. The decay induced by artificial ageing of the polymer coating was also studied in deep because it directly affects the outcome of the cleaning process. After that, stone substrates coated with both unaged and aged polymer were cleaned by applying the considered nanostructured emulsions in three different way (direct contact, cellulose pulp method, and gel method) in order to assess the cleaning perfomance on the emulsions as well as of the procedures.

2. Results and Discussion

Polymer ageing processes were examined by chromatic variations, contact angle measurements, optical microscope, FTIR, and SEM-EDS analyses. Colorimetric measurements showed that oven ageing affects the color of polymer, which increased with time without depending on the substrate: after 35 days ageing ΔE^* values increased up to 6.1 and 6.2 for coated LS and AS, respectively. Moreover, the changes (darkening of the surface due to the polymeric material degradation) induced by ageing can be noted even by naked eye. Contact angle measurements showed a slight reduction of hydrophobic properties following oven ageing. The salt crystallization test induced a drastical damage of the polymer layer on both the stone substrates. SEM-EDS and Optical microscope (OM) analyses indicated that ageing induced a change in the texture of polymer films (in all the substrate) which showed some "melted" areas. This behavior increased with exposition time and can be easily noted even by naked eye on 25- and 35-days aged samples. After investigating thoroughly the ageing process of polymer coating, preliminary cleaning operations with organic solvents were done by direct immersion method: glass samples as well as stone samples were examined both before and after ageing in order to understand any possible behavior change due to ageing. The results showed that some solvents (ethyl acetate, 2-butanone, and butyl acetate) easily remove the polymer film, while ethanol and water are not able to remove the polymer. 2-butanol (BuOH) showed middle properties. In order to understand the cleaning properties of the three emulsions, all the considered samples were directly exposed to them. The results showed that NSE1 does not provide a satisfactory removal of paraloid B-72 (partial removal), while NSE2 and NSE3 completely removed the polymer film. However, direct contact with organic solvent, although it is emulsified in water is not recommended for the heritage building materials and can be hardly applicable in real cases. As recommened by the literature, there are two main methods used in this field: cellulose pulp method, and hydrogel cleaning method [2]. In this study, a comparative work using both methods has been done in order to understand the best one for all the considered substrates. The samples were examined by OM, FTIR (ATR mode), SEM-EDS, and iodine vapour test. Considering all the preliminary analyses, NSE2/cellulose mixture was applied on the considered samples and results revealed that the cleaning process have to be repeated two times in order to remove completely the polymer from the substrates as can be seen in the Figure 1. Hydrogel was prepared according to the literature method [3]. After preparing thin hydrogel films (1 cm thickness), they were applying on the coated substrates after inglobing inside the emulsions. According to the preliminary analyses, the hydrogel cleaning method seemed to be better than cellulose pulp method.

3. Conclusions

All the preliminary analyses suggested that the direct cleaning performed by nano-emulsions NSE2 and NSE3 was able to completely remove acrylic polymer from stone substrates, despite this method is not recommened for artifacts and can be hardly applicable in real cases. On the other hand, the cellulose pulp method was succefully applicable for this purpose. Moreover, preliminary results obtained by hydrogel cleaning method suggested that it is the most promising procedure for polymer coating removal.

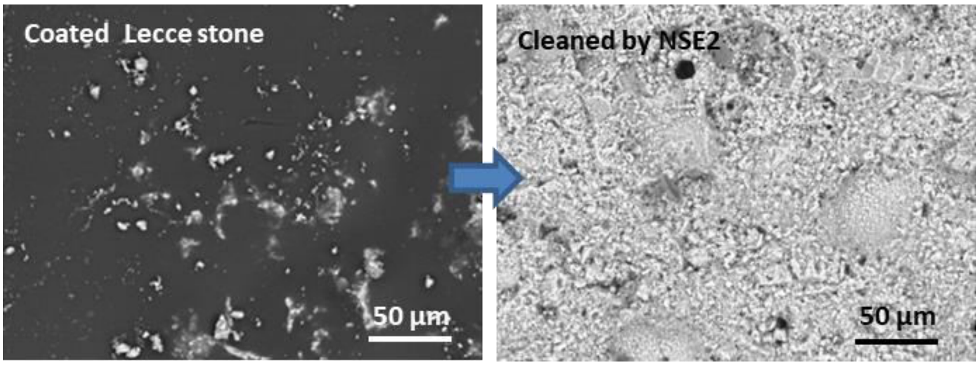

Figure 1. SEM images of coated LS before and after cleaning by NSE2/Cellulose pulp method

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OP29

METHODOLOGICAL APPROACHES AND FIELD EXPERIENCES FOR THE MOLECULAR CHARACTERIZATION OF AIRBORNE MICROORGANISMS IN CRITICAL ENVIRONMENTS

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1. Introduction

COVID19 pandemic has highlighted the relevance of characterization studies on pathogens in ambient aerosol/particulate matter [1] to a wide public. Beside the COVID 19 pandemic, Antimicrobial Resistance is an issue of enormous health impact that requires bioaerosol research [2] and methodological optimization [3] also in the frame of One Health paradigm and initiatives [4]. Both microorganism targeted analysis [5] and extended characterization of viruses, bacteria, fungi present in bioaerosol can be faced by molecular/genetic approaches, even if the latter approach is not trivial [6].

2. Results and Discussion

After having tested sampling using Condensation Growth Tubes CGT for targeted RT-PCR and infectivity assessment and parallel detection of bioaerosols by biosensors based on CANARY (Cellular Analysis and Notification of Antigen Risks and Yields) technology, in both Geriatric and Infective Diseases wards, Emergency Rooms were sampled, seeking COVID-19 infected emitters in early abundant viral shedding phase. Traces of SARS CoV 2 RNA were sampled and detected by RT-PCR at 39 amplification cycles, without reaching levels activating CANARY detection on field.

In order to check presence of airborne pathogens in a community Waste Water Treatment Plant monitoring has been proposed [7] and develop a method for continuous sampling of such contaminants, an intercomparison of sampling devices able to preserve infectivity has been started at the aeration section of raw influents in the main WWTP of Trieste, considering CGT Aerosol Devices BioSpot ViVAS sampling condensates on small petri dish @8lpm, impingement in SKC Biosampler sampling on 20ml of modified MEM@12,5lpm, and filtration by Sartorius MD8 Airport on gelatine filters @50lpm. Samples are processed for barcode molecular RT-PCR characterization, and sampling methods are compared on the basis of detected microorganisms diversity and abundance.

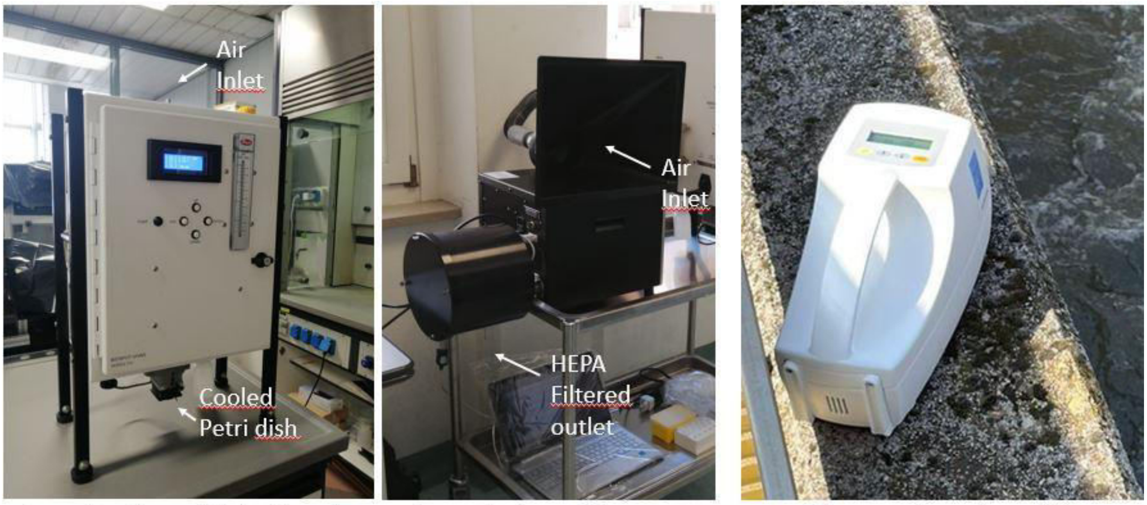
Capability of CGT of collecting nanometric bioaerosol droplets directly in concentrated liquid, requiring moderate pretreatment before analysis, has a trade off with sampling length, weight and cost of instrumentation, if gelatine filter sampling by portable pumps is considered in comparison. Glass impingers have the drawback of fragility and poor compactness if we consider the need of a separate pump. Portability and robustness are also issues in recently started public transport monitoring.

Depending on application, droplet sizes of interest can limit to > 300 nm if focus is on bacteria or fungal spores, or requires collection of smaller particles, if focus is posed on smaller viruses; air volumes to be considered can be relatively small in case of sampling intense sources as wastewater tanks, or larger (several cubic meters) in case of ambient air monitoring. Experimental intercomparison of bioaerosol samplers for bacteria and virus, working in parallel, does not results to be available in literature at the moment; samples one cubic meter of ambient air sampled by different technologies

Moreover, samples have to be stored and analyzed, and eventually pretreated before analysis; the considered technologies collect bioaerosol on liquids or soluble filters, simplifying aliquotation and limiting relevance of partitioning of biomolecular analytes on sampling supports; liquid samples are adequate for use in residual infectivity assays by Cytopathic effect assay on permissive cell cultures, as Vero E6.

3. Conclusions

For indoor air, evidences of low number of viral copies from healthcare settings, suggest to carefully control the air exchanges in rooms -by CO2 monitoring- that can dilute bioaerosol particles; more, they point at the need of accurately position sampling devices even in indoor environments; adequate CFD simulations can provide criteria for such relevant task, as for instance by the Advanced Simulator for Airborne Pathogen Propagation [8]. Pathogenic bioaerosol sampling instruments still require definition of desirable features in terms of flows, sampling support, required sampling efficiency for different bioaerosol size fraction, especially for standardization of airborne pathogen research. High volume portable samplers have been prototyped, based on wet cyclone technology.



Condensation Growth Tube Sampler
Aerosol Devices BioSpot ViVAS

Airborne biohazard detector
(CANARY Technology)
Smiths Detection BioFlash

Portable pump for gelatine filters
at wastewater aeration tank
Sartorius MD8 AirPort

Bioaerosol samplers (ViVas, AirPort) and detector (BioFlash)

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OP30

NEW HYBRID POLYAMIDO-AMINES AND -AMINOACID WITH SOL-GEL PROCESSABLE SILOXANE MOIETIES AND THEIR USE IN TOXIC METAL SEQUESTRATION

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1. Introduction

In the last decades, toxic metals contamination in water systems has become a global environmental problem due to the harmful effects towards living organisms. The main toxic metals found in aqueous systems are Cu, Cd, Hg, Pb, Ni and Zn (divalent ions) and Cr, As and Se (multivalent ions).

To remove toxic metal ions from water systems, several processes have been proposed. Among these, the adsorption is one the most efficient techniques thanks to the easy tuning for different targets, versatility in design, low cost and recyclability. Many efforts have been made to develop highly selective non-toxic and biocompatible adsorbent materials.

Chelating agents containing amines and carboxylate groups, such as the linear biocompatible polymers polyamidoamines (PAA) [1] are promising candidates to form stable complexes with metal cations and therefore to act as effective sequestering materials for metal in waste waters [2]. In order enhance their chelating properties and to form insoluble reticulated materials, aminoacidic functions and sol-gel processable siloxanic functions have been inserted in their structure and here we present the results obtained in the case of Co^{2+}, Ni^{2+} and Cu^{2+}.

2. Results and Discussion

Three PAA species have been synthesized by the well-known aza-Michael addition between a nitrogen nucleophile and an activated vinyl group. The addition between methylenebisacrylamide (MBA) and L-Glycine and/or 3-Aminopropyltriethoxysilane in equimolar ratio leads to the formation in high yield (99%) of the polymers named PAAGly, SiPAA (showed in Fig.1) and SiPAAGly, respectively. A model molecule was also synthesized by reacting acrylamide with glycine in 2:1 molar ratio (AAGly). The completeness of the polymerization reaction has been monitored by FTIR, Raman and ^{1}H NMR spectroscopies, all evidencing the disappearance of the double bond typical of the MBA.

Moreover, the condensation degree of Si-functionalized PAA calculated by 29Si CP/MAS NMR results about 80%: two intense signals are visible and associated to T3 [$R\text{-}Si(OSi)_3$] at 67 ppm and T2 [$R\text{-}Si(OSi)_2OR$] at 58–59 ppm units, respectively.

The coordination ability of AAGly and relevant polymers towards Cu^{2+}, Ni^{2+}, Co^{2+} in water has been studied by the Job's plot method getting insight into the nature of the metal complexes.

The metal sequestration ability were tested by adding rigid membranes made by SiPAA and SiPAAGly in aqueous solutions (0.0125 mol/L) of Cu(II), Co(II) and Ni(II) prepared starting from metal acetates in molar ratio M/L = 1/4. The adsorption capacity (mg/g) of the system was obtained by ICP measurements. Both polymers are able to remove the metal ions from the solution, SiPAAGly being more efficient: in 6 hours the removal percentage was ca. 85% for Cu(II)

To verify the reusability of the polymers, the membranes were cleaned with a solution of disodium ethylenediaminetetraacetic salt and again exposed to a metal solution for the adsorption test. After the third experiment the adsorption capacity remains almost unchanged.

3. Conclusions

The removal of toxic metal ions from wastewater is one of the most important current research goals due to the harmful effects these pollutants can have on human health and the environment.

For this purpose, the functional polymers PAA/amino acids, here presented, are capable to give stable complexes with metal cations. Moreover, in the form of reticulated membranes, obtained by insert a sol-gel processable siloxane moiety, they have revealed high metals sequestration power in aqueous solution. Their easy recovery and regeneration allow them to be reused several times, making them promising materials in wastewater remediation.

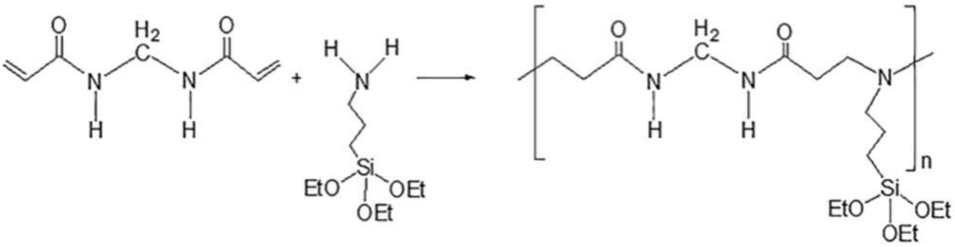

Figure 1. Reaction scheme of SiPAA

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OP31

NON-INVASIVE ANALYTICAL APPROACH TO CHARACTERIZE ITEMS PRODUCED BY PINNA NOBILIS

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1. Introduction

This study is part of a project conceived to characterize and valorize the original collection of the Commodity Science Museum of the University of Bari [1]. It includes a set of the bivalve mollusk, sedentary and endemic to the Mediterranean, Pinna nobilis (Linnaeus, 1758) (Fig.1).

From a cultural heritage perspective, the value of the fan mussel's collection is amplified by the presence of secrete byssus threads produced to anchor themselves to seagrass meadows. Indeed, this specific byssus was the raw material used to produce sea-silk, a stunning iridescent amber-golden textile [2]. Until the mid-20th cent. Taranto in Apulia and Sardinia were centers of sea-silk manufacturing. They are again important today, where the focus lies on raising awareness of the artisanal knowledge and to transfer it to next generations.

Our aim is to characterize Pinna nobilis set. In this way, there will be a systematic and scientific trace of an oral tradition, not yet well-known.

The samples investigated are valves, pearls and several phases of byssus production.

Since they are valuable, rare and exhibited items, non-destructive analytical techniques have been preferred to characterization.

2. Results and Discussion

Different techniques were used to study the valuable set.

Sea-silk manufacturing phases

Processed sea-silk can hardly be distinguished from mulberry silk with the naked eye, nevertheless in cross-section it can easily be recognized. Indeed, investigations by Optical Microscopy (OM) and Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS) highlighted its typical elliptical or almond-shaped and remarkable encrustations of salts deposits in raw byssus.

The nanostructure of the fibers during weaving was also examined by small and wide-angle X-ray scattering (SAXS and WAXS) [3] as well as infrared spectroscopy (IR) revealing the presence of hydroxyapatite on the initial fibers and the crystalline beta-sheet domains within the fibers. Finally, a WAXS-based method reveals a decrease in the crystalline/amorphous ratio with crafting.

Metals release of threads in deionized water was investigated by Inductively Coupled-Mass Spectrometry (ICP-MS) analysis showing a marked metal depletion from not-treated byssus to the final textile, confirming the oral handing down of the know-how: basically, byssus cutting followed by several water washing (some sources reported lemon juice addition) -and successive steps to carding, spinning, and weaving, and finally obtaining the knitted patterns.

Nacre and pearls

By means of Surface Enhanced Raman Spectroscopy (SERS) and Attenuated Total Reflection (ATR) nacre and pearls were investigated [4-6]. Aragonite, calcite, polyenes and probable conchiolin were revealed in nacre flakes and shell fragment. Also, spectra highlighted the presence of calcite, aragonite, polyenes and carotenoids, organic pigments, responsible for the pink/orange color of natural and cultivated pearls.

3. Conclusions

Up to now all results observed confirmed that the complete assemble exhibited belongs to Pinna nobilis, offering important results of sea-silk manufacturing procedure and nacre and pearls characterization.

The data obtained could be used for a better classification and valorization of the fan mussel's samples of the museum collection, and for a deeper knowledge about the goods there preserved.

Equally important is to bring light and preserve, by scientific data, a demoethno-anthropological heritage about the precious and rare textile produced in Southern Italy.

Perspectives

To check possible differences in the protein pattern of different byssus manufacturing steps proteomic investigations will be carried on. As well as further SERS investigations.

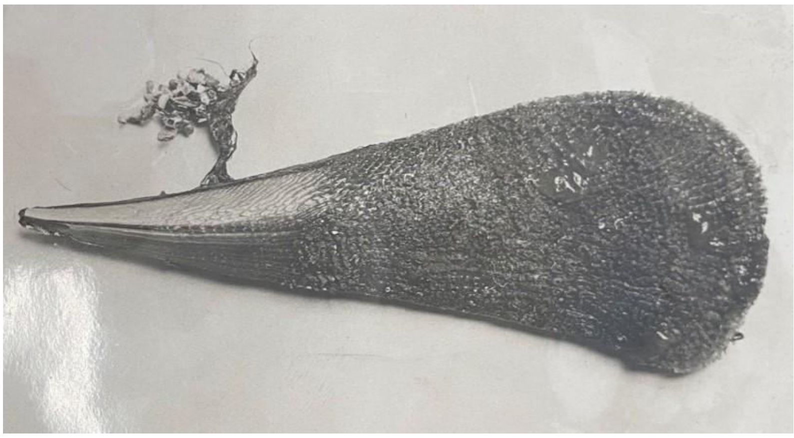

Figure 1. Photographic image of Pinna nobilis with a tuft of regenerated byssus from Table 1 of the Museum.

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OP32

ON THE SURFACE: RAW MATERIALS, FIRING CONDITIONS AND TECHNOLOGICAL FEATURES OF POTTERY SURFACE TREATMENTS IN RED FIGURE VASES FROM APULIA (ITALY)

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1. Introduction

Raman spectroscopy and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy are used to investigate the black and red surfaces of Apulian red figure vases coming from some of the most important locations in Apulia (Italy) in order to identify production techniques and raw materials.

The definitive archaeometric objective is to recognize the interconnections between 4thcentury BC Apulian and Attic production so as to validate the hypothesis of the Apulian production being independent from the Attic one also in terms of manufacturing and technology.Red figure technology is based on painting a black gloss background, saving figures from the ceramic body (e,g. the color of the red figure is the "natural" one for ceramic bodies). The significant color difference between the ceramic body and the red surfaces[1-2] clarify the study of red surfaces on Apulian vases, as well as the need to confirm or disprove the hypothesis about the export of dried Attic black glaze to Greek colonies[3].

The final purpose of this study is clarifying painting practices and firing conditions, still under debate[4-5].

2. Results and Discussion

According to our results, two different clays were employed for the black gloss and ceramic body in Apulian red figure pottery. Based on all analytical data it can be assumed that the raw material is terra rossa, namely its finest fraction (< 2 μm), which is the richest in kaolinite and illite, as well as Fe and Al oxides, and is easily attainable through a refining process. Terre rosse are continental sedimentary layers found throughout Apulia. They are composed mainly of partially crystalline Fe and Al oxides and hydroxides, clay minerals (illite and kaolinite), traces of quartz, feldspars, micas, pyroxenes, and other minerals. No organic material was added to the clayey suspension. The carbon traces on the surfaces were caused by fly ash produced during the fire process. As concern the Apulian red surfaces, the ability of obtaining information on the size of hematite particles from the position of hematite distinctive Raman bands was successfully examined, enabling -in a non destructive approach- to obtain indications on the presence of a surface layer. The method is based on the comparison of particle sizes in the ceramic body and on the surface [6].The analysis of finds from different Apulian sites allowed to widen the range of procedures used by Apulian ceramists to color red the whitish/grayish surface of vases produced with local clayey raw materials. "Miltos" (ferruginous water) treatment, application of a clayey layer added with Fe oxides and a clayey engobe layer, obtained refining the raw material employed for the paste, were recognized on the Apulian ceramic bodies. A smaller size of hematite crystals on the surface was deduced for all the engobed vases, whereas a larger size for "miltos" and fine silty-grain clayey layer ones.

As concerns the firing temperature, the mineralogical phases observed in the black gloss (e.g. coexistence of Fe-spinels hercynite and magnetite as well as the newly-formed phases – pyroxenes and gehlenite – found in the ceramic bodies of all vases) allowed to hypothesize that the maximum firing temperature was about 900 °C. Moreover, all results support the multi-step firing (ox-red-ox) practice.

3. Conclusions

Although the visual aspect of Apulian and Attic red figure vases is very similar, Raman microspectroscopy and SEM-EDS revealed that they are distinct, since they were manufactured with locally sourced raw

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materials and comparable, but not identical, production techniques. The analytical results might be explained by familiarity rather than actual and genuine continuity with the Attic ceramic tradition.

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OP33

A QUANTITATIVE INDEX TO INCORPORATE TRANSCRIPTOMIC DATA INTO WEIGHT OF EVIDENCE APPROACHES FOR ECOLOGICA RISK ASSESSMENT

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1. Introduction

In the context of ecological risk assessment, with time more types of scientific evidence have been added to infer waterbody quality status. In particular, investigation of aquatic environments includes now multiple and heterogeneous pieces of evidence, for example chemistry, bioavailability, ecotoxicological bioassays, survey of benthic communities and cellular biomarkers, which should then be combined together to determine the hazard posed by the chemical contaminants of concern. The integration of different studies can be pursued with a Weight of Evidence approach [1]. Extending the modules available in classical WoE, for example by including new ecotoxicogenomics evidence, such as transcriptomics studies of genomic-scale changes in RNA expression, could foster our understanding on the biological changes linked to chemicals exposure. In this work, a methodology is presented to quantitatively elaborate transcriptional data obtained from aquatic organisms exposed to chemicals with the aim of integrating this information into a Weight of Evidence approach to support ecological risk assessment.

2. Results and Discussion

The methodology makes use of results from the application of Gene Set Enrichment Analysis (GSEA, [2]) to recent studies investigating the response of Mytilus galloprovincialis and Ruditapes philippinarum exposed, under controlled laboratory conditions, to environmentally realistic concentrations of contaminants, i.e. per-fluoroalkyl substances, pharmaceutics, herbicides, and fragrances, and to environmental stressors, i.e. acidification.

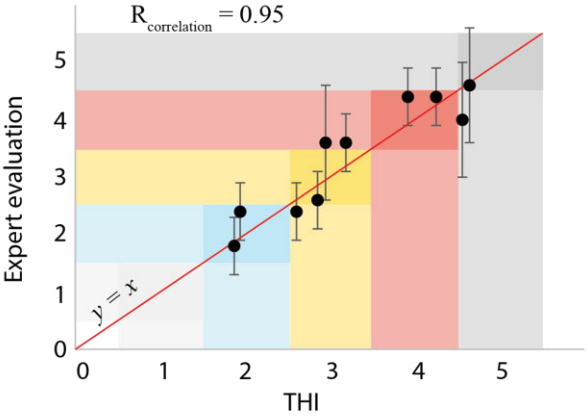
A set of mathematical algorithms was designed to translate the severity of transcriptional alterations in exposed organisms into a quantitative hazard index. The degree of de-regulation of gene sets organised into higher biological themes together with the relevance of each biological theme in terms of physiological reactions contribute to the calculation of the hazard index. The outcome, expressed on the scale 0-100%, is classified according to five hazard classes (from 1-absent to 5-severe), providing an evaluation of the early individual effects of chemical exposure. The ability of the synthetic index to mirror the subjective expert judgment of transcriptional alterations is tested with both experimental and simulated altered transcriptomics profiles of aquatic organisms. By adding realistic in-silico transcriptomics profiles, it was possible to create a broader variety of transcriptional scenarios proving that the model can effectively discriminate different levels of adverse transcriptomic response when compared with expert judgement. The fitness of the transcriptomics index was further tested by peer-evaluation of ten datasets of GSEA outputs picked from both experimental and simulated data so that their risk ranged from slight to severe.

The transcriptomics index proved to be a good indicator of the different levels of adverse transcriptomic response by never falling far from the expert judgment, as indicated by the Spearman correlation coefficient of about 0.95. Specifically, the synthetic index seems to work in conjunction with the qualitative class of hazard by complementing the indication of the transcriptomics hazard that would result in the simple use of a “label” (absent to severe) and by giving an indication of the degree of risk for borderline situations, where also experts’ evaluations were shown to difficulty align.

The consistency of predicted and resulted hazard is promising, and it encourages further testing and refinement of the quantitative transcriptomics index proposed in this work to support environmental risk assessment in aquatic ecosystems, something that has been sought for long. The framework presented in this work is the first step in this direction, but its transferability and reproducibility require further testing. The quantitative hazard tool has been applied to only laboratory-controlled exposures and the ability to interpret transcriptomics adverse outcome should be established also for in situ scenarios characterized by multiple stressors and mixture of chemicals.

3. Conclusions

The proposed methodology is not meant to be definitive, but it can serve as a proof of concept for the integration of genomic tools in ecological risk assessment based on multidisciplinary investigations. To this end, the synthetic index would also benefit of an advancement in the delineation of a set of shared protocols and guidelines for managing transcriptomics data. In the meantime, within the multidisciplinary vision adopted by ecological quantitative WoE approaches, our proposed method seems to suggest a possible opening towards the construction of a supportive line of evidence based on transcriptional data that could complement the interpretation of results from other disciplines.



Index values against the averaged expert evaluation converted into nominal scale (1 to 5) of hazard

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OP34

MICROPLASTICS IN WASTEWATER TREATMENT PLANTS: OCCURRENCE, REMOVAL AND FATE

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1. Introduction

The high presence of microplastics (MPs) of varying sizes, types and concentrations is a key environmental concern due to their potential impact on water bodies and related ecosystems. MPs are not properly retained by the filtration systems of wastewater treatment plants (WWTPs), which represent often a major source of release into rivers and seas. Nevertheless, as the issue of MPs is relatively recent, there are no standardised analytical procedures for sample pre-treatment and instrumental analytical procedures to date.

In this context, the present study aims to investigate the effectiveness of treatment processes in removing MPs from wastewater in different mixed civil and industrial WWTPs, located in central-northern Italy, and to define an optimal protocol for the analysis of complex samples, such as wastewater.

2. Results and Discussion

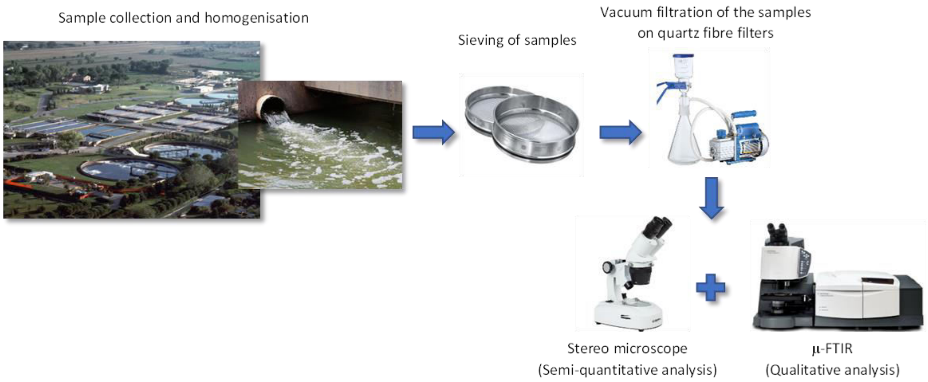
The study allowed the optimisation of an experimental procedure applied to real samples taken at the inlet and outlet of different WWTPs through the centre and north of Italy and included the evaluation of the sieving, filtration and digestion conditions and subsequent instrumental analysis. A semi-quantitative analysis was carried out using a stereo microscope, followed by a qualitative analysis performed by a Fourier transform infrared spectrometer (FTIR), coupled to an optical microscope, with an FPA detector in reflection mode.

The data obtained made it possible to highlight two main macro-categories of MPs, fibres and fragments, with a clear prevalence of the former representing over 70% of the total in the samples from all the plants. The MPs determined were characterised by almost similar colours and shapes, with a predominance of transparent and blue fibres and, in terms of shape, a prevalence of filaments, as well as fragments and scales. The main plastic polymers identified in these samples were nylon, polyamide, ABS and PET. There was also a high percentage of cellulosic fibre, a natural polymer widely used in various human activities such as fishing, agriculture, textiles and many others. Natural fibres, such as cotton, can easily lead to overestimation of plastics because of their colour, shape or buoyancy. Cellulose may not be an environmental hazard in itself, but dyes or additives associated with it could be potentially harmful.

It was also estimated that more than 80% of the plastic material identified in all the plants studied was removed during the water purification process, in agreement with other literature studies conducted on similar samples.

3. Conclusions

Despite the high removal rates, non-negligible amounts of MPs are still present in the outflows from the WWTPs and can be discharged into the receiving water bodies, posing a threat to aquatic ecosystems. Due to the large water volumes treated, in fact, even small quantities released per litre can result in a considerable amount of MPs being spread into the environment. Clearly, the extent of contamination is linked to the type of effluent and fluctuates according to the seasons of the year; for this purpose, it would be interesting to carry out additional sampling to assess the the variation in the presence of fibres during periods of minimum load and to compare them with data from the same installations during periods of maximum load.



Schematic representation of sample pre-treatment and instrumental analysis steps.

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OP35

A METHOD TO ASSESS THE IMPACT OF BIOPLASTIC ON TALITRID AMPHIPODS

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1. Introduction

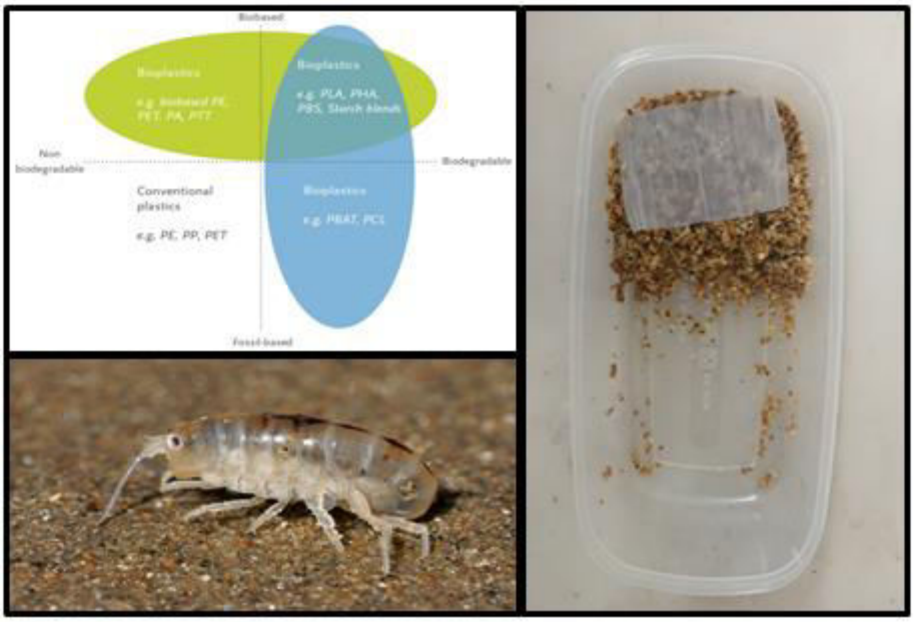
Over the last 60 years plastics production is widely increased owing to their inexpensice, durable, versatility and lightweight nature, and plastic demand will still continue to grow over the coming years. Therefore, in recent years, bioplastics are being touted by industry marketers as the solution to plastics pollution to reduce the plastic environmental impact and petro-dependence. The littoral and supralittoral zones are characterized by high biodiversity, including the presence of talitrid amphipods [2], which are considered good bioindicators. A variety of chemical additives, as phthalates (PAEs), are used as plasticizers in numerous plastic and bio-plastic applications and thus can be ingested by marine organisms exposed to plastics [3]. Moreover, PAEs are considered to be toxic and endocrine disruptors linked with a long list of reproductive, developmental, and other health issues even at very low concentrations. To this aim, a lab experiment was conducted to observe the toxic effects that bioplastics can cause to amphipod communities.

2. Results and Discussion

A laboratory experiment was set up nursing for one month homogenous pools of about 30 individuals of amphipods with two different types of bioplastics (Experimentals) or with a mixture of dried fish food and paper (Control) in the same experimental conditions. Adults T. Saltator were collected on the beaches of Talamone, Grosseto and Regional Natural Park of Migliarino. Two different types of starch-based bioplastics (BIO1 and BIO2), classified as biodegradable and compostable according to UNI EN 13432, were chosen. BIO1 and BIO2 were characterized by FTIR in ATR mode and GC-MS analyis to evaluate the presence of PAEs. H-NMR analysis were also performed and fecal materials were analysed by high-resolution 3D microtomography to evidence any structural differences. The mortality was recorded in the three homogeneous groups and was significantly higher in BIO2 compared to BIO1 and control pools, with a minimum of 5% of survivors in BIO2 and a maximum of 90% in BIO1 experiment, respectively. The feces of the BIO1- reared T. Saltator were characterized by visible short bioplastic filaments, while those individuals feeded with BIO2 showed larger quasi-leaf structures inside probably related to the plastic material. The composition of the fecal pellets of individuals from BIO1 and BIO2 experiments was also characterized by FTIR and 1H-NMR, and compared with that of BIO1 and BIO2 items. The ATR analyses evidenced that both bio-plastic materials are characterized by the presence of PET (polyethylene terephthalate). The comparison of the ATR spectrum of the feces of individuals from the experimentals and control pools revealed a significant difference in composition, not found superimposing the spectra of the feces of BIO1 and BIO2 fed individuals. From NMR analysis a significative difference between BIO1 and its fecal pellets was also observed. This would indicate a higher ability of T. Saltor to consume the lipidic component present in BIO1 and thus it could probably explain the increased survival rates observed when amphipods are fed with this polymer. The data obtained suggest that biobased plastics behave in similar way to ordinary plastics, i.e. they seem not metabolized by the body but are essentially excreted as they are. Among ten target phthalates, the presence of DHEP, DNIP and DIPB,which represent the most common plasticizing agents, was observed in all samples; BBZp was determined in 85% of the analysed samples with concentrations significantly lower than the other three. Moreover, a decrease in the concentration of these analytes in terms of absolute concentration of all these compounds in the samples of batch BIO1 was observed. This result seems to indicate that virgin microplastic fragments, whatever their nature, have a scavenger role concerning a wide range of organic compounds.

3. Conclusions

This study confirms the ability of T. Saltor to consume and ingest bioplastics. The ATR and NMR spectra indicated a slight difference between the fecal pellets and BIO1 suggesting potential assimilation of bioplastic probably related to the increased survival rate and higher lipid content. The results indicate a significant decrease in the total concentration of phthalates in individuals fed with BIO1 compared to T. saltator not subjected to experimental conditions. The high concentrations of phthalates in untested individuals suggest the presence and ability of amphipods to assimilate these compounds. While a decrease in the concentration of phthalates in BIO1-fed individuals compared to controls can be attributed to the scavenger effect of virgin plastic material.



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OP36

MICROPLASTICS IN SEA ICE: DETECTION BY FTIR AND ELUCIDATION OF VERTICAL DISTRIBUTION PATTERNS

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1. Introduction

Recent investigation showed that sea ice may be heavily contaminated by microplastics (MPs) but at the present time the mechanism determining their accumulation and distribution in this environmental compartment are still unclear [1]. Previous observation seems to indicate that the acculumation of MPs along the vertical profile of icecore is size-specific and time variable [2]. Starting from this basis we investigated the level of contamination and vertical distribution of MPs in the ice of the Novik bay (Peter the Great Bay, Sea of Japan). Ice cores (thickness ~40 cm) was segmented into 5-cm thick layers and analyzed for MPs content using µ-FTIR .

2. Results and Discussion

MPs particles of size ranges comprised between 20 and 3000 µm were found in all layers of the ice cores. Contamination in upper\lower layers resulted up to 3 times larger than in the middle of the cores. The majority (45%) of MPs were 1-2 mm in size and were distributed on the top layers of the ice cores confirming a certain deficit of smaller MPs within the ice. Considering shape, fibers (53%) were the most represtented followed by fragments (44%). Considering polymers, chemically modified cellulose and polyolefin were the most represented (up to 74%). Vertical distribution of the particles along the icecore appeared to be related to the ice salinity profile. Specifcally, correlation with the presence of weathered particles (presenting fuctional groups related to photooxidation and/or hydrolisys) was highlighted.

3. Conclusions

The distribituion of MPs in ice core looks stonglty determined both by environmental conditions and physical processes. The hydrophobicity of the material seems to be the key factor involved in the particle retention during the ice formation. Photoxidation and mechanical fracturing determined by the freeze/thaw cycle deserve to futher investigation as main drivers of the particle segregation

Example of ice core sampled from the Sea of Japan

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OP37

FIRST DETECTION OF MICROPLASTICS IN REEF-BUILDING CORALS FROM A MALDIVIAN ATOLL

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1. Introduction

Synthetic polymers, due to their widespread use, have become the predominant human-made debris in the oceans. Only recently, the possible impacts of plastic pollution on the health of reef-building corals have been started to be investigated. Feeding experiments carried out in tanks demonstrated that stony corals can actively ingest microplastics and face health impacts [1]. Since these studies were performed in laboratories, employing high concentrations of commercial plastics, it was questioned if the results may be totally representative of what happens in the "real" environment. Under this view, there is an urgent need of studies carried out on field to evaluate the impacts of microplastics in coral reef ecosystems. Starting from this basis, we carried out an unprecedented survey regarding the contamination of reef-building corals in the Maldives, archipelagic state suggested to be potential sink of plastics, due to the monsoonal regime that dominates the Northern Indian Ocean [2]. Specifically, we aimed to investigate the possible effect of exposure, depth and species onto microplastic distribution.

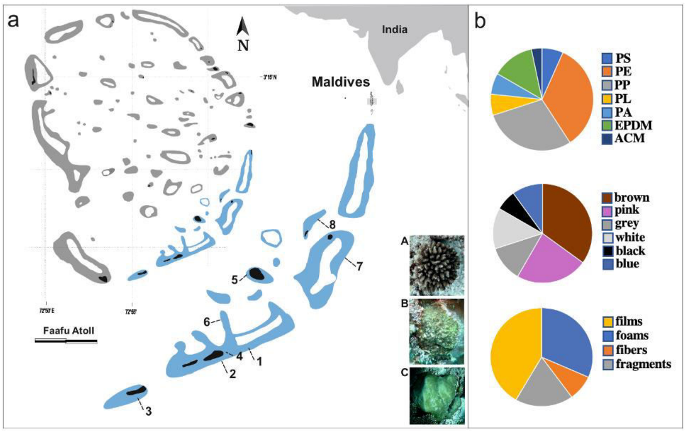
2. Results and Discussion

60 microplastics within the size range 25-150 μm were detected in 58% of the surveyed colonies by μ-FTIR. The average concentration was 1.8 ± 0.4 particles/g. The most abundant polymers were polyethylene (PE) followed by polypropylene (PP), representing 63% of the total detected particles. 35% of the microplastics were brown, followed by the 23% that was pink. Grey (12%), white (13%), black (7%) and blue (10%) particles were also detected. Considering the shape, four different types were detected: films (42%), foams (32%), fragments (18%) and fibers (8%). The contamination did not display a clear pattern across sites, species and environments, but was rather ubiquitous. A possible explanation of this outcome may be found in the large number of sources of plastic debris present along the Maldivian archipelago and in the mechanism of vertical mixing that involve plastic particles. We observed the greatest average concentration of plastic particles (2.8 ± 0.9 particles/g) in P. verrucosa, coral displaying a branching morphology which significantly differ from the massive one, typical of the other two surveyed species (P. varians and P. lutea), and that reasonably is capable to induce a higher degree of particle entrapment. Moreover, we found that site 4 (near Magoodhoo island) and site 5 (near Bileddhoo island) showed the highest average particle concentration (3.9 ± 2.1 particles/g and 4.0 ± 1.8 particles/g respectively), while site 8 (Adanga island) resulted the least impacted (0.28 ± 0.28 particles/g). Being Magoodhoo and Bileddhoo inhabited islands (~ 900 inhabitants), it's reasonable that the local contribution affects the corals of these sites. On the other hand, Adanga is a desert uninhabited island, therefore less subject to the anthropic pressure. Inner and outer reef corals displayed similar amount of microplastics (1.8 ± 0.75 particles/g, and 1.8 ± 0.50 particles/g, respectively). Since the detected microplastics showed clear signs of surface oxidation (presence of hydroxyl and carbonyl groups), we can assert that their genesis was likely to be via photo-oxidative degradation of larger items (secondary microplastics). Thus, it is reasonable that the particles derive from larger items transported from the open ocean and then trapped in the corals of the inner atoll rim. This finding is in line with our previous study, in which even microplastic contamination of the sea surface in the inner atoll rim resulted relatively higher than outside, suggesting that the inner atoll rim may represent an accumulation zone [3]. Noteworthy, slightly higher concentration of microplastics was detected in individuals sampled at shallow depth (5-10 m), in accordance with the low density characterizing the predominant detected polymers, polyolefin (PE and PP). However, since even deep coral samples showed a relatively high contamination, somehow these polymers were removed from the seawater surface. A possible mechanism

involved in the removal of plastic microparticles from seawater surface is transport by marine snow, but it has not been examined in the Maldives yet. The last part of the work was dedicated to the analyses of 5 PAEs through the SPME/LC-MS/MS method to highlight correlation between the presence of microplastics and of 5 PAEs within the investigated coral colonies, but no significant correlations were found.

3. Conclusions

In conclusion, we reported for the first time the presence of microplastics in wild-collected corals from the archipelago of the Maldives. Plastic particles up to 25 μm in size were found in 58% of the analyzed colonies and this may be viewed as an alarming sign of the current contamination of the Indian Ocean. Morevor, we detected no significant correlations between presence of microplastics and PAEs in the investigated colonies. The availability at the present time of only few on field studies, concerning the problem of microplastic contamination in reef building corals, summarize the scarcity of data and recall the need of further effort in determining the impacts of this growing issue onto the health of coral reef ecosystems worldwide.



Graphical abstract

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OP38

XPS STUDY ON THE DEGRADATION OF CALCARENITE STONES OF TWO RUPESTRIAN CHURCHES IN THE "SASSI" OF MATERA

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1. Introduction

Understanding the complex phenomenology that affects the degradation of Cultural Heritage is fundamental for their conservation. Two important cases study are represented by the rupestrian churches in the Sassi of Matera (San Pietro Barisano and Madonna dei Derelitti) which show extensive degradation phenomena linked to the porosity of the stone and to particular environmental and microclimatic conditions [1]. The environment of the churches is, in fact, characterized by high relative humidity, water infiltrations and poor ventilation. As part of the MIUR project "Smart Cities, n. SCN_00520" a study was started on the internal walls of the churches and the hypogeum of San Pietro Barisano, to correlate the types of degradation given by the composition of the surface patinas with their location within the churches. The research relied on a multidisciplinary approach and one of the main diagnostic contributions was provided by XPS, the surface analytical spectroscopy that proved useful for analyzing the powdered samples, taken from degraded surfaces, in a simple and rapid way, without requiring particular sample treatments.

2. Results and Discussion

The first phase of the investigation involved the visual and macroscopic analysis of the state of the surfaces; this made it possible to assess the presence of considerable degradation in various areas, mainly deriving from water infiltrations, internal microclimate influenced by inadequate ventilation and high concentration of CO_2, linked above all to tourist turnout. In some areas, a significant chromatic alteration of the stone surfaces was observed with the presence of patinas, drips, efflorescence, alveolization and detachment of portions of the walls. For the XPS investigations, the sampling was carried out in specific areas with different degradation in the churches and in two areas in the hypogeum of San Pietro Barisano. The sampling was carried out by gently removing a small portion of patina or surface layers from the walls with a spatula, avoiding collecting samples from deep layers. The powdered samples were homogenized in an agate mortar, pressed on double-sided copper tape, suitably fixed on a steel sample holder and safely introduced into the analysis chamber of the SPECS Phoibos 100-MCD5 spectrometer. To identify the main elements composing the samples under examination, the "wide" spectra were first acquired, with a channel widths of 1 eV, over the entire range of kinetic energies (KE) that can be explored by the X-ray source (100-1500 eV) in use, either in FAT (Fixed Analyzer Transmission) and FRR (Fixed Retarding Ratio) modes. This allows to associate each peak to specific orbitals of the identified elements and to select the regions of interest to be acquired at higher resolution (detailed spectra) in FAT mode with a constant pass energy of 9 eV and channel widths of 0.1 eV. The detailed spectra are then resolved in the component peaks by the "curve-fitting" procedure, using the Googly program [2]. In this way, a "fine structure" can be obtained for each element which combines qualitative (chemical states) and quantitative (by evaluating the areas of the peaks) information for the characterization of each sample. As a short outcome, from the results obtained by curve-fitting, it was noted that the organic carbon fraction (intended as the sum of all the identified organic carbon groups) was present in all the samples with an average value of 60%. The presence of oxalate was found in the black crusts probably deriving from the microbial metabolism present in the patinas, while the presence of magnesium and sodium salts (NaCl) was highlighted in the zones with evident phenomena of efflorescence.

3. Conclusions

Qualitative and semi-quantitative analysis, possible with the XPS technique, made it possible to associate chemical compounds with various types of stone degradation and biodegradation of the internal areas of the rupestrian churches, also by means of PCA statistical analysis. The results obtained, through the curve-fitting procedure of the spectral regions, allowed discriminating the different types of degradation, constituting an important knowledge base of data for any conservation treatment.

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OP39

ECODESIGN LIFE CYCLE ASSESSMENT OF A WASTE TREATMENT PLANT

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1. Introduction

This paper aims to provide an exhaustive comparison of alternative waste management scenarios for the integrated waste treatment centre of Saliceti through a gate-to-grave comparative LCA study of four different possible scenarios for the management of future OFMSW (Organic Fraction of Municipal Solid Waste) and Green-waste streams. Specifically, the scenarios selected are A) production of Biogas utilizing a biodigester, B) construction of a composting plant, C) current condition (i.e., sending the flows to other regions plants) and, D) hybrid treatment plant, a mix of B and C scenarios. The study was conducted from May to July 2019 through the application of the ReCiPe method at midpoint level using the DTU Environment EASETECH software through primary information provided by the plant managers and the manufacturer in collaboration with ARPA Liguria, and secondary information collected from the Ecoinvent v3.3 database. The study demonstrates that building the biodigester is the least impactful scenario for the environment given all alternatives are considered equally valid on an industrial level.

2. Results and Discussion

To address the impacts, the ReCiPe method at the midpoint level has been selected [1]. Specifically the study was carred out through Characterization and Normalization at european level [2]. Within the study, the OFMSW and Green-waste streams managed by the integrated waste treatment centre of Saliceti were considered as raw materials. Since it was not possible to have access to a complete characterization of the waste, it was substituted with data from scientific literature. Energy flows have been considered for analysis according to the European and Italian consumption mixes identified in Ecoinvent. For transportation involved in Scenarios A and B, an average of 30 km from the integrated waste treatment centre was considered, while for Scenario C, the actual waste delivery distance to inter-and intra-regional facilities was considered. Avoided impacts related to energy produced by biomethane fed into the network was modelled using average National energy consumption.

The Characterizarion results of the comparative Eco-design study between scenarios A, B, C and D are reported in the Figure. As can be seen, scenario A (Saliceti bio-digester) always has less or equal negative impacts and greater or equal positive impacts to the other scenarios for all impacts. This result is due to the Biogas generation process which allows scenario A to reduce atmospheric emissions deriving from composting and at the same time to avoid the impacts associated with the generation of gas from other sources. On the other hand, the most impactful scenario emerged to be scenario B involving a possible evolution of the current situation with the creation of a composting-only plant for the treatment of the identified waste streams, this because the beneficial effect brought by the avoided impacts of the biodigester is lacking. As regards scenario C, inherent to the status quo delivery in different treatment centers, it reports better results than scenario B, despite the long distances travelled by trucks, thanks to the presence of some plants producing Biogas. Finally, scenario D, which involves a mixed treatment from scenarios B and C, is the second-worst scenario after B in almost all impact categories analyzed. This is due to the benefits brought by the avoided impacts from biodigestion plants present in scenario C reduced by the negative environmental impacts of the composting plant in scenario B. It can therefore be observed that the creation of the Biodigester for the integrated waste treatment centre in Saliceti is the best choice given the flows and treatment technologies considered in this eco-design LCA study.

3. Conclusions

This "gate to grave" study made it possible to highlight that the creation of a Biodigester is the least impactful scenario among those considered. Indeed, the improvements of scenario A are mainly due to both the production of clean energy and the compost from a material that previously would have created only negative impacts on the environment. In conclusion, in a situation where citizens' commitment to the separate waste collection is taking shape, the future is identified by an increase in the flows of green waste and OFMSW. For this circumstance, the results presented in this study can be used as a benchmark for new forms of waste management of other plants.

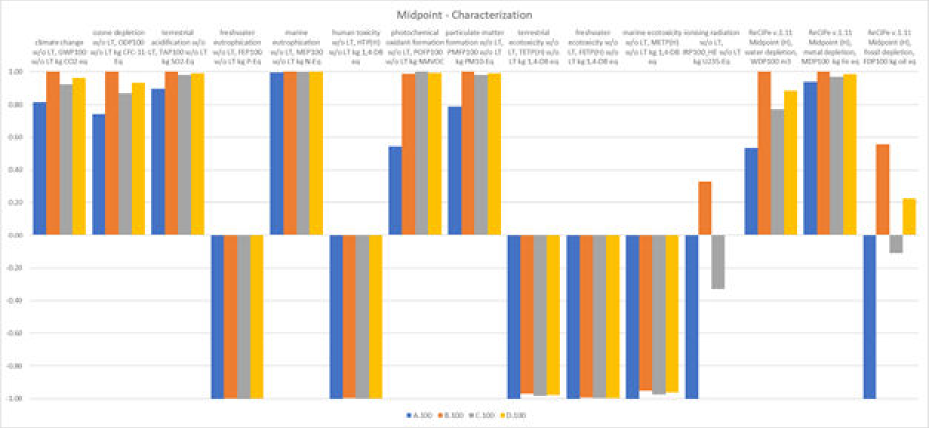

Figure: negative and positive midpoint characterization impact

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OP40

INVESTIGATION ON SOURCES OF AIR POLLUTANTS IN BLACK CRUST SAMPLES FROM THE MONUMENTAL CEMETERY OF MILAN (ITALY)

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1. Introduction

Exposure to atmospheric pollutants (e.g. CO_2, NOx and SOx) causes the damage of cultural heritage, expecially the degradation of stone surfaces of buildings and monuments located in the historic centers of large cities. The chemical interaction of stone materials with air pollutants is known to be at the origin of the blackening of surfaces, one of the most dangerous phenomena that occur in architectural heritage. The atmospheric deposition accumulates on stone surfaces together with the products of the chemical transformation of materials, forming dark-coloured deposits, called black crusts (BCs) [1]. Different pollutants can be detected on BCs, including organic matter, metals and polycyclic aromatic hydrocarbons [2]. Knowing the nature and source of degradation products could be very precious for the identification of the proper strategies for the preservation of historical monuments. This study is focused on the identification of sources of air pollution in BCs collected from the Monumental Cemetery of Milan (figure1). The importance of this investigation lies in the great cultural interest of this site due to its numerous architecture and sculpture works of art.

2. Results and Discussion

Several analytical techniques, including X-ray Diffraction (XRD) and Fourier Transform-Infrared spectroscopy (FT-IR), Ionic chromatography (IC), High Performance Liquid Chromatography (HPLC), and isotope ratio mass spectrometry (IRMS) were used for the characterization of BC samples. Concerning mineral composition, black crusts are mainly made of calcite and gypsum. HPLC measurements were carried out on Soxhlet extracts to identify the presence of polycyclic aromatic hydrocarbons (PAHs) in the collected samples. Different PAHs (acenaphthene, benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, fluoranthene and pyrene) were detected in BC samples. In particular, fluoranthene and pyrene are the more abundant (concentrations up to 10 µg/g of dry matrix). Based on the ratio of the different isomeric PAHs, the presence of these chemicals is mainly attributable to anthropogenic emissions. In addition, stable isotope ratio of sulphur and oxygen have already been used for the identification of the source of sulphur in black crusts [3]. Carbon stable isotope ratio is used to evaluate the sources of such carbonaceous pollutants on BC samples, whereas sulfur and oxigen stable isotope ratio are employed to assess the origin of sulfates.

3. Conclusions

In this study, pollutants on black crusts collected from the Monumental Cemetery of Milan, one of the most important and best-known Italian cemeteries, have been analysed. Several PAHs were detected in all samples analysed, at concentrations up to 10 µg/g of dry matrix. Moreover, stable isotope ratios of carbon, sulfur and oxygen are used for the identification of sources of hazardous pollutants accumulated on BCs samples.

OP40

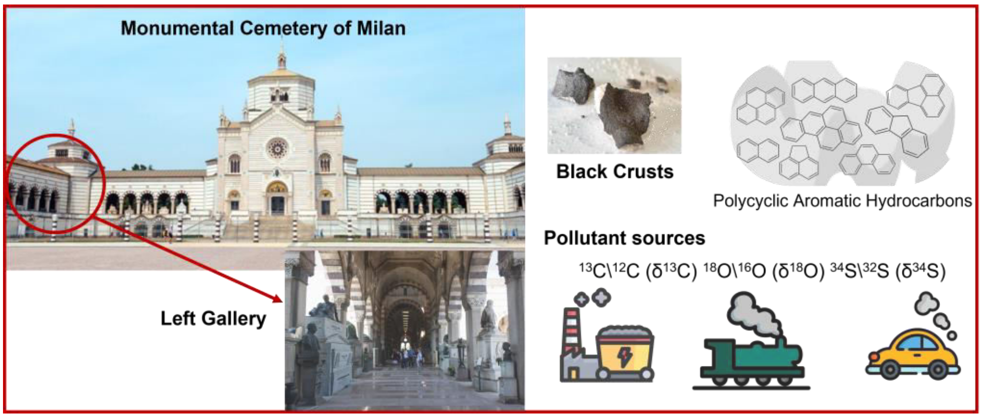

Figure 1. Schematic representation of the main objectives of the present study.

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OP41

DEVELOPMENT OF INNOVATIVE STRATEGIES FOR POLLUTANTS ABATEMENT IN AQUACULTURE SYSTEMS

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1. Introduction

In recent times, aquaculture has been the fastest growing food producing sector in the world and is expected to be the only way to meet the increasing demand for seafood in the future. However, one of the main problems in recirculating aquaculture systems is the accumulation of unpleasant odorous molecules, such as Geosmin and 2-methylisoborneol (MIB), in water and in the fish meat. They can be perceived at extremely low concentrations making fish unsuitable for commercialization and human consumption [1]. Water used for aquaculture can also be subjected to contamination by potentially toxic elements (PTEs) such as heavy metals and contaminants of emerging concern (CECs). Therefore, finding and developing efficient methods with a low environmental impact for the removal of a wide range of pollutants is of great usefulness and importance. In this context, we aimed of exploiting both the catalytic properties of laccase enzymes and the photodegradation performances of ZnO-based photocatalysts toward the abatement of heavy metals, CECs and odorous molecules.

2. Results and Discussion

Biotic transformation of pollutants was achieved by means of fungal laccases, extracellular monomeric glycoproteins, which belong to the group of the multirameic oxidase family. Laccases produced by fungi of the Trametes pubescens (Tp) and Coriolopsis gallica (Cg) species were tested on a wide range of contaminants of emerging concern since in the literature several studies that attest the particular effectiveness of laccases in the degradation of aromatic substrates, in particular proton donors such as phenols or aromatic amines are reported [2]. Excellent performances were obtained in the abatement of Bisphenol A, 2,4-dichlorophenol, 2,4,6-trichlorophenol, acetaminophen and triclosan and good results, albeit with longer half-life, were gained for fenoterol and chlorotetracycline. Experiments were performed on single target molecules and on their mixture, using the laccases one at a time and simultaneously in order to evaluate a possible synergistic effect deriving from different secondary metabolites that trigger the oxidation cascade. No substantial changes were recorded varying conditions, although Tp laccase showed a slightly higher efficiency. Once these preliminary results were obtained using small volumes, a scale-up of the process was carried out using larger volumes, in order to approach the real conditions of use of laccases in the aquaculture field. The increase of utilized volumes did not lead to a worsening of the degradative capacity of the laccases, on the contrary, results consistent with the preliminary ones were obtained. However, the biotic process is not sufficiently efficient for the abatement of odorous molecules and heavy metals.Therefore, ZnO-based photocatalysts with enhanced absorption in the visible region were tested on these classes of pollutants, in particular on Geosmin, MIB, mercury and other recalcitrant CECs (benzotriazole, diclofenac, sulfamethoxazole and bisphenol A). Pristine ZnO, Ce-doped ZnO and Ce/Cu-doped ZnO were synthetized via hydrothermal route and their efficiency was tested using a Solarbox ($\lambda>340$ nm) that simulated the solar irradiation on solutions containing the three individual classes of analytes and on a mixture of them. CECs were analyzed by HPLC-UV, mercury was detected by ICP-OES analyses, whereas a solid phase micro extraction (SPME) method combined with gas chromatography-mass spectrometry (GC-MS) was developed for the analysis of odorous compounds. A medium polar SPME fiber Divinylbenzene/Carboxen/Polymethylsiloxane was used and extraction conditions such as extraction time, sample volume and temperature were optimized. Results showed a good efficiency of all catalysts, in particular of CeO_2-ZnO heterojunction impregnated with Cu_2O thanks to the better spatial separation of the photoinduced charge carriers, with consequent enhancement of the oxidative process carried on by holes [3].

Interestingly even better performances were obtained when the degradation of the mixture containing CECs, mercury and odorous molecules was performed, in comparison to those achieved for single analytes making the process suitable in real conditions.

3. Conclusions

Biotic and abiotic processes were explored for the abatement of pollutants, typically present in the water exploited in aquaculture. Biological treatment with fungal laccase was not efficient for the degradation of odorous molecules, Geosmin and MIB, but provided good results as regards the abatement of different types of CECs: antibiotics, drugs, antibacterials and plastic components. Conversely, a more promising approach for achieving the degradation of odorous molecules together with PTEs is constituted by co-doped photocatalysts. In the perspective of a real application in an aquaculture plant, the two processes could be coupled and enzymes and photocatalysts could be supported on materials such as membranes or hydrogels to produce self-standing systems.

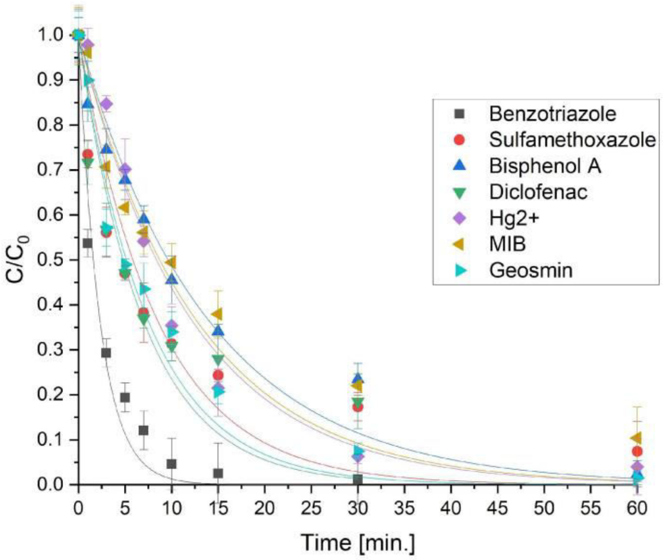

Figure 1. Contaminants degradation achieved by photocalyis with CeO_2-ZnO heterojunction impregnated with Cu_2O.

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OP42

STUDY OF THE EVOLUTION OF THE ANTHROPOGENIC IMPACT ON THE TRASIMENO LAKE (CENTRAL ITALY) USING LEAD ISOTOPIC RATIOS AND TRACE ELEMENTS CONCENTRATIONS

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1. Introduction

Freshwater ecosystems are known to easily accumulate chemical species produced by surrounding anthropogenic activities. Therefore, the lake's sediment cores can be used to reconstruct the history of the local pollution. [1,2]

In particular, it is documented in different studies that anthropogenic pollution is an important input of trace elements into the environment [3,4] and they can have a relevant impact on local basins.

Lead is considered a good indicator for human-derived pollution since it is emitted by several kinds of anthropogenic activities and, once it is embedded with a natural matrix, just as sediments, it easily becomes immobilized. Since anthropogenic pollution sources have a different lead isotopic composition compared to an uncontaminated soil, sediment cores can be used to investigate the modification of the human impact on the environment over the decades. [5]

The present work is focused on the Trasimeno Lake, located in Central Italy, which has been severely affected by human activities in the last decades; this resulted, since the beginning of the 20th century, in a modification of its hydrological status.

2. Results and Discussion

In this study, three deep sediment cores were sampled (C1, C2 and C3) from the Trasimeno Lake in 2007, respectively in the northern, central and southern area of the lake, in order to assess the history of the past anthropogenic pollution. It was estimated, in fact, that these cores were representative of the last 150 years, from 1850 to 2007.

Sub-samples were obtained after extruding and cutting the cores every 1 cm in the first 30 cm, and every 2 cm for the lower part. These sub-samples underwent homogenization and acid digestion and were then analyzed. The quantification of major and trace elements was carried out, for all of the cores, using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Ultima 2, HORIBA Scientific): in addition, for the central core (C2), the lead isotopic composition was measured using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS QQQ, 8900, Agilent). [6]

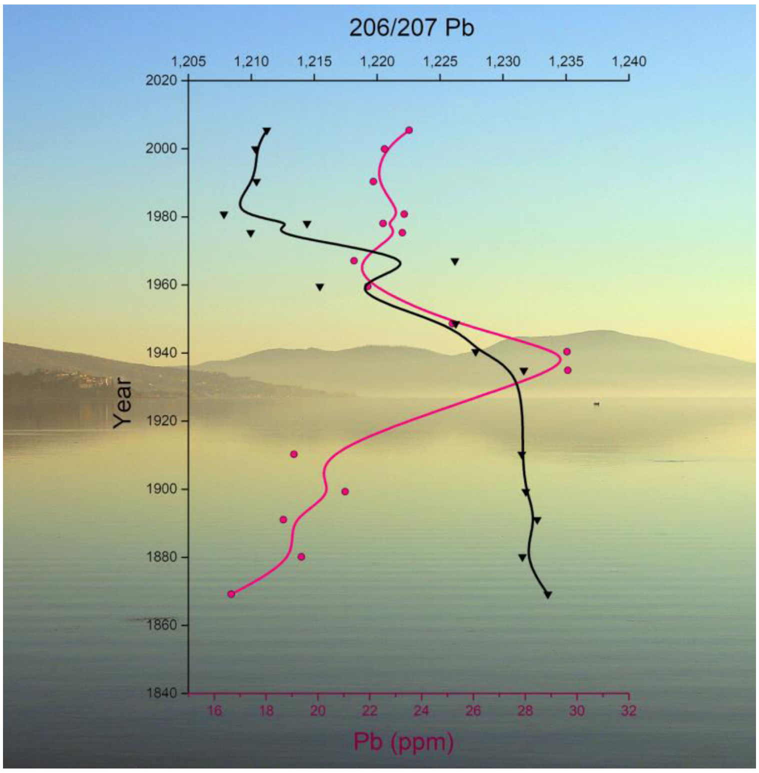
The central lake core was the one with highest concentrations compared to C1 and C3, which is an effect probably due to the different sedimentation rates of the lake and the distance from the shore. Nevertheless, the trends for most of the metals were overall similar between the cores. Some of these elements' trends* presented an evident peak in concentration corresponding to the years going from 1930 to 1945. Since the metals involved were, respectively, V, Cr, Zn, Co, Ni and Pb, an industrial source was hypothesized. This observation was confirmed by the fact that the "Società Aeronautica Italiana" (SAI) moved an air-plane industry to Passignano, located nearby the lake in this same period, and by the increase of productivity derived by the beginning of the Second World War. While the other elements' concentrations decreased after the peak, lead slightly increased again after 1960, which is probably due to the use of leaded gasoline.

Looking at the results obtained for the 206/207Pb isotopic ratio, the impact of human activities on the lake became clear. In fact, even though there is a great variability between the isotopic signature of soils coming from different areas [7], it has been demonstrated that the values of that particular lead isotopic ratio is always lower in contaminated samples compared to uncontaminated ones; in the central core of the Trasimeno Lake, the 206/206Pb ratio evidently decreased in correspondence of the peak in lead concentration. Moreover this isotopic ratio, presents a minimum around 1980, connected to the use of lead as additive to the oil, followed by a modest increase in the last few decades.

3. Conclusions

Three sediment cores were sampled in the Trasimeno Lake in Central Italy in order to investigate the anthropogenic pollution that occurred in the last 150 years. Trace and major elements were quantified and lead isotopic ratios were measured in order to investigate the evolution of anthropogenic pollution in the area.

The results showed a clear impact of the local human activities, with a strong peak dated 1930-1945 for V, Cr, Zn, Co, Ni, Pb, connected with an air-plane industry during World War II and a minor increase in lead concentrations after 1960 linked to the use of leaded gasoline. The anthropogenic impact on this natural system was confirmed by the values of 206/207 Pb: this value dropped in the same moment in which the concentrations of the metals increased.



Trends of lead concentration (pink) and 206/207 Pb isotopic ratio (black) versus time.

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OP43

TAILORED UV-BASED PROCESSES FOR THE DEGRADATION OF FLUORINATED ORGANIC POLLUTANTS IN REAL CONTAMINATED GROUNDWATER

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1. Introduction

Per- and poly-fluoroalkyl substances (PFAS) include over 4700 fluorinated aliphatic compounds used in a wide variety of commercial products and industrial applications [1]. Current knowledge shows that most of PFAS are persistent under environmental conditions, thus posing concern regarding their bioaccumulation.

Among the PFAS removal technologies, granular activated carbon (GAC) filtration is the most effective technology operating at full-scale in drinking water treatment plants (DWTPs) but, because of the complex adsorption mechanisms of PFAS on carbon-based materials, GAC must be replaced frequently with very high operative cost. In addition, it has to be pointed out that the use of GAC is not environmentally friendly because it allows the mere transfer of the PFASs from one matrix to another without destroying them.

In the present work it was investigated the effectiveness of UV-based processes that already showed promising results, to transform long-chain PFAS, short-chain PFAS and fluorinated harmeless derivatives. Specifically, it was investigated i) photolysis by vacuum ultra-violet (VUV), ii) photocatalysis (PC) and iii) photoelectrocatalysis (PEC).

2. Results and Discussion

Real contaminated was sampled from those Veneto area where it is well known that the PFAS contamination is still present. Analyses, carried out by liquid chromatography interfaced to high resolution mass spectrometry also employing an online preliminary step of solid phase extraction, revealed that the concentration of C4-C10 organic fluorinated acids as well as organic fluorinated sulphonates ranged between 7 and 2090 ng/L.

Experiments with VUV were carried out with a 7 L lab-scale reactor equipped with an excimer lamp of 200 W emitting at 172 nm. PC and PEC experiments were performed with a 1 L lab-scale reactor equipped with a low pressure UV lamp emitting mainly at 254 nm but also having a lower emission at 185 nm. Detailed description of the employed set-up is reported elsewhere [2]. In brief, PEC synergistically combines electrochemical phenomena with heterogeneous photocatalysis. Upon suitable irradiation of a semiconductor catalyst, electrons in the valence band are excited to the conduction band, leaving holes in the valence band which will be responsible for the direct or indirect oxidation of organic species. The catalyst is immobilized on a conductive anode, thus the electron-hole recombination, which usually hampers PC processes, can be minimized by the application of the electrical bias which brings the electrons to the cathode. This mechanism increases the photocatalytic efficiency of the supported semiconductor, up to the point of over-performing dispersed catalytic powders preferentially used in PC and photolysis.

Experiments with VUV showed that the process is able to remove most of the PFAS present in the contaminated groundwater. Specifically, the fluorinated pollutants that were easily removed were the long-chain acid ones while the short chain sulphonated ones were removed only to a very limited extent.

The results obtained with PEC were slightly better. Specifically, the investigation showed that 61.7% of initial PFOA was degraded in 2 h by 185 nm VUV light. Pseudo-first-order kinetics well simulated PFOA degradation and defluorination and main fluorinated products were detected by the employed analytical technique. Several fluorinated carboxylic acids consecutively formed and further degraded with irradiation time, suggesting that the starting pollutants are initially decarboxylated by 185 nm light and the radical thus formed reacts with water to form shorter-chain fluorinated carboxylic acids with one less CF2 unit.

Overall, such tests demonstrated that (see Fig.1) total PFAS concentration was reduced by more than 60% (from 2500 to 914 ng/L) by PEC combined with H2O2. According to Acque Veronesi, which has been testing several technologies to remove PFAS including ozonation + UV, this was the first time that AOPs significantly reduced the concentration of PFAS of Lonigo groundwaters.

3. Conclusions

The present investigation demostrated that UV-based processes can be usefully employed for the remediation of PFAS in real contaminated groudwater. further investigation is needed in order to get information about the scale-up of the process (initially at a pilot scale stage). Such a step would allow to acquire information about the operative costs of the processes.

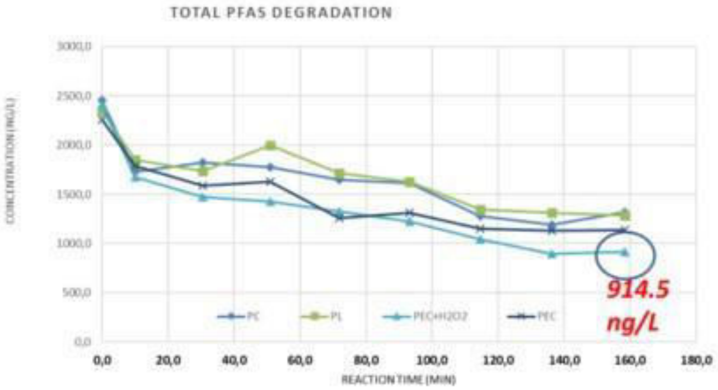

Fig.1 – Degradation of L-PFOS in real contaminated groundwater by UV-based processes.

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OP44

MICROPOLLUTANTS OCCURENCE AND TRASPORT IN TICINO VALLEY GROUNDWATER: A CASE STUDY

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1. Introduction

The present study is part of the wider project funded by Lombardy Region "Research and Innovation Hub" namely "CE4WE – Circular economy for Water and Energy" and aimed to the assessment of the ground waters quality along the Ticino Valley between Abbiategrasso (Milan) and Vigevano (Pavia). This higly populated area supports many agricultural and industrial activities, thus it is a good model to evaluate the anthropogenic impact in terms of traditional and emerging pollutants occurrence and the role of aquatic environment as a potential reservoir for spread and evolution of antibiotic resistance genes [1]. Indeed, micropollutant are naturally or synthetically substances that enter the environment through different pathways, e.g. pesticides applied on agricultural fields, pharmaceuticals and personal care products used every day by humans and not completely abated by wastewater treatment plants [2,3]. The main goal of this work is to investigate the occurrence of a selection of inorganic and organic pollutants to individuate a spatial marker for a field case study coupling hydrochemical, isotopic and microbiological approaches.

2. Results and Discussion

Water samples from 14 natural (risorgive) and 9 artificial (fontanili) springs, 6 wastewater treatment plants (outlet), and 2 (upstream and downstream) Ticino River, were collected in two periods according to the phases of rice cultivation (September 2020 and March 2021). All samples were characterized according to the main physico-chemical parameters and the results highlighted a distinction between ground waters sampled near or far wastewater treatment plants.

$\delta^{18}O(H_2O)/\delta^{2}H(H_2O)$ isotope analyses were carried out on the spring samples to determine their origin, while $\delta^{18}O(SO_4)/\delta^{34}S(SO_4)$, and $\delta^{18}O(NO_3)/\delta^{15}N(NO_3)$ to get information about the source of sulphates and nitrates. Trace elements analyzed in ICP-MS did not show significant difference in distribution between the sampling points.

The most representative organic micropollutants were selected from the literature [2,3] and based on anthropic activities present in the area. The main classes selected were: pesticides, natural and synthetic steroid hormones and antibiotics belonging to cephalosporines, fluoroquinolones, sulfonamides, macrolides, tetracycline and diaminopyridines. The heterogeneous set of micropollutants required different extraction procedures and analytical conditions, thus specific analytical methods based on solid phase extraction and liquid chromatography tandem mass spectrometry analysis were developed for the quantitative analysis of the selected organic pollutants of each class. All the methods were evaluated based on the main figures of merit (accuracy, linearity, method detection and quantification limits).

Generally, most of the investigated contaminants were found in concentrations from a few ng/L to hundreds ng/L. However, Glyphosate and its metabolite AMPA (belonging to the class of pesticides) were observed in the highest concentrations in our research, achieving up to µg/L levels in some sampling points.

The most frequently detected (60% samples) pesticide was Tricyclazole, a fungicide specially used in the prevention and control of rice blast, although banned from 2016. It is possible to witness that samples from the second campaign (March 2021) highlighted both the presence of a greater number of quantified pesticides and a higher frequency of finding, probably ascribable to different patterns of use in the different seasons.

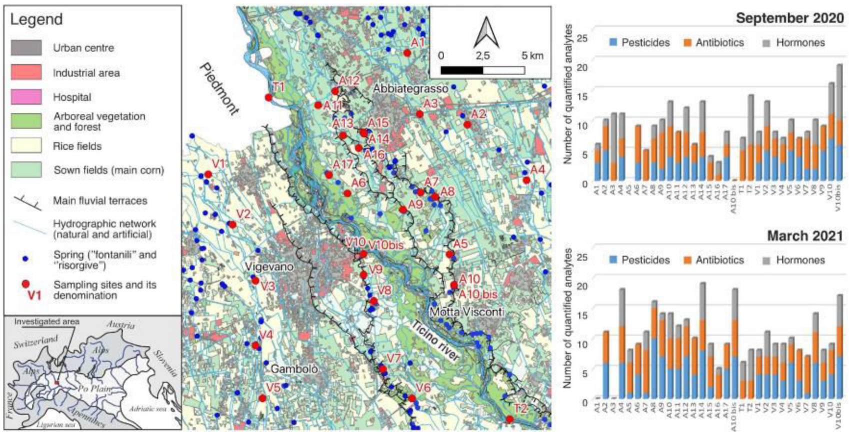
Among steroid hormones, the most frequently detected (~45% samples) was the glucocorticoid Dexamethasone.

The results of these monitoring campaigns highlighted the ubiquity of Trimethoprim together with a recurrent presence of fluoroquinolone antibiotics in all sampled sites. Moreover, the antibiotics were the most detected class of organic micropollutants in the samples of both campaigns, as pointed out in the figure. In fact a high microbial load was found in both campaigns, in particular in those sampling sites close to wastewater treatment plants. In each campaign more than 200 Gram-negative isolates have been identified with Klebsiella spp., Escherichia coli and Citrobacter spp. as the most frequent. The highest resistance levels were detected for broad spectrum penicillins and III and IV generation cephalosporins. In addition, at least the 25% of Klebsiella spp. and Escherichia coli isolates resulted multidrug-resistant (β-lactams, fluoroquinolones, aminoglycosides and trimethoprim/sulfamethoxazole).

3. Conclusions

Although this study shows a snapshot of the contamination in a well-establish area, it contributes to improve the knowledge of the occurrence of multiple classes of micropollutants in a highly urbanized, industrialized, and agricultural area of the Northern of Italy.

The results show that concentration of the measured compounds in this area is generally low (few ng/L) with a few exceptions (Glyphosate and AMPA, two widely used herbicides, up to µg/L). The occurrence of antibiotics at most sites, although at very low levels, is of environmental and public health concern due to the problem of antibiotic resistance, as highlighted by the results of the microbiological investigation.



Site plan with sampling sites and micropollutants' distribution chart

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OP45

CHARACTERIZATION AND MONITORING OF UV FILTERS IN SUNSCREENS BY VOLTAMMETRIC METHODS

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1. Introduction

Sunscreens are useful since they protect the skin against radiations, which may be responsible for harmful photochemical reactions to the body. Sunscreens involve the use of appropriate sun-blocking agents. In particular, ultra-violet filters (UVF) are inorganic and organic chemicals used to attenuate the negative effects of sunlight exposure on both human skin and synthetic materials. In order to enhance the sun protection factor values, several combinations of UVF are used, so their total concentration in the final products increases. Organic substances containing chemical groups that can filter UVA and UVB radiation are used as active ingredients of sunscreen formulations. Some of those approved in the manufactured formulations are octocrylene (OCR) and 2-Hydroxy-oxybenzone (BENZO-3) [1]. However, some chemical sun-blocking agents can be almost as damaging as UV radiation itself, making the effects of some sunscreens questionable and are considered as contaminants of emerging concern (CEC). Despite many organic UVF are electroactive, only few papers reporting electrochemical methods for their determination are reported [2].

2. Results and Discussion

In this context, the present work aims at evaluating the applicability of voltammetry to monitor sunscreen quality and composition. The sunscreens under study were purchased in pharmacies and supermarkets in the province of Turin. Carbon Paste Electrodes (CPEs) have been obtained by mixing an aliquot of graphite powder and an aliquot of each sunscreen were used to test the resistance of creams to exposure to sunlight using a solar box. The redox anodic and cathodic profiles of each sunscreen embedded in the paste were recorded by square wave voltammetry (SWV). The voltammograms of each sample were recorded just after opening the cream vessel and after 1h, 3h and 5h of exposure in the solar box. Some modifications in the redox profile at different times was observed; in particular, a significant decrease of the peak intensities was observed. Also, the stability of a standard OCR in seawater exposed to sunlight for several days was tested, in comparison with another aliquot of the same sample solution stored in the dark and in the fridge. A rapid decrease in the peak of the OCR for the sample exposed to the sun was observed.

In the second part of the work the possibility to apply voltammetry to monitor and to quantify the concentration of some sunscreen agents was tested. For this purpose, a Glassy Carbon Electrode (GCE) was used. Different solutions were used as supporting electrolyte (NaCl) and a buffer (Britton-Robinson). Suitable experimental parameters were identified and the linearity, the repatability, the detection limit, and the accuracy were determined. Then, the applicability of the proposed technique for the determination of UV-filter residues in seawater was evaluated. In this case, aliquots of seawater were spiked with different amounts of products, and the standard addition method was used to quantify sunscreen agents (for example, octocrylene) as shown in Figure 1.

3. Conclusions

The results obtained demonstrated the good applicability of voltammetry for the quality control of sunscreens and for their monitoring in seawaters. In particular, this method coupled with the use of portable instrumentation could permit the application of the technique for on-site analysis. The proposed methods is easy, fast and quite cheap if compared with other official techniques.

Our technique could be used as a screening for the presence or absence of UVF in different environmental matrices, as for example seawater, lake water and solar cream.

The next steps of the work concern the further optimization of the method, the analysis of other UV filters and other types of matrices, and an increase in the number of samples analyzed.

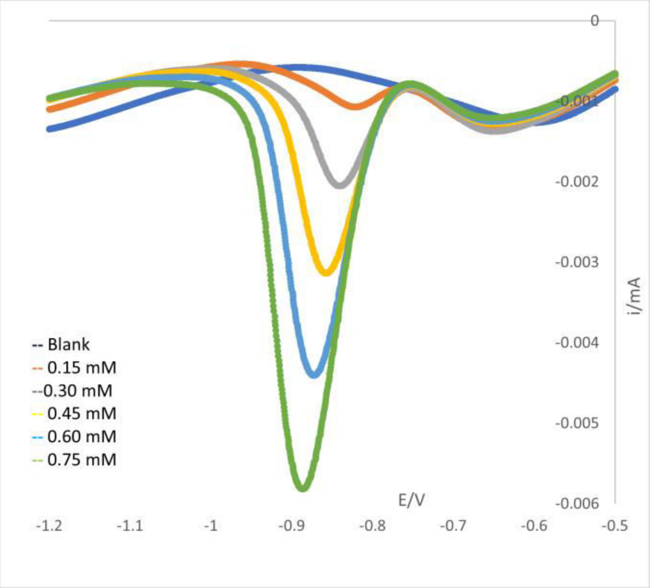

Figure 1. Standard additions (0.15 mM each) of octocrylene in a seawater sample.

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OP46

HPLC-HRMS CHARACTERIZATION OF TRANSFORMATION PRODUCTS OF DROPERIDOL INDUCED BY TiO_2 MEDIATED PHOTOCATALYSIS AND THEIR QUANTITATION IN WATER SAMPLES

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1. Introduction

The “Direttiva Quadro delle Acque” 2000/60/EC states that “water is not a commercial product like any other, but a heritage that must be protected, defended and treated as such” [1]. The evaluation of environmental pollution is therefore of fundamental importance [2]. Pharmaceutical Active Compounds are drugs for human or veterinary use, while personal care products are mainly used to improve the quality of daily life. These two categories are merged into pharmaceuticals and personal care products (PPCPs) and are classified as emerging contaminants (ECs) [3]. The presence of PPCPs in the environment leads to the progress of studies regarding their toxicity and the environmental fate of both parent compound and its metabolites and transformation products (TPs). The research and characterization of TPs of ECs are then required and a valid tool to obtain these goals are the application of photocatalysis mediated by semiconductor such as TiO_2 and high resolution mass spectrometry [4, 5]. The aim of the presented work was the development of a HPLC-HRMS method for the identification and characterization of TPs TiO_2 induced of the drug droperidol and the application of the method to water

2. Results and Discussion

The identification and characterization of the TPs of droperidol induced by heterogeneous photocatalysis mediated by TiO_2 were performed using as instrumentation an HPLC (Ultimate 3000 Dionex, Thermo Scientific) coupled through an ESI source with an Orbitrap Tribrid Fusion (Thermo Scientific) high resolution mass analyzer.

A Philips (Monza, Italy) TLK/05 lamp (40 W/m2) with maximum emission at 340 nm was used to execute irradiation experiment. The lamp irradiance over the irradiated solutions was around 30 W/m2 in the wavelength range of 290−400 nm (measured with a powermeter from CO.FO.ME.GRA., Milan, Italy).

An aqueous suspension of droperidol (20 mg/L) and TiO_2 (200 mg/L) was placed in a Pyrex glass cells and irradiated at different times with a temperature of 25±2 °C. The irradiation times were: 0, 5, 10, 15, 30, 60, 80, 100, 120, 140, 160, 180, and 360 minutes to follow the decrease of the droperidol concentration and the TPs formation during the treatment.

We started testing four different columns (reverse phase C18, biphenyl and pentafluorophenyl, and HILIC) to obtain the better characterization of TPs. Although the biphenyl column gave the best results for signals intensity, the classic C18 chromatographic column arose to the identification of the higher number of TPs, included several isomers.

In the same way, we tested the polarity of ionization mode of the ESI source and we found that the positive ionization mode gave the superior signal intensity for droperidol and many TPs. However, we also used the negative ionization mode to detect TPs able to easily lose protons.

The high resolution mass spectrometry analyzer was used to identify the TPs with a resolution of 60K for full mass spectra and of 50K for tandem mass spectra. As usual, we started with the characterization of the fragmentation pathway of the parent compound, droperidol, and then we tried to identify the structural formulae of the TPs. With the developed method we identified and characterized 28 TPs (17 ESI+ and 11 ESI-), most of them showing multiple isomers.

Under photocatalytic conditions, droperidol was almost completely degraded within 120 min following a pseudo-first order kinetic decay. The remaining concentration after this time was 0.21% of the initial one.

Most of the characterized TPs showed kinetics similar to droperidol and disappeared after 120 min of treatment. Instead, the higher concentrations of TPs were found after 5 or 10 minutes of photocatalysis.

The next phase for the characterization of the environmental fate of droperidol involved the analysis of water samples from Po and Reno rivers. After setting up an SPE procedure with Bond Elut PPL cartridges (Agilent), 10 river water samples were analyzed from 7 sampling points searching for parent compound and TPs. The parent compounds were identified in samples by retention time, accurate mass (mass error <5 ppm) and MS2 spectra. Droperidol was found in all samples except for one. The average concentration of droperidol (recovery 70%) in the samples was 0.17 ppt in 500 mL of water. Four TPs were identified in water samples with a concentration always at least one order of magnitude lower than the mean droperidol concentration.

3. Conclusions

The developed HPLC/HRMS method was effective both for quantitation of droperidol (targeted analysis) and identification of its transformation products (untargeted determination). The high resolving power of the orbitrap allowed to identify the accurate mass of specific neutral losses of the molecules and to hypothesize the structural formula of newly formed products. 28 TPs of droperidol were identified and tentatively structural characterized. The method was then applied to real water samples coming from two Italian rivers, Po and Reno. The compounds were quantified in environmental samples with high sensitivity.

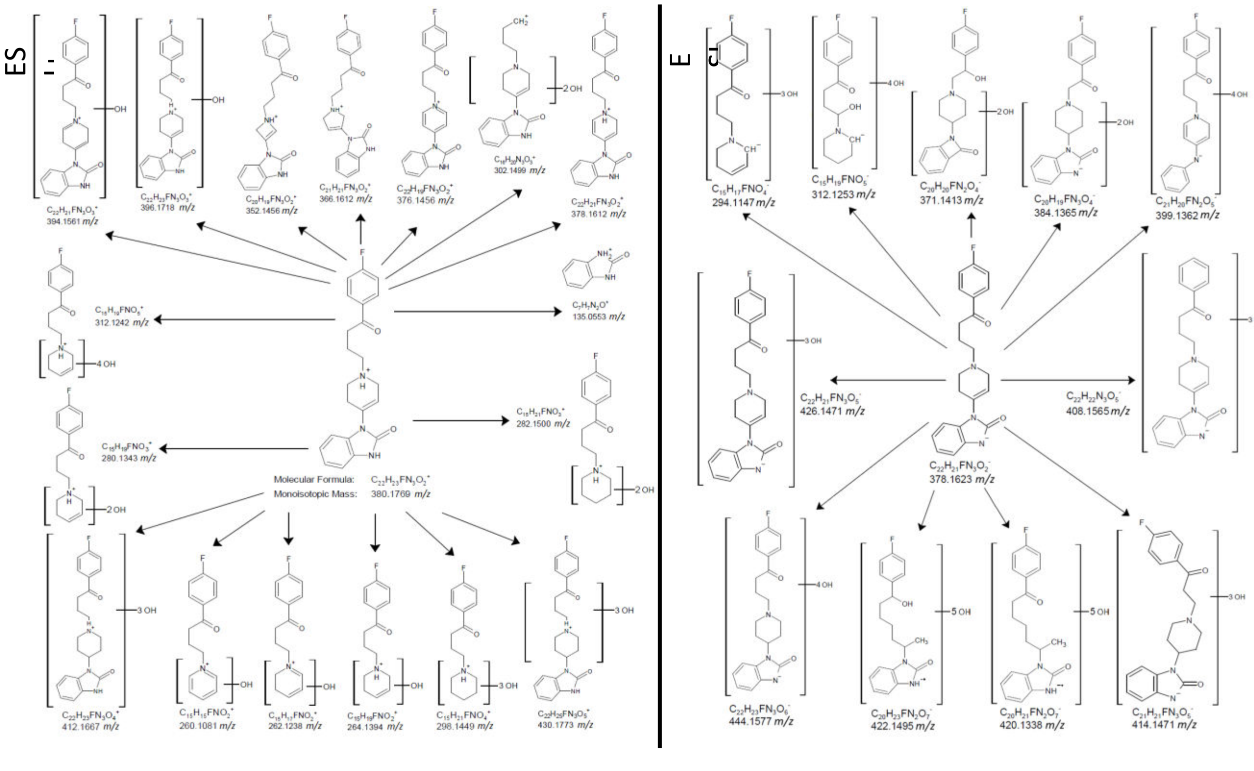

Figure 1. Scheme of droperidol TPs detected in positive (ESI+) and negative (ESI-) ionization modes.

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OP47

RELEVANCE OF A LOCAL ENVIRONMENT FOR ASSESSING TOXICITY IMPACTS OF CHEMICAL EMISSIONS IN USETOX

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1. Introduction

Nowadays the environmental problem most feared by our society and, in particular, by the new generations, is climate change. The effects of climate change are visible on global scale, but if attention is shifted to local-scale effects, chemicals (and plastics) pollution is of greatest concern to people.

The Life Cycle Assessment (LCA) methodology provides a quantification framework to assess the damage caused by chemical emissions on ecosystems, through characterizing chemical emissions in terms of their multimedia fate, human and ecological exposure and toxicological effects.

However, the local dimension of damage on human and ecosystem health is not fully considered in the calculation models or limited to certain compartments (e.g. air in the urban scale).

The aim of this study was to develop an assessment model to provide an answer to citizens and public administrations about damage on human health and ecosystem caused by local emissions that occur near settlements. This was achieved by introducing a local scale into USEtox 2.12, the UNEP/SETAC scientific consensus model for characterizing human and ecotoxicological impacts of chemical emissions in life cycle impact assessment.

2. Results and Discussion

The relevance of the local scale, i.e. a small scale box with an extension of 1 x 1 km^2 nested in a continental box and including the point of ground-level emissions in air, water natural soil and agricultural soil compartments and an exposed population of 4166 people, was assessed in terms of damages on human health and ecosystem health, based on the assumption of well-mixed boxes. This assumption simplifies the comparison of magnitude of impacts with the other scales (mainly continental), but it is not intended to represent local phenomena that are better represented by appropriately spatialized models and flows.

The results are analyzed at two levels, by assessing the magnitude of the local and continental impacts in the modified USEtox model (called "USEtox local") and by assessing the relevance of the introduction of the local scale by comparing the total impact score generated by the "USEtox local" model, calculated by sharing a defined amount of emitted chemical between local and continental scale, with the impact score of the USEtox model, assuming the whole amount of chemical is emitted at the continental scale.

For the first analysis, considering an emission of 1 kg d^{-1} of benzene, chosen as reference chemical to explore the behavior of the newly introduced scale, the local scale always has higher concentrations for an emission in the same scale compared to the concentrations found in the continental emitting scale.

This result can be attributed to the smaller volume of the local scale, which maximizes the concentration of the incoming mass. The concentration increase range is more limited for air compartment (+ 5 orders of magnitude) compared to the other local compartments (+ 8 orders of magnitude for freshwater and + 7 orders of magnitude for soils), thanks to the effective removal via advection.

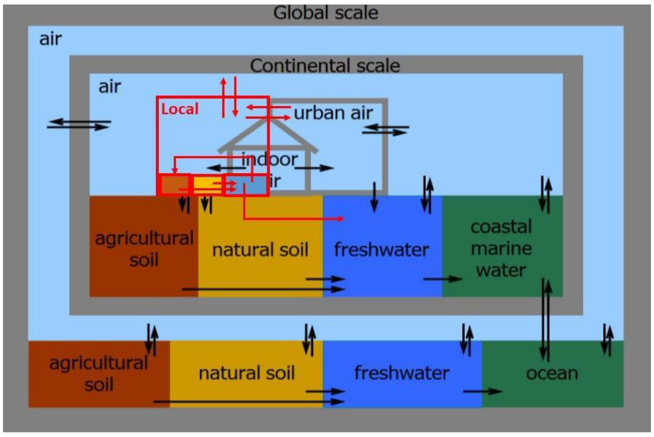
After evaluation of the exposure and effect according to the current framework of USEtox, the endpoint human health toxicity potential on all the receiving scales expressed in disability adjusted life years per kg emitted (DALY kg^{-1}) and the endpoint freshwater ecotoxicity potential on all the receiving scales expressed in potentially disappeared fraction of species multiplied with compartment volume and the chemical residence time per kg emitted (PDF m^3 d kg^{-1}) were assessed and compared for each emitting scale. Local emissions always produce the highest toxicity results, particularly for human health, where a more limited increase occurs for air compartment (twice the damage of the continental result) compared to the other local compartments (+ 2 orders of magnitude for freshwater and natural soil and + 1 order of magnitude for agricultural soil).

In the comparison between the two models, in a first scenario of unit emissions, the "USEtox local" impact score (IS) by 1 kg d^{-1} emitted in the local scale and 1 kg d^{-1} emitted in the continental scale was compared to the IS of the USEtox model, taken as reference, where 2 kg d^{-1} were emitted in the continental scale.

Endpoint toxicity for human health shows a significant increase in these emitting conditions, ranging from +61% for air to +7150% for freshwater emissions, while ecotoxicity increase is less relevant for the local scale, i.e. not exceeding +7.6% (freshwater emissions).

3. Conclusions

Preliminary results about the assessment of local impacts compared to larger emitting scales were obtained by introducing a 4 compartments small scale into USEtox v.2.12. Considering a unit emission, the local scale results to be relevant in terms of damage, mainly due to the high concentration to which the local population and the ecosystem are exposed to. Limitation of this study is the absence of modeling of very local phenomena that could not be represented by the well-mixed box assumption. Moreover, real European amounts of chemical emitted should be considered in order to provide a realistic estimate of the relevance of local emissions, as well as a larger number of chemicals. The local compartments will be proposed for formal inclusion in the global consensus model USEtox.



Introduction of the local scale in USEtox. Image adapted from Rosenbaum et al. 2008

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OP48

INDOOR AND OUTDOOR AIR QUALITY IN TWO HIGH SCHOOLS OF SALENTO (SOUTH ITALY)

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1. Introduction

It is well known that children are more sensitive to air pollution than adults. In fact, children are constantly growing and, in propotion to their weigh, they breathe more air. Moreover they spend large amounts of their time in school buildings, where they may be exposed to unknown levels of indoor pollutants[1].

In our study, results obtained by indoor and outdoor monitoring campaigns of Volatile Organic Compounds (VOC) performed in two high schools of Salento (Apulia region, South Italy) will be shown. One campaign was performed in Galatina municipality (Lecce province) from January to March 2019 and the other was performed in Squinzano, located in the suburban area of Lecce, from May to June 2019.

2. Results and Discussion

Passive VOC measurements were carried out using diffusive samplers in radial symmetry with adsorbent cartridges Rad 130 (Radiello® — Fondazione Salvatore Maugeri-IRCCS, Padova, Italia). The sampling time covered a 3-day period from Tuesday morning until Friday afternoon, and a 4-day period from Friday afternoon to Tuesday morning next week.

In the school located in Galatina, sampling indoor places investigated were: male bathroom, female bathroom, classroom 4B, classroom 4E, and external balcony of classroom 4E. In the school located in Squinzano the samplers were positioned in two bathrooms (female and male), classroom (4B) and an external site located on a lateral terrace.

The results highlighted that indoor TVOC concentrations were systematically larger than those outdoors, with a mean value of the I/O ratio equal to 1.41 for Galatina campaing. This suggests indoor pollutants sources. It is plausible to assume that the higher TVOC concentrations registered throughout the daytime school hours were due to student occupancy and poorly ventilated classrooms in the cold investigated period [2]. Toluene/Benzene ratio has been used to discriminate the different pollutants sources. Observing figure 1, the T/B ratios found at locations B1(bathroom), B2 (bathroom), and 4B (classroom) are higher with respect to 4E (classroom) and the outdoor site. For site 4B, for which the ratio is higher than 1, a possible contribution from outdoor traffic is plausible, while for 4E and O4E sites cigarette smoke emission can be plausible, as detailed in Ielpo et al. 2021 [2]. Differences and similarities between the two schools will be discussed.

3. Conclusions

The results suggest some recommendations to protect the students' health: increasing ventilation in classrooms during school activities, and after cleaning; limiting smoking activities in bathrooms, and also possibly in outdoor spaces; involving students in discussions regarding the use of acrylic paints, permanent markers, perfumes and deodorants, with a suggestion to limit the use of these products indoors all together.

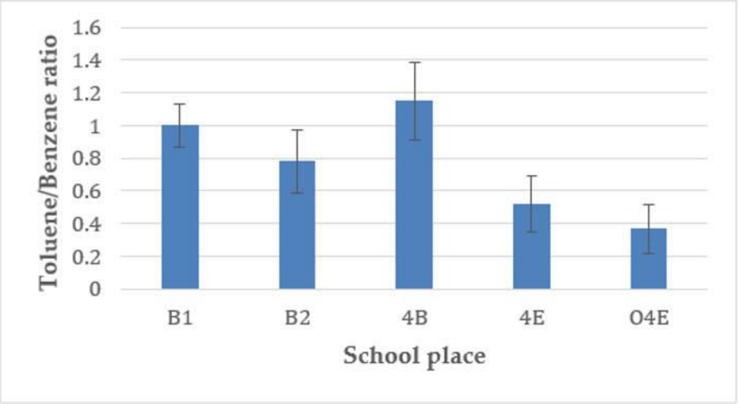

Figure 1. Toluene/Benzene ratio in the monitored areas of school located in Galatina.

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OP45

POLYMERS' IDENTIFICATION IN SPRAY PAINTS BY COMBINING MATRIX ASSISTED LASER DESORPTION IONIZATION MASS SPECTROMETRY AND SPECTROSCOPIC TECHNIQUES

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1. Introduction

A thriving research branch in analytical chemistry has been dedicated to the characterization of spray paints [1,2]. Py-GC-MS is mostly employed allowing the identification of alkyd resins as well as acryilic/styrene copolimers in real specimens collected from graffiti murals [2]. Matrix-assisted laser desorption/ionization-time of flight-mass spectrometry (MALDI-ToF-MS) is very suitable for polymeric matrices analyses [3]. Soft ionization processes prevent the fragmentation of oligomers, thus allowing the detection of intact chains. MALDI generally promotes single charging of the analytes thus facilitating spectra interpretation [3]. Despite these favorable features, application of MALDI to the analysis of polymeric binders in modern paint formulations is rare in scientific literature. The study herein presented is intended to develop a MALDI-ToF-MS methodology for the analysis of various polymer in spray paints. Acrylic spray paints of two brands were tested with different solvents and MALDI matrices to choose the best conditions for analysis.

2. Results and Discussion

First experiments were conducted on acrylic based yellow spray from brands Arexons and Ral. About 10 mg of painting film were tested for solubilization into 200 µL of different solvents: methanol, tert-butyl methyl ether (MTBE), ethyl methyl ketone (MEK), acetone, dimethyl sulfoxide (DMSO) and chloroform. Methanol and DMSO were ruled out because they were not suitable to solubilize the varnishes. Each sample was then tested for MALDI-ToF-MS analysis with different MALDI matrices, in positive or in negative ionization mode. The following matrix solutions were prepared for analysis in positive mode:

- (E)-2-cyano-3-(naphthalen-2-yl)acrylic acid 10 mg/mL in 95% acetonitrile and 5% H_2O;
- 1,5-Diaminonaphthalene (DAN) 5 mg/mL in methanol;
- Dithranol 20 mg/mL in 70% acetonitrile and 30% NaCl 2 mM;
- α-Cyano-4-hydroxycinnamic acid (CHCA) 10 mg/mL in 70% acetonitrile, 30% H_2O and 0.1% formic acid.

For negative mode analysis, other matrixes were used:

- 2′,4′,6′-Trihydroxyacetophenone (THAP) 10 mg/mL in H_2O:acetonitrile 1:1 (v:v);
- Dithranol 10 mg/mL in H_2O:acetonitrile 1:1 (v:v).

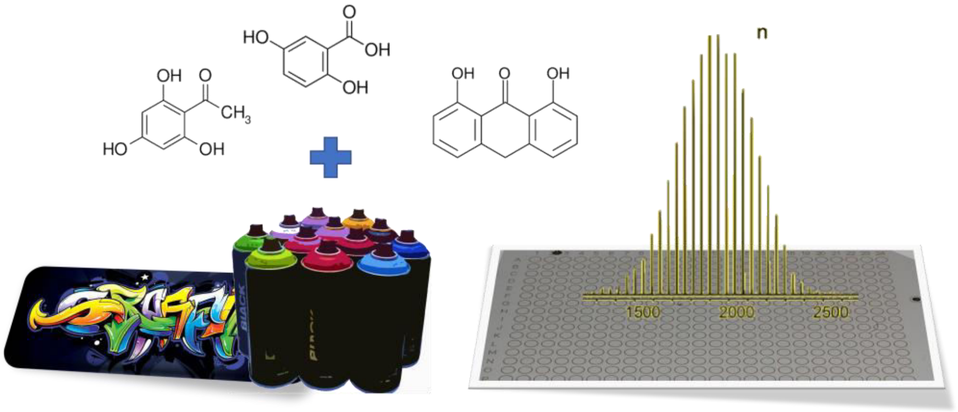
1 µL of a mixture of matrix:analyte 1:1 (v:v) was deposited on the MALDI plate and dried at room temperature. Analysis were conducted using a 5800 MALDI-ToF/ToF analyzer (AB SCIEX) equipped with a neodymium-doped yttrium lithium fluoride laser (345 nm), in reflectron mode as well as in positive and negative mode. Mass accuracy was 10 ppm. Mass calibration in the range 800 to 4000 m/z was performed using external peptide standards, namely adrenocorticotropic hormone, renin and angiotensin I. A typical value of 1000 laser shots were accumulated, at laser pulse rates of 400 Hz. Each mass spectrum was averaged upon the accumulation of at least five single mass spectra. Spectra were acquired between m/z 100-4000 and subranges of that interval. Both in positive and negative ionization mode, dithranol was found to be the most suitable matrix. Matrix (E)-2-cyano-3-(naphthalen-2-yl)acrylic acid proved to be inadequate since it generates interfering signals in the range m/z 100-1300. DAN appeared to be unable to promote oligomers ionization. By coupling dithranol with MEK or acetone as a solvent, spectra of polyethylene glycol (PEG), used as additive in the spray formulation, were obtained.

Yellow spray paints were also characterized with ATR-FTIR analysis using a Spectrum Two Perkin Elmer instrument provided with the universal ATR accessory and equipped with a diamond prism. Spectra were acquired in transmission mode in the range 4000–400 cm^{-1} with 4 cm^{-1} resolution and collecting 32 scans. Comparisons with database of ATR-FT-IR spectra of conservation-related materials in the MID-IR and

FAR-IR region [4] allowed the identification of polyethylmethacrylate/polymethylmethacrylate composition of Arexons spray and polystyrene/polymethylmethacrylate presence into Ral spray paints. These different outcomes demonstrates how the characterization of these polymeric matrices is challenging. In particular, MALDI MS seems to favor the ionization of more polar PEG oligomers; in this context, the use of specific dopants will be tested soon and X-ray photoelectron spectroscopy (XPS) analysis will be carried out

3. Conclusions

In this contribution we presented preliminary results of a MALDI-ToF-MS approach for the characterization of polymeric binders in spray paints. Different solvents and MALDI matrices were tested. First analysis shows the combination of dithranol, as matrix, and acetone or MEK, as solvents, to be the best condition for the PEG used as additive in the paint formulation. This work was supported by project Progetto di Ricerca di Interesse Nazionale—PRIN 2020MNZ579—"Sustainable Preservation Strategies for Street Art - SuPerStAr", financed by the Italian Ministero per l'Istruzione, l'Università e la Ricerca (MIUR).



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OP50

BIOLOGICAL AND CHEMICAL CHARACTERIZATION OF BRONZE AND MARBLE PATINAS TO STUDY TYPICAL BACTERIA COMMUNITY

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1. Introduction

Epilithic bacteria play a fundamental role in the conservation of cultural heritage materials. Bacteria communities are involved in both the degradation and protection of stones in several ways. Bronze biocorrosion in non-burial conditions is rarely studied. Only a few research studies examine the relationship between the bacteria community and the chemical composition of patina (surface degradation layer). The present study aims at: (1) characterise the bacteria community on bronze and marble statues; (2) evaluate the differences in bacteria community composition occurring between different patina types on different statues; (3) provide a representative bacteria community to be included in laboratory ageing tests for simulating the biological ageing. Biological and chemical characterization of different patina were performed by sampling bronze and marble statues in Bologna and Ravenna (Italy). Non-invasive sampling with sterile swabs was performed. DNA extraction, amplification of 16S rRNA gene, sequencing by Oxford Nanopore technology using MinION and data analysis by EPI2ME software were carried out. Chemical analyses were done via SEM/EDS and Raman spectroscopy.

2. Results and Discussion

To study the bacteria community living on different patina types on bronze and marble artefacts in outdoor conditions, characterization and evaluation of the bacteria community living were performed using a non-invasive sampling method and a metabarcoding approach.

Differences in environmental DNA concentration were clearly observed between the two materials: marble and bronze. Lower environmental DNA concentration was detected on bronze patinas likely due to copper and lead alloying elements. Indeed, bacteria characterization was achieved for all types of marble patinas except for the case of the greenish area of the marble basement interested in the leaching of copper from the above bronze artefact. Our findings highlight statistical differences in bacterial community structure between bronze and marble patinas, for all the considered biological indexes (total taxa richness, Margalef's index, Pielou's index and Shannon's index). Bronze patinas generally show less alfa diversity than marbles ones. No statistical differences in biological community structure were observed among bronze patinas. We note that bacteria communities, growing on both bronze patinas and green marble patinas subjected to copper leaching, are effectively known to be resistant to metal biocide effects. This may be the consequence of bacteria growth inhibition. No clear effects may be attributed to a different microclimate.

Indeed, the bacteria community on bronze is resulted mainly composed of only one phylum, Proteobacteria with the most abundant genus Methylobacterium (Fig.1).

Marble patinas are characterized by more complex bacteria composition (Fig.1) and are in line with other studies. Statistical differences were found between patina types within the same marble statues and between patinas belonging to different statues. All detected bacteria communities are in line with current climatic conditions because, especially for marble, show at both phylum and genus levels the presence of bacteria resistant to desiccation, high radiation level, wide and rapid temperature and moisture changes. The characterization performed in this work can help the identification of representative bacteria communities to be included in ageing laboratory tests to also consider the biotic factor in the study of the decay mechanisms in the Mediterranean areas. At the genus level, for marble patinas, the proposed bacteria community could be composed mainly of Aliterella, Gloeocapsopsis Truepera and Rubellimicrobium. For what concerns bronze surfaces, the proposed bacteria community could be composed mainly of Methylobacterium. Moreover, for marble we suggest to include also copper-resistant genera such as Roseomonas, Sphingomonas and Methylobacterium, in case the interest is in bacteria communities on marble artefact close to bronze one.

3. Conclusions

Highly statistical differences in bacteria composition between marble and bronze patinas and between patinas of the same material were found.

This study can find applications in cultural heritage conservation since it suggests a possible bacteria community composition to be applied in artificial ageing tests for CH in the Mediterranean and polluted areas. These are going to be integrated with future biological characterizations to get and provide biological communities more representative of different environmental conditions. This is necessary for the ongoing changes in climate and atmospheric composition, exacerbating the vulnerability of materials in outdoor conditions. These changes are determining higher degradation also via biological actions.

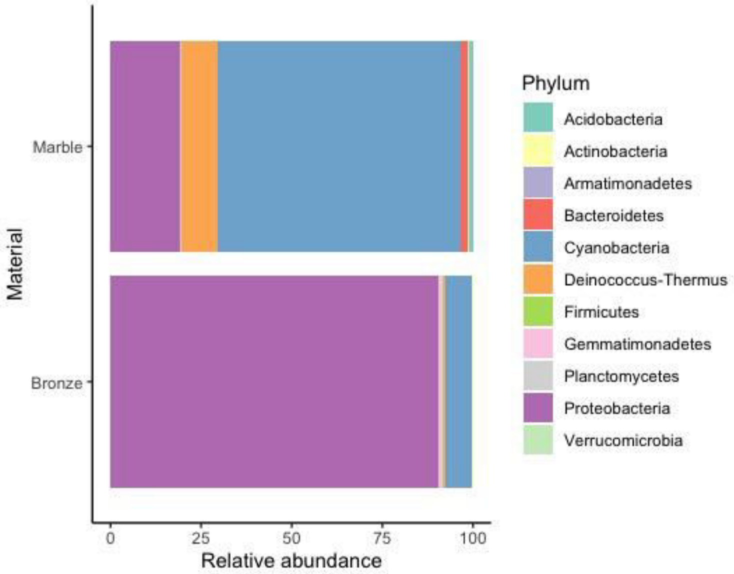

Figure 1. Bacterial abundance in Bronze and Marble statues at the phylum level.

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OP51

TREATMENT OF GREYWATER BY FOAM FRACTIONATION AND PHOTO-FENTON LIKE PROCESSES

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1. Introduction

Greywater (GW) is defined as wastewater produced from washing processes (shower, hand basin, dishwasher, washing machines and kitchen sink) [1] and it is considered an underutilized water source [2]. Among the different physical processes found in the literature for GW treatment, foam fractionation could be a rapid and cost-effective alternative for treating this matrix rich in surfactants and other foaming agents [3]. To guarantee an adequate GW quality standard a combination of physical, biological or chemical processes with a disinfection step is required [4]. Photo-Fenton like using Fe-IDS (iron iminodisuccinate) complexes as catalyst have not been tested for GW treatment and this innovative application could overcome some drawbacks of Advanced Oxidation Processes [5]. The aim of this work was to evaluate, for the first time, the efficiencies of the combination of foam fractionation and photo-Fenton like process Fe-IDS/H_2O_2/UV-C for GW treatment in terms of removal of organic matter as chemical oxygen demand (COD) and 5 days biochemical oxygen demand (BOD_5).

2. Results and Discussion

The foam fractionation process and photo-Fenton with Fe-IDS were tested for the first time for the treatment of GW. When the two processes were tested individually, a COD removal of 82.5% and 63.8% and a BOD_5 reduction of 43% and 50%, for foam fractionation and photo-Fenton like process were reached respectively. The foam fractionation process was found to be very efficient for greywater treatment in terms of COD removal, with a treatment time of 120 minutes. Also, important BOD_5 reductions were observed, which results in a considerable increase in the biodegradability of the final effluent, measured as BOD_5:COD ratio. Fe-IDS catalyst allowed to perform photo-Fenton process at circumneutral pH in 180 minutes, using a low amount of iron(III) and H_2O_2, with positive effects in terms of management costs. It should be noted that although IDS is stable during the process, it is biodegradable and self-degrades almost completely (96%) after 28 days. To reduce COD and BOD_5 to make the effluent in compliance with international standards for reuse of wastewater for non potable application, the combination of the two processes in series was tested (Figure 1). Removals of about 95% and 93.4% were achieved for COD and BOD_5 respectively. Subsequently UV-C radiation was replaced by solar radiation in the AOP to improve treatment sustainability both in economic and environmental terms. In this case there was only a little decrease in the efficiencies, in particular COD removal decreased from 95.3% to 89.5% while BOD_5 removal from 93.4% to 75.8%. To better evaluate the applicability of combined processes, a cost analysis was performed. It resulted in a unit cost for combined process with solar radiation (1.99 €/m^3) which is significantly lower than that for for combined process with UV-C radiation (15.33 €/m^3), making the solar driven solution the most sustainable and attractive option for a full-scale application.

3. Conclusions

In this study, the combination of foam fractionation process and photo-Fenton with Fe-IDS was tested for the first time in the treatment of greywater. Combined processes permitted to reach a GW quality in agreement with Italian regulatory limits for non potable water reuse. In particular COD and BOD_5 removals up to 95.3% (final value of 31 mg/L) and 93.4% (final value of 9 mg/L) were obtained. The replacement of UV lamps with sunlight allows to reduce operating costs from 15.33 €/m^3 to 1.99 €/m^3, thus the solar solution is the most sustainable and attractive option for a full-scale greywater treatment.

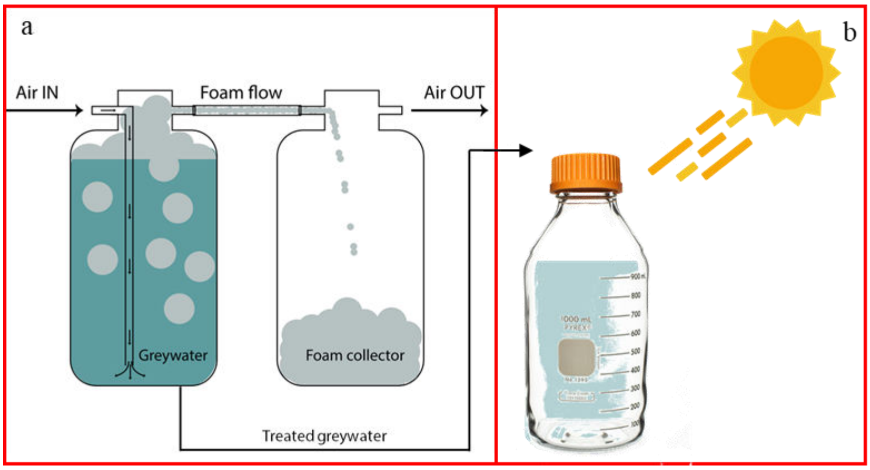

Figure 1. Schematic representation of the experimental set-up for solar driven combinated process.

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OP52

VERTICAL DISTRIBUTION OF HG IN SEDIMENT CORES OF THE WESTERN-CENTRAL AND SOUTHERN ADRIATIC SEA

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1. Introduction

Some trace elements (TEs) (e.g., Al, As, Ba, Bi, Cd, Pb, Hg, Ni, Pt, and Ag) are characterized by relatively high density, toxicity at low concentrations, environmental persistence and, in some cases, bioaccumulation processes. Therefore, they represent one of the most relevant anthropogenic impact in marine ecosystems (water, sediments and biota). Their presence in surface sediments is generally related to recent pollution phenomena and is influenced by the bottom water-column status, while the deeper part of the sediment cores are generally used to evaluate the historical trends. Mercury is considered a priority pollutant in marine environments according to Water Framework Directive 2013/39/EC (WFD) for its high toxicity and capability to interact with organic matter in the form of metilmercury and its bioaccumulation along the food chain.

For these reasons, total particulate Hg distribution has been studied in core sediments collected in the Central and Southern Adriatic Sea bottom. For further understanding of the depositional setting of the core sediments also geochemical and grain size parameters were determined.

2. Results and Discussion

Surface and core sediment samples (n=107 stations) were collected during the oceanographic cruise PERTRE, from 16 September to 4 October 2016, along the western central-southern Adriatic Sea (Fig. 1) by using a box corer. Details of the study area, sample collection and hydrographic parameters are reported in [1].

In these stations four cores (ST23, ST28, ST40, ST42; Figure 1b, 1c, 1d, 1e) have been selected for the analysis of the vertical profiles of Hg, Al and grain-size. Each core, about 25 cm long, has been sub-sampled for Hg and grain size determination with 0.5 cm resolution in the surface layers (0-4 cm) and with 1 cm resolution from 4-cm depth to the bottom. Hg was analysed by Direct Mercury Analyser (DMA) while grain size by X-Ray-sedigraph. Aluminium content, used as fine grain size indicator, was determined by XRF core scanner and expressed as clicks per second (cps), with a resolution of about 1 cm for the entire core length.

Grain size showed that the ST23 core mainly consists of silty-clay (clay% ~60%) while the ST42, ST40, ST28, collected in the southern part of the study area, are mainly clays (clay >75%). The vertical profile of the clay percentage remained almost constant within each core but varied in the different stations.

The four cores showed different Hg concentrations, ranging from0.136 mg/kg (St23) to 0.022 (St40), with a mean value of 0.074 mg/kg. Hg content decreases from around 15 cm to the bottom depth with different percentages (from 20% to 50%) depending on the site and depth (Figure 1). A Hg north-south gradient was recognised with concentrations decreasing from 0.12 ± 0.02 mg/kg at the ST23 to 0.04 ± 0.01 at ST40. In any case, all Hg values were well below the sediment's Hg Environmental Standard Quality (EQS) included in the WFD (0.3 mg/kg). Aluminium showed a general decreasing with depth suggesting a changing of the continental inputs probably due to the decreasing of the solid loads of the Italian rivers and their trapping in the coastal area for the protection works in the last decades. In the St23 core a correlation between Hg, Al and Clay is evident ($r \geq 0.7$). This is connected also to the higher Hg content in the St23, probably related to northern anthropogenic sources of pollution. The Hg content tends to decrease southward due to the dilution effect of the southern sedimentary processes and inputs. St40 core, as well, showed a strong association between Hg and Al (r=0.76), enlightening the fact that Hg tends to accumulate in the finest fraction of the sediments.

Further investigations including sediment dating are necessary to understand the vertical Hg distribution and the North-South gradient, thus better understanding possible anthropogenic inputs from the last industrialized periods.

3. Conclusions

In the present work preliminary results on the total particulate Hg concentrations, Al content and grain size were reported for four cores of the western central-southern Adriatic Sea. All samples showed Hg concentrations well below the limit of 0.3 mg/kg indicated by the WFD 2013/39/EC.

Hg concentrations increased in the surface layers of the sediment cores, probably due to the increasing anthropogenic input of the last decades.

A North-South decreasing gradient of Hg values can be observed, following by the higher anthropogenic inputs of Hg in the northern part of the Adriatic Sea.

During the last 10 years Al content increased, due to the recent large-scale river and coastal anthropization and also decreasing rainfalls which affect the riverine outflows and marine sediment dispersal.

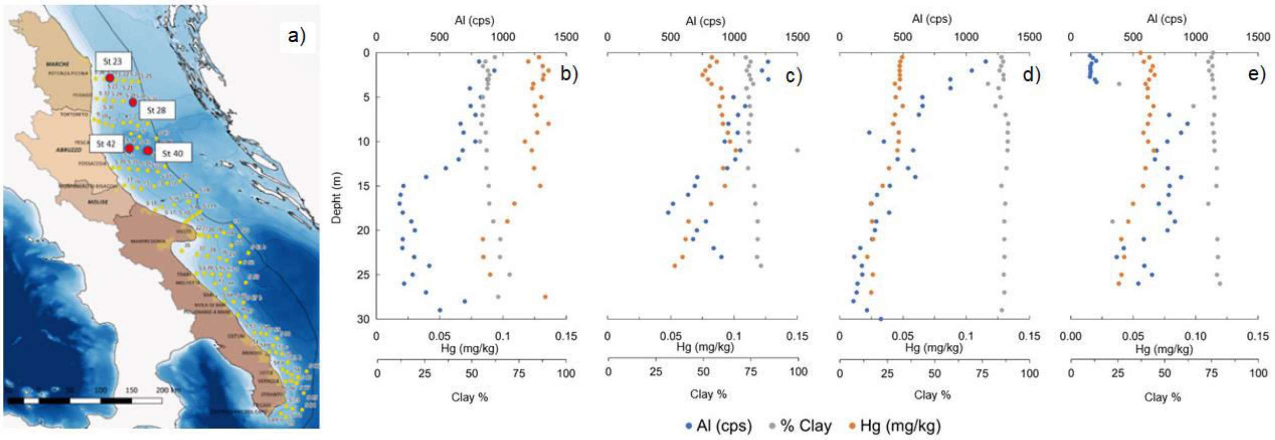

Figure 1. a) Map of the study area and profiles of Clay, Hg and Al in b) St23, c) St28, d) St40, e) St42.

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OP53

CHEMICAL COMPOSITION AND HYGROSCOPICITY OF AEROSOL DEPOSITED ON THE INSULATORS OF THE ITALIAN POWER LINES

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1. Introduction

The reliability of any national power lines is clearly of huge importance in modern society for energy distribution. Insulators are a relevant part of the power lines because of their role in the isolation of conductors from the tower and mechanical support for the line. Atmospheric pollution is among the main natural causes of flashover accidents [1]. Hygroscopic aerosol particles in the deposit layers can quickly light up with partial discharge activity once dirty surfaces are wetted; the water-soluble fraction of aerosol particles dissociate in ions, acquiring conductive characteristics and causes flashover accidents [2]. In this context, the University of Milano-Bicocca and RSE worked at the determination of the chemical composition of the aerosol deposits on insulators over the whole Italian territory by means of ion chromatography analysis, by thermo-optical and X-Ray techniques. Moreover, synthetic aerosol with the same chemical composition was generated in laboratory and deposited on glass speciements enabling the determination of deliquescence and crystallization relative humidity and the conductance in an Aerosol Exposure Chamber.

2. Results and Discussion

About 75% of aerosol mass deposited on insulators was due to the presence of water-soluble inorganic component, while the remaining was due to insoluble carbonaceous and crustal material. In Figure 1 it is possible to see how the major fraction of the deposit in Insular regions (Sardegna and Sicilia) is explained by the water-soluble ions analyzed in solution (72.42%). The insoluble fraction represents just over a quarter of the total residue (27.58%) present on the sampled insulators in the Sicily and Sardinia regions. Of these, 65.2% is represented by the carbonaceous fraction (WINSOM and BC), while 34.8% is represented by the crustal material. Based on the ambient chemical composition, synthetic aerosol was generated in laboratory and analysed in the Aerosol Exosure Chamber to assess the water uptake and conductance change while varying the relative humidity of the atmosphere inside the chamber. All the obtained humidograms showed a mass variation due to the absorption of water vapor which reaches a maximum at 90% RH of 2.01 ± 0.26 mg water/mg of deposit. All three macro-regions show the evident presence of a hysteresis cycle (an example is reported in Figure 1), the amplitude of which is variable depending on the chemical composition of the deposit. The deliquescence relative humidity values are greater in Sardegna and Sicilia and decrease going north, till the Po Valley area, from 71±1% to 62±1% RH.

Conductance measurements were conducted and related to the aqueous content measured as a function of relative humidity. A growth in conductance is observed in parallel with the increase in mass of the deposit, while during the supersaturated conditions of evaporation the conductance remains high due to the increase in ion concentration up to values higher than the Italian limit for flashover discharge potential (5 μS). For predictive purposes, the relationship between conductance and mass increase was investigated. An example is presented in Figures 1. The empirical relationships reported represent a starting point of a predictive system for the modeling determination of conductance on insulator deposits as a function of aqueous mass. The different slope identified along the Italian Peninsula reflects and integrates the information linked to a different chemical composition which determines (even with the same mass of the deposit and aqueous content) a different mobility of ions for each macro-region.

3. Conclusions

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The reported study investigated for the first time in Italy the chemical composition of the deposited aerosol mass on insulators of the National power lines. The results highlighted the presence of an hazardous layer of inorganic ions which generates sharp phase transitions of the deposited material in function of the ambient relative humidity. The consequent conductance can generate flashover discharges. Therefore, the obtained results are actually implemented in a protocol for reducing the amount of deposited material in a preventive maintenance perspective.

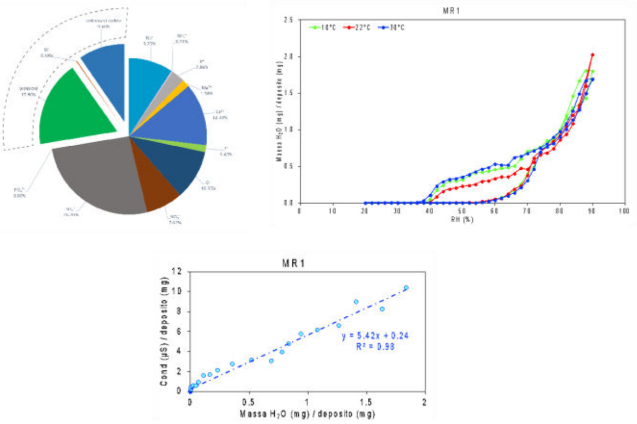

Figure 1. Chemical composition of deposit, the related humidograph and water-conductance relation.

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OP54

EVALUATION OF SARS COVID 19 RESTRICTION ON PM10 IN A SUB URBAN SITE OF SOUTH ITALY

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1. Introduction

Atmospheric particulate matter (PM) has been identified as an important source of pollutants for environment, especially near urban area where anthropogenic activities (i.e. traffic, combustion, nearby industrial plants) can introduce different pollutants, influencing the composition of air [2]. The main objective of this study was to investigate the influence of SARS-covid19 restrictions on PM10 in an sub urban area.

The sampling site of PM10 is inside of the University Campus Ecotekne of Lecce, located in the Apulia region and it can be considered a suburban background station. Soluble salts, metals and organic and elemental carbon were analysed. In this work the PM10 concentration and its inorganic chemical composition have been studied. Source apportionment has been carried out with: the mass reconstruction method and the Positive Matrix Factorization (PMF) [1].

2. Results and Discussion

In this study PM10 concentrations measured during the lockdown months of 2020 were compared to those measured during the same period in previous years (2007 and 2011) and in the following months, showing a decrease in concentrations. Lowest monthly average PM10 values were observed in June 2020 (18±3 µg/m3) caused by limited number of people at University Campus Ecotekne and March 2021 (19±9 µg/m3), probably due to the introduction of strong restriction measures in "Red Zone". The average values of PM10 during No Lockdown, Orange Zone and Red Zone (figure) are of 26±9 µg/m3, 26 ±13 µg/m3 and 20±6 µg/m3, respectively. The restriction measures in the people's movement have determined a decrease of PM10 levels in atmosphere for 3% and 23% during Orange and Red zone, respectively. During Orange zone respect to No lockdown period, OC and EC showed an increase of 52% and 82%, while in Red zone, with the introduction of strong restriction measures on travels/movements OC and EC showed a decrease of 20% and 16%, respectively. Considering concentration levels and pollution roses, OC, EC and Ni, Cr and Cu levels are greater during No lockdown period and present higest concentrations at lowest wind speeds. PMF shows the presence of: crustal, resuspended, combustion, SIA and marine sources. Combustion and resuspended sources showed lowest values during lock down periods.

3. Conclusions

The present study has shown the decreasing of PM and of pollutants related mainly to combustions in relationship to the restriction introduced with Sars covid 19 regulamentations. The main sources affected by restrictions were combustion and resuspension one that lead to the decreasing of pollutants in air of the sub urban site.

OP54

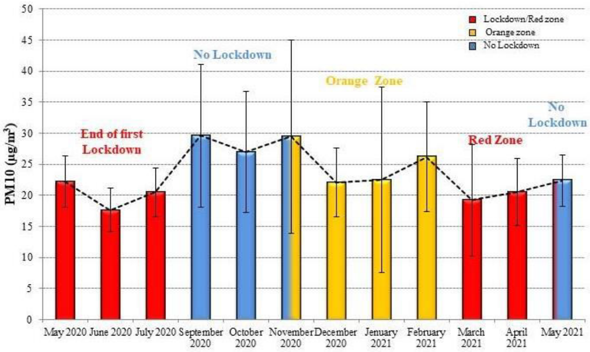

Figure 1. Effect of Lockdown periods, Orange and Red Zone on PM10.

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OP55

DIRECT AND NITRITE-SENSITIZED PHOTOLYSIS OF VANILLIN IN ARTIFICIAL SNOW

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1. Introduction

Methoxyphenols are semi-volatile organic compounds emitted by biomass burning (e.g., wildfires, combustion/pyrolysis of agricultural residues) into the atmosphere. The atmospheric lifetime of these compounds can be of some days, allowing their long-range transportation from, e.g., midlatitudes to the Poles, where they eventually undergo deposition [1]. Indeed, methoxyphenols have been detected in snowpacks and ice cores in the Arctic and Antarctic. For this reason, they are used as environmental markers of biomass burning in ice cores, sometimes allowing paleo-estimates of past wildfires events [2].

However, previous works have shown that methoxyphenols undergo (photo)chemical transformation in the atmosphere, producing nitrophenols and oligomers as sources of aqueous secondary organic aerosols [1]. This process represents a bias for the use of methoxyphenols as markers of biomass burning. To date, moreover, little is known about the photochemistry of methoxyphenols in snow, which is an effective environmental photoreactor [3].

In this work we investigated the photoreactivity of vanillin (VN) in artificial snow (243 K) with and without added sodium nitrite.

2. Results and Discussion

Artificial snow samples were prepared inside a walk-in cold room, set at 243 K, by nebulization of synthetic aqueous solutions containing VN (5-50 μM), sodium sulfate (to fix the total solute concentration = 200 μM as a continental snow) and, sometimes, sodium nitrite (5-50 μM). VN was here used as a proxy for methoxyphenols emitted by biomass burning, while nitrite as photosensitizer of HO radicals and NO_x. Indeed, nitrite plays an important photochemical role in environmental snowpacks. Snow samples were then irradiated under a UVA lamp at 243 K, and the evolution of both VN and nitrite concentration was monitored over irradiation time by HPLC-DAD after snow melting.

In the absence of nitrite, VN direct photolysis was sluggish in snow and the observed degradation rate coefficient was anticorrelated to VN concentration. This finding may be accounted for by considering that the direct photolysis proceeds through a self-sensitized mechanism, where the photoproduced excited triplet state of VN reacts with ground state VN to form the radicals VN^+ and VN^- [4]. These radicals can undergo further degradation, but can recombine as well, in particular at the surface of ice crystals, where VN molecules would be segregated during freezing reaching high concentration. As a consequence, this back-reaction process would limit the direct photolysis of VN in snow.

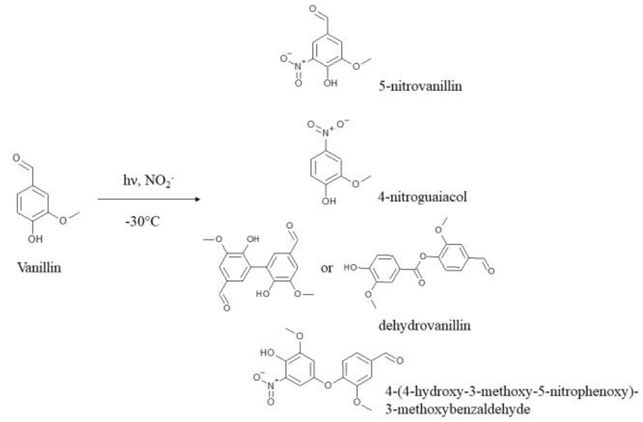
When nitrite was added to artificial snow, the measured rate coefficient of VN photodegradation increased almost linearly with nitrite concentration, and was higher than that observed for direct photolysis. A suitable kinetic model showed that NO_x would play a major role in VN photodegradation in the adopted snow conditions. In support of this hypothesis, phototransformation products were tentatively identified by HPLC-MS/MS analysis, showing that formation of 5-nitrovanillin, 4-nitroguaiacol, dehydrovanillin and a nitrophenoxy-substituted 3-methoxybenzaldehyde were produced (Fig.). Formation of nitrophenols highlights the involvement of NO_x in VN photodegradation. Furthermore, the formation of VN oligomers caused the observed increase of the absorbance of the (melted) snow samples in the visible, as similarly found for the photodegradation of some methoxyphenols in the atmospheric liquid-phase [5].

The same irradiation experiments were carried out in liquid water at room temperature, for the sake of comparison between VN photochemistry in the atmospheric liquid-phase and that in snow. Direct photolysis was found to be the main photodegradation pathway of VN in liquid water, even in the presence of nitrite. Furthermore, VN direct photolysis was faster than that observed in snow, and showed the same decreasing trend with the increase of VN concentration. Nitrite had scarce effects on VN direct photolysis, although it partially acted as a limiting agent possibly because of (i) a light-screening effect and/or (ii) as scavenger of the VN excited triplet state. The latter process (i.e., the oxidation of nitrite to NO_2 by the VN triplet state) may be responsible for the production of nitrophenols during the direct photolysis of vanillin, as observed by HPLC-MS measurements. Finally, dehydrovanillin was formed as well by VN direct photolysis.

3. Conclusions

This work shows that VN, a proxy for methoxyphenols emitted by biomass burning, is photoreactive in artificial snow in the presence of nitrite as photosensitizer of HO radicals and NO_x. The reactions responsible for VN photodegradation in snow would be led by NO_x, while direct photolysis prevails in liquid water at room temperature under the same irradiation conditions. Despite the different mechanisms, the same nitrophenols and VN oligomers were produced in the two scenarios, suggesting that NO_x production may take place also during VN direct photolysis in the presence of nitrite.

Since VN undergoes significant photodegradation both in liquid-phase and in snow, its use as an environmental marker of biomass burning should take into account this process.



Tentative by-products of VN photodegradation observed in artificial snow.

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OP56

SUSTAINABLE PRESERVATION STRATEGIES FOR STREET ART

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1. Introduction

Street art is now recognized as a valuable contemporary cultural heritage. Unfortunately, the ephemeral character and exposure to natural and anthropic threats, make public paintings vulnerable to neglect, removal, vandalism and decay. In recent years, some projects at local and international level have begun to address the various aspects that should be taken into consideration in conservation projects of street art works, highlighting their complexity.

The SuPerStAr Sustainable Preservation Strategies for Street Art project aims to deepen the knowledge of street art materials and their degradation processes through innovative multi-analytical methods and to develop conservation protocols aimed at reducing the impact of physical and environmental factors on street art works.

2. Results and Discussion

The three-year project started in March 2022 and is moving its first steps. This contribution presents the results obtained so far and the research methodology that will be adopted during the project implementation. Relevant case studies have been selected, located in different environmental urban contexts, and exposed to different types of risk. Based on the identified case studies in Pisa, Turin and Milan, the collected documentation and previous experiences, different sets of paints models have been prepared, with different combinations of materials and stratigraphy, in order to effectively investigate issues related to the stability of binders and organic pigments, to cleaning and protection procedures. Acryl, styrene and alkyd wall paints and sprays have been considered, admixed with organic pigments, including fluorescent pigments, that present stability issues.

These models will be artificially aged to simulate long-term outdoor exposure and will be used to investigate degradation processes and test materials and conservation treatments that, at a later step of the project, will be tested also on-site.

Non-invasive multi-analytical in-situ methodologies for the study of street art works will be set-up comprising both point-analysis spectroscopies (FT-IR, UV-Vis-NIR reflection and fluorescence, Raman and XRF) and imaging hyperspectral techniques. The implementation of remote sensing will be crucial to cover wide areas, thus a novel application of unmanned air vehicle (UAV) platforms equipped with i) a hyperspectral camera, ii) a multispectral imager in the visible range and iii) a thermal camera in the IR region will integrate portable hyperspectral cameras and scanning systems.

Laboratory microanalytical methods based on mass spectrometry coupled with chromatography and with analytical pyrolysis (Py-GC-MS) and other thermo-analytical (TGA, DSC, EGA-MS), chromatographic (size exclusion chromatography, SEC, HPLC-DAD), and mass spectrometric techniques (HPLC-ESI-Q-ToF, MALDI-MS) will be developed for the in-depth characterization of modern paints and for the study of their degradation phenomena. The non-invasive and micro-invasive analytical methods will be then integrated in a modular analytical protocol for the identification of materials, the monitoring of the conservation state, and the assessment of the effects of conservation treatments.

Novel eco-compatible materials and procedures for the cleaning of non-painted and painted wall surfaces will be developed to selectively remove surface deposits and unwanted graffiti. Green gels loaded with non-toxic solvents obtained from renewable sources will be considered, alone or complemented by laser cleaning.

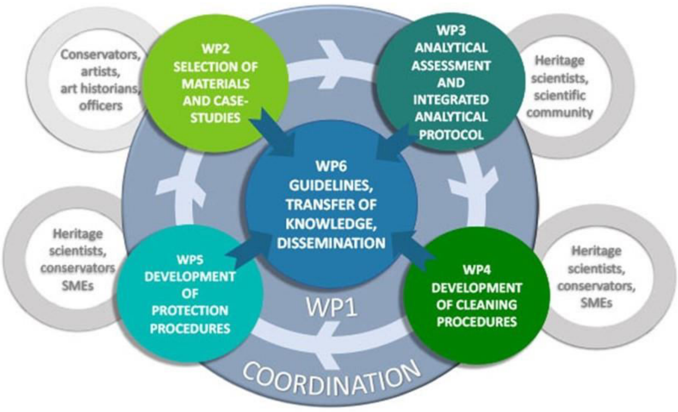
In addition, protective treatments to preserve contemporary murals will be identified and optimized paying attention to critical issues like the application method, compatibility with the substrate, protection efficacy, durability of the coating and re-treatability of the painted surface.

All these activities will result in the drafting of protection, monitoring and maintenance guidelines for street art preservation.

3. Conclusions

The SuPerStAr project will promote a synergistic advancement in the knowledge of contemporary paint materials and conservation methods, providing a timely response to current needs for the management of urban art.

Thanks to the strong collaboration between partners with complementary skills and with conservation institutions, the project will deliver the following results: innovative cleaning procedures optimized for the restoration of outdoor murals and for the removal of vandalized graffiti; protective coating materials selected with particular attention to the aspects of durability; and an integrated protocol for long-term sustainable monitoring and conservation.



SuPerStAr project at a glance

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OP057

INVESTIGATION OF THE ANTHROPOGENIC IMPACTS ON THE SURFACE OF THE STONE-BUILT HERITAGE IN VENICE: THE VENETIAN WELL-HEADS AS CASE STUDIES

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1. Introduction

Stone surfaces are potentially a reliable 'recorder' of past environmental changes to read. Reading the subtle clues embedded on the surface of a stone-built architectural element gives us a frame of the complex relationship between stone, environment and society [1]. This paper aims to visually and qualitatively investigate some of the possible anthropogenic impacts on the surface of the stone-built heritage in Venice. The Venetian well-heads have been chosen as case studies due to their importance as cultural assets of the city, their well-distribution in the urban area, and their high exposure to the environment and anthropogenic factors. So far, no implemented scientific study has been done yet on the surface of the Venetian well-heads. Thanks to a photographic archive (photos taken from 2003 to 2013), visual surveys have been conducted and some significant parameters have been evaluated and compared with the past situation. According to the visual exploration, in situ analyses (Raman Spectroscopy), and in the laboratory investigation (FTIR-ATR and XRD) are conducted to possibly evidence the presence of substances deriving from anthropogenic impacts on well-heads.

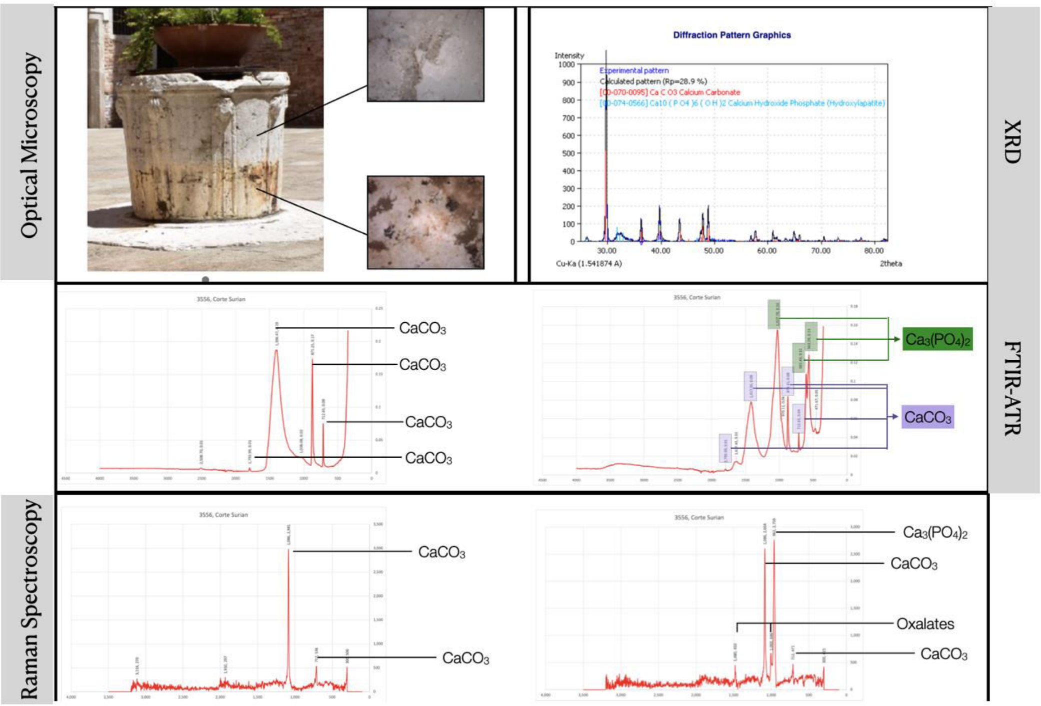
2. Results and Discussion

One hundred twenty-seven case studies from four sestieri of Castello, San Marco, Dorsoduro, and Cannaregio have been visually observed and photographed. Discoloration and deposit, biological colonization, material loss, cracks, and vandalism (presence of graffiti) have been the five factors considered for a semi-quantitative analysis of the anthropogenic impacts on the well-heads. The comparison between the current situation and archive photos indicates, in terms of cracks and material loss, a mainly unchanged situation. Biological colonization, on the contrary, shows a significant increase in many sites. Considering the parameter of "vandalism" and its relationship with tourism, the situation in San Marco seems to be more controlled than in the other sestieri, probably due to higher surveillance. Chromatic alteration of the well-heads surface (such as discoloration and deposits) are the most relevant changes visually relevable. These surface modifications are observed mainly on the lower part of the well-heads; its color varies from whiteish to yellowish with different intensities. This alteration may be linked to the impact of high tide (acqua alta) on the materials and there seems to be a correlation between the altimetry of area where the well-heads are positioned. In order to investigate the chemical composition of the lower (presence of color change) and upper (no evidence of color change) stone surfaces, spectroscopic analyses were conducted. The analyses performed by Raman spectroscopy, FTIR-ATR, and XRD confirm the diffused presence of calcium phosphate only on the lower part of the well-heads (generally below 50 cm). The presence of phosphate is probably related to pollution in the urban effluents (2), which could come into contact with the stone surfaces at the time of flooding.

3. Conclusions

The comparison between past and current photos based on a semi-quantitative evaluation of well-defined parameters could give an important indication of the state of conservation and of the main anthropogenic factors impacting the stone surface. Chromatic changes were observed on the lower part of many well-heads in Venice, and the presence of calcium phosphate was also detected for the first time. The possible relationship between the presence of calcium phosphate and the high tide events has been proposed.

OP057



The presence of calcium phosphate on the lower-part surface of the studied well-head

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OP58

HOW DIFFERENT DISPERSION PROTOCOLS AND CELL CULTURE CONDITIONS CAN INFLUENCE THE MULTICOMPONENT NANOMATERIALS PROPERTIES AND IN VITRO TOXICITY RESULTS

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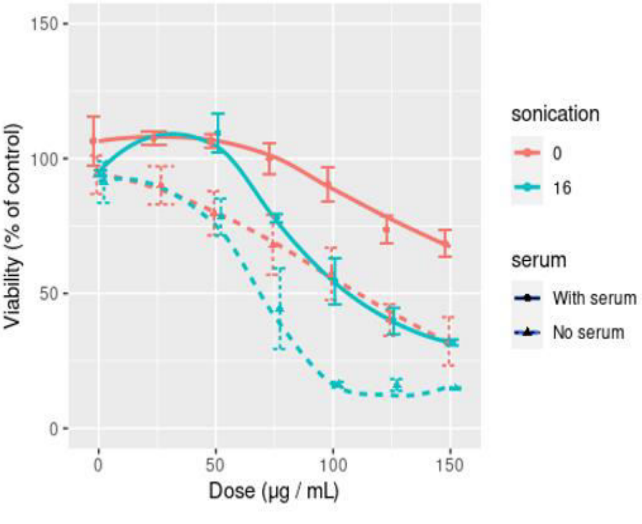
1. Introduction

Over the last decade, significant efforts [1-2] have been devoted to understand if a generally applicable dispersion protocol for different kind of engineered nanomaterials (ENMs) could be provided prior to toxicological testing. However, the high degree of variability in the main physicochemical properties of ENMs, including size, morphology, surface area, chemical composition and surface chemistry, have represented a barrier to this harmonization, even more by considering the complexity of multi-component nanomaterials (MCNMs), composed of two or more distinctly definable condensed nanoscale domains. Therefore, within the Horizon2020 SUNSHINE project, the colloidal characterization of both single- (i.e. SiO2, ZnO, SiC and TiO2) and SiO2-ZnO and SiC@TiO2 MCNMs, intended to be used in cement and ceramic nanocomposite coatings respectively, was investigated to highlight how the different dispersion protocols and cell culture conditions can affect the MCNMs properties and toxicity results.

2. Results and Discussion

Hydrodynamic diameter, surface charge, sedimentation velocity of MCNMs were investigated after performing either the Nanogenotox [3] or the dispersion protocol proposed by Deloid et al. [4] in relevant cell-culture medium, either with or without the addition of serum. Cell viability and release of inflammation markers were tested using both epithelial and macrophages cell lines. The set of information from both the colloidal characterization and from the in vitro toxicity assays performed were exploited to understand if and which are the main parameters of the dispersion- and exposure protocols which could influence the MCNMs properties and their in vitro toxicity. Preliminary results indicate that the use of serum in the cell culture medium decreases the toxicity of SiO2-ZnO MCNM, which is probably related to the formation of a protective protein corona at the particle surface.



3. Conclusions

These findings could have relevant implication on the MCNM risk evaluation. Especially in relation to the Green Deal ambitions to develop materials that are safe-by-design (SbD), materials should be tested in a realistic manner without changing characteristics. Extensive sonication could damage a material surface treatment, thereby interfering with the SbD intervention. A generally applicable dispersion protocol is not suitable for all ENM and MCNM. We propose to tailor sonication to the specific MCNM, supported by thorough colloidal characterization. This approach should result in better understanding of what drives MCNM toxicity, enabling SbD solutions.

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OP59

INTERACTION BETWEEN METRONIDAZOLE WITH TOXIC METAL CATIONS IN AQUEOUS SOLUTION: A SPECIATION STUDY FOR APPLICATIONS IN ENVIRONMENTAL FIELD

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1. Introduction

The persistence of pharmaceutical products in environment fluids has led to greater attention on the characterization and study of methods for their removal [1]. Among them, metronidazole (MNZ), shown in Figure 1, widely used in clinical therapies against bacterial infections, led to serious damage to the environment and to humans due to its high resistance to current purification processes. For this reason, and for its high solubility in marine environments under atmospheric conditions, MNZ has been included in the class of new emerging contaminants. A speciation study was carried out on MNZ with the toxic metal cations Pb^{2+}, Cd^{2+} and $(CH_3CH_2)_2Sn^{2+}$ (Et_2Sn^{2+}), commonly present in natural waters, with the aim of defining the type of interaction and the thermodynamic picture of the species formed in solution.

2. Results and Discussion

Potentiometric titrations were carried out at three values of temperature (t = 15, 25, 37°C) and ionic strength ($I = 0.15, 0.5, 1$ mol L^{-1}) on NaCl aqueous solutions containing different metal(M) - ligand(L) ratios, in order to select the best speciation model and to determine the values of the formation constants of the species formed in solution. For all three M-L systems, the speciation models obtained are quite simple, characterized by the single species ML for the Cd^{2+}-MNZ system, ML and ML_2 for the Pb^{2+}-MTZ system, and ML, MLH and MLOH for the Et_2Sn^{2+} system. Solutions with different M-L ratios were also investigated by UV-Vis titrations at 25°C and $I = 0.15$ mol L^{-1} in order to confirm the speciation models and the values of the formation constants, as well as to investigate the spectrophotometric behavior of the complex species. Furthermore, the results of ^1H-NMR titrations, employed on solutions containing Et_2Sn^{2+} and MNZ at t = 25°C and $I = 0.15$ mol L^{-1}, are in full agreement with the results gained by potentiometry. Enthalpy change values were determined by the dependence of the formation constants on the temperature. The dependence of the formation constants on the ionic strength was also evaluated. The sequestering ability of MNZ towards Et_2Sn^{2+}, Pb^{2+} and Cd^{2+} was obtained under different conditions of pH, ionic strength and temperature by an empirical parameter known as $pL_{0.5}$, i.e., cologarithm of the ligand concentration required to sequester 50% of the metal ion present in traces [2].

3. Conclusions

The assessment of the thermodynamic data of species formed by Et_2Sn^{2+}, Pb^{2+} and Cd^{2+} with MNZ, an emerging contaminant present in natural waters, is crucial to make simulations and to predict the environmental behavior of these species under real conditions and therefore useful for setting up effective removal processes.

OP59

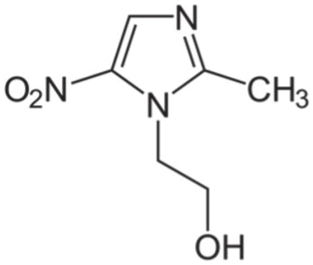

Figure 1: Metronidazole (2-Methyl-5-nitroimidazole-1-ethanol, MNZ)

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OP60

ELEMENTAL CHARACTERIZATION OF ANTARCTIC PM_{10} (DOME C): WHERE DOES IT COME FROM?

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1. Introduction

The analysis of the elemental composition of the atmospheric particulate matter (PM) by ICP-SF-MS is a well-known tool to study the processes that control the production, transport, and deposition of PM. The correlation between the elements can be related to the origin of the material which composes the PM (crustal, marine, anthropogenic) [1]. The variability of the element in samples of different times reflects the temporal variability in the strength of the sources and removal processes, as well as the mutation of the main pathways of the air masses along the seasons and the years [2]. Moreover, the study of the PM preserved in the paleoclimate proxies (ice cores and snow samples) allows for studying these evolutions along the centuries and the geologic eras. In the context of the project SIDDARTA, elemental, ionic, and isotopic characterization of Antarctic PM_{10} has been performed for the recognition of its sources. We present here the elemental characterization of the PM_{10} collected every month from 2017 to 2020 at the Concordia Station (Dome C, East Antarctica), and those of soil samples from Australia and South America, considered potential source areas (PSA) [3].

2. Results and Discussion

Principal components analysis (PCA) has been performed to highlight similitudes between the PM_{10} samples and correlations between the elements over the four years under investigation. PCA returns three principal components that explain the 31%, 18%, and 13% of the whole information, respectively. All the considered elements have positive loadings for PC1, which, therefore, can be considered as an index of the amount of PM_{10} in the Antarctic troposphere. Considering the scatter plot of PC2vsPC3 (Figure 1.a), the elements with marine origin (Na, Mg, K, and Sr) are grouped at high and positive loading values on PC2, with very low values for PC3; The other elements, instead, have little loading values for PC2 and are grouped along PC3 between three clusters, mixing elements with a clear crustal origin and those usually related to anthropic sources: Zn, Mn, Ti, and Pb (loadings > 0.30); As, Ni, Cd, Cu, Sc, Al, and V (loading between ±0.15); Ba, Ca, Fe, Co, and Cr (loading $\leq$ -0.2). The absence of separation between the elements with crustal and anthropogenic origin can be due to the low concentrations of these elements in the Antarctic air (down to tenths of pg m^{-3}) and a low level of anthropic contamination. The samples collected during 2018 present a higher load in the atmosphere (higher score on PC1), and a significantly lower contribution of the elements of marine origin. Even if Mg, K, and Sr can be associated to marine sources, the crustal enrichment factors (CEF) reveal a not negligible contribution of crustal source for these elements with 60%, 80%, and 88% of the distributions, respectively, lower than the threshold value of 10, usually used to recognize if a fortification/contamination has occurred.

The study of the elemental composition of the soil samples from the PSA reveals some peculiar differences between the two types of soil: Australia and South America. For instance, using Al, Ca, and K is possible to separate the two types of soil in a ternary plot. In fact, the Australian soil samples have a higher amount of Al and a lower amount of Ca and K than those from South America. These same variables can be used to infer the relative importance of these PSA as active sources for PM_{10} at Dome C. However, few PM_{10} samples fall close to one of the two clusters (prevalence of one of the sources) or between them (mixing of the sources) (Figure 1.b). This could indicate a not negligible contribution of other sources with a different proportion between Al/Ca/K. However, this aspect will have to be confirmed by the analysis of PM_{10} samples from subsequent years. From the ternary plot emerges again that the samples of 2018 are quite different from those of the other years. In fact, these samples present a higher relative amount of Ca, and a lower amount of Al and K. Moreover, between the samples of 2018, there is lower dispersion respect to the samples of the other years.

3. Conclusions

Elemental analysis by ICP-SF-MS and multivariate techniques have been used to study the composition of Antarctic PM_{10} (2017-2020) and soil samples from PSAs (Australia and South America) for the source recognition of the aerosol reaching the inner regions of Antarctica (Dome C). The composition of PM_{10} highlights the origin of the material that composes the aerosol (marine and crustal). PSAs' soil shows a significant difference in the elemental composition respect to the PM_{10}, which could be due to the presence of other sources with not negligible contributions. Further studies for a better characterization of the Australian and South American soils, and the continuation of the sampling campaign of PM_{10}, are necessary to improve the knowledge of the origin of the Antarctic aerosol.

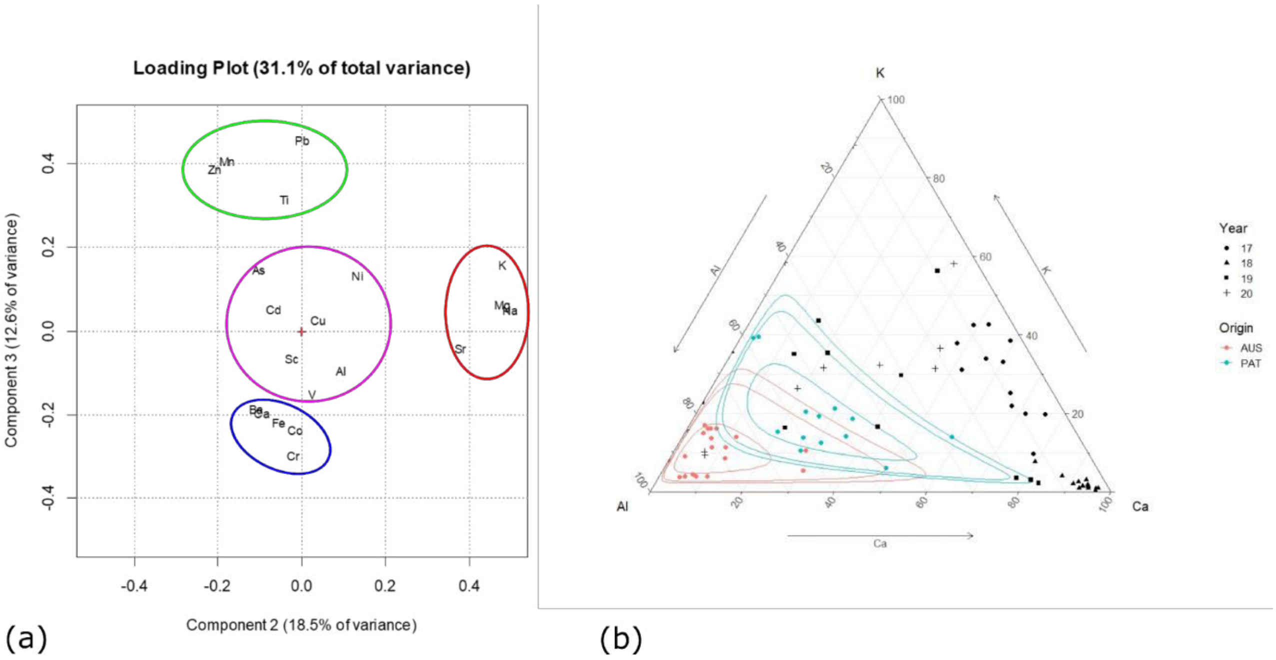

Figure 1. (a) PCA for the elemental composition of Antarctic PM_{10} (2017-2020) and (b) ternary plot.

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OP61

SEEPING PLASTICS: SOLVENT AND SOLID PHASE EXTRACTIONS TO EVALUATE THE POTENTIALLY HARMFUL MOLECULAR FRAGMENTS LEACHED OUT FROM MICROPLASTICS

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1. Introduction

Sampling, separation, detection and characterization of micro- and nano-plastic pollutants dispersed in the environment is a challenging and critical goal to understand their distribution, fate, and the related hazards for ecosystems. Microplastics have now been detected in all the main environmental compartments, and the associated environmental and health hazards have been the focus of intense social, scientific, and media attention. Recent researches demonstrate that plastic debris should be considered by no means as chemically stable persistent pollutants, but rather as reactive materials. Indeed, synthetic polymers exposed to the environment undergo chemical and physical degradation processes leading not only to mechanical but also molecular fragmentation. In this work we tested different extraction procedures in order to evaluate the potentially harmful molecular fragments leached out from microplastics in the environment.

2. Results and Discussion

Samples of micronized reference polymers (low- and high-density polyethylene, polypropylene, and polystyrene) were photoaged in SolarBox and investigated at different aging times. The aged polymers were extracted with solvents in conditions specifically optimized to selectively extract the degraded (oxidized) fractions produced during irradiation. We applied evolved gas analysis-mass spectrometry (EGA-MS), analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS), size exclusion chromatography (SEC) to characterize the bulk polymers at different ageing times, the extractable fractions, and the corresponding extraction residues. The analysis performed on the extracts and the extraction residues allowed us to gain information on the products of oxidation/fragmentation and on the complex microplastics degradation processes, such as the formation of short chain carboxylic acids from polypropylene and of long chain carboxylic acids from polyethylene. The use of microwave assisted extraction combined with multi-shot Py-GC-MS analysis allowed us to detect the same degradation products in environmental sand beach samples.

To evaluate the possible leaching of these chemical species in water, the same reference microplastic were then subjected to accelerated photo-oxidative ageing in artificial seawater to perform a molecular characterization and quantification of chemical species leached out after selective extraction, derivatization, and GC/MS analysis. The analysis allowed us to characterize different classes of compounds. The analysis allowed us to identify more than 60 different compounds, such as linear and branched mono and dicarboxylic acids, and benzene derivatives. The results obtained from the reference microplastics were then compared with those obtained by analyzing leachates in artificial seawater from aged plastic debris collected in natural environment.

Finally, solid phase extraction approach was also tested directly on water leachates obtained for environmental microplastics in order to evaluate the possibility to obtain complementary and more accurate information in respect to the solvent extraction approach.

Selected ion flow tube mass spectrometry (SIFT-MS) was also applied in order to evaluate the volatile organic compounds (VOCs) emitted both from artificially aged microplastics and environmental plastic debris. The research was supported by the JPI Ocean project HOTMIC – Horizontal and vertical oceanic distribution, transport, and impact of microplastics (2020-2023).

3. Conclusions

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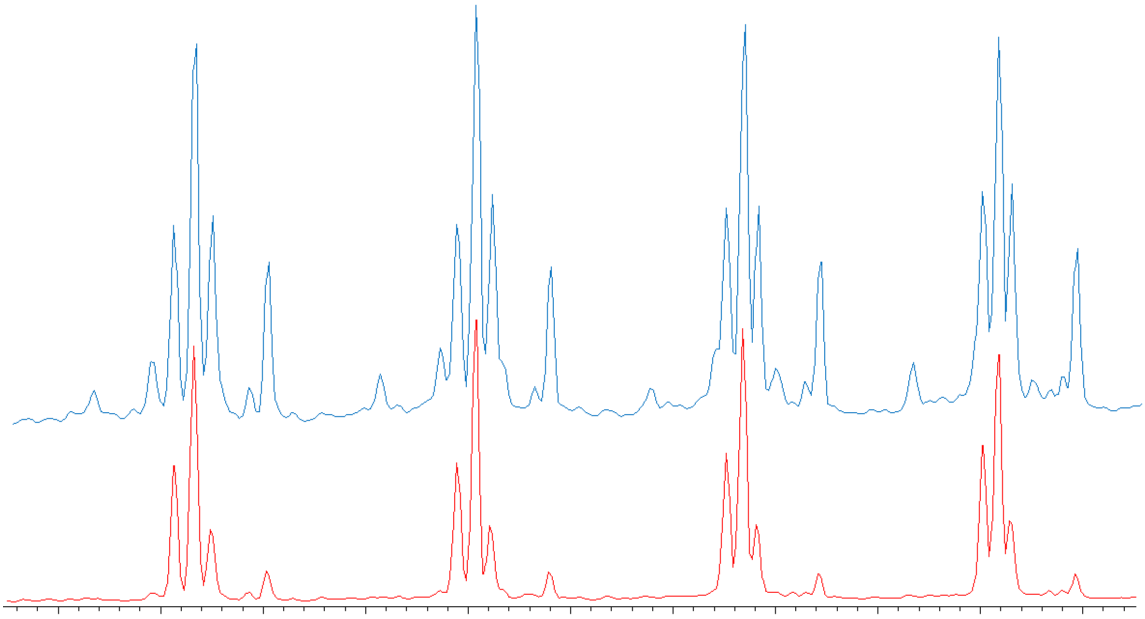
The combination of extraction procedures and analytical approaches based on pyrolysis and gas chromatography achieved significant information for a better understanding of the chemical nature of degradation products released by different polymers present as microplastics in the environment.



Chromatograms (15.20–17.20 min) obtained in the Py–GC–MS analysis of LDPE-0w (red))and LDPE-4w (blue

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OP62

ARSENIC REMOVAL FROM WATERS: A HEAD-TO-HEAD COMPARISON BETWEEN BARE AND SUPPORTED NANOSTRUCTURED IRON OXIDES AND OXYHYDROXIDES ADSORBENTS

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1. Introduction

Arsenic pollution represents a criticism in the water and soils availability in more than 70 countries worldwide, due to its high toxicity in low concentrations.[1,2] The presence of As in the environment is due to both natural and anthropogenic processes, such as dissolution of As-bearing minerals, mining, use of pesticides, etc. The use of As adsorbents assures high efficiency, low cost, possibility of designing regenerable and versatile multipollutants-active sorbents. Arsenate and arsenite species are known to adsorb on the surface of iron oxides and oxyhydroxides thanks to the presence of surface hydroxyl groups, depending on the pH and consequently surface charge. The use of these Fe-based compounds is favourable due to their low-cost, ease of synthesis, biocompatibility, and, in some cases, their possible magnetic separation.[3] Moreover, the design of nanostructured materials allows the enhancement of the efficiency due to the increase of the reactive surface area. In this study, nanostructured iron oxides and oxyhydroxides, in form of single phases or dispersed in porous silica supports, were tested as adsorbents for As(III)/As(V) species from As-spiked water.

2. Results and Discussion

Akageneite, ferrihydrite, maghemite, and a Fe_2O_3-SiO_2 composite were tested for their As(V)/As(III) removal from water in the pH range 2–8. All sorbents were characterized for their structural, morphological, textural, and surface properties to understand the differences in the exhibithed performance. Akageneite was found to be the most promising adsorbent in the whole pH range for As(V) (89 mg/g at pH 3 and 52 mg/g at pH 8) and to keep good removal ability also for As(III) (ca. 80% at 100 mg/L; q_e = 91 mg/g at 500 mg/L and pH 8), whose best adsorbent was ferrihydrite (ca. 95% at 100 mg/L; q_e = 144 mg/g at 500 mg/L and pH 8). The results were explained in terms of surface properties, arsenic speciation, and ability of the adsorbents in modifying the pH of the As-spiked solutions upon solid-liquid contact. Additional removal tests were carried out on the best adsorbent, akaganeite, to deepen the effect of initial concentration, contact time, ionic strength, and presence of competitors. Other tested adsorbents were developed based on the incorporation of Fe_2O_3 nanoparticles within the ordered porous structures of SiO_2 scaffolds, with the idea of using these latter as versatile platforms to anchor active phases for different pollutants (all-in-one removers). Therefore, the growth of Fe_2O_3 nanoparticles was induced by two-solvents impregnation strategies into meso-(SBA15, pore size (Ø) = 7–8 nm) and macrostructured (MOSF, Ø = 70-120 nm) SiO_2-based supports. The final Fe_2O_3 nanoparticles were affected by the textural properties of SiO_2 supports in terms of both structural and morphological properties: 4-6 nm Fe_2O_3 nanoparticles were obtained in the SBA15 support, and a mixture of 18–20 nm-hematite and 3–5 nm-maghemite for MOSF one. The first sorbent was found to be more efficient, and further compared with an amino-grafted SBA15. Possible secondary-pollution phenomena derived from the use of the SiO_2-based sorbents, usually ignored in the literature, were studied, revealing the occurrence of silicon releases, due to the detachment of silica nanoparticles.

3. Conclusions

Different head-to-head comparisons of the As-removal ability were carried out by batch tests on: (a) iron oxides (maghemite) and oxyhydroxides (akaganeite, ferrihydrite); (b) bare Fe_2O_3 and silica-embedded Fe_2O_3;

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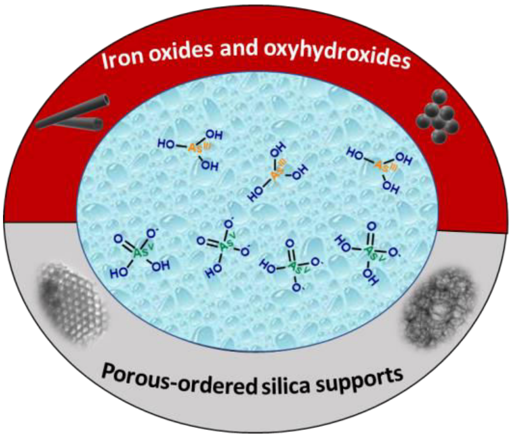
(c) meso- and macrostructured silica-based adsorbents; (d) inorganic (Fe_2O_3) and organic (amine groups) active phases loaded on the same silica-based support. The batch tests were conducted under different experimental conditions by changing the arsenic species, pH, initial As concentration, contact time, ionic strength, and presence of competitors. Iron oxyhydroxides were the best removers, while the occurrence of silica release revealed to be critical issue to be considered in the design of the sorbents.



Arsenic removal study by bare and silica-supported nanostructured iron oxides and oxyhydroxides

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INDOOR AIR QUALITY EVALUATION IN ONCOLOGY UNITS AT TWO EUROPEAN HOSPITALS: LOW-COST SENSORS FOR TVOCS, PM2.5 AND CO2 REAL-TIME MONITORING

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1. Introduction

Indoor Air Quality (IAQ) evaluation is a crucial issue for general public health protection and should be a priority in sensitive indoor environments such as hospitals and health care centers where high level quality standards in terms of human health and well-being must be guaranteed [1,2]. The present study has been carried out with the purpose of contributing to filling the knowledge gap regarding IAQ in oncology units elucidating how these microenvironments are impacted by the human occupancy, routine medical treatments and other human activities. IAQ evaluation was performed inside oncology units at two European hospitals, one in Italy (Bari) and one in Spain (Barcelona). IAQ parameters were selected due to their relevance as traces of outdoor infiltration (PM2.5), indoor particle resuspension (PM2.5, PM10), ventilation (CO2) and indoor emissions from chemicals, cleaning agents or humans (TVOCs). Low-cost sensors were used for high temporal resolution monitoring combined with information on human activity patterns and micro-environmental parameters. Moreover, to evaluate PM sensor performance, field and laboratory comparisons were performed with scientific-grade equipment.

2. Results and Discussion

2.1 TVOCs, CO2 and fine particles monitoring data in Bari

The TVOCs profile (Fig. 1a) clearly shows a daily regular pattern on weekdays (Monday-Friday) when the oncology ward is open to the public for medical assistance. The increase in TVOCs concentration was systematically observed in the daytime hours (08:00–15:00) characterized by higher human occupancy in the ward corridor for scheduled chemotherapy treatments, with concentration peaks in the range 0.60–1.40 ppm from background levels varying from 0.12 to 0.37 ppm. The reported profiles are representative of the pollutants behavior throughout the entire monitoring campaign. The hypothesis of an association between TVOCs concentration peaks and increased human occupancy and scheduled activities in the ward is strengthened by the consistency observed between TVOCs and CO2 concentration profiles, for both weekdays and weekend days. The daily increase in CO2 concentration on working days, from approximately 400 ppm to 500–600 ppm, occurs concurrently with an increase in human density in the outpatient waiting areas of the ward and remarks the TVOCs diurnal trend. A consistent association was also observed between CO2 and PM2.5 concentration profiles over the time (Fig. 1b). The daily increase in CO2 concentration generally observed at high occupancy hours (08:00–15:00) is associated to a variation of PM2.5 concentration from 5 to 20–30 µg/m3, with the highest peaks likely related to cleaning activities and walking-induced particles resuspension due to medical personnel and patients movement in the ward [3].

2.2 Fine particles monitoring at oncology hospital in Barcelona

The two patient rooms assessed in the Barcelona hospital evidenced almost identical concentrations and daily patterns as in Bari. The PM2.5 data from Barcelona, in accordance with those collected in Bari, show a diurnal pattern with higher concentrations during daytime hours (concentration range: 10–60 µg/m3) characterized by higher occupancy with respect to the late evening-night hours. Furthermore, weekly trends clearly evidenced weekend decreases in PM2.5 concentrations, as expected due to the fact that the daycare unit was closed on weekends.

3. Conclusions

The oncology hospitals are enclosed environments of high concern with regard to the environmental inhalation exposure due to the presence of patients with weakened immune system. In the present study two extensive monitoring campaigns inside two oncology hospitals in two EU cities (e.g., Bari and Barcelona) were performed deploying low-cost sensors for high temporal resolution monitoring of TVOCs, PM2.5 and CO2. Temporal profiles of target pollutants show a regular pattern on weekdays with concentration peaks observed in the daytime hours characterized by higher human occupancy for scheduled chemotherapy treatments and by cleaning activities. Human occupancy, the use of pharmaceutical and cleaning products were recognized as the main sources affecting TVOCs and particle concentrations.

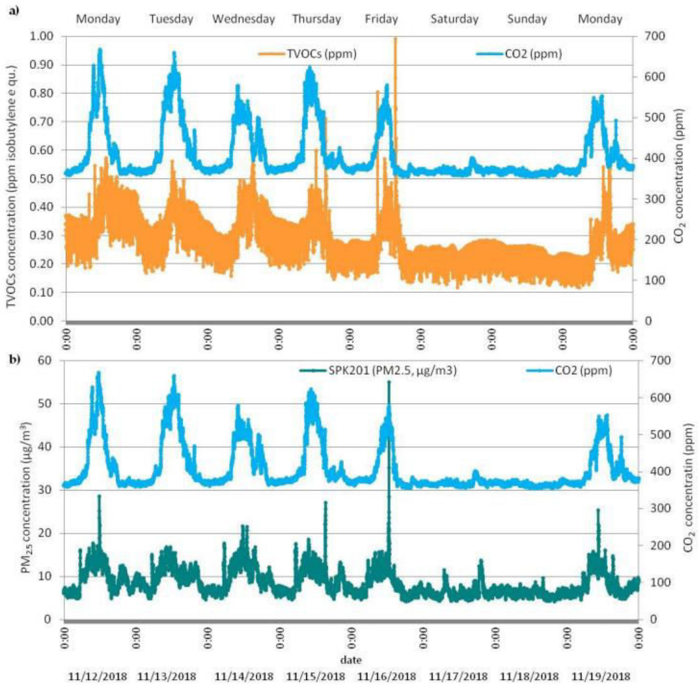

Figure 1:Weekly variation of TVOCs, PM2.5 and CO2 concentration in the Oncology ward in Bari

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STUDY ON DEGRADATION OF NANOPLASTIC AND SMALL MICROPLASTICS

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1. Introduction

Plastic pollution has been widely reported since the 1970s and nowadays it is an important environmental, social and economic problem. Plastic represents the main fraction of marine debris, indeed between 4.8 and 12.7 million tons of plastic enter the ocean every year and plastic pollution now reaches even the most remote areas of the Earth [1]. Plastic debris undergo a slow process of transformation in the environment, which lead to transformation and fragmentation of plastic polymers. Therefore, the size of plastic debris in the environment can cover different orders of magnitude (from cm to nm); microplastics (MPs) and nanoplastics (NPs) are defined as having size between 1 µm and 5 mm and lower than 1 µm, respectively [2]. MPs and NPs are not inert, and they can react and interact with chemical species that occur in the surrounding environment [3]. In particular, when a plastic piece degrades down to parts with sizes in the nanometre scale, the exposed area increases drastically and so does the surface reactivity. However, the dependence of plastics degradation kinetics upon their particle size is almost unknown, and the environmental fate and impact of NPs is still unclear.

2. Results and Discussion

In this study, we investigated the reactivity of NPs and small MPs toward light and chemical oxidants. Aqueous suspensions of polymers in nano and micro-size range were exposed to light and hydroxyl radicals. Reactivity constants between hydroxyl radicals and plastic particles were calculated using a competition kinetic method; a linear correlation between reactivity and exposed surface of particles was found. Degradation products (mainly short chain carboxylic acids) realised in liquid phase were identified by ion chromatography (IC) and high-resolution mass spectrometry (HR-MS); also the total organic carbon (TOC) released by plastic degradation was measured. The possible morphology changes of particles due to the oxidation processes were investigated using a Scanning Electron Microscopy (SEM). We studied the degradation of different types of plastic particles: polystyrene (PS), polystyrenedivinylbenzene (PSDVB), polyvinylchloride (PVC), polyethylene (PE), polytetrafluoroethylene (PTFE) and polymethylmetacrylate (PMMA). The size range of plastic particles used varied from 200 nm up to 35000 nm and we investigated both monodisperse and polydisperse samples. For monodisperse polystyrene samples we find a correlation between the size of the particles and the reactivity, for polydisperse samples it is more difficult to calculate the relationship between exposed surface and the reactivity. For most of the investigated plastic samples, degradation leads to formation of small organic molecules and of compounds with molecular mass up to 200 Da. For example, the degradation of PS particles induced by hydroxyl radicals, leads to formation of formic, acetic, lactic and benzoic acid as shown in Figure 1. We do not observe in the mass spectra higher weight (>200 Da) compounds derived by the breakup of large segment of the polymer chain. Therefore, these preliminary results suggest that polymer oxidation takes place little by little at the chain extremities, but further investigations are needed to confirm this hypothesis.

3. Conclusions

In this work, we found that plastics in nano- and micro-size can react with oxidants and the degradation can lead to formation of small organic compounds (released in aqueous solution) and a change in the particle morphology. The reactivity constants can be used to simulate the reactivity of plastic debris in the environment and to estimate the contribution of NPs and MPs degradation to the dissolved organic matter in natural waters.

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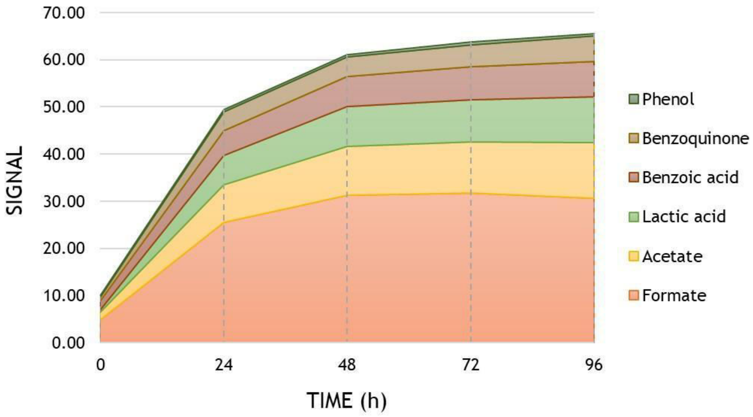

Figure 1. Products formation during PS irradiation in presence of photogenerated hydroxyl radicals.

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OP65

MICROSAMPLING TECHNIQUES PROVIDE NEW INSIGHTS ON SOIL FERTILISATION: A HIGH-RESOLUTION SPATIOTEMPORAL STUDY OF PHOSPHORUS

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1. Introduction

Phosphorus (P) is an essential nutrient for plants, so much that it is also one of the major limiting nutrients for crops yield [1], hence global food production relies on P fertilizer application. However, P-fertilisers efficiency is limited by phosphorus removal from the local soil solution either by absorption onto soil particles or by runoff, which can cause pollution and eutrophication of water bodies. Consequently, P concentrations in the soil solution are reportedly very low [2] and its diffusion in soil is very slow as it is influenced by both abiotic, like dissolution and adsorption, and biological processes.

In order to maximise crops yield while minimising side-effects such as P runoff, precision agriculture strategies have to be implemented, however, they would require information on on the spatiotemporal scales of P release from fertiliser granules and its mobility in soil. This study aims at determining the spatial and temporal scales of P movement in soil at high resolution by using minimally invasive sampling (microdialysis) and imaging (X-ray Computed Tomography) techniques.

2. Results and Discussion

In this study [3], we developed an experimental assay for investigating P release from the fertilizer pellets, and its movement through soil. We implemented non-invasive microsampling techniques and the collected samples were analysed by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). We also used X-ray Computed Tomography for a 3D reconstruction of the system and for monitoring changes in the fertiliser granule and soil structure throughout the whole experiment.

Microdialysis is a passive sampling technique that relies on the diffusion of solutes through a semi-permeable membrane. It is performed with minimally invasive probes that allow to collect multiple samples of the soil solution from the same spot without disrupting the soil structure.

Microdialysis results showed a rapid single pulse release of P from the granule within the first 2 hours from soil wetting followed by a gradual decrease over time. This observation is supported by X-ray computed tomography (XCT) 3D imaging, which showed a progressive wetting of the granule taking place in the first 24 hours from soil wetting.

We have also investigated the effect of the soil bulk density on P movement. We have conducted twin experiments using two different fractions of the same soil. The fine soil fraction comprised all the particles with a diameter below 2 mm, while the coarse soil fraction corresponded to the fraction of particles with diameter ranging between 1.18 mm and 2 mm. The results of this experiment showed that higher soil bulk densities (and in turn lower soil porosities) contribute in slowing down and reducing the maximum concentration of the P pulse. Moreover, the total phosphorus concentration profile, measured at the end of the experiment by soil digestion and analysis, showed a more homogeneous distribution of P in the soil column in the coarse case rather than in the fine case.

Finally, we have compared microdialysis with more widely used microsampling probes named suction cups [4]. Suction cups provide an active sampling of the soil solution and could therefore be more invasive than microdialysis. Suction cups samples in fine soil resembled the trend observed with microdialysis in coarse soil, showing that suction cups have an impact on soil water flow dynamics that can also influence the system under observation.

3. Conclusions

In this study, we demonstrated that phosphorus fertiliser granules release all the phosphorus within a very limited time from their application (less than 2 hours) in a single pulse. Moreover, phosphorus' free path is very short due to soil particles binding, therefore, the P patch is accessible to plant roots only at a specific depth which doesn't necessarily match the area explored by the roots for the whole lifespan of the plant. Understanding the fundamental processes taking place at the fertiliser pellet scale can guide precision agriculture decisions on fertilisation timing for maximising crop yields whilst minimising runoff.
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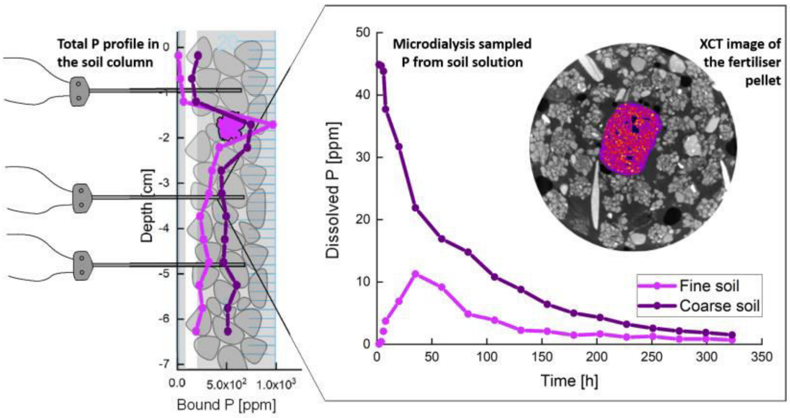

Graphical abstract showing the main results of the study

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OP66

FE-IDS: A NEW BIODEGRADABLE CATALYST FOR PHOTO FENTON-LIKE PROCESSES AT NEUTRAL PH

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1. Introduction

Fenton and photo Fenton processes are among the most effective advanced oxidation processes (AOPs) in industrial wastewater treatment. However, they are still barely faesible for full-scale applications due to the requirement of a strongly acidic pH to ensure the solubility of iron ions [1].

To cope with this limitation, alternative processes have been proposed as (photo) Fenton-like processes, involving the use of chelating agents to form with iron or other transition metals, complexes soluble at neutral and circumneutral pH and active in Fenton-type mechanism [2,3].

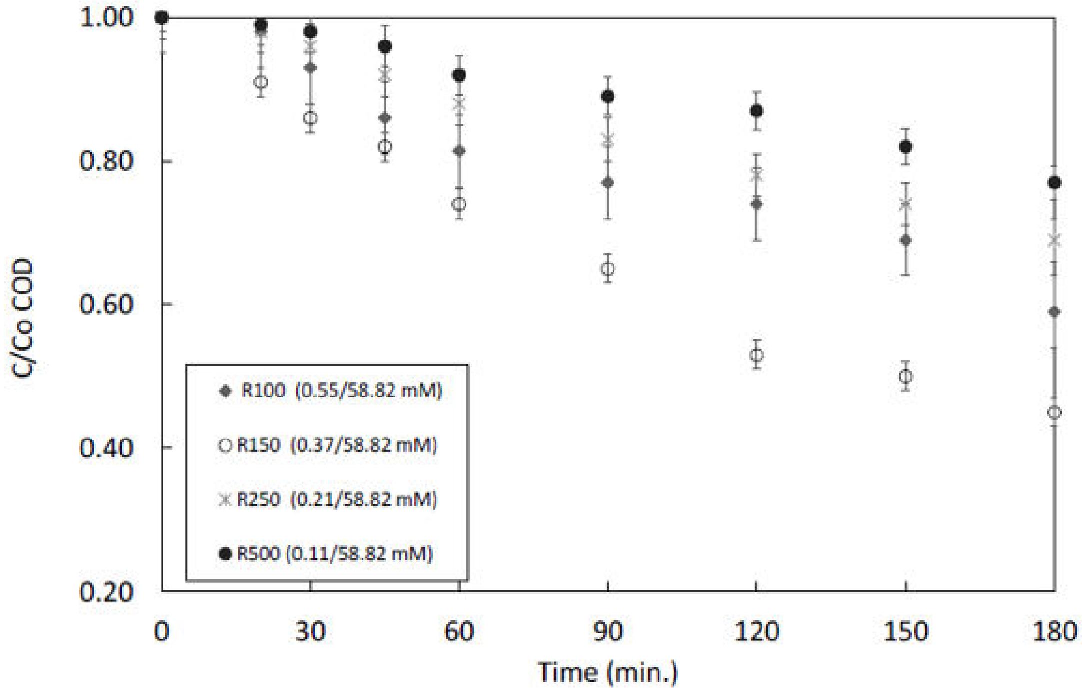
Thus, following the benign-by-design approach , a new, green, active and fully biodegradable complex, ferric iminodisucinate (Fe^{III}-IDS), able to promote the Fenton-like process is presented herein for the treatment of an industrial olive mill wastewater (OMW) [4].

2. Results and Discussion

First, the aerobic biodegradability of Fe-IDS was assessed (96% in 28 days). Then, the complex was tested as catalyst for Fenton-like and photo Fenton-like processes for degradation of phenol as target model compound. Experiments were performed in dark, and under both UV-C and solar irradiation to evaluate the effect of the light surce. Since solar-activated photo Fenton-like process gave the best results in terms of COD removal, this process was also investigated for the treatment of an industrial OMW. The process was optimised varying the catalyst loading at fixed hydrogen peroxide initial concentration (58,8 mM), in order to achieve the highest COD removal. In the best scenario, with a Fe-IDS loading of 0.37 mM gave a COD removal of 55%. Furthermore, the biodegradability of treated samples was increased from 0,16 up to 0,45, making the treated wastewater suitable for a biological treatment.

3. Conclusions

To summarise the main achievments of this work, Fe-IDS was found to be completely biodegradable (96% in 28 days) and it was proved to be a suitable environmental friendly catalyst in Fenton-like and photo Fenton-like processes for industrial OMW. The catalyst was active in both UV-C and solar activated processes. As matter of facts, it was even more active when supported by solar radiation, with a COD removal of 55% and improved biodegradability of the wastewater (from 0.16 to 0.45). The possibility to work at circum-neutral pH and with solar irradiation allows to significanty lower the managing costs usually associated with this kind of processes, and the results obtained make this process a suitable pretreatment before a biological one for OMW.



COD removal by solar photo Fenton-like processes at different Fe-IDS/H_2O_2 ratios

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OP67

TREATMENT OF WEATHERING STEEL AFFECTED BY VANDALIC ACTS

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1. Introduction

Weathering steels are low alloy steel resistant to atmospheric corrosion thanks to their protective oxide layer, called patina. These materials are highly appreciated in construction and art since they have good mechanical properties, appreciable chromatic characteristics and, if properly applied, low maintenance needs. The protective surface layer can develop throught both natural or artificial processes, but if not properly developed it can lose its properties and degrade due to unfavorable conditions (absence of wet/dry cycling, very long wetness times, atmospheres with a marine component, polluted environment, wrong exposure conditions) [1, 2]. As already stated, this material is widely applied in several fields and in some cases it is affected by diverse forms of degradation caused by improper use or vandalism. The aim of this work is to investigate the corrosion behaviour of the patina and possible interventions on anthropogenic degradation (graffiti).

2. Results and Discussion

Naturally aged weathering steel samples were investigated, they were characterised by a heterogeneous natural light-brown patina with a few orange areas and some small darker spots. The FTIR and XRD analyses allowed us to identify lepidocrocite as the main corrosion product present on the weathering steel patina, together with magnetite and maghemite. These data were in accordance with literature on XRD analyses performed on natural weathering steel patinas [2]. Electrochemical characterisation was performed on the following order in each investigated area: potential monitoring, linear polarisation resistance (LPR), electrochemical impedance spectroscopy (EIS), followed by a cathodic or anodic polarisation. The trend of LPR curves together with the polarisation resistance (Rp) value provides an indication of the protectiveness of the patina: when a curved trend is observed this indicates that the corrosion layers are protective, while a linear trend is typical of active surfaces (Fig. 1a). Higher Rp and higher corrosion potentials were always associated to curved trends of LPR measurements. Considering EIS results, it was observed that the Nyquist plots reported a longer diffusion tail (diagonal line at the high frequencies) when associated to a protective LPR curve than to a linear one (Fig. 1b). Regarding the patination techniques in the case of degradation phenomena of the patina, a simulation of graffiti (spray paint and scratches) was considered. Firstly, weathering steel samples were sprayed with a commercial blue spray paint, then they were cleaned with different techniques: using a polypropylene (PP) sponge and acetone, with a commercial acetone spray, with a cotton ball soaked in acetone, and with a latex sponge soaked in acetone and a brush. The results of each method were analyzed with the microscope, the colorimeter, and the FTIR spectrometer. Two samples were scratched using a micro-scratch tester in order to simulate the incisions on the patina (Fig. 1c). Two different patination techniques were proposed. The surfaces were treated with a chemical tannin-based commercial product (Fig. 1d) and with a 10%wt solution of sulfuric acid (H_2SO_4) [3] (Fig. 1e). The application of the tannin-based product caused a darkening of the patina which become black; while the sample treated with sulfuric acid assumed the characteristic orange-brown color of the patina. The first technique in not accepltable since it produced an important change in color on the patina, which is not allowed from the point of view of restoration instances. Instead, the sulfuric acid patination method produces more acceptable results, even though the patina resulted brighter than the original one. In both cases the scratches are not anymore clearly visible after the chemical treatments since they were covered by corrosion products. Moreover, in line with literature, in both cases the artificial patinas do not develop protective properties [3, 4].

3. Conclusions

The outcomes of the characterisation of a natural weathering steel patina showed that the patina presented different trends (protective or active) when the analyses were applied on different points of the same surface. No clear correlation in terms of color or composition could be identified. In the case of spray paint application, the coupling between acetone application and brushing removed the spray paint residues under the patina. Regarding the removal of the scratches, results indicated that sulfuric acid is preferable with respect to the tannin product, even although neither treatment was completely satisfactory.

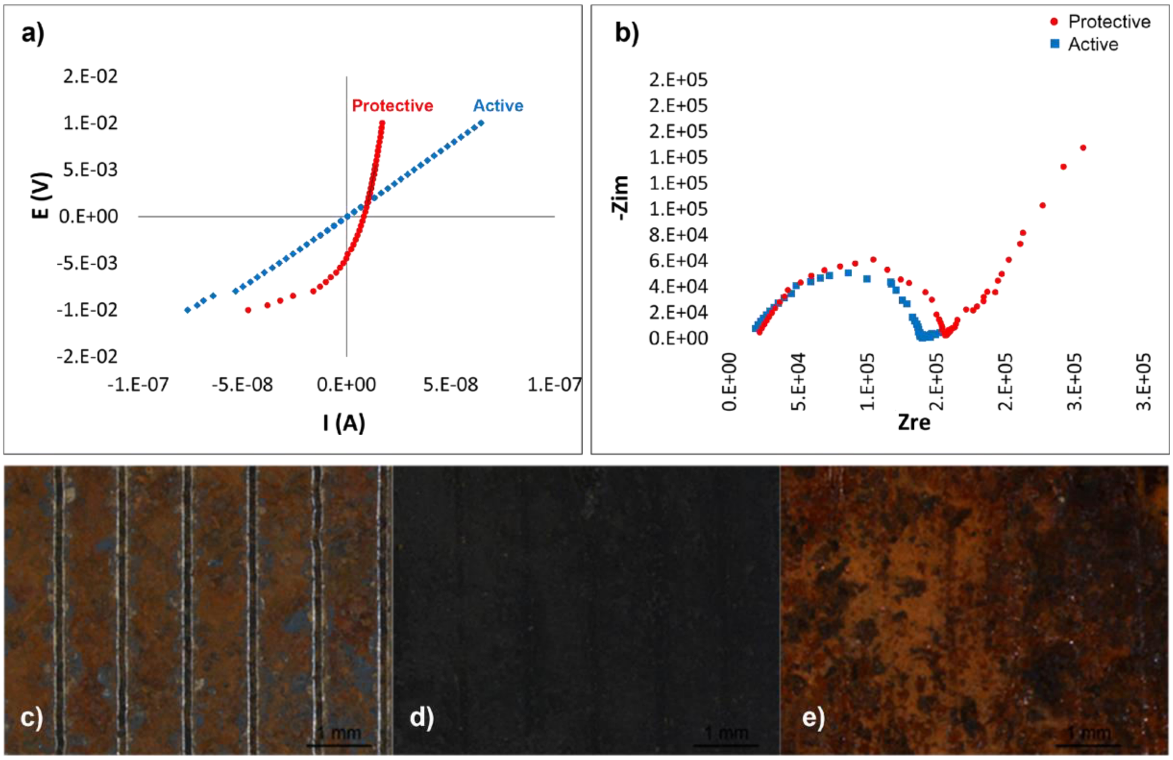

Fig. 1 a) LPR graph ; b) Nyquist graph. c) scratches; d) tannin product; e) H_2SO_4

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OP68

SPITZ-RUND (1925) BY WASILIJ KANDINSKIJ: DIAGNOSTIC ANALYSES FROM KNOWLEDGE TO CONSERVATIVE TREATMENTS

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1. Introduction

SPITZ-RUND (1925) by Wasilij Kandinskij is an oil painting on cardboard 4 millimetres thick, subsequently glued on a wooden support. Due to the historic labels stuck on the back of the wood board, the authors suppose that the intervention was made in a period between the 1930s and 1970s. After having been applied on the wood, the painting was varnished with a keton resin, generally used as a protective varnish after the 50s.

The conservation treatment on Spitz-Rund presented in this work has been divided into two steps: the first phase (2018-2019) focused on studying the object through a multidisciplinary approach by means of non-invasive and micro-invasive techniques. The second phase of the project (2021) has been focused on the conservative treatment aiming at improving the aspect fruition of the painting and its future preservation. More specifically, the aim of the second phase of intervention has been the thinning of the synthetic varnish that was present on the surface. The cleaning treatment has been carried out after a preliminary experimental phase on mockups.

2. Results and Discussion

The first diagnostic campaign, carried out by means of non-invasive and micro-invasive analyses (multispectral imaging, XRF, Raman spectroscopy and FORS spot analyses, Macro-XRF, and after micro-sampling FTIR spectroscopy, PY-GC/MS and cross sections analysed by OM and SEM/EDS) has allowed to hypothesize the painting stratigraphy as reported in fig. 1. The original cardboard has been glued on a not original wooden support by means of synthetic adhesive (PVAc). The painted layers have been spread on a white ground, composed by a zinc white and proteinaceous glue layer. The different colors used are made of organic and inorganic pigments either in drying oil or natural resin, or in a mixture of both binding media, to obtain the desired chromatic effects.

After this first analytical campaign seeking to characterize the materials and technique used by the artist, further investigations have been carried out specifically to monitor the cleaning process.

The aim of the intervention was the thinning of the ketone resin varnish that was present on the painting surface. For this purpose, a preliminary stage of experimental tests has been carried out. Different kinds of model samples have been set to simulate the stratigraphy constituting the pink background area. The film layers have been brushed onto a paper support. After accelerated ageing, different cleaning solutions have been tested. Free solvents and supported on gels have been tested to find a correct methodology to remove the varnish on the painting as safely as possible.

Treatments were evaluated by means of portable optical microscopy in visible and UV light, 3D-OM and Mid-infrared (MIR) reflectance spectroscopy, before and after cleaning. Furthermore, in order to assess the effect of the chosen methodology on some mockups, microscopic samples have been taken from areas corresponding to the transition between the cleaned and uncleaned surfaces and analyzed with optical microscopy.

After the trials, the selected cleaning treatment has been monitored by means of the same non-invasive analytical techniques applied to the mockups. Furthermore, all the cleaning procedure has been achieved under OM observation.

3. Conclusions

The two-phases analytical protocol developed for the study of the oil painting on cardboard allowed to reconstruct the artistic technique and to follow the cleaning processes in detail, almost exclusively through a non-invasive approach.

Moreover, the potential of UV fluorescence imaging, 3D microscopy and Mid-infrared (MIR) reflectance spectroscopy to monitor cleaning processes has been verified, allowing to achieve the thinning of a previous non-adequate treatment.

Figure 1. Reonstructed stratigrafphy of the panting

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OP69

A MULTI-ANALYTICAL APPROACH FOR DETERMINATION OF SAFFRON QUALITY

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1. Introduction

Crocus sativus, commonly known as saffron, is a spice widely used both in the culinary and cosmetic fields for its well-known coloring, flavouring and aromatic properties. Furthermore, it is used in traditional medicine for its therapeutic properties, such as eupeptic, sedative, antispasmodic, analgesic and exciting effects; it is also recognized to stimulate appetite and digestion and can be used to treat ailments such as coughs, insomnia and asthma [1]. Saffron spice is constituted by the dried stigmas of the C. sativus flowers, which are manually or mechanically separated and dried to produce commercially available saffron in filaments, or powder if the final product is crushed. Due to its unique organoleptic attributes and the difficulties involved in its cultivation, harvesting and handling, saffron is considered an high value agricultural product and the most expensive spice in the world [2]. It follows that this spice is an important candidate for adulterations, especially the product sold in powder form, into which the foreign material can be introduced more easily. Therefore, proper quality control of saffron is an important issue for the food industry and for consumers.

2. Results and Discussion

In the present work 21 samples of saffron of different types and origins were analyzed; among them, 13 samples from small Italian producers were in the form of stigmas, while the remaining 8 samples from foreign or commercial sources were in the form of powder. All the samples have been subjected to the quality analyses required by the ISO 3632:2011 standard, and therefore have been divided, where possible, into the product classes required by the cited standard. The analysis of the percentage of humidity and volatile substances and the consequent analysis by UV-Vis spectroscopy have shown that most of the samples considered cannot be assigned to one of the three product classes provided as at least one of the analysis parameters exceeds what required by the standard, and bring out its limits. The samples were then subjected to morphological analysis by SEM-EDX, to analyse their characteristics and evaluate a possible contamination. The results obtained show characteristics common to stigmas samples, directly attributable to their intrinsic nature and their geographical origin and thus providing further information on their quality. Moreover, the EDX data provided valuable information on the natural contaminants of an accidental nature found in them, useful for building the history of the sample. The same kind of analyses, carried out on the powder samples, confirmed their origin from the trituration of the stigmas; in some cases it was possible to identify the presence of contaminants of floral or vegetable origin, or particles of inorganic origin. Moreover, the samples were subjected to FT-IR-ATR analysis, to evaluate if this technique could be a valid support for the verification of the quality of the products. In this case, the data collected are in line with the provisions for saffron samples, but do not allow to evaluate the possible presence of small contaminants; the technique for these samples is therefore not enough sensitive in assessing the quality. Finally, the data collected were used for a preliminary chemometric study which, in particular in relation to the SEM-EDX measurements, made it possible to better visualize the common characteristics of the samples under examination.

3. Conclusions

This study shows that the parameters considered by the ISO 3632:2011 standard should not be fully capable of assessing the quality of saffron. On the one hand, the FTIR-ATR and SEM-EDX analyzes confirmed that the samples falling into the first commercial category according to the ISO method were indeed of high quality and no contamination or adulteration was detected. Furthermore, a correlation between the concentration of some target elements (K, P, S, Ca, Al, Si, Fe) and the quality of the samples was preliminarily established.

Figure 1. Crocus flower with stigma well visible and, on background, a SEM image of single stigma.

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OP70

INNOVATIVE HYBRID AIR QUALITY MONITORING NETWORK IN THE CITY OF TURIN

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1. Introduction

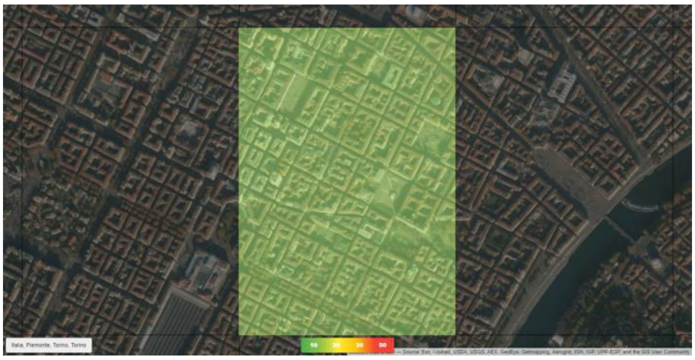
Air quality is an issue that has involved many subjects in recent years. Cities with a high degree of urbanization and industrialization are the most interesting places for monitoring air quality [1]. To map the urban context with a high resolution, the real-time on-road monitoring networks for air quality - ROMS [2] have been developed in recent years. These networks allow the pollution levels definition with a resolution of 1kmq thanks to the measurement devices positioning on moving vehicles. The sensors used are based on IoT technology and allow the measurement of PM10, PM2.5, PM1 and microclimate parameters with a resolution of 1 minute. The installed monitoring network is hybrid and consists of the ROMS network made up of 22 vehicles and a fixed network made up of 8 measuring devices. In this way, a pollutant concentration map with a high spatial and temporal resolution will be obtained. In this case study, the sensors are located on the maintenance vehicles of Sirti, one of the largest companies involved in telecommunications, systems integration, infrastructure and, security.

2. Results and Discussion

The ROMS network provides air quality data with a resolution of 1 km^2, however these systems have limitations related to the operating range of the measuring devices that are connected to the vehicles. There is a lack of data on holidays and in the evenings when vehicles are stationary. Furthermore, the urban context does not allow the passage of vehicles in limited traffic zones (LTZ) or green or pedestrian areas. To make up for the lack of data, either modeling techniques are used to estimate missing data [3] or, as in this case, a fixed monitoring network for the air quality measurements with high spatial and temporal resolution is implemented to support ROMS. In this way, the lack of data by the ROMS network is compensate for the fixed network that provides data in real time 7/7 days 24/24 hours. In addition, the fixed control devices not only provide information on microclimate as pressure, temperature, relative humidity but also on the wind intensity and direction which are fundamental for the dispersion models definition and for the pollutants tracking. The fixed air quality monitoring network installation preceded by a preliminary study to identify the correct positioning points of the measuring devices. To do this, vehicles GPS routes data on which the measuring devices would have been installed were first analyzed to verify which areas remained uncovered in the monitoring. Following this analysis, eight macro-areas were identified in which to install the fixed measuring devices. The analysis of macro-areas to identify sensitive points to pollution such as schools, parks, pedestrian areas and areas with high traffic flow was carried out to define the correct installation points on the territory. The measured data can be reported directly on the map of the considered area using, for example, a color scale. A color scale ranging from green to red was used to display the pollution levels. Green indicates a condition of absence of pollution while the tendency towards yellow-orange indicates a progressive approach to the limit value and the reaching of red represents the overrun of this limit. The daily limits are defined by the Legislative Decree. 155/2010 and for PM10 it is set at 50 $\mu g/m^3$ while for PM2.5 it is set at 25 $\mu g/m^3$. In Figure 1 it is shown that, for a cell with an area of 1km^2 it is possible to define the pollutants concentrations given by the first fixed monitoring device installed. The cell taken as an example shows a low concentration of PM10 and is representative of the city center. As can be seen from the satellite map (Figure 1), the area considered has a high degree of urbanization and the roads pattern is very dense, indicating a high traffic. Considering the meteorological conditions corresponding to the measurement date shown, the high wind speed measured explains the low levels of pollution although we are referring to a potentially very polluted area. The high wind speed in fact allows a rapid dispersion of pollutants and therefore reduces pollution levels. Maps produced every 30 minutes, hourly, daily, weekly, monthly, will allow in depth pollution analysis in the areas considered to support any actions introduced by policy makers for the abatement of environmental pollution.

3. Conclusions

A hybrid network for air quality monitoring was implemented in Turin (Italy). The network consists of 22 mobile measuring devices and 8 fixed measuring devices that provide information on the particulate matter concentrations and meteorological parameters. The positions choice where to install the fixed measurements devices was carried out with a preliminary analysis of the vehicle routes and areas sensitive to pollution. The data are reported directly on a map with a resolution of 1kmq. The time resolution of 1 minute with which the data are collected, combined with the resolution of 1kmq allows the detailed definition of the pollution levels. Deep information on pollution levels will help the implementation of strategies for the air pollution reduction.



PM10 daily concentration measured in Turin (Italy) with the fixed measuring device installed.

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OP71

POLLUTION LEVELS OF METALS AND RARE EARTH ELEMENTS (REES) IN DIFFERENT SITES IN SOUTHERN ITALY

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1. Introduction

Heavy metal pollution is a serious threat to environment due to their high toxicity, non-degradability, bioaccumulation and biomagnification. To date, 12 species of heavy metals have been classified as priority pollutants, including As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Ti, and Zn. In addition to metals, also rare earth elements (REEs) have become of great interest to the scientific community. They have been used widely in numerous industrial processes such as in the production of superconductors, supermagnets, catalysts, pigments in glasses, plastics, additives, medicines and cosmetics as well as fertilizers. In recent years, the environmental behaviour of REE has attracted conspicuous attention, especially the study of their geochemistry along with an increased interest in their ecotoxicity [5-7]. The level of pollution by metals and rare earth elements (REEs) was studied in various contaminated sites in Italy, such as the sediments of the Gulf of Pozzuoli (NA), the soils near the industrial site of Taranto, Augusta and Priolo.

2. Results and Discussion

The distribution of metals in surface sediments of Gulf of Pozzuoli (GoP), showed the presence of As, Cd, Hg, Pb, Zn largely exceeded the legal limits. The mercury has an average value of of 5.8 mg/kg, twentyfold higher the limit, accumulating primarily near Bagnoli industrial site. The mean effective range quotient, m-ERM-Q, revealed a high potential for negative biological effects especially in the area nearby the Bagnoli site. The enrichment factor (EF) values were outstandingly high,> 1.5 with values which were often ≥100. The geoaccumulation index, Igeo, was very critical for Cr, Cu, Hg and Ni, showing an Igeo in the range of strongly polluted ($4 < \text{Igeo} < 5$) and very strongly polluted ($\text{Igeo} > 5$). The REE, Y, Th and Sc pollution in sediments of the Gulf of Pozzuoli showed the presence of Ce, La, Nd and Pr had the highest percentage distribution of rare earth elements normalized respect to chondrite with 31.19, 28.35, 19.51 and 8.41% individually. It was observed a marked enrichment of these elements, from west to the east from 26.39 to 111.04 mg/kg and from onshore to offshore from 31.67 to 217.74 mg/kg. The output of the principal component analysis revealed that the REE were mainly of anthropic origin being clearly linked to that of PAHs, metals and organic matter. This, together with their distribution patterns, highlighted the role of the former Bagnoli metallurgical plant in the pollution of the gulf [1,2].

The analysis of the Taranto topsoils showed the highest levels of iron and of total (excluding iron) metals. Sites 1, 3, 7, and 9 (Statte, power plant, and Tamburi 1 and 3) also showed high levels of chromium and/or zinc. The levels of individual metals (from Fe to Sn, including REEs) at different sampling sites were evaluated by PCA [3].

Analysis of the level of soil pollution in the vicinity of the petrochemical plants located in the vicinity of Augusta and Priolo (Sicily SE). they showed higher levels of contamination in the sampling sites located near some petrochemical plants defined as, for example, the “Punta Cugno” site. Furthermore, the analyzes showed the presence of total REEs higher than at other sites. This observation was consistent with the recognized roles of REEs both in oil refining and in the use of catalytic additives in the formulation of diesel fuel. In turn, this finding is in agreement with occupational exposure to REE in workers exposed to diesel exhaust microparticulate.

3. Conclusions

Different studies were conducted to verify the distribution of pollution levels of metals and rare earth elements (REEs) in different contaminated sites in southern Italy. The analyzes showed the presence of high levels of metals and rare earths mainly near the sampling points located nearby to industrialized areas or former industrial areas. In any case, the presence of these elements is almost always attributable to an anthropic origin.

Study areas:Gulf of Pozzuoli (NA), Taranto and Augusta - Priolo

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OP72

CARBONATE SYSTEM PROPERTIES AND DISSOLVED IRON DATA AS CHEMICAL TRACERS OF THE SEA WATER MASSES IN THE EASTERN ROSS SEA (ANTARCTICA)

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1. Introduction

The Eastern Ross Sea (Antarctica) is a key area to understand the role of the Amundsen sea glaciers in driving the thermohaline characteristics of the westward current that can influence the Ross Sea water properties. Nevertheless, only few observations have been collected in this area. For the first time, in the framework of the ESTRO (Effect of the eaSTern inflow of water on the ROss Sea salinity field variability) project a comprehensive physical and chemical dataset was collected. The carbonate system properties (total alkalinity, total inorganic carbon and pH) and dissolved iron data are presented. A principal component analysis (PCA) was used to investigate the main drivers affecting their variability in the samples.

The addition of fresh water together with the increase of atmospheric CO_2 affect the carbonate system parameters, such as pH and carbonate saturation grade (Ω) which are key variables for monitoring the state of ocean acidification. The melting of glaciers could supply Fe to the surrounding waters and an enhancement of this source of Fe may thus stimulate the carbon biological pump representing a mitigating feedback to the increase of atmospheric CO_2 [1].

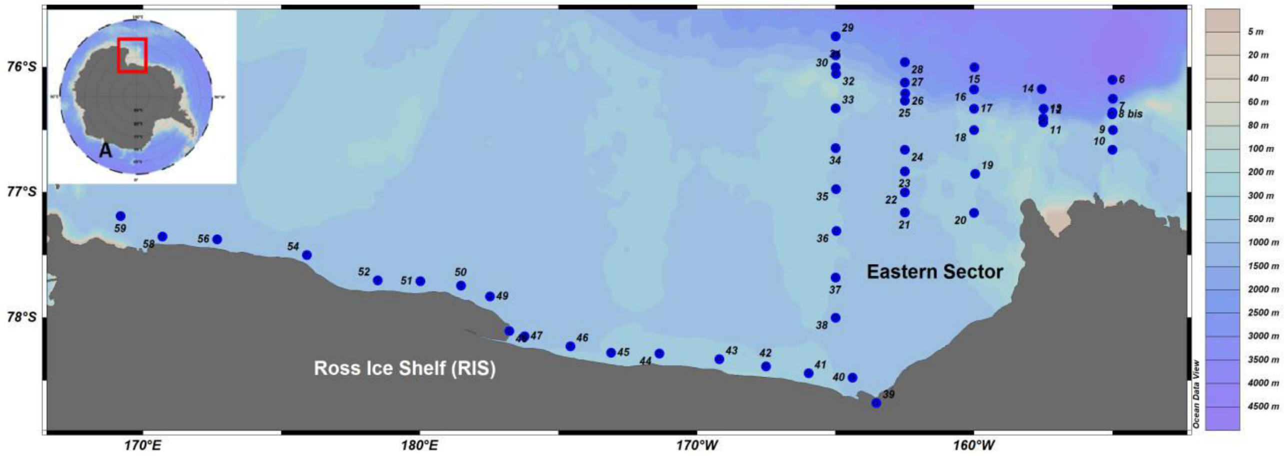
2. Results and Discussion

The less explored area of the Ross Sea is the eastern sector. Only sparse observations, both in time and space, have been collected in the eastern region in the framework of several Antarctic national programmes. On the other hand, the eastern sector is the entrance gate of waters coming from the Amundsen and Bellingshausen Sea, where a strong input of fresh water, due to an accelerated glacial melting, has altered and is altering the freshwater budget of both seas and of the downstream areas. The carbonate system parameters and Ω are key variables to monitor the state of ocean acidification. As part of the ESTRO project, 283 samples were collected at 58 stations (Figure), at different depth between the surface and the bottom, based on CTD profiles. Total alkalinity (AT) values ranged between 2266 and 2374 μmol kg sw^{-1} for the eastern sector and between 2296 and 2376 μmol kg sw^{-1} along the Ross Ice Shelf (RIS), while total inorganic carbon (CT) values ranged between 2131 and 2284 μmol kg sw^{-1} and between 2150 and 2272 μmol kg sw^{-1} for the same areas, respectively. pH ranged between 7.83 and 8.13 in the eastern sector and between 7.96 and 8.21 along the RIS. The concentration of dissolved iron (dFe) ranged from 0.28 to 3.69 nM. Principal component analysis was applied at the whole dataset and then separately to surface and deep samples. PCA applied to the full dataset subdivided the samples on the basis of the depth, in particular identifying the surface, the intermediate (depth<500 m) and the deep (depth>500 m) samples. As regards the surface samples, they were mainly distributed along PC1, that represented the longitudinal variability, moving from the samples collected in the western part of the RIS, characterized by high values of dissolved oxygen (O_2), pH, fluorescence and Ω, to the stations belonging to the eastern Ross Sea. These results underlined the difference in factors affecting the surface variability in the carbonate system in the eastern and western sector of the Ross Sea, where it was more driven by the phytoplankton activities than by the dilution due to sea ice melting [2]. The application of the PCA to the deeper samples dataset allowed us to identify different groups of samples characterized by different hydrographic and chemical properties, principally distributed along PC1, that similarly to the surface samples displayed the longitudinal variability. Based on the potential temperature and salinity (θ/S) plot and O_2 concentration, several intermediate and deep-water masses were identified moving from the eastern sector of the Ross Sea to the western side of the RIS: Amundsen Winter Water (AWW), Circumpolar Deep Water (CDW), Shelf Waters (SW), Deep Ice Shelf

Waters (DISW), High Salinity Shelf Waters (HSSW) and shelf waters sampled along the RIS being neither DISW nor HSSW (RIS). AT and pH were rather conservative and allowed us to distinguish the water masses on the basis of their mean values, resulting a good chemical tracer. On the contrary, dFe displayed a less conservative behaviour and for this reason did not result a good chemical tracer.

3. Conclusions

The results allowed us to obtain information on the chemical characteristics of the eastern area of the Ross Sea that has not yet been studied and to compare it with the western area that has already been well studied. Based on our results, the distribution of the carbonate system parameters in surface waters was more controlled by dilution due to the sea ice melting than by biological activities. PCA analysis highlighted the differences between the eastern sector and RIS area, allowing us to distinguish the different water masses. AT and pH were good conservative tracers of the intermediate and deep water masses unlike dFe which showed a less conservative behavior.



Position of the Ross Sea in the Antarctic continent and sampling stations of the ESTRO project.

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POS01

LETRASET® LIGHT AGEING
UNCONVENTIONAL ARTISTIC MATERIAL DEGRADATION

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1. Introduction

Transfer lettering or Letraset®, the name of the brand who developed the dry transfer technology in 1961, results from the extensive development of synthetic material that occurs during the last two centuries. The dry transfer technology reflects the predominance of plastics in our daily routine and their inevitable occurrence in museums and collections, fact that challenge conservators with the unclear outcomes of their interactions and combinations [1,2].

The relative short lifetime of those when compared with traditional artistic material is a determinant factor that implies the necessity to improve the existent knowledge in regards to Letraset®'s constitution, degradation and the necessary measures to prolong its stability [1].

Contribute to the long-term collection care and consolidation of artworks of Letraset® is the aim of a PhD research in course at the University of Turin which has among its primary research purposes the characterization of the composition and degradation products of Letraset® using ATR-FTIR, EGA-MS, Py-GC/MS) alongside accelerated light and humidity tests.

2. Results and Discussion

Accelerated ageing tests were planned considering the degradation of cellulose nitrate, Letraset®'s main component. Cellulose nitrate, at room temperature, undergoes a combination of acid or alkaline hydrolysis and oxidation, that reaction is catalysed by its breakdown products and acid impurities from the manufacturing process in the presence of light [1,2].

Mock-ups were produced with naturally aged (black and white) Letraset® letters respectively applied to white and black cartridge paper, with additional samples produced on microscopy glass. The samples were light aged for 1100 hours in an irradiation chamber with xenon lamp reproducing the electromagnetic spectrum of sunlight with filter (window Q) with nominal cut-off at 310nm to simulate sunlight indoor exposure filtered by windows.

Measurements of the performing colour and ATR-FTIR data were collected before ageing and after each 24 hours until the first 96 hours, to track the first signs of degradation. After that the analyses were developed each 100 hours until 1100 hours of exposure. Complementary analyses by Py-GC/MS and gloss measurements were done before and after ageing.

The colorimetric data were elaborated according to CIELAB 1976, a metric system for the calculation of colour differences, with no significative alteration observed on the set with black indicia with the variations in colour considered not perceptible by the human eye [3].

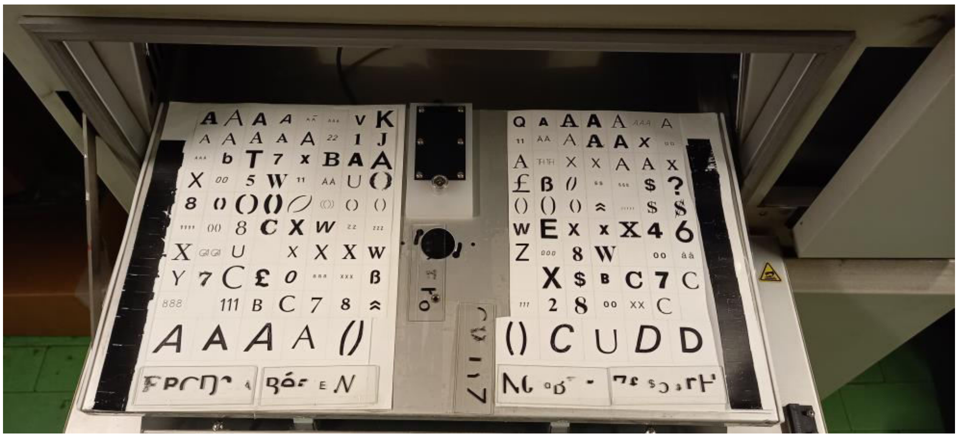
The tests with white indicia, on the other hand, show more significative changes when compared with the data collected with the black set of samples. Although still hardly detectable by the average human eye, more intense changes were observed after 24 and 300 hours [3].

Surrounding elements such as the intense fade of the paper support and some level of transparency observed on the white indicia may have influenced the alterations observed and further analyses are required.

3. Conclusions

Letraset®'s characterization and degradation patterns is challenging not only by the limited trade secret ingredients or changings in formulation, it is also largely influenced by the variety of conservation conditions of the sheets used for the analyses, all naturally aged in unknown conditions and acquired or collect from different locations.

The relative stability observed during the light ageing test are partially due the fact that cellulose nitrate is particularly vulnerable to wavelength between 360-400nm, which is not present in indoor exposure filtered by windows that was recriated during the tests considering that items of Letraset® applied to paper are not expected to be exposed to outdoor conditions [1,2].



Black set of samples during light ageing

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POS02

Photo-induced luminescence imaging for the non-invasive investigation of Cadmium pigments degradation

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1. Introduction

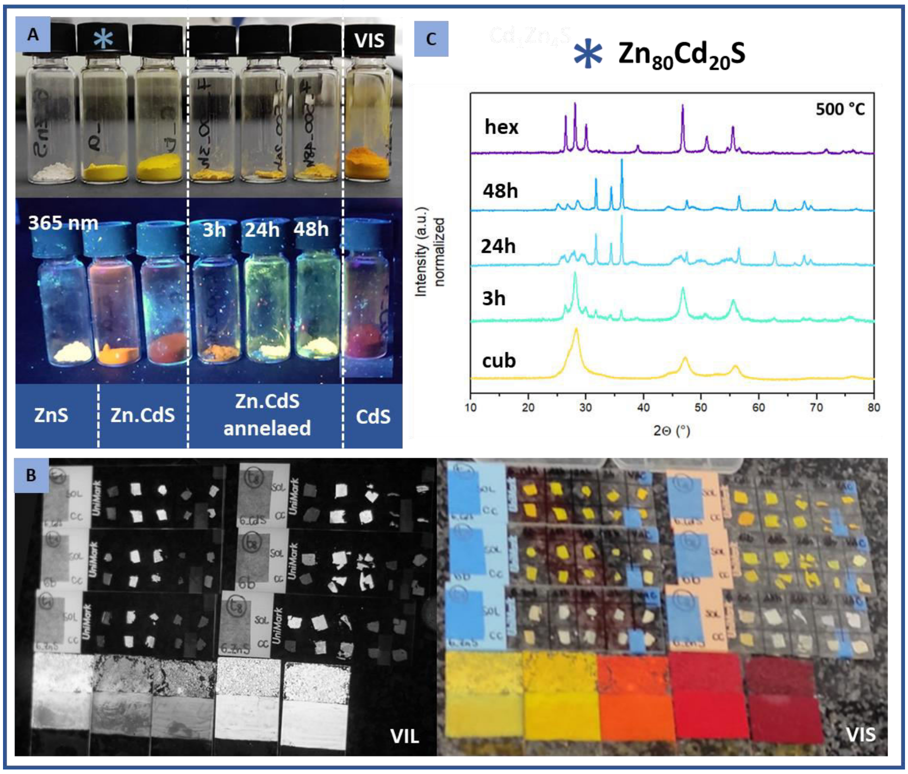
Cd1-xZnxS and CdSexS1-x solid solutions have been employed as pigments since the 1840s and 1910s, respectively, thanks to their bright shades from yellow to orange to red. Paintings in which these pigments were used show remarkable signs of degradation after limited time periods; for example, zinc and cadmium carbonates, sulfates, oxides, and oxalates were reported as deterioration products [1-3]. Thanks to their optical properties, they respond to the photo-induced luminescence imaging, allowing a quick identification and spatial distribution information[4]. The aim of this work is to establish if this technique can be exploited to discriminate the different compositions and can be sensitive to the presence of secondary and deterioration products, either formed as residual form synthesis or from paint degradation.

2. Results and Discussion

Pigments with progressive substitution of Cd or S were synthetized according to the historical synthesis [5,6]. Moreover, Cd.ZnS powders were mixed with oxides and sulfates in increasing amounts to test the limit of detection of the method. The powders have been used to reproduce paint samples. XRD, SEM, PL, FTIR-ATR and Reflectance spectroscopy were employed to characterize the initial powders; while Visible-Induced Infrared Luminescence (VIL) and UV-induced visible luminescence (UVL) imaging coupled with XRF mapping were used to trace the presence of cadmium pigments and degradation products. Different synthesis routes were performed to obtain powders with a broad array of properties. Particular attention has been put on the thermal treatment step to which the sample has been subjected, since this is the synthesis step in which unwanted phases are formed. Thermal treatment has been performed from 3 to 48 hours, both in air or under vacuum. Pigments with different structure, morphology and crystallinity were obtained. All pigments were optically investigated through both Reflectance Spectroscopy and colorimetric measurements with a portable spectrophotometer in order to obtain spectra as well as color coordinates in the L*a*b* color space [7]. In regard to the production of a series of yellow pigments with increasing substitution of Zn with Cd (0% - 20% - 40% - 60% - 80% - 100%), two different routes were performed. The result of both is an intense yellow precipitate. XRD shows how the route employed has a strong influence on the final pigment, producing powders with different structure. Cd-yellow obtained with the first method presents a cubic form – F43m, whereas the pigments obtained with the second one have an hexagonal – P63mc lattice. The hexagonal structure yields a pigment with higher L* values and, while literature agrees that annealing of the powders is required to obtain it, the hexagonal form was achieved at the precipitation step. The thermal treatment performed under vacuum produced, nevertheless, hex-Cd.ZnS when performed on starting cub-Cd.ZnS; annealing in air resulted in formation of secondary products. In regard to Cadmium Reds, XRD showed that the main phase for all samples is Cadmium Selenide, hexagonal form (P63mc); Se – S substitution through the dry method proved to be less efficient than the Zn -Cd one. Interestingly, powders of the same color show different emission under UV light (365 nm): in the case of the series of yellow pigments with different Cd amount, emission changes proportionally to the increasing substitution. Moreover, intensity changes, and increases, in concordance to the amount of secondary product present. The painted layers examined revealed that: I) the organic binder does not interfere with the VIL response, opposite to excitation under the UV light where a strong fluorescence is detected; II) all cadmium pigments show emission; III) the more intense response is given by the samples annealed for 3 and 24h, while, unexpectedly, samples treated for 48h are less bright; IV) pigments containing selenium are more emissive than the zinc-cadmium ones.

3. Conclusions

In conclusion, a broad dataset of Cd-based pigments has been synthetized, gaining insight into the historical process of production. Moreover, the imaging method has been proved to be sensitive to the presence of residual and secondary products, that show different emissions than the pristine samples, and allowed to collection of spatial information and the discrimination among set of pigments with the same colour but different composition, without the use of invasive techniques.



A),B) powders and painted samples in visible and UV light (365 nm) and VIL imaging; C)XRD plots

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POS03

ANALYSIS OF BLACK CRUSTS COLLECTED FROM HISTORICAL BUILDINGS IN THE URBAN AREA OF NAPLES

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1. Introduction

It is well known that domestic combustion and vehicular traffic in urban areas contribute to the emission of substances such as sulfur dioxide, carbon monoxide, nitrogen oxides ad unburnt hydrocarbons, in addition to organic and elemental carbon also emitted by biomass combustion in restoration activities [1, 2]. All these chemical species are responsible for a great part of adverse effects on human health and of the deterioration processes observed on cultural heritage; in particular, the facades of the historic buildings and monument surfaces often suffer from the effects of the atmospheric substances that directly or indirectly act as both oxidizing and acidifying agents. The chemical characterization of these deposits (BCs) is an important goal to achieve because it is the basis for identifying the best intervention strategy, choosing the most suitable methodologies and substances for the deposit to be removed or proposing new approaches. In addition, recent studies indicate that the analysis of BCs chemical composition in urban areas can help to identify the emission processes involved in this type of degradation, in order to propose policies for reducing pollutants [3].

2. Results and Discussion

The study area of this work was the urban center of Naples, a very densely populated area in southern Italy.
Naples is characterized by the presence of different emission sources, principally combustion processes, responsible for the production of chemical species causing surface damages, including particulate matter, volatile compounds, organic and elemental carbon [4]. Further, Naples hosts one of the largest harbors dedicated to both touristic and commercial activities in the Mediterranean area that contributes to the local emissions [2]. The interest for this town is also justified by the presence of a great number of historical buildings and ancient churches (Palazzo Penne, Palazzo Casacalenda, Palazzo Carafa, Chiesa del Gesù Nuovo, Chiesa e Monastero di Santa Chiara, San Giovanni a Carbonara, Chiesa della Santissima Annunziata, etc.) and museums hosted in ancient buildings (Museo Acheologico Nazionale di Napoli, Museo Filangieri, Castel Nuovo, Pio Monte della Misericordia, etc.). In addition, there are also many works of arts and ancient fountains distributed in the historical center (Corpo di Napoli, Obelisco di Piazza del Gesù, Fontana di Monteoliveto, Fontana della Sellaria) and many sites declared UNESCO World Heritage.
The black crusts samples were collected and stored in inert containers; each sample was divided in two parts and characterized by performing the chemical analyses for soluble fraction and hydrocarbons (C12-C40) determination; in particular, Ionic chromatography (IC) and GC-MS techniques were respectively performed. The sampling sites considered were: SS. Annunziata, S. Giovanni a Carbonara, S. Maria La Nova, S. Maria di Costantinopoli, Chiesa del Gesù Nuovo, each of them characterized by a different impact of anthropic activities. The influence of different urban contexts and different ages of the analyzed deposits is clearly displayed by the distribution of chemical species; in particular, in Fig 1 were shown the results related to the ionic composition of deposits from SS. Annunziata (samples collected from four points of the dome, in the directions DD-NW, AA-NE, BB-SE, CC-SW) and S. Giovanni a Carbonara church (samples collected from the facade).

POS03

In this case, the highest concentrations were observed for ionic species (with the exception of nitrite) in the BCs collected from the SS. Annunziata dome; this result, in agreement with other published data, can be explained by the longest deposition period of these deposits [5]. Ammonium showed a different behavior, with the greatest concentration in the deposits collected from S. Giovanni a Carbonara facade; this result can be explained by the proximity of this site to a very busy road. The presence of potassium and acetate was well correlated with the influence of biomass burning in the wood-fired ovens of restaurants and pizzerias. Significant differences were observed also for hydrocarbons; in this case the greatest concentrations were observed for the S. Giovanni a Carbonara and SS. Annunziata BB-SE sites, with values of 0.1789 mg/g. This result can be explained, respectively, by the proximity to the road and the impact of air masses from the port area.

3. Conclusions

The chemical description of black crusts shown in this work will represent an important data set for: studies aimed to compare the black crusts composition in different urban areas; studies on air pollution and its effects; studies on air quality, based on the use of black crusts as passive samplers. In addition, these data will represent an important support for the restores, contributing to the deepening the knowledge on black crusts formation, depending on substrate typology and sampling point typology; also, the spatial analysis of these data, will help the restores in the choice of the most appropriate diagnostic approach and of the better intervention strategy for the cleaning, determining a reduction of process time and costs.

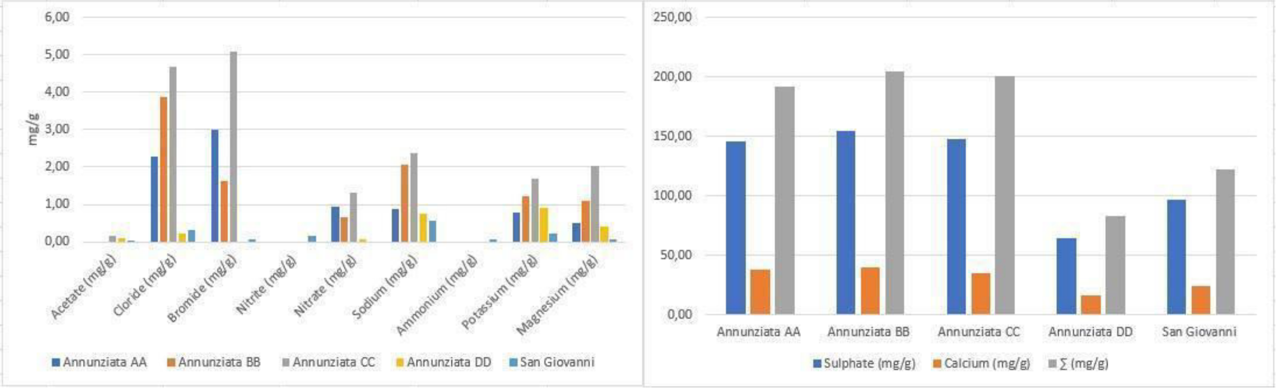

Fig 1. Ionic composition of BCs from SS. Annunziata and S. Giovanni a Carbonara churches.

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POS04

CORRELATION BETWEEN SURFACE ROUGHNESS AND SPECTRAL FEATURES IN IR-REFLECTION SPECTROSCOPY

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1. Introduction

The FTIR is one of the most diffuse techniques for material characterization. In the last 15 years, technology allowed the development of portable and non-invasive systems. An Alpha Bruker, with an External Reflection (ER) module, and a Cary 630 Agilent customized by Madatec with a non-invasive Diffuse Reflection (DR) accessory, were compared. While the ER predominantly collects the specular component of the reflected radiation, the DR intercepts most of the diffuse one. Modifications of spectral features were already reported for surfaces with diverse morphologies, affecting both their properties and generated spectra. In this work, a comparison between two sets of spectra non-invasively acquired on malachite, with five surfaces at different average roughness (S_a), was performed.

2. Results and discussion

The surface microroughness was measured for all investigated areas. A gradual increase of the average surface roughness (S_a) from 0.30 to 6.30 μm was detected in the five (SR1-5) surfaces realized. Both SEM-BSE images and 3D surface height maps further allowed for appreciating morphological differences between different surfaces. The diffusion reflection (DR) spectral profile was found to match quite well with the spectra available from literature. For the analysis of the spectral profiles produced by the two different reflection modules, the following five ranges were considered: (I) 5000-3750 cm^{-1}, (II) 3500-3000 cm^{-1}, (III) 2750-1700 cm^{-1}, (IV) 1700-1250 cm^{-1} and (V) 1250-600 cm^{-1} (ER spectra) or 1250-400 cm^{-1} (DR spectra). The specular reflection bands with $k<1$, properly transformed into absorbance ones by KKT, fall in the II and V ranges, whereas the Reststrahlen bands fall in the IV region. The diffuse reflection bands which fall in the I range (i.e. $2\nu_3(CO_3^{2-})$ at 4510 cm^{-1}, $\nu+\delta(OH)$ at ca. 4400 cm^{-1}, $3\nu_3$ / $\nu+\delta(OH)$ at 4240 cm^{-1}, $\nu+\delta(OH)$ at ca. 4150 cm^{-1} and unassigned at ca. 3890 cm^{-1}) consistently increased in intensity moving from SR1 to SR5. A comparison between the two modules in the I range showed that the ER one allowed for following the evolution of spectral features in the whole S_a range considered. On the other hand, the DR head - specifically developed for rough substrates - coherently performed at its best on SR4 and SR5 surfaces. Alike the I range, also the III one was characterized by weaker absorptions if compared to the features of the other spectral regions. In the SR5 area, on the contrary, the ER spectrum showed all main characteristic bands of malachite, while the DR spectrum provided the same faintly informative profile of SR4. The Alpha-R module started to be sensitive in the III range with an average surface roughness (S_a) of 6.30. The MADAIR module, instead, was able to detect one spectral feature already at S_a=3.20 (SR4), but its sensitivity did not improve when a surface with a nearly double average surface roughness (S_a=6.30, SR5) was analysed. The specular reflection KKT bands, falling in the II range, generally decreased in intensity and broaden in shape from SR1 to SR2, while no significant variations were observed when moving from SR3 to SR5. The Alpha-R module exhibited, in the range 3500-3000 cm^{-1}, a relatively low sensitivity in revealing the specular reflection contribution of areas with $S_a \geq 2.70$, contrary to the MADAIR module, despite being optimized for detecting the diffuse reflection. The strongest features of the entire spectral region were found in the IV range. The intensity of the Reststrahlen bands at 1505 cm^{-1} and 1400 cm^{-1} ($v_{as}(CO_3^{2-})$) did not show a linear trend as the roughness increased, neither in ER nor in DR mode. By the comparison of the two series in the IV interval, it was possible to note that the ER spectra were characterized by a greater intensity of the Reststrahlen bands than the DR ones. The specular behaviour of the two spectral sets resulted to be quite consistent with the roughness of the investigated areas, which did not exceed the S_a value of 3. In the DR mode, instead, the intensity of these bands did not vary with S_a, except for SR1.

3. Conclusions

The acquisition of spectra on malachite surfaces at different roughness, as well as on powder, allowed for evaluating the effectiveness of two portable MID-IFT spectrometers in different spectral ranges. The employed ER module demonstrated high performances, both in terms of sensitivity and flexibility, allowing for the acquisition of cleaner and more resolved bands, compared to the DR module. Interestingly, intervals hosting diffuse reflection bands could be also properly investigated with the ER optics. The DR module allowed the collection of particularly intense specular reflection bands in the 3500-3000 cm^{-1} interval, despite its optical geometry optimized for the preferential collection of the diffuse reflected fraction of radiation.

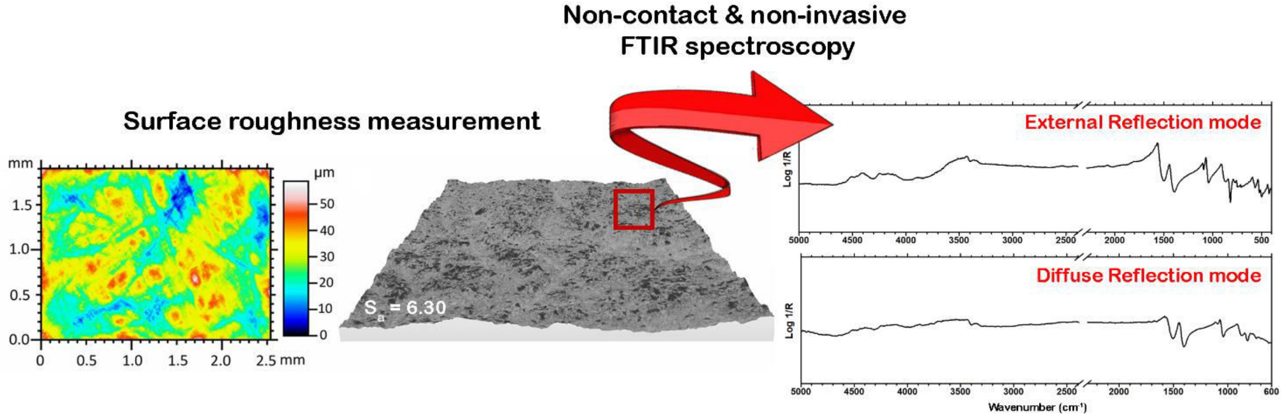

Fig. 1. Graphical abstract of the investigation.

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POS05

DEVELOPMENT OF A MULTI-ANALYTICAL PROTOCOL TO STUDY THE “VINEGAR SYNDROME” ON FILMS MADE OF CELLULOSE ACETATE

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1. Introduction

Motion picture films made of cellulose triacetate (CTA, a material widely used as support in the first half of the 20th century) are subjected to degradation mainly due to the “vinegar syndrome” [1,2]. This phenomenon concerns the side-chain cleavage through ester hydrolysis induced by moisture, with the formation of hydroxyl groups and the release of acetic acid. This reaction is strictly influenced by temperature, humidity and acidity: when the acetic acid concentration increases, the acetic acid formed acts as a catalyst for the deacetylation reaction and induces an autocatalytic process. A secondary effect induced by the acetic acid formed through vinegar syndrome is the hydrolysis of the glycosidic bonds between the glycosidic units constituting the CTA backbone. Then, in addition to the smell, vinegar syndrome’s macroscopic symptoms are the shrinkage and the embrittlement of the film and a consequent detachment of the emulsion.

The main aims of this study are to develop an accelerating aging method to stress CTA in order to artificially induce the vinegar syndrome and to set up a multi-analytical protocol to monitor the evolution of this process.

2. Results and Discussion

We artificially aged both standard CTA-based films and real motion picture films, made of an emulsion layer (silver nanoparticles dispersed in a proteinaceous matrix) and a support layer (CTA with plasticizers). The aging was carried out in hermetically closed chambers in an acid atmosphere for different times in order to induce the vinegar syndrome. Before and after the aging procedure, the samples were characterized with a multi-analytical protocol to study the chemical, physical and mechanical variations induced by the aging itself. We chose to perform Fourier Transform Infrared – Attenuated Total Reflectance (FTIR-ATR) spectroscopy, Derivative Thermogravimetry (DTG) and Tensile strength measurements.

From a first, qualitative observation of the samples, the effects of the aging were evident in terms of shrinkage and embrittlement of the support (Figure 1).

FTIR-ATR spectroscopy was performed to detect the decrease of the acetyl content in a non-invasive way. We monitor the rate between the intensities of the peak corresponding to the C-O stretching of the acetyl group and the peak assigned to the C-O-C of the glycosidic ring, chosen as an internal standard [3,4]. We assumed that the first value decreases with aging while the second one doesn’t change. We observed a decrease in this rate during the aging process for both the CTA-films standard and the real motion picture films. We noticed also that the deacetylation evolves through two phases: a first phase during which the reaction progresses slowly, called induction period, and a second phase in which a rapid increase in the deacetylation rate is detected, due to the autocatalytic nature of the reaction. In the case of real films, it has been observed that the induction period is longer (9-12 days) than in CTA films (4-6 days), probably due to the presence of the emulsion that acts as a protective layer.

The validity of this method was confirmed by gravimetric analysis, titration and free acidity tests [5].

Tensile strength measurements were also carried out to evaluate how the mechanical properties of real motion picture films change with aging: it was possible to observe a decrease in Young's modulus (from 32 N/m² for the unaged film to 20 N/m² for the sample aged for 25 days) up to the breaking in the most degraded samples (films aged 20 and 25 days). This behavior is probably due to various factors, such as the lowering of the average molecular weight of the polymer chains and the loss of plasticizers and emulsion.

Also from the DTG measurements, it was possible to observe a decrease in the thermal degradation temperature of the polymer in the most aged samples [6] (we observed a narrow peak at 365 °C for the unaged film and a wider band centered at about 254 °C for the sample aged for 25 days).

3. Conclusions

In conclusion, the just described multi-analytical protocol based on FTIR-ATR analysis, tensile strength and DTG measurements allowed to monitor in a micro-invasive way the evolution and the effects of the vinegar syndrome induced in an acid environment on standard films and real motion picture films. In the latter case, further investigations will be needed, regarding the influence of plasticizers and emulsion on the final results. The future steps of this project will concern the development of a treatment to inhibit the vinegar syndrome and the evaluation of its effectiveness through the just described protocol.

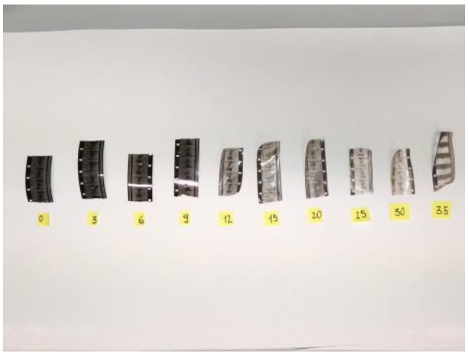

Figure 1. Real motion pictures films subjected to accelerated aging.

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POS06

AN EXTENSIVE STUDY OF ARCHAEOLOGICAL GLASS FROM LAZIO: THE INGOT-EL PROJECT

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1. Introduction

INGOT-EL - INvestigation of Glass Origin and Technology in Etruscan Lands - is a project that aims at bringing new analytical data into the discussion on glass production and circulation in the Iron Age Italy. Currently, Iron Age objects attracts a lot of attention and papers dealing with archaeometric investigations are available [1,2]. Glass underwent its own way of technological evolution in many production centers and chemical analyses can give clues to investigate its origin, although conclusions are not always straightforward.

The ongoing project relies on a large number of glass beads and a wide selection of analytical techniques. Archaeological objects are protected in the museum collections and cannot be evidently damaged for analytical purposes, therefore, in order to obtain adequate information on raw materials, colourants and opacifiers by overcoming the limitations due to the inevitable glass alteration while meeting the requirements of museums, a compromise approach has been applyed. The integrity of the valuable objects was mostly preserved while still obtaining reliable data on a wide set of elements and compounds.

2. Results and Discussion

Feasibility of the project is a primary concern for the stakeholders. Several museums and laboratories were involved, as more than 300 glass beads have been considered. The research is proceding stepwise, by selecting samples to be included in the next step of analysis based on the previous analyses' data. It is the optimal way for processing large sets of samples.

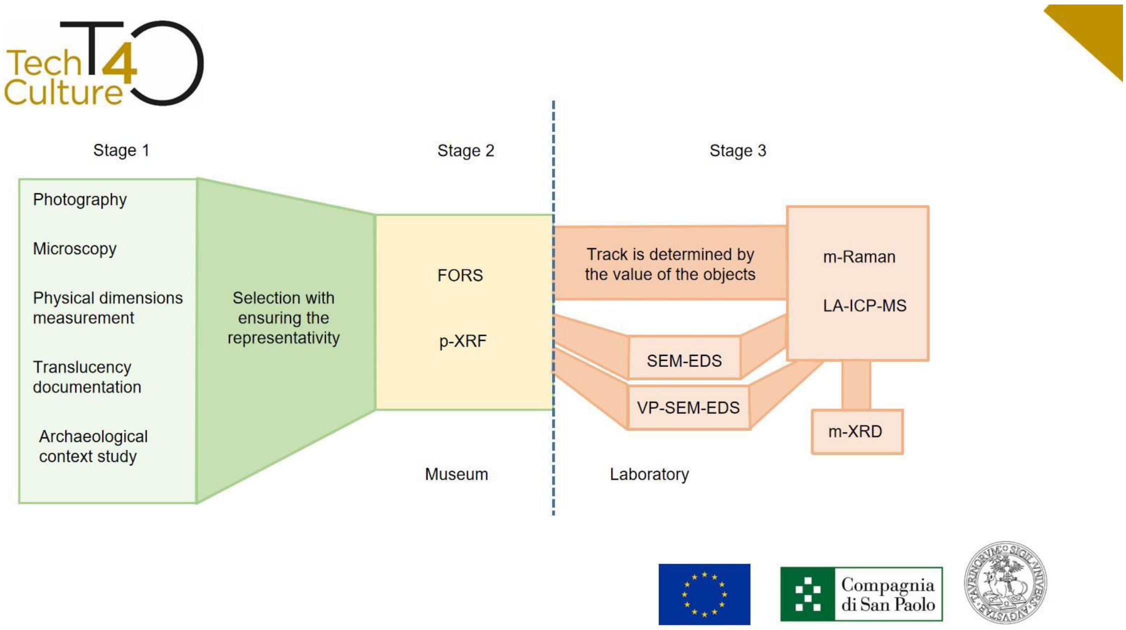
By the kind of work, the questions faced and the analytical approach, the project can be divided into 3 stages: stage 1 includes familiarisation with the beads through the study of their archaeological context and a close visual examination with a comprehensive documentation through digital photography and microscopy of the significant features; stage 2 involves non-invasive analyses with portable X-ray fluorescence (p-XRF) and Fiber Optics Reflectance Spectrometry (FORS) in order to be able to collect data from a large number of samples; stage 3 is an in-depth micro-morphological and chemical study of selected/available beads by means of Scanning Electron Microscopy-Energy Dispersive Spectrometry (SEM-EDS), micro-Raman, micro-X Ray diffraction (m-XRD), Laser Ablation-Induced Coupled Plasma-Mass Spectrometry (LA-ICP-MS). Samples involved in stage 3 are processed through either invasive track (preparation of a cross section) or micro-invasive track (laser ablation analysis on the object as it is). Moreover, samples for which composition or appearance suggests the presence of suspended crystalline phases are analysed with techniques that allow the identification of such phases (Raman and m-XRD). These steps are outlined in the image below. Stage 1 and 2 actions were performed within the museums without the need for taking large number of objects to the laboratory's facilities. All these techniques are widely used for studying ancient glasses [see 3 and references therein]. Compositional data undergoes quality control such as quantification limit determination, precision and accuracy checks.

There are two assumptions that are made when selecting samples: a) beads of the same type have similar chemical composition unless there are differences in appearance; b) conclusions obtained by processing results from stage 3 can be extended to all samples involved in stage 1 and 2 that have similar composition based on p-XRF results.

Preliminary information about main glass batch constituents derived from stage 2 through raw data elaboration for K, Rb, Ca and Sr. Some transition metals might be interpreted as silica source impurities. The presence of specific ions (for example Fe^{2+} and/or Fe^{3+}) can be detected by FORS and provides the clues on the redox conditions inside the furnace. p-XRF and FORS are particularly suitable for detecting the species responsible for glass color and translucency, whereas microscopy is invaluable in guiding the selection of the analytical spots, and also provides information about how the glass beads were formed. In this way, stage 2 results provide an understanding of major divisions within the set of samples. We are dedicating significant attention to ensure the full compatibility of the data obtained in different museums with different p-XRF equipment. The data collected are being compared to the ones obtained during the stage 3 of the analyses, as data processing is still ongoing.

3. Conclusions

Sounding conclusions are possible only when data from several sources will be reconciled, including the archaeological evidence. Some limitations of the specific analytical approaches emerged, as the constraints set by the institusions that keep the objects of public cultural property. They can be detrimental for accuracy of the quantitative analytical data. These issues need to be taken into careful condiseration and will be properly managed. Nevertheless, several trends already emerged from raw data, highlighting differences that will be discussed with the archaeologists, in order to interpret them in view of the the technological development of glass production, connections and trade routes among different regions in the Iron Age Mediterranean.



Scheme of the techniques used for glass characterisation within the INGOT-EL project

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POS07

A CHEMOMETRIC APPROACH FOR THE DEVELOPMENT OF A NEW CLEANING STRATEGY OF IRON STAINS ON CARRARA MARBLES AND ITS EVALUATION THROUGH IMAGE ANALYSIS

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1. Introduction

Chromatic alterations affecting the stone materials making up the Cultural Heritage, represent a problem that is not easy to solve. Of particular note are the stains due to the diffusion of iron corrosion products on marble surfaces. Iron chelants have usually been used for the removal of these stains: one of the most used complexing agents was citrate [1], although other methods involving the use of EDTA have also been tested [2]. Previous studies dedicated to the development of innovative "green", two chelators such as Deferiprone and Glutathione supported on gel have proved effective for the removal of iron corrosion stains from Carrara marble surfaces. In this work, based on XPS results before and after cleaning treatments, Deferiprone (3-hydroxy-1,2-dimethylpyridin-4 (1H) -one) was chosen as the best chelant for the removal of iron stains, to develop a Multivariate Design of Experiment (MDOE). To this aim, to evaluate the optimal composition of the gel based on sodium alginate and polyvinyl alcohol supported by calcium chloride and the effectiveness of the chelating treatment, statistical analysis and image processing were coupled with sensory investigations.

2. Results and Discussion

The effectiveness of the chelant Deferiprone was evaluated with tests performed on Carrara marble samples (100x100x20 mm); the stains were obtained by placing iron bars on the surface of the marbles and promoting corrosion through outdoor exposure for one year. This type of exposure was chosen to obtain a mediated action of the environmental conditions of temperature and rainfall over the four seasons. Oxidation was favored by rain and by the presence of atmospheric humidity and gave rise to the formation of stains. Subsequently, 18 samples were selected with dimensions of 10x15x10 mm, analyzed before and after the treatment by XPS spectroscopy. In order to evaluate the effect on the chelating capacity, the variables relating to the percentage composition of the gel and the operating environmental conditions (indoor/ outdoor) were evaluated using the MDOE procedure. Different compositions of the gel were then obtained to be applied on the stains both in indoor and outdoor conditions and the images of the samples were collected before and after the treatment. A rectangular ROI was obtained from each acquired image to eliminate the background and make them comparable before and after the treatment. Visual evaluation analysis was subsequently used to confirm the goodness of the image analysis strategy. The color intensities of each image were then represented as a frequency histogram, taking into account together red, green and blue channels. The shape of this graphical representation well explains the ROI behavior both in terms of color shade and uniformity, defined by the mean and the standard deviation, respectively. For an effective evaluation of the changes that occurred after the gel treatment, mean and standard deviation were expressed as a relative percentage. This strategy allows us to focus on the improvement, independently from the initial level of contamination.

3. Conclusions

The data processing of the images made it possible to automate the evaluation of the improvement of the samples due to the treatment and, using the Pareto strategy between mean and standard deviation, it was possible to choose the best specimens. Deferiprone proved to be an excellent chelating agent for cleaning marble surfaces affected by metal contamination and DoE represented a rational design of sample preparation in order to evaluate all sources of variability and significantly reduce the number of experiments.

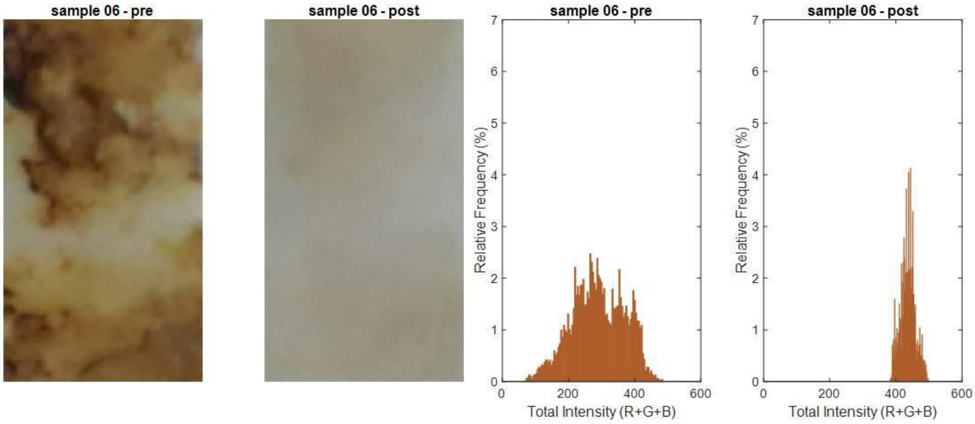

Fig.1 Sample 6 before (left) and after (right) treatment. Relative frequency histograms of ROI

Acknowledgements

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POS08

ARTIFICIAL AGEING TESTING FOR CULTURAL HERITAGE MATERIALS EXPOSED TO A CHANGING TROPOSPHERE: UPDATED GUIDELINES FOR AGEING SOLUTION AND PM

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1. Introduction

Outdoor Cultural Heritage (CH) suffers severe damage due to the interaction among physical and chemical atmospheric factors [1]. To study these mechanisms of degradation of materials and to test the effectiveness of new protective treatments, accelerated ageing tests and artificial rains are widely used in the field of material science and outdoor CH Conservation. In a scenario where climate and tropospheric composition are changing, the compositional variation of atmospheric deposition could strongly contribute to the gap between the results obtained in the laboratory with respect to those from real outdoor exposure. In order to reduce this gap, updated synthetic solutions and particulate matter composition, representative of changed deposition, seem necessary for material testing. Actually, no ready-to-use updated formulations are available which take into account these atmospheric changes. The study herein presented aims at providing updated environmental parameters for the formulation of synthetic depositions of both rainwater and particulate matter to fine-tune accelerated ageing tests and so to set up better conservative and preventive strategies.

2. Results and Discussion

This study provides a suitable range of particulate matter composition and hydrometeor ion concentrations to formulate both synthetic PM and precipitation, following their long-term evolution. The formulation of ageing solutions was obtained by source and trend analysis of a long-term (22 years) series of the chemical composition of bulk depositions samples [2]. Our findings highlight pH values ranging from 4.5 to 7.4 with both the average and median value of around 6 (Fig. 1). This average pH can be classified as alkaline, as the neutral pH for rainwater is assumed to be 5.6. The observed neutralizing action is mainly attributable to calcium carbonate and ammonia of crustal and agricultural origin, respectively. The contribution of mineral carbonates is increasing under the effect of increasing temperature and dry conditions and by an increasing mineral dust contribution from the African desert. The trend analysis was applied to all the following variables: EC, pH, Alkalinity, Na^+, NH^{4+}, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-} as well as NH_4^+/NO_3^- and NH_4^+/SO_4^{2-} ratios. Both the Seasonal Kendall test and the Mann Kendall test were applied and the results obtained reveal statistically significant trends, especially using the Seasonal Kendall test. This suggests the presence of a strong seasonality within the time series in agreement with the local climatology, characterized by a bipolar precipitation pattern. The mean change per year indicates a slightly decreasing trend for all parameters except for sulphate concentration, which shows a more marked decline and for the NH_4^+/SO_4^{2-} ratio which shows a positive trend. pH shows an increasing trend with a mean change per year of about +0.02, suggesting decreasing acidity. Indeed, since the NH_4^+/SO_4^{2-} ratio shows an increase of 0.05 per year with high significance and the high abundance of NH_3, the pH trend is mostly associated with the decrease in H_2SO_4 due to the well-known reduction of sulfur oxides emission/concentration because of the mitigation policy adopted in EU in the past decades. The analyses performed clearly show how not only meteo-climatic but also environmental conditions have changed in terms of atmospheric composition in the recent decades. The ready to use hydrometeor ion concentration formulated considers the sources and trend analysis performed. Concerning the synthetic PM, a formulation is proposed based on the statistical elaboration of current urban PM compositional data from a wide bibliographical survey.

Results are compared with other Mediterranean locations, to provide an effective compositional range for both synthetic rainwater and particulate matter valid for the southern European region, to be applied in material testing, especially for cultural heritage material conservation.

3. Conclusions

This study provides updated ready-to-use ion concentrations for synthesizing atmospheric deposition solutions and a suitable range of particulate matter composition to test materials in the context of climate change, specifically for southern European locations. The rainwater formulation was obtained by source and trend analysis of a long-term dataset of the chemical composition of atmospheric bulk deposition from Po Valley (Italy). The PM formulation is proposed based on the statistical elaboration of current urban PM compositional data from a wide bibliographical survey. The proposed ageing media reflect the compositional change in particular for the pH value increased, the reduced importance of sulfate and nitrate and, the alkalinization provided by calcium, carbonates and ammonium.

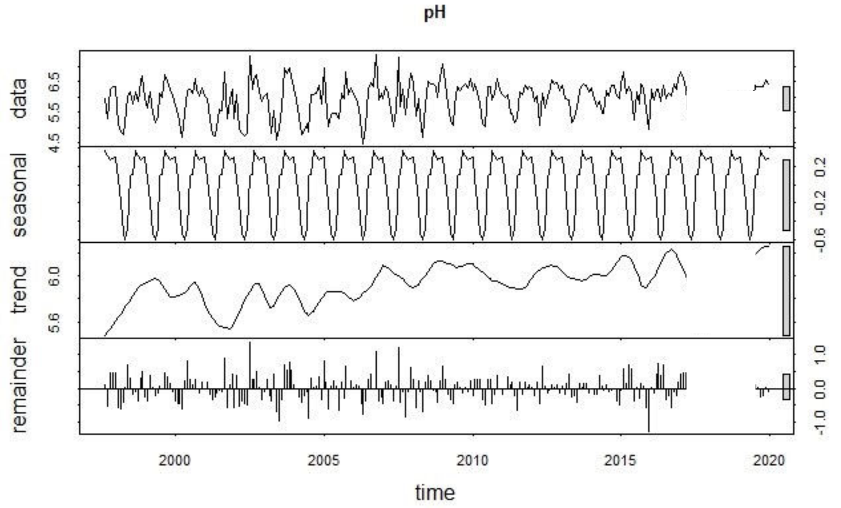

Figure 1. STL decomposition for the time series of pH, from 05-1997 to 12-2019.

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POS09

CONSERVATIVE AND CONSOLIDATING TREATMENTS BASED ON POLYAMIDOAMINES AND CELLULOSE NANOCRYSTALS FOR THE RESTORATION OF TRACING PAPER

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1. Introduction

The tracing paper, also called transparent or translucent paper, was commonly used for architectural, engineering, and design drawings since the end of the 19th century.

As all lignocellulosic materials, tracing paper is subject to natural deterioration through physical, chemical and biological agents, such as UV radiation, humidity, fire, insects and microorganisms. In addition, as a support for architectural drawings and other technical projects, they are often treated directly by the worker, causing mechanical damage such as bending, folds, tears, cuts or stains.

To improve the durability to biotic attacks and hardness, here we propose an innovative treatment, based on polyamidoamines (PAA), whose biostatic activity is known both against insects and molds [1] and cellulose nanocrystals (CNC), as nanoscale constituent for renewable reinforcing agents [2]. The work was carried out in collaboration with Centro Studi e Archivio della Comuniazione (CSAC) Parma, one of the most important museums of the visual arts of the last century, including more than a million of architectural project, design, and art drawings.

2. Results and Discussion

Water and alcohol soluble polyamidoamines (PAA) are synthesized by Michael-type reaction, adding ethanolamine to methylenebisacrylamide in ethanol. The addition reactions have been followed by NMR and Raman spectroscopy, monitoring the decrease of the intensity of the C=C stretching mode of bisacrylamide.

Aqueous suspensions of CNC were successfully produced by sulfuric acid hydrolysis with high yield starting from cotton linter. The crystallinity index estimated by XRD analysis is about 80% (Fig. 1a). The CNC characterized by Raman and FTIR spectroscopy, show the typical features of a highly crystalline material.

The PAA solution was mixed with CNC or commercial cellulose micro-fiber (CMF) powders to obtain a final concentration of 2%.

The treatments, in alcoholic medium, were applied on the tracing paper samples (Canson paper and 1950s paper from CSAC) in different ways: by brush, by exposure to solution vapors and by impregnation. The morphological analysis SEM shows that the brush application is suitable for small samples, while on large areas the exposure to solution vapors is preferable, which guarantees a uniform distribution of the treatment.

Thanks to the deacidification properties of PAA [3], treated papers gave neutral/basic pH. The treatments do not induce significative colorimetric changes on samples (ΔE 1.6) even after artificial ageing (ΔE 2.3). FTIR analysis confirms that no oxidation processes occur.

The reinforcement of samples by treatment in particular with CNC and CMF, has been demonstrated by mechanical tests, performed for each direction (machine- and cross–directions): about the 30% with respect the untreated sample, in machine-direction (fig. 1b) and about 15 % in cross-direction.

The biocidal efficacy of treatments was tested on four bacterial strains (Pseudomonas aeruginosa Pantoea spp., Bacillus subtilis., Staphylococcus aureus) and on four fungal strains (Aspergillus spp., Penicillium spp., Scedosporium spp., Rhodotorula spp.) by means of Kirby-Bauer method.

The results on PAA-based treatments show that Pseudomonas aeruginosa, one the most resistant bacterial species and Bacillus Subtilis were inhibited by the presence of PAA, while the other bacterial species are resistant or minimally sensitive to PAA (zone of inhibition about 3 mm). Among the fungal species only Aspergillus niger and Penicillium spp. were sensitive to PAA biocidal effect; also paper samples treated with PAA-based preservative show significantly lower growth Aspergillus niger and Penicillium spp compared to pure paper.

3. Conclusions

The PAA and CNC based coatings strengthen the interactions among the fibers allowing for stress transfer which, in turn, leads to greater resistance to tensile deformation of the paper. Furthermore, the treatments are effective in preserving the tracing paper from biodeterioration.

The new preservative and consolidating treatments based on polyamidoamines and cellulose nanocrystals can therefore be used for the conservation of lignocellulosic materials as a "green" and bioinspired consolidant with biocidal activity, as an alternative to existing products for restoration.

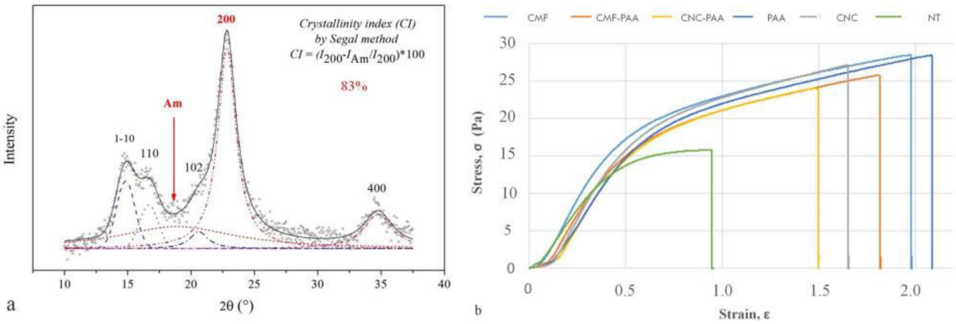

Fig.1 Crystallinity Index of CNC (a); Stress vs. strain for untreated (NT) and treated samples (b)

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POS10

MULTI-ANALYTICAL APPROACH FOR THE STUDY OF INNOVATIVE AND ECO-FRIENDLY COATINGS FOR OUTDOOR BRONZE ARTWORKS

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1. Introduction

Bronze is one of the few metal alloys we are used to perceive covered by corrosion effects. According to personal taste, some people may even prefer the patinated surface rather than its pristine colour.[1]The patina could not only enhance the aesthetic of artworks but it also protects the metallic substrate. However, the constantly growing air pollution, together with more frequent acidic rain phenomena lead to a remarkable alteration of the composition of the patina and the chemical structure in outdoor exposed bronzes. During latter years, the protecting properties of these patinas have become weaker and weaker causing a persistent corrosion, which can only be terminated by means of an efficient and uniform coating.[2]The actual conservation perspective focuses on new eco-friendly and safe treatments. An ideal coating should prevent the object from degradation without modifying its appearance; the application method should be straightforward and the chemical nature of the treatments should allow their removal with a safe and non-toxic approach. Eventually, the properties of these treatments should assure a good protective performance, long-term durability and low-cost maintenance.[3]

2. Results and Discussion

In this work, several formulations of a possibly new non-hazardous coating was investigated: Paraloid® B44, (ethyl acrylate/methyl methacrylate copolymer) was employed in solution with different percentages of a corrosion inhibitor, MPT (5-mercapto-1-phenyltetrazole), and two UV stabilizers, Tinuvin®312 and Tinuvin®5050, whose acting mechanisms sensibly differ. The formulations were artificially aged in a UV chamber for one thousand hours. A multi-analytical approach was adopted for studying the efficacy of the additives on photostability, solubility, glass transition point and colour changes of the coating film over time. FT-IR analyses, colorimetric measurements and glass transition temperatures pointed out that the coatings prepared without the UV stabilizers perform worse. FT-IR analyses highlighted that the only-MPT coatings undergo oxidation phenomena: the signal pertaining to the carbonyl group increases proportionally to its concentration within the first hours. This phenomenon is contained by the addition of Tinuvin®312. Colourimetric measurements (figure 1) displayed a colour change that was more significant at higher concentrations of MPT in the formulations. On the other hand, the coatings including UV stabilizers were affected by a lighter colour change. All coatings exhibited an increase in glass transition temperature after aging: for those containing inhibitor, the increase was higher. Also in this case, the presence of UV stabilizers seems to reduce glass transition temperature variation. Furthermore, in order to test the reversibility of the coatings, their insoluble fractions were analysed. Their amount increases inversely proportional to the concentration of MPT, becoming particularly relevant at minimum concentration. This outcome is promising, taking into account that the anti-corrosive efficiency of MPT increases proportionally to its concentration.

3. Conclusions

In conclusion, the MPT appears to have a different influence on degradation phenomena according to its concentration. At the beginning, cross-linking reactions prevail and cleavage reactions take place over time, promoting an improvement in reversibility. UV stabilizers seems to reduce colour change and oxidation phenomena. Further analyses will be addressed to verify the efficacy of UV stabilizers by testing different concentrations, as well as the anti-corrosive properties of MPT, by applying it on bronze mock ups.

POS10

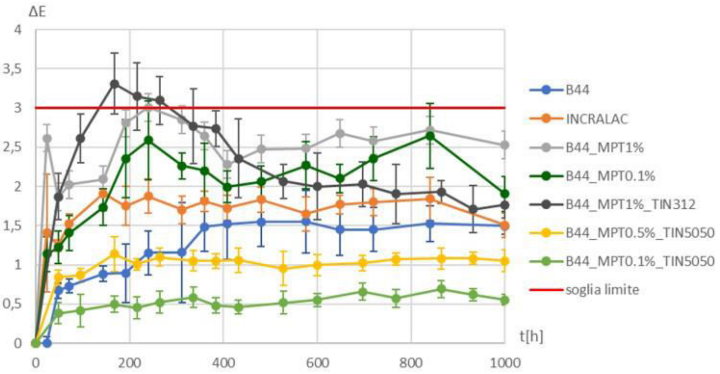

Figure 1: Colour change of some coatings compared to Incralac and Paraloid B44.

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POS11

CHARACTERIZATION OF MODERN STARCHES FROM PLANTS POTENTIALLY AVAILABLE DURING LATE MARINE ISOTOPIC STAGE 3

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1. Introduction

The retrieval of starch grains entrapped inside the pores of ground stone tools of Late Pleistocene [1], provided the evidence that Homo sapiens (HS) was mechanically grinding tubers, fruits, and seeds during its dispersal into Eurasia, occurred between 60-25 ka BP. Starch is the reserve of polysaccharides accumulated in the amyloplasts of plants storage organs, and its high energetic value might have played a vital role for HS to survive at the Northern latitudes' new environments, during the harshening of the climate occurred across the late Marine Isotopic Stage 3 (MIS 3). Starch grains, which are characterized by the presence of concentric rings of amylose and amylopectin, have a micrometric size, and their identification is conventionally carried out by means of optical microscopy with bright and polarized light [2]. In this context, an exhaustive reference collection of starches extracted from plants potentially available during MIS3 could be extremely helpful to recognize the starch still adhering to the ground stones and thus to enhance the narrative on the exploitation of the available resources by the hominins thriving in a given territory.

2. Results and Discussion

To build a reference collection viable to recognize the grains retrieved from macro-lithic tools (ground stones), a careful selection of more than 50 plants putatively available across the Eurasian Steppe during MIS 3 was performed, and the plants were collected along the year, according to their maximum starch yield. A procedure to extract starches from the storage organs was developed and a morphological characterization of the isolated starches by means of both optical and electronic microscopy (OM, Polarized, SEM) was performed. As example, images of the starches extracted from the Aesculus hippocastanum seeds are reported in Figure 1.

In addition, a preliminary physicochemical characterization of the extracted starches was carried out by means of spectroscopic and spectrometric analyses, aiming at overcoming the limits of the sole morphological attribution in use at present.

3. Conclusions

This is the first reference collection of MIS 3 plants that can be used for comparison, which makes available data from imaging, and spectroscopic and spectrometric techniques. The comparative analysis already allowed the identification of several starchy plants that have been processed by HS in key sites where both modern humans and Neandertals were present. The presence of starch on the stone tools used by HS can be interpreted as a dietary adaptation that enhanced modern humans' capacity to thrive in a very cold climate and one of the reasons for its evolutionary success.

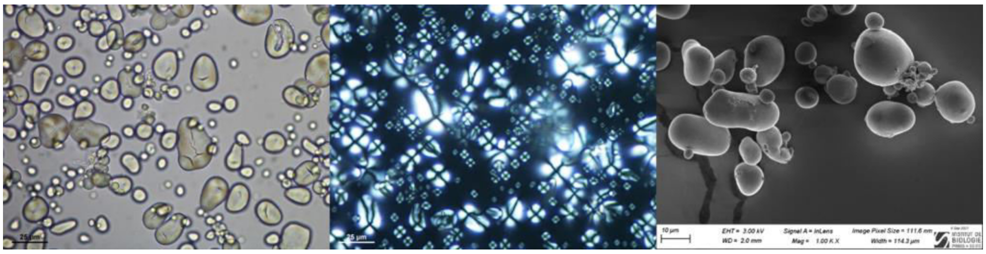

Figure 1. a) Optical microscopy, b) polarized optical microscopy, c) SEM images.

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POS12

ARCHAEOMETRIC INVESTIGATIONS ON PREHISTORICAL ADHESIVES FROM THE VALLESE SITE OF OPPEANO 4D

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1. Introduction

This work presents the results of archaeometric investigations conducted on small ready-to-use mastic ingots but also on residues taken from repaired ceramic pots and wooden objects, such as a sickle (at the welding point of the flints), found in the 'pile-dwelling settlement of Vallese of Oppeano site 4D, one of the most important sites in a humid environment, dated to the Middle Bronze Age, and discovered in recent decades, due to the incredible state of conservation of the structures and the peculiar characteristics of the archaeological context (unit domestic and artisanal). The ingots were concentrated in certain areas of the settlement, since it would suggest an environment dedicated to the preparation of the mastic. These ancient adhesives were probably extracted from the bark of trees and plants readily available in the area, by means of pyrolytic treatments (heating in the absence of oxygen) or boiling [1].

2. Results and Discussion

All samples were analyzed by Fourier Transformed Infrared Spectroscopy (FTIR) in the range 5000-100 cm-1 at the Chemical and Life Sciences branch of the SISSI beamline of Elettra Sincrotrone, Trieste. The data collected were compared with the reference literature and with reference open-source databases [2]. Out of a total of 13 samples (all analyzed in triplicate by taking very small quantities of sample), 12 of them showed the characteristic IR signals of a triterpene resin, most likely of the Betulaceae (birch) family [3,4]. Only one of the ingots was instead composed of a mix of carbonates and silicates of a clayey nature, probably a residue deriving from the production of ceramics.

Furthermore, all the samples were also analyzed by using gas chromatography coupled with mass spectrometry (GC-MS) and it was confirmed the presence of Betulaceae resin-derived molecules.

3. Conclusions

Our intent is to confirm or exclude the possibility that birch resins were mixed with small percentages of other types of organic substances (for example diterpene resins or vegetable gums) and to obtain more detailed information on any extraction and preparation procedures of these mastics from the Bronze Age.

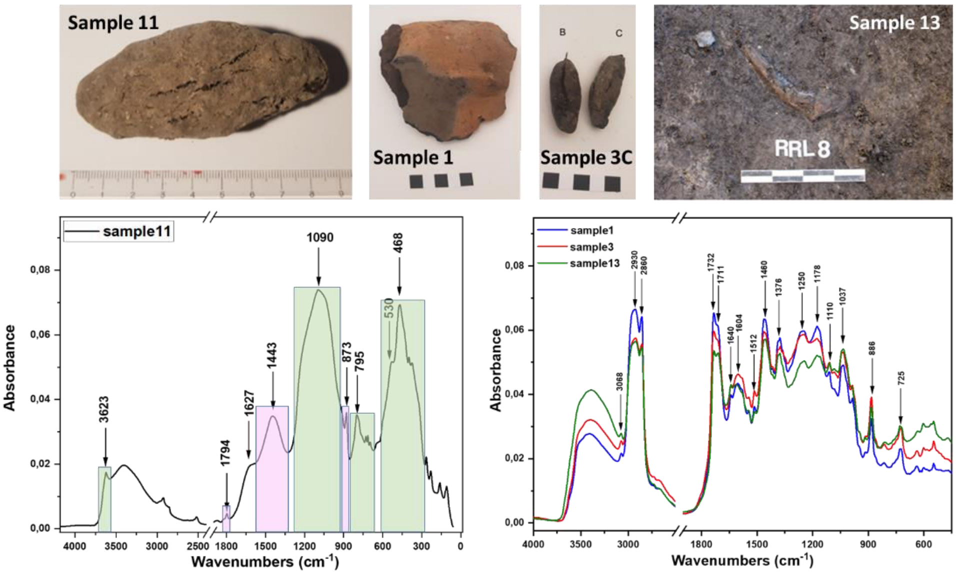

Figure 1. FT-IR of samples 1, 3, 11, 13.

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POS13

THE CHARACTERISATION OF PIGMENTS OF AN EGYPTIAN ANTHROPOMORPHIC SARCOPHAGUS COVER OF THE LATE DYNASTIC PERIOD: A MULTI-ANALYTICAL STUDY

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1. Introduction

Since ancient times, man has attributed symbolic meaning to colours, many of which have had different meanings depending on the civilisation. Throughout millennia, the charm of colours has always pushed Man to search for various natural materials to be used as pigments and/or dyes and, since antiquity, to produce colours synthetically. In ancient Egypt, where colour's symbolism was rigidly established, the tint was considered an indicator of a thing's essence rather than its appearance.

In this context, bearing in mind the high technical skills of Egyptians, it does not seem strange that what is considered the first synthetic pigment in history was Egyptian blue, whose production began around 3000 BC. This research aimed to characterise the colour palette employed for decorating the cover of an Egyptian anthropomorphic coffin attributed to the Late Period. The artefact, which is part of a private collection, was analysed by exploiting a multi-technique approach that employed Raman, scanning electron microscopy equipped with an X-ray fluorescence probe (SEM-EDXS), and total reflectance Fourier transform infrared spectroscopy (ATR/FTIR).

2. Results and Discussion

The first measurements were performed in situ directly on the artefact's surface. Blue-black, red, green, white, black and bright blue areas, which represented the entire colour palette of the coffin cover, were analysed through a BWTek i-Raman EX portable spectrometer equipped with a fibre optic probe and a 1064 nm Nd-YAG laser source. Despite the excitation in the near-infrared region, the collected spectra were mainly characterised by a very strong fluorescence signal, which was not surprising [1]. However, the peaks of calcite at 1086, 712 and 284 cm-1 and the bands at about 220, 290, 403 and 608 cm-1 attributable to red ochre were relieved by Raman spectra acquired respectively on the white and red area of the sarcophagus [1, 2]. Six micro-samples were then collected from the same points already investigated by Raman spectroscopy in order to verify the obtained results and deepen the analysis of the pigments through SEM-EDXS technique and ATR/FTIR spectroscopy.

After having observed the samples through a stereomicroscope to evaluate their hue from a microscopic perspective, they underwent morphologic and elemental semiquantitative analysis by a Hitachi TM 1000 scanning electron microscope equipped with an energy dispersive X-ray spectrometer (Oxford Instruments SwiftED). None of the SEM-EDX measurements required a coating application. All the samples appeared basically characterised by a relevant percentage of calcium, averaging in range from 65 to 80% in the coloured samples and reaching 90% in the white piece, and by the presence of silicon (5-15%), aluminium (averaging 1,5%), potassium (1-4%) and sulphur (2-5%). Then, for each sample, a chromophore element responsible for the colour was identified, namely copper for blue-black, bright blue and black samples, calcium for the white sample and iron for green and red samples.

Those results allowed hypothesising the presence of calcium carbonate in the white sample, red ochre in the red one, and green earth in the green one. The high percentage of copper was attributed to the employment of copper-based pigments in bright blue, blue-black and black fragments, the ones on black samples being quite surprising outcomes.

The subsequent ATR/FTIR measurements elucidated the presence of the characteristic bands of calcite (particularly abundant in the white sample) and the features of silicate minerals in all samples. Furthermore, white, green, and blue-black samples also exhibited peaks of calcium sulphate. Then, the presence of red ochre, previously evidenced by Raman spectroscopy, was confirmed, especially because of the bands ascribable to iron oxide. In contrast, green earth, specifically the minerals celadonite and glauconite, were recognised in the FTIR spectrum of the green sample. Finally, the typical features of Egyptian blue (figure 1) were highlighted in the FTIR spectrum of the bright blue sample, whereas no evidence of anything came as far as the black pigment was concerned.

3. Conclusions

This study highlighted the usefulness of disposing of several complementary techniques. In fact, that multi-analytical approach allowed the characterisation of the entire colour palette, with the exception of the black pigments. Based on the high percentage of copper and the absence of any other element or Raman/IR features responsible for that dark colour, the contemporary presence of carbon black and Egyptian blue was hypothesised in black and blue-black samples. Further analyses will be performed to prove the latter conjecture. It is also worth noting that Raman in situ measurements enabled recognising some of the pigments in a totally non-destructive way. Finally, the identified colours were compatible with what is reported in the literature for analogous artefacts.

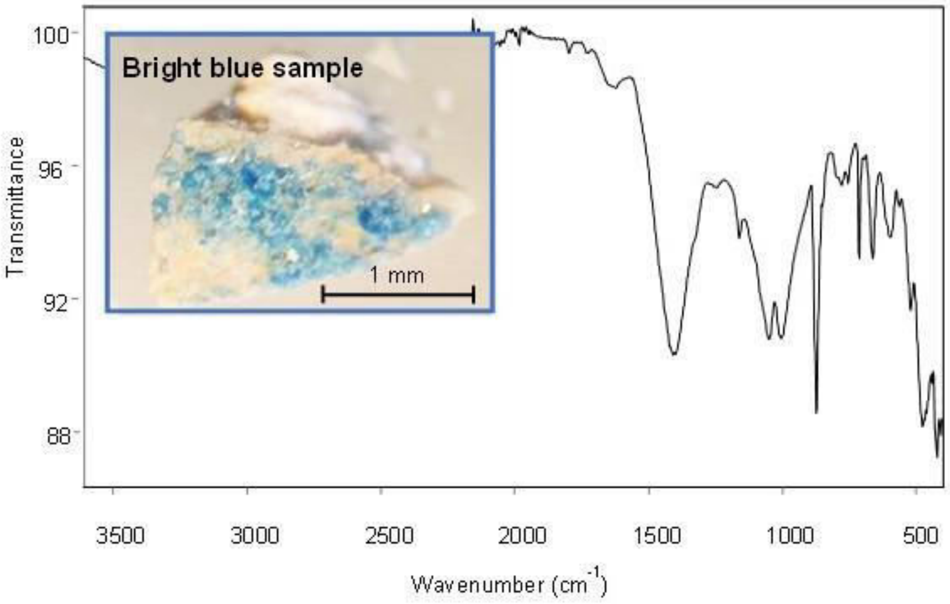

Fig.1 – ATR/FTIR spectrum of Egyptian blue obtained from the bright blue sample

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POS14

MODELLING ANALYTICAL PROCESSES AND CURATING DIGITAL DATA: EXAMPLES FROM THE BE-ARCHAEO ARCHAEOMETRIC ENDEAVOUR

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1. Introduction

Finds from archaeological sites or archaeological museums are often investigated with advanced, instrumental scientific techniques, leading to the growing production of digital data. These data need to be stored properly and interlinked in order to become a true source of (new) knowledge in the digital world.

Many models have been developed to account for the encoding of the archaeological processes in a database. However, the many archaeometric processes – which use instrumental scientific equipment to yield knowledge on how artefacts were made, when they were produced, and the provenance of raw materials – have yet to be addressed.

This results in an archipelago of diverse, specialised, but rather isolated information systems. Nevertheless, there is a strong need for interlinked and transdisciplinary approaches.

2. Results and Discussion

Researchers from the various disciplines involved in archaeometric investigations, including chemists, are presently engaged in using and developing representational models. The aim is to ensure that the overall transdisciplinary endeavour related to archaeological sites and objects is properly represented in the digital world (Fig. 1).

Semantics-based reference models–such as those relying on the CIDOC Conceptual Reference Models (CRM) family [1]–ensure the coherence of disciplinary information and knowledge and allow varied audiences to query the data and evaluate (or re-evaluate) conclusions.

The BE-ARCHAEO project, with archaeological excavations and archaeometric analyses carried out by an international and interdisciplinary team, represents a suitable playground to develop these representation models. In particular, we have already devised computational ontologies to model the digital archaeological records and we aim to implement a transdisciplinary vision to provide an interlinked representation of the archaeometric knowledge.

As a first step, the preliminary conceptualisation and formalisation of the data was performed based on the CRMsci model (a member of CIDOC-CRM family). The model covers a large variety of processes related to archaeometric investigations. Besides standard ontologies, non-ontological resources [2] were also included.

For a comprehensive view, we have adopted a Digital Data Curation (DDC) approach [3] throughout the project to support reflectivity, fertilise transdisciplinarity, and enhance the exploitation of the data.

The DDC model starts as soon as the archaeological find is uncovered and the objectives of the scientific investigations are defined. As a specific example, we can consider the investigation of a set of ceramic fragments from decorated cylindrical pedestals found at the Tatetsuki burial mound (Kurashiki City, Okayama Prefecture, Japan), one of the largest mounds of the Late Yayoi period. Scientific investigation has been performed in order to determine if the fragments share a common origin.

In the archaeometric domain, this question is approached by combining the contribution of researchers from various disciplines (from chemistry to Earth science); here we will focus on elemental composition determined using ICP-OES and micro morphological/compositional features obtained by SEM-EDS. The scientific investigations generate digital objects such as images and tables. In the DDC, this is set as "data acquisition". Then, the DDC task of "data modelling and processing" enriches the digital objects with metadata that reveals some features of the investigated archaeological fragment. As an example, SEM elemental maps (which are produced as JPEG images) may show that a coating was actually present on the fragment. This is an outcome of "data modelling and processing". Similarly, the elemental composition of the fragment is another outcome of "data modelling and processing". Then, the "data interpretation" process includes the features extracted in the previous step (through the ICP-OES and SEM-EDS analyses) into a larger set of the investigated fragments and produces a dispersion graph with some hypothesis about their possible common origin. These conclusions are then stored and/or disseminated.

3. Conclusions

The BE-ARCHAEO endeavour demonstrates that interdisciplinary teams can effectively support the development of semantic-based representational models and must carefully curate their digital data. This ensures that the many disciplinary processes are correctly reported in the digital world, that transdisciplinary knowledge arises from the overall effort, and that data become valuable sources of (new) knowledge in an interlinked system. Some significant examples from the BE-ARCHAEO database are presently displayed as an installation of the Content Management System Omeka-S [4].

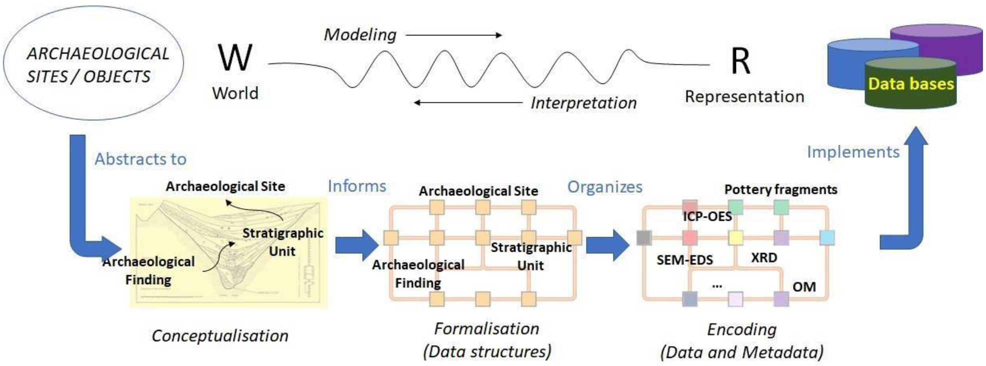

Figure 1: From the real world to the digital one

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POS15

STRENGTHENING OF THE ATMOSPHERIC OBSERVATORY WITHIN THE ACTRIS AND ICOS INFRASTRUCTURES FOR THE SYNERGISTIC STUDY OF AEROSOLS AND GHG AT CNR-IMAA

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1. Introduction

Atmospheric particulate matter and greenhouse gases (GHG) represent two of the major environmental concerns: the former for the direct impact on human health, on climate and precipitation cycle, and the latter for their pivotal role in global warming. The study of their physical and chemical characteristics as well as the understanding of their environmental cycles is the basis for the pollution reduction policies aimed at safeguarding the Earth. At the "Istituto di Metodologie per l'Analisi Ambientale" of the Italian National Research Council (CNR-IMAA) is operative since 2000 an advanced remote sensing atmospheric observatory, called CIAO (CNR-IMAA Atmospheric Observatory) operating within ACTRIS project (The Aerosol, Clouds and Trace Gases Research Infrastructure). In addition, it is currently in progress within CIAO the implementation of an ICOS (Integrated Carbon Observation System)-compliant Class 1 atmosphere station for the study and monitoring of GHG, planned to be operative within the end of 2022.

2. Discussion

The observatory is located in Tito Scalo, Potenza, Southern Italy (40.60° N, 15.72° E, 760 m asl) in a plain surrounded by low mountains (<1100 m asl), less than 150 km from the West, South and East coasts. Due to its characteristics, the site is particularly interesting for the study of the properties of aerosols and greenhouse gases. Referring to aerosols of natural origin such as desert dusts and volcanic aerosols, it is important to note that the site is affected by a rather high number of Saharan dust intrusions per year [1] and is located at 300 km from the volcano Etna. CIAO consists of several advanced systems capable of providing complementary long-term high-quality information of aerosols and cloud properties; the station has instruments such as lidar, radar, ceilometers, radiometers and currently represents one of the largest ground remote sensing stations in the Mediterranean Basin and is one of the main atmospheric observatories in Europe [2]. The site also represents a novelty in the ICOS atmospheric network, being the Class 1 station at the lowest latitude and the first in the Mediterranean basin. The co-presence of the two research infrastructures and the considerable amount of information available represents an opportunity to obtain synergistic and in-depth investigations of GHG and atmospheric aerosols. In this context, the CIAO observatory is currently under upgrade including a laboratory for the aerosol in situ measurements and characterization. The CIAO aerosol in situ sampling station is located in a shelter just outside the CNR-IMAA institute and will be equipped with several on-line and off-line instruments. The combination of on-line and off-line measurements is a fundamental feature of the Observatory and the chemical information related to the physical characteristics of the atmospheric particulate, can provide an excellent knowledge base for understanding the source and evolution of the particulate. The ICOS station will be located about 1 km away from the institute and will be equipped with several instruments for the analysis and the sampling of GHG/trace gases. The upgrade of CIAO laboratory is funded by the Italian project PER-ACTRIS-IT aimed at enhancing the Italian contribution to ACTRIS and this aerosol in situ facility will be proposed as ACTRIS National Facility for the aerosol in situ component. The ICOS station implementation is supported by MIUR (Italian Ministry of University) PON ICOS PRO MED, aimed at strengthening the ICOS-Italy observational network in the Mediterranean area. Measurements at the CIAO in situ aerosol facility and at the ICOS station will start in the second half of 2022.

Conclusions

The reported above PON projects and in particular the strengthening of the CIAO observatory will increase the competitiveness of Italian research in the European panorama, providing tools to face present and future socio-economic challenges, linked to air quality, climate change and protection from environmental risks.

Acknowledgements

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POS16

HYGROSCOPICITY OF AEROSOL SAMPLED DURING THE EUREC4A CAMPAIGN

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1. Introduction

EUREC4A field campaign took place in the downstream winter trades of the North Atlantic, eastward and south-eastward of Barbados, and lasted more than four weeks, during which atmospheric, surface and oceanic processes operating across a very wide range of scales were investigated [1]. The main purpose of EUREC4A is to improve our understanding of the factors that influence clouds in the trades at different scales, how they will respond to warming, and their link to other components of the earth system, such as the mesoscale and sub-mesoscale dynamics of the upper ocean, the life-cycle of particulate matter, or air-sea gas exchange [1].

On the particle scale, aerosol properties and turbulence both imprint themselves on the cloud microstructure, and therefore affect the formation of precipitation [2,3,4,5]. Particles can serv as seeds from which liquid water droplets initiate and grow and these particles are called cloud condensation nuclei (CCN). The potential for an atmospheric particle to act as CCN, termed its CCN activity, is ranked by the atmospheric water vapor pressure required for it to nucleate into a droplet and depend on both its size and chemical composition [6].

2. Results and Discussion

For this work, measurements were performed to characterize aerosols, using the R/V L'Atalante as a privileged platform. The ship performed a cruise from 20 January to 23 February 2020, collecting ocean and atmosphere data from 6°N to 15°N and from 60°W to 52°W surveying the Tradewind Alley and the North Brazil Current eddy corridor[1]. It was equipped with a high volume sampler ECHO-PUF (by Tecora), which allowed to collect TSP on filters and infer the chemical composition and the hygroscopic properties of the aerosol. Water-Soluble Inorganic Ions concentration was determined by ion chromatography. The hygroscopic properties and growth (necessary for the aerosol particles to act as CCN), related to the chemical composition, were determined by carrying out deliquescence and crystallization cycles inside an Aersol Exposure Chamber, which made it possible to control the air temperature and relative humidity (the RH was varied by 2% at a time, from 20% up to 90% and vice versa). Therefore Deliquescence relative humidity (DRH) and crystallization relative humidity (CRH) (and the related phase transition regions) were identified coupling the gravimetric sampling method for TSP with a gravimetric hygroscopic determination [7]. The chemical composition is typical of marine aerosol, with a clear predominance of chlorine and sodium ions. The other cations (Ca, Mg and K), which are among the major constituents of sea water, are present but in lower percentages. Sulfates concentrations are also important; indeed SO42- is due to primary emissions of sea spry, secondary formation from DMS precursor, emitted by phytoplankton activities, (both represent a natural marine origin) and also to long-range transport from the continents favored by its stability in the atmosphere (anthropogenic origin). NO3- is less abundant than the sulphate ion because it comes only from anthropogenic sources (i.e. continental sources, except for ship emissions) and because it is less stable in the atmosphere and then tends to volatilize during the long-range transport. Aerosol hygroscopicity measurements carried out in the AEC are presented here averaged in Figure 1. By the knowledge of the aerosol mass deposited on teflon filters and the mass of the water absorbed by the aerosol, the mass Hygroscopic Growth Factor (HGF) as computed as total wet mass (aerosol+water) divided by the dry aerosol mass at the beginning of each cycle (20% RH). The average DRH is clearly visible between 70% (DRHstart) and 76% (DRHend), with the highest gradient at 74 RH, in keeping with the aerosol chemical composition dominated in mass by sea spray aerosol. A further increase in the RH leads to hygroscopic growth due to the continuous condensation of water. Similarly the CRH started from 58% (CRHstart) ending at 44% (CRHend) when the aerosol came back to a dry state; the highest gradient was at 48% RH, again in keeping with the aerosol chemical composition.The data from ion chromatography was also used in the of Extended AIM Aerosol Thermodynamics Model. Comparing the deliquescence curve from experimental data with the modelled data, the humidographs closely resemble each other. From the experiment we find DRH is 72±1%, while from the model the value is 73%. The shapes of the curves are similar, but there is difference in scale: the modelled mass of water is about 28%more than the experimental one

3. Conclusions

In this work we studied the chemical composition and the hygroscopicity properties of total suspended particles collected during EUREC4A campaign. The chemistry is typical of marine aersol, with high concentrations of chlorine and sodium and lower concentrations of ions of (at least partially) anthropogenic origin, such as sulphates and nitrates. The analyzes in the Aerosol exposure chamber of the hygroscopic growth factor and of the RH values of deliquescence and crystallization of the particulate are concordant with the chemical composition, dominated by the sea salt. The agreement between experimental and modelled curves suggests that data obtained from future chemical analysis can be applied to the AIM model to interpret the deliquescence process occurring in other regions.

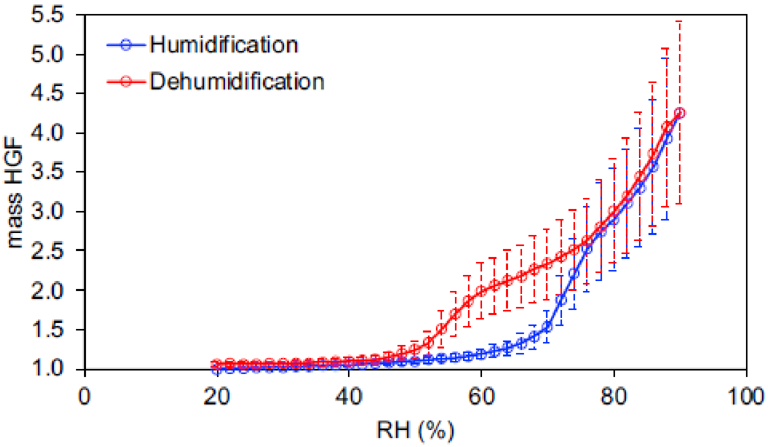

Figure 1. Average curves of mass HGF obtained on teflon filters sampled during EUREC4A

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POS17

ENVIRONMENTAL IMPACTS EVALUATION OF CANNABIS SATIVA L. AGRONOMIC PRACTICES BY LIFE CYCLE ASSESSMENT

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1. Introduction

Cannabis sativa L., also named hemp, has been cultivated everywhere even if during the 20th century the prohibition of hemp culture due to the D9-tetrahydrocannabinol content led to a decline of its production. Nowadays, the decriminalization of C. sativa has caused a renewed interest. A considerable amount of legal cannabis is cultivated for several purposes, but the magnitude of the industry's environmental impacts has not been yet fully quantified.

This study is aimed to evaluate the environmental impacts of Cannabis sativa L., through the implementation of Life Cycle Assessment (LCA) framework. Results are supported by a comparative analysis of three different hemp agronomic practices: conventional (indoor and outdoor) and organic and the available literature. This study is focused on just the agriculture phase considering that it accounts for more than 90% of the total impact. Most of data used are primary i.e., directly provided by the local producers.

2. Results and Discussion

The selected indicators are the most used for the ecosystem quality evaluation: Global Warming Potential, eutrophication and acidification potential, terrestrial ecotoxicity, ozone layer depletion and water footprint. The Functional Unit (FU) chosen is 1 ha of cultivated land. The environmental impacts of the three hemp cultivations are summarized in Fig. 1.

The comparative analysis of agronomic practices indicates that both conventional and organic outdoor produce a lower environmental impact than indoor.

Forthemore for both conventional and organic outdoor, inputs and processes are similar for all impact categories: e.g. for the Global Warming Potential the contribution of direct emissions is relevant (more than 30% of the total). These emissions are due to the consumption of fossil fuels and to crop residues left in cropland. The seeds impact of the conventional outdoor system is less than the seedlings purchased and contained in plastic jars used in the organic outdoor practice, due to the relevant contribution of plasticized materials.

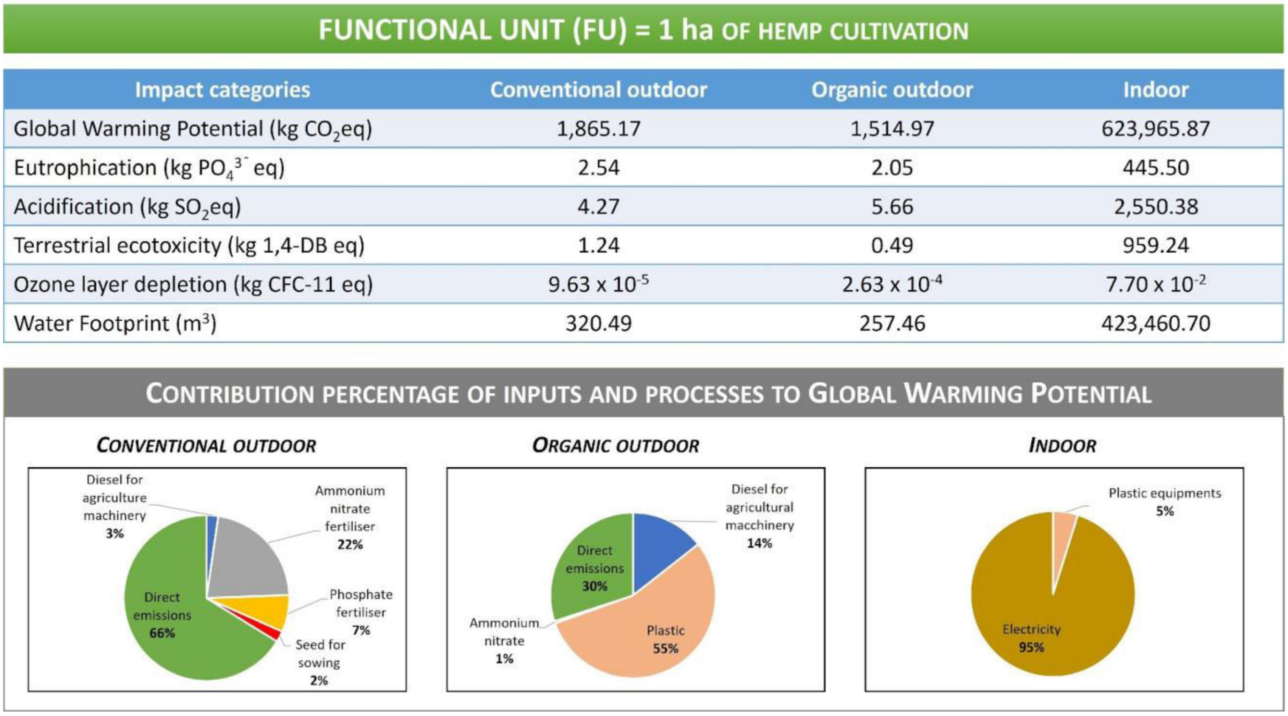
On the other hand, the hemp indoor production is energy-intensive and depends on lighting and microclimate control input in man-made greenhouse.

Then, these results are compared with other similar studies [1,2]. Disparities between the results are observed, probably due to several issues: different accounting methodologies, system boundaries, specific climatic and soil conditions related to site of cultivation, etc.

3. Conclusions

This study assesses the potential environmental impacts of hemp culture, highlighting the differences between three agricultural practices. Since there is no a wide availability of information on this issue, this research experience addresses the knowledge regarding the sustainability of this type of industry and provide an examination of possible pathways to further reduce the relative environmental impacts.

POS17



FUNCTIONAL UNIT (FU) = 1 ha OF HEMP CULTIVATION

Impact categories	Conventional outdoor	Organic outdoor	Indoor
Global Warming Potential (kg CO_2eq)	1,865.17	1,514.97	623,965.87
Eutrophication (kg PO_4^{3-} eq)	2.54	2.05	445.50
Acidification (kg SO_2eq)	4.27	5.66	2,550.38
Terrestrial ecotoxicity (kg 1,4-DB eq)	1.24	0.49	959.24
Ozone layer depletion (kg CFC-11 eq)	9.63×10^{-5}	2.63×10^{-4}	7.70×10^{-2}
Water Footprint (m^3)	320.49	257.46	423,460.70

CONTRIBUTION PERCENTAGE OF INPUTS AND PROCESSES TO GLOBAL WARMING POTENTIAL

Fig. 1: Potential environmental impacts of three hemp agronomic systems.

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POS18

REMOVAL EFFICIENCY OF PHARMACEUTICAL COMPOUNDS BY VERTICAL-FLOW CONSTRUCTED WETLANDS INTEGRATED WITH BIOCHAR, TREATING URBAN WASTEWATER

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1. Introduction

A proper treatment of wastewater is essential before its discharge into natural water reservoirs or before its reuse. Constructed wetlands (CWs) are a worldwide sanitation technology for wastewater treatment because it owns the advantages of low external energy requirements, aesthetic value and easy operation. Biochar may be attractive as a robust multifunctional medium in CWs for adsorbing micropollutants, supporting plant growth, and providing environments for microbe communities because of its unique physicochemical properties [1]. This study aims at evaluating the removal efficiency towards selected pharmaceutical compounds (PhCs) and their transformation products (TPs) by a vertical-flow CW implemented by using granular biochar (average diameter 10 mm), together with sand and gravel with different diameters as filling media, and planted with Phragmites australis (CW-BC-P). The removal efficiency of this system was compared to the ones obtained by a CW filled as CW-BC-P, but unplanted (CW-BC-U) and a planted CW in which the biochar was replaced with gravel of the same diameter (CW-G-P). All CWs were fed with urban wastewater from the Sidi Thabet municipality (Tunisia).

2. Results and Discussion

Quantitative determination of PhCs in wastewater was performed by liquid chromatography coupled with electrospray ionization tandem mass spectrometry (LC-MS/MS). Influent and effluent of an Imhoff tank, the latter feeding the three CWs were analyzed to obtain information on the concentration of PhCs before and after each treatment. Nineteen out of the thirty-nine investigated PhCs and TPs were detected in at least one sample. These compounds belong to the following categories. (i) Non-steroidal anti-inflammatory drugs: Diclofenac (DIC), Ibuprofen (IBU), Naproxen (NAP), 2-Hydroxyibuprofen, (2-HYIBU), 4-Hydroxydiclofenac (4-HYDIC), and O-desmethylnaproxen (O-DMNAP). (ii) Beta-blockers: Bisoprolol (BIS). (iii) Antibiotics: Ciprofloxacin (CIP), Clarithromycin (CLA), Erythromycin (ERY), Levofloxacin (LVF), Sulfamethoxazole (SMX), and Trimethoprim (TMP). (iv) Psychiatric drugs: Carbamazepine (CBZ) and O-Desmethylvenlafaxine (O-DMVEN). (v) Antihypertensives: Ramipril (RAM). (vi) Antifungals: Fluconazole (FLC) and Miconazole (MCL). (vii) Statins (Atorvastatin (ATO) [2]. MCL, IBU, HYIBU, and O-DMNAP were found only occasionally and therefore they are not discussed here. Most of the detected compounds were characterized by a significant removal in at least one CW, being it ≥ 70% for NAP, 4-HYDIC, BIS, CIP, CLA, ERY, LVF, TMP, RAM, ATO, and O-DMVEN, and around 50% for DIC and SMX (see Figure 1). CW-BC-U showed the highest efficiency, as it reduced the concentrations of eleven out of nineteen PhCs by more than 70%. CBZ exhibited a negative removal in all three CWs with values of -94 ± 142%, -69 ± 97%, and -37 ± 110% in the CW-BC-P, CW-G-P, and CW-BC-U, respectively, thus highlighting a recalcitrant behavior in these kind of treatment systems. Poor or even negative removal of CBZ is a finding already observed in literature and ascribed to the conversion of its TPs into the parent compound via biological or photochemical processes [3,4]. FLC showed a negative removal, as well, with values as high as -119 ± 59% in CW-BC-P, probably to transformation, recombination and/or accumulation phenomena, which on the other hand may affect the fate of all compounds in CW systems [5]. Overall, these results indicate that vertical CWs play an important role in the reduction of the concentrations of most of the studied PhCs, with the exceptions of CBZ and FLC, due to their peculiar behavior in these systems. However, the removal efficiency shown by the CW-BC-U was surprisingly lower than the corresponding unplanted CW, thus suggesting that the sorption ability of biochar could be decreased by the presence of the root system due to a number of reasons. One hypothesis is that the release of plant exudates may contribute to saturate the sorption ability of biochar, while another refers to the creation of hydraulic short-circuiting inside the planted system that decrease the contact between wastewater and biochar. A lower efficiency of plants to support the degradation of PhCs can also be hypothesized in the presence of biochars since CW-BC-P shows in some cases a removal lower than CW-G-P.

3. Conclusions

This study demonstrated that CWs can be a cost-effective and sustainable alternative for removing selected PhCs. The three investigated CW systems led to a considerable reduction of a broad range of pharmaceuticals typically present in treated wastewater. On the other hand, the use of sorbent media inside the bed does not seem to offer clear advantages in terms of PhCs removal, probably due to complex chemical and physical interactions between plant and biochar.

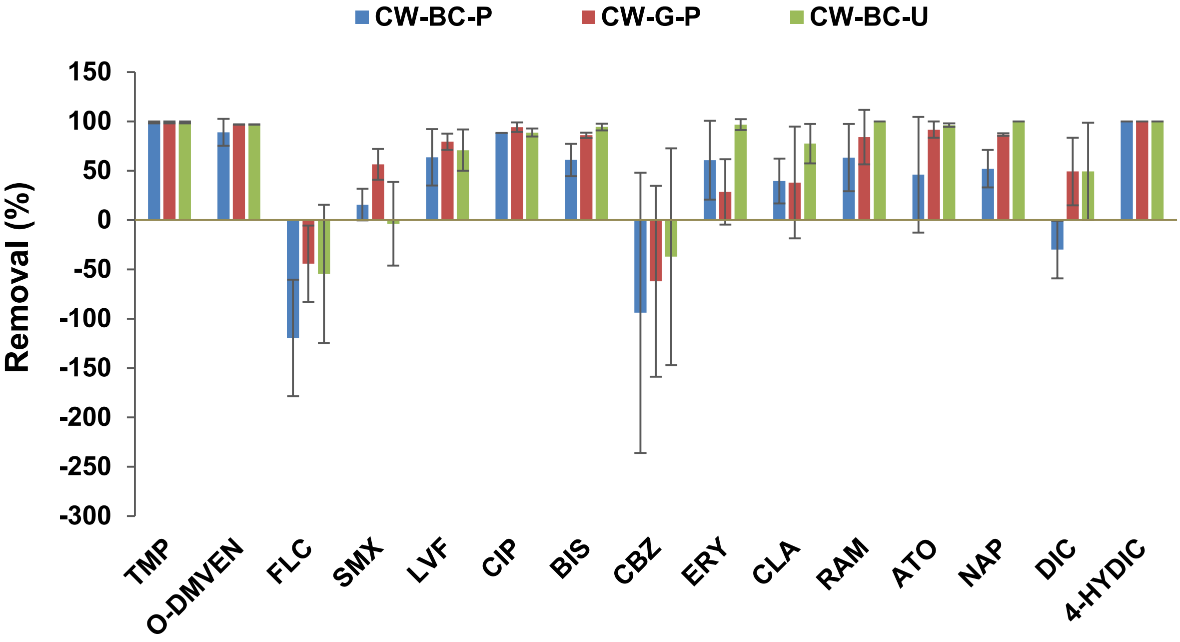

Figure 1 – Removal percentages of PhCs compounds in the vertical flow constructed wetlands

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POS19

PRELIMINARY STUDY ON THE POLLUTANT EMISSIONS OF WOOD-FIRED PIZZA OVENS

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1. Introduction

Biomass combustion contributes the emission of several major air pollutants, including methane, carbon dioxide (CO_2), carbon monoxide (CO), nitrous oxides (NO_x), sulphur dioxide (SO_2), volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs) [1]. Wood combustion is also a significant source of fine particulate matter (PM), which is the fraction that poses the most severe threat to human health [2]. In fact, studies based on epidemiological data estimate that the contribution of biomass smoke to premature mortality in Europe amounts to at least 40,000 deaths per year [1]. In this regard, the European Commission is tackling the problem by introducing source-specific emission standards for biomass combustion. Specifically, in the Ecodesign Directive (EDD) sets emission limits targeting small-scale domestic appliances for PM, organic gaseous compounds (OGC), CO and NO_x [3]. Despite the efforts of international institutions towards tackling the problem, no standards or regulations currently exist regarding wood-fired ovens. Moreover, very few literature data exists on the emissions of this source and this work aims to start filling this gap.

2. Results and Discussion

The pollutants monitored during the course of the experimental tests were: CO, CO_2, NO_x, OGC and total particulate matter (TPM). The sampling system employed was constructed by adapting the dilution tunnel test rig facility described in the UNI EN 16510-1:2019 technical standard to a traditional fixed top wood-fired oven (Figure 1). The fuels chosen for the execution of tests were beechwood logs and beechood briquettes. Measurements were carried out before and after dilution in the tunnel, except for OGC which was monitored only on the hot flue gases. New combustion cycles were designed specifically for the execution of the tests on the oven in order to simulate real-life operating conditions. These included five operational phases: cold ignition, pre-heating, hot re-ignition, cooking and shutdown. The emissions were measured exclusively during the cooking phase by carrying out cycles with and without pizza cooking. Other parameters which were measured and kept under control were: the draught, the temperature of the cold flue gases and the dilution factor.

The results of this preliminary study indicate that the emissions of the wood-fired ovens are in line with literature data for domestic wood-burning appliances such as stoves, cookers, and fireplaces [1]. The cycles conducted using smaller amounts of beechwood logs emitted higher concentrations of CO and OGC, whereas the ones conducted with greater amounts revealed higher emissions of NO_x and CO_2. Based on experimental observations, smaller amounts of fuel were associated with lower temperatures inside the oven and a lower flame intensity, especially during the final minutes of the sampling period.These conditions caused the levels of CO and OGC to rise during this time frame, inevitably impacting the overall average values. Instead, for similar mass loadings, the beechwood briquettes showed lower emissions of all the gaseous pollutants, with the exception of CO_2 which was in line with the concentrations observed for the wood logs.

Differently, particulate matter concentrations seemed to be directly influenced by the amount of fuel used, regardless of the form (wood logs or briquettes). Unlike other similar studies conducted on small-scale appliances burning woody biomass [4], the results of these experiments did not highlight a significant degree of condensation of semi-volatile organic compounds (SVOCs). This is possibly due to the fact that the difference between TPM concentrations of the diluted and concentrated fumes is generally smaller for open systems like ovens and open fireplaces [4]. However, further tests will need to be carried out to clarify this point, considering that the average OGC concentrations was consistently above 10 mg/m³.

The cycles conducted with pizza cooking highlighted a significant impact of this activity on the concentrations of OGC, whereas no statistically significant differences could be observed in terms of the other pollutants.

3. Conclusions

Wood-fired pizza ovens represent a potential source of air pollutants, especially in urban areas where there is a high concentration of commercial acitivities which make use of such systems. Considering the negative effects that biomass combustions has on human health, being albe to identify and quantify the pollutants emitted by wood-fired ovens is of the upmost importance. The current work is a preliminary study which enabled the identification and quantification of the major air pollutants emitted by this source. Further experimental tests will be carried out in order to obtain a full characterization of the emission profile of wood-fired ovens; possible developments include: investigating different fuels, different oven types and analyzing other classes of pollutants such as PAHs.

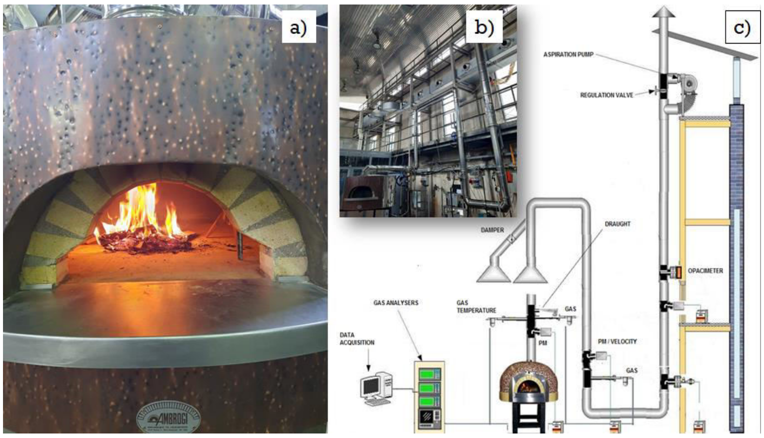

Figure 1. a)Traditional fixed top oven; b)Sampling system; c)Sampling system scheme (not to scale)

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POS20

EFFECTS OF WASTEWATER TREATMENTS ON ALPINE STREAM NUTRIENT DYNAMICS UNDER WATER SCARCITY CONDITIONS: PRELIMINARY RESULTS

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1. Introduction

Alpine streams are highly sensitive to climate change: the raising average temperatures and the changing precipitation patterns cause an alteration of the flow regime and a deterioration of water quality, with consequent effects on the ecosystems [1]. Exacerbated by anthropogenic activities, these events can undermine the supply of water for irrigation, energy production, drinking and waste dilution and prevent rivers from offering ecosystem services. This conflicts with the augmenting demand of water.

While it is known that effluents from WWTPs cause physical and chemical discontinuities along the receiving water body, increasing nutrient concentrations and introducing toxic substances, few studies have addressed this problem in conjunction with water scarcity: the increasing droughts driven by climate change result in water shortage and altered flow regimes in alpine rivers, which consequently lose part of their dilution potential [2]. This leads to an over-concentration of nutrients, pollutants and pathogens in watercourses, with severe implications on the ecosystem functions and on the overall water quality [3].

2. Results and Discussion

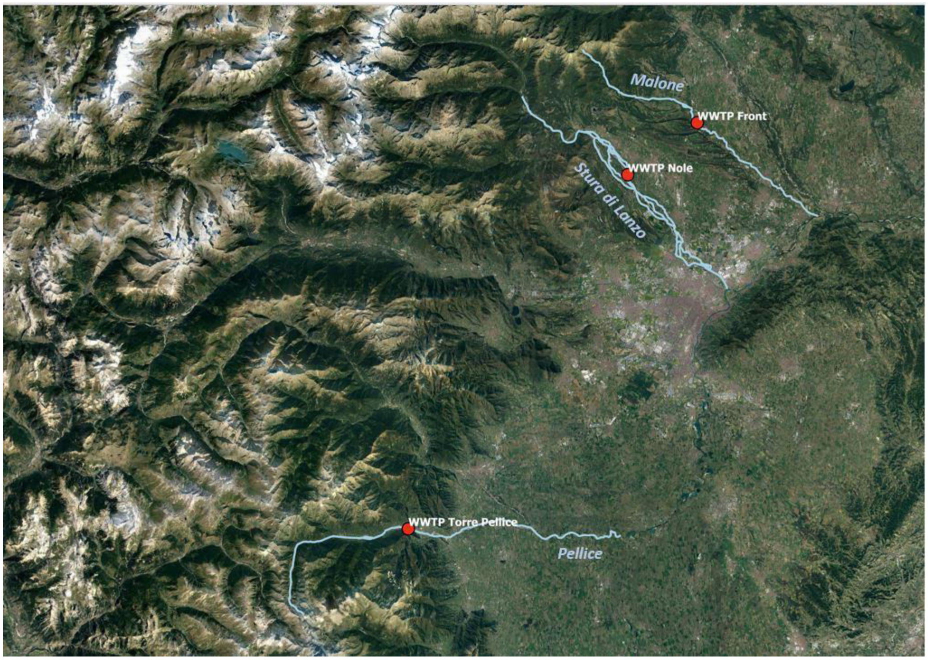
The purpose of this research was to gain deeper insight on the effects of wastewater treatment plants inputs on the nutrient dynamics of three alpine streams belonging to the Po basin and located in Piedmont (NW Italy): Stura di Lanzo, Malone and Pellice. All the selected rivers are experiencing a high seasonal variability in their flow regime and strong water scarcity conditions. Each stream was sampled in three points: upstream, at the discharge and downstream the respective wastewater treatment plants, with the downstream points located at a maximum distance of 500 metres from the discharge inlet. The possible presence of secondary tributaries was taken into account, as well as the land use and the anthropogenic pressures insisting on the watershed.

Samples of 1 dm^3 of water were monthly collected at each sampling site, starting from January 2022, and the main chemical features were analyzed. Anionic and cationic contents were measured by using ionic chromatography, while $N\text{-}NH_3$, $N\text{-}NO_2$, $N\text{-}NO_3$, Si, P and anionic surfactants were measured by using spectrophotometric methods. Total C and N were also measured using a TOC analyzer. Physical and chemical parameters (pH, temperature, conductivity, %DO) were measured directly in field, by using a multiparameter probe.

The trends in the concentrations of each nutrient were monitored through the year, with the objective to analyze the relationship between their budgets and the variability of water amounts in the receiving body, and their content changed seasonally. The data were also correlated to the observed biodiversity (density, structural and functional organization of benthic macroinvertebrate and diatom communities) and microbiological asset (presence of pathogens and bacterial indicators), which were evaluated in parallel samplings following the same experimental design.

3. Conclusions

Climate change and variability are expected to have an influence both on water quantity and on water quality. This is particularly evident for alpine environments and has been here highlighted. Being water quality subjected to local hydrology and punctual sources of contamination, the increasing water scarcity and the reduced wastewater dilution capacity of streams are establishing themselves as key factors to be considered while thinking water management in the years to come. This study investigates their effect on the operation of wastewater treatment plants, using a multidisciplinary approach that strived to underline correlations between the nutrient load trends and the biological composition of the chosen rivers.



Satellite image of the three target streams. The respective WWTPs are highlighted.

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POS21

ECOTOXICITY ASSESSMENT OF THE FINER FRACTION OF THE RESUSPENDED LAGOON SEDIMENT

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1. Introduction

The Venice lagoon is a fragile ecosystem characterized by an irregular bathymetry, with extensive shallow water areas, where sediment resuspension may occur during both natural and anthropogenic disturbance events. This may cause the remobilization of sediment-associated pollutants, which are released in the water column both in soluble form and in association with suspended particulate matter, becoming available for water column organisms. In shallow water systems, resuspension involves mainly the fine fraction of sediments. The pollutant-enriched finest particles remain in suspension longer and, besides acting as pollutant carriers, could themselves affect vital functions of organisms, due to the unique properties of particles below a certain size.

Objective of this work was an in-depth investigation on the finer fraction of the resuspended lagoon sediment, going beyond its usual definition (< 63 µm), with a focus on particles with an average diameter approximately <4 µm. The study aimed at isolating this fraction and assessing its influence on sediment quality by performing ecotoxicological testing with Aliivibrio fischeri, Acartia tonsa and Mytilus galloprovincialis.

2. Results and Discussion

The study required the development of a novel procedure for post-sampling treatment and for the proper isolation of the finer fractions of the resuspended surface sediment, without altering their properties and using artificial marine water (AMW), for the purpose of ecotoxicity testing with marine organisms. Ecotoxicity assay methods as well had to be adapted and optimized for this type of samples.

Sediments were collected at three sites with different characteristics and pollution levels. The different fractions were obtained as dispersions in AMW, which were characterized by means of laser diffraction and Dynamic Light Scattering (DLS) to determine their particle size distribution and assess the effectiveness of the separation procedure.

The two fractions F0 and F1 showed an effective difference in particle size (average diameter between 4 and 5 µm for F0 and between 1.5 and 3 µm for F1), with similar distribution among sites, and for both sampling periods.

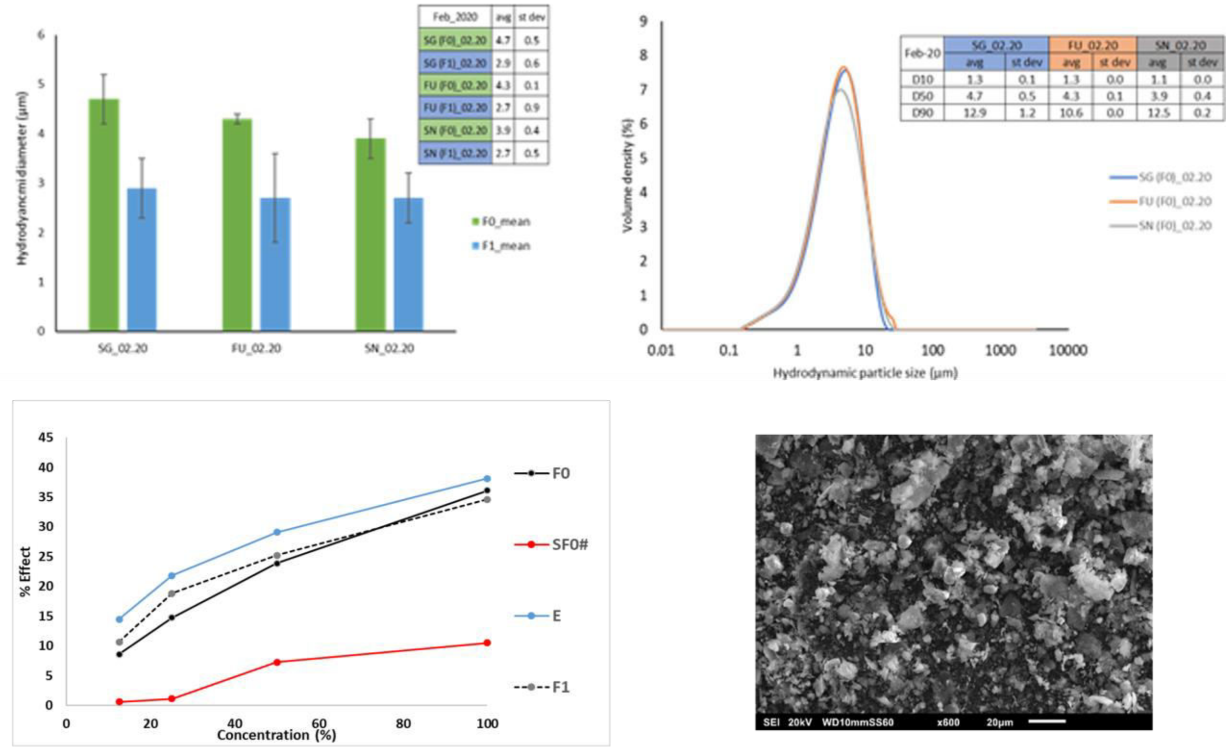
Bioluminescence inhibition assays with the bacterium A. fischeri carried out with the different fractions showed that, in general, inhibition was below 50%, and the results did not provide a clear distinction among the different sampling sites based on their pollution levels. Moreover, with the purpose to discriminate the effects due to suspended particles and to the chemicals released in water following resuspension, particles were completely precipitated by centrifugation, separated and re-dispersed in fresh AWM (sample SF0#). These last samples showed no significant inhibitory activity, while the supernatants (sample E) elicited a toxic effect more similar to the F0 and F1 dispersions.

These results seem to show that the suspended particles provide a modest contribution to the total inhibitory effect, suggesting that this is mainly due to pollutants released in the water phase during sediment resuspension. However, this could be due to a low concentration of solid particles in F0 and F1, below the amount necessary to severely inhibit the luminescence of A. fischeri.

Therefore, to further investigate the possible toxic effects exerted by fine particles per se, the original sediment samples were treated by an ad hoc procedure aimed at removing the pollutant-bearing phases, followed by the isolation of different fine fractions as solid materials. Moreover, diatomaceous earth (DE) and kaolinite (KA) were used as reference materials for the bioassays, and toxicity was assessed also with the copepod A. tonsa and the bivalve mollusc M. galloprovincialis, which may be target species in the lagoon environment. The results highlighted effects of the fine fraction (average diameter 5 µm) with all bioassays and allowed the calculation of EC50 values, which ranged between 1 and 2 g/L for A. fischeri and below 1 g/L for the A. tonsa larval development assay and for the M. galloprovincialis embryotoxicity assay, which showed similar values.

3. Conclusions

The study provided novel information about the role played in shallow water systems by the finer fraction of sediments, which is known as a major carrier of contaminants. Resuspension events may cause the release of chemicals that may impact water column organisms, but also the finer particles per se could exert adverse effects, which are not usually investigated. The results obtained with the most sensitive life stages of lagoon organisms suggest that this possibility cannot be excluded, but additional investigation is needed to provide further support to the observed effects.



Feb_2020	avg	st dev
SG (F0)_02.20	4.7	0.5
SG (F1)_02.20	2.9	0.6
FU (F0)_02.20	4.3	0.1
FU (F1)_02.20	2.7	0.9
SN (F0)_02.20	3.9	0.4
SN (F1)_02.20	2.7	0.5

Feb-20	SG_02.20		FU_02.20		SN_02.20	
	avg	st dev	avg	st dev	avg	st dev
D10	1.3	0.1	1.3	0.0	1.1	0.0
D50	4.7	0.5	4.3	0.1	3.9	0.4
D90	12.9	1.2	10.6	0.0	12.5	0.2

Characterization of the finer fraction of resuspended sediment and toxic effect on A. fischeri

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POS22

A NOVEL INTEGRATED APPROACH FOR ASSESSING THE IMPACT OF SHIPPING EMISSIONS CONTROL TECHNOLOGIES ON THE MARINE ENVIRONMENT IN THE NORTHERN ADRIATIC SEA

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1. Introduction

A significant increase in the use of shipping emission abatement technologies such as exhaust gas cleaning systems (scrubbers) has been estimated for the next decades as an alternative to the use of low-sulfur fuels mandated by the recent global application of limits on the sulfur content for marine fuels.

Due to the evidence of the negative effects on marine organisms of the discharge of acidified and contaminated scrubber discharge water, an integrated assessment framework to evaluate the impacts of these emissions on marine ecosystems, while considering also the environmental and health benefits of reducing emissions of air pollutants, and associated costs, is needed. This is the main objective of the H2020 EMERGE project, which aims to jointly evaluate environmental and health impacts of shipping emissions reduction technologies under future scenarios through the integration of experimental and modeling approaches.

2. Results and Discussion

The approach developed in the EMERGE project is being applied to five EU case-studies, including the Northern Adriatic Sea, a shallow marine basin subjected to the presence of several anthropogenic activities posing chemical pressures on the environment. The first component of the modeling chain is the STEAM model, which estimates shipping-related emissions of pollutants and nutrients based on Automatic Identification System data.

The data estimated from this model is integrated with the emissions of contaminants to the water and air compartments originating from land-based sources, then high resolution models are used for estimating the transport of selected pollutants in the air and water compartments.

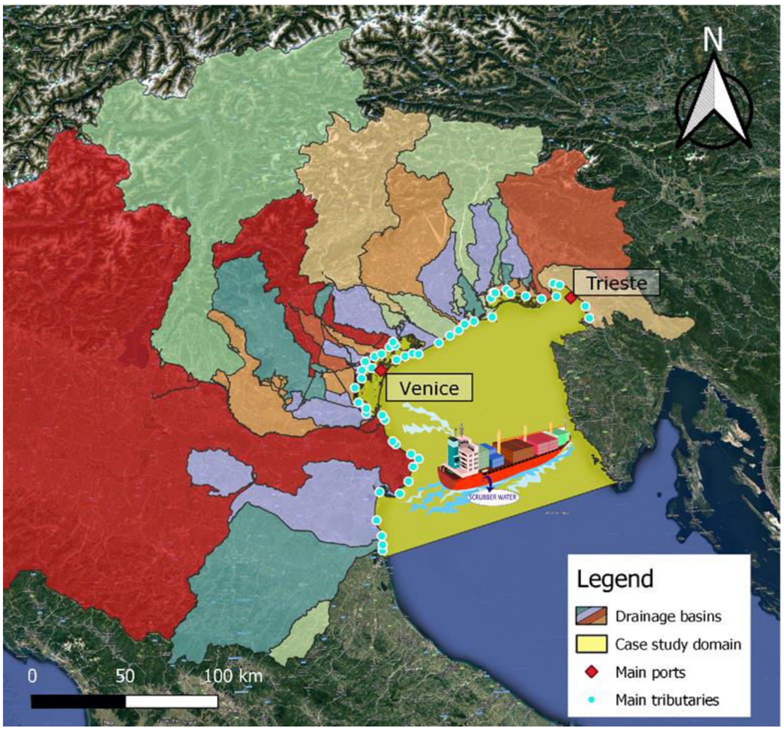
The obtained fluxes of contaminants in the case study area are then used for investigating: (i) the concentration, persistence, and fate of target pollutants using the ChemicalDrift model, (ii) the effects of changing nutrients loads on biogeochemical processes using the Biogeochemical Flux Model, and (iii) the bioaccumulation of pollutants using the MERLIN-Expo model.

Ecotoxicological tests carried out on real scrubber water using planktonic bioindicators (i.e. Aliivibrio fischeri, Acartia tonsa and Mytilus galloprovincialis) and considering different life stages and exposure times complement the modeling activities and support the comprehensive impact assessment for the case study area.

3. Conclusions

A novel approach integrating modeling and experimental activities has been developed and applied to estimate the impact on the marine ecosystem and the human health of the use of different emission control technologies in the shipping industry. Preliminary results from the Northern Adriatic Sea case-study are illustrated.

POS22



Case study domain (yellow area) and drainage basin of its tributaries

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POS23

HOW DID THE LOCKDOWN RELATED TO COVID-19 IMPACTED ON AIR QUALITY AND HUMAN HEALTH IN CAMPANIA REGION?

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1. Introduction

In many urban and suburban areas around the world, air quality is frequently affected by pollution problems. Among the air pollutants, ozone (O_3), nitrogen dioxide (NO_2) and particulate matter (PM) are the most hazardous [1], because they can cause adverse health effects on respiratory and cardiovascular systems, as well as negative impacts on the ecosystems such as vegetation growth, acidification, etc. [1-3]. In this study, several air pollutants were analysed in 23 towns of Campania region (Southern Italy) between 2019 and 2021, using Environmental Protection Agency Campania Region (ARPAC) data collected by 37 ground level monitoring stations, in order to evaluate the effects of lockdown regulations, enforced from March 9th to May 4th to limit COVID-19 spread. Monthly and hourly changes of benzene, CO, NO_2, O_3, PM_{10} and $PM_{2.5}$ quantity as well as the correlation of their concentration with weather parameters were also studied. General air quality was quantified computing the Air Quality Index (AQI) developed by EPA-USA [4], whereas the influence of air pollution on human health was carried out using the AirQ+ software v. 2.1.1 (WHO, 2021).

2. Results and Discussion

The rigid lockdown restrictions, implemented during the period March – May 2020 to contrast and limit the spread of COVID-19, impacted air quality positively. Compared to the same period of the previous year, all measured air pollutants showed a concentration decrease (average value of all sampling stations, NO_2: -46%; benzene: -24%; PM_{10}: -16%; CO: -15%; O_3: -9%). A weak increase (+3%) was only shown for $PM_{2.5}$, suggesting that for this pollutant other sources than traffic and industrial activities has to be considered.

A positive effect can be also seen after the end of lockdown period. In fact, the highest values reached by all pollutants in the years 2020 and 2021, were generally lower than the ones reported for the 2019.

Higher concentration of the primary pollutants as benzene, CO, NO_2, and PM were detected during the colder months rather than during the warmer ones. An opposite behaviour was observed for O_3, with higher values recorded during spring and summer than in winter season. The hourly trend of those pollutants showed two maximum concentration values: the first in the range 07:00-09:00 and the second in the range 19:00-21:00 corresponding to morning and evening rush hours. Conversely, O_3 showed a broad peak at midday. These patterns have been also observed in other studies done in different urban areas around the world [1-3; 5; 6]. Benzene, CO, and NO_2 showed a high positive correlation with atmospheric pressure and relative humidity, instead a negative one was observed with air temperature, solar irradiance, precipitation, UV, and wind speed; PM behaved similarly but in a less evident way. O_3 presented a negative correlation with relative humidity, no correlation with atmospheric pressure and precipitation, and a positive correlation with the other parameters. NO_2 and PM concentrations were overall lower than the limits fixed by EC [7], but substantially higher than that proposed by WHO [8, 9]; a more serious state was observed for traffic and industrial sites. It is worth to note as the background stations exceeded the EC limit for 8 hours mean concentration of O_3. This can be ascribed to the lower number of sinks in the rural area and/or to the arrival of precursors transported from mid and long distances [4].

According to our results, the air quality index of the monitored sites ranges from good ($0 < AQI < 50$) to hazardous ($301 < AQI < 500$), for all three years. Among those considered, the most impacting pollutants on the air quality were: $PM_{2.5}$ and O_3 during winter and summer, respectively. Overall, air quality was better in background stations whereas the worse conditions were found in traffic sites although some of them presented better conditions than others. All sites showed an improvement of air quality in summer 2020 compared to the previous year due the lower ozone concentrations reached, likely linked with the reduction of NO_2 emissions caused by the lockdown restrictions, as shown in Figure 1.

To estimate how much of specific health outcomes are ascribable to long-term exposure to benzene, NO_2, O_3, PM_{10}, and $PM_{2.5}$ concentration, AirQ+ software was used. A sharp decrease of adult mortality related to NO_2 was observed during the March, April and May 2020 compared to the same months of 2019 (-62%, -95% and -87%, respectively).

3. Conclusions

The effect of lockdown to limit the spread of COVID-19, on air quality in Campania region (Italy) was analyzed with respect to pollutants' concentration and healthy effects. The considered pollutants showed a seasonal and hourly periodic pattern and a positive correlation with some weather parameters. Overall air quality matched the limits imposed by EC regulations but the concentration values did not comply the WHO ones. The 2020 lockdown positively impacted on air quality, causing a decrease of most pollutants' concentration during March and April and influencing the air quality during the summer, due to less NO_2 as a precursor to O_3 formation. An overall better AQI score and a decrease in the incidence of respiratory diseases and deaths caused by air pollution were recorded.

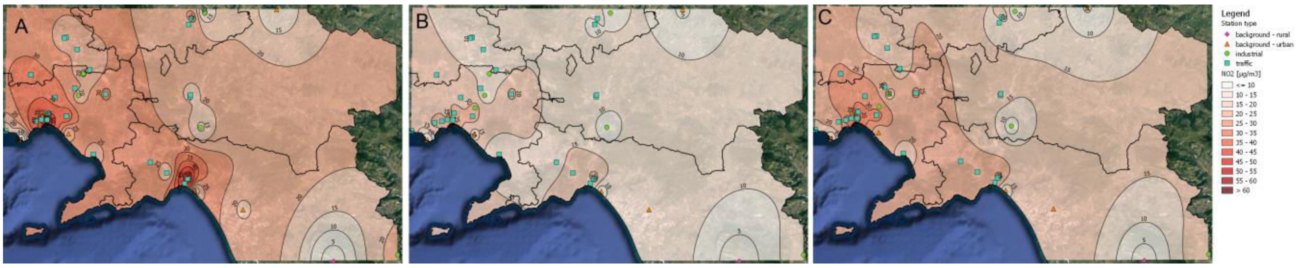

Figure 1 Spatial distribution of NO_2 in March-April period: A) 2019, B) 2020, C) 2021.

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POS24

COMPARISON OF TWO METHOD FOR DETERMINATION OF FORMALDEHYDE IN STACK EMISSION

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1. Introduction

Formaldehyde (HCHO) is a chemical compound extremely common in many industrial productions [1] but since January 2016 it has been re-classified as carcinogenic (H350) and mutagenic (H341); this fact caused big limitations in emission limit of formaldehyde, down to the limit of 5 mg/Nm3 actually implemented by Italian Environment Ministry.

As Formaldehyde was thought not to be very dangerous up until 2004, no European validated method for emission control was scheduled and, for this reason, a specific working group WG 40 in the framework of CEN TC 264 has been created in order to produce a qualified and tested method for it's quantification in emissions of stationary sources.

In the field of biomasses, the importance of formaldehyde is given by its presence in emissions from spark engines that burn (bio)methane, with expected values far above the limit of 5 mg/Nm3.

From a first examination of candidate methods, two analytical principles were selected: spectrophotometry (EPA 323) and HPLC (VDI 3862-2), using impingers with an absorption solution, as such technique is the most common also for other compounds.

2. Results and Discussion

To investigate and to deepen the characteristics of the methods identified within the CEN TC 264 WG 40, a first experimental plan was created.

A real biomass plant that produces biogas (biomethane) was selected. The selected plant implements the best available techniques like an emission thermal oxidiser and implements a good quality management system.

Simultaneous samplings were realized by two laboratories: APPA Trento Labora-tory (Lab A) and RSE Laboratory (Lab B). The measurements were achieved using dif-ferent sampling solutions, different probes and analytical methods: DNPH (VDI 3862-2) and Acetylacetone (EPA 323).

The data seem to show that the derivatization reaction takes time to take place completely, for this reason it was chosen to place at least 24 hours between the time of derivatization and that of the analysis.

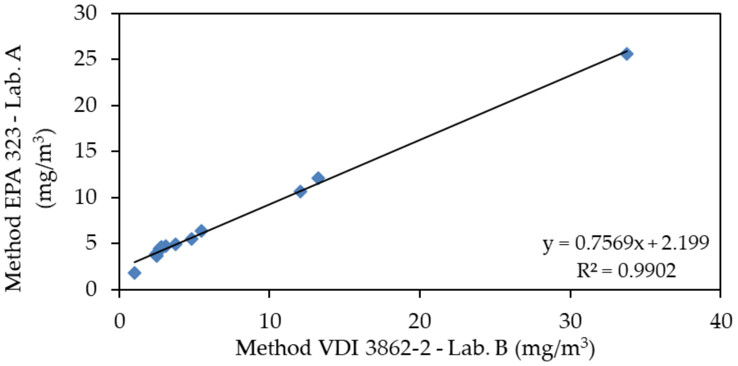
To compare the two sampling methods was calculated the correlation between the values obtained by the two different methods (Figure 1).

3. Conclusions

Sampling of formaldehyde is critical as regards the formation of condensation, which absorbs formaldehyde in an unpredictable way and which must be absolutely avoided. The capture of formaldehyde in pure water is unstable, so the use of a solution of H_2SO_4.

If the measurement method VDI 3862-2 is used, the solution must be treated, within 24 hours of sampling, with DNPH and kept at least 48 hours before analysis, which can be done in the following 15 days, if the samples are stored at 4 ° C.

The relationship between EPA 323 methods and VDI 3862-2 is good but it is necessary to carry out new evaluations in order to better evaluate reproducibility and repeatability.



Correlation of samples according to the EPA 323 analyzed by Lab. A and VDI 3862-2 analysed by Lab. B

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POS25

MICROBIOLOGICAL, CHEMICAL AND AGRONOMIC STUDY ON SOILS TREATED WITH BIOCHAR AND BIOSTIMULANTS

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1. Introduction

This research is part of the FERTILIAS project funded by the Emilia-Romagna Region. An eco-sustainable methodology that combines innovative technologies and agro-industrial/agronomic practices was applied to limit the use of fertilizers and pesticides, by using novel amendments and specific biostimulants. In this study, biochar derived from wood residues was used to improve soil quality in industrial tomato cultivation, applied in limited quantities (about 1 ton per hectare) both alone and in combination with commercial microbial consortia (bacteria and fungi) on different farms in Parma and Ferrara provinces. The aims of the combined action of biochar and biostimulants were to increase the global primary production of agricultural land, the organic matter (OM) content in soils, decrease the release of nitrates in vulnerable areas and greenhouse gas emissions. Agronomic studies and different analytical techniques were applied to assess whether biochar could be an alternative to the common chemical input in agriculture to investigate the impact on dissolved OM (DOM) and other nutrients. Soils were sampled before, during and after the tomato cultivation.

2. Results and Discussion

The monitoring of plant performance in different farms and experimental plots was carried out through several agronomic parameters, concerning morphology, physiology, productivity and quality of tomato plants, measured at harvest. Moreover, the content of chloropyll was measured during growth with non destructive spectral analysis. Conventional fertilisation and treatments with biochar was compared over two seasons and few significant differences was observed, indicating that biochar, applied either with or without microbial consortia, can sustain growth of tomato in such conditions. In farms located in Ferrara Province, the combined treatment with biochar and microbial consortia led to a significant reduction in the percentage of fruits with rotting symptoms. In the farm located in Parma, yield of marketable tomato fruits was higher when biochar was applied.

To study the variation in the content of OM, TOC (total organic carbon) measurements were made both in solid samples and in water leachates. No changes were observed with different treatments in solid samples, while DOC exhibited a wide variability. A slight decrease in carbon mobilization was observed over the period.

Nitrogen speciation was investigated by ion chromatography. It showed the predominance of nitrate, low levels of nitrite in some sanples, while ammoniacal nitrogen was negligible.

Molecular spectroscopy allowed the determination of the fluorescence index (FI) and specific UV-Vis absorbance at 254 nm wavelength (SUVA254), which are linked to aromatic moieties in DOM. There were significant differencies between soils, however, not dependent on treatments. These two parameters exhibited lower values in pure biochar than in soil leachates. 3D fluorescence spectra were processed by excitation-emission matrices (EEM) with parallel factor analysis (PARAFAC). Four components have been identified for biochar in different regions corrisponding to proteins, humic and fulvic acids.

Combining analytical pyrolysis (Py-GC-MS) and optical techniques evidenced variations in DOM molecular composition between untreated and amended soils.

The potential retention of nitrates, not evidenced in the leachates, was further investigated though percolation tests by filling a column with 10 cm of treated soil and a filter in the bottom made of sand and glass wool. Water passed through this column and the filtrate was collected and analyzed. A comparison between treated soil and a control soil was made to study the role of biochar in nitrate retention.

3. Conclusions

An important result of this project is the constancy of yield, physiological parameters, and fruit quality in different treatments; the ones with biochar and microbial consortia did not receive the same amount of nutrients as in the conventionally fertilised control. These results can support the adoption of soil amendments and biostimulants. A complete metagenomic analysis on the rizhospheric soils in different parcels showed suggestive results of a population dynamic also in relation with the treatments.

In general, no relevant improvement has been detected in amended soils for properties concerning carbon and nitrates. It is known that biochar addition to soils induces changes in DOM content and composition in a way which is strongly depending on soil type and amendment rate.

Acknowledgments. This research was part of the project "Green strategies for bioremediation of soils, with a better management of water resources, fertilizers and pesticides - FERTILIAS", supported by Regione Emilia-Romagna, Italy, through the Rural Development Programme 2014–2020—Operation Type 16.1.01—Focus Area 4B. www.gofertilias.it
We owe our special thanks to Azienda Agricola Ganazzoli (Parma),Azienda Agricola Contarini (Ferrara), Azienda Agricola Trombini (Ferrara), and to Technopole of Rimini.

POS26

EVALUATION OF PM_{10} AND $PM_{2.5}$ PRE AND DURING COVID-19 LOCKDOWN IN THE MUNICIPALITY OF POMIGLIANO D'ARCO, NAPLES (ITALY)

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1. Introduction

The coronavirus disease 2019 (COVID-19) created unique environmental conditions for the study of air pollution, due to reduction of many economic activities and mobility limitations starting from March 2020.

One of the most important features that are analyzed in terms of atmospheric aerosols are the dimensions of the particles. The size is very important, because it is directly connected to the ability of the particles to remain suspended in air. The smaller particles will be longer in suspension in the atmosphere, since the sedimentation speed is directly related to the size and weight of the particles [1]. The smaller particles pose a greater danger to human health, as they can penetrate deeply into the respiratory system; for this reason environmental monitoring is carried out on PM10 and PM2.5.

In the present study, average daily concentrations of PM10 and PM2.5 were evaluated in a medium-sized town located north of Naples, Pomigliano D'Arco, between 2019 and 2021, within the MONAIR project [2]. The annual and seasonal trend was investigated to be related with some limitations that have been taken during and pre COVID-19 pandemic period.

2. Results and Discussion

The concentration values of PM10 and PM2.5 have been obtained from an automatic air pollution measurement station Dual Channel (Fai Instruments) located on the roof of the city Hall of Pomigliano d'Arco. The daily meteorological data (max. temperature in °C, min. temperature in °C, wind speed in km/h, relative humidity in %, rain in mm and air pressure in mbar) have been collected from a meteo validated website [3].

The seasonal variation of PM10 and PM2.5 shows similar trends and the highest value was recorded in winter and lowest value was registered in spring. In case of PM10 the highest monthly average was 104.4 µg/m^3 in January 2020 while the lowest monthly average was 22.5 µg/m^3 in the May 2019.

The several studies show that the concentration of PM10 and PM2.5 is higher in the winter season and followed by spring, autumn and summer [4,5], but in Pomigliano d'Arco municipality the variability of weather conditions does not allow to identify a trend in the seasons. In 2019, the concentration of PM10 and PM2.5 was higher in summer season and followed by spring and autumn. In 2020, autumn season concentrations of PM were higher than in summer and in spring, while in 2021 spring concentrations were higher than summer and autumn ones.

The start of lockdown in March 2020 showed a downward trend of particulate matters and monthly average value gradually declined from March until August 2020 in which there is the maximum of reduction of PM10 equal to 46% compared to both 2019 and 2021.

In case of PM2.5 monthly average concentration, the significant decrease is recorded in the month of June 2020 with a reduction of 49.8% compared to 2019 and 40.2% compared to 2021.

The decrease in particulate matter stops starting from September 2020 which showed higher values than 2019 and 2021 and no significant difference follows in autumn season.

Overall, the number of exceedances of the daily limit of 50 µg/m^3 is equal to 89 in 2020, lower than the exceedances recorded in 2019 equal to 98 and equal to 100 in 2021.

The evaluation can be completed considering the effect of rain on suspended particulate matter [6]. In particularly rainy months (November 2019) the number of overrun days is drastically reduced. We considered rainy days if it has rained at least 2 mm in the day. Analyzing the three years of interest we can highlight that although 2020 was the least rainy of the three, with 94 rainy days compared to 130 in 2109 and 125 in 2021, it was also the year that recorded the least overruns of PM daily limit.

It is evident that the concentration of PM10 and PM2.5 has been significantly reduced during lockdown period of 2020 in comparison with pre-lockdown phase (in 2019) and recovery phase in 2021. This may be due to the limitations and changes in habits due to the pandemic.

3. Conclusions

Both the meteorological and anthropogenic factors regulate the seasonal and diurnal variation of PM10 and PM2.5 in the municipality of Pomigliano d'Arco, Naples. The trend of the particulate matter recorded in the period of interest (2019-2021) shows dependence on the limitations and changes in habits of pandemic period.

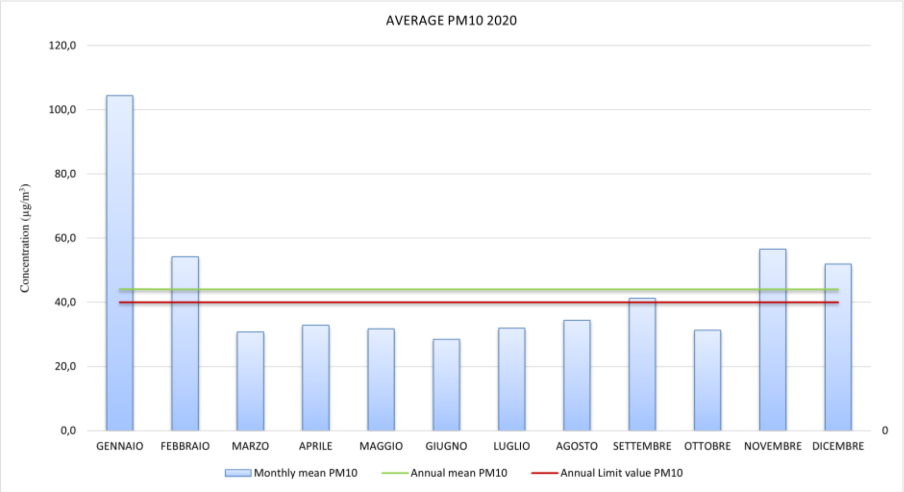

Figure 1. Monthly mean concentrations of PM10 during 2020 in Pomigliano d'Arco city.

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POS27

GLYCIDOL: OVERVIEW ON MAIN SYNTHESES AND CONVERSIONS INTO VALUE-ADDED COMPOUNDS

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1. Introduction

The use of biobased building blocks for the preparation of chemicals is one of the 12 principles of green chemistry [1] and one of the major investigated research fields within this community [2–6]. Glycerol valorization through catalysis (glycerochemistry) represents a valuable example with several repercussions at industrial level [7]. Among glycerol derivatives, following the benign-by-design approach [8,9], we propose a mini-review on glycidol (2,3-epoxy-1-propanol), a versatile molecule (e.g. applications in laundry detergents, disinfectants, cosmetics, skin creams, moisturizing lotions, shampoos, etc.) with high reactivity due to oxiranic and alcoholic functionalities. Glycidol market value reaches USD 20 per kg [10], with a global size over USD 130 million (2019) and an expected projection up to USD 180 million in 2026 [11].

2. Results and Discussion

Glycidol may be produced from fossil resources (e.g. allyl alcohol epoxidation with H_2O_2 and tungsten oxide/salts of tungstic acid [12] or TS-1 [13,14] as catalytic system) or from bio-based glycerol a platform molecule with a market projected to reach 4 Mt by 2027 (Global Industry Analysts Inc., 2021). At least 15 alternative routes are available. As described, its high versatility may lead to the synthesis of 1,2-propanediol or 1,3-propanediol (precursor of polyethers, propylene [15], unsaturated polyester resins or as monomer in the synthesis of polypropylene terephthalate and polyesters [16]), glycerol carbonate (one of the most valuable molecules for the possibility to be used as a solvent, lubricant, coating agent, ingredient in pharmaceutical/personal care and as building block in organic and polymer chemistry [17–20]) and monoalkyl glyceryl ethers (MAGEs, that serve several industrial areas, e.g. C1-C6 solvents, C1-C24 detergents and surfactants, C1-Cx additives for lubricants, inks, etc., C4-C18 cosmetics). In addition, glycidol may be used as monomer to produce poly(glycidyl-ether)s, sustainable and biodegradable polymers obtained through anionic polimerization with protected glycidols, and glycidyl esters, a valuable epoxy resin monomers obtained through the selective transformation of glycidol catalyzed by a quaternary alkyl ammonium salt by transesterification of methyl esters.

3. Conclusions

To sum up, glycidol synthesis and valorization to value-added chemicals has been reviewed. The preparation of bio-based allyl alcohol through glycerol deoxydehydration represents, to date, the major challenge to speed up the transition from a fossil-based production to a renewable one. In this context, glycidol obtained as glycerol derivate could increase the interest towards the glycerol biorefinery

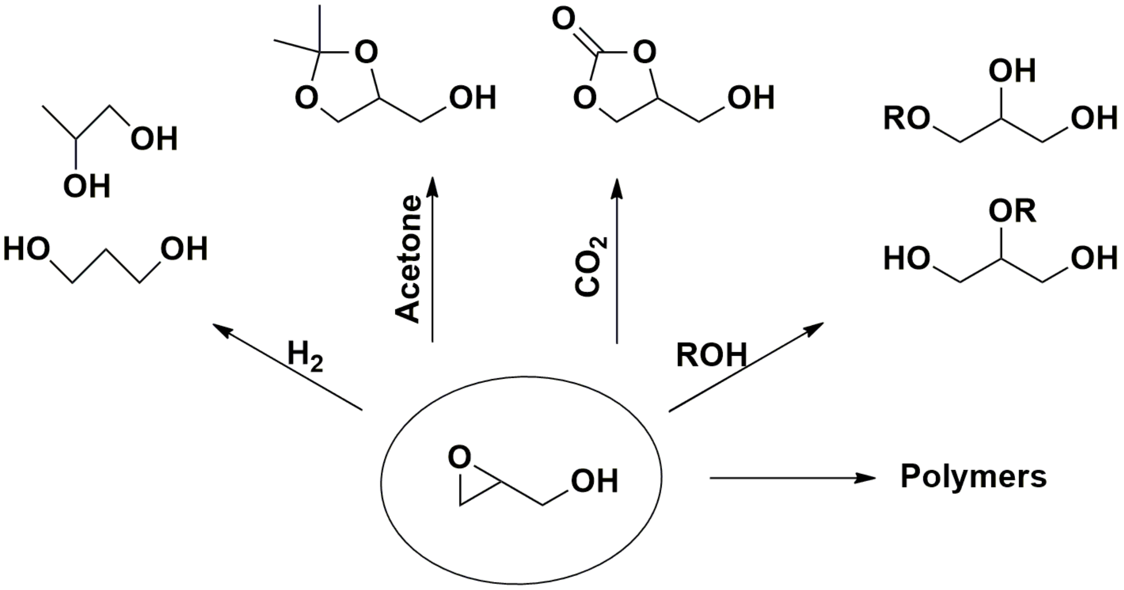

Figure 1. Glycidol valorisation pathways.

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POS28

AMINOPOLYCARBOXYLIC ACIDS-BASED CATALYSTS FOR (PHOTO-) FENTON-PROCESSES AT CIRCUMNEUTRAL PH

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1. Introduction

According to the UN sixth sustainable development goal, the design of new active catalysts for water and wastewater treatment represents a key aspect to fulfill this goal. This approach became more and more important also in the light of an increasing number of chemical substances that are continuously released into the aquatic environment from urban wastewater treatment plants, not being removed by traditional treatment processes. Advanced oxidation processes (AOPs), based on the generation of radical species with high oxidizing power, represent a promising solution for the tertiary treatment of urban water and wastewater.Among AOPs, Fenton and particularly photo-Fenton, generally carried out in the presence of Fe^{2+} /H_2O_2, have gained considerable interest. These processes have not represented a feasible option for the tertiary treatment of urban water and wastewater so far because they require acidic pH (<3) with significant repercussions on the management costs due to an acidification and a necessary subsequent neutralization before disposal/reuse, with the concomitant formation of sludge (precipitation of iron as hydroxides) [1].

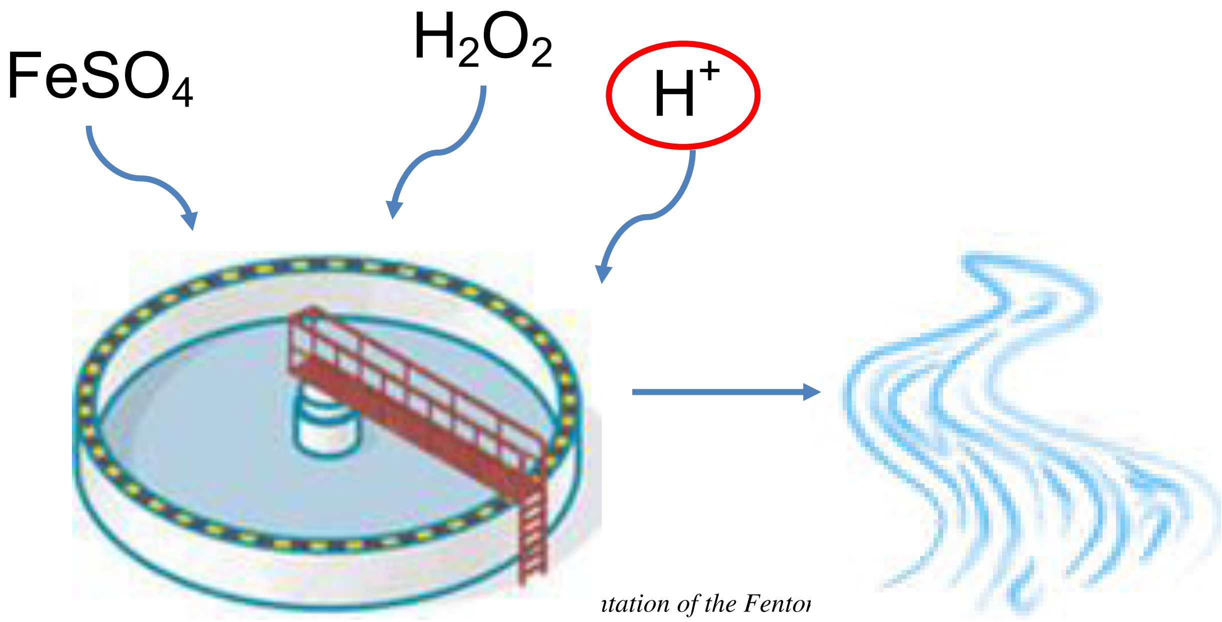
2. Results and Discussion

To overcome this limitation, several studies have been carried out in the presence of homogeneous metal complexes (M= $Fe^{2+}/^{3+}$; Cu^{2+}, Ag^{+}, Co^{2+} and Mn^{2+} in the so-called photo-Fenton-like processes) able to work at circumneutral pH. For instance, Fe^{3+} ions form stable complexes with aminopolycarboxylic acids (APCAs), in an extensive range of pH and depending on the ligand with higher quantum yields than iron aquo complexes. APCAs are an interesting class of ligands and their application in Fenton and photo-Fenton processes has increased over years [2]. Among APCAs, ethylene diaminetetraacetic acid (EDTA), ethylenediamine- N,N-disuccinic acid (EDDS), iminodisuccinic acid (IDS), diethylenetriaminepentaacetic acid (DTPA) and nitrilotriacetic acid (NTA) represent some examples tested for this purpose [3].

3. Conclusions

The design of APCA-based complexes for Fenton and photo-Fenton processes is reviewed. Efforts toward the necessity to improve catalyst biodegradability represent a forthcoming research topic to be investigated. The design of biomass-derived ligands is another crucial aspect to consider. Catalytic activity evaluation needs to be deeper addressed favouring the use of some parameters generally used in catalysis (turnover frequency, turnover number) in combination with the life cycle assessment. The proposed holistic approach could improve the greenness of future contributions to this research field.

POS28



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POS29

ELECTRO-OXIDATION TREATMENT OF AMMONIUM IN WASTEWATER USING BDD ELECTRODES

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1. Introduction

Ammonia (NH_3) and ammonium ion (NH_4^+) effluents cause high levels of contamination of water and it can involve eutrophication [1], and significant environmental-health risks. The excessive use of fertilizers, and the incorrect management of slurry from livestock farms are among the most common sources of ammoniacal nitrogen in water and wastewater. Traditional techniques, such as anaerobic digestion treatments, are ineffective towards the removal of NH_3/NH_4^+ from polluted waters, thus the development of innovative methods is required. Among the advanced oxidation processes (AOPs), the electro-oxidation (EO) treatment of ammonium has attracted considerable attention over the last years, due its simplicity and no need to add chemical reagents. In the present contribution, experimental investigations on NH_4^+ removal from synthetic wastewater, by means of EO using BDD electrode, on a lab-scale reactor were carried out. In details, the effects of operating parameters, such as the electrolyte composition and electrolyte concentration, on the NH_4^+ degradation efficiency, were investigated.

2. Results and Discussion

In aqueous solution, NH_3 and NH_4^+ are in a pH-controlled equilibrium, but in alkaline media the dominant species is NH_3, while at pH under 7, NH_4^+ prevails. In this study, several EO of NH_4Cl experiments were performed, and in each of them an initial pH of 6.6 has been encountered, meaning that the ammonium ions were the main species in solution.

The electrochemical reactor consisted of two BDD electrodes of 100 x 50 mm, connected to a DC Power supply BPS-305 (Lavolta). BDD electrode have been widely employed for electrochemical treatment of wastewater due to their high current efficiency and high performances. As reported in several studies, the EO process is commonly impacted by the composition of electrolyte. To evaluate the influence of the latter parameter on the NH_4^+ degradation efficiency, different EO tests were carried out using 3 types of salts: NaCl, Na_2SO_4, $NaClO_4$. In all of the experiments, the NH_4Cl starting concentration was 50 mg/L, the electrolyte concentration was 250 mg/L and applied current intensity was kept constant at 0.15 A.

The findings are shown in Fig.1. The NH_4^+ degradation efficiency is the highest running in presence of NaCl (74.9 %) rather than Na_2SO_4 and $NaClO_4$ (2.0 and 1.0 %, respectively), after 120 minutes of treatment. Therefore, basically no NH_4^+ degradation occurs operating with both Na_2SO_4 or $NaClO_4$ as electrolytes. As known, the EO of NH_4^+ on BDD electrode under acidic pH, is mediated by the electro-generation of active free chlorine, therefore favoring indirect oxidation to direct oxidation process. Conversely, acting with Na_2SO_4 or $NaClO_4$ as electrolytes, no active chlorine species were produced, hence corroborating the extremely low degradation efficiencies obtained [2].

So, these results would seem to confirm that active chlorine species are strong electrochemically generated oxidants for indirect oxidation of ammonium, in acidic media. Consequently, in order to examine the influence of indirect oxidation mediated by active chlorine, the effect of NaCl concentration was investigated. The NaCl concentration was varied between 100 and 750 mg/L, and each experiment was conducted at a current intensity of 0.15 A. The results exhibited in Fig. 2 clearly state that the lowest NH_4^+ degradation efficiency was achieved operating with the lowest NaCl concentration (100 mg/L), after 180 min of treatment. However, at the end of the EO treatment, no improvements in degradation efficiency were obtained by increasing the NaCl concentration above 250 mg/L. In details, basically the same degradation efficiencies of 75.2%, 76.8%, 76.1% were achieved, operating with 250, 500 and 750 mg/L of NaCl, respectively. Thus, the results suggested that the rise of NaCl concentration above 250 mg/L did not promote the generation of more active chlorine species, which are fundamental to the ammonium oxidation. This outcome is probably due to the high chlorine overpotential of the BDD electrode, resulting in a low generation of active chlorine at the applied current intensity of 0.15 A [3].

3. Conclusions

EO process was investigated for ammonium removal from synthetic wastewater, using BDD electrodes. Electrolyte composition and electrolyte concentration were investigated because they are the two main operating parameters on ammonium removal. The results highlighted that the highest ammonium degradation efficiency of 74.9 % was achieved operating in presence of NaCl. This process is mediated by indirect oxidation under acidic pH, which involves the generation of active chlorine species. However, no improvements in terms of NH_4^+ degradation efficiencies were obtained by enhancing the initial NaCl concentration above 250 mg/L. This result is probably due to the high chlorine overpotential of the BDD electrode, which does not allow to obtain a high generation of active chlorine species.

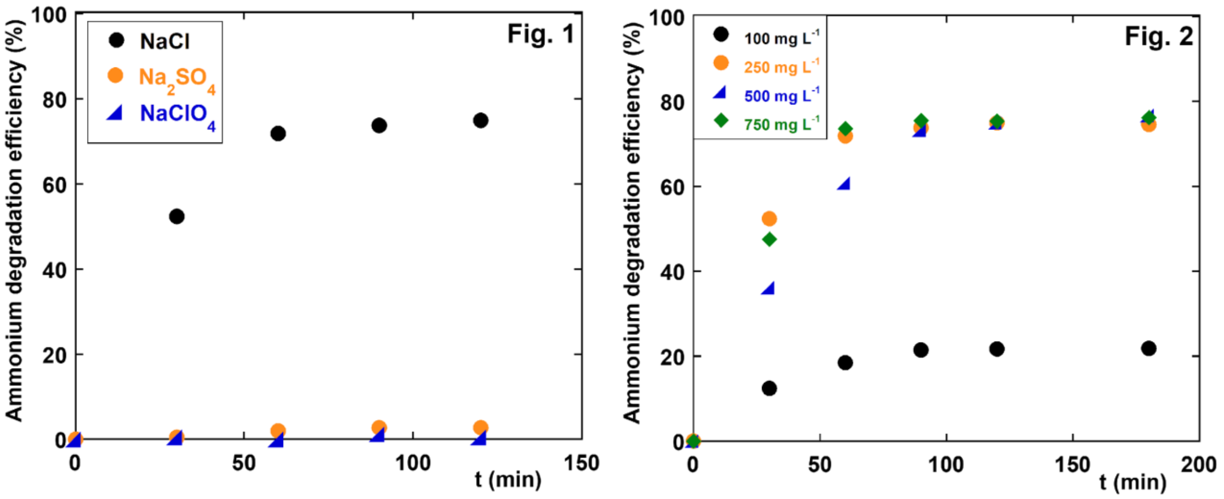

Fig.1: Effect of electrolye composition; Fig.2:Effect of NaCl concentration.

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POS30

ABATEMENT OF POLLUTANTS FROM WATER BY FENTON LIKE PROCESSES

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1. Introduction

Nowadays, dyes are being used in all production processes in industry and valuable alternatives are seldom available. The estimated dye production is in the order of 700,000 tons per year. So, colored effluents from production sectors such as paper, leather and so on are a major source of environmental pollution. Moreover, herbicides like Glyphosate are another major source of concern due to their potential human health effects. Conventional methods (biological oxidation, activated carbon adsorption, coagulation and flocculation) are not sufficient to remove contaminants that are at the same time recalcitrant a water soluble. An attractive, inexpensive and sludge free alternative for the removal of wide range of pollutants in wastewaters is use of advanced oxidation processes (AOPs). Among AOPs, Fenton-like processes have been used as a source of hydroxyl radicals from H2O2 in the presence of iron species and mild reaction conditions [1,2]. Fe0 or ferrous ions (Fe(II)), released from Fe0 corrosion, react with oxygen to produce H2O2, which further reacts with Fe(II) via the well-known Fenton reaction to produce ˙OH.

2. Results and Discussion

Different dyes including Rhodamine B, Malachite Green and Acid Blue 74 have been degraded using Zero valent iron (ZVI, i.e., Fe0) and hydrogen peroxide at different pH values ranging from acidic (3) to near neutral, i.e., 6. Rhodamine B was degraded with different amounts of ZVI ranges (0.01-0.02 g/L) along with 50-100 µM of H2O2. At pH 5 and 6, stepwise addition of hydrogen peroxide was required to degrade the remaining concentration of the dye. In case of Malachite green, at pH 3 and 4, ZVI (0.01 g/L) and hydrogen peroxide (50-100µM) were the concentrations needed for optimal degradation, while at pH 5 and 6 ZVI (0.06g/L) with 100 µM H2O2 (as an alternative, 0.02 g/L ZVI and 50µM H2O2) were the optimum concentrations for maximum degradation. Acid blue 74 (AB74) reacted very fast (much faster than malachite green or rhodamine B): at pH 3, ZVI (0.01g/L) with H2O2 50µM degraded AB74 within 5 minutes. At pH 4 and other identical conditions, AB74 was degraded in 15 minutes. At pH 5 and 6, stepwise addition of H2O2 was used to remove AB74. ZVI (0.02g/L) with hydrogen peroxide (50+50 µM (after every 10 minutes)) were added to achieve maximum removal within a total reaction time of 60 minutes. All reactions were quenched by 1ml of methanol and, after regular intervals, the same amount of sample was taken and absorbance was measured by UV-Vis spectrophotometry.

A persistent emerging pollutant, Glyphosate, has been degraded with the same procedure. Ion chromatography with conductivity detection was used for the analysis, with 17 mM NaOH as the eluent. The main experiment involved 2ppm glyphosate solution, and pH was maintained by sulfuric acid. The amount of ZVI was 0.01-0.02 g/L with hydrogen peroxide 50-300µM, for a total reaction time of one hour. After one hour, few ml from the solution were filtered and injected to analyse the concentration of glyphosate. Adsorption of glyphosate was also investigated to compare the degradation and adsorption percentages. At pH 3, almost 20% removal was observed with 0.01g/L ZVI alone, due to adsorption on ZVI. With 0.01g/L of ZVI and 300µM of hydrogen peroxide, almost 99% glyphosate removal was achieved. At pH 4, adsorption was almost 43% and degradation+adsorption was almost 87% with 0.01g/L ZVI and 150+50 µM H2O2 (added initially and after 30 minutes). At pH 5 and 6, there was almost no removal of glyphosate by using different combinations of ZVI and H2O2.

3. Conclusions

Organic dyes were degraded using a Fenton process involving ZVI + H2O2. Almost all dyes exhibited promising results concerning Fenton removal, and the degradation parameters were optimized at different pH values. Glyphosate was also degraded at 3 and 4 pH with the same strategy used for the dyes, but it did not show any degradation at pH 5 and 6. Adsorption of Glyphosate on ZVI was also investigated, to check for the actual adsorption/degradation percentages.

Mechanism of Fenton like processes using zero valent iron (ZVI) and H2O2 for pollutant removal

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POS31

MICROALGAL-BASED CARBON ENCAPSULATED IRON NANOPARTICLES FOR THE REMOVAL OF MICROPOLLUTANTS FROM WASTEWATER

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1. Introduction

Hydrothermal carbonization (HTC) is a low-impact thermochemical process [1] that can be used to produce microalgal-based carbon encapsulated zero-valent iron nanoparticles (ME-nFe) to be used for wastewater treatment popruse. Due to the high sorption capacity and the reducing power of this particular adsorbent Me-nFe can be used to remove micropollutants from wastewater, providing a new option for their removal that still need to be optimized in most wastewater treatment plants [2]. Here we present a laboratory-scale adsorption study focusing on the removal of specific organic pollutants: Amisulpride (AMS), Ofloxacin (OFX), Metoprolol (MET), Sulfamethoxazole (SMX), Clarithromycin (CLM), Gabapentin lactam (GBP), Propifenazone (PHP), Carbamazepine (CBZ) and Diclofenac (DCF) from aqueous solutions made with ultrapure water. The effect of different doses of ME-nFe (0.1, 1, and 3 g/L), and contact time (2 and 10 minutes) were evaluated to treat solutions containing all the compounds at 1.5 μg/L and 500 ng/L. Samples properly filtered at 0.2 μm, were stored in autosampler vials and were then analyzed by UPLC-MS.

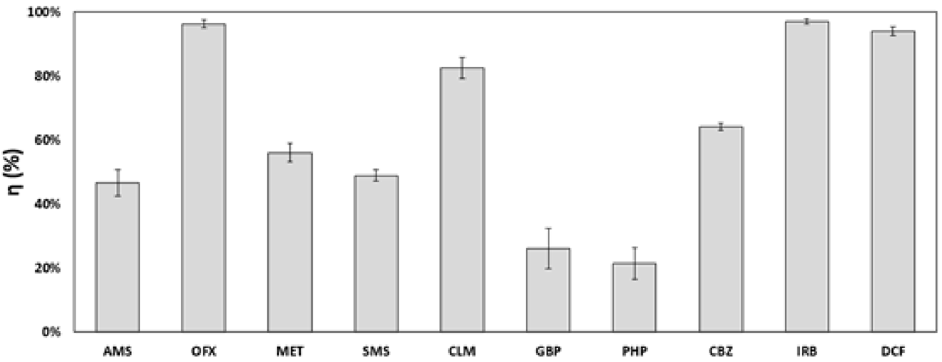
2. Results and Discussion

Adsorption tests on the 1.5 μg /L solution were used as preliminary tests to understand the overall affinity among the nanoparticles and the selected pharmaceutical compounds, also allowing the definition of the best operative parameters to optimize the use of the Me-nFe. Sulfamethoxazole (SMX), Gabapentin lactam (GBP), Propifenazone (PHP), Carbamazepine (CBZ), and Diclofenac (DCF) were adsorbed very quickly (2 minutes) except for being subject to partial desorption already after 10 minutes. At the same time, Amisulpride (AMS), Ofloxacin (OFX), Metoprolol (MET), and Clarithromycin (CLM) were not affected by the same fate as no desorption occurred after 10 minutes. Because of these trends, ensuring short contact times seems the better strategy to use the nanoparticles. Higher Me-nFe doses were not always matched by better purification effects. This was apparent with Diclofenac, for which the removal efficiency increased from 76% to 94% using a dose of 3 and 0.1 g/L, respectively. Considering all the compounds, the best results were obtained using a Me-nFe concentration of 1 g/L with two minutes of contact time. This configuration led to removal yields that were excellent for Ofloxacin and Diclofenac (90% and 92%, respectively) and fair for Amisulpride, Metoprolol, Sulfamethoxazole, and Carbamazepine (51%, 53%, 49%, and 62%). While Gabapentin lactam and PHP were never adequately removed (35% and 20%), this was not the case for CLM, which was characterized by a very large variation among the samples, deserving further investigation. Based on the results of the 1.5 μg/L Jar test, the best contact time and Me-nFe dose were selected for the next part of the study which was aimed at assessing the performance of the nanoparticles on lower contaminant concentrations (500 ng/L). Diclofenac, Ofloxacin, Clarithromycin and Irbesartan were removed efficaciously (94 ± 1 %, 96 ± 1 %, 83 ± 3 %, 97 ± 1 %, respectively); Amisulpride, Metoprolol, Sulfamethoxazole, and Carbamazepine concentrations were basically halved (47 ± 4 %, 56 ± 3 %, 49 ± 3 %, 64 ± 1 % respectively). However, the removal was not adequate for Gabapentin lactam and Propifenazone (26 ± 6 %, 22 ± 5 %). Pearson correlation was performed on the 500 ng/L test results to understand if a linear correlation could be detected between the experimental data (removal efficiency) and the main physico-chemical characteristics of the pharmaceutical compounds. The only significant correlation was found between the removal efficiency and the hydrophobicity of the compounds (r=0.73 p value=0.015).

d

3. Conclusions

The Me-nFe had similar effectiveness while dealing with both levels of contamination (1.5 µg/L and 500 ng/L) that were chosen to recreate reasonable scenarios for municipal wastewater. The lab-scale tests clearly showed different efficiencies in the removal of ten micropollutants, in particular Diclofenac, Ofloxacin, Clarithromycin, and Irbesartan were the ones with higher affinity for the nanoparticles. These results, despite positive, still need to be confirmed for municipal effluents where the nanoparticles are likely to interact with many other contaminants that can compete for their active sites. However, using microalgal biomass to produce this type of adsorbent seems a promising technology to deal with emerging pollutants.



Removal efficiencies (η) for the 500 ng/L test. Data are shown as mean ± standard deviation (n=5)

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POS32

BARN SWALLOWS AS BIOINDICATOR OF TRACE ELEMENTS ENVIRONMENTAL CONTAMINATION

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1. Introduction

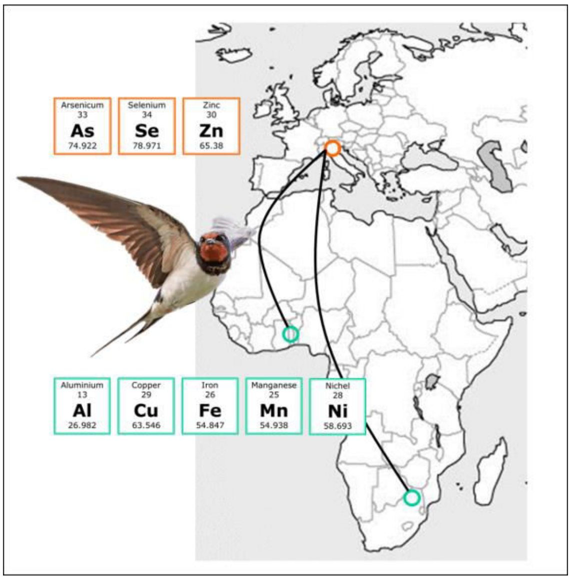
Trace elements are among the main stressor for wild animals. Although some of them are essential for organisms, others may have toxic effects that impact on population dynamics [1]. The biomonitoring of trace elements is therefore pivotal in environmental risk assessment. Birds are excellent biomonitors for trace elements since they are ubiquitous, easy to sample and, depending on their migratory behaviour, can be indicators of either long-range or local pollution. This work aimed at analysing the contamination fingerprint of trace elements of African non-breeding grounds and European breeding areas in a long-distance migratory bird, the barn swallow (Hirundo rustica). To do so, a first tail feather (R4af, hereafter) was plucked in Northern Italy from 59 individuals upon arrival from migration; as barn swallow undergo a complete moult during wintering, this feather represents the contamination profile of the African quarters. The removal of this feather induced a regrowth of the same one; therefore, about 1 month after the first sampling, the individuals were re-captured and the re-grown feather (R4it, hereafter), that accumulated trace elements in the breeding quarter, plucked.

2. Results and Discussion

Trace element concentrations were measured by an inductively coupled plasma quadrupole mass spectrometer (ICP-MS) equipped with a standard ICP torch, cross-flow nebulizer, nickel sampler and skimmer cones and dynamic reaction cell. Focal trace elements (namely Al, Fe, Zn, Cu, Mn, Ni, Pb, Hg, Se, Cr, As, Cd, listed in order of decreasing concentration) were detected in each sample with the exception of Cd, found in measurable concentration only in 44% of them. As expected, variability in trace element concentrations was lower in R4it as compared to R4af feathers; indeed, while the firsts were grown within the same small area (~20 km in radius), the latter were moulted across a broad African non-breeding range, characterized by different elemental compositions. The redundancy analyses disclosed statistically significant differences in the elemental composition according to the interaction between feather growth location and individual age, while no effect of individual sex and body condition was found. Differences in the overall elemental composition of feathers were further investigated with univariate analyses. Feathers grown in Africa showed higher concentrations of Al, Cu, Fe, Mn and Ni, while concentrations of As, Se and Zn were higher in feathers grown in Italy. In addition, trace element concentrations were lower in individuals at their first breeding season as compared to the others, with the exception of Se and Zn, that showed the highest concentrations in R4it feathers of individuals at their first breeding season. This is interesting, since Zn ad Se are known to be deficient in soils of the Sub-Saharan Africa, where multiple deficiencies of micronutriens are widespread [2]. The differences in the profile of trace elements accumulated in tail feathers grown in Africa and Italy likely reflect dissimilarities in the elemental profile of soil, water, vegetation and food sources occurring between the wintering and the breeding grounds. A further analyses also investigated the correlation patterns among trace elements within the two groups, with some interesting results. In particular, focusing on the feathers grown in the wintering area, two clusters of elements were found: the first one included Al, Fe, Mn, Hg and Cd, while the second one included Zn, Cu, Ni, Pb, Se, Cr and As. This finding suggests that the population of breeding barn swallow studied in the present work spend the wintering period in Africa in two different geographical area, characterised by different elemental composition. This was not unexpected: barn swallows show migratory connectivity at the continental scale, and are known to cluster in two groups of individuals wintering in Africa to the south and the north of approximately 5° S. Individuals breeding in Italy generally spend the non-breeding staging period to the north of the equator, but geolocator tracking of individuals breeding in the same geographical area where we collected feathers revealed that some individuals arrive much further south, up to South Africa [3]. Therefore, the observed patterns of trace element covariation may reflect these two groups of individuals.

3. Conclusions

In this work we described the trace elements fingerprint of barn swallow tail feathers grown in breeding (Italy) and non-breeding (Africa) areas. The most abundant elements were Al, Fe and Zn, while the levels of toxic elements, including Pd, Ni, Cd and Hg, were very low. The elemental fingerprint differed between feathers grown in breeding and non-breeding areas, with overall lower levels in feathers grown in Italy, with the exception of Zn and Se, suggesting different environmental sources of trace elements. Considering the toxicity of some trace elements, further researches are necessary to investigate the sources and the accumulation pathways of trace elements in barn swallows. Finally, this work underlines the suitability of feathers as a tool to monitor trace element contamination.



Trace elements in barn swallow feathers grown in breeding (Italy) and non-breeding (Africa) areas

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POS33

OPTIMIZING LVDI-LC-HRMS SENSITIVITY FOR NON-TARGETED ENVIRONMENTAL ANALYSIS BY DESIGN OF EXPERIMENTS

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1. Introduction

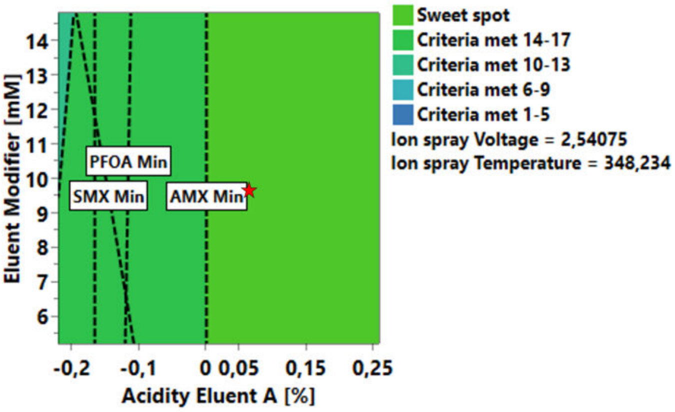
Non-targeted analytical approaches based on liquid chromatography coupled with high-resolution mass spectrometry (LC-HRMS) are gaining attention for the comprehensive detection and identification of chemicals of environmental concern (CECs) occurring in environmental samples, alleviating the need for reference standards [1]. LC-HRMS non-targeted approaches are playing a relevant role in monitoring CEC occurrence in surface waters and effluents from wastewater treatment plants, in both of which transformation products (TPs) can occur after chemical, photochemical, and biological degradation processes. Consequently, non-targeted approaches tend to lower selectivity by reducing sample handling, without drastically affecting sensitivity often performing large-volume direct injection (LVDI) [2]. On this basis, a Design-of-Experiment (DoE) optimization workflow is here presented for increasing the sensitivity of a LVDI-LC-HRMS method, performed using a training set of 42 CECs (e.g., PFASs and estrogens) and TPs from 2013-2020 regulations and watch lists, covering a wide range of physicochemical properties, being thus characterized by different chromatographic and ionization behaviours.

2. Results and Discussion

Experiments were performed on a TriPlus™ RSH EQuan 850 LC System coupled with an Orbitrap Exploris 120 mass spectrometer by an Ion Max Source operating in ESI mode. Chromatographic analysis was performed in reversed phase mode on a F5 Kinetex analytical column, using MS grade water and methanol as aqueous and organic solvents, respectively. DoE was implemented evaluating four critical factors for the in-source ionization process: (i) acidity of aqueous eluent, expressed as percentage of formic acid, (ii) eluent modifier, expressed as mM concentration of ammonium formate, (iii) source ion spray voltage (kV), and (iv) temperature (°C), each one investigated at 3 levels through a D-optimal design (n=3 center points), considering mixed and two-factors interactions. All the experiments were acquired in triplicates. The dependent variables (or responses), i.e. the averaged chromatographic areas of critical CECs in the investigated training set, were fitted using PLS algorithm, and the obtained models transformed and refined by removing not significant coefficients, where needed. For the optimization step, only a reduced set of responses was kept. In fact, chromatographic areas that exhibited a non-significant and non-valid model were removed to reduce the uncertainty in prediction. The only exception was made for miconazole, as one of the novel CECs introduced in the watch list 2020/1161/EU. The analysis of model coefficients and contour plots evidenced very interesting results, some of them briefly reported below, as relevant examples. The response of perfluorinated compounds was negatively affected by the quadratic term of source voltage, as its increase can cause a higher rate of in-source dissociation phenomena, involving the loss of the ionizable polar groups in these molecules. Clarithromycin and azithromycin responses increased with increasing source temperature, whereas estrogens chromatographic areas were significantly reduced by the acidity of the aqueous eluent. Subsequently, by the analysis of the sweet-spot plot, i.e. the region of the experimental domain where the chromatographic areas of the selected set of analytes were maximized, 3 optimal set points were identified, which exhibited the highest values of the desirability function. The ratio between the experimental chromatographic areas obtained in each set point and the relative predicted values was used to estimate the best analysis parameters. Thus, the optimized conditions to increase LVDI-LC-HRMS sensitivity were as follows: acidity of aqueous eluent = 0.057%, eluent modifier = 9,7 mM, ion spray voltage = 2,5 kV, and ion spray temperature = 348 °C.

3. Conclusions

This study allowed for identifying the optimal conditions to increase the sensitivity of a LVDI-LC-HRMS platform by means of DoE, evaluating an experimental domain defined by eluents composition and ESI source parameters. Even if a varied and complex scenario was outlined for the optimization of the chromatographic areas of the analytes inside the selected training set, 3 optimal set points were identified by sweet-spot plot analysis. The identified optimal method will be applied, as a further perspective, to the non-targeted analysis of surface and ground water samples related to the potabilization and depuration management of several urban areas in Tuscany (Italy), in order to identify known and unknown CECs and TPs that can potentially impact drinking water safety.



Chromatographic area Sweet-spot plot highlighting the optimized conditions (star point).

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POS34

ASSESMENT OF MICROPLASTICS AND PHTALIC ACID ESTERS IN BARCELLONA CONTINENTAL SHELF

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1. Introduction

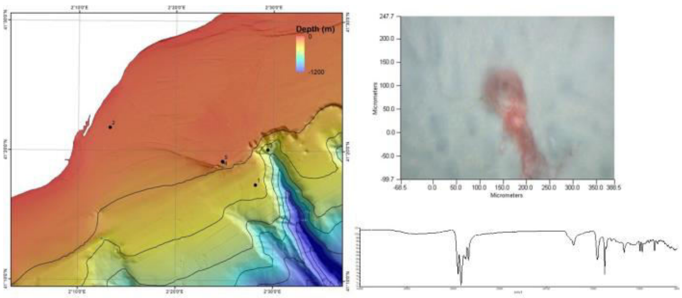
The seafloor has been recently indicated as possible final sink for the plastic debris that enters the ocean [1], 2004). The collection of data regarding the presence of microplastics (MPs) and plastic associated contaminants in the seabed is currently a relevant topic [2]. At the present time, only a few studies considered the correlation between the presence of microplastic and of plastic associated contaminants in the deep sea environment. In this baseline assessment we investigated for the first time the presence of microplastic together with the presence of phthalate acid esters (PAEs) in the continental shelf of Barcelona.

2. Results and Discussion

Following a shelf-slope-deep basin continuum approach, we sampled seafloor sediments from five collection points, and we performed analysis by means of infrared micro spectroscopy and liquid chromatography tandem mass spectrometry. Plastic fragments were found to range from 90 to 931 items/kg and PAEs resulted comprised between 2.05 to 1.32 mg/kg. Statistical analysis did not show any significant correlation between the concentration of PAEs and microplastic detected in each sampling station.

3. Conclusions

Contamination of MPs of the continental shelf of Barcellona was investigated for the first time. Analysis revealed the presence of both plastic microparticles and pthaltic acid ester plasticizer.



The sampling station and idenfication of a plastic particle by μ-FTIR

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POS35

MICROPLASTIC IN THE PO DELTA: A PRELIMINARY INVESTIGATION IN THE SUBAQUEOUS REALM

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1. Introduction

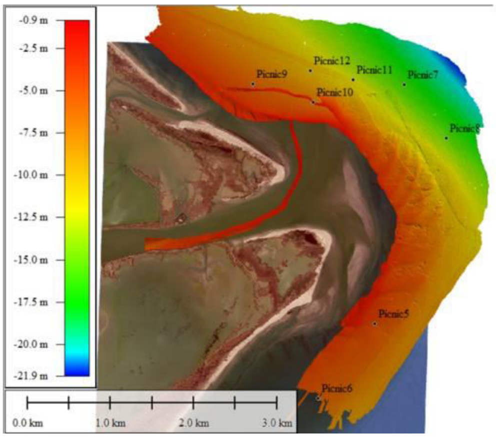
The presented work aimed to preliminary asses the presence of Microplastics (MPs, concentration and type) at the river mouth of the Po considered as a possible hotspot of MPs sedimentation [1,2] and to discuss the observed distribution in light of morphological information. Bathymetric survey after the November 2019 allows to collect samples from twelve stations that are representetive of the subaqueous sector of the Po delta where both depositional and erosional features coexist as a result of the interaction between river floods and along-shore current.The samples were treated with $ZnCl_2$ to induce particle floatation and collected surnatant were filtered on stainless steel and submitted to microFTIR analysis for particles characterization. Moreover, the presence of plastic associated contaminants was determined by LC-MS/MS

2. Results and Discussion

Analysis of the twelve samples showed an average of 183 microplastic/Kg with a maximum of 574 found in the sampling point 04 retrieved from the channel thalweg. Mayor part of the detected microplastics were fragment (54%) and fibers (37%) by shape.Most abundant polymer was rayon (45%), followed by PVA (22%), PP (22%) and PL (11%). 34% of the detected microplastics were film in shape, 33% were fibers, 22% fragments and 11% foams. Three different colors were found: grey (78%), brown (11%) and red (11%).Plastic associated contaminants (pthalates, BPA, and related metabolites) were detected in all the samples with total concentration spanning from 3 to 34 mg/kg.

3. Conclusions

The presence of microplastics and plastic associated contaminants in the Po river delta was assesed for the first time. Data were disccused considering the sediment volume maps



The Po Delta samplng area

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POS36

PASSIVE SAMPLING OF ORGANIC CONTAMINANTS AS A NOVEL APPROACH TO MONITOR SEAWATER QUALITY IN AQUARIUM OCEAN TANKS

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1. Introduction

Coastal waters are subjected to several anthropogenic stressors such as runoff, shipping traffic and wastewater treatment plant discharge. Aquarium water is collected from the sea (supply water) and subjected to treatments (treated water). The detection of pollutants in marine water, especially emerging contaminants (ECs), represent an analytical challenge due to the low concentration levels and the complexity of the matrix. Thus, selective and sensitive methods are required, such as chromatographic techniques coupled to mass spectrometry. Furthermore, the performance of the whole analytical method could be improved employing proper sampling techniques[1]. The use of passive samplering permit to enhance the method sensitivity combining in-situ sampling and preconcentration.

In this work, the presence of organic contaminants at trace and ultra-trace levels was assessed in the Genoa Aquarium supply, treated and shark tank water. Three monitoring of two weeks were performed between March 2017 and January 2018. The Polar Organic Chemical Integrative Sampler (POCIS)[2] was employed as passive sampling device. Both untargeted and targeted approaches were used for the analyses.

2. Results and Discussion

The untargeted analysis by gas chromatography coupled to mass spectrometry showed the presence of hydrocarbons, diphenyl sulfone (DPS) and 2,4-di-tert-butyl-phenol (2,4-DTBP). In particular, hydrocarbons were detected in all the samplers extracts and the chromatographic profile showed their petrogenic origin. The concentrations of the industrial pollutants DPS and 2,4-DTBP presented a seasonal trend, with the higher amounts found during the spring samplings.

Nineteen ECs, belonging to different classes (pharmaceuticals, UV-filters, hormones, perfluorinated compounds), were selected for the liquid chromatography tandem mass spectrometry targeted analysis. Thirteen analytes were detected, although the majority of them were below the quantitation limit. Two UV filters (octocrylene and ethylhexyl methoxycinnamate) were the most concentrated among ECs, both in supply and treated waters. Bisphenol-A, Gemfibrozil and Carbamazepine were also observed in the supply water.

The water treatment system efficacy was evaluated comparing supply and treated waters. In general, the analyte concentrations were lower after treatment, confirming the good performance of the Aquarium water treatment system in the abatement of seawater contaminants.

3. Conclusions

The use of POCIS to monitor Genoa Aquarium water quality allowed the detection of some ECs with endocrine disruptor capacity and other substances with aquatic toxicity. The passive sampling approach permitted to enhance sensitivity and to obtain data mediated over time. The use of POCIS permitted to consider fluctuations and episodic events, unlike the classical spot sampling approach that provides only a snapshot of the pollution levels.

Example of the system configuration for the sampling of supply and treated water using POCIS.

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POS37

ENHANCING CIRCULARITY TO LIMIT ENVIRONMENTAL IMPACT OF A COMPOSITE SYSTEM: A QUANTIFICATION FRAMEWORK

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1. Introduction

Circular Economy (CE) is a paradigm aimed at generating wealth, protecting the environment, and preventing pollution [1] by shifting from a typical linear material consumption pattern to a more sustainable, efficient, and circular one [2].

This practice can be implemented on systems of different dimensions and complexity such as an industry, a cluster of industries, a city, or a region. Until now the research focused on how and how much a CE system can improve material circularity and resource productivity. Therefore, most studies in literature provide aggregated indicators that refer to materials, waste and recycling, generation of municipal or other waste, recycling rates, and derivatives of such scores. However, CE also aims at minimizing impacts [3]. The aggregated indicators until now proposed fail in quantifying these aspects because it is not certain that the most circular solution is also the most environmentally preferable one. Therefore, it is necessary a tool able to detect the direction toward circularity, while assessing the environmental performance in terms of several different impact categories.

2. Results and Discussion

We proposed a framework that aims to investigate circularity and the environmental performance of a CE system using, as a case study, a generic territorial system populated by several productive sub-systems (e.g., firms), not including population and relative consumption.

The framework should investigate the system's environmental performance using a standardized methodology that allows for assessing the overall potential environmental impacts of the different flows of energy and material that cross the system and how they change due to the implementation of circular practices. Therefore, a comparison between the system in exam and a reference system should be proposed.

To better point out the benefits of circular practices, the reference system should be an ideal system that works in the complete absence of circularity and has the same output and system boundaries as the studied system. Moreover, to better understand the evolution toward circularity, the framework should allow to monitor the system over time collecting useful information and quantify how much the change in the environmental performance depends on the implemented circular practices. A methodology, suitable to underpin such framework, can be the Life Cycle Assessment that enables quantification of impacts and assignment of them to single process or phase. Since Life Cycle assessment provides a number of impacts categories, the framework results in a set of indexes easy to calculate, understand, and communicate, with the main problem consisting in the collection of the necessary data.

3. Conclusions

A framework for measuring circularity in an economic system is a useful instrument in decision-making processes. This framework would be used not only to investigate territorial systems or macro-system such as cities or regions but also micro and meso systems such as industries in a "symbiosis". The framework focuses on investigating the direction toward circularity while assessing the environmental performance of a CE system. In order to follow up on the gaps in the measurement of the level of circularity and the assessment of the environmental performance of CE system that is evident in the literature.

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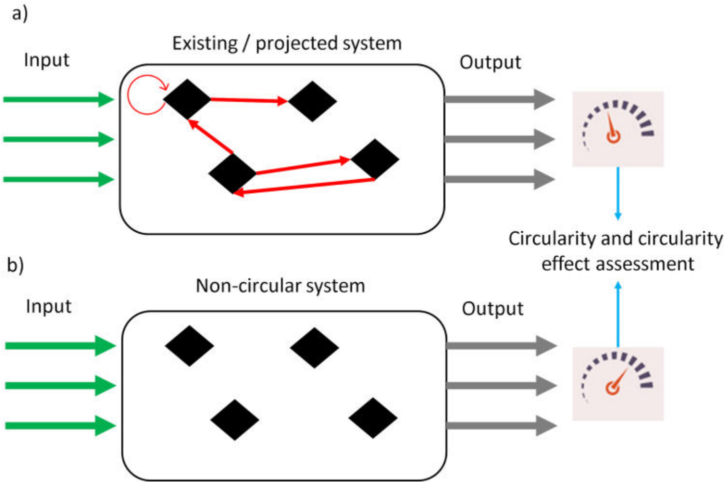

Generic territorial system populated by productive sub-systems a)existing/projected b)non-circular.

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POS38

THE ANTHROPOGENIC ELEMENTAL CYCLE OF MANGANESE, NICKEL AND NATURAL GRAPHITE IN THE EU

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1. Introduction

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 (Mn), nickel (Ni), and natural graphite (C), 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) is among the assessment tools for mapping materials flows through the economy and ultimately to achieve quantitative understanding of industrial development and potential environmental impact about the flows of resources, the ways in which industry utilizes them, and the magnitude of interaction with the environment, ultimately informing strategies for elemental ciruclar economy. We summarize the main findings of the anthropogenic Mn, Ni and C cycles in the EU investigated in [1].

2. Results and Discussion

Our work provides detailed characterization of Mn, Nin and C material stocks, flows, and changes in selected performance. The achieved results may inform decision-makers engaged with raw materials recovery and recycling as well as the strategic securement of a reliable material supply to the EU for resilient industrial ecosystems.

More specifically, a few applications cover the majority of the targeted materials accumulated in use: that is, building and construction, transportation and engineering products for manganese (in total, about 92% of its in-use stock) and nickel (72%), while refractories (56%) for natural graphite. These application sectors have relatively long useful lifespans and have embodied historically large material inflows to use, mainly driven by a consolidated and wide use of steel products in the anthroposphere.

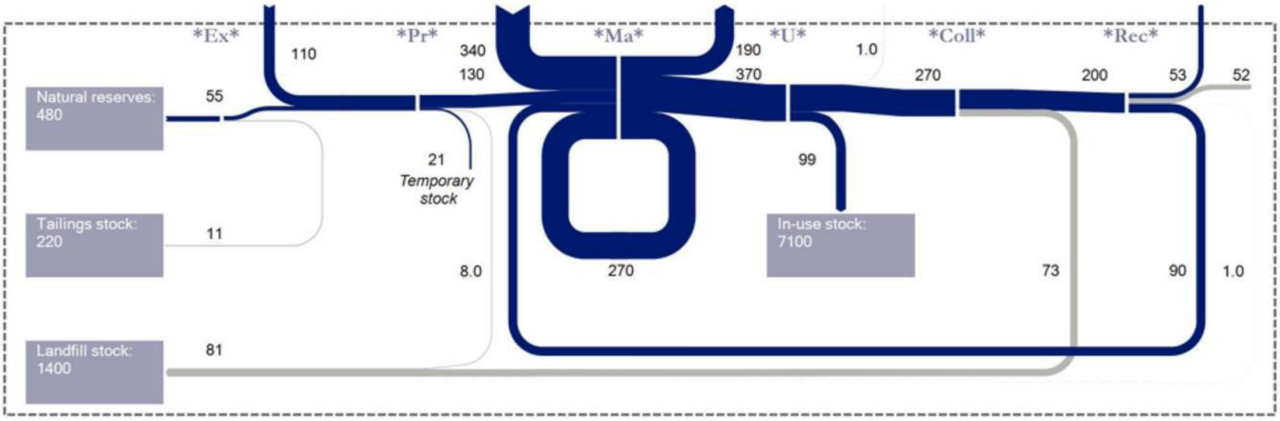
Building and construction, transportation, engineering equipment, and refractories are also the main applications driving annual inflow to use of the targeted raw materials, although some stabilization has occurred in developed countries in recent years [2]. This characteristic is likely dictated by the achievement of initial levels of iron products in-use saturation [3-5] and it is enhanced by material efficiency strategies such as lightweighting of certain goods (e.g., vehicles) and product lifetime extension (Hertwich et al., 2019. Compared to metallurgy uses, the battery market is evolving quickly. Despite the relative contribution of this sector to in-use stock accumulation is still marginal compared to more traditional uses of the targeted materials, but the overall trend is increasing [2,6].

The enhancement of the recycling industry and improvement of process efficiencies at end-of-life are the main areas where supplemental benefits could be very likely achieved if appropriate efforts were implemented. The average EoL–RR resulted in 49% (± 8%) for Ni, 51% (± 3%) for Mn and 8% (± 0%) for C. Despite annual variations of material flows may affect these estimations, the computed end-of-life recycling performance of Mn and Ni is much higher than that of C and many other metals in use today [7]. These outcomes also demonstrate that contemporary anthropogenic material cycles are far behind an ideal material circularity even in the case of the most efficiently used metals in our society.

On the other hand, constraints in technology development and the manufacturing industry set conditions to fully operational implementation of economically feasible strategies for material recovery and sustainable material supply [8]. This varies from material to material. Although the three targeted materials need to face a similar set of issues (such as high import reliance, lack of natural deposits, interconnection with steel cycle, pivotal role in energy storage systems, and limited end-of-life recycling), each material has its own inherent life cycle and no set of indicators can alone represent the complex nature of its manufacturing network [9] that, in the end, determines the level to which these strategies can be successfully implemented.

3. Conclusions

Descriptive and quantitative modeling approaches like MSA constitute an evidence-based approach to the setting of boundary conditions for efficient resource use and contribute to a full achievement of the circular economy. This evidence may support future decision-making on targeted strategies toward raw material recovery. Ultimately, enhancing the resilience of recycling industry in the EU, which is currently far from ideal performance for the targeted materials, requires an improved understanding of the interlinkages between these materials and it introduces a new facet to supply constraints that should be further investigated to characterize the elemental presence in modern society and set leverages for driving viable patterns of material production and consumption.



The anthropogenic nickel cycle, flows in kt/year [2]

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ACKNOWLEDGEMENTS

The current work was developed using the results achieved from the MSA of five battery raw materials, which are described in a JRC MSA report (https://doi.org/10.2760/519827) and individual publication of the authors (Ciacci, L., et al. (2022). Material system analysis: Characterization of flows, stocks, and performance indicators of manganese, nickel, and natural graphite in the EU, 2012–2016. Journal of Industrial Ecology, 1-14).

DISCLAIMER

The presented data are also part of a separate technical report (Matos, C. T. D., et al. (2020). Material system analysis of five battery-related raw materials: Cobalt, lithium, manganese, natural graphite, nickel, EUR 30103 EN. Publication Office of the European Union. https://doi. org/10.2760/519827). Views expressed are those of the authors and do not reflect an official position of the European Commission.

POS39

USE OF WASTE MATERIALS TO REMOVE ORGANIC CONTAMINANTS FROM WATER

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1. Introduction

The increase of the population and the exploitation of natural resources by human beings have resulted in a deterioration in the water quality by pollution, uncontrolled dumping or release of hazardous chemicals and materials. Therefore, protecting and restoring water-related ecosystems is crucial in agreement with the Sustainable Development Goals (SDGs) adopted by all United Nations Member States in 2015 [1]. On the other hand, managing natural resources efficiently for a sustainable development encourages the recycling and the reuse of wastes to realize a circular economy. Within this framework, the present work aimed to extract the cellulose and the enzyme Soybean Peroxidase (SBP) from soybean hulls, destined to become a waste, in order to prepare alginate-cellulose hybrid hydrogels to remove organic pollutants from water. In particular, the goal was to promote both the adsorption and the degradation of organic pollutants by means of a combined effect due to the adsorbent characteristics of the gel and the catalytic action of the SBP, a redox enzyme capable of oxidizing a large number of aromatic compounds in the presence of H_2O_2 [2].

2. Results and Discussion

The first part of this work was focused on the extraction of SBP and cellulose from soybean hulls. The former was extracted by immersion in phosphate buffer, followed by a step of concentration and purification. The cellulose was obtained by subjecting the same peels to three successive hydrolyses and functionalized with APTES (3-Aminopropyltriethoxysilane) and glutaraldehyde. Finally, the extracted SBP was immobilized on the cellulose. The same functionalization was also carried out on the silica for comparison purpose. The synthesis of the hydrogels was performed by gelation: the functionalized cellulose or silica was suspended in a viscous solution of alginate (2.5 w/w) which is dripped by a syringe in a solution of $CaCl_2$ kept under stirring. The hydrogels were characterized by activity tests, swelling tests, scanning electron microscopy and FTIR. The adsorption and degradation capacity of alginate-based hydrogels containing cellulose (or silica) and SBP (3.5 mg/g of cellulose or silica) were then tested to remove triclosan (TCS), trichlorophenol (TCP) and Bisphenol A (BPA), chosen as pollutant model in the presence of H_2O_2 ($1x10^{-4}$ M) in MilliQ water and in a real matrix (aquaculture water).

In the presence of four alginate-based hydrogels containing cellulose with SBP, the half-life time of the contaminants were less than 60 minutes thanks to a combined effect of adsorption and degradation. When the pollutants were present in a mixture, the removal rate of substrates decreased and the complete disappearance of TCP and TCS was achieved in a shorter time (ca 150 min) than that observed for BFA (300 min).

To evaluate the stability and reusability of the prepared materials, the same hydrogels were employed for 8 successive degradation cycles and the results demonstrated that the hydrogels maintained their efficiency.

Finally, degradation tests performed in aquaculture water showed that BPA disappeared completely after 120 minutes, whereas the removal rate observed for TCP and TCS instead significantly decreased, probably due to the dissolved organic matter (DOM) present in water.

Finally, acute toxicity of the mixture of pollutants in the two matrices was assessed using an assay that exploits the natural bioluminescence of *Vibrio fischeri* bacteria both at the beginning of the process and after the treatment. After 60 minutes of reaction a significant decrease in the initial toxicity was observed reaching a residual value of 10-20% after 24 hours in both matrices.

3. Conclusions

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The extraction of SBP and cellulose from soybean hulls represent a valid approach to reuse a waste material and to obtain efficient promising hybrid materials for the decontamination of aqueous solutions. Although the immobilization of the protein undoubtedly involves a loss of activity, these preliminary results showed that the investigated hydrogels can be employed for organic pollutants removal in water matrices exploiting their adsorbing / degradative capacity and therefore be recovered easily from the aqueous solution after the treatment.

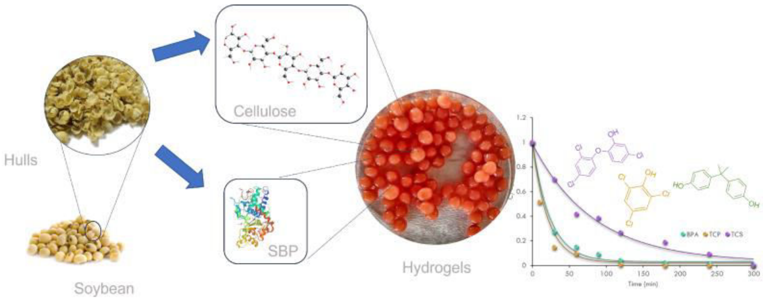

Figure 1. Schematic representation of preparation/application of hydrogels.

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POS40

A SUSTAINABILITY DECISION-MAKING FRAMEWORK TO SUPPORT THE ASSESSMENT, ADOPTION, AND IMPLEMENTATION OF CORPORATE SUSTAINABILITY

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1. Introduction

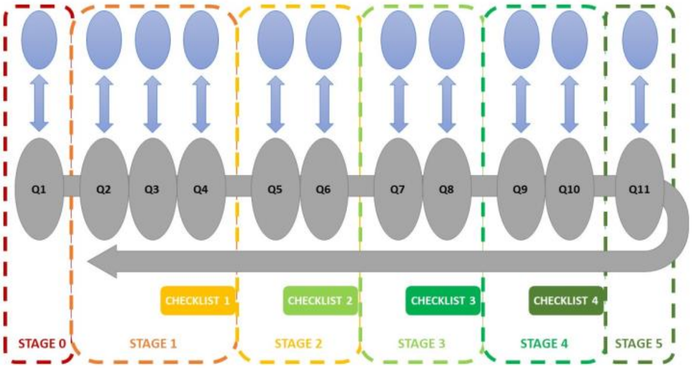
In recent decades, sustainability concepts applied to organizations have become an integral part of society and governments as stakeholders are increasingly aware of the negative externalities of companies' operations and require them to implement sustainable strategies in their business models [1]. To address these issues, various tools (i.e., ratings, standards and frameworks) have been developed to assist organizations in the transition towards sustainable practices [2]. However, the lack of shared procedures, often not standardized, cause uncertainty in the identification of the most suitable tools to reach this objective. The purpose of this work is to design a Sustainability Decision Making Framework (SDMF) that can support companies in the process of identifying an objective and strategic path towards sustainability. Specifically, the rationale behind the SDMF is to guide companies in i) the assessment of key materiality externalities through stakeholders' engagement and ii) the assessment and implementation of sustainability through a proactive approach in a way that is tailored to the specific needs of the company under assessment.

2. Results and Discussion

With the aim of developing a robust and scientifically based tool that allows organizations to understand how to objectively deal with sustainability implementation, both scientific publications and gray literature on sustainability tools were examined. Therefore, the most important reporting tools were studied. They included both voluntary (e.g., GRI and SASB) and mandatory such as the Directive 2014/26/EU and the Corporate Sustainability Reporting Directive, along with ESG ratings, frameworks (e.g., BS8001, the Natural Step, etc.) and European strategies such as the Green Deal, and the European Taxonomy. The SDMF took inspiration from these tools and integrated them within a PDCA (Plan, Do, Check and Act) decision-making approach. Accordingly, the SDMF was conceived as a modular, adaptable and multispatial procedure composed of a vertical and a horizontal dimensions, which led to the creation of a guideline on sustainability. It consists of i) 6 phases, from red to dark green ii) 11-questions, show in grey, iii) different sustainability strategies, blue section and iv) 4 checklists, from yellow to dark green, as shown in the figure. The phases make up the macro-areas and are characterized by specific consequential themes (0 sustainability and theoretical principles, 1 definition of the initial position, 2 future priorities, 3 priority interventions, 4 progress assessments, and 5 final reporting). The questions that compose the survey, the strategies and the checklists have been structured within the different phases. The horizontal dimension of the SDMF is defined by the survey, which is the core part of the tool. The survey allows organizations to either continue to travel horizontally, or to move vertically within the SDMF when a non-compliance section is reached. The vertical dimension is composed of the sustainability strategies which includes different methodologies (i.e., materiality matrices, MCDA, morphological schemes, stakeholder engagement) that could be used to approach the identified non-conformities and therefore, once solved, to resume horizontal development. At the transition boundary of each phase (excluding the initial one), checklist have also been included that allows an organization to proactively and in advance check whether the sustainability strategies required within the relevant phase have been completed correctly. If an organization has not completed the strategies suggested in the checklists, it is asked to start over from the first question of that stage and to check all the suggested strategies. Furthermore, the SDMF has been modelled through a closed-loop approach that allows an organization to be supported in the constant attempt to improve its sustainability activities, albeit it has already completed the survey and implemented the priority strategies. Indeed, this tool has been designed considering that sustainability is a process of continuous and never-ending improvements. Accordingly, after completing the first cycle, an organization will have reached a greater awareness and ability in identifying and managing its materiality and in the implementation of methodologies for mitigating negative externalities and will be prepared to start over the process, being more critical and seeking to investigate other priority aspects to improve its sustainability.

3. Conclusions

In conclusion, a modular decision-making framework (SDMF), developed within VeniSIA Project code 2120-0004-204-2019, to support companies in the process of adopting and implementing sustainability has been presented. The SDMF acts both as a guideline on corporate sustainable development and as a tool to understand how to implement long-term sustainability visions objectively and concretely. The modularity of the SDMF is a crucial characteristic since makes the SDMF proactive and preventive to future pressures and strategies such as for example the European taxonomy. Moreover, the questionnaire, which is the core part of the SDMF, is potentially adaptable to different organizations' characteristics and can constantly lead them in the implementation of sustainability interventions over time.



The consequential stages leading to increased sustainability awareness are reported from a dark red, low sustainability awareness, to a dark green, high sustainability awareness. Within the stages, it is also possible to notice both the survey present in grey, which defines the horizontal development of the SDFM and, the different strategies that make up the vertical development, represented in blue. Indeed, for each question, different vertical strategies are reported. Finally, from yellow to dark green, the checklists that act as a control element between one stage and the next are shown.

Figure: flowchart representation of the SDMF

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LEARNING ENVIRONMENTAL SUSTAINABILITY THROUGH DIGITAL ESCAPE ROOMS

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1. Introduction

Multimedia tools are widely used in schools nowadays. In addition, people sometimes seem to have more confidence in Internet information than in scientific research, which is probably related to the difficulty of communicating the academic results to a wide audience: these factors could lead to disinformation and many misunderstandings. Moreover, sustainability is one of the most important concerns of the current century, so the right information is crucial to raise everyone's awareness.

2. Results and Discussion

With the "Escape to Learn" project we aimed to narrow the gap between lower grades and scientifical research by using digital escape rooms (DERs) as a fun way to teach environmental knowledge. The goal is not only to teach something the younger generation, but also to engage students in an fun way and get them involved in their own learning. On DER students have to find some information (videos, texts, images) and then use them to solve quiz and minigames necessary to leave the room.

The project is divided into several steps. The first is to decide which topic to cover in the DERs: 1. reuse of treated wastewaters, which is a good alternative to using freshwater for agricultural purposes; 2. renewable energy sources, evaluating the advantages and disadvantages compared to fossil energy sources; 3. waste recycling, as a way to prevent the depletion of natural resources and promote a circular economy.

For each topic, a design table was first created that listed the subjects, objectives, activities and a possible assessment of student learning at the end of each area of DER. This first step was very useful in schematizing information and ideas and gave the opportunity to create a rough plot for the DER. DERs were then created and targeted students between the ages of 6 and 19. Different communication language was chosen for each age, and each room was assigned a main storyline, to make it more likable for students. The DERs about reusing of treated wastewaters and renewable energy sources were intended for second grade students in a secondary school, while the DERs about waste recycling were created for elementary school students. The digital implementation of the DERs was done through free online platforms that offer settings and games which can be customized.

In each area, clues, information, games (which can be solved by finding the clues) and sometimes access to new areas of DER were added. Once students found all the clues and played all the games, they could "escape" from the space.

Once created, the DERs were reviewed and validated by the researchers and finally tested by selected teacher from the partner schools and their classes. To assess the impact of the DERs on the students, surveys were conducted, a first one immediately before the game, a second one immediately after, and a third one after about twenty days.

3. Conclusions

The project is currently in full swing: the first Escape Rooms have been set up and tested in the partner schools. The students seem enthusiastic and very interested in solving the games and finding clues, while their teachers find that even the most lively children are completely immersed into the Escape Rooms. The results of the feedback forms are still in the evaluation sheet.

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