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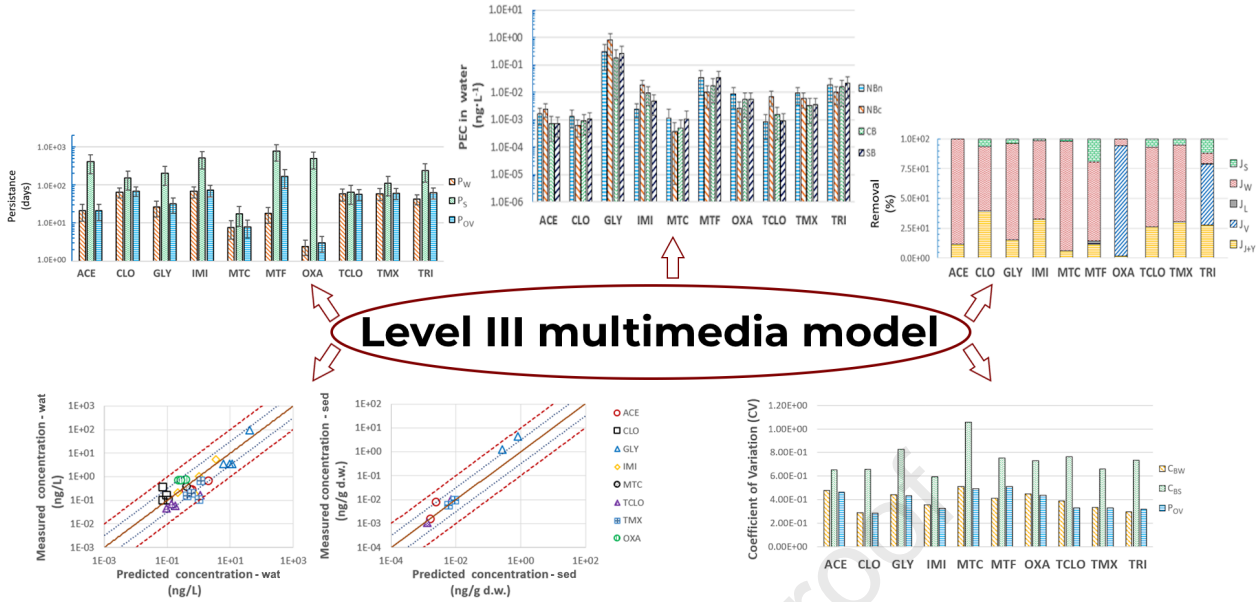

Fate and transport of ten plant protection products of emerging concern in a coastal lagoon: application and evaluation of a multimedia level III fugacity model

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Abstract

Multimedia fugacity models are effective tools for studying the environmental behaviour and occurrence of contaminants of emerging concern (CECs) and assessing associated risks, especially when experimental data is limited. These models describe processes controlling chemical partitioning, transport, and reactions in environmental media using mathematical statements based on the concept of fugacity.

To aid in identifying and prioritizing CECs for future local monitoring, we present here the application of a level III multimedia fugacity model assuming non-equilibrium between compartments and steady-state conditions. This model estimated predicted environmental concentrations (PECs), persistence, distribution, and transport of ten plant protection products (PPPs) in the Venice Lagoon, a complex coastal environment under high anthropogenic pressure.

The model was evaluated through uncertainty and sensitivity analysis using the Monte Carlo approach and by comparing PECs with PPP concentrations measured during four sampling campaigns. Results showed good agreement with field data, with the highest concentrations in water and sediments estimated for glyphosate, followed by imidacloprid, metaflumizone, and triallate. The model indicated accumulation of all investigated PPPs in sediments. For most chemicals, advection outflow and degradation in the water column were the main removal mechanisms, while volatilization was significant only for oxadiazon and triallate.

Sensitivity and uncertainty analysis revealed that degradation rates, organic carbon/water partitioning coefficients (K_{OC}), and parameters describing air-water interactions had the strongest influence on the model's results, followed by inputs accounting for sediment sinking and resuspension. The lack of data on PPP degradation in brackish waters accounted for most of the uncertainty in model results.

This work shows how a relatively simple multimedia model can offer new insights into the environmental behaviour of PPPs in a complex transitional waterbody such as the Venice lagoon, providing useful data for the identification of the CECs to be prioritised in future local monitoring efforts.

Keywords

Emerging contaminants, Environmental pollution, Venice Lagoon, Plant protection products, Exposure and risk assessment.

Highlights

- The first multimedia modelling of plant protection products in the Venice Lagoon
- Concentration and environmental fate of ten plant protection products were simulated
- The highest modelled and measured concentration in water and sediments was of glyphosate and imidacloprid
- The study provides data to support ecological risk assessment for the Venice Lagoon
- Degradation rates, partitioning coefficients, and air-water interactions had strong effects on model results

1. Introduction

Water pollution has been widely recognized as a severe worldwide problem (Geissen et al., 2015), due to a multitude of contaminants detected across the world's water bodies (Sharma and Bhattacharya, 2017). For several decades, the attention of the scientific community has been focused on conventional pollutants, which include many compounds whose high environmental persistence is linked to their lipophilicity and stability, such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzodioxins and furans (PCDDs/PCDFs), and pesticides (Calza et al., 2013). In more recent years, thanks to the development of improved methods of detection, identification, and quantification of organic substances in many environmental media (Stefanakis and Becker, 2015), the presence in several environmental compartments of many "contaminants of emerging concern" (CECs) has been brought to attention. In detail, CECs are defined as "synthetic or naturally occurring chemicals that are not commonly monitored in the environment but which have the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects" (Geissen et al., 2015). The release to the environment of these contaminants may have occurred for a long time (e.g. wastewater treatment, agriculture, and industry), but it may not have been recognized until sufficient detection methods were developed. In other cases, both the synthesis of new chemicals or changes in the use and disposal of existing chemicals could have created new sources of these substances (NORMAN, 2020). In this context, more than 700 compounds (i.e. CECs, their transformation products, and their metabolites) have been detected in surface waters, groundwater, and marine waters (Geissen et al., 2015).

In particular, plant protection products (PPPs) have been widely recognized to have adverse impacts on both the environment and human health. The presence in the environment of such chemicals can be attributed to several phenomena, such as leaching into groundwater, surface run-off, and drift into non-target areas (Lupi et al., 2019), leading to acute and chronic (e.g., neurotoxicity, immunotoxicity, endocrine disruption, and behavioural changes) negative effects for both soil-dwelling (e.g. earthworms and microorganisms) and non-soil dwelling (e.g. molluscs, fish, pollinators, birds, and larger mammals) organisms (Christen et al., 2018; Pogăcean and Gavrilescu, 2009). Furthermore, plant protection residues on food and in drinking water have been identified among the main factors leading to human exposure (FAO and ITPS, 2017).

In these circumstances protecting water quality becomes of fundamental importance to minimize environmental and human risk, therefore starting from the EU 2000/60/EC directive (European Commission, 2000), several actions have been undertaken by the European Union for a better management of hydric resources. Within this framework, due to the potential impact that these substances may have on ecosystem and human health, the lack of knowledge regarding their behaviour in the environment and the deficiency in analytical and sampling

techniques (Geissen et al., 2015), the need of detailed ecological risk assessment (ERA) evaluations for these substances has been widely recognized (Stefanakis and Becker, 2015).

Among the available tools to carry out these evaluations, the use of models has been identified as a reliable low-cost tool for estimating, identifying, and managing environmental and ecological risks (Şimşek et al., 2019). The models used within this framework may vary in relation to their purpose, scope, and level of analysis. In particular, the models used during different stages of the ERA process include fate-exposure models, exposure-effect models, and integrated models (Vaz, 2019).

Fate-exposure models cover the first half of the source-to-outcome continuum (Williams et al., 2010) and simulate the transport and transformation of pollutants in the environment to predict the concentrations of these substances in different environmental media (e.g., atmosphere, water, soil, and sediments) (Vaz, 2019). Since the results of these models represent concentrations to which target organisms could be potentially exposed, this data is often used instead of measured concentrations as an input to exposure-effect models, which are applied in the final part of the source-to-outcome continuum of the ERA (Vaz, 2019).

One of the most used approaches used to develop multimedia fate models is to describe the processes controlling chemical partitioning and reactions in the environment by developing and applying mass balance equations based on the concept of fugacity developed by Mackay and co-workers (Mackay et al., 1985, 1983a; Mackay and Diamond, 1989). These equations are solved combining information regarding environmental compartments characteristics, chemicals' emissions, transport and elimination processes, in order to estimate the distribution and concentrations of the target substances in each media of the modelled system (Mackay and Paterson, 1991), provide a quantitative analysis of the emission sources, transport and transfer routes, as well as estimate where contaminants may accumulate within the system under investigation (MacLeod et al., 2010; Su et al., 2019; Vaz, 2019; Wang et al., 2020a).

Multimedia fugacity model models can be set-up considering different levels of complexity depending on the specific requirements of the study, data availability, and the desired accuracy of predictions. In particular, fugacity models considering i) adjective and diffusive (both intra- and inter-media) transport processes, ii) non-equilibrium conditions between different compartments, and iii) steady state mass-balance (i.e., level III fugacity models) are one of the most diffused multimedia fugacity models (Wang et al., 2020b), which have been applied to investigate the fate of a multitude of both conventional (e.g., DDT, PCBs, and PAHs) (Fang et al., 2016; Mackay and Diamond, 1989; Xu et al., 2013) and CECs (e.g., pharmaceuticals, herbicides, and hormones) (Tan et al., 2007; Wang et al., 2020b) within several environmental systems such as rivers, lakes, estuaries, wetlands, catchments, and lagoons (Cancelli et al., 2019; Fang et al., 2016; Kilic and Aral, 2009; Mugnai et al., 2010; Warren et al., 2005).

This study aimed to simulate, using a multimedia level III fugacity model, the environmental fate and distribution of ten PPPs in the Lagoon of Venice with the objective of improving the understanding about the processes governing their environmental behaviour, especially those involved in their natural attenuation. Moreover, this work aimed at estimating the exposure of lagoon ecosystems to these chemicals to support future risk assessment efforts, in particular to facilitate the identification of priority contaminants for the case study area to be included into dedicated future monitoring campaigns.

2. Materials and methods

2.1 Study area

The lagoon of Venice (Figure 1b) is the largest transitional water body in the Adriatic Sea and it is composed by a complex ensemble of aquatic and terrestrial environments, covering a half-moon shaped area of about 550 km^2 (Umgiesser et al., 2004). The prevailing direction of the wind is NE–SW and water temperature ranges from 0 to 30 °C (Umgiesser et al., 2004). Its drainage basin is situated in a highly populated area (ca. 635 people/km^2) (ISTAT, 2012; Veneto Region, 2020a), corresponding to about 1600 inhabitant equivalents per km2 if industrial and agricultural activities are also taken into account (Dalla Valle et al., 2003). This causes the

lagoon's ecosystem to be subjected to several pressures due to numerous stressors such as contaminant loadings from transports, industry, agriculture, human settlements, and fishing activities.

The lagoon is mainly composed of a mix of shallow waters with an average depth of about 1 m and mudflats, which is crossed by a complex system of channels (maximum depth > 15 m) (Ferrarin et al., 2019), thus creating a quite complex hydrological system. The lagoon has been subdivided into four m ain basins (NBn, NBc, CB, and SB) according to modelled hydro-dynamic circulation patterns (Solidoro et al., 2004) considering the three inlets (Lido, Malamocco, and Chioggia) that allow water exchange with the Adriatic Sea (Dalla Valle et al., 2003) and the freshwater inflow from 12 major tributaries, whose drainage basin covers an area of about 2530 km^2 (Veneto Region, 2020a). In detail, the subdivision of the Venice lagoon and the average net flows of water (m^3/s) to and from each segment are reported in Figure 1b.

2.2 Target plant protection products and emission inventory

Ten PPPs (i.e. methiocarb (MTC), metaflumizone (MTF), and glyphosate (GLY), oxadiazon (OXA), triallate (TRI), imidacloprid (IMI), thiacloprid (TCLO), thiamethoxam (TMX), clothianidin (CLO), and acetamiprid (ACE)) were selected for this study after a review of the existing knowledge on CECs in Europe, Italy and the lagoon of Venice and its watershed, considering also the two versions of the Watch List already established when this work was planned (i.e., DIR 2015/495 EU and DIR 2018/840 EU (European Commission, 2015; European Commission, 2018)).

Mean emission rates in each region of the Venice lagoon drainage basin for the target chemicals were calculated starting from PPPs annual sales data by applying the approach reported in a previous work (Calgaro et al., 2023). In some detail, we assumed the use and release into the environment of the studied PPPs to be proportional to the area dedicated to agriculture present in each of the lagoon drainage sub-basins. These areas were estimated by GIS-based spatial analysis of the Veneto Region land-use census map of 2018 (Veneto Region, 2020b) and of the shapefiles reporting the confines of each of the lagoon's sub-regions drainage basin (Veneto Region, 2019).

Finally, concentration of each PPP in the riverine inflow water of each sub-basin (C_{IW}, $ng \cdot L^{-1}$) was calculated by applying Eq. 1 (Table S1):

$$C_{IW} = [(E_{PPPi})/(J_I \cdot 8760\ h)] \cdot 10^9 \qquad \text{Eq. 1}$$

where E_{PPPi} ($kg \cdot year^{-1}$) is the annual average emission of the target PPPs to each sub-area of the Venice lagoon drainage basin, and J_I ($m^3 \cdot h^{-1}$) is the corresponding average annual riverine input (Solidoro et al., 2004). Since there is no significant cropland within the Venice lagoon, we assumed that no direct emission of PPPs was present (i.e. $E_W = 0$). Also, we assumed that no adjective inflow of the target chemicals in the air occurred for the Venice lagoon due to their low volatility (EPPO, 2003) or quick removal from the atmosphere after application by wet deposition (Chang et al., 2011; Messing et al., 2011; Ravier et al., 2019).

2.3 Modelling approach

2.3.1 Model description

A multimedia level III fugacity model based on the approaches of Mackay and colleagues (Mackay et al., 1983a, 1983b; Mackay and Diamond, 1989; Mackay and Paterson, 1991) was set-up to investigate the distribution and fate of several plant protection products in the lagoon of Venice.

The conceptual diagram of the model presented in Figure1a shows that air, water, and sediment were defined as three bulk compartments, while six additional sub-compartments were included in the three bulk compartments as follows: i) air, and particles in the air, ii) water, and suspended solids in water, iii) pore water and solids in sediment. The processes taken into consideration are shown in Figure1a, while additional details are given in paragraph 2.3.2.

Similarly to Sommerfreund and co-workers (2010a, b) (Sommerfreund et al., 2010b, 2010a), we focused our modelling exercise on the sub-basins of the Venice Lagoon (NBn, NBc, CB, and SB) defined by Solidoro et al. (2004) and shown in b, using the reference scenario of ‘‘no wind’’ to represent the steady-state hydrologic circulation pattern of the lagoon (Solidoro et al., 2004). In particular, water flow between each sub-basin was considered as a unidirectional net flux having the same concertation in the water of suspended particle matter (SPM) and contaminant of the stating water body, while no transfer of sediment between sub-basins was contemplated in the model.

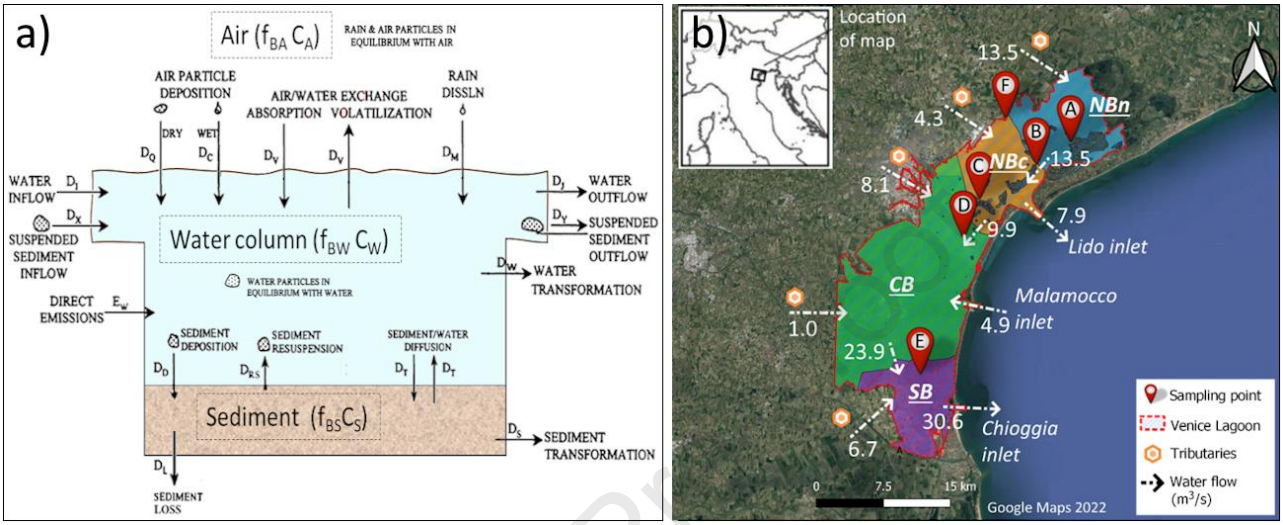


Figure 1: a) Transport and transformation processes treated in the multimedia level III fugacity model, consisting of a defined atmosphere with water and sediment compartments. Adapted from Mackay et al. (2001); b) Subdivision of the Venice Lagoon into four main basins (i.e., NBn, NBc, CB, and SB) according to modelled hydro-dynamic circulation patterns. Red symbols denote the selected sampling points, while arrows indicate average annual flows of water expressed as m^3/s. Adapted from Solidoro et al. (2004) and Sommerfreund et al. (2010b).

The concentrations of the target chemicals in each compartment and the transfer fluxes between adjacent compartments and sub-basins were modelled under a steady-state assumption by using a MS Excel version of a multimedia level III fugacity model, as reported by Mackay and co- workers (Mackay et al., 2014).
The model calculates the predicted environmental concentration (PEC) of the target chemical in each compartment based on the linear relationship between fugacity (f, *Pa*) and concentration (C, mol/m^3), as shown in Eq. 2.

$$C = Z \cdot f \qquad \text{Eq. 2}$$

Where Z (fugacity capacity, $mol \cdot m^{-3} \cdot Pa^{-1}$) is a proportionality constant dependent on the temperature, on the nature of the compartment and the physical-chemical properties of the compound. In detail, Z values are calculated from the relationships reported in Table 1 (Mackay, 2001).

Table 1. Fugacity capacities (Z, $mol{\cdot}m^{-3}{\cdot}Pa^{-1}$) and D values (D values, $mol{\cdot}Pa^{-1}{\cdot}h^{-1}$) for each segment of the level III multimedia fugacity model to calculate intermedia and reaction rates and the corresponding multiplying fugacity used to calculate each process' flux (Franco and Trapp, 2010; Mackay, 2001).

Process	D value	Definition of D Value	Multiplying Fugacity	Fugacity capacity
Volatilization	D_V	$\left[K_{AW}/(\frac{K_{AW}}{k_{VW}}+\frac{1}{k_{VA}})\right]\cdot A_W\cdot(1/H)\cdot$	f_W	$Z_{BA}=Z_A\cdot f_A+Z_Q\cdot f_Q$
Adsorption	D_V	$\left[K_{AW}/(\frac{K_{AW}}{k_{VW}}+\frac{1}{k_{VA}})\right]\cdot A_W\cdot(1/H)\cdot$	f_A	$Z_A=1/RT$
Rain dissolution	D_M	$G_M\cdot Z_W\cdot$	f_A	$Z_Q=(1/RT)\cdot[(6\cdot10^6)/P^V]$
Wet particle deposition	D_C	$G_C\cdot Z_Q\cdot$	f_A	$Z_{BW}=[Z_W\cdot(1-f_P)]+(Z_P f_P)$
Dry particle deposition	D_Q	$G_Q\cdot Z_Q\cdot$	f_A	$Z_W=[(1/H)\cdot(I+1)]$
Sediment deposition	D_D	$G_D\cdot Z_P\cdot$	f_W	$Z_P=K_{OC-P}\cdot\rho_P\cdot Z_W\cdot f_{OC-P}/H$
Sediment resuspension	D_{RS}	$G_{RS}\cdot Z_S\cdot$	f_S	$Z_{BIW}=[Z_{IW}\cdot(1-f_{IP})]+(Z_{IP}f_{IP})$
Sediment to water diffusion	D_T	$k_T\cdot A_S\cdot Z_W$	f_S	$Z_{IW}=[(1/H)\cdot(I+1)]$
Water to sediment diffusion	D_T	$k_T\cdot A_S\cdot Z_W$	f_W	$Z_{IP}=K_{OC-IP}\cdot\rho_{IP}\cdot Z_{IW}\cdot f_{OC-IP}/H$
Water inflow	D_I	$G_I\cdot Z_W$	f_I	$Z_{BS}=[Z_{SPW}\cdot(1-f_S)]+(Z_S f_S)$
Water particle inflow	D_X	$G_R\cdot Z_P$	f_I	$Z_{SPW}=[(1/H)\cdot(I+1)]$
Sediment loss	D_L	$G_L\cdot Z_S$	f_S	$Z_S=K_{OC-S}\cdot\rho_S\cdot Z_W$
Sediment transformation	D_S	$k_S\cdot V_S\cdot Z_S$	f_S	$Z_{RS}=K_{OC-RS}\cdot\rho_S/1000$
Water transformation	D_W	$k_W\cdot V_W\cdot Z_W$	f_W	$Z_M=[(1/H)\cdot(I+1)]$
Water outflow	D_J	$G_J\cdot Z_W$	f_W	
Water particle outflow	D_Y	$G_Y\cdot Z_P$	f_W	
Direct emissions in water	–	E_W	-	

Subscripts indicate the environmental compartment corresponding each parameter: BA = bulk air, A = air gas phase, Q = air particulate, BW = bulk water, W = water, P = particulate matter in water, BIW = bulk inflow water, IW = inflow water, IP = particulate matter in inflow water, BS = bulk sediment, S = sediment solids, SPW = sediment pore water, RS = resuspended sediment, and M = rain. R = ideal gas constant ($J{\cdot}mol^{-1}{\cdot}K^{-1}$); P^V = vapour pressure (Pa); ρ = density ($kg{\cdot}m^{-3}$); K_{OC} = organic carbon–water partition coefficient; f_{OC} = organic carbon fraction; f = volume fraction. k_S and k_W are transformation rate constants (h^{-1}) for sediment and water, respectively. k_T is a sediment-water mass transfer coefficient ($m{\cdot}h^{-1}$) while k_{VW} and k_{VA} are overall the water–side and air-water mass transfer coefficients ($m{\cdot}h^{-1}$), respectively. A_W and A_S are the air-water and water-sediment interfaces area (m^2), respectively. V_W and V_S are water and sediment volumes (m^3). K_{AW} is the air-water partition coefficient. For additional details see Table S2, Table S3, and Table S4.

The Henderson-Hasselbalch relationship was used to calculate the ratio of ionic to non-ionic forms (I) for the target chemicals that dissociate in the water (Mackay, 2001) (i.e. CLO, IMI, ACE, MTF, and GLY) by applying Eq. 3, then the effect of dissociation on the adsorption of the target chemicals on organic matter was considered by using Eq. 4.

$$I = 10^{(pH - pK_a)} \qquad \text{Eq. 3}$$

$$K_{OC} = [(I/(I+1)) \cdot K_{OC\,diss}] + [(1/(I+1)) \cdot K_{OC\,undiss}] \qquad \text{Eq. 4}$$

$$K_{OC\,diss} = 10^{(0.11 \cdot \log K_{OW} + 1.54)} \qquad \text{Eq. 5}$$

In detail, the organic carbon to water partition coefficient of the undissociated chemical ($K_{OC\,undiss}$) was taken from the literature, while $K_{OC\,diss}$ was estimated from the water/octanol partitioning coefficient (K_{OW}) by means of Eq. 5, as reported by Franco and colleagues (Franco and Trapp, 2008; Vitale and Di Guardo, 2019) if no experimental data was available (Table S2).

Furthermore, following the approach reported by Franco and co-workers (Franco and Trapp, 2010), only the undissociated form a chemical was assumed able to diffuse through the air-water interface. For this reason, DV was calculated using the equations reported in Table 1 and an additional factor (1/(I+1)) accounting for the target chemical dissociation was added to the water compartment mass balance equation.

All input and removal pathways (J_i) related to transport and transformation processes are assumed to occur simultaneously and instantaneously once a contaminant enters the system. They were calculated as the product of each process flow rate (D_i values, $mol \cdot Pa^{-1} \cdot h^{-1}$) and the relative compartment fugacity (f, *Pa*) using the equations shown in Table 1 (Mackay, 2001). In particular, we included both sediment burial (for NBn, NBc, and SB) and sediment erosion (for CB) (Sommerfreund et al., 2010b) into a sediment loss pathway (D_L) to permanently remove the contaminant from the system.

Then, the results were used to solve the mass balance equations for the water (Eq. 6) and sediment (Eq. 7) compartments under a steady-state assumption (i.e. constant emissions, air fugacity, and inflow water fugacity) since air fugacity was assumed equal to that of the atmosphere outside the modelled system (Mackay et al., 2014).

$$E_W + \left[\sum f_{I_i} \cdot \left(D_{I_i} + D_{X_i}\right)\right] + f_A \cdot \left(D_v + D_M + D_C + D_Q\right) + f_S \cdot (D_{RS} + D_T) = f_W \cdot \left([D_v \cdot (1/(I+1))] + D_W + D_D + D_T + \left[\sum \left(D_{J_i} + D_{Y_i}\right)\right]\right) \qquad \text{Eq. 6}$$

$$f_W \cdot (D_D + D_T) = f_S \cdot (D_R + D_T + D_S + D_L) \qquad \text{Eq. 7}$$

Following the guidelines reported by OECD on overall persistence (P_{OV}) and long-range transport potential (LRTP) estimation (Gomis et al., 2015; MacKay et al., 2020; OECD, 2020; Whelan, 2013), persistence of the selected PPPs in the whole lagoon and in each sub-basin (Eq. 8) was estimated as the ratio of the quantity (*kg*) of chemical in each region to the respective total rate of loss ($kg \cdot day^{-1}$) from each system, including degradation and transport processes. Persistence of the target and sediment pollutants was also investigated separately for the water (P_W) and sediment (P_S) compartments, as shown in Eq. 9 and Eq. 10.

$$P_W = Q_W / J_{W-OUT} = Q_W / (J_{(J+Y)} + J_W + J_V) \qquad \text{Eq. 8}$$

$$P_S = Q_S / J_{S-OUT} = Q_S / (J_S + J_B) \qquad \text{Eq. 9}$$

$$P_{OV} = Q_{TOT} / J_{TOT-OUT} = Q_{TOT} / (J_{(J+Y)} + J_W + J_V + J_S + J_B) \qquad \text{Eq. 10}$$

Where Q_W, Q_S, and Q_{TOT} represent the quantity of each PPP (*kg*) in the bulk water phase, the bulk sediment phase, and in the whole lagoon system at steady state, respectively. Furthermore, J_{W-OUT}, J_{S-OUT}, and $J_{TOT-OUT}$ are, respectively, the fluxes ($kg \cdot h^{-1}$) of each PPP out of the bulk water phase, the bulk sediment phase, and out

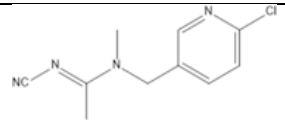
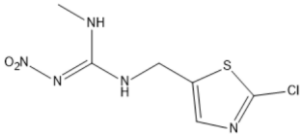
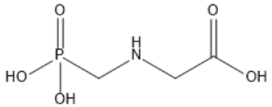
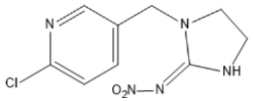
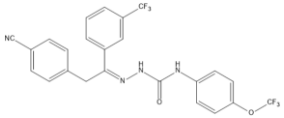
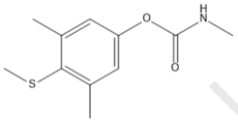
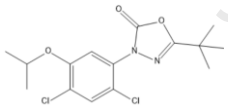
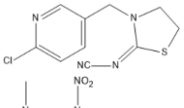
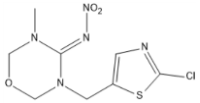
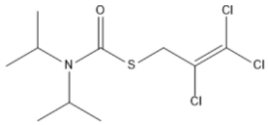
of the whole sub-basin system. In detail, J_{W-OUT} is composed of the following components: outflow of dissolved and particle-associated chemical ($J_{(J+Y)}$), volatilization (J_V), and transformation (J_W). Finally, J_{S-OUT} is comprised of the selected chemical's outflow due to sediment loss (J_L) and transformation (J_S). The exchanges between the water column and the sediment were not included because they do not represent net system losses (Mackay, 2001; MacKay et al., 2020). Mass balance equations were also used to calculate the predicted environmental distribution (PED) of the selected PPPs over the different environmental compartments, following the approach reported by Mackay and co-workers (Daam et al., 2012; Mackay, 2001).

2.3.2 Model parameters

All model parameters including environmental, physical, chemical, and process kinetic ones were selected after a careful literature review, save for C_{IW}, which was calculated by model calibration following the approach described in paragraph 2.2.

Environmental parameters (i.e., sediment active layer, sediment solids volume fraction, concentration of particles in water, organic carbon content of SPM and sediments, sediment deposition/resuspension rate, and sediment burial/erosion rate) regarding each sub-basin of the Venice Lagoon (i.e. NBn, NBc, CB, and SB) were taken from Sommerfreund et al. (2010a, b) and calculated as the average of the weighted values according to the area of each basin's sub-segments. Furthermore, the average SPM concentration (i.e. C_{PI}) in each sub-basin riverine input was calculated as the average of the weighted values according to the discharge of each tributary using the measurements reported by Collavini *et al.* (2005). No contaminant was assumed to be present within CB inflow from the sea, and its SPM concentration (i.e. 9.6 $mg \cdot L^{-1}$) was taken from ARPAV monitoring data for the period 2008-2019 (ARPAV, 2019). As reported by Dalla Valle *et al.* (2005b, 2003) dry deposition rate of atmospheric particulate and organic carbon content of riverine SPM were assumed equal for all basins, and organic carbon content of SPM flowing from the sea was considered equal to that of the other lagoon inflows. In detail, the symbols, descriptions, values, and sources of all model inputs values for environmental parameters are presented in Table S3 and Table S4, while the inputs regarding the selected PPPs chemical properties are reported in Table 2 and Table S2.

Table 2: Physico -chemical properties of the selected PPPs. For references and additional information on model parameters see Table S2.

PPP	Structure	Henry's law constant	K_{OC}_undiss	K_{OC}_undiss	Log(K_{OW})	pKa
		$Pa \cdot m^3 \cdot mol^{-1}$	$L \cdot kg^{-1}$	$L \cdot kg^{-1}$	-	-
Acetamiprid (ACE) CAS: 135410-20-7		9.58E-09	2.67E+02	4.25E+01*	8.00E-01	6.80E-01
Clothianidin (CLO) CAS: 210880-92-5		1.90E-11	5.88E+02	4.36E+01*	9.00E-01	1.11E+01
Glyphosate (GLY) CAS: 1071-83-6		6.94E-08	2.00E+04	1.42E+03	2.00E+04	2.54E+00
Imidacloprid (IMI) CAS: 138261-41-3		1.09E-10	2.93E+02	8.85E+01*	3.70E+00	1.11E+01
Metaflumizone (MTF) CAS: 139968-49-3		1.50E-03	3.38E+04	-	4.60E+00	-
Methiocarb (MTC) CAS: 2032-65-7		9.43E-05	6.60E+02	7.56E+01*	3.08E+00	1.48E+01
Oxadiazon (OXA) CAS: 19666-30-9		1.09E+07	6.76E+02	-	5.33E+00	-
Thiacloprid (TCLO) CAS: 111988-49-9		2.74E-10	6.15E+02	-	1.26E+00	-
Thiamethoxam (TMX) CAS: 153719-23-4		3.56E-10	3.82E+02	-	-1.30E-01	-
Triallate (TRI) CAS: 2303-17-5		8.63E-01	2.94E+03	-	4.06E+00	-

*: Estimated using the approach reported by Franco et al (Franco and Trapp, 2008; Vitale and Di Guardo, 2019).

2.3.3 Sensitivity and uncertainty analysis on model results

The variability in the model predictions due to the uncertainty associated with input values was quantified by using the Monte Carlo simulation approach, as already reported by several authors for multimedia fugacity model uncertainty analysis (Cao et al., 2004; Kim et al., 2013; Wang et al., 2015, 2020a; Zhang et al., 2013).
Monte-Carlo analysis (5000 iterations) was used to propagate variance in inputs to the model results (Wang et al., 2020a) by applying the Oracle Crystal Ball® software (ver. 11.1.2) (Oracle, Redwood City, CA, USA), a Microsoft Excel add-on capable of describing each model input as a probability density function, thus accounting for both the range of values and the likelihood of the parameter having that value. In detail, all the chemical and environmental parameters were assumed to follow a log-normal distribution (Na et al., 2021; Xu et al., 2013) and estimated inputs' uncertainty was quantified using confidence factors (*Cfs*), where 95% of possible values lie between *Cf* times the median and the median divided by *Cf* (MacLeod et al., 2002). *Cfs* values for each input parameter were taken from the literature and are reported in Table S5. The results obtained from the uncertainty analysis are reported as coefficients of variation (CVs), calculated as the ratio of standard deviation and mean values of a population (Wang et al., 2020b).
Sensitivity analysis was carried out identify the key input parameters and explore the role of individual parameters on the outcome variance of the multimedia model (Cacuci et al., 2003). In some detail, first the overall sensitivity was determined by the Spearman rank-order correlation coefficient between the input and output data. The individual contribution of each input to the total variance of the outputs (contribution to sample variance, CSV) (Tarantola et al., 2012) was estimated as the square of the correlation coefficient normalized to the sum of the squared correlation coefficients following the approach reported by Mackay and co-workers (Mackay et al., 2014).

2.3.4 Calibration and evaluation of model performance

Data on the measured environmental concentrations (MECs) of the studied PPPs in the case study area were available from a recent baseline field study carried out by Pizzini et. al (2024) in the framework of the Venezia2021 project and used for model evaluation and calibration.
In some detail, the work reported by Pizzini and colleagues included four sampling campaigns: spring 2019 (end of April-beginning of March), autumn 2019 (end of October-beginning of November), summer 2020 (end of July-beginning of August), and winter 2021 (end of January-beginning of February). Water and sediment samples were collected in six sampling sites, shown in Figure 1b and Table S6. Details on analytical methods, results, and sampling procedures are reported in Pizzini et. al (2024).
Model calibration was performed by using the Oracle Crystal Ball® software interfaced with the level III fugacity model to locate the parameter value corresponding to the simulation output that best fitted the target chemical average measured environmental concentrations (MECs) (Table S8) by automatically varying, in the range defined in the literature (Table S5), the value assigned to the selected input (Wang et al., 2020b).
As reported by several authors, to calculate each PPP average MEC in both water and sediment, the samples that were below the limit of detection (LOD) were assigned a value of half of LOD (LOD/2) (Masiá et al., 2013). Model calibration was carried out for the PPPs whose average MEC in the water or in the sediments exceeded the detection limit and for those chemicals whose PECs exceeded LOD/2 when the corresponding MECs were below the detection limit for all the samples.
Model results were evaluated by comparing each target chemical's average MEC in water (Table S6) and sediments (Table S8) with the corresponding PEC estimated by the model according to Eq. 11.

$$PEC/MEC_{PPP} = \mathrm{PEC}_{PPP}/MEC_{PPP} \qquad \text{Eq. 11}$$

In detail, the model results were considered acceptable if the PEC fell within an order of magnitude of the MEC (i.e. if the PEC/MEC_{PPP} ratio ranged between 0.1 and 10) (Lamon et al., 2012) or if the predicted concentrations in both water and sediment were less than LOD/2 when the corresponding MECs were below the detection limit for all the samples.

3. Results and discussion

3.1 Predicted environmental concentrations (PECs), transport, and persistence

The concentration in bulk water (C_{BW}) sediments (C_{BS}) of the target chemicals estimated for each segment of the Venice lagoon is reported in Figure 2a-b and Table S9.

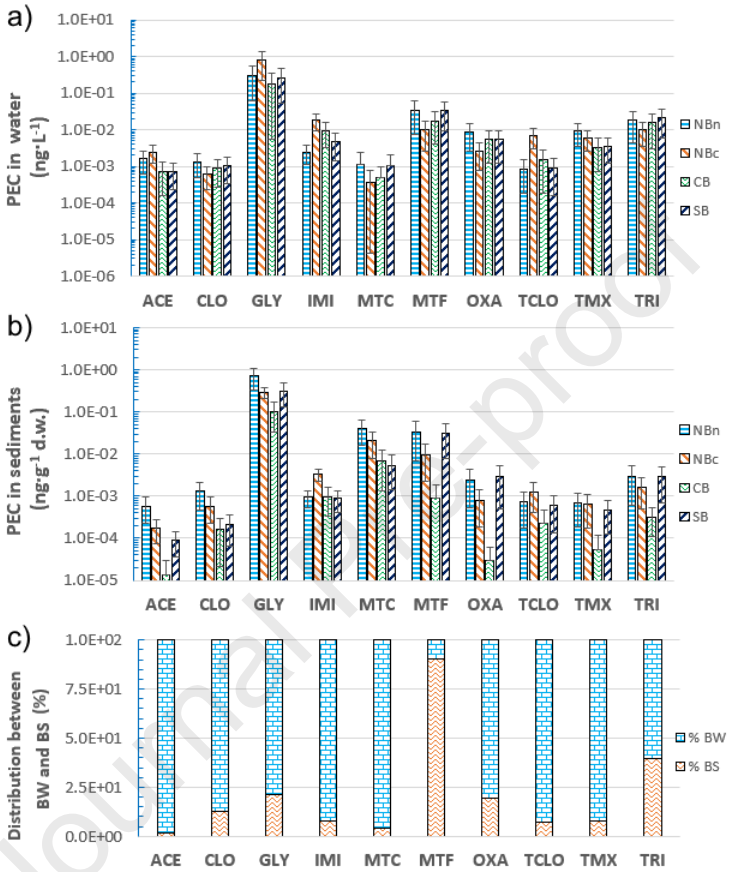


Figure 2. Predicted environmental concentrations (PECs) of the selected PPPs in bulk water (C_{BW}) (a) and bulk sediment (C_{BS}) (b). Distribution of the studied PPPs among bulk sediments (BS) and bulk water (BW) (c). Error bars represent standard deviation of the results.

Since these estimations reflect a combination of substance properties, emission rates, and lagoon characteristics, they can used to obtain important information on the interaction of these chemicals with the environment. In detail, the results showed remarkable differences in the presence and geographical distribution of the studied PPP across the lagoon. The model estimated similar concentrations in the water column across the lagoon for GLY (6-40 ng·L^{-1}), TMX, ACE, MTC, TRI, OXA (0.2-2.0 ng·L^{-1}) CLO, and MTF (0.02 – 0.1 ng·L^{-1}), while the concentration of IMI and TCLO changed more than one order of magnitude between the different subbasins (0.1- 3.4 ng·L^{-1}). In particular, slightly higher levels of TRI, OXA, CLO, and MTF were estimated for NBn and SB subbasins with respect to the other parts of the lagoon, while for the other PPPs the highest concentrations in water were obtained for the NBc waterbody. The results reported in Figure 2a-b and Table S9 shows that this spatial distribution could be also found for the sediment compartment, where the highest concentrations were estimated for GLY (0.2 - 0.8 ng·g^{-1} d.w.) and MTF (~ 0.02 ng·g^{-1} d.w.). These trends could be ascribed to both different consumption patterns and transport due to leaching and run-off after application in the various regions of the lagoon drainage basin, highlighting the importance of improving PPPs emission estimation methods accounting for soil characteristics, crop type and degradation during transport in the drainage basin.

Furthermore, model results (Figure 2c and Table S10) showed that only a small part of the quantity of ACE, IMI, MTC, TCLO and TMX discharged into the lagoon would accumulate in the sediments, due to a combination of several factors such as low affinity to organic matter, high solubility, and persistence in water. On the contrary, a significant fraction of CLO, GLY, MTF, OXA, and TRI would accumulate in the sediments, possibly leading to secondary pollution phenomena due to sediment erosion, maintenance of navigable canals or illegal fishing practices (Dalla Valle et al., 2005a, 2003). This was particularly evident in the case of MTC due to its fast degradation in the water column and for TRI thanks to a combination of high stability and affinity to organic matter. This is a very important aspect for the management of the lagoon, especially for the areas subjected to high inflows of suspended particulate matter either from a tributary or one of the inlets (Zonta et al., 2020).

The average mass transport fluxes of the target chemicals can provide a systematic view on their environmental behaviour, in particular of the processes involved in their natural attenuation and of the interaction between the sediments and the overlaying water column (Kong et al., 2018).

As can be seen from the results reported in Figure 3a and Table S11, degradation in the water (J_W) accounted for most of the elimination of ACE, CLO, GLY, IMI, MTC, MTF, TCLO, and TMX while transformation in the sediments (J_S) was much more limited, reflecting both their half-lives and distribution within the lagoon compartments. Considering the several degradation pathways (e.g. oxidation, hydrolysis, photolysis, and microbial degradation) and products reported for the studied PPPs (e.g. aminomethylphosphonic acid, 6-chloronicotinic acid, and, 5-dimethyl-4-methylsulfonyl-phenyl-N-methylcarbamate) (Anjos et al., 2021; Chakraborty et al., 1999; Lopes Catão and López-Castillo, 2018; Pang et al., 2020; Plácido et al., 2013) this confirms the need for further studies on the presence and effects of their metabolites and degradation products, as reported by several other authors (Geissen et al., 2015; Tang et al., 2019). Figure 3a shows also that water outflow (JJ+Y) contributed significantly to the removal of ACE, CLO, GLY, IMI, MTC, TCLO, and TMX while volatilization (JV) was a relevant elimination mechanism only in the case of OXA and TRI, due to their slight volatility and low solubility in water (Comoretto et al., 2008; Yates, 2006). Sediment loss (JL) accounted only for a small part of the overall loss of the target chemicals, but its contribution to the elimination of the investigated PPPs with high affinity to organic matter within the CB basin sediments was significantly more relevant.

The transfer fluxes between water and sediments calculated for each PPP are detailed in the Supplementary Information (Table S12), while Figure 3b shows the net fluxes due to diffusive (i.e. J_T) and non-diffusive (i.e. J_D and J_{RS}) processes. As confirmed also by the results on the PPPs' distribution (Figure 2c) there is a net flow of all chemicals from the water column to the sediments, especially in the case of GLY, MTC, and TRI, suggesting that the sediment could serve as a sink for these pollutants in the lagoon. Similar trend have already been reported for other CECs and POPs (Wang et al., 2020b; Xu et al., 2013).

The predicted persistence of the target chemicals is reported in Figure 3c and Table S13, showing the longest overall residence time for MTF (about 6 months) due to its accumulation in the sediments where it is degraded significantly slower than the other PPPs (Table S2). Similar overall residence times in the water column and the whole lagoon (about 1-2 months) were estimated for ACE, CLO, GLI, IMI, TMX, TCLO, and TRI, reflecting the fact that these contaminants have similar water half-lives and were predicted to be for the most part in the water (Table S2 and Figure2c). Furthermore, a much shorter stay in the lagoon (about 3-7 days) was predicted for OXA and MTC due to a combination of limited accumulation in the sediments, rapid volatilization, and quick degradation in the water (Table S13 and Figure 3). From Figure 3c it can also be seen that all the studied chemicals exhibited a tendency to remain in the sediments much longer then in the water column, due to the absence of significant sediment transport and longer half-lives with respect to the water compartment, indicating a possible risk for benthic organisms (Whelan, 2013). Moreover, PPPs with high affinity to organic matter showed an estimated persistence in the sediments significantly lower than their respective degradation half-lives, highlighting the relevance of sediment burial or erosion in their overall environmental fate.

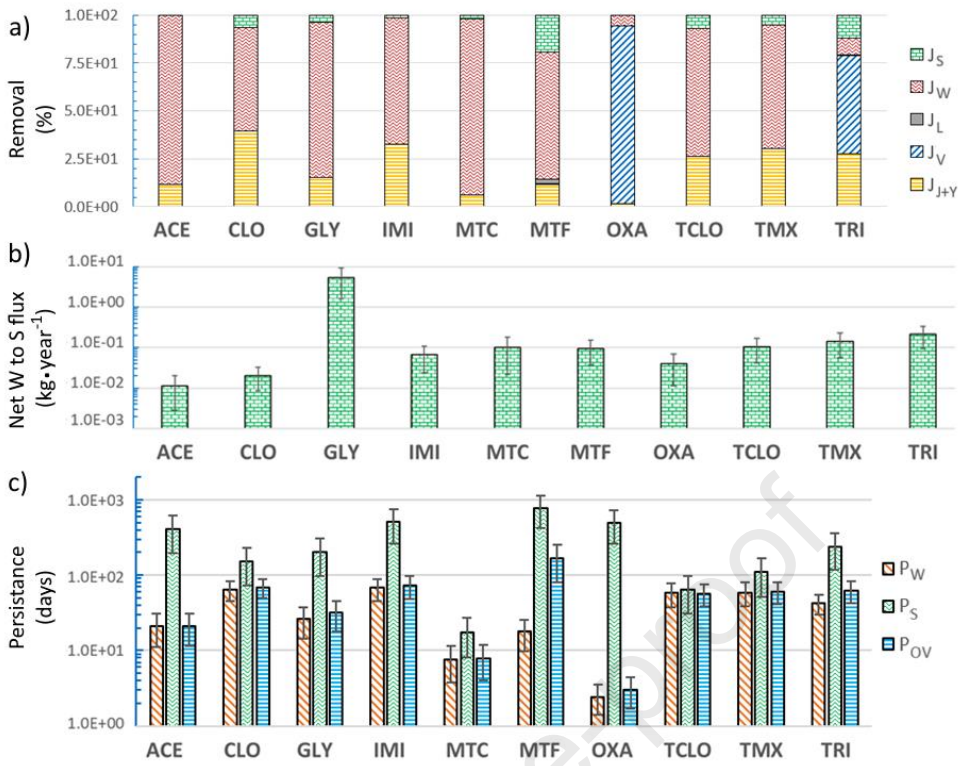


Figure 3. Predicted mass transfer fluxes, expressed as a percentage of all loss processes, for the studied PPPs in the Venice lagoon (a). Predicted net transfer fluxes of PPPs across the water–sediment interface in the Venice Lagoon. Positive values indicate net transfer from the water to the sediments. (b). Estimation of the selected PPPs' persistence in the water column (P_W), in the sediments (P_S), and in the lagoon (P_{OV}) (c). Error bars represent standard deviation of the estimation.

3.2 Evaluation of model performance

The model was evaluated by comparing PECs of the PPPs in the water (i.e. C_W) and the sediments (i.e. C_{BS}) with the arithmetic mean of the measured concentrations detected during the four sampling campaigns (Pizzini et al., 2024), and the results are shown in Figure 4 and detailed in Table S14. In particular, when experimental results above the detection limit were available the agreement between calculated and measured values was always within the acceptable range (i.e., 0.1 < PEC/MEC < 10), in particular in the case of OXA, ACE, IMI, MTC, and TCLO whose PEC/MEC ratio ranged between 0.3 and 3.0. Furthermore, most of the measurements in the sediments compartment were always below the instrument's detection limits, therefore it was only possible to conclude that the model did not overestimate the concentration of these contaminants within the sediments. This shows the importance of developing accurate and sensitive analytical methods for the detection of CECs in such matrices, especially in the case of chemicals that have a high affinity for organic matter (Hajeb et al., 2022). For ACE and GLY the model showed a tendency to overestimate their concentration in the water and underestimate it in the sediments (Figure 4 and Table S14), and this could be attributed to an underestimation of their water half-life or of their dissociated form's affinity to organic matter (Table 2) (Franco and Trapp, 2010; Lamon et al., 2012). From the results reported in Figure 4 and Table S14 it can also be seen that the concentration of CLO and OXA in the water was underestimated in all subbasins except for SB, while the PEC in the sediments was always less than LOD/2, indicating either a possible overestimation of these PPPs' water half-life or an underestimation of their annual emissions (Kong et al., 2018).

These differences between modelled and predicted concentrations could also be ascribed to the inherent simplified nature of the fugacity model with respect to real conditions, for an environment as complex as the Venice Lagoon.

For example, the model considers only the annual average concentration and deposition rate of SPM in the lagoon, while not accounting for the seasonal variations of zooplankton and phytoplankton's concentration. In fact, these factors have been identified as a key factor on the fate and transport of organic pollutants both in freshwater and marine environments (Dachs et al., 2000; Kong et al., 2018) due to their influence on air-water exchange, sorption, accumulation, and SPM sinking flux (Nizzetto et al., 2012; Tao et al., 2006). The integration of the multimedia fate model with an aquatic ecosystem model (Lovato et al., 2013; Pastres et al., 2001) accounting for other biotic and abiotic processes may be a solution, but it would greatly increase model complexity and the results' uncertainty (Kong et al., 2018).
Furthermore, more in-depth sampling campaigns would permit to evaluate model results with a more detailed spatial discretization of the lagoon, thus deepening our knowledge on the spatial and temporal variability of these PPPs distribution in the Venice Lagoon.

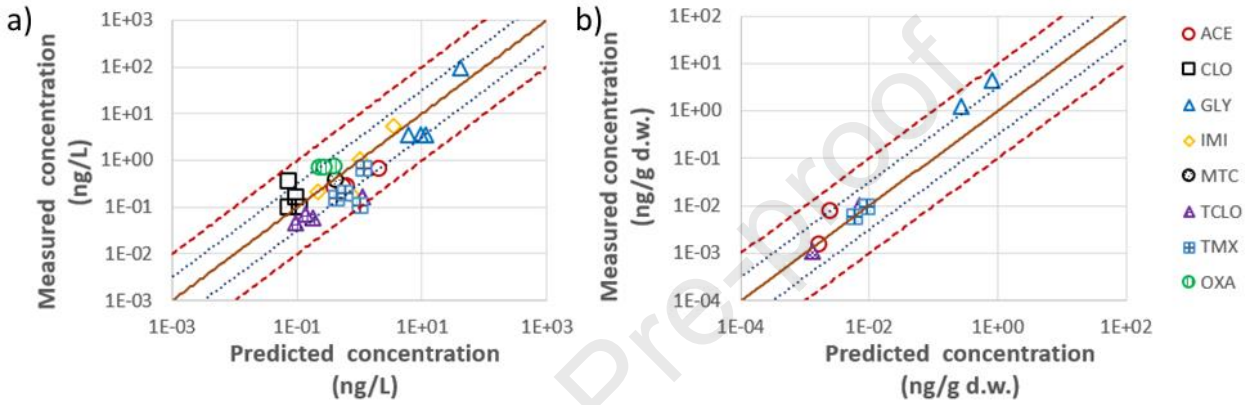


Figure 4. Comparisons between the predicted (PEC) and measured (MEC) concentration of the selected PPPs in water (C_W) (a) and bulk sediment (C_{BS}) (b). Diagonal lines indicate perfect agreement, while the dotted and hatched lines represent agreement within factors of $10^{0.5}$ and 10, respectively.

3.3 Sensitivity and uncertainty analysis

3.3.1 Sensitivity analysis

Model output sensitivity with respect to the concentration of the studied PPPs chemicals in the water and in the sediments was investigated and results are reported in Figure 5 and Table S15-S17. The outcomes of sensitivity analysis showed that half-life in water accounted for most of the variance (76-92%) attributed to C_{BW} for all the studied chemicals, except for TRI and OXA. For the concentration in the water of these two chemicals the most important input data were those describing water-air interface processes, and this could be ascribed to their higher vapor pressure with respect to the other studied substances (Mackay, 2001). In detail, the highest values of CSV for OXA and TRI were shown by the water-side mass transfer coefficient and the air-water partitioning coefficient, respectively. This can be related to the value of their Henry's constant, showing that the volatilization of OXA is controlled by the processes at the water side of the air-water interface, while the volatilization of TRI is controlled by the processes at the air-side (Schwarzenbach et al., 2016). The concentration in the water column of the studied PPPs characterized by a high affinity to organic matter (i.e. TRI and MTF) was also slightly influenced (CSV ≈ 1-3%) by the variation of some of the inputs that describe the exchanges between water and sediments, such as K_{OC}, sediment depth, and resuspension rate. From the results reported in Figure 5 and Table S16 it can also be seen that for all the studied PPPs a significant portion of the variance attributed to C_{BS} could ascribed be K_{OC} (5-25%), sediment porosity (15-30%), and sediment density (3-10%) variation. For all PPPs, with the exception of TRI and OXA, a relevant portion (20-60%) of the remaining variance attributed to C_{BS} could be linked to their half-lives in the water, thanks to a combination of their higher stability in the sediments with respect to their degradation rate in the water column and their limited affinity to organic matter due to dissociation phenomena. In the case of TRI and OXA, similarly to what was found for C_{BW}, a significant contribution to C_{BS} variance (12 and 40 %, respectively) was given by

the mass transfer coefficients describing water-air interface processes. Both the height of the sediments active layer and the degradation rate in the sediments contributed to a significant portion (10-20%) of the variance attributed to C_{BS} for those PPPs that are less persistent in the sediments (i.e. MTC, TCLO, TMX, CLO, GLY, and TRI), while for the other selected chemicals the contribution of this parameter was much more limited (1-5%), highlighting the necessity to accurately estimate the degradation rates of the less stable contaminants (US EPA, 2020). The quantity of each chemical discharged into the lagoon of Venice also accounted for a significant part of the total variance of C_{BW} and C_{BS} (5-12%), showing how the uncertainty linked to this input influenced most of the model outputs.

The results reported in Figure 5 and Table S17 showed also that the half-life in water of TCLO, CLO, GLY, TMX, IMI, MTC, and ACE accounted for most of the variance (90-99%) attributed to P_{OV} in the lagoon, while the most important inputs for estimating TRI and OXA overall persistence (CSV ≈ 55-95%) were the mass transfer coefficients between water and air. On the contrary, MTF was the only PPP whose residence time in the lagoon was significantly influenced by the variation of parameters directly linked to sediments dynamics (i.e. K_{OC}, SedRate, and ReSusRate) due to its low degradation rate in the sediments and high affinity to organic matter.

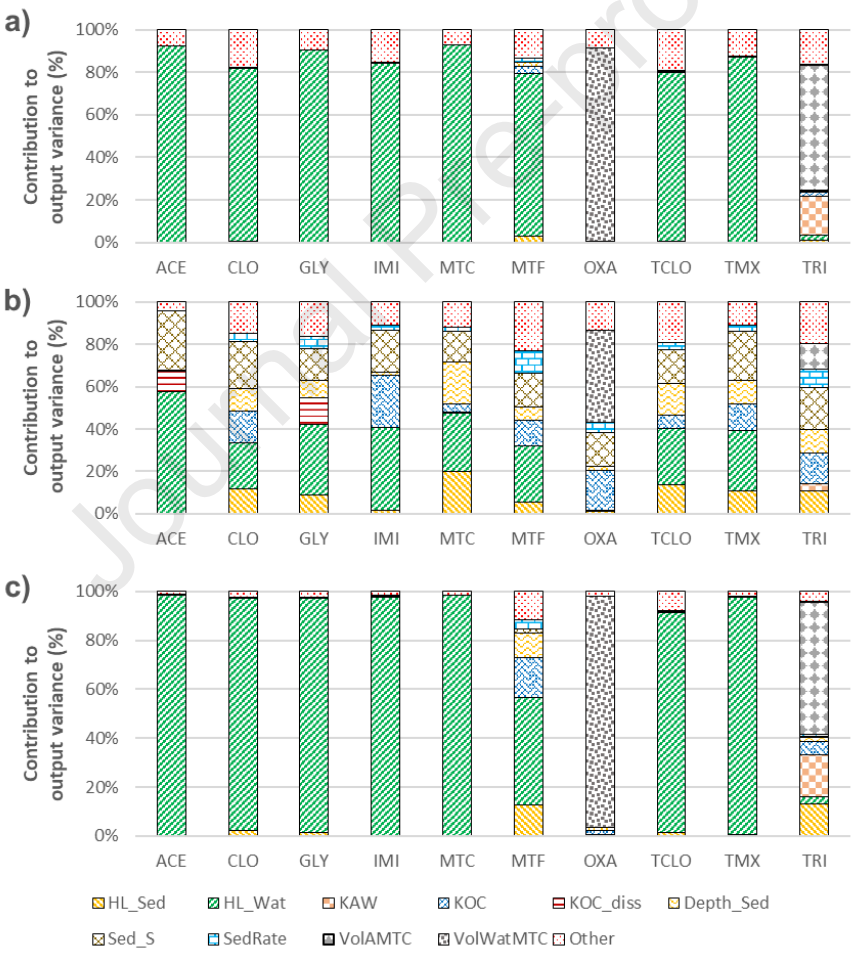


Figure 5: Main parameters contributing to CV for the estimation of C_{BW}, C_{BS}, and P_{OV}. Each value represents the arithmetic mean of the values obtained for each sub-basin.

3.3.2 Uncertainty analysis

Monte Carlo simulation approach was also used to assess model outputs' uncertainty, and coefficients of variation (CV) related to C_{BW}, C_{BS}, and P_{OV} are shown in Figure 6, while the CVs related to other outputs are detailed in the Supporting Information (Table S9-S13). There was moderate uncertainty (0.20 < CV < 0.40) for the concentration of the target PPPs in the water compartment, while the CV related to the concentration

in the sediments was markedly higher (CV > 0.60), due to the contribution of parameters describing sediments' dynamics (i.e. K_{OC}, SedRate, and ReSusRate). Similarly, there was high uncertainty (0.50 < CV < 0.85) also for the estimation of studied chemicals' fluxes across the water-sediment interface and out of the system due to sediment loss. The uncertainty pertaining the overall persistence of all PPPs, except for MTF, was similar to that associated to the estimation of C_{BW} (Figure 6), reflecting the distribution of these chemicals between the environmental media in the lagoon (Figure 2).

The high uncertainty related to the model results can also be attributed the high *Cfs* (i.e. 3.0) assigned to degradation half-lives and active layer sediments depth to account for the scarcity of data on the removal of the studied chemicals in brackish waters, such as coastal lagoons and river deltas, and the high re-suspension and deposition rates of sediments and SPM in the lagoon (Dalla Valle et al., 2005a).

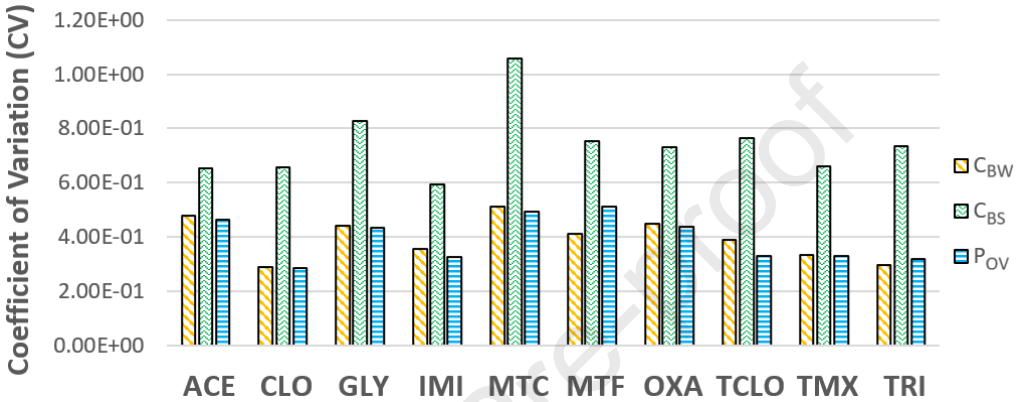


Figure 6: Summary of CV values for C_{BW}, C_{BS}, and P_{OV} for the selected PPPs. Each value represents the arithmetic mean of the values obtained for each sub-basin.

3.4 Strengths, limitations, and implications for environmental risk assessment of the modelling approach

The use of level III multimedia fugacity models has been recognized as a suitable tool to support risk assessments alongside monitoring studies, as it allows to estimate long-term exposure to chemicals and investigate the mechanisms, processes, and emission sources controlling the environmental fate of chemicals in complex environments, while requiring a relatively limited amount of information on the modelled system (Su et al., 2019). On the contrary, this steady-state modelling approach has been shown to be unsuitable to describe the presence of pollution hotspots or sporadic emissions. The use of multimedia fugacity models (level IV) assuming unsteady-state distributions and processes (i.e., input rates, mass fluxes, concentrations, and fugacity vary with time) was shown to better resolve the presence of such phenomena (Contreras et al., 2008; Lu et al., 2024). However, these models require much more specific knowledge on the temporal and spatial variation of environmental parameters (e.g., temperature, and SPM concentration) and processes (e.g., water flows, SPM deposition/resuspension, and atmospheric deposition), as well as considerable computing resources if high spatial-temporal resolution is required (Guo et al., 2023; Yang et al., 2015)

The results of this study offer a first evaluation of the environmental fate and distribution of the selected PPP in the Venice Lagoon and highlight the need to further investigate the risks caused by the presence of such chemicals and their degradation products in the water and sediments of complex environments like lagoons and other brackish water bodies. In fact, the lack of data on the removal of the target PPPs in brackish waters accounted for a relevant portion of the overall uncertainty of the model results, indicating the need for more studies focused on the degradation of PPPs in such conditions.

The modelling exercise carried out in this work also provided valuable insights into the environmental processes regulating the fate of the selected PPPs within a complex transitional environment such as the Lagoon of Venice.

These findings can serve a valuable resource to guide the development of experimental studies focusing on the degradation of PPP in coastal and transitional environments, as well to support future risk assessments and investigations focusing on exploring the impact of diverse emission management strategies, such as usage restrictions or substitution, on the environmental exposure to the studied PPPs and other CECs.

4. Conclusions

In this study a level III multimedia fugacity model was applied to simulate the fate and transport of ten PPPs in a complex coastal lagoon, such as the lagoon of Venice, and the concentration of the selected chemicals predicted in the water and sediments showed good agreement with field data.

The highest concentrations in water were estimated for GLY and IMI, reflecting their high discharge from the lagoon drainage basin estimated in a previous work (Calgaro et al., 2022). Furthermore, the highest concentrations in the sediments were predicted for GLY, MTF, and TRI despite the difference of two to three orders of magnitude of their emissions. Model results also showed a net accumulation in the sediments for all the studied chemicals, indicating the possibility for sediments to act as sinks for PPPs and, as a consequence, as secondary source of pollution.

The main removal mechanisms for GLY, IMI, ACE, MTC, MTF, TMX, TCLO, and CLO resulted degradation in the water column and adjective outflow, while volatilization was a key factor for the elimination of OXA and TRI. Sensitivity and uncertainty analysis highlighted that degradation rates, K_{OC}, and the parameters describing air-water interactions had the strongest influence on model's results, followed by the inputs accounting for sinking and resuspension of sediments.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CRediT author statement

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: