



Importance of environmental and biomass dynamics in predicting chemical exposure in ecological risk assessment



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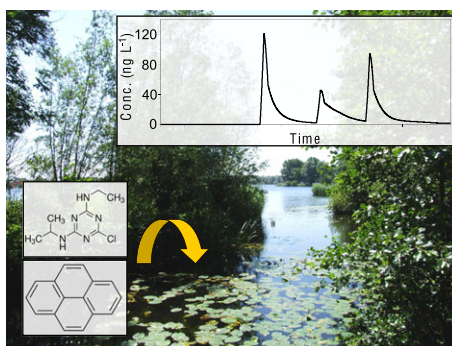
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HIGHLIGHTS

- Exposure is generally modelled using static environmental and biomass conditions.
- The spatio-temporal heterogeneity of such conditions may cause exposure variations.
- A new dynamic spatially-explicit model for aquatic environments was developed.
- Spatial and temporal dynamics were predicted for four organic chemicals.
- Variations of bioavailable concentrations can be up to several orders of magnitude.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 9 March 2015

Received in revised form 16 April 2015

Accepted 17 April 2015

Editor: D. Barcelo

Keywords:

ChimERA

Fate modelling

Dynamic exposure

Bioavailability

Surface water

Organic chemical

ABSTRACT

In ecological risk assessment, exposure is generally modelled assuming static conditions, herewith neglecting the potential role of emission, environmental and biomass dynamics in affecting bioavailable concentrations. In order to investigate the influence of such dynamics on predicted bioavailable concentrations, the spatially-resolved dynamic model “ChimERA fate” was developed, incorporating macrophyte and particulate/dissolved organic carbon (POC/DOC) dynamics into a water-sediment system. An evaluation against three case studies revealed a satisfying model performance. Illustrative simulations then highlighted the potential spatio-temporal variability of bioavailable concentrations after a pulsed emission of four chemicals in a system composed of a pond connected to its inflow and outflow streams. Changes in macrophyte biomass and POC/DOC levels caused exposure variations which were up to a factor of 4.5 in time and even more significant (several orders of magnitude) in space, especially for highly hydrophobic chemicals. ChimERA fate thus revealed to be a useful tool to investigate such variations and to identify those environmental and ecological conditions in which risk is expected to be highest.

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1. Introduction

Ecological risk assessment of chemicals (ERA) is a procedure which is commonly used to evaluate the impact of chemicals on ecosystems.

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This is generally done comparing the environmental exposure and the potential (ecological) effect threshold levels. The need for regulating a large number of chemicals and the complexity of the ecosystems to protect led to the development of simple and standardized tools (EPA, 1998; EC, 2003). However, most of these approaches do not properly address environmental realism in terms of, for example, the spatial and temporal variability of exposure and ecological scenarios (affecting both exposure and effects) (De Laender et al., 2014, 2015), the interactions among individuals and populations and the co-occurrence with other stress factors (such as chemical or physical ones). A recent joint scientific opinion document from the three scientific committees of the European Commission (EC, 2013; Vighi, 2013) tried to address the new challenges for risk assessment for human health and the environment. Among the points devised, a number were related to the improvement of environmental exposure assessment (EEA) in ERA. It was underlined that EEA deserves particular attention when predictions should cover a large variety of habitats at different spatial scales, as well for terrestrial as aquatic environments (Di Guardo, 2014). Moreover, in a recent publication specifically devoted to challenges for EEA (Di Guardo and Hermens, 2013), the need of accounting for the bioavailability of chemicals (here defined as the freely dissolved concentration of a chemical, in e.g., water) is remarked. This concentration, which is regarded as available for uptake by organisms, can exhibit spatio-temporal variations in surface water bodies in response to the presence of relevant amounts of organic carbon-rich materials like primary producers (e.g., algae and/or macrophytes) (Taylor et al., 1991; Berglund et al., 2001; Leistra et al., 2003), particulate/dissolved organic carbon (POC/DOC) (Schwarzenbach et al., 2003), or sorbing materials (e.g., organic matter or soot) in sediment (Gustafsson et al., 1997). Despite the fact that a number of exposure models exist accounting for the presence of primary producers (e.g., Armitage et al., 2008; Nfon et al., 2011) or incorporating variable degrees of environmental complexity (e.g., Adriaanse, 1997; FOCUS, 2001), there is a need to develop a model unit incorporating such processes to reflect realistic ecosystem heterogeneity and suitable for regulatory purposes. Indeed, most of the exposure models adopted for regulatory purposes (such as EUSES in the European Union; EC, 2004) rely on simplistic assumptions (such as steady-state) or they use fixed values for environmental parameters (temperature, organic carbon fractions, volumes of compartments and phases, etc.).

The aim of this study was to develop a new dynamic, spatially-explicit fate model for shallow-water environments (“ChimERA fate”), capable of accounting for spatio-temporal variability of emissions and compartment properties and considering the role of macrophytes, POC and DOC dynamics in affecting bioavailable concentrations. Although phytoplankton can be relevant in affecting exposure in shallow waters, its modelling will be included in a following paper. Comparisons between model predictions and experimental observations for three case studies allowed a preliminary assessment of model performance. The results of illustrative simulations run for chemicals with different hydrophobicity and persistence are then presented in order to show (I) the potential temporal and spatial variability of bioavailable concentrations after a pulsed emission in a stream-pond-stream system, (II) the role of macrophytes, POC and DOC and their dynamics in influencing bioavailability and (III) the added value of adopting time-variable profiles of macrophyte biomass and POC/DOC concentrations compared to the use of constant or averaged values.

2. Materials and methods

The ChimERA fate model is based on the fugacity approach (Mackay, 2001) and was developed starting from an existing dynamic water-sediment model (Di Guardo et al., 2006). New compartments and sub-compartments were added and different model units were connected to obtain a spatial discretization. In this first version of ChimERA fate, the model incorporates the macrophyte compartment, while the

inclusion of the phytoplankton compartment will be the object of future work. In Fig. 1a, a schematic representation of the model unit is provided. Moreover, the temperature dependence of properties and degradation rates was included, as explained in Text S1. Details concerning model development and parameterization are presented in the following sections and in the SI. A complete list of Z- and D-values can be found in Tables S1 and S2.

2.1. Model background

ChimERA fate was grounded on the DynA Model (Di Guardo et al., 2006), developed to investigate the fate of organic chemicals in dynamic water-sediment systems. In DynA, time-varying chemical emissions and environmental parameters (e.g., water temperature and fluxes) can be specified, and model output (chemical concentrations and fluxes) is provided on an hourly basis. Suspended solids are modelled as a water sub-compartment (in equilibrium with water), and POC is simulated by specifying the organic fraction of suspended solids. In the original DynA Model, the presence of DOC is neglected. The model was calibrated and validated for herbicides in rice paddy scenarios, but no vegetation compartment was simulated (Infantino et al., 2008). More recently, an organism compartment was included and the model was applied to simulate uptake of DDTs by fish in an Italian sub-alpine

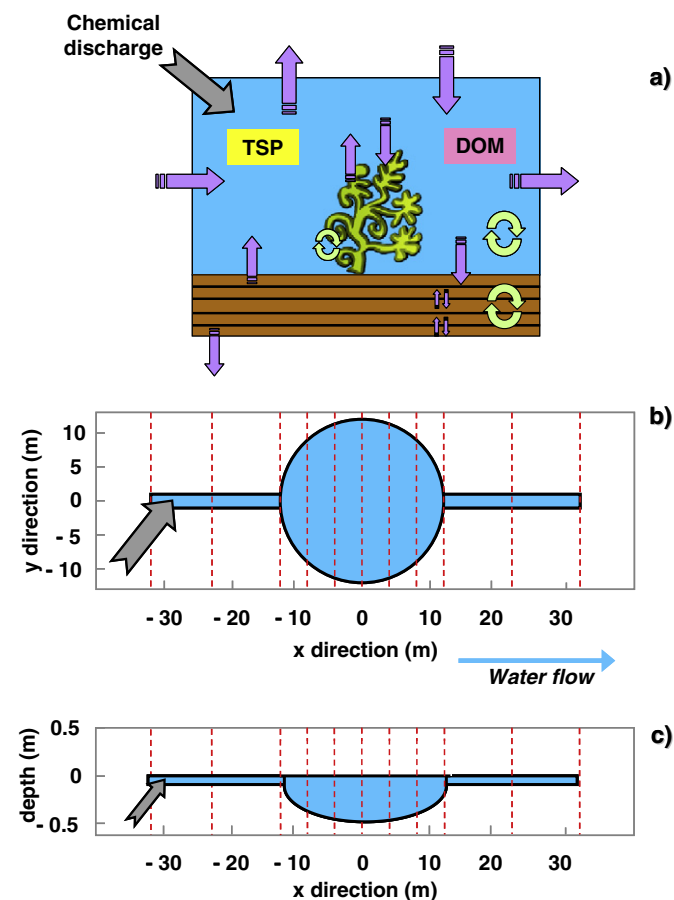


Fig. 1. Schematic representation of (a) the ChimERA fate model unit, with purple arrows indicating chemical fluxes between compartments or accessing/leaving the system and circular green arrows indicating degradation processes; (b) top-view and (c) side-view of the environmental system simulated in the model illustration. TSP is total suspended particles while DOM is dissolved organic matter.

lake (Infantino et al., 2013) and of a number of POPs by macroinvertebrates in a glacier-fed stream (Morselli et al., 2014).

2.2. Model formulation

2.2.1. Macrophyte compartment

Macrophytes play a vital role in aquatic ecosystems, not only as primary producers, but also because of their ability to sequester pollutants, trap suspended solids containing them, and enhance degradation and thus their irreversible removal from water bodies (Hinman and Klaine, 1992; Jeppesen et al., 1998; Karen et al., 1998; Hand et al., 2001). For these reasons, the macrophyte compartment has been incorporated into a number of fate modelling approaches (e.g., Armitage et al., 2008; Park et al., 2008; Renaud et al., 2008; Rose et al., 2008; Nfon et al., 2011). In ChimERA fate, macrophytes were included following the approach of Armitage et al. (2008), which is based on the relationships between $\log K_{OW}$ (octanol–water partition coefficient) and uptake/deposition rate constants derived by Gobas et al. (1991) for hydrophobic organic substances. Modelled processes include diffusive exchanges with water, degradation in macrophytes, and particle-mediated deposition onto macrophyte leaves. For simplicity, only the above-sediment portion of vegetation biomass was modelled in the present version of the model, thus neglecting diffusive exchange between roots and the sediment compartment. It was also assumed that macrophyte losses through mortality and excretion processes could occur, implying a chemical flux to total suspended particles (TSP) and dissolved organic matter (DOM), respectively (Park et al., 2008; De Laender et al., 2008). Details concerning the calculation of the D -values for macrophyte-related processes are reported in Text S2.

2.2.2. TSP and DOM sub-compartments

As in the original DynA Model (Di Guardo et al., 2006), suspended particles were modelled as a water sub-compartment (i.e., in equilibrium with water), characterized by a given fraction of organic carbon representing POC. Moreover, in order to account for the presence of DOM, a new water sub-compartment was added and its fugacity capacity (Z_{DOM} , mol m⁻³ Pa⁻¹) was calculated as described in Armitage et al. (2008) (Table S1). Processes involving water sub-compartments are TSP deposition to aquatic vegetation and sediment and resuspension from sediment and, for both TSP and DOM, inflow and outflow with water and chemical transfer from macrophytes through mortality and excretion. A complete list of D -values can be found in Table S2.

2.2.3. Sediment vertical discretization

In ChimERA fate, the sediment compartment can be divided into a number of layers, in order to obtain a more accurate reconstruction of chemical vertical movement. The total number of layers can be user-selected and for each layer the different properties (e.g., depth, density, solids and organic carbon fractions) can be specified, in order to simulate specific sub-environments. Each sediment layer was modelled as a well-mixed box composed of two phases (i.e., solids and pore water), between which equilibrium was assumed. Chemical exchanges between adjacent layers included upward and downward diffusive fluxes. For simplicity, the top sediment layer (at the water–sediment interface) was assumed to be the only one to exchange with water, and therefore to be affected by diffusion from and to water, and particle deposition and resuspension. Similarly, the bottom sediment layer was assumed to be the one to lose chemical through burial. All D -values are listed in Table S2.

2.2.4. Chemical mass balance, numerical solution and model code

Chemical mass balance in ChimERA fate is described by a system of 1st-order ordinary differential equations (ODEs), one for each

compartment. These ODEs are solved using a 5th-order accurate, diagonally implicit Runge–Kutta method with adaptive time stepping (Semplice et al., 2012). For a system consisting of water, macrophytes and one sediment layer, the equations are:

$$\frac{dmol_{Mf}}{dt} = a \cdot mol_W - b \cdot mol_{Mf} \quad (1)$$

$$\frac{dmol_W}{dt} = c + d \cdot mol_{Mf} + e \cdot mol_S - g \cdot mol_W \quad (2)$$

$$\frac{dmol_S}{dt} = h + i \cdot mol_W - j \cdot mol_S \quad (3)$$

where mol_{Mf} , mol_W and mol_S represent the moles in the three compartments at a certain time, while each coefficient (from a to j) represents a transformation or a transport flux (single D -value or sum of D -values) divided by the proper product of volume and fugacity capacity Z (Table 1).

Except for the hydrological module described in the following section and more in detail in Text S3, the ChimERA fate model was coded using Microsoft Visual Basic 6.0 and was provided with a graphical user interface through which input data can be selected and uploaded and results can be visualized and processed. The model can be downloaded from the Insubria University website ().

2.2.5. Spatial discretization

The spatial discretization was obtained by connecting multiple model units by means of water flow. For this purpose, the ChimERA fate model was provided with a hydrological module capable of computing water volumes (m³) and fluxes (m³ h⁻¹) on an hourly basis in a user-specified number of adjacent boxes. Water flow was described using the Saint-Venant equations for a rectangular-section channel with variable width and depth (Balbas and Karni, 2009), with the Manning's friction term (Gordon et al., 2004). The numerical approximation of the equations was performed with a finite-volume conservative method, so that the total mass of water can change only through the inflow and outflow at the beginning and end, respectively, of the simulated portion of the water body and no artificial sources or losses can occur at the internal interfaces. For more details on the hydrological module see Text S3. Similarly, a mass-conservative approach was adopted for the chemical flow by firstly computing the flow across any given interface and secondly subtracting that amount from one compartment and adding it to the neighboring one. Such discretization allows the simulation of complex environments such as systems of

Table 1

Coefficients appearing in the 1st-order differential equations describing the chemical mass balance in a water–macrophyte–sediment system (see Section 2.2.4). For Z -, D -values and other parameters see Tables S1 and S2.

Coeff.	Explanation	Equation
a	Water to macrophytes	$(D_{W_Mf} + D_{TSP_Mf}) / (V_W * Z_{Wbulk})$
b	Losses for macrophytes	$(D_{Deg_Mf} + D_{Mf_W} + D_{Mf_TSP} + D_{Mf_DOM} + D_{lfail}) / (V_{Mf} * Z_{Mf})$
c	Sources for water	$Discharge + G_I * C_I + FugAir * (D_V + D_M + D_C + D_Q)$
d	Macrophytes to water	$D_{Mf_W} / (V_{Mf} * Z_{Mf})$
e	Sediment to water	$(D_T + D_{S_TSP}) / (V_S * Z_{Sbulk})$
g	Losses for water	$(D_V + D_W + D_J + D_T + D_{W_Mf} + D_{TSP_Mf} + D_{W_Phyto1} + D_{W_Phyto2} + D_{Out_TSP} + D_{Out_DOM} + D_{TSP_S}) / (V_W * Z_{Wbulk})$
h	Sources for sediment	$Starting\ contamination$
i	Water to sediment	$(D_T + D_{TSP_S}) / (V_W * Z_{Wbulk})$
j	Losses for sediment	$(D_S + D_{S_TSP} + D_B + D_T) / (V_S * Z_{Sbulk})$

ponds and ditches (see Sections 2.3.2 and 3.2) and the description of peculiar sub-environments in water bodies (e.g., presence/absence of macrophytes, and content of TSP or DOM). In the present version of ChimERA fate, no vertical discretization of the water compartment was included since the model was designed to deal with shallow-water systems (1 m or less), where stratification phenomena due to temperature or density can be neglected and water can be assumed as “well mixed” in the vertical direction.

2.3. Model parameterization

2.3.1. Model evaluation

A model evaluation was performed for ChimERA fate in order to assess model performance against experimental observations for three case studies differing in applied chemical and environmental system characteristics (Knuth et al., 2000; Leistra et al., 2003; Armitage et al., 2008). Such effort, following the terminology introduced in a recent paper by Augusiak et al. (2014), can be considered as a “model output verification”, which implies the critical assessment of how well model output matches observations and of the degree of calibration necessary to obtain a good fit between model output and data. For this purpose, ChimERA fate was parameterized by selecting values for the environmental parameters (e.g., water volumes, sediment depth, vegetation biomass and characteristics, and TSP and DOM concentrations) equal to the ones characterizing the experimental systems (Knuth et al., 2000; Leistra et al., 2003), as also done by Armitage et al. (2008) for testing their modelling approach. More details on model parameterization are reported in Text S4. Model performance was assessed by means of calculating the modelling efficiency (EF; Mayer and Butler, 1993), a dimensionless statistics which directly relates model predictions to observations:

$$EF = 1 - \frac{\sum (y_i - \hat{y}_i)^2}{\sum (y_i - \bar{y})^2} \quad (4)$$

where y_i are observations, \hat{y}_i are predictions and \bar{y} is the average of observations. For such statistic, the “perfect fit” results in 1, and the degree of fit declines as it falls away from 1. EF between 0 and 1 still indicates good model performance, while negative values could indicate model bias or need for model re-calibration (Mayer and Butler, 1993).

2.3.2. Model illustration

One-year simulations were performed for four chemicals in a macrophyte-dominated spatially-resolved system in order to illustrate the potential of the ChimERA fate model in predicting concentration variability in response to spatio-temporal environmental heterogeneity. The system was composed of a 450-m², 50-cm deep (maximum depth) pond overlaying a 1-cm deep sediment compartment connected to its 10-cm deep and 1-m wide inflow and outflow streams and was split into 10 adjacent boxes along the water flow direction (Fig. 1b and c). A constant water flow was selected to obtain an average residence time in the pond boxes of about 20 days. The modelled chemicals were a herbicide (atrazine), a polycyclic aromatic hydrocarbon (pyrene) and two polychlorinated biphenyls (PCB 1 and PCB 153), selected in order to cover a range of $\log K_{OW}$ and environmental half-lives, which is wide enough to allow investigating the influence of such properties on bioavailable concentrations (Table S5). Realistic information on macrophyte biomass, POC and DOC concentrations (Fig. S1a) and water temperature (Fig. S1b) was derived from the literature (de Figueiredo et al., 2006; Parszuto and Kaliszewska, 2007; Desmet et al., 2011). It should be remarked that no effort was made to simulate a specific environmental situation and that the present scenario was adopted for illustration purposes only, since time-resolved data concerning macrophyte biomass densities, POC/DOC concentrations and other environmental parameters are often lacking for a single environmental system.

In order to investigate the influence of the different organic phases (macrophytes, POC and DOC) on bioavailable concentrations, the model was run using four scenarios accounting for different biomass and POC/DOC conditions: the first one (“A”) included all phases, “B” excluded macrophytes and accounted for POC and DOC only, “C” included DOC only, while in scenario “D” no organic phases (except for the organic carbon fraction of sediment) were simulated. In addition, three different exposure scenarios characterized by pulsed emissions were adopted in order to illustrate (1) the influence of biomass, POC and DOC dynamics on levels and temporal variability of bioavailable concentrations (three pulses, scenario “Em1”), (2) the influence of organic phases on bioavailable concentration trends in space (one pulse, scenario “Em2”) and (3) the added role of simulating biomass, POC and DOC dynamics when assessing exposure concentrations (four pulses, scenario “Em3”). The same emission profiles were adopted for all chemicals. The relationships between exposure and biomass/POC/DOC scenarios are depicted in Fig. S2. More details on model parameterization are reported in Text S4.

3. Results and discussion

3.1. Model evaluation

The results of the comparison between ChimERA fate predictions and experimental observations for Case 1 are presented in Fig. 2, while the ones for Cases 2 and 3 are reported in SI (Figs. S4 and S5, respectively).

While for Cases 1 and 2 chemical inventories of the different compartments were compared expressed as percentage of the applied dose, for Case 3 the comparison was based on concentrations. Model calibration concerned (1) particle deposition velocity, for which the best fit was obtained at 0.5 m d⁻¹ (value in the range of those suggested in the literature; e.g., Schwarzenbach et al., 2003; Mackay, 2001), and (2) the water-sediment diffusion mass transfer coefficient (MTC), for which a value 5 times higher the default one (i.e., $1 \cdot 10^{-4}$ m h⁻¹; Morselli et al., 2014) was finally adopted.

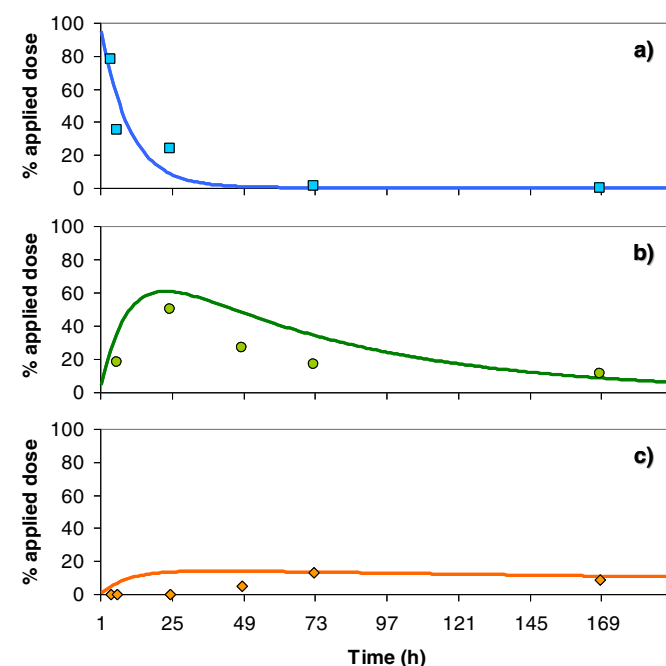


Fig. 2. Results of the model output verification for water (a), macrophytes (b), and sediment (c): Case 1 (lambda-cyhalothrin, high vegetation; Leistra et al., 2003; Armitage et al., 2008). Lines represent model predictions, while markers depict experimental observations.

Concerning Cases 1 and 2, simulations indicated an excessively rapid chemical transport from water to macrophytes and sediment in both cases, which led to a general overestimation of concentrations in these two compartments (charts b and c). Such overestimation was particularly evident for Case 2 (lambda-cyhalothrin, low vegetation biomass), at least in the first 25–50 h ($EF < 0$ for macrophytes and sediment). However, predictions were generally within an order of magnitude with respect to observations and, especially in Case 1, overprediction in macrophytes was only moderate (within a factor of 2). Dominant fluxes were particle deposition onto macrophyte and sediment surfaces (at least two orders of magnitude higher than the other losses for the water compartment; results not shown). This confirmed the importance of TSP concentrations and deposition velocity on exposure levels revealed by the sensitivity analysis for the more hydrophobic chemical (Fig. S3b). Armitage and co-workers ascribed the poor representation of the uptake of lambda-cyhalothrin by sediment in the first 1–2 days to two factors: (1) the assumption that the contaminant immediately became well-mixed in the water column and (2) the assumption of equifugacity between suspended solids and water (Armitage et al., 2008). Our simulations confirmed such hypotheses, since looking at the calculated chemical fluxes a fast particle-mediated deposition onto sediment (and macrophyte leaves) immediately after dosing was observed, also due to the high $\log K_{OW}$ of lambda-cyhalothrin. Results for Cases 1 and 2 suggested that, at least for highly hydrophobic chemicals, an accurate model parameterization in terms of suspended solid concentration and deposition velocity could be vital to obtain accurate results. They also suggested that the simulation of suspended solids as a separate compartment (instead of water sub-compartment) could avoid the initial overestimation of deposition fluxes to macrophytes and sediment. This will be the object of future work.

From the simulations for azinphos-methyl (Case 3) (Fig. S5) a different picture appeared. Results revealed a good model performance, at least for water and macrophytes (within a factor of 1.5 or less, with $EF_W = 0.92$ and $EF_{Mf} = 0.96$). The fit was lower for sediment, but nevertheless satisfying ($EF = 0.35$). Given the lower $\log K_{OW}$ of azinphos-methyl with respect to lambda-cyhalothrin (2.75 vs. 7), particle-mediated deposition processes were less important, and degradation in water was the dominant flux in determining chemical depletion from water (results not shown). However, the poorer fit for sediment suggested that more data concerning the physical environment (e.g., sediment properties with depth) and water-sediment exchange in the investigated system may be needed to improve model performance. In all cases, the lack of depth-related input data and concentrations in the studied systems led to the application of ChimERA fate considering one sediment layer only. This evaluation process indicated, however, a satisfying model performance, with an agreement between predictions and observations that in many cases was within a factor of 2 for all compartments.

3.2. Model illustration

3.2.1. Influence of compound properties on exposure levels

The first set of illustrative simulations was run using the exposure scenario “Em1” (three chemical pulses) and investigating all biomass/POC/DOC scenarios (“A” to “D”). This allowed assessing the influence of physical-chemical properties and half-lives on predicted concentrations in different ecological conditions. Some preliminary considerations can be derived from Fig. 3, where the water-dissolved concentrations (“WD conc.”, mol m^{-3}) of the modelled chemicals in three locations of the investigated system predicted using scenario “A” are reported. For comparative reasons, concentrations for all chemicals were reported in mol m^{-3} . The selected locations were Box 1 (1st box of the inflow stream, where emission occurred), Box 3 (1st box of the pond, representative, in terms of morphology, of “littoral” conditions) and Box 5 (middle box of the pond, representative of “pelagic” conditions).

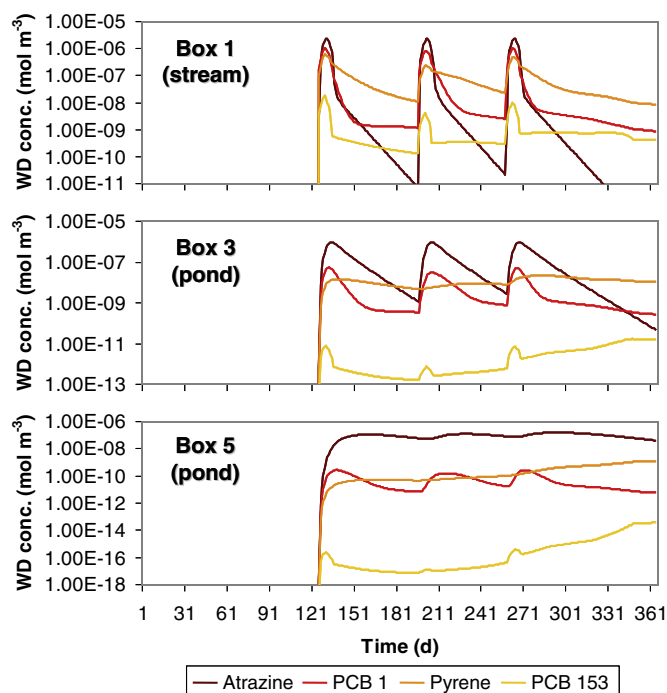


Fig. 3. Water-dissolved concentrations (“WD conc.”, mol m^{-3}) of the modelled chemicals in three locations of the investigated system: Box 1 (stream, where emission occurred), Box 3 (1st box of the pond) and Box 5 (middle box of the pond). Predictions are reported for the biomass/POC/DOC scenario “A”. y axis is in log scale.

In Box 1, the highest peak concentrations were predicted for atrazine ($2.3 \cdot 10^{-6} \text{ mol m}^{-3}$), followed by PCB 1 ($8 \cdot 10^{-7}$ to $1 \cdot 10^{-6} \text{ mol m}^{-3}$), pyrene ($2.2 \cdot 10^{-7}$ to $5.9 \cdot 10^{-7} \text{ mol m}^{-3}$) and PCB 153 ($3.8 \cdot 10^{-9}$ to $1.7 \cdot 10^{-8} \text{ mol m}^{-3}$). Such discrepancies were related to the differences in physical-chemical properties (mainly solubility, vapour pressure and $\log K_{OW}$) of the modelled compounds (Table S5). For example, the higher atrazine water-dissolved levels were due to its low $\log K_{OW}$ (2.5), which explained its reduced sensitivity to the presence of macrophytes and POC/DOC. This appears to be in contrast with a number of experimental evidences which showed that also atrazine can experience rapid removal in the presence of vegetation (e.g., Alvord and Kadlec, 1996; Moore et al., 2000). This behaviour was generally ascribed to enhance reaction in biofilms and would suggest the need for the inclusion of a biofilm/periphyton compartment in a modelling approach such as ChimERA fate. However, the non-detectable levels in macrophytes observed by Moore et al. (2000) indicate that the negligible influence of aquatic vegetation predicted by ChimERA fate for atrazine was plausible. In contrast, the effect of organic phases on more hydrophobic chemicals (especially pyrene and PCB 153) was more pronounced, and concentrations were lower than atrazine ones by 1 to 3 orders of magnitude (Fig. 3). This was confirmed by investigating chemical losses from the water compartment, reported in Fig. S6 for Box 1. While for atrazine the dominant loss was outflow with water (maximum flux = $1.35 \cdot 10^{-7} \text{ mol h}^{-1}$), followed by definitely lower diffusion to sediment, particle deposition and diffusion to macrophytes (maximum $\sim 2 \cdot 10^{-9} \text{ mol h}^{-1}$), for PCB 1 volatilization, particle deposition and diffusion to macrophytes were as important as outflow with water. For pyrene, losses were dominated by transfer to macrophytes (mainly particle-mediated), followed by outflow with water and particle deposition to sediment, while PCB 153 mainly left water by particle deposition to macrophytes and sediment, and outflow mainly occurred through DOM and TSP. The dominant role of particle-mediated chemical deposition on macrophyte surfaces for hydrophobic chemicals ($\log K_{OW} > 5.5$) has already been highlighted (Section 3.1 and Armitage et al., 2008). This process can be of particular importance considering the enhanced deposition and retention

of particulate matter occurring in vegetated aquatic environments (Elliot, 2000; Pluntke and Kozerski, 2003). Similar considerations on losses from water can be made for Boxes 3 and 5 (Fig. 3), for which however outflow with water was progressively less important (due to the higher residence time in such boxes) and, for the less persistent chemical (atrazine), degradation in water gradually increased (results for fluxes not shown).

The higher influence of organic phases on exposure levels of hydrophobic chemicals was also evident from results for scenarios “B” to “D” (Figs. S7–S10). Such consideration can be easily deduced from the temporal trends of bioavailable concentrations predicted in the three boxes for all chemicals and biomass/POC/DOC scenarios. When macrophytes (“B”), POC (“C”) and DOC (“D”) were neglected, atrazine concentrations were not affected substantially (Fig. S7). For PCB 1, peak concentrations only slightly changed, while discrepancies between scenarios were more evident after emission pulses, when chemical release from macrophytes and POC resuspension with TSP contributed to increase concentrations with respect to scenarios “C” and “D” (DOC only and no organic phases, respectively) of about 1 order of magnitude (Fig. S8). Pyrene concentrations were much more influenced by changes in organic phases' presence and abundance, and the discrepancy between “A” and “B” (all organic phases and POC + DOC, respectively) with respect to “C” and “D” increased with increasing distance from Box 1, where the chemical was emitted (Fig. S9). This was caused by the lower importance of chemical transport by water (due to the higher water residence time) while moving from stream (Box 1) to “pelagic” (Box 5) conditions. As a consequence, macrophytes and POC became more efficient in sequestering pyrene from water. For PCB 153, DOC was also important, and the comparison between scenarios “C” and “D” (especially for Box 5) suggested that this phase was capable of retaining more chemical in the water compartment with respect to the simulation with no organic phases, competing with transport to sediment and other loss processes (Fig. S10).

3.2.2. Exposure variations in time

From Fig. 3 and the stream conditions (Box 1), it can be deduced that emission pulses of the same entity were able to cause temporal variations in exposure levels. Such variations became more important with increasing chemical $\log K_{OW}$ and were related to the seasonal dynamics of the modelled organic phases (Fig. S1). For example, while for atrazine peak concentrations were substantially unvaried, the higher macrophyte density (and, therefore, exchange area) and POC/DOC concentrations in

July contributed to reduced bioavailable concentrations (with respect to the first peak) by a factor of 1.3 for PCB 1, 2.9 for pyrene and 4.5 for PCB 153. A similar temporal variability was also observed in the pond (Boxes 3 and 5) (Fig. 3) and for the scenario excluding macrophytes (“B”) (Figs. S8–S10), in which the reduction in the middle concentration peak was caused by the higher POC concentration and, consequently, by the increased amount of particle-bound chemical deposited to sediment. Finally, for PCB 153, DOC dynamics (scenario “C”) were also able to determine a temporal variability in exposure concentrations, which was up to a factor of 2.4 (Fig. S10). Despite the fact that large fluctuations in macrophyte biomass (and, consequently, of POC/DOC levels) are common in both natural and managed systems (Carpenter and Lodge, 1986), very few studies exist which explicitly addressed the effects of changes in ecologic conditions on the fate of hydrophobic organic compounds (Roessink et al., 2010). For this reason, given the fully-dynamic nature of the ChimERA fate model, it could represent a vital tool for the investigation of such relationships and for the planning of informative monitoring campaigns.

3.2.3. Exposure variations in space

In order to illustrate the potential spatial variability of exposure deriving from a pulsed chemical emission to the investigated system, simulations for all the modelled chemicals and biomass/POC/DOC scenarios (“A” to “D”) were performed using the simplified one-peak exposure scenario “Em2”. Results are depicted in Fig. 4 for pyrene and in Figs. S11–S13 for the other chemicals. In the figures, the spatial distribution of concentrations (mol m^{-3}) at four selected hours is reported using different colours; the first hour corresponds to the middle of the emission pulse, the following 2 h were selected with a 1600-h interval, while the last one represents the last simulation hour.

All chemicals experienced a decrease in concentrations in the transition between stream and pond conditions (from Boxes 2 to 3) of at least 1 order of magnitude. This effect can be partially ascribed to the dilution caused by the increased water volume (from about 0.8 m^3 in Box 2 to 11 m^3 in Box 3). In contrast, atrazine was the only chemical affected by the increase in concentrations due to the water volume reduction when returning from pond to stream conditions (from Boxes 7 to 8), since for all other chemicals the concentration effect caused by the decreased water volume (from about 11 m^3 in Box 8 to 0.9 m^3 in Box 9) was fully counterbalanced by the higher losses from water (due to volatilization, particle deposition to macrophytes and sediment, etc.). As already discussed, atrazine was poorly affected by the presence of

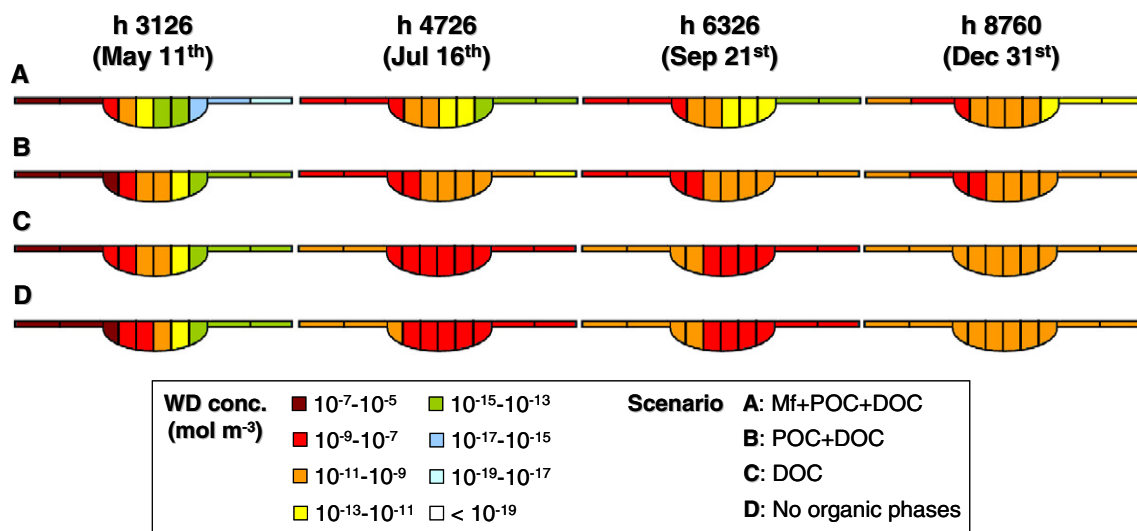


Fig. 4. Spatial distribution of pyrene water-dissolved concentrations (mol m^{-3}) during (h 3126) and after (h 4726, 6326 and 8760) the emission peak (exposure scenario “Em2”). Predictions for all biomass/POC/DOC scenarios (A–D) are reported. Water flux was from left to right.

organic phases, and for all scenarios a similar picture appeared, with highest concentrations progressively moving from the inflow stream (where emission occurred) towards the outlet of the system. However, even for such a hydrophilic chemical, exposure variability in space ranged from 4 to 12 orders of magnitude for all scenarios (Fig. S11). PCB 1 concentrations generally showed higher spatial variability during the first 2 h (6–10 orders of magnitude), which then decreased to 4–7 orders of magnitude (Fig. S12). Being more influenced by the presence of organic phases and given its high vapour pressure, a concentration wave was not visible for PCB 1 as for atrazine since it was retained (by macrophytes), deposited (with particles) and volatilized from the system. The reduction of exposure variability with time was much more evident for pyrene (Fig. 4), which experienced a progressive “homogenization” of concentrations with time (up to a variability of 1–2 orders of magnitude), with such process being faster in the absence of macrophytes and POC (“A” and “B”). Similar considerations can be made for PCB 153 (Fig. S13), for which spatial variability of exposure was the highest (up to 17 orders of magnitude), especially when accounting for all organic phases.

3.2.4. Why accounting for biomass and POC/DOC dynamics?

Further illustrative simulations were run to assess the potential added value of adopting a temporally dynamic biomass and POC/DOC concentrations with respect to a constant one. For this purpose, the exposure scenario “Em3”, characterized by an additional emission peak in mid February (when macrophyte biomass, POC and DOC were around their minimum; Fig. S2), was adopted. Fig. 5 reports the water-dissolved concentrations predicted for all chemicals using the dynamic scenario depicted in Fig. S1 (black lines) and the corresponding

constant scenario obtained by averaging water temperature, macrophyte biomass density and POC/DOC concentrations (red lines).

While for atrazine almost no differences were observed, the first two concentration peaks of all other chemicals were underestimated using the constant scenario. The level of underprediction was up to a factor of 1.3 for PCB 1, 3.8 for pyrene and even by more than one order of magnitude (factor 36) for PCB 153. This demonstrated the importance of accounting for environmental and biological dynamics such as seasonal variations in primary producer biomass and, consequently, POC/DOC levels, especially when dealing with hydrophobic chemicals ($\log K_{OW} > 5$).

4. Conclusions

The development and application of the new dynamic, spatially explicit model ChimERA fate allowed the assessment of (1) the influence of physical–chemical properties on exposure levels and variability and (2) the potential magnitude of exposure variability in space and time deriving from a pulsed emission in a natural system consisting of a pond and its inflow and outflow streams. In particular, it was observed that such variations can reach orders of magnitude in both space and time, and are higher for hydrophobic chemicals ($\log K_{OW} > 5$) and in the presence of primary producers and POC/DOC. The importance of accounting for biomass dynamics was also highlighted, suggesting the strong need for more time- and space-resolved datasets concerning both input data (e.g., organic phase properties and abundance) and chemical concentrations after static or pulsed emissions. This would also allow a more complete evaluation of the modelling approach presented here.

The crucial role of aquatic vegetation in influencing the fate and distribution of hydrophobic organic chemicals is evident from numerous laboratory and field studies (e.g., Hinman and Klaine, 1992; Karen et al., 1998; Hand et al., 2001; Moore et al., 2002; Rose et al., 2008; Roessink et al., 2010). The experiments conducted by Roessink and co-workers demonstrated the strong influence of aquatic vegetation on chemical fate also for sediment-bound organic compounds. For these reasons, future efforts will imply (1) the inclusion of periphyton and litter compartments, which can be crucial in determining chemical fate in lentic systems such as ponds or wetlands, where most of dead biomass remains in-place and enters the detrital pool (Kuehn et al., 2000; Chimney and Pietro, 2006) and (2) a description of the exchange between macrophytes and sediment. The implementation of a phytoplankton compartment, together with the exploration of exposure variability in a range of European-based scenarios, will be the object of future work. Moreover, in the framework of the new challenges devised for ERA (EC, 2013), the ChimERA fate model will be integrated with selected effect models and tested to explore the improved level of realism and the benefits deriving from such an approach (De Laender et al., 2014, 2015). The model developed here and the following integrated exposure-effects modelling approach could be valuable tools to assess and regulate the behaviour of chemicals in shallow-water systems.

Acknowledgments

The Chimera project is financed by the Long Range Initiative of CEFIC (www.cefic-lri.org) (project code: LRI-ECO19). Andreas Focks, from Alterra, Wageningen University and Research Centre (Wageningen, The Netherlands), is kindly acknowledged for the suggestions given at the first version of the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2015.04.072>.

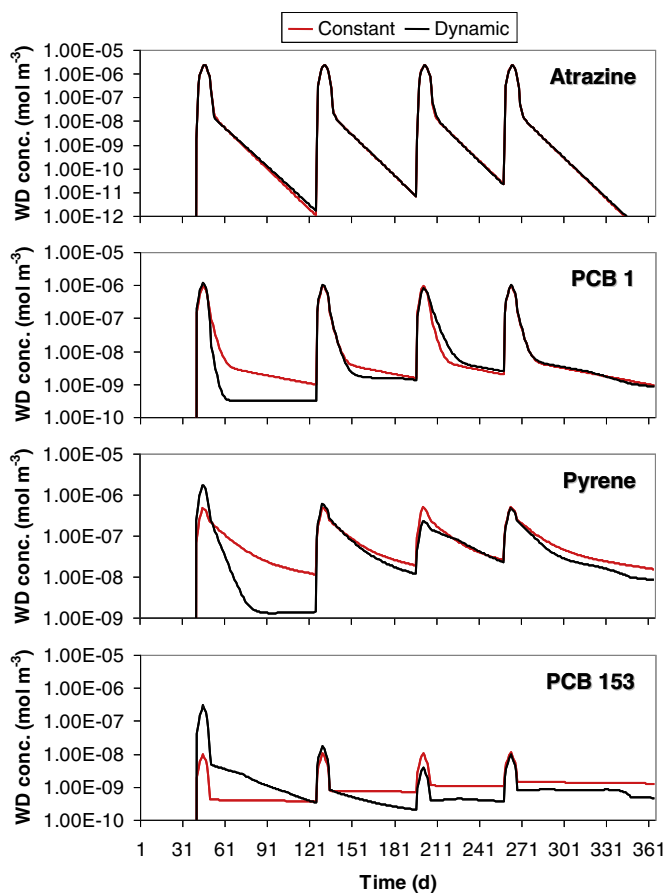


Fig. 5. Comparison between the water-dissolved concentrations (mol m^{-3}) predicted using the dynamic scenario depicted in Fig. S1 and the ones predicted using the corresponding constant scenario (exposure scenario “Em3”). y axis is in log scale.

References

- Adriaanse, P.I., 1997. Exposure assessment of pesticides in field ditches: the TOXSWA model. *Pestic. Sci.* 49, 210–212.
- Alvord, H.H., Kadlec, R.H., 1996. Atrazine fate and transport in the Des Plaines wetlands. *Ecol. Model.* 90, 97–107. [http://dx.doi.org/10.1016/0304-3800\(95\)00150-6](http://dx.doi.org/10.1016/0304-3800(95)00150-6).
- Armitage, J.M., Franco, A., Gomez, S., Cousins, I.T., 2008. Modeling the potential influence of particle deposition on the accumulation of organic contaminants by submerged aquatic vegetation. *Environ. Sci. Technol.* 42, 4052–4059. <http://dx.doi.org/10.1021/es702439u>.
- Augusiak, J., Van den Brink, P.J., Grimm, V., 2014. Merging validation and evaluation of ecological models to 'evaluation': a review of terminology and a practical approach. *Ecol. Model.* 280, 117–128. <http://dx.doi.org/10.1016/j.ecolmodel.2013.11.009>.
- Balbas, J., Karni, S., 2009. A central scheme for shallow water flows along channels with irregular geometry. *ESAIM: M2AN* 43, 333–351. <http://dx.doi.org/10.1051/m2an:2008050>.
- Berglund, O., Larsson, P., Ewald, G., Okla, L., 2001. Influence of trophic status on PCB distribution in lake sediment and biota. *Environ. Pollut.* 82 (4), 199–210. [http://dx.doi.org/10.1016/S0269-7491\(00\)00166-4](http://dx.doi.org/10.1016/S0269-7491(00)00166-4).
- Carpenter, S.R., Lodge, D.M., 1986. Effects of submersed macrophytes on ecosystem processes. *Aquat. Bot.* 26, 341–370.
- Chimney, M.J., Pietro, K.C., 2006. Decomposition of macrophyte litter in a subtropical constructed wetland in south Florida (USA). *Ecol. Eng.* 27, 301–321. <http://dx.doi.org/10.1016/j.ecoleng.2006.05.016>.
- de Figueiredo, D.R., Reboleira, A.S.S.P., Antunes, S.C., Abrantes, N., Azeiteiro, U., Gonçalves, F., Pereira, M.J., 2006. The effect of environmental parameters and cyanobacterial blooms on phytoplankton dynamics of a Portuguese temperate lake. *Hydrobiologia* 568, 145–157. <http://dx.doi.org/10.1007/s10750-006-0196-y>.
- De Laender, F., De Schampelaere, K.A.C., Vanrolleghem, P.A., Janssen, C.R., 2008. Validation of an ecosystem modelling approach as a tool for ecological effect assessment. *Chemosphere* 71, 529–545. <http://dx.doi.org/10.1016/j.chemosphere.2007.09.052>.
- De Laender, F., Van den Brink, P.J., Janssen, C.R., Di Guardo, A., 2014. The ChimERA project: coupling mechanistic exposure and effect models into an integrated platform for ecological risk assessment. *Environ. Sci. Pollut. Res.* 21, 6263–6267. <http://dx.doi.org/10.1007/s11356-014-2605-5>.
- De Laender, F., Morselli, M., Baveco, H., Van den Brink, P.J., Di Guardo, A., 2015. Theoretically exploring direct and indirect chemical effects across ecological and exposure scenarios using mechanistic fate and effects modelling. *Environ. Int.* 74, 181–190. <http://dx.doi.org/10.1016/j.envint.2014.10.012>.
- Desmet, N.J.S., Van Belleghem, S., Seuntjens, P., Bouma, T.J., Buis, K., Meire, P., 2011. Quantification of the impact of macrophytes on oxygen dynamics and nitrogen retention in a vegetated lowland river. *Phys. Chem. Earth* 36, 479–489. <http://dx.doi.org/10.1016/j.pce.2008.06.002>.
- Di Guardo, A., 2014. Environmental exposure assessment. In: Wexler, P. (Ed.), 3rd ed. *Encyclopaedia of Toxicology* vol. 2. Elsevier Inc., Academic Press, pp. 366–371.
- Di Guardo, A., Hermens, J.L.M., 2013. Challenges for exposure prediction in ecological risk assessment. *Integr. Environ. Assess. Manag.* 9 (3), e4–e14. <http://dx.doi.org/10.1002/ieam.1442>.
- Di Guardo, A., Ferrari, C., Infantino, A., 2006. Development of a Dynamic Aquatic Model (Dyna Model): estimating temporal emissions of DDT to Lake Maggiore (N. Italy). *Environ. Sci. Pollut. Res.* 13 (1), 50–58. <http://dx.doi.org/10.1065/espr2006.01.009>.
- EC (European Commission), 2003. Technical Guidance Document on Risk Assessment; Part II. European Chemical Bureau, Joint Research Centre, Ispra (Italy) (EUR 20418 EN/2). http://echa.europa.eu/documents/10162/16960216/tgdpart2_2ed_en.pdf.
- EC (European Commission), 2004. European Union System for the Evaluation of Substances 2.0 (EUSES 2.0). National Institute of Public Health and the Environment (RIVM), Bilthoven (the Netherlands) (Background report No.: 601900005/2004. <http://www.pbl.nl/sites/default/files/cms/publicaties/601900005.pdf>).
- EC (European Commission), 2013. Addressing the New Challenges for Risk Assessment. SCHER (Scientific Committee on Health and Environmental Risks), SCENIHR (Scientific Committee on Emerging and Newly Identified Health Risks), SCCS (Scientific Committee on Consumer Safety) (Mar. http://ec.europa.eu/health/scientific_committees/consumer_safety/docs/scscs_o_131.pdf).
- Elliot, A.H., 2000. Settling of fine sediment in a channel with emergent vegetation. *J. Hydraul. Eng.* 126 (8), 570–577. [http://dx.doi.org/10.1061/\(ASCE\)0733-9429\(2000\)126:8\(570\)](http://dx.doi.org/10.1061/(ASCE)0733-9429(2000)126:8(570)).
- EPA (U.S. Environmental Protection Agency), 1998. Guidelines for Ecological Risk Assessment. U.S. Environmental Protection Agency, Risk Assessment Forum, Washington (DC) (Apr. EPA/630/R-95/002F. <http://www.epa.gov/raf/publications/pdfs/ECOTXTBX.PDF>).
- FOCUS (Forum for Co-ordination of pesticide fate models and their Use), 2001. FOCUS surface water scenarios in the EU evaluation process under 91/414/EEC; rev. 2. FOCUS Working Group on Surface Water Scenarios (EC Document Reference SANCO/4802/2001).
- Gobas, F.A.P.C., McNeil, E.J., Lovett-Doust, L., Haffner, G.D., 1991. Bioconcentration of chlorinated aromatic hydrocarbons in aquatic macrophytes. *Environ. Sci. Technol.* 25 (5), 924–929. <http://dx.doi.org/10.1021/es00017a015>.
- Gordon, N.D., McMahon, T.A., Finlayson, B.L., Gippel, C.J., Nathan, R.J., 2004. *Stream Hydrology. An Introduction for Ecologists*. 2nd ed. Wiley, West Sussex (UK).
- Gustafsson, O., Haghseta, F., Chan, C., MacFarlane, J., Gschwend, P.M., 1997. Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability. *Environ. Sci. Technol.* 31, 203–209. <http://dx.doi.org/10.1021/es960317s>.
- Hand, L.H., Kuet, S.F., Lane, M.C.G., Maund, S.J., Warinton, J.S., Hill, I.R., 2001. Influences of aquatic plants on the fate of the pyrethroid insecticide lambda-cyhalothrin in aquatic environments. *Environ. Toxicol. Chem.* 20 (8), 1740–1745. [http://dx.doi.org/10.1897/1551-5028\(2001\)020-1740:IOAPOT>2.0.CO;2](http://dx.doi.org/10.1897/1551-5028(2001)020-1740:IOAPOT>2.0.CO;2).
- Hinman, M.L., Klaine, S.J., 1992. Uptake and translocation of selected organic pesticides by the rooted aquatic plant *Hydrilla verticillata* Royle. *Environ. Sci. Technol.* 26, 609–613. <http://dx.doi.org/10.1021/es00027a026>.
- Infantino, A., Pereira, T., Ferrari, C., Cerejeira, M.J., Di Guardo, A., 2008. Calibration and validation of a dynamic water model in agricultural scenarios. *Chemosphere* 70, 1298–1308. <http://dx.doi.org/10.1016/j.chemosphere.2007.07.047>.
- Infantino, A., Morselli, M., Di Guardo, A., 2013. Integration of a dynamic organism model into the DynA Model: development and application to the case of DDT in Lake Maggiore, Italy. *Sci. Total Environ.* 454–455, 358–365. <http://dx.doi.org/10.1016/j.scitotenv.2013.03.026>.
- Jeppesen, E., Søndergaard, M., Søndergaard, M., Christoffersen, K. (Eds.), 1998. *The Structuring Role of Submerging Macrophytes in Lakes*. Springer, New York.
- Karen, D.J., Joab, B.M., Wallin, J.M., Johnson, K.A., 1998. Partitioning of chlorpyrifos between water and an aquatic macrophyte (*Elodea densa*). *Chemosphere* 37 (8), 1579–1586. [http://dx.doi.org/10.1016/S0045-6535\(98\)00141-6](http://dx.doi.org/10.1016/S0045-6535(98)00141-6).
- Knuth, M.L., Heinis, L.J., Anderson, L.E., 2000. Persistence and distribution of azinphosmethyl following application to littoral enclosure mesocosms. *Ecotoxicol. Environ. Saf.* 47, 167–177. <http://dx.doi.org/10.1006/eesa.2000.1945>.
- Kuehn, K.A., Lemke, M.J., Suberkropp, K., Wetzel, R.G., 2000. Microbial mass and production associated with decaying leaf litter of the emergent macrophyte *Juncus effusus*. *Limnol. Oceanogr.* 45, 862–870. <http://dx.doi.org/10.4319/lo.2000.45.4.0862>.
- Leistra, M., Zweers, A.J., Warinton, J.S., Crum, S.J.H., Hand, L.H., Beltman, W.H.J., Maund, S.J., 2003. Fate of the insecticide lambda-cyhalothrin in ditch enclosures differing in vegetation density. *Pest Manag. Sci.* 60, 75–84. <http://dx.doi.org/10.1002/ps.780>.
- Mackay, D., 2001. *Multimedia Environmental Models: The Fugacity Approach*. 2nd ed. Lewis Publishers, Boca Raton (FL).
- Mayer, D.G., Butler, D.G., 1993. Statistical validation. *Ecol. Model.* 68, 21–32. [http://dx.doi.org/10.1016/0304-3800\(93\)90105-2](http://dx.doi.org/10.1016/0304-3800(93)90105-2).
- Moore, M.T., Rodgers, J.H., Cooper, C.M., Smith, S., 2000. Constructed wetlands for mitigation of atrazine-associated agricultural runoff. *Environ. Pollut.* 110, 393–399. [http://dx.doi.org/10.1016/S0269-7491\(00\)00034-8](http://dx.doi.org/10.1016/S0269-7491(00)00034-8).
- Moore, M.T., Schulz, R., Cooper, C.M., Smith Jr., S., Rodgers Jr., J.H., 2002. Mitigation of chlorpyrifos runoff using constructed wetlands. *Chemosphere* 46 (6), 827–835. [http://dx.doi.org/10.1016/S0045-6535\(01\)00189-8](http://dx.doi.org/10.1016/S0045-6535(01)00189-8).
- Morselli, M., Semplice, M., Villa, S., Di Guardo, A., 2014. Evaluating the temporal variability of concentrations of POPs in a glacier-fed stream food chain using a combined modeling approach. *Sci. Total Environ.* 493, 571–579. <http://dx.doi.org/10.1016/j.scitotenv.2014.05.150>.
- Nfon, E., Armitage, J.M., Cousins, I.T., 2011. Development of a dynamic model for estimating the food web transfer of chemicals in small aquatic ecosystems. *Sci. Total Environ.* 409, 5416–5422. <http://dx.doi.org/10.1016/j.scitotenv.2011.08.070>.
- Park, R.A., Clough, J.S., Wellman, M.C., 2008. AQUATOX: modeling environmental fate and ecological effects in aquatic ecosystems. *Ecol. Model.* 213, 1–15. <http://dx.doi.org/10.1016/j.ecolmodel.2008.01.015>.
- Parszuto, K., Kaliszewska, E.A., 2007. The evaluation of the trophy of selected Olsztyn lakes by means of indices of particulate organic carbon (POC) and dissolved organic carbon (DOC). *Limnol. Rev.* 7 (2), 87–93.
- Pluntke, T., Kozerski, H.P., 2003. Particle trapping on leaves and on the bottom in simulated submerged plant stands. *Hydrobiologia* 506, 575–581. <http://dx.doi.org/10.1023/B:HYDR.0000008569.29286.ec>.
- Renaud, F., Bellamy, P.H., Brown, C.D., 2008. Simulating pesticides in ditches to assess ecological risk (SPIDER): I. Model description. *Sci. Total Environ.* 394, 112–123. <http://dx.doi.org/10.1016/j.scitotenv.2007.11.038>.
- Roessink, I., Moermond, C.T.A., Gillissen, F., Koelmans, A.A., 2010. Impacts of manipulated regime shifts in shallow lake model ecosystems on the fate of hydrophobic organic compounds. *Water Res.* 44, 6153–6163. <http://dx.doi.org/10.1016/j.watres.2010.07.013>.
- Rose, M.T., Crossan, A.N., Kennedy, I.R., 2008. The effect of vegetation on pesticide dissipation from ponded treatment wetlands: quantification using a simple model. *Chemosphere* 72, 999–1005. <http://dx.doi.org/10.1016/j.chemosphere.2008.04.059>.
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2003. *Environmental organic chemistry*. 2nd ed. Wiley, Hoboken (NJ).
- Semplice, M., Ghirardello, D., Morselli, M., Di Guardo, A., 2012. Guidance on the selection of efficient computational methods for multimedia fate models. *Environ. Sci. Technol.* 46, 1616–1623. <http://dx.doi.org/10.1021/es201928d>.
- Taylor, W.B., Carey, J.H., Lean, D.R.S., McQueen, D.I., 1991. Organochlorine concentrations in the plankton of lakes in southern Ontario and their relationship to plankton biomass. *Can. J. Fish. Aquat. Sci.* 48, 1960–1966. <http://dx.doi.org/10.1139/f91-233>.
- Vighi, M., 2013. New challenges for ecological risk assessment. *Integr. Environ. Assess. Manag.* 9 (3), e1–e3. <http://dx.doi.org/10.1002/ieam.1422>.