



Development of a dynamic model for estimating the food web transfer of chemicals in small aquatic ecosystems

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ABSTRACT

A dynamic combined fate and food web model was developed to estimate the food web transfer of chemicals in small aquatic ecosystems (i.e. ponds). A novel feature of the modeling approach is that aquatic macrophytes (submerged aquatic vegetation) were included in the fate model and were also a food item in the food web model. The paper aims to investigate whether macrophytes are effective at mitigating chemical exposure and to compare the modeling approach developed here with previous modeling approaches recommended in the European Union (EU) guideline for risk assessment of pesticides. The model was used to estimate bioaccumulation of three hypothetical chemicals of varying hydrophobicity in a pond food web comprising 11 species. Three different macrophyte biomass densities were simulated in the model experiments to determine the influence of macrophytes on fate and bioaccumulation. Macrophytes were shown to have a significant effect on the fate and food web transfer of highly hydrophobic compounds with $\log K_{OW} > 5$. Modeled peak concentrations in biota were highest for the scenarios with the lowest macrophyte biomass density. The distribution and food web transfer of the hypothetical compound with the lowest hydrophobicity ($\log K_{OW} = 3$) was not affected by the inclusion of aquatic macrophytes in the pond environment. For the three different hypothetical chemicals and at all macrophyte biomass densities, the maximum predicted concentrations in the top predator in the food web model were at least one order of magnitude lower than the values estimated using methods suggested in EU guidelines. The EU guideline thus provides a highly conservative estimate of risk. In our opinion, and subject to further model evaluation, a realistic assessment of dynamic food web transfer and risk can be obtained using the model presented here.

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1. Introduction

Several models for assessing the uptake, fate and distribution of organic chemicals in food webs have been developed (e.g. Clark et al., 1990; Thomann et al., 1992; Gobas, 1993; Morrison et al., 1996; Nfon and Cousins, 2007). Common features in these models are (i) their general applicability to large ecosystems and (ii) the use of a steady-state assumption. These steady-state models however are not appropriate for predicting the fate and food web uptake of chemicals in small aquatic ecosystems where emissions are often periodic (e.g. in the case of pesticides; Crossland, 1982; Rand and Clark, 2000), and chemical levels therefore fluctuate substantially over time.

Carbonell et al. (2000) addressed some of these concerns when they developed a simple, generic and dynamic (time dependent or unsteady-state) food web model. They demonstrated that bioaccumulation becomes important for hydrophobic chemicals even if the chemical is only moderately persistent. The approach of Carbonell et al. (2000) has gained acceptance at the European level for registration

of pesticides by being incorporated into the Aquatic Guidance Document on Aquatic Ecotoxicology as a higher tier study in the context of the Directive 91/414/EEC (EU 2002).

There is interest among regulators, the agrochemical industry and researchers in the ability of aquatic vegetation (macrophytes) to mitigate against chemical exposure (e.g. Maund et al., 2002; Bouldin et al., 2004). Apart from playing a vital role in aquatic ecosystems as primary producers at the base of aquatic food webs, macrophytes may reduce the dispersion and assist the removal of chemical from aquatic environments by sorbing residues or trapping particulate containing chemicals (Hinman and Klaine, 1992; Karen et al., 1998) and thus limiting the ability of the chemical for aquatic transport or uptake from the water-phase (reducing the exposure of aquatic animals). Aquatic plants have also been shown to enhance the overall degradation of chemical residues facilitating the irreversible removal of toxic compounds from contaminated water bodies (Muir et al., 1985; Hand et al., 2001). Armitage et al. (2008) developed and applied a fugacity-based model to describe the fate of chemicals in small ponds and specifically their mass transfer to macrophytes. They concluded that uptake by macrophytes is particularly strong for hydrophobic chemicals ($\log K_{OW} > 5.5$), where the mass transfer is dominated by particle deposition.

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This study describes a dynamic food web model for studying the food web transfer of chemicals in small-scale ecosystems such as ponds, streams, ditches or mesocosms. It represents a logical extension of the work of Carbonell et al. (2000) because (i) uptake/elimination parameters are derived from chemical properties using similar approaches used in large-scale steady state food web models (ii) the transfer of chemical residues between environmental compartments and biota is explicitly calculated using the fugacity concept (iii) aquatic macrophytes are included as component of the aquatic ecosystem and as a food item for food web species and (iv) a realistic pond food web is modeled. The paper aims to investigate whether macrophytes are effective at mitigating chemical exposure and to compare the modeling approach developed here with the previous modeling approaches recommended in the aforementioned EU guidance document, including the approach of Carbonell et al. (2000).

2. Methods

The general structure of the model consists of a chemical fate module linked to a food web bioaccumulation model representative of a generic pond ecosystem.

2.1. Pond fate model

The pond fate model is represented by three compartments (water, sediment and submerged vegetation) and has been previously described in Armitage et al. (2008). The water compartment is modeled as three phases (water, suspended solids and dissolved organic matter); the sediment compartment comprises two phases (pore water and sediment solids) and the submerged vegetation is modeled as a single phase. The model uses the fugacity concept (Mackay, 2001). The different methods used to calculate fugacity capacities (Z-values) (mol m⁻³ Pa⁻¹) and transport D-values (mol Pa⁻¹ h⁻¹) are explained in full in Armitage et al. (2008).

Three differential equations representing the mass distribution (or fugacity) of the chemical in the pond were generated in fugacity format as:

$$V_W Z_W df_W/dt = f_S D_{SW} + f_M D_{MW} - f_W D_{TW} \tag{1}$$

$$V_S Z_S df_S/dt = f_W D_{WS} + f_M D_{MS} - f_S D_{TS} \tag{2}$$

$$V_M Z_M df_M/dt = f_W D_{WM} + f_S D_{SM} f_M D_{TM} \tag{3}$$

where V, Z, f and D are the volumes (m³), fugacity capacities (mol m⁻³ Pa⁻¹), fugacities (Pa), and the fugacity transport coefficients or D-values (mol Pa⁻¹ h⁻¹), respectively, the subscripts W, S and M refer to the water, sediment and macrophyte compartments and the subscripts on the D-values refer to different D-values for intermedia transport (W, S and M again refer to water, sediment and macrophytes, thus D_{SW} refers to intermedia transport from sediment to water and so on) and total loss (i.e. D_{TW} refers to the total loss D value for the water compartment which comprises several processes; degradation, volatilisation, diffusive and particulate deposition to sediments and macrophytes).

A solution of the system of equations is generated by numerical integration (with initial conditions f_S = f_M = 0 and f_W = C_{W0}/Z_W) and the output is the change in fugacity with time for each compartment in the modeled system. C_{W0} is the concentration in the system following an initial pulse release of chemical. With modification, the model can be used to model other emission scenarios such as continuous steady inputs or time-varied inputs. Full details of the pond fate model are given in Armitage et al. (2008).

2.2. Pond food web model

The pond food web model comprises five trophic levels of 11 guilds (see Fig. 1). Defining guilds rather than specific organisms was preferred because it allows a more generic representation of the pond ecosystem. The food web is representative of a typical pond food web, but the selection of number/type of species and guilds is arbitrary. The food web modeling approach is based on the model developed by Campfens and Mackay (1997) using the fugacity approach of Mackay (2001) with the main difference that the model is dynamic (concentrations can be calculated as a function of time) rather than steady-state. Eleven equations of the form of Eq. (4) describing the fugacity of each species in the food web were generated

$$V_i Z_i df_i/dt = \sum (D_{Aji} f_j) + D_{Vi} (f_W \cdot X_{Wi} + f_S \cdot X_{Si}) - D_{Ti} f_i \tag{4}$$

where i can be any one of eleven species; V is volume, f is fugacity and Z is fugacity capacity, D_{Aji} is the food uptake D-value to species i

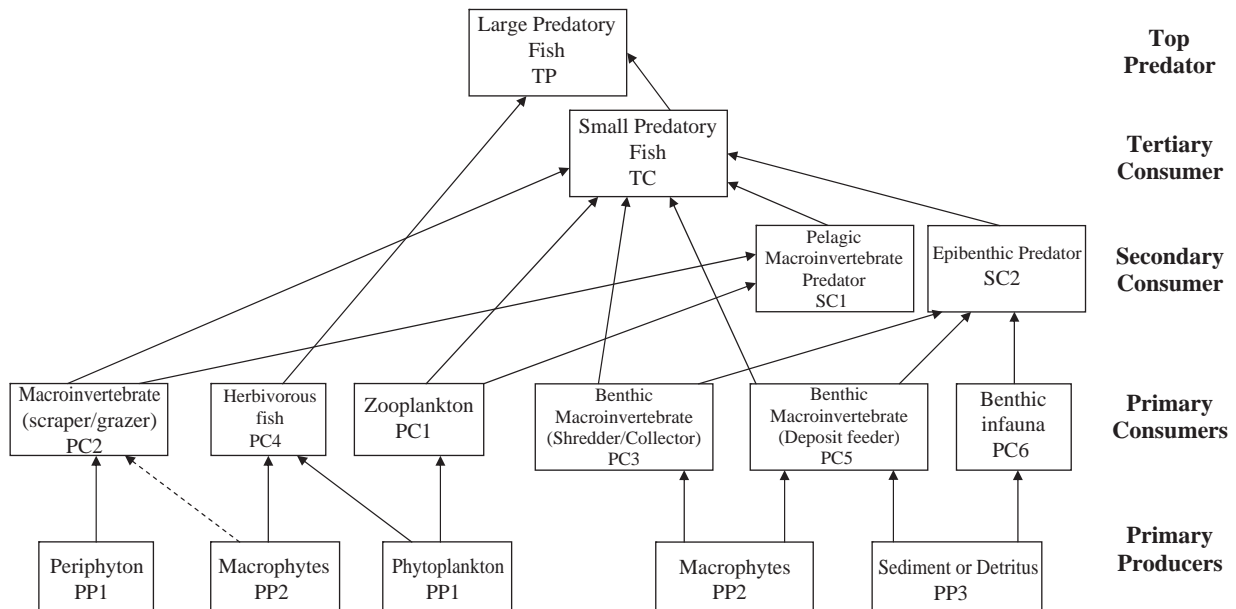


Fig. 1. Pond food web structure showing representative species in the different trophic levels. The arrows indicate feeding relationships.

occurring from consumption of species j in the food web, D_{vi} is the respiration D -value, x_{wi} and x_{si} are the proportion of water column water and sediment pore-water respired by organism i . D_{Ti} is the sum of the loss D -values for organism i (includes respiration, egestion, metabolism and growth dilution). A full description of the methods used to estimate Z - and D -values for the food web model is given in the Supplementary content.

The abiotic fugacities generated from Eqs. (1)–(3) are used as input to drive the food web model to give fugacities or concentrations in species as a function of time (Eq. (4)), thus quantifying the time response characteristics of the system. Mass balance checks were performed on the chemical in the model compartments and no mass leakage was observed.

The combined fate and food web model was implemented in Microsoft Office Excel® (Visual Basic for Applications (VBA) 6.5® v.1053). Integration was performed using a simple Euler method programmed in VBA, which proved to be mathematically stiff (stable) for all model simulations conducted. To ensure stability an integration time step was chosen that was 5% of the shortest half-time for transport and transformation and the stability of the result checked by decreasing the time step systematically as described in Mackay (2001). The equations included in the Supplementary content allow implementation of the model in any model platform. The model and model code are freely available from the corresponding author on request.

2.3. Pond environmental characteristics

Required parameters for the hypothetical pond were either assumed or obtained from the literature. Parameters included compartment surface area (m^2) and depth (m), fraction of organic carbon and the concentration of particulates in water (g particulates m^{-3}), volume of water, sediment and submerged vegetation (m^3) leaf area index (LAI) (m^2 leaf m^{-2} water) and area of vegetation (m^2). A summary of the input parameters used for the model simulations are presented in Table S3 in the Supplementary content. The parameters are also explained in more detail in the original publication of the pond model (Armitage et al., 2008).

2.4. Physical–chemical properties of hypothetical chemicals

Several physical chemical properties are required to run the pond fate and food web models in tandem. Key properties specific to the pond fate model include for example the octanol–water partition coefficient (K_{OW}) and the first-order degradation rate constants (water, sediment and aquatic macrophytes). The pond fate model also requires the loading of chemical as a pulse input at time zero.

We chose to assess hypothetical rather than specific chemicals primarily to avoid the uncertainty and controversy associated with selecting degradation rate constants, which can be highly variable depending on actual field conditions. We modeled three hypothetical chemicals (CHEM1, CHEM2 and CHEM3) which were assigned different hydrophobicities (i.e. $\log K_{OW}$ was set at 3 for CHEM1, 5 for CHEM2 and 7 for CHEM3). The degradation and metabolism half-lives for the three hypothetical chemicals were set at 55,000 h (6.3 yr) in all media/species i.e. all chemicals were considered to be highly persistent. Although we are aware that for modern pesticides the assumption of high persistence is not always representative, it helps (i) ensure that differences in fate and food web uptake for the three chemicals are dependent only on variability in hydrophobicity and (ii) gives us a worst-case of biomagnification in the food web model that can be compared to the worst-case calculation used in the EU guidelines (see Section 3.2). It should be noted that the model can also be used to simulate real, as well as hypothetical, chemicals that do degrade (e.g. modern pesticides). The representative physical–chemical property data for the hypothetical chemicals required to run the model are summarized in Table S4 in the Supplementary content.

Furthermore, to investigate the effects of the assumed degradation rate constants on the observed fate of the selected chemicals, we also performed a series of simulations with degradation rate constants of 55 h, 550 h and 1700 h in all abiotic media (using the same K_{OW}).

2.5. Food web structure

Feeding relationships among the 11 representative species (Fig. 1) were estimated based on the known behavior of the types of species within each guild in the food web and macrophytes were included as a food item for some species (See Table S5 and Table S6 in the Supplementary content). Feeding rates and growth rates are typical values for the different trophic positions based on Campfens and Mackay (1997). The fractional respiration from water was set as 1.0 for species respiring exclusively in water, zero for species respiring exclusively in pore water or as a fraction (i.e. between 0 and 1.0) for species migrating between the water column and sediment (see Table S7 in the Supplementary content).

2.6. Model application

The model was applied to simulate the fate of the three hypothetical chemicals in a pond with varying macrophyte biomass densities. We consider three scenarios; a high biomass density (0.145 kg dry m^{-2} water, see Leistra et al., 2003); low biomass density (0.045 kg dry m^{-2} water, see Knuth et al., 1992, 2000) and medium biomass density (0.08 kg dry m^{-2} water, geometric mean of the high and low biomass densities).

In all simulations, a fixed pulse of 1 g of the hypothetical chemical was emitted into the pond assuming the three different biomass densities. The output of interest was the modeled concentrations of the compounds in water, sediment, macrophytes and all species over the length of the simulation (30 days).

2.7. Model sensitivity analysis

A sensitivity analysis of the fate model was carried out to assess the effect of variation in individual input model parameters on key model output. The predicted water concentration (after 5, 10 and 30 days of simulation) was selected as the output to be monitored. A wide range of model input parameters (see Table S3 and S4 in Supplementary content) were varied within the same range ($\pm 10\%$ of their initial value) using a Monte Carlo analysis technique. One hundred trials were run using the Crystal Ball® software add-on (Oracle, v.11.1.1.0.00) for Microsoft Office Excel® assuming a uniform distribution for the sampling of values across the range of each input parameter. The contribution to variance in predicted water concentrations attributable to model input parameters under these assumptions are presented in Table S9. These outputs are estimated by calculating the rank correlation coefficients between every assumption and forecast, then squaring these coefficients and normalizing them to 100%. We chose a relatively high variation in input values (10%) for a model sensitivity analysis, but previous experience (MacLeod et al., 2002, and personal communication from Macleod) with undertaking sensitivity analyses on food web models has shown that varying inputs by either 0.1, 1 or 10% has only a minor impact on the results.

3. Results and discussion

3.1. Influence of hydrophobicity and macrophyte biomass density on food web bioaccumulation

The model produces a time course of concentrations in water, sediments, macrophytes and all species in the food web. Concentrations in the different species in the food web increase during the model simulations until they peak and then decline, with the exact timing

of the occurrence of the peak concentration dependent on both the species' uptake/depuration rate and the fugacity capacity of the species for the chemical (the higher the K_{OW} the higher the fugacity capacity of the species for a given chemical). Fig. 2 shows the variation in concentration of CHEM3 in a primary producer (PP1) and top consumer (TP). Observe that PP1 immediately responds to changes in the water phase concentration since uptake is dominated principally by passive diffusion (Fig. 2, top). However, the larger species at higher trophic levels (e.g. TP in bottom Fig. 2) require longer periods to respond, even though dietary uptake is considered, due to the fact that uptake and elimination kinetics have an inverse relationship with body size (i.e. larger organisms have slower kinetics) (Hendriks et al., 2001). Fig. 3 shows the peak concentrations of CHEM3 in food web species normalized to the low density scenario (normalization is performed by adjusting the peak predicted concentration in the low density scenario to 1 mg kg⁻¹ and then using the same normalization factor to adjust the two other scenarios). Peak concentrations in each trophic level were highest for the scenario assuming low macrophytes biomass density, and this was also observed for the other compounds.

Fig. 4 shows the concentration of the three compounds CHEM3, CHEM2 and CHEM1 in water. Concentrations in water are highest at the beginning of the simulations and decline rapidly for CHEM3 and CHEM2 and gradually for CHEM1 during the model simulations. The influence of macrophytes on modeled peak concentrations of TP was related to the hydrophobicity of the chemicals. Peak TP concentrations assuming low macrophytes density were approximately two times higher than the high macrophytes biomass density scenario for CHEM3 with $\log K_{OW} = 7$ (Table S8). For CHEM1 with $\log K_{OW} = 3$, peak concentrations assuming low macrophytes density were approximately equal to the high macrophytes biomass density scenario (Table S8).

The predicted concentrations in water of CHEM3 and CHEM2 are affected by the assumed biomass density and decline most rapidly under the assumption of high biomass density. Calculated dissipation half-lives (DT_{50}) (note: dissipation includes all possible loss processes) for the different biomass densities ranged from 1 to 3 d for CHEM3 and

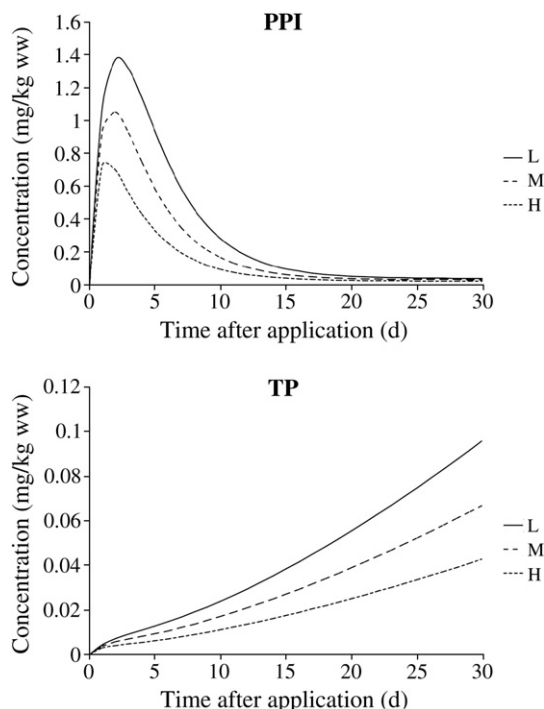


Fig. 2. Model predicted concentrations of CHEM3 in a primary producer (PP1) and a top consumer (TP) in mg/kg wet weight. L, M and H indicate the macrophytes biomass density scenario.

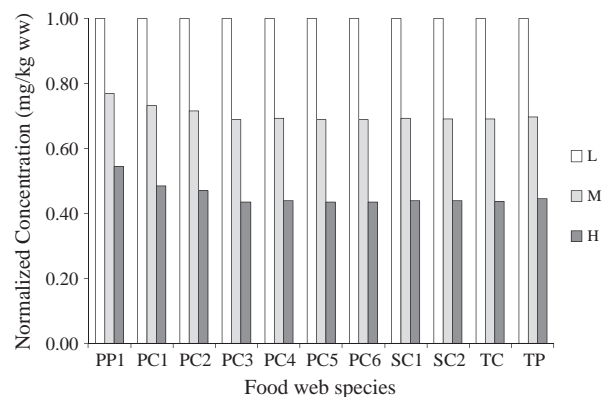


Fig. 3. Peak concentrations of hypothetical compound CHEM3 in food web species. All concentrations are normalized to the low density scenario. Normalization is performed by adjusting the peak predicted concentration in the low density scenario to 1 mg/kg and then using the same normalization factor to adjust the two other scenarios. L, M and H indicate the macrophytes biomass density scenario.

CHEM2. This behavior is due to the fact that these substances associate extensively with suspended solids and were therefore removed from the water column via particle settling to macrophytes and sediments (see Figs. S2 and S3 in the Supplementary content). Conversely, the predicted concentration of CHEM1 in water (top of Fig. 4), and macrophytes and sediment (Fig. S4 in Supplementary content) remain relatively unchanged. Dissipation from the water compartment was much slower ($DT_{50} > 30$ d) because particle dynamics are much less effective at transporting this chemical out of the water column. This behavior reflects the fact that CHEM1 is predominantly in the dissolved phase of the water column and the influence of macrophytes biomass density is also low. In more realistic assessments, degradation in the water column will likely dominate the dissipation kinetics since most current-use pesticides are far less persistent than assumed here (Wauchope et al., 1992; Augustijn-Beckers et al., 1994).

K_{OW} is an important factor controlling the partitioning of chemicals in the environment and uptake by aquatic species. Degradation (abiotic and biotic) exerts an important influence counteracting accumulation and can substantially reduce concentrations throughout the food web in absolute terms if the reaction rate constants are of sufficient magnitude (see Table S8 in Supplementary content). However, the results of the simulations performed using the same K_{OW} and shorter, more realistic degradation half-lives for the pond media (i.e. water, sediments and macrophytes) indicated similar patterns in relative terms to those presented above using much longer degradation rate constants of 55,000 h for the compounds (see Fig. 5). This finding is important as it demonstrates that the relative patterns describing the environmental fate of the compounds investigated are not sensitive to assumptions regarding degradation rate constants in water, sediments and macrophytes (i.e. hydrophobicity remains a key driver in aquatic systems). It is noteworthy that in this model experiment we did not lower the metabolism half-lives in organisms, which would additionally lower the uptake in the food web and top predator.

The influence of macrophyte density on model output can be understood by considering the two processes (diffusive exchange between water and macrophytes and particle deposition to macrophytes) used to model uptake and elimination of chemicals by aquatic macrophytes (see model description in Armitage et al., 2008). The higher the K_{OW} of a chemical the faster the uptake rate (or the slower the elimination rate) and the larger the amount sequestered in macrophytes. As reported in Armitage et al. (2008), passive diffusion and particle deposition are comparable for chemicals with $\log K_{OW}$ up to 5.5, after which point deposition begins to strongly dominate. As K_{OW} increases, there is a greater tendency for the macrophytes to bioconcentrate the chemical in the water column, but more importantly for mass transfer via particle deposition, leading to an increased proportion of the mass of chemical

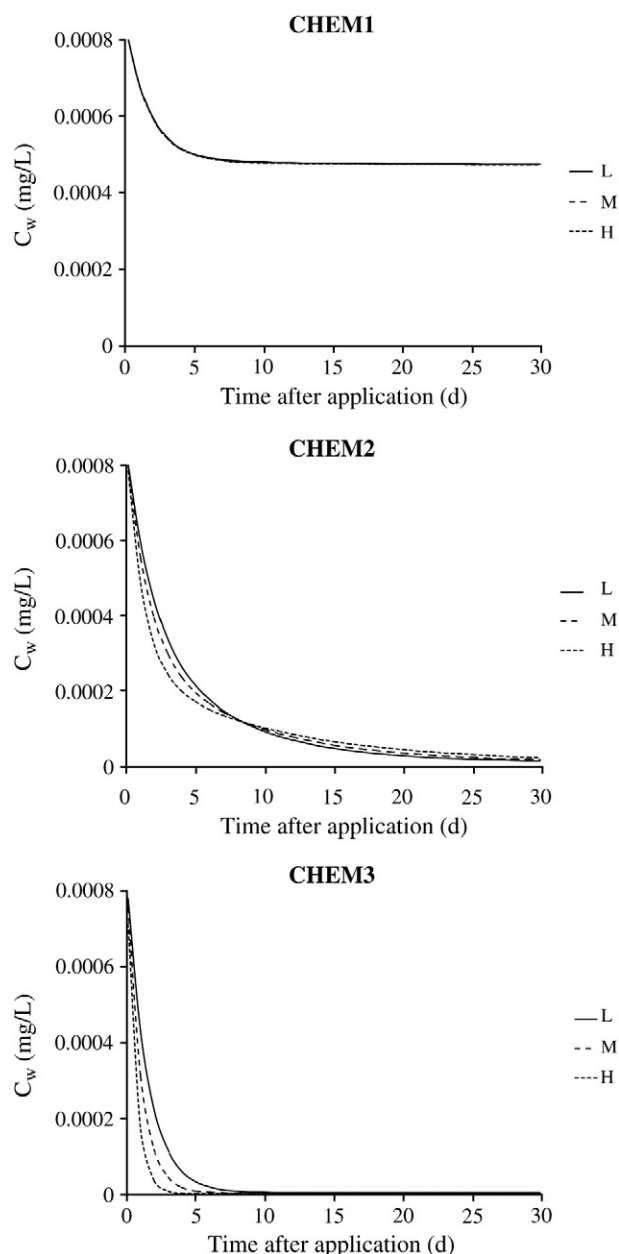


Fig. 4. Simulated dynamics of CHEM3, CHEM2 and CHEM1 in water (C_w is the total concentration i.e. dissolved + particle bound). H, L and M indicate the macrophytes biomass density scenario.

being associated with macrophytes. Thus it is apparent that both passive diffusion and mass transfer of chemical to macrophytes predominantly control the fate of the hydrophobic compounds with high $\log K_{OW}$ (5–7) in the model environment. For chemicals with relatively low $\log K_{OW}$ ($\log K_{OW} = 4$) there is no strong tendency for macrophytes to bioconcentrate the compound through passive diffusion nor does particle deposition result in substantial mass transfer. In addition, the volume of the macrophytes compartment in the present model was at least 3 orders of magnitude smaller than the volume of the water column. Accordingly for CHEM1, the mass of chemical associated with macrophytes is negligible in comparison to the water column and sediments (see Fig. S5 in Supplementary content).

It is possible that some chemicals may sorb more strongly to macrophytes than estimated using absorption models based on K_{OW} (e.g. they adsorb strongly) (Hand et al., 2001). The algorithm used by the model to estimate K_{OC} from K_{OW} was recently shown to be in good

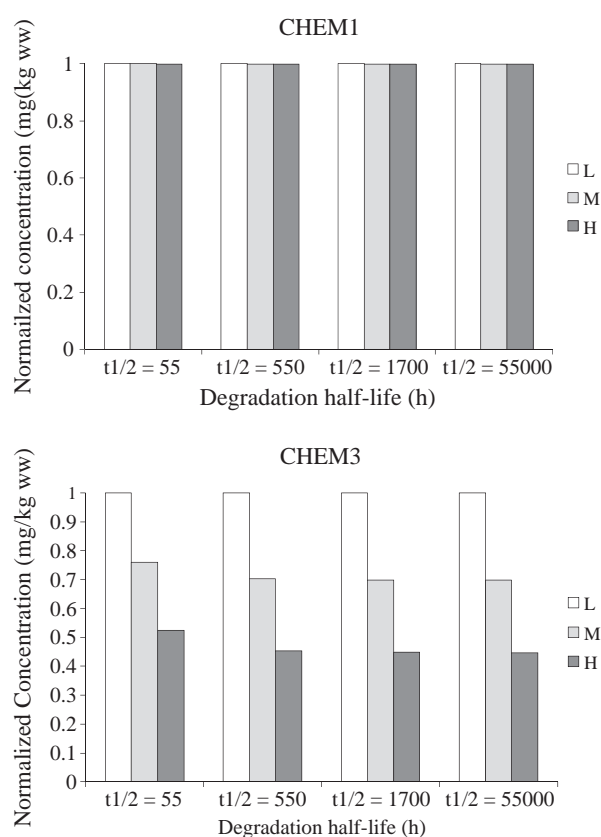


Fig. 5. Predicted concentrations of CHEM3 and CHEM1 in top predator (TP) for different degradation half-lives. All results are normalized to the low density scenario. Normalization is performed by adjusting the peak predicted concentration in the low density scenario to 1 mg/kg and then using the same normalization factor to adjust the two other scenarios. H, L and M indicate the macrophytes biomass density scenario.

agreement with experimental values for neutral organic compounds (Niederer et al., 2006). However, if the required input parameters are available, we recommend the use of poly-parameter linear free energy relationships (p,p-LFERS) (e.g. based on Abraham-type LFERS; Platts and Abraham, 2000) for more polar compounds since it is likely that K_{OC} is underestimated by our modeling approach (Niederer et al., 2006). Regardless, the fate model output suggests that the distribution of compounds with $\log K_{OW} \leq 4$ ($\log K_{OC} \leq 3.6$) is not influenced by the presence of macrophytes (Armitage et al., 2008). Many persistent organic pollutants (POPs) are strongly hydrophobic and we would therefore expect the fate and transport of such compounds in aquatic systems to be influenced to some extent by the presence of macrophytes. These compounds may also be more practical to use in laboratory and field-studies to evaluate this model further since degradation tends to be more limited.

It is also important to recognize that the conclusions of this study refer to the influence of macrophytes on the distribution of chemicals between the components of the abiotic system only. Macrophytes can potentially influence chemical fate indirectly as well through (i) altering water pH due to photosynthetic activity and (ii) providing a substrate for microbial communities. Both of these factors would tend to increase degradation of susceptible chemicals in the system. For example, it has been observed that photosynthetic activity can elevate the pH of natural waters above 9 during peak sunlight hours (Prins et al., 1980; Kersting and Van den Brink, 1997), potentially influencing the rate of base-catalyzed hydrolysis of susceptible chemicals such as azinphos-methyl. The degradation half-life of this compound declines from approximately 28 days at pH 8.6 to 2.5 days at pH 9.6 (Heuer and Yaron, 1974). In this context, higher macrophyte biomass densities

could cause larger alterations to the physical/biological environment the chemical experiences resulting in enhanced degradation in comparison to water bodies with low and medium biomass density. For hydrophobic chemicals, it can be argued that these processes are unlikely to change the basic patterns of fate behavior reported here since the lowest modeled concentrations are found in high macrophytes biomass density scenarios already. For more water-soluble chemicals (e.g. azinphos-methyl), these processes could possibly result in greater differences between biomass density scenarios. However, specific data would be required to develop model scenarios allowing for more quantitative assessments of the influence of these processes.

The influence of the varied input parameters on the predicted water concentration of the hypothetical chemicals is presented in Table S9 of the Supplementary content. The values (%) represent the contribution of the varying parameter to the variance of the selected output parameter (this is the standard way of representing input sensitivity in the Oracle Crystal Ball Software package and is a relative measure of sensitivity). The results show that the predicted water concentration was most sensitive to K_{OC} , fraction of organic carbon in sediment and the sediment deposition mass transfer coefficient. For CHEM2 and CHEM3, the leaf area index of macrophytes was also a sensitive parameter. The sorption coefficient and the sediment deposition mass transfer coefficient determine the proportion of chemical that remains in the water column. Increasing K_{OC} decreases the amount of chemical in solution reflected in the slightly lower contribution from K_{OC} for CHEM1 compared to CHEM2 and CHEM3. The model predictions for CHEM2 and CHEM3, which are more hydrophobic, were also sensitive to the biomass of macrophytes per water surface area and the leaf area index of macrophytes because increasing the K_{OW} of the chemical results in a faster uptake and a slower elimination by macrophytes thus decreasing the amount of chemical in the water column. Note that these results are based on simulations with negligible degradation rate constants; model output will become increasingly sensitive to assumed degradation rate constants as higher values more representative of modern pesticides are used (i.e. when degradation becomes a dominant fate process).

In terms of the broader relevance to pesticides and in a regulatory perspective, it is interesting to note that many current-use pesticides are not sufficiently hydrophobic to be greatly influenced by the presence of macrophytes in a pulse exposure (i.e. they are more similar to the compound CHEM1). For example, less than 5% of the compounds on the SCS/ARC/CES Pesticides Properties Database (Wauchope et al., 1992; Augustijn-Beckers et al., 1994) have $\log K_{OW} > 5.5$, while the median value is ~ 3.1 . Some modern pesticides (e.g. pyrethroids such as deltamethrin) are hydrophobic and macrophyte sorption is thus relevant for them. As noted above, modern pesticides are also typically much more degradable and thus food web uptake will be limited compared to the hypothetical highly persistent chemicals considered here.

3.2. Comparison to previous modeling approaches and implications for risk assessment

The concentration at the top of the food web (for the tertiary consumer and the top predator) is a relevant metric for assessing the exposure of fish eating birds and terrestrial mammals that feed at the top of aquatic food webs. The EU guideline for risk assessment of pesticides sets out a fast and expedient procedure to estimate a worst case exposure of fish eating birds and mammals. According to this guideline, the maximum concentration attainable in a fish species (CF_{max} , $mg\ kg^{-1}$) in higher tier risk assessment may be estimated as

$$CF_{max} = C_{Wi} BCF \quad (5)$$

where BCF is the theoretical bioconcentration factor calculated from the K_{OW} and lipid fraction (L_f) (using $BCF = L_f K_{OW}$) and C_{Wi} is the dissolved

concentration of the pesticide ($mg\ L^{-1}$). It is therefore assumed that the aquatic species achieves instantaneous equilibrium with the initial concentration in water and the compound is not metabolized (i.e. is highly persistent). However, based on the rate constants estimated in the model, the time to reach near steady state (95%) concentrations ($t_{95\% SS} = 3/\sum k_{elimination}$) assuming a constant water concentration (for CHEM3 and high macrophytes density scenario) is approximately 930 and 1100 days for the tertiary consumer and top predator respectively (assuming negligible metabolism) compared to approximately 10 and 6 days for PP1 (e.g. phytoplankton) and PC1 (e.g. zooplankton) respectively. The rapid dissipation of CHEM3 from the water column therefore limits the peak concentration achieved by the larger species in the food web. It should also be noted that if we had assumed some metabolism for the three hypothetical chemicals, as is more typical e.g. for modern pesticides, we would expect even faster dissipation. Assuming high persistence allows us to examine the worst-case exposure.

For the three different hypothetical chemicals and at all macrophyte biomass densities, values for CF_{max} estimated according to EU guidelines using Eq. (5) were many times higher than model maximum estimated peak concentrations (PCF_{max}) in the 11 food web species values. For example, CF_{max} for CHEM3 in the tertiary consumer (TC) and top predator (TP) were approximately 55–110 and 13–20 times respectively higher than PCF_{max} . Conversely, the model previously developed by Carbonell et al. (2000) predicted that top predators are exposed to higher concentrations than estimated using CF_{max} in Eq. (5). Carbonell et al. (2000) reason that food web transfer was not considered in Eq. (5) and therefore the equation used in the EU guidelines underestimates risk. However, our reported PCF_{max} takes into account the contribution from food web transfer and contrary to the findings of Carbonell et al. (2000) estimates PCF_{max} values that are consistently lower than CF_{max} from Eq. (5). We reason that the dissipation of chemicals from the water column limits the theoretical peak concentration CF_{max} from being achieved. On further examination, the modeling approach of Carbonell et al. (2000), unlike our model, does not mechanistically model the distribution and dissipation of chemical in the water column. Instead the model uses overall dissipation half-lives for chemical in the water column and bottom sediments. The model does not explicitly estimate phase distribution and therefore the “available” dissolved concentrations. Instead, these concentrations must be directly entered by the user. Furthermore, the influence of macrophytes on reducing exposure is neglected. We believe that by mechanistically modeling both the fate and food web accumulation our combined model more accurately represents the food web accumulation in small aquatic systems than the simpler Carbonell et al. approach.

The implication of the findings of this modeling study is that using CF_{max} from Eq. (5) in risk assessment would result in a large overestimation of the risk of fish eating birds and terrestrial mammals that feed from the aquatic environment, rather than an underestimation as suggested by Carbonell et al. (2000). The method in the EU guideline thus provides a highly conservative estimate of risk. In our opinion, and subject to further model evaluation, a realistic assessment of dynamic food web transfer can be obtained using the model presented here. To date it has only been possible to use the food web model developed here for evaluative model scenarios, although we were able to test the fate model against real datasets (see Armitage et al., 2008). We are aware that datasets in which concentrations in pond species are measured are generated during pesticide registration by pesticide manufacturers (although these are often confidential). These datasets if made available in the public domain could be used to evaluate the accuracy of our food web model, and thus authenticate its use as a higher-tier regulatory tool for risk assessment. The model can additionally be a useful tool for interpreting laboratory, mesocosm and field measurements, especially for assessing the aquatic behavior of pesticides that associate with macrophytes i.e. those with high K_{OW} values.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.scitotenv.2011.08.070.

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