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AGRO-2014: A time dependent model for assessing the fate and food-web bioaccumulation of organic pesticides in farm ponds: Model testing and performance analysis

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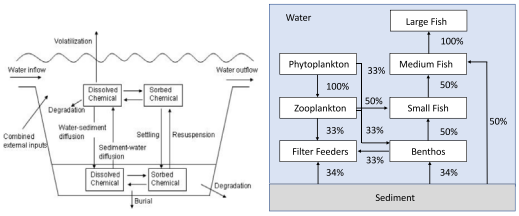
HIGHLIGHTS

- Time-dependent environmental fate & food-web model for neutral hydrophobic organic pesticides is developed & tested.
- Model accurately assesses concentrations after episodic pesticide applications.
- Time dependent model exhibits better accuracy than corresponding steady-state model.
- Model can be used for estimating concentrations of neutral hydrophobic organic pesticides in water, sediments and biota.
- Model is freely available for use and further study.

GRAPHICAL ABSTRACT



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ABSTRACT

A time-dependent environmental fate and food-web bioaccumulation model is developed to improve the evaluation of the behaviour of non-ionic hydrophobic organic pesticides in farm ponds. The performance of the model was tested by simulating the behaviour of 3 hydrophobic organic pesticides, i.e., metaflumizone (CAS Number: 139968-49-3), kresoxim-methyl (CAS Number: 144167-04-4) and pyraclostrobin (CAS Number: 175013-18-0), in microcosm studies and a Bluegill bioconcentration study for metaflumizone. In general, model-calculated concentrations of the pesticides were in reasonable agreement with the observed concentrations. Also, calculated bioaccumulation metrics were in good agreement with observed values. The model's application to simulate concentrations of organic pesticides in water, sediment and biota of farm ponds after episodic pesticide applications is illustrated. It is further shown that the time dependent model has substantially better accuracy in simulating the concentrations of pesticides in farm ponds resulting from episodic pesticide application than corresponding steady-state models. The time dependent model is particularly useful in describing the behaviour of highly hydrophobic pesticides that have a potential to biomagnify in aquatic food-webs.

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1. Introduction

Hydrophobic organic pesticides have a natural tendency to avoid the water phase when introduced in aquatic environments. This causes them to transfer into non-aqueous media such as suspended and deposited particulate matter and biological organisms. Because of their ability to be efficiently absorbed by organisms, organic pesticides can enter and move through aquatic food-webs. Assessing the extent to which this occurs is of importance in managing and controlling pesticide applications. As a result, several models have been developed and used to assess the potential impacts of non-intentional, off-target applications of hydrophobic organic pesticides in aquatic systems. These models include the Exposure Analysis Modeling System (EXAMS) model (Burns, 2004), the Variable Volume Water (VVW) model of the Pesticide in Water Calculator (Young, 2014), an earlier version of the AGRO model (CEMC, 2007), and the KOW (based) Aquatic BioAccumulation Model (KABAM) model (Garber, 2009). These models are often used in combination with other models such as the Pesticide Root Zone Model (PRZM) (Suarez, 2005) to make assessments of pesticide concentrations in abiotic and biotic media and to assess risks to off-target fish-consuming species such as birds and mammals.

Recently, Padilla et al. (2015) reviewed the environmental fate component of the AGRO model for assessing the risks of pesticides with persistent, bioaccumulative and toxic characteristics. The authors noted that the AGRO model is the only model of those mentioned above that explicitly models the impact of variation in suspended sediment and sedimentation on the benthic-limnetic exchange of pesticides. This feature of the model makes the model particularly suitable to simulating the behaviour of hydrophobic organic pesticides in food-webs because uptake and bioaccumulation of pesticides in exposed wildlife results from both direct (via respiration) and indirect (via the diet) uptake of the pesticide from water and suspended and deposited sediments.

The USEPA KABAM model can utilize pesticide concentrations in water and sediments calculated by the AGRO model to estimate concentrations in organisms of an aquatic food-web. However, one of the disadvantages of the KABAM model is that the model is a steady-state (or time-independent) model which is not expected to be adequate for calculating concentrations of hydrophobic organic pesticides in biota resulting from time-variable concentrations of pesticides in water and sediments following episodic pesticide applications. Hence, applying the steady-state KABAM model to time-dependent concentration output from time-dependent environmental fate models such as AGRO or EXAMS can cause substantial error, especially for substances that are very hydrophobic and for which bioconcentration and biomagnification play an important role in the environmental behaviour and potential effects of pesticides.

It is the goal of this study to investigate the ability of the time-dependent AGRO model to estimate concentrations of hydrophobic organic pesticides in water, sediments and biota in aquatic systems. The focus of this paper is on the assessment of concentrations in biota. An accompanying paper emphasizes the estimation of the concentrations of pesticides in water and sediments of farm ponds. The objectives of this paper are fourfold. First, we summarize the time-dependent AGRO environmental fate and food-web bioaccumulation and discuss its parameterization for estimating concentrations of hydrophobic organic pesticides in organisms of an aquatic food-web as a result of time-varying pesticide application rates. Secondly, we test the model by calculating concentrations of pesticides in water, sediments and biota of experimental microcosm and comparing calculated to measured concentrations in an effort to characterize the model's performance. Thirdly, we apply the model to illustrate the model's capacity to assess pesticide concentrations in wildlife species that can be used for risk assessment. Fourth, we compare the behaviour of the time dependent and steady-state environmental fate and food-web bioaccumulation models to investigate their differences and the effect that these differences may have on environmental risk assessments of pesticides.

2. Theory

The AGRO-2014 model consists of two sub-models, i.e. (i) a water-air-sediment exchange model and (ii) an aquatic food-web bioaccumulation model for non-ionic hydrophobic organic pesticides. The first sub-model was originally developed by Mackay et al. (1994) as the quantitative water-air-sediment interaction QWASI model and estimates fugacities and concentrations of chemicals in various abiotic media of aquatic systems resulting from inputs (or loadings) of the chemical into the system. The second sub-model, developed by Arnot and Gobas (2004) after an earlier version of the model (Gobas, 1993), estimates concentrations of organic chemicals in various organisms of aquatic food-webs from the concentrations of the chemical in water and sediments of aquatic systems. The model equations used in the food-web bioaccumulation model of AGRO are identical to those used in the USEPA KABAM, as the KABAM model is based on the Arnot and Gobas (2004) model. The combination of the two sub-models makes it possible to assess the effect of inputs of organic pesticides in aquatic systems (such as farm ponds) in terms of resulting concentrations in biota, which can be compared to various toxicity reference values for risk assessment. The two sub-models of AGRO were originally developed as steady-state models to assess concentrations of organic chemicals in environmental media after a prolonged steady input of the chemical in an aquatic system. To make the model applicable to time-varying pesticide applications rates, the models were converted into time-dependent models for AGRO (CEMC, 2007). AGRO-2014 was updated as described in Padilla et al., 2015. In addition, the environmental fate and bioaccumulation sub-models are presented in this paper in terms of rate-constants and concentrations instead of transport parameters and fugacities. The fugacity and concentration based equations are mathematically identical. A description of the model is presented and a copy of the model is freely available and can be downloaded from http://www.stone-env.com/news-and-insights/resource-library or https://www.sfu.ca/rem/toxicology/our-models/agro.html.

2.1. Time-dependent environmental fate sub-model

Fig. 1 illustrates the conceptual diagram describing the input, distribution, loss and transformation of the pesticide in the farm pond. The pesticide is released into the water as a result of a combination of processes including direct application, wind drift and/or run-off. The input or loading of the pesticide refers to the combined inputs from all sources. In the water, the pesticide can volatilize to the atmosphere and partition into suspended particulate matter or sediments and diffuse into deposited sediments. When associated with sediment particulate matter, the pesticide is subject to deposition, resuspension and sediment accretion (or burial), the latter being considered a loss of the pesticide from the system. The pesticide can also be transformed in both water and sediment. Transformation is also treated as a loss of the (parent) pesticide from the system. The mathematical representation of this behaviour includes two mass balance equations, i.e. one for the water and one for the deposited (or bottom) sediments.

The mass balance equation for bulk water describes the change in mass (g) of the pesticide in water (M_W) as a function of time t as:

$$dM_W/dt = L(t) + k_{SW} \cdot M_S - (k_V + k_O + k_{WR} + k_{WS}) \cdot M_W \quad (1)$$

where

dM_W/dt = net flux of the pesticide in the water compartment at time t (g/day)
M_W = mass of pesticide in water (g)
$L(t)$ = input or loading of the pesticide at time t into the water (g/day)
k_{SW} = overall sediment to water transport rate constant (day^{-1})
M_S = mass of pesticide in sediment (g)

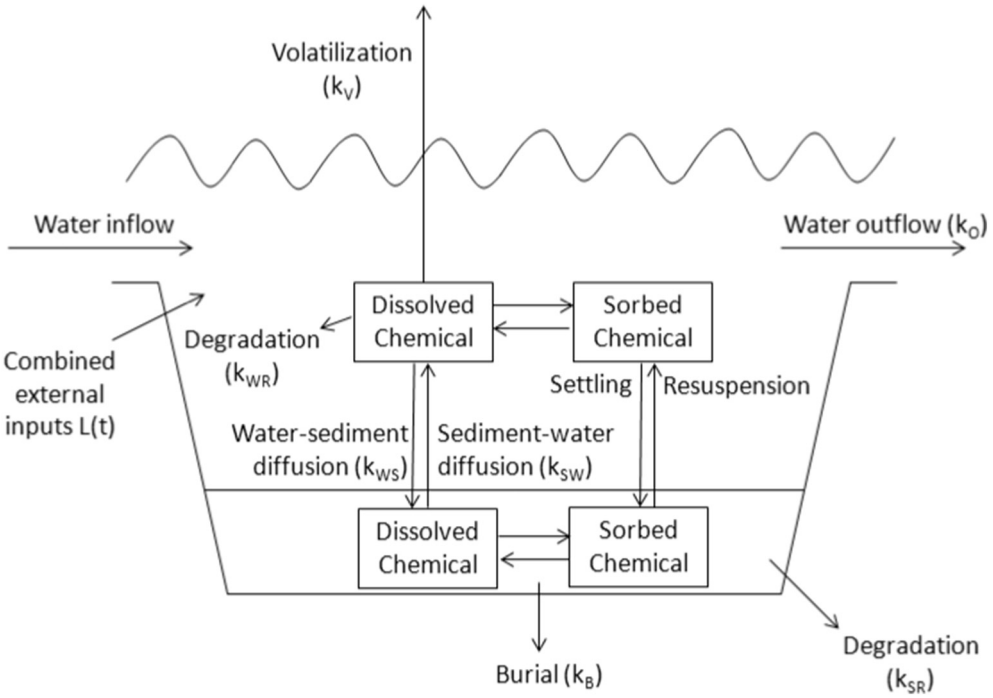

Fig. 1. Conceptual diagram of the distribution of a pesticide in a farm pond in the AGRO-2014 environmental fate sub-model.

k_V = rate constant of pesticide volatilization to the atmosphere (day^{-1})
k_O = water outflow rate constant from the system (day^{-1})
k_{WS} = overall water to sediment transport rate constant (day^{-1})
k_{WR} = reaction rate constant of chemical in water (day^{-1})

The corresponding mass balance equation for the bottom sediments describes the change in mass (g) of the pesticide in the sediment (M_S) as a function of time t:

$$dM_S/dt = k_{WS} \cdot M_W - (k_{SW} + k_B + k_{SR}) \cdot M_S \quad (2)$$

where

dM_S/dt = net flux of pesticide into the sediment compartment at time t (day)
M_S = the mass of pesticide in sediment (g)
k_{WS} = overall water to sediment transport rate constant (day^{-1})
M_W = the mass of pesticide in water (g)
k_{SW} = overall sediment to water transport rate constant (day^{-1})
k_B = rate of sediment burial rate constant (day^{-1})
k_{SR} = pesticide degradation rate in sediment (day^{-1})

Methods used for calculating the rate constants in Eqs. (1) and (2) are presented in Table S1. An Euler-type numerical-integration method was used to solve the mass balance equations (Eqs. (51)–(56), Table S1). Corresponding concentrations of the pesticide in water and sediment were calculated by dividing the total pesticide mass in each compartment by the volumes of the respective water and sediment compartments.

2.2. Time-dependent food-web bioaccumulation sub-model

A conceptual diagram of the food-web bioaccumulation sub-model illustrating the major routes of pesticide uptake and elimination in consumer organisms of an aquatic food-web is shown in Fig. 2. Organisms can absorb pesticide via the respiratory route and (with the exception of phytoplankton and algae) through the consumption of food. For phytoplankton, algae and aquatic macrophytes, a similar approach is used but dietary uptake and fecal egestion is not included. The conceptual diagram illustrates that in this model, organisms are viewed as individual homogenous compartments. Hence, the model is best applied in situations where the concentration of the pesticide in the whole organism (rather than in specific organs) is of interest. Growth of the organisms is described in terms of a dilution effect due to the increase in organism's volume and weight during growth. Growth dilution is therefore viewed as a pseudo elimination process although no loss of pesticide mass occurs. Because growth is associated with an increase in dietary consumption, the growth dilution effect is counteracted by uptake of pesticide from diet. The balance of these processes controls the ultimate concentration in the organism. A single mass balance equation, treating the organism as a single compartment describes the exchange of hydrophobic organic pesticides between the organism and its ambient environment:

$$dC_B/dt = (k_1 \cdot [m_O \cdot \Phi \cdot C_{WT.O} + m_P \cdot C_{WD.S}] + k_D \cdot \Sigma(P_i \cdot C_{D.i})) - (k_2 + k_E + k_M + k_G) \cdot C_B \quad (3)$$

where

C_B = pesticide concentration in the organism (g/kg)
k_G = growth rate constant of the organism (day^{-1})
k_1 = the clearance rate constant (L/kg/day) for pesticide uptake via the respiratory area (e.g., gills and skin)
m_O = fraction of the respiratory ventilation that involves overlying water
m_P = fraction of the respiratory ventilation that involves sediment-associated pore water
Φ = fraction of the total pesticide concentration in the overlying water that is freely dissolved and can be absorbed via membrane diffusion (unitless)
$C_{WT.O}$ = the total pesticide concentration in the water column above the sediments (g/L)
$C_{WD.S}$ = the freely dissolved pesticide concentration in the sediment associated pore water (g/L)

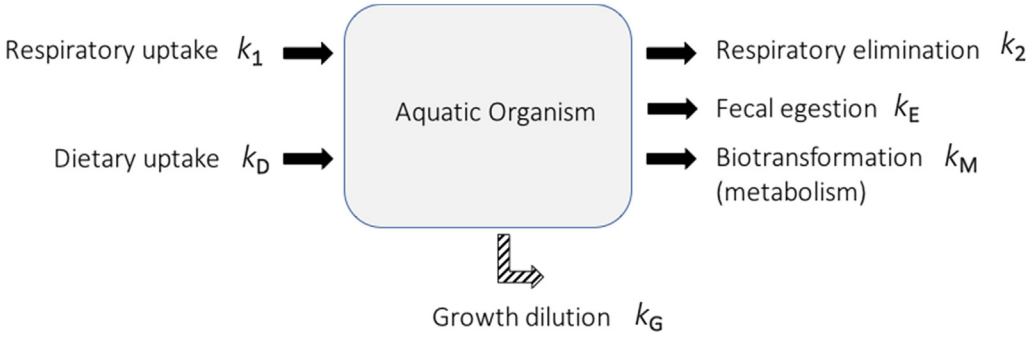

Fig. 2. A conceptual diagram of the major routes of pesticide uptake and depuration in consumer organisms of an aquatic food-web.

P_i = the fraction of the diet consisting of prey item i (unitless)
$C_{D.i}$ = the concentration of pesticide (g/kg) in prey item i
k_2 = the rate constant (day^{-1}) for pesticide elimination via the respiratory area
k_M = the rate constant (day^{-1}) for metabolic transformation of the pesticide
k_D = the clearance rate constant (kg/kg/day) for pesticide uptake via ingestion of food and water
k_E = the rate constant (day^{-1}) for pesticide elimination via excretion into egested feces

Methods used for calculating the rate constants in Eq. (3) are presented in Table S2. An Euler-type numerical-integration method is used to solve the mass balance equations for all species except phytoplankton and zooplankton. Due to the small body weight and large corresponding pesticide elimination rate constant (k_2) in phytoplankton and zooplankton, the time required for the pesticide to reach steady state can be very short. For these organisms, a steady-state expression is used to evaluate the pesticide concentrations in phytoplankton and zooplankton. This reduces the number of required simulations and associated computation time. The equations that are used to describe the pesticide concentrations in phytoplankton, algae, macrophytes and zooplankton are respectively:

$$C_P = (k_1/(k_2 + k_G)) \cdot (m_O \cdot \Phi \cdot C_{WT.O} + m_P \cdot C_{WD.S}) \quad (4)$$

$$C_Z = (k_1 \cdot [m_O \cdot \Phi \cdot C_{WT.O} + m_P \cdot C_{WD.S}] + k_D \cdot \Sigma(P_i \cdot C_{D.i}))/(k_2 + k_E + k_G + k_M) \quad (5)$$

where

C_P = pesticide concentration in phytoplankton, algae and macrophytes (g/kg wet weight)
C_Z = pesticide concentration in zooplankton (g/kg wet weight)

The individual mass balance equations for each aquatic organism are linked together via feeding interactions (food-web). The default food-web structure in the model (Fig. 3) follows the food-web structure that has been used in the USEPA KABAM model. Other feeding relationships can be used as well. It is important to stress that the mass balance equations for biota are not included in the mass balance equations for the water and sediment. It is often assumed that the biomass is too small to have a significant effect on the mass balance of the pesticide in water and sediments. However, this assumption is most likely to fail for primary producers (including phytoplankton, algae and macrophytes), which may in certain systems encompass a biomass that affects the overall distribution of mass of the pesticide between water, sediments and biota. Several models have included algae and macrophyte biomass in the overall mass balance of pesticides (Dachs et al., 1999; Nizzetto et al., 2012; Adriaanse, 1997; Armitage et al., 2008; Nfon et al., 2011; Morselli et al., 2015; Di Guardo et al., 2017). Since information on the biomass of algae and macrophytes in farm ponds is often not available, it is advantageous for a model not to require specific information on algae and macrophytes biomass. Also, since measurements of the concentrations of particulate matter in water and sediment (and associated organic carbon contents) often include both biotic and abiotic particulate matter, a significant fraction of primary producers and plankton is included in the water-sediment mass balance for the system when the model is parameterized to represent the aquatic system. For evaluating the performance of the model, we parameterized the model using the conditions of the laboratory and microcosm studies.

The application of Eqs. (1)–(3) to estimate concentrations of pesticides in water, sediment and aquatic organisms can be limited by the availability of time-dependent model input parameter values, i.e., concentrations of the pesticide in water and sediment. In such situations, a steady-state assumption, i.e. dM_W/dt, dM_S/dt, and dC_B/dt equal zero, can be applied to make time-independent calculations. The steady-state assumption is reasonable for applications in the field in which the organisms have been subject to constant pesticide inputs for a long period of time. The steady-state assumption can also be applied to less hydrophobic organic pesticides, small aquatic organisms and to pesticides that are quickly metabolized because, under those conditions, steady-state is achieved rapidly. The application of time-dependent calculations is most important in situations where pesticide concentrations in water and sediments are time variable and for

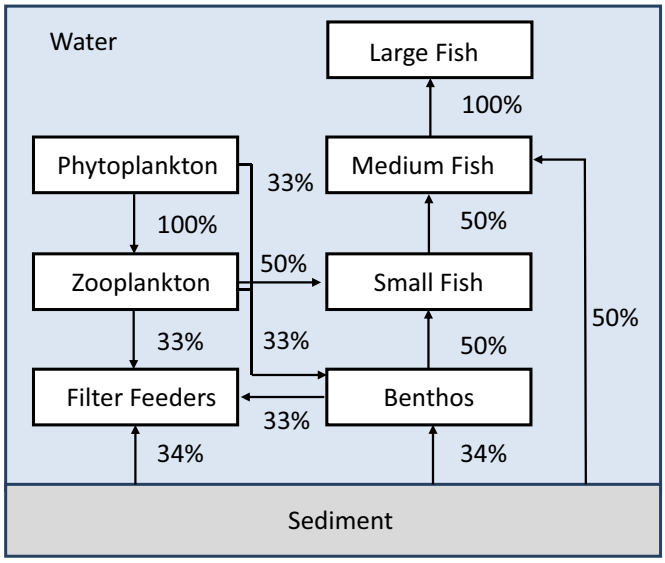

Fig. 3. Conceptual diagram of the default aquatic food-web composition and structure used in the model. Arrows represent feeding interactions and the percentages represent the fraction of the predator's diet consisting of various prey items. This food-web model structure is similar to that used in the USEPA KABAM model (Garber, 2009). Other food-web structures can be used in the model as well.

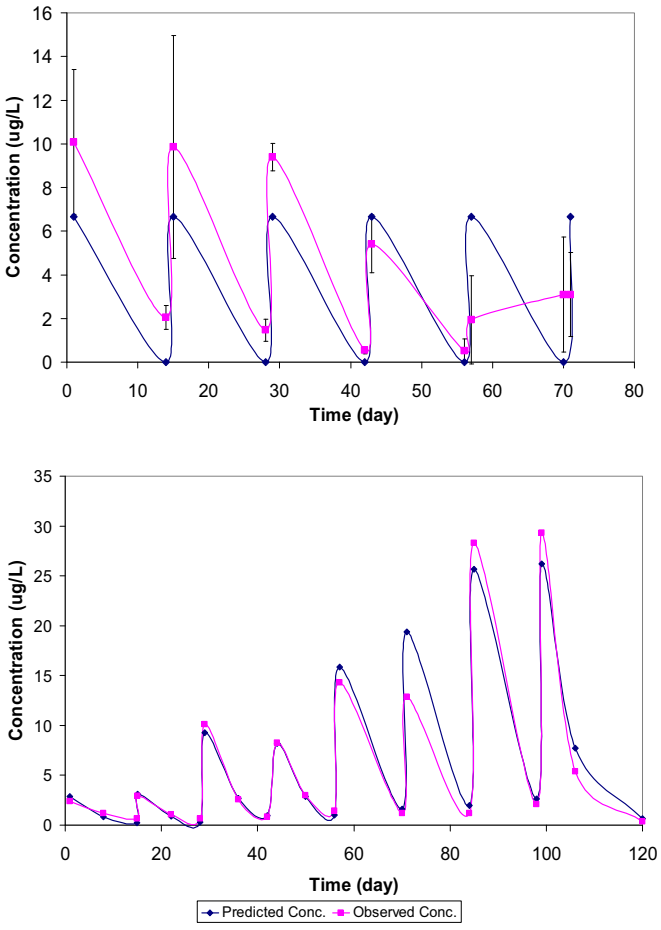

Fig. 4. Comparison of model-calculated and observed arithmetic mean concentrations of kresoxim-methyl (top) and pyraclostrobin (bottom) in bulk water of microcosms. Error bars represent one standard deviation of the mean of observed concentrations in water.

pesticides that are depurated from the organisms slowly, e.g. due to a lack of metabolic transformation and/or high K_{OW}. The steady-state mass balance equations are presented in Table S3.

3. Methods

3.1. Model implementation

The AGRO-2014 model was developed as a spreadsheet model in Microsoft EXCEL. The model parameters and the mass balance equations of each sub-model were calculated within the spreadsheet. The excel spreadsheet was also used for model performance analysis and model application.

3.2. Default model parameterization

The Environmental Fate and Effect Division (EFED) of the USEPA has suggested a range of default model parameters that can be used to simulate pesticide applications and to estimate concentrations of pesticides in water, sediment and different aquatic organisms in ponds near pesticide application areas. The EFED recommended parameter values (Table S4) were used as the default values for the application of the environmental fate sub-model of AGRO-2014. The default values for the parameters used in the food-web bioaccumulation model (Tables S5 and S6) were obtained from USEPA's KABAM model (https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/models-pesticide-risk-assessment).

3.3. Model performance analysis

To test the ability of the model to simulate concentrations of pesticides in farm ponds, several performance analyses were conducted. They include: (i) An evaluation of the model performance by simulating concentrations of the pesticides kresoxim-methyl (CAS No: 144167-04-4) and pyraclostrobin (CAS No: 175013-18-0) (Table S7) in water of a microcosm and comparing estimated concentrations to observed concentrations reported in Dohmen (1995, 2000). The active ingredient kresoxim-methyl was applied to the microcosm in six applications of 0.0421 g at 14-day intervals. Pyraclostrobin was applied to the microcosm in the form of eight applications at 14-day intervals at application rates increasing from 60 to 160 g a.i./ha during the season (Table S8). The model water body was parameterized to represent the conditions in the microcosm study (Table S9); (ii) An evaluation of the performance of the bioaccumulation model for fish by estimating the uptake clearance rate constant k_1, the depuration rate constant k_T, i.e. the sum of (k_2, k_E, k_G and k_M) and the bioconcentration factor (BCF) of metaflumizone (CAS number: 139968-49-3) in the fish used in the test and then comparing estimated to empirical values from Afzal (2004). Metaflumizone is a hydrophobic pesticide consisting of two isomers (i.e., an E and a Z isomer in a 9:1 ratio). The physical-chemical properties used for the calculations are summarized in Table S10. The bioaccumulation model for fish was parameterized (Table S11) to reflect the conditions in the bioconcentration experiment; (iii) An evaluation of the model performance by simulating concentrations of the pesticide metaflumizone in water, sediment and different aquatic organisms in microcosms after application and comparing the estimated concentrations to observed concentrations in Funk (2004). The model parameterization is discussed in the Supporting Information and

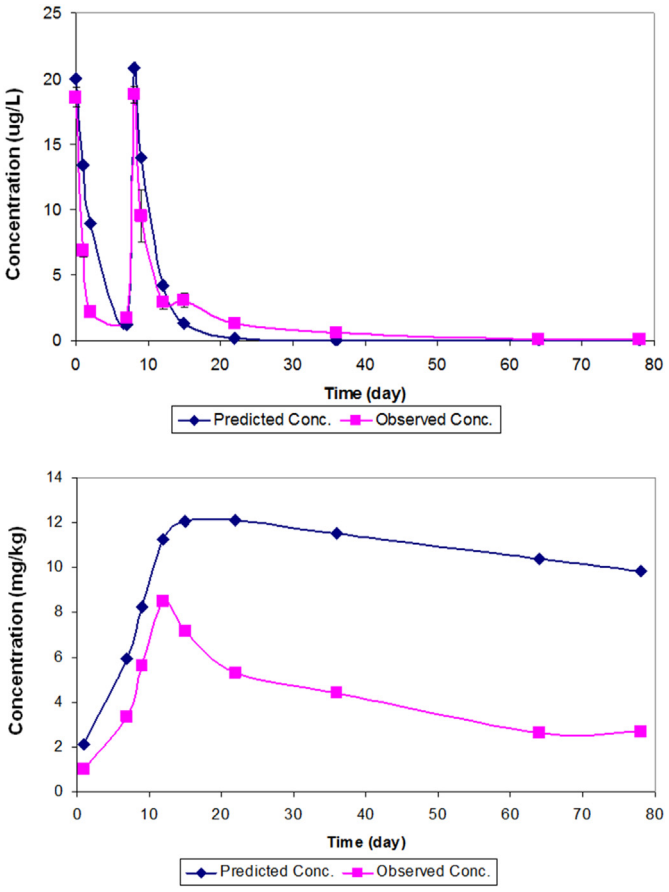

Fig. 5. Model-calculated and observed concentrations of metaflumizone in bulk water (top) (n = 3) and sediment (bottom) (n = 1) of the microcosm. Error bars represent the standard deviations of the mean of observed metaflumizone concentration in water.

model parameters are summarized in Tables S12 and S13. Two performance evaluations were conducted. The first evaluation focussed on the food-web bioaccumulation sub-model using the measured concentrations of metaflumizone in the water and sediments as external input parameters in the model. The second evaluation involved the combined environmental fate and food-web bioaccumulation sub-models and used the metaflumizone application rate as the external input parameter.

Model performance was assessed by (i) comparing the model-predicted chemical concentrations to observed chemical concentrations from laboratory and microcosm studies and (ii) calculating the mean model bias (MB) and its 95% confidence interval for concentrations in a single medium or organism and all media and organisms combined:

$$MB_j = 10^{\sum_{i=1}^{n} \frac{|\log C_{pred,i}/C_{obs,i}|}{n}} \quad (6)$$

where

MB_j = the mean model bias for concentration observations in medium j
n = number of comparisons between estimated and measured concentrations at time point i
$C_{pred,i}$ = estimated chemical concentration at time point i
$C_{obs,i}$ = observed chemical concentration at time point i

The overall model bias, combining the results for all n time points in all m species is calculated as:

$$MB_{tot} = 10^{\left[\sum_{j=1}^{m} \frac{\sum_{i=1}^{n} \frac{|\log(C_{pred,i,j}/C_{obs,i,j})|}{n}}{m}\right]} \quad (7)$$

where

MB_{tot} = the mean model bias for all species for all time points
n = total number of time points
m = total number of species
$C_{pred,i,j}$ = model-calculated concentration of the chemical in species j at time point i
$C_{obs,i,j}$ = observed concentration of the chemical in species j at time point i

MB_{tot} is the geometric mean (assuming a log-normal distribution of the ratio $C_{pred,i,j}/C_{obs,i,j}$) of the ratio of model-calculated and observed chemical concentrations for all time points in all species for which empirical data were available. If MB is greater than 1, then the model over predicts the chemical concentrations by a factor equal to the MB value. If MB is less than 1, then the model underestimates the chemical concentrations by a factor equal to the MB value. Ideally, the MB equals 1.

The 95% confidence interval of the geometric mean represents the range that includes 95% of the MB values. The mean MB value and the

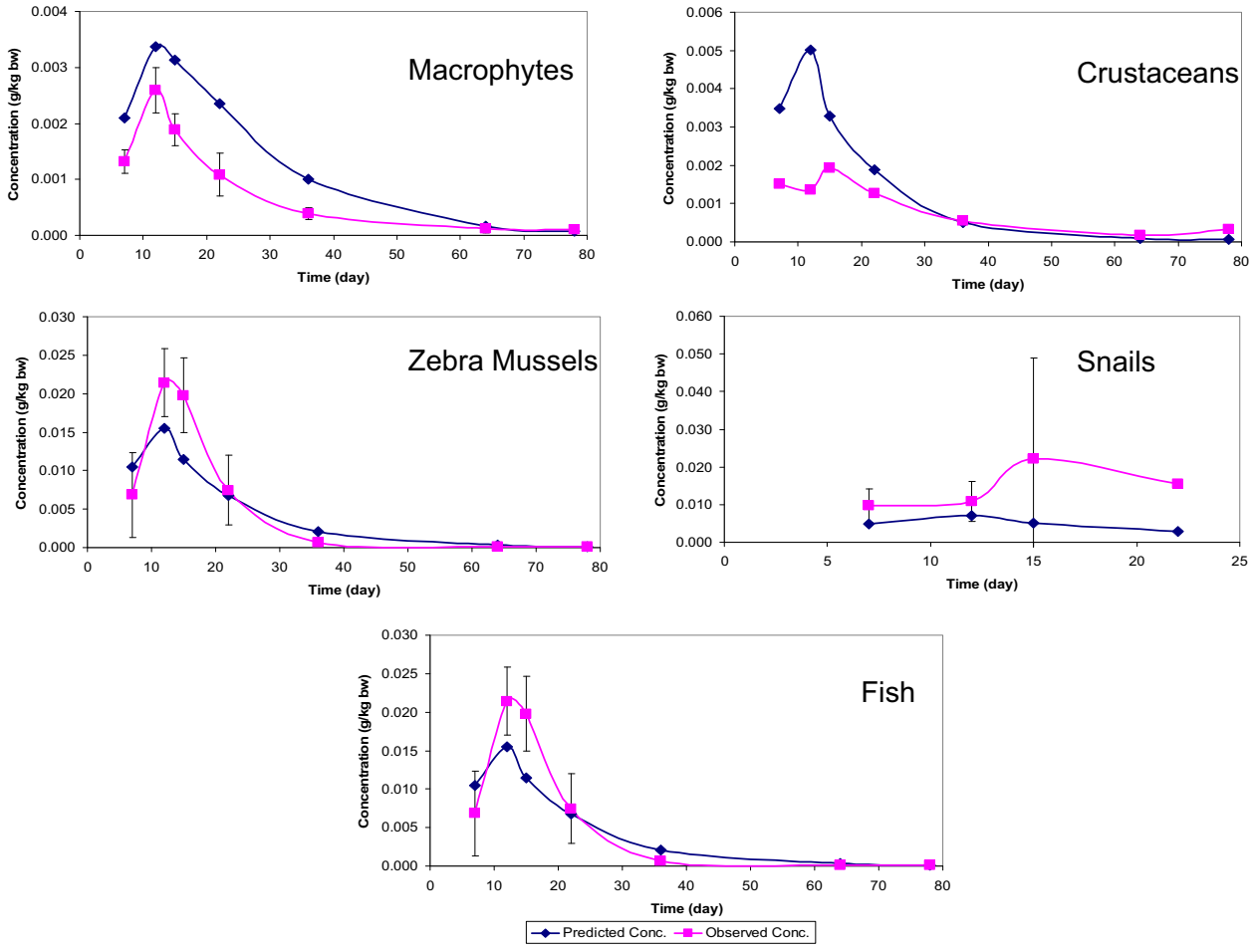

Fig. 6. Model-calculated and observed concentrations (in units of g/kg wet body weight) of metaflumizone in macrophytes (n = 3), crustaceans (n = 3), Zebra mussels (n = 3), snails (n = 3 for the first 3 data points; n = 1 for the last data point) and fish (n = 3) in a microcosm study. Observed concentrations depict the arithmetic mean and the error bars represent one standard deviation of the observed mean metaflumizone concentration. n represents the number of samples. This simulation calculates concentrations in biota based on concentrations of metaflumizone in bulk water and sediment solids as input.

associated 95% confidence intervals reflect all sources of error in the model calculations, including model parameterization errors, errors in model structure, analytical errors in the empirical data and variability in the empirical data used for the model performance analysis.

3.4. Model application

To illustrate how AGRO-2014 can be used, we applied the model to estimate the concentrations of the pesticide metaflumizone in water, sediment and biota in a farm pond conforming to specifications recommended by EFED (Table S4) and the USEPA KABAM model. For this illustrative application of the model, we used an application rate of 280 g/ha, four times annually at 7-day intervals over a 10 year period. Wind drift was assumed to be 5%, producing releases of 14 g (5% of 280 g) into a 1 ha farm pond. The physical-chemical properties of metaflumizone used in the model are listed in Table S10. Estimated concentrations of metaflumizone in water were compared to the NOEC of 0.015 mg/L for reproduction and survival in zebrafish (*Danio rerio*) reported by Schäfers (2004). Estimated metaflumizone concentrations in sediment were compared to toxicity reference values derived for *Chironomus tentans* (Aufderheide and Lucash, 2002), *Leptocherius plumulosus* (Aufderheide and Holmes, 2004a) and *Hyalella azteca* (Aufderheide and Holmes, 2004b). The lowest reported no-effect concentration (NOEC) was 0.93 mg active ingredient/kg sediment in a 10-day survival test for *Chironomus tentans*. All model parameters used for the model calculations are presented in Table S14.

3.5. Model comparison

To investigate the difference in chemical concentration calculations between a steady-state model and a time-dependent model, we calculated concentrations of metaflumizone in a farm pond that was parameterized following EFED recommendations using both time dependent and steady-state expressions of the mass balance equations for water, sediment and biota. The time dependent model calculations were based on an application rate of 14 g/d, four times annually at 7-day intervals over a 5 year period, producing a total input into the farm pond of 280 g metaflumizone over 5 years. Two steady-state calculations were performed. One using a metaflumizone application rate of 14 g/d and a second using a metaflumizone application rate of 280 g/(5 × 365) d or 0.15 g/d. The second steady-state scenario introduces the same amount of metaflumizone into the farm pond over a 5 year period as the time-dependent scenario. Concentrations in water, sediment, and different aquatic organisms calculated for each scenario were then compared. The model input parameters for the calculations are summarized in Table S15.

4. Results and discussion

4.1. Model performance analysis

Time-dependent Environmental Fate Sub-model: Fig. 4 shows that model-calculated concentrations of the pesticides kresoxim-methyl and pyraclostrobin in water were in good agreement with observed concentrations. The mean MB value for concentrations of kresoxim-methyl in water (n = 11) was 1.19 with 95% confident intervals of 0.31 and 4.65. The mean MB value for concentrations (n = 21) of pyraclostrobin in water was calculated to be 1.00 with 95% confident intervals of 0.48 and 2.10. There were insufficient data for concentrations of the two pesticides in sediment to conduct a model performance analysis. The results suggest that the environmental fate sub-model can be used to estimate chemical concentrations in water with reasonable accuracy.

Metaflumizone Bluegill Bioconcentration Study: The model-calculated uptake rate constant (day^{-1}) k_1, and depuration rate constant (day^{-1}) k_T, were 389 $L.kg^{-1}.day^{-1}$ and 0.041 day^{-1} respectively. The reported k_1 and k_T were 380 ± 38 $L.kg^{-1}.day^{-1}$ and 0.048 ± 0.0057 day^{-1} respectively. The reported BCF for metaflumizone in Bluegill was 7800 ± 1200 L/kg ww (Afzal, 2004). The predicted BCF was 7730 L/kg ww. The calculated values are within one standard deviation of the reported values and the values are also close to the mean observed values suggesting that the model predictions are in good agreement with the empirical data.

Metaflumizone Microcosm Study: Fig. 5 illustrates the comparison of model-calculated and observed metaflumizone concentrations in bulk water and sediments solids of the microcosm study following an application of metaflumizone. The mean model bias (MB) and its 95% confidence interval (in brackets) for the calculation of the concentrations of metaflumizone in the water (n = 12) was 0.62 (0.05–7.24) suggesting reasonable agreement between observed and calculated concentrations with some tendency for underestimation of the observed concentrations. The mean model bias (MB) for the calculation of the concentrations of metaflumizone in the sediment (n = 1) was 2.71, indicating considerable over-estimation of concentrations in the sediment especially in the latter part of the study. However, sample size of the sediment was limited to single samples and error in the concentration measurements could not be adequately quantified.

Fig. 6 illustrates the comparison of model-calculated and observed concentrations of metaflumizone in the aquatic organisms in the microcosm of the metaflumizone microcosm study when using the observed concentrations of metaflumizone in the water and sediments as starting points for the model calculations. The mean model bias (MB) and their 95% confidence intervals (in brackets) were 1.48 (0.60–3.66) for

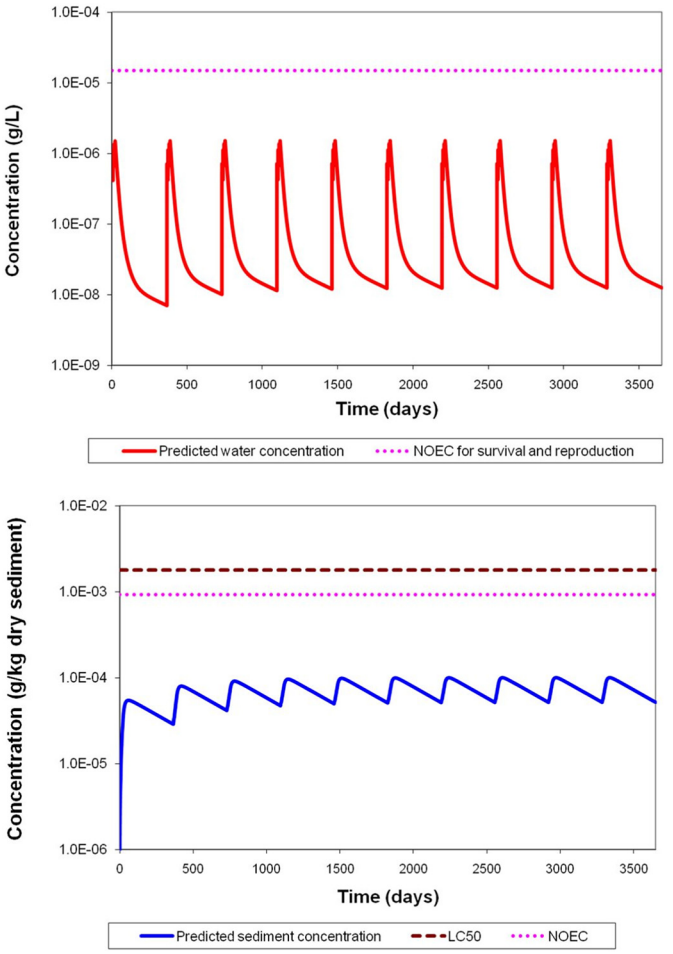

Fig. 7. Comparison of model-calculated concentrations of metaflumizone in bulk water (top) and sediment (bottom) to respectively the LC50 in Zebra fish and the NOEC of metaflumizone in *Chironomus tentans*.

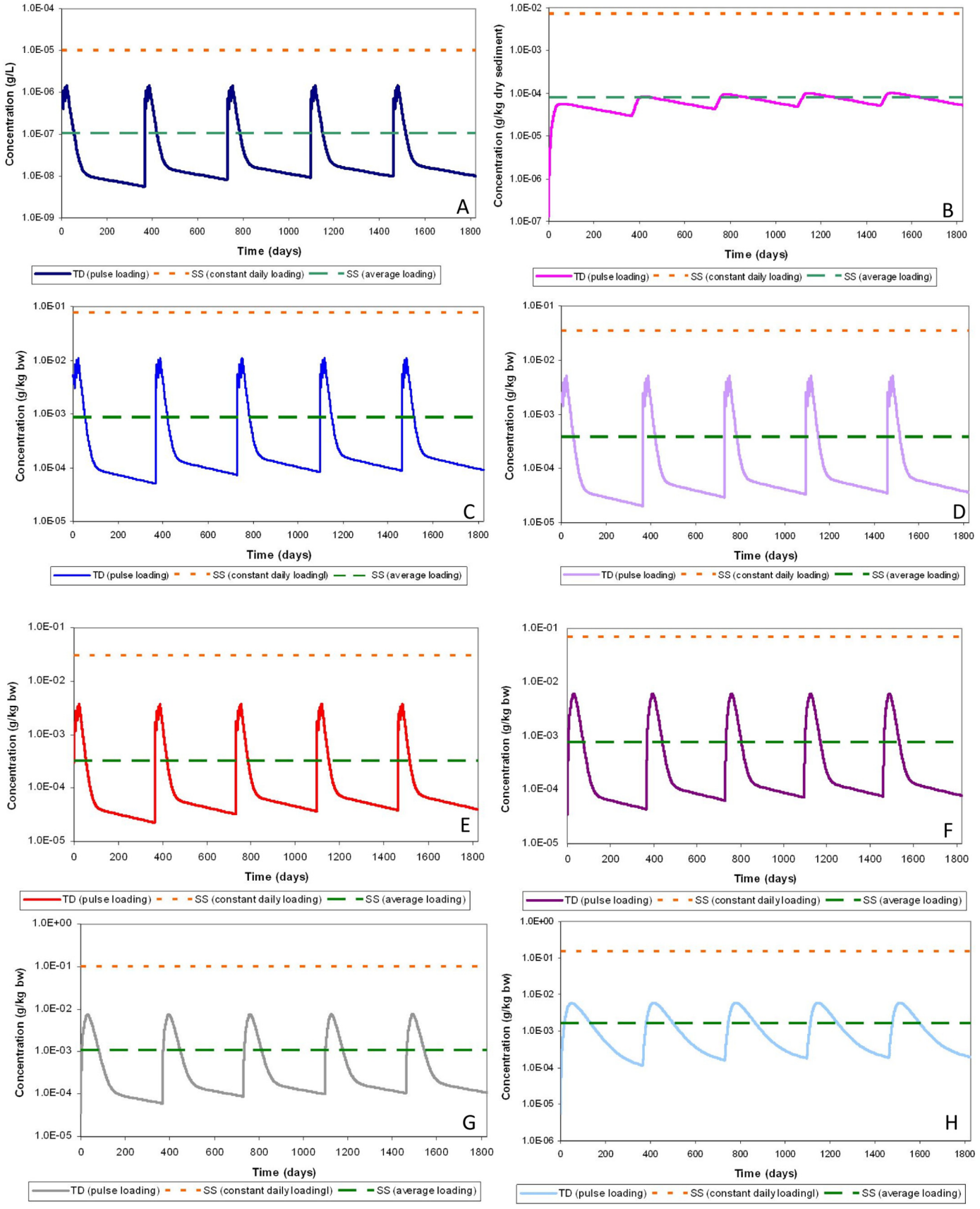

Fig. 8. Comparison of concentrations of metaflumizone in bulk water (A), sediment (B), phytoplankton (C), zooplankton (D), benthos (E), small fish (F), medium fish B (G) and large fish (H) of a farm pond, calculated by (i) the time-dependent model for an annual pulse loading of 4 times 14 g metaflumizone at 7-day intervals; (ii) the steady-state model for a constant daily loading of 14 g of metaflumizone per day; and (iii) the steady-state model for a constant daily loading of 0.153 g of metaflumizone per day, over a 5 year period.

macrophytes, 1.09 (0.14–7.91) for crustaceans, 1.51 (0.50–4.58) for Zebra mussels, 0.35 (0.11–1.12) for snails, 1.41 (0.38–5.20) for fish and 1.04 (0.30–3.52) for all species combined (Table S16). Given that a value for MB of 1 represents no systematic bias in terms of a systematic over or underestimation of the concentrations, it follows that, in general, the model is in good agreement with the observed behaviour of metaflumizone in the microcosm food-web. The only exception to this general behaviour was for the calculated concentrations of metaflumizone in snails, which were underestimated. The large variation in the observed metaflumizone concentrations on the 3rd sampling day and the lack of adequate sampling on the 4th sampling day may play a role in this apparent departure from the model's general behaviour. Considering the variability in the observed concentrations data, calculated concentrations were not statistically different from the observed concentrations in all species tested.

Despite the apparent overestimation of the concentrations in the sediment (Fig. 5), the fit of the model to the observed concentrations in biota was not greatly affected when using the model-calculated concentrations of metaflumizone in the water and sediments as input parameters for the calculation of the concentrations in the biota of the microcosm. Fig. S2 illustrates the comparison of the model predicted and observed metaflumizone concentrations in various organisms in the microcosm study when using the metaflumizone application rate as the main external input parameter for the model. The mean MB values calculated for the aquatic organisms were: 1.41 for macrophytes; 0.78 for crustacean; 0.72 for zebra mussel; 0.61 for snail and 1.29 for fish (Table S17). The mean MB for all organisms was calculated to be 0.91 with 95% intervals of 0.44 and 1.88. The main reason for the limited effect of the concentrations in the sediments on the fit of the model to the observed concentration data is that the aqueous concentrations largely control the uptake of metaflumizone in the biota of the microcosm, and the fit of the model to the aqueous concentrations in the microcosm was reasonably adequate (Fig. 5). The concentrations in the sediments appeared to have little effect on the model outcomes, indicating that water is the main source of chemical uptake in aquatic biota.

4.2. Model application

Fig. 7 shows calculated concentrations of metaflumizone in water and sediment of a farm pond following the illustrative application of this pesticide of 280 g/ha, four times annually at 7-day intervals over a 10 year period and a 5% wind drift. Fig. 7 illustrates the large temporal variations of the metaflumizone in the water and sediment, with variations in water being greater than those in sediments. In this pesticide application scenario, concentrations of metaflumizone in sediment solids and bulk water can be expected to stay below the corresponding NOECs in Zebrafish *and Chironomus tentans* throughout the 10 year duration of application.

It is common practice for conducting assessments of potential impacts of pesticide application to compare concentrations in water and/or sediments to toxicity reference values expressed in terms of concentrations water and sediments because the toxicity data are typically measured in terms of concentrations in water and sediments. The food-web model of AGRO also has the capacity to estimate concentrations in biota which can be compared to toxicity reference values expressed in terms pesticide body burdens or dietary dosages for aquatic life consuming organisms such as birds or mammals. Often body burden based toxicity reference values are not available because their measurement involves (often difficult) analysis of biological matrices. However, they can often be estimated, e.g. by multiplying a NOEC in fish by the bioconcentration factor of the chemical if the bioconcentration factor is known. Reference doses for chemical substances are often available. The advantage of using the food-web model of AGRO and toxicity reference values presented in terms of body burdens or dietary dosages is that the role of dietary bioaccumulation and food-web biomagnification can be included in the calculations. Including dietary bioaccumulation in the assessment is particularly important for pesticides that can biomagnify in food-webs, e.g. very hydrophobic pesticides that are not or poorly metabolized.

4.3. Model comparison

Fig. 8 shows the results of time-dependent calculations of the concentrations in the various media of the farm pond following a pulse loading event. Fig. 8 shows that concentrations fluctuate substantially over time. The temporal fluctuations in concentrations are greatest for water, phytoplankton and zooplankton and smallest for sediments. In all cases, the peak concentrations are far below the concentrations calculated by the steady-state model that uses a loading rate equal to the pulse loading rates. Hence, simulating a pulse loading scenario with a steady-state model using a loading rate equal to the pulse loading rate can be expected to overestimate the peak concentrations that are reached in water, sediments and biota of the farm pond. If the steady-state model calculations use a loading rate that introduces the same annual amount of pesticide into the farm pond as that in pulse loading scenario, then the steady-state model will calculate a concentration that is equal to the mean concentration in the time dependent simulation but that underestimates the peak concentrations that are reached in the farm pond. The model comparison clearly shows that steady-state models are likely inadequate in accurately estimating concentrations of pesticides in media and organisms of farm ponds after pulse loading applications. When simulating concentrations of pesticides resulting from episodic pesticide application events, time dependent models generally perform better than steady-state models and should be preferred for risk assessment.

5. Conclusion

This study investigated the performance of the environmental fate and organism sub-models of AGRO-2014 using empirical data of laboratory experiments and microcosm studies from several sources. The model bias, a metric used to quantify the extent of model performance, ranged between 0.35 and 2.71 with a median value of 1.14 for all tests. A model bias of 1 presents perfect model agreement. Model-calculated concentrations were within a factor of 3 of observed concentrations and on average slightly overestimated observed concentrations by approximately 14%. The study illustrates that because pesticide loadings to water bodies vary with seasonal agronomic practices, crop growth, pest pressure, weather and other factors, a time dependent model is a more appropriate and likely a more accurate model of the concentrations of pesticides in farm ponds than a corresponding steady-state model. The AGRO-2014 model appears to be a useful model for assessing the concentrations of non-ionic hydrophobic organic pesticides in farm ponds under time variable pesticide application scenarios. It may also be useful in assessing if pesticide application rates can be expected to cause concentrations of pesticides in water, sediment and biota below target or toxicity values. We encourage further application and testing of the model to further improve the assessment of the environmental fate and effects of pesticides in environmental systems.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.05.115.

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