DEVELOPMENT, VALIDATION AND APPLICATION OF A TIME-DEPENDENT FOOD WEB BIOACCUMULATION MODEL FOR ORGANIC PESTICIDES IN AQUATIC ECOSYSTEMS

by

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ABSTRACT

Currently, steady-state based bioaccumulation models are used by regulators to assist environmental guideline development and to conduct legislation of pesticides. For high Kow chemicals that do not reach steady-state in environmental compartments quickly, the steady-state based models could overestimate chemical concentrations and lead to errors in environmental evaluation. A time-dependent food web bioaccumulation model was developed to improve the evaluation of the fate and effects of pesticides in aquatic environments. The performance of the model was evaluated by simulating a Bluegill bioconcentration study for metaflumizone and microcosm studies for three pesticides, metaflumizone, kresoxim-methyl and pyraclostrobin. The model predictions were compared with the empirical data to determine the accuracy of model predictions. Model predictions for these three pesticides are in good agreement with the empirical data. The model can be applied to ecological risk assessment to provide exposure concentrations, internal body burden and remediation target for the impacted aquatic ecosystems.

Keywords: food web; bioaccumulation; time-dependent; model; pesticide; metaflumizone

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GLOSSARY

Bioaccumulation	The process by which the chemical concentration within an organism achieves a level that exceeds that in its environment as a result of chemical uptake through all possible routes of exposure (eg., dietary, dermal, respiratory). Gobas & Morrison, 2000
Bioaccumulation factor	The ratio of the chemical concentration in organism to the chemical concentration in water. The concentration can be expressed on a wet weight; dry weight or lipid weight basis. Gobas & Morrison, 2000
Bioconcentration	The accumulation of the dissolved phase of the compound in water by the organism via respiratory surfaces or skin. Connell, 1988
Biomagnification	The process in which the chemical concentration in an organism achieves a level that exceeds that in the organism's diet, due to dietary absorption Gobas & Morrison, 2000
Biota-sediment accumulation factor	The ratio of the chemical concentration in an organism to the chemical concentration in the sediment in which the organism resides Gobas & Morrison, 2000
Ecological risk assessment	Ecological risk assessment is a process that evaluates the likelihood that adverse ecological effects are occurring or may occur as a result of exposure to one or more stressors US EPA, 1992
Lowest observed adverse effect limit	The lowest concentration or dose in a test which produces an observable adverse effect. US EPA, 2007

No observed adverse effect limit	The maximum concentration or dose in a test which produces no observed adverse effects. US EPA, 2007
Octanol-water partition coefficient	The ratio of a chemical's solubility in octanol versus water. Mackay, 1991
Steady-state	A condition where the total flux of chemical into an organism equals the total flux out with no net change in mass or concentration of the chemical Gobas & Morrison, 2000

LIST OF ACRONYMS

BAF	Bioaccumulation factor
BCF	Bioconcentration factor
BSAF	Biota-sediment accumulation factor
EC50	Effect concentration that cause adverse effects in 50% of the population
EFED	Environmental Fate and Effects Division
ERA	Ecological Risk Assessment
EXAMS	Exposure Analysis Modeling System
DOC	Dissolved organic carbon content
Kow	Octanol-water partition coefficient
LC50	Lethal concentration that cause lethality in 50% of the population
LOEC	Lowest observed effect concentration
MB	Mean model bias
NOEC	No observed effect concentration
OC	Organic carbon
POC	Particulate organic carbon content
PRZM	Pesticide Root Zone Model
TOC	Total organic carbon content
US EPA	United States Environmental Protection Agency

CHAPTER 1: INTRODUCTION

1.1 Background

In recent years, several bioaccumulation models have been developed to estimate chemical concentrations in the environment (EXAMS, Arnot and Gobas, 2004, Mackay, 1994 and Gobas et al. 1995, 2003, 2004). The majority of these models were developed based on mass balance equations. A mass balance is an accounting of material entering and leaving a system. Based on the "conservation of mass" principle, the mass that enters a system must either leave the system or accumulate within the system. Therefore, by considering the chemical kinetics in and out of a system, mass balance equations can be developed to describe the chemical partitioning in different environmental compartments (e.g., water, sediment and biota).

Bioaccumulation is the process by which the chemical concentration in an aquatic organism achieves a level exceeding that in the water as a result of chemical uptake through all possible routes of chemical exposure (e.g., dietary absorption, respiration, dermal absorption) (Webster, 2004). The level of bioaccumulation can be expressed by the bioaccumulation factor (BAF), the steady-state ratio of the chemical concentration in the organism, resulting from uptake from water and food, and the chemical concentration in the water. The bioaccumulation potential of a chemical in aquatic organisms depends on the

organism and the nature of the chemical (Thomann, 1989). The octanol-water partition coefficient, Kow, is a key property of the chemical that describes the degree of chemical bioaccumulation. The octanol-water partition coefficient is the ratio of the concentration of a chemical in octanol and in water at equilibrium at a specified temperature. Since octanol resembles the solution properties of lipid and other organic matrices, the Kow of a chemical is often used to assess the fate of the chemical in the environment and in the aquatic organisms (Mackay, 1982).

Currently, the U.S. EPA and Environment Canada have been using steady state based bioaccumulation models as tools to estimate environmental concentrations to derive environmental guidelines and to curtail chemical emission into the environment. These models assume that chemicals will reach steady state. This assumption is reasonable for applications where the organisms have been exposed to chemicals for a long period of time and for chemicals that are subject to relatively fast exchange kinetics (e.g. lower Kow substances, small organisms); since, under these situations, steady-state is achieved rapidly. However, when the exchange kinetics are relatively slow (e.g., slowly metabolizable chemicals of high Kow in large, lipid-rich organisms), steady state takes a long time to achieve. When applying steady state bioaccumulation models to these situations, the model may overestimate the chemical concentrations in the environment and in the aquatic organisms. For chemicals (e.g., pesticides and industrial products) that have economic values or are

beneficial to human life, these errors may affect the economic values and potential benefits of these chemicals.

By developing a time-dependent food web bioaccumulation model, some of the key limitations of steady-state based models can be addressed. The time-dependent food web bioaccumulation model provides a more realistic estimation of chemical concentrations in the environment. The model can also be used to screen new and existing chemicals for their potential to bioaccumulate, to develop water- and sediment-quality criteria, to develop total maximum daily loadings and remediation targets for contaminated aquatic ecosystem.

The objectives of this study are:

1. Develop a time-dependent food web bioaccumulation model for organic chemical in water, sediment and aquatic ecosystems that can be used to estimate chemical concentrations in certain aquatic organisms over time.
2. Evaluate the performance of the model by comparing model predictions with empirical data.
3. Use the time-dependent food web bioaccumulation model to investigate the potential over-prediction of chemical concentrations in the environmental compartments by the steady-state based food web bioaccumulation model.

4. Apply the time-dependent model to derive the maximum allowable pesticide loadings from pulse exposures so that the pesticide concentrations in the environment will not exceed the environmental guidelines.

To achieve the research objectives, the research project is divided into three major components. The first component is the development of a new time-dependent food web bioaccumulation model based on a steady-state food web bioaccumulation model (Arnot and Gobas, 2004) and Level III fugacity model (Mackay and Paterson, 1991). The new model is capable of estimating concentrations for hydrophobic organic chemicals in different environmental compartments such as water, sediment and in key aquatic organisms at different time points. The theory of model development is discussed in chapter 2. The second component is the investigation of model performance. Here the performance of the environmental fate sub-model, food web sub-model and the combined time-dependent food web bioaccumulation model are determined by conducting model performance analyses comparing model predicted chemical concentrations in different environmental compartments to empirical data. Model stimulations are performed to mimic a bioconcentration study using metaflumizone (BAS 320 I) and microcosm studies for three pesticides, i.e., metaflumizone (BAS 320 I), kresoxim-methyl (BAS 490 02F) and pyraclostrobin (BAS500 00F). Mean model bias (MB) is calculated for each model performance analysis to quantitatively express model performance. The third component is the

model's application. Here the model is used to illustrate the model's application in deriving pesticide application rates consistent with pesticide regulations and in ecological risk assessment. In addition, the time-dependent food web bioaccumulation is used to illustrate that it can solve the potential overestimation problems of the steady state based bioaccumulation model.

CHAPTER 2: MODEL THEORY

A time-dependent food web bioaccumulation model for organic chemicals for aquatic ecosystems was developed based on the bioaccumulation model of Arnot and Gobas (2004). The time-dependent food web bioaccumulation model contains an environmental fate sub-model which was developed following a previous model by Gobas et al. (1995) which was developed after Mackay et al. (1994). The time-dependent food model provides time-dependent estimations of chemical concentrations in water and sediment based on the amount of chemical released into the water. The resulting concentrations in water and sediments served as the model input parameters for the food web model; since, the aquatic organisms are exposed to the chemicals in water and/or sediment. By linking the two models together, time-dependent chemical concentrations in the aquatic organisms can be estimated as a result of time varying pesticide application rates.

The theories for the development of time-dependent environmental fate sub-model and time-dependent food web sub-model are explained in chapter 2.1 and 2.2 respectively.

2.1 Time-dependent environmental fate sub-model theory

The time-dependent environmental fate sub-model includes two mass balance equations (Equation 1 and 2) describing the net movement of chemical in and out of the water and sediment in an aquatic ecosystem. Figure 2.1 illustrates the conceptual diagram describing the major routes of chemical uptake and elimination in the water and sediments.

The amount of chemical released into the water in an aquatic ecosystem can be described as the total chemical inputs into the water minus the total chemical outputs from the water. The total inputs of chemical into the water include: direct chemical release to the water and chemical partitioning from sediment to water through the sediment-water diffusion and sediment resuspension. Total chemical outputs away from water include: volatilization to the atmosphere, outflow from the ecosystem, chemical degradation in water and chemical diffusion from water to sediment and settling to sediment.

The change in mass of chemical (g) in water as a function of time (with a defined time increment) can be calculated as:

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

Where

dM_W / dt = the net flux of chemical in water at any point in time t (g/day)

L = direct chemical inputs to the water (g/day)

k_{SW} = overall sediment to water transport rate constant (day^{-1})

M_s = the mass of chemical in sediment (g)

k_V = rate constant of chemical volatilization to the atmosphere (day^{-1})

k_O = outflow rate constant from the ecosystem (day^{-1})

k_{WS} = rate constant of chemical diffusion from water to sediment (day^{-1})

M_W = the mass of chemical in water (g)

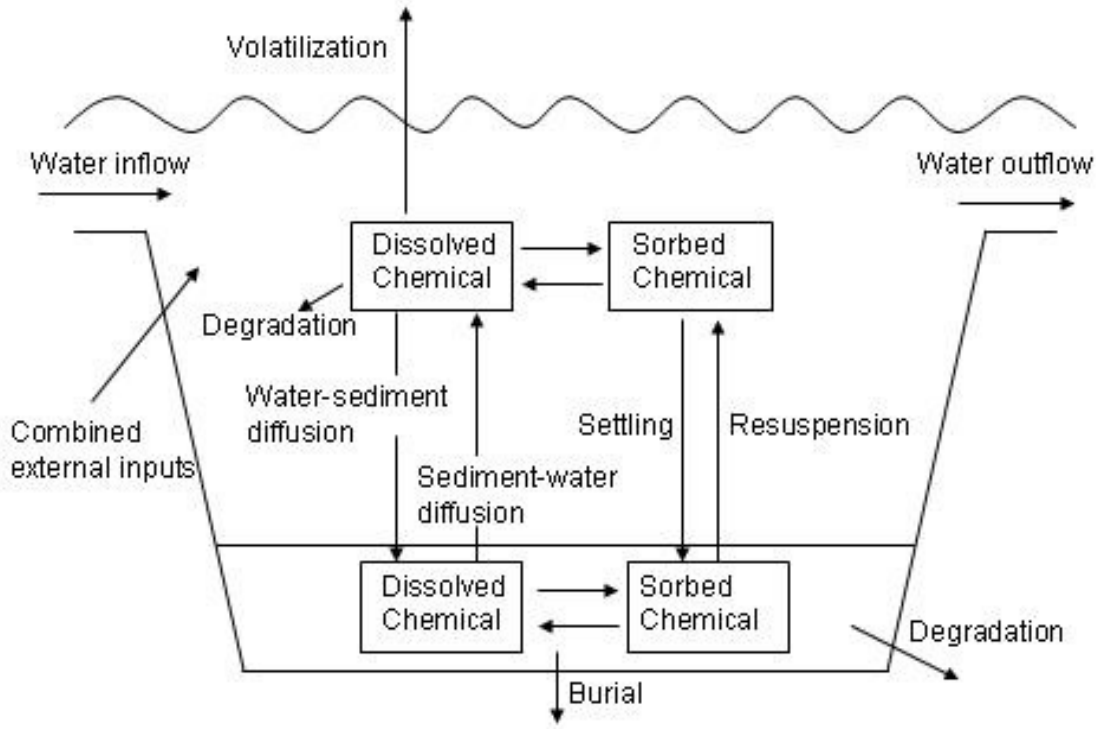

Figure 2-1 Conceptual diagram of the distribution of an organic chemical in an aquatic ecosystem as described by the environmental fate sub-model.

A similar approach was applied to derive the mass balance equation for the sediments. The input of chemical into the sediment is through transport through sediment settling and diffusion. Chemical transports out of the sediment compartment are via sediment burial, settling of suspended solids, and chemical diffusion from sediment to water and through chemical degradation in the sediments. The change in the mass of chemical in sediment as a function of time is described as:

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

Where

dM_S / dt = the net flux of chemical in sediment at any point in time (day).

k_{WS} = overall water to sediment transport rate constant (day^{-1})

M_W = the mass of chemical 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} = chemical degradation rate in sediment (day^{-1})

M_S = the mass of chemical in sediment (g)

The following equations describe how each rate constant is calculated.

Outflow rate constant (k_O):

$$k_O = F / (1000 \cdot V_W) \quad [3]$$

Where

k_O = outflow rate constant (day^{-1})

F = water in- and out-flow (L/day)

V_W = volume of water (m^3)

Volatilization rate constant (k_V):

$$k_V = (S_{aw} \cdot f_{DW} \cdot ve) / V_W \quad [4]$$

Where

k_V = volatilization rate (day^{-1})

S_{aw} = lake surface area (m^2)

f_{DW} = fraction of freely dissolved chemical in water (unitless)

ve = volatilization mass transfer coefficient (m/day)

V_W = volume of water (m^3)

Overall water to sediment transport rate constant (k_{WS}):

$$k_{WS} = k_{WS1} + k_{WS2} \quad [5]$$

Where

k_{WS} = overall water to sediment transport (day^{-1})

k_{WS1} = solids settling rate (day^{-1})

k_{WS2} = water-to-sediment diffusion rate (day^{-1})

Overall sediment to water transport rate constant (k_{SW}):

$$k_{SW} = k_{SW1} + k_{SW2} \quad [6]$$

Where

k_{SW} = overall sediment to water transport (day^{-1})

k_{SW1} = solids resuspension rate (day^{-1})

k_{SW2} = sediment-to-water diffusion rate (day^{-1})

Solids settling rate constant (k_{WS1}):

$$k_{WS1} = S_{aw} \cdot vs \cdot (1 - f_{DW}) / V_w \quad [7]$$

Where

k_{WS1} = solids settling (day^{-1})

S_{aw} = lake surface area (m^2)

vs = solids settling rate (m/day)

f_{DW} = fraction of freely dissolved chemical in water (unitless)

V_w = volume of water (m^3)

Water to sediment diffusion rate constant (k_{WS2}):

$$k_{WS2} = S_{as} \cdot v_D \cdot f_{DW} / V_W \quad [8]$$

Where

k_{WS2} = water to sediment diffusion (day^{-1})

S_{as} = sediment surface area (m^2)

v_D = water to sediment diffusion mass transfer coefficient (m/day)

f_{DW} = fraction of freely dissolved chemical in water (unitless)

V_W = volume of water (m^3)

Solids resuspension rate constant (k_{SW1}):

$$k_{SW1} = (ResFlux / C_{SS}) \cdot (1- f_{DS}) / (1000 \cdot V_S) \quad [9]$$

Where

k_{SW1} =solids resuspension (day^{-1})

ResFlux = sediment solids mass balance and resuspension flux (kg/d)

C_{SS} = concentration of solids in sediment (kg/L)

f_{DS} = fraction of freely dissolved chemical in sediment (unitless)

V_S = volume of sediment (m^3)

Sediment to water diffusion rate constant (k_{SW2}):

$$k_{SW2} = S_{as} \cdot v_D \cdot f_{DS} / V_S \quad [10]$$

Where

k_{SW2} = sediment to water diffusion (day^{-1})

S_{as} = sediment surface area (m^2)

v_D = water to sediment diffusion mass transfer coefficient (m/day)

f_{DS} = fraction of freely dissolved chemical in sediment (unitless)

V_S = volume of sediment (m^3)

Sediment burial rate constant (k_B):

$$k_B = v_B \cdot S_{as} \cdot (1 - f_{DS}) / d_{SS} \cdot 10^{-6} / V_S \quad [11]$$

Where

k_B = sediment burial rate constant (day^{-1})

v_B = sediment burial mass transfer coefficient (m/day)

S_{as} = sediment surface area (m^2)

f_{DS} = fraction of freely dissolved chemical in sediment (unitless)

d_{SS} = density of sediment solids (kg/L)

V_S = volume of sediment (m^3)

Chemical degradation rate in water (k_{WR}):

$$k_{WR} = Ln(2) / hlw \quad [12]$$

Where

k_{WR} = chemical degradation rate constant in water (day^{-1})

hlw = water half life of chemical (day)

Chemical degradation rate in sediment (k_{SR}):

$$k_{SR} = Ln(2) / hls \quad [13]$$

Where

k_{SR} = chemical degradation rate constant in sediment (day^{-1})

hls = sediment half life of chemical (day)

Volatilization mass transfer coefficient (v_E):

$$v_E = 1 / (1 / v_{EW} + 1 / (K_{AW} \cdot v_{EA})) \quad [14]$$

Where

v_E = volatilization mass transfer coefficient (m/day)

v_{EW} = water-sediment evaporation mass transfer coefficient (m/day)

K_{AW} = partition coefficient of suspended particles in the water

v_{EA} = air-side evaporation mass transfer coefficient (m/day)

Partition coefficient of suspended particles in the water (K_{PW}):

$$K_{PW} = 0.35 \cdot OC_{PW} \cdot K_{OW} \quad [15]$$

Where

K_{PW} = partition coefficient of suspended particles in the water (L/kg)

OC_{PW} = organic carbon content of particles in water (unitless)

K_{OW} = octanol-water partition coefficient of the chemical (unitless)

0.35 = proportionality constant (L/kg)

Partition coefficient of bottom sediment particles (K_{PS}):

$$K_{PS} = 0.35 \cdot OC_{SS} \cdot K_{OW} \quad [16]$$

Where

K_{PS} = partition coefficient of bottom sediment particles (L/kg)

OC_{SS} = organic carbon content of bottom sediment (unitless)

K_{OW} = octanol-water partition coefficient of the chemical (unitless)

0.35 = proportionality constant (L/kg)

Air-water partition coefficient (K_{AW}):

$$K_{AW} = H / (8.314 \cdot (273 + T_W)) \quad [17]$$

Where

K_{AW} = air-water partition coefficient (unitless)

H = Henry's law constant ($Pa \cdot m^3/mol$)

T_W = water temperature (^oC)

Temperature dependence of Henry law constant ($H(T_W)$) for PCBs:

$$\ln H(T_W) = \ln H(298) + 20.18 - (6013.6 / Tw) \quad [18]$$

Where

$\ln H(T_W)$ = temperature dependence of Henry law constant (H) for PCBs

T_W = water temperature (^oC)

Fraction of freely dissolved chemical in water (f_{DW}):

$$f_{DW} = 1 / (1 + (C_{PW} \cdot 0.35 \cdot OC_{PW} \cdot K_{OW} / d_{PW}) \quad [19]$$

Where

f_{DW} = fraction of freely dissolved chemical in water (unitless)

C_{PW} = concentration of particles in water (kg/L)

OC_{SS} = organic carbon content of particles in water (unitless)

K_{OW} = octanol-water partition coefficient of the chemical

d_{PW} = density of suspended solids (kg/L)

0.35 = proportionality constant (L/kg)

Fraction of freely dissolved chemical in sediment (f_{DS}):

$$f_{DS} = 1 / (1 + (C_{SS} \cdot 0.35 \cdot OCss \cdot K_{OW} / d_{SS})) \quad [20]$$

Where

f_{DS} = fraction of freely dissolved chemical in sediment (unitless)

C_{SS} = concentration of solids in sediment (kg/L)

OC_{SS} = organic carbon content of bottom sediment (unitless)

K_{OW} = octanol-water partition coefficient of the chemical

d_{SS} = density of sediment solids (kg/L)

0.35 = proportionality constant (L/kg)

Settling of sediment solids flux (SetFlux):

$$SetFlux = 1000 \cdot C_{PW} \cdot k_{WS1} \cdot V_W \quad [21]$$

Where

SetFlux= settling of sediment solids flux (kg/day)

C_{PW} = concentration of particles in water (kg/L)

k_{WS1} = solids settling (day^{-1})

V_W = water volume (m^3)

Burial flux of sediment solids (BurFlux):

$$BurFlux = 1000 \cdot C_{SS} \cdot k_B \cdot V_S \quad [22]$$

Where

BurFlux= burial flux of sediment solids (kg/day)

C_{SS} = concentration of solids in sediment (kg/L)

k_B = sediment burial rate constant (day^{-1})

V_S = sediment volume (m^3)

Sediment solids mass balance and resuspension flux (ResFlux):

$$ResFlux = SetFlux - BurFlux \quad [23]$$

Where

ResFlux = sediment solids mass balance and resuspension flux (kg/day)

SetFlux = settling of sediment solids flux (kg/day)

BurFlux = burial flux of sediment solids (kg/day)

Water volume (V_W):

$$V_W = S_{aw} \cdot D_W \quad [24]$$

Where

V_W = water volume of lake (m^3)

S_{aw} = water body surface area (m^2)

D_W = average water depth (m)

Sediment volume (V_S):

$$V_S = S_{as} \cdot D_S \quad [25]$$

Where

V_S= sediment volume (m^3)

S_{as} = sediment surface area (m^2)

D_S = depth of active sediment layer (m)

Concentration of particulate organic carbon (X_{POC}):

$$X_{POC} = C_{PW} \cdot OC_{PW} \quad [26]$$

Where

X_{POC} = concentration of particulate organic carbon (kg/L)

C_{PW} = concentration of particles in water (kg/L)

OC_{PW} =organic carbon content of particles in water (unitless)

Volume of sediment solids (V_{SS}):

$$V_{SS} = C_{SS} \cdot (V_S \cdot 1000) \quad [27]$$

Where

V_{SS} = volume of sediment solids (kg)

C_{SS} = concentration of solids in sediment (kg/L)

V_S = sediment volume (m^3)

$$V_{SSL} = V_{SS} \cdot (1 / d_{SS}) \quad [28]$$

Where

V_{SSL} = volume of sediment solids (L)

V_{SS} = volume of sediment solids (kg)

d_{SS} = density of sediment solids (kg/L)

Volume of pore water in sediment (V_{WS}):

$$V_{WS} = V_S \cdot 1000 - V_{SSL} \quad [29]$$

Where

V_{WS} = volume of pore water in sediment (L)

V_S = sediment volume (m^3)

V_{SSL} = volume of sediment solids (L)

A numerical-integration method was used to solve the mass balance equations. By adding the change in chemical mass in water (dMw) and sediment (dMs) to the chemical mass from the previous time step, the total amount of chemical in water and sediment at time t can be calculated.

$$M_W(t) = M_W(t\text{-}1) + dM_W \quad [30]$$

$$M_S(t) = M_S(t\text{-}1) + dM_S \quad [31]$$

Where

$M_W(t\text{-}1)$ = mass of chemical (g) in water at the previous time step (t – dt)

dM_W = change in chemical mass in water that occurs over the time step dt.

$M_S(t\text{-}1)$ = mass of chemical in sediment at the previous time step (t – dt)

dM_S = change in chemical mass in sediment that occurs over the time step dt.

The corresponding chemical concentrations in water and sediment at different time points can be calculated by dividing the total chemical mass by the total volume of the environmental compartment (i.e., volume of water and sediment respectively).

2.2 Time-dependent food web sub-model theory

The time-dependent food web sub-model is developed following Arnot and Gobas (2004). It is assumed that the exchange of hydrophobic organic chemicals between the organism and its ambient environment can be described by a single mass balance equation. A conceptual diagram is shown in Figure 2.2 to describe the major routes of chemical uptake and elimination in aquatic organisms. The organisms can absorb chemical from their diet through food consumption and from water through gill uptake.

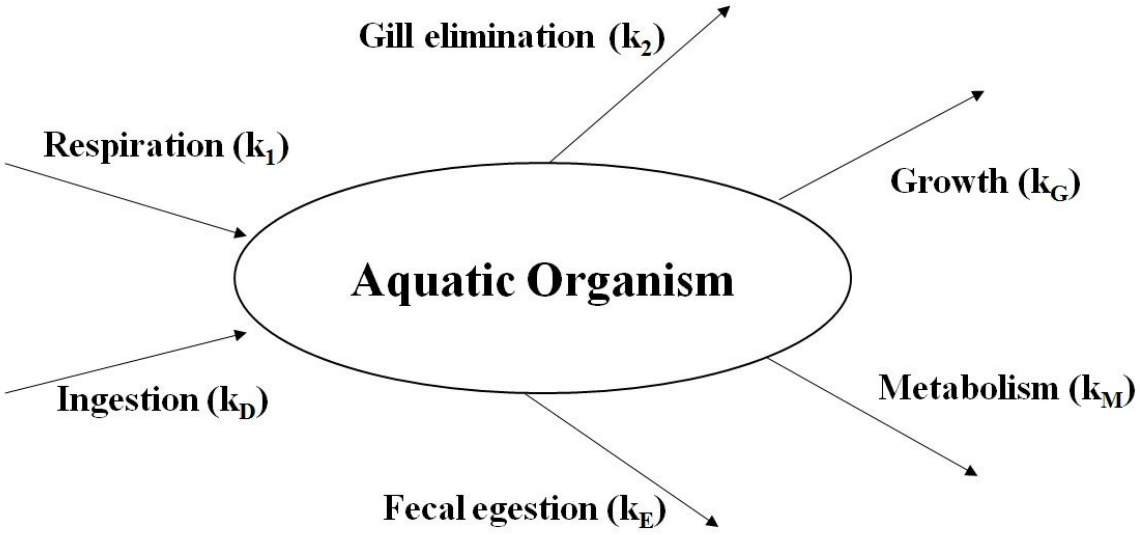

Figure 2-2 A conceptual diagram representing the major routes of chemical uptake and elimination in an aquatic organism. k_D = dietary uptake rate constant; k_1 = gill uptake rate constant; k_2 = gill elimination rate constant; k_M = metabolic transformation rate constant; ; k_G = growth rate constant; k_E = fecal egestion rate constant.

The mass balance equation describing the change in mass of chemical uptake over change in time is shown as:

$$dM_B/dt = \{W_B \bullet (k_1 \bullet [m_O \bullet \Phi \bullet C_{WT.O} + m_P \bullet C_{WD.S}] + k_D \bullet \Sigma(P_i \bullet C_{D.i})) - (k_2 + k_E + k_M) \bullet M_B \quad [32]$$

Where

dM_B/dt = the net flux of chemical being absorbed at any point in time t (day)

W_B = weight of the organism at time t (kg)

k_1 = the clearance rate constant (L/kg/day) for chemical uptake via the respiratory area (i.e., 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 chemical concentration in the overlying water that is freely dissolved and can be absorbed via membrane diffusion (unitless)

$C_{WT.O}$ = the total chemical concentration in the water column above the sediments (g/L)

M_B = the mass of chemical in the organism (g)

$C_{WD.S}$ = the freely dissolved chemical concentration in the sediment associated pore water (g/L)

$\Sigma P_{.i} C_{D.i}$ = the total chemical in the diet

P_i = the fraction of the diet consisting of prey item $_i$ (unitless)

$C_{D.i}$ = the concentration of chemical (g/kg) in pretty item $_i$

k_2 = the rate constant (day^{-1}) for chemical elimination via the respiratory area

k_M = the rate constant (day^{-1}) for metabolic transformation of the chemical

k_D = the clearance rate constant (kg/kg/day) for chemical uptake via ingestion of food and water

k_E = the rate constant (day^{-1}) for chemical elimination via excretion into egested feces

Equation 32 can be simplified by dividing both sides of the equation by the weight of the organism (Wb) as:

$$dC_B/dt = (k_1 \bullet [m_O \bullet \Phi \bullet C_{WT.O} + m_P \bullet C_{WD.S}] + k_D \bullet \Sigma(P_i \bullet C_{D.i})) - (k_2 + k_E + k_M + k_G) \bullet C_B \quad [33]$$

Where

C_B = chemical concentration in the organism (g/kg)

k_G = growth rate constant of the organism (day^{-1})

This equation was used in the spread-sheet to estimate chemical concentrations in different aquatic organisms. By using the simplified equation [33], we can calculate chemical concentrations in organisms directly instead of calculating the mass of chemical in the organism first and then dividing the value by the organism weight. This simplified equation reduces the number of calculations in the excel spread-sheet and speeds up the simulation time. Also, it can make use of the growth rate constant, which is used in the steady-state model.

In the food web sub-model, the change in chemical concentrations in aquatic organism over a time step *d*t can be calculated as:

$$dC_B = \{ (k_1 \bullet [m_O \bullet \Phi \bullet C_{WT.O} + m_P \bullet C_{WD.S}] + k_D \bullet \Sigma(P_{.i} \bullet C_{D.i})) - (k_2 + k_E + k_M + k_G) \bullet C_B \} \bullet dt \quad [34]$$

Due to the small body weight and large chemical elimination rate constant (k_2) of phytoplanktons and zooplanktons, the time required for the chemical to reach steady state in these organisms is very short. For these organisms, a steady-state expression can be used to evaluate the chemical concentrations in phytoplankton and zooplankton. This also reduces the number of required simulations. The equations that are used to describe the chemical concentrations in phytoplankton and zooplankton are:

$$\text{Phytoplanktons: } C_p = (k_1 / (k_2 + k_G)) \bullet (m_O \Phi \bullet C_{WT.O} + m_P \bullet C_{WD.S}) \quad [35]$$

$$\text{Zooplanktons: } C_z = ((k_1 \bullet [m_O \bullet \Phi \bullet C_{WT.O} + m_P \bullet C_{WD.S}] + k_D \bullet \Sigma(P_i \bullet C_{D.i})) / (k_2 + k_E + k_G + k_M)) \quad [36]$$

A numerical integration approach was used to calculate the chemical concentrations in each aquatic organism at time t.

$$C_B(t) = C_B(t\text{-}1) + dC_B \quad [37]$$

Where

C_B (t-1) = chemical concentration (g/kg) in biota at the previous time step (t – dt)

dC_B = change in chemical concentration (g/kg) that occurs over the time step dt

The mass balance equation describing the chemical partitioning into aquatic organism was applied to each of the aquatic species with the exception of phytoplankton and zooplankton. The individual sub-models for each aquatic organism are linked together through feeding interactions (food web). The default food web structure in the model was shown in Figure 2-3. This default food web structure is the food web structure used by the US EPA. However, other feeding relationships can be used as well.

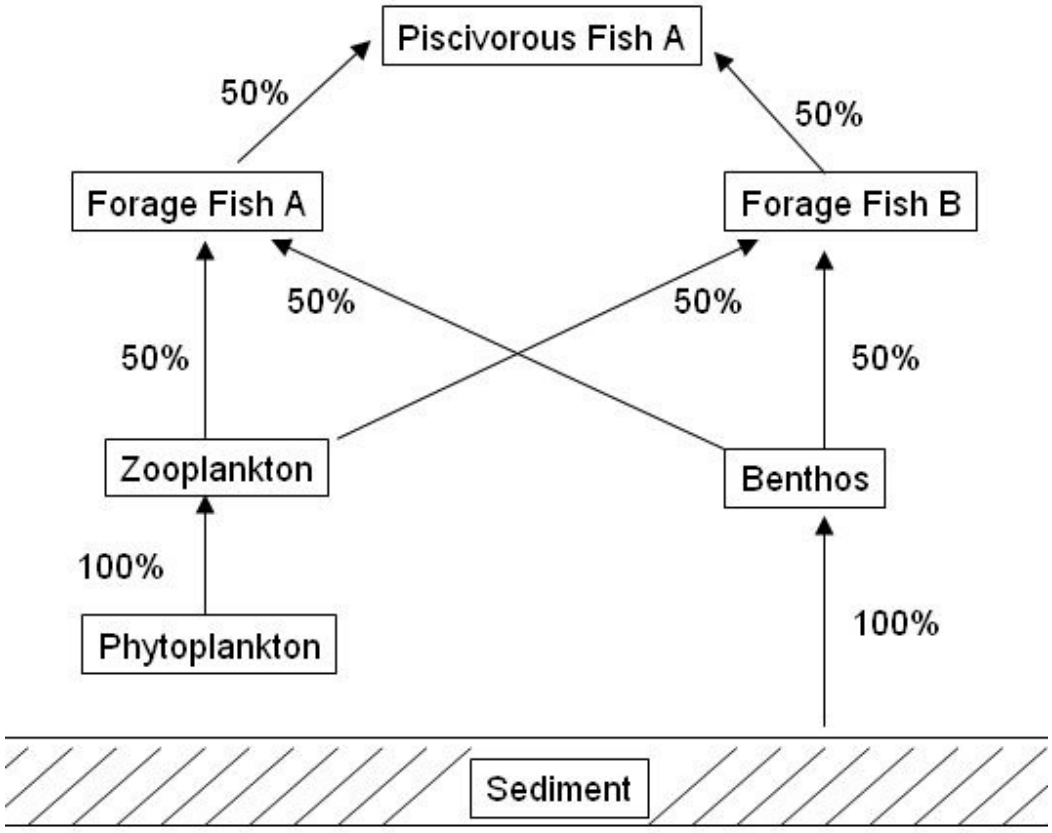

Figure 2-3 The default food web structure in the model. The arrows represent the feeding interactions and the percentages represent the fraction of the predator's diet consisting of various prey items.

The various sub-models for calculating the model parameters are described below.

The ratio of the freely dissolved chemical concentration in water to the total chemical concentration in water (ϕ):

Hydrophobic organic chemicals tend to have a high binding affinity for organic matters, such as particulate organic carbon (POC) and dissolved organic carbon (DOC) in the water column (McCarthy 1983). The chemical will become unavailable for uptake via diffusion into aquatic organism if the chemical binds to these organic materials. The ratio of the freely dissolved chemical concentration in water to the total chemical concentration in water is estimated as:

$$\phi = C_{WD} / C_{WT} = 1 / (1 + X_{POC} \cdot D_{POC} \cdot \alpha_{POC} \cdot K_{OW} + X_{DOC} \cdot D_{DOC} \cdot \alpha_{DOC} \cdot K_{OW}) \quad [38]$$

Where

ϕ = the ratio of the freely dissolved water conc. to the total water conc.

X_{POC} = the concentrations of POC in the water (kg/L)

X_{DOC} = the concentrations of DOC in the water (kg/L)

D_{POC} = the disequilibrium factors for POC partitioning

D_{DOC} = the disequilibrium factors for DOC partitioning

We have assumed that α_{POC} can be estimated as 0.35 L/kg (Seth et al.,1999), and α_{DOC} to be 0.08 L/kg (Burkhard et al., 2000).

Uptake clearance rate constant for fish, invertebrates and zooplankton (k_1):

$$k_1 = E_W \cdot G_V / W_B \quad [39]$$

Where

k_1 = chemical uptake rate from water via the respiratory surface (L/kg · day).

E_W = the gill chemical uptake efficiency (unitless)

G_V = the ventilation rate of the chemical across the respiratory surface area (L/d)

W_B = the wet weight of the organism (kg)

Gill chemical uptake efficiency (E_W):

$$E_W = (A_{EW} + (B_{EW} / K_{OW}))^{-1} \quad [40]$$

Where

E_W = gill chemical uptake efficiency (unitless)

constant A_{EW} = 1.85

constant B_{EW} = 155

Ventilation rate of the chemical across the respiratory surface area (G_V):

$$G_V = 1400 \cdot W_B^{0.65} / DO \quad [41]$$

Where

G_V = ventilation rate (L/day)

W_B = the wet weight of the organism (kg)

DO = the dissolved oxygen concentration in the water (mg O_2/L)

Chemical uptake rate constant for algae, phytoplankton and aquatic macrophytes (k_1):

$$k_1 = (A_P + ((B_P / K_{OW}))^{-1} \quad [42]$$

Where

k_1 = chemical uptake rate constant for algae, phytoplankton and aquatic macrophytes (L/kg/day)

A_P = a constant describing the resistance to chemical uptake through the aqueous phases of the algae, phytoplankton or macrophyte (day)

B_P = a constant describing the resistance to chemical uptake through organic phases of the algae, phytoplankton or macrophyte (day)

Default values for constant A_P and B_P are $6.0 \cdot 10^{-5}$ (day) and 5.5 (day) respectively according to Arnot and Gobas (2004).

The respiratory elimination rate constant (k_2):

$$k_2 = k_1 / K_{BW} \quad [43]$$

Where

K_{BW} = the biota-water partition coefficient (L/kg wet weight)

k_2 = the rate constant (day^{-1}) for chemical elimination via the respiratory area

k_1 = the clearance rate constant (L/kg/day) for chemical uptake via the respiratory area

Organism-water partition coefficient K_{BW}:

$$K_{BW} = k_1 / k_2 = v_{LB} \cdot K_{OW} + v_{NB} \cdot \beta \cdot K_{OW} + v_{WB} \quad [44]$$

Where

K_{BW} = Organism-water partition coefficient

k_1 = the clearance rate constant (L/kg/day) for chemical uptake via the respiratory

k_2 = the rate constant (day^{-1}) for chemical elimination via the respiratory area

v_{LB} = the lipid fraction (kg lipid/kg organism ww)

v_{NB} = the non-lipid organic matter (NLOM) fraction (kg NLOM / kg organism wet weight)

v_{WB} = the water content (kg water/kg organism ww) of the organism

β = a proportionality constant expressing the sorption capacity of NLOM to that of octanol

Phytoplankton-water partition coefficient (K_{PW}):

$$K_{PW} = v_{LP} \cdot K_{OW} + v_{NP} \cdot 0.35 \cdot K_{OW} + v_{WP} \quad [45]$$

Where

K_{PW} = phytoplankton-water partition coefficient

v_{LP} = the lipid fraction in phytoplankton (kg lipid/kg organism ww)

v_{NP} = the non-lipid organic matter in phytoplankton (NLOM) fraction (kg NLOM/kg organism ww)

v_{WP} = the water content in phytoplankton (kg water/kg organism ww) of the organism

Fraction of time the organisms is in contact with overlaying water (m_O) and sediment associated pore water (m_P):

Benthic fish and some invertebrates have close contact with bottom sediment. These organisms can exchange chemical with sediment associated pore water. For organisms that have no direct contact with pore water, m_P is zero. In all cases m_O equals 1 - m_P.

Freely dissolved concentrations in pore water ($C_{WD,P}$):

$$C_{WD,P} = C_{S,OC} \cdot \delta_{OCS} / K_{OC} \quad [46]$$

Where

$C_{WD,P}$ = the freely dissolved chemical concentration in the pore water (g/L)

$C_{S,OC}$ = the chemical concentration in the sediment normalized for organic carbon content (g/kg OC)

δ_{OCS} = the density of the organic carbon in sediment (kg/L)

K_{OC} = the organic carbon-water partition coefficient (L/kg)

Dietary uptake clearance rate constant (k_D):

$$k_D = E_D \cdot G_D / W_B \quad [47]$$

Where

k_D = dietary uptake rate constant (kg/kg·day)

E_D = dietary chemical transfer efficiency (unitless)

G_D = the feeding rate (kg/d)

W_B = the weight of the organism (kg)

Dietary absorption efficiencies of the chemicals (E_D):

$$E_D = (A_{ED} \cdot K_{OW} + B_{ED})^{-1} \quad [48]$$

Where

E_D = dietary chemical transfer efficiency (unitless)

constant $A_{ED} = 8.5 \cdot 10^{-8}$

constant B_{ED} = 2.0 for zooplankton, invertebrates and fish

Feeding rates in fish species and aquatic invertebrate species (G_D):

$$G_D = 0.022 \cdot W_B^{0.85} \cdot e^{(0.06 \cdot Tw)} \quad [49]$$

Where

G_D = the feeding rate (kg/day)

W_B = the weight of the organism (kg)

T_W = the mean water temperature in degrees Celsius

Dietary feeding rate for filter feeding species (G_D):

$$G_D = G_V \cdot C_{SS} \cdot \sigma \quad [50]$$

Where

G_D = the feeding rate (kg/d)

G_V = the gill ventilation rate G_V (L/d)

C_{SS} = the concentration of suspended solids (kg/L)

σ = the scavenging efficiency of particles (%) absorbed from the water

Fecal elimination rate constant (k_E):

$$k_E = G_F \cdot E_D \cdot K_{GB} / W_B \quad [51]$$

Where

k_E = fecal elimination rate constant (day^{-1})

E_D = dietary chemical transfer efficiency (unitless)

K_{GB} = the partition coefficient of the chemical between the GIT and the organism (kg-feces/kg-organism · day)

W_B = the weight of the organism (kg)

G_F = feeding rate (kg/day)

$$G_F = \{(1-\varepsilon_L) \cdot v_{LD}) + (1-\varepsilon_N) \cdot v_{ND} + (1-\varepsilon_W) \cdot v_{WD}\} \cdot G_D \quad [52]$$

Where

ε_L = the dietary absorption efficiency of lipid

ε_N = the dietary absorption efficiency of nonlipid organic matters (NLOM)

ε_W = the dietary absorption efficiency of water

v_{LD} = the overall lipid content of the diet

v_{ND} = the overall NLOM content of the diet

v_{WD} = the overall water content of the diet

The partition coefficient of the chemical between the contents of the GIT and the organism (K_{GB}):

$$K_{GB} = (v_{LG} \cdot K_{OW} + v_{NG} \cdot \beta \cdot K_{OW} + v_{WG}) / (v_{LB} \cdot K_{OW} + v_{NB} \cdot \beta \cdot K_{OW} + v_{WB}) \quad [53]$$

Where

v_{LG} = the lipid (kg lipid/kg digesta ww) contents in the gut

$v_{NG,}$ = NLOM (kg NLOM/kg digesta ww) contents in the gut

v_{WG} = water (kg water/kg digesta ww) contents in the gut

β = proportionality constant expressing the sorption capacity of NLOM to that of octanol

The sum of these fractions (i.e. total digesta) approaches 1 and are dependent on the absorption efficiency for each component of the diet as:

$$v_{LG} = (1-\varepsilon_L) \cdot v_{LD} / \{(1-\varepsilon_L) \cdot v_{LD} + (1-\varepsilon_N) \cdot v_{ND} + (1-\varepsilon_W) \cdot v_{WD}\} \quad [54]$$

$$v_{NG} = (1-\varepsilon_N) \cdot v_{ND} / \{(1-\varepsilon_L) \cdot v_{LD} + (1-\varepsilon_N) \cdot v_{ND} + (1-\varepsilon_W) \cdot v_{WD}\} \quad [55]$$

$$v_{WG} = (1-\varepsilon_W) \cdot v_{WD} / \{(1-\varepsilon_L) \cdot v_{LD} + (1-\varepsilon_N) \cdot v_{ND} + (1-\varepsilon_W) \cdot v_{WD}\} \quad [56]$$

Growth rate constant (k_G):

The following generalized growth equations, based on Thomann et al., 1989, were used to provide approximation for the growth rate constant k_G (day^{-1}) of the aquatic species.

Growth rate constant for zooplankton and invertebrates (k_G):

$$k_G = I_{GR} \cdot W_B^{-0.2} \quad [57]$$

Where

k_G = the growth rate constant k_G (day^{-1}) of the aquatic species representative for temperatures around 10°C

I_{GR} = Based on an average water temperature of approximately 15°C, I_{GR} is the invertebrate (0.00035) growth rate coefficients

Growth rate constant for fish (k_G):

$$k_G = F_{GR} \cdot W_B^{-0.2} \quad [58]$$

Where

F_{GR} = Based on an average water temperature of approximately 15°C, F_{GR} is the fish (0.0007) growth rate coefficients

Metabolic transformation rate constant (k_M):

The rate at which a parent compound is eliminated via metabolic transformation is represented by the metabolic transformation rate constant k_M (day^{-1}). To simplify the model and to be conservative, k_M was set to zero as the default value. The result of k_M being zero will cause the model to overestimate chemical concentrations for chemicals that are metabolized quickly. However, if the model is used to develop environmental guidelines for chemicals, it is important to set a conservative value so that all the organisms could be protected. If the metabolic transformation rate constant is available, it can be applied to the model for a more accurate estimation of chemical concentrations.

2.3 Steady-state food web bioaccumulation model theory

The application of equation 1, 2 and 32 to estimate chemical concentrations in water, sediment and aquatic organisms can be limited by the availability of the time-dependent model input parameter values. The equations can be simplified using steady-state assumptions if the time-dependent model input parameters are not available. The steady-state assumption is reasonable for applications in the field in which the organisms have been exposed to the chemical for a long period of time. The steady-state assumptions can also be applied to lower-Kow substances, small aquatic organisms and chemicals that are quickly metabolizable since steady-state is achieved rapidly in these situations.

The chemical mass at steady state can be calculated by setting the change in chemical mass over the change in time to be zero. The calculations of chemical mass in water and sediment at steady-state are shown below:

$$dM_W / dt = L + k_{SW} \cdot M_S - (k_V + k_O + k_{WR} + k_{WS}) \cdot M_W = 0$$

$$L + k_{SW} \cdot M_S = (k_V + k_O + k_{WR} + k_{WS}) \cdot M_W$$

$$M_W = [L + k_{SW} \cdot M_S] / (k_V + k_O + k_{WR} + k_{WS}) \quad [59]$$

$$dM_S / dt = k_{WS} \cdot M_W - (k_{SW} + k_B + k_{SR}) \cdot M_S = 0$$

$$k_{WS} \cdot M_W = (k_{SW} + k_B + k_{SR}) \cdot M_S$$

$$M_S = k_{WS} \cdot M_W / (k_{SW} + k_B + k_{SR}) \quad [60]$$

After substitution of equation [60] into equation [59], it follows that:

$$M_W = \{L + k_{SW} \cdot [k_{WS} \cdot M_W / (k_{SW} + k_B + k_{SR})]\} / (k_V + k_O + k_{WR} + k_{WS})$$

After rearranging the above equation, the mass of chemical in water is calculated as:

$$M_W = L / ((k_V + k_O + k_{WR} + k_{WS}) - ((k_{WS} \cdot k_{SW}) / (k_{SW} + k_B + k_{SR}))) \quad [61]$$

The chemical mass at steady-state in water and sediment can be calculated using equation [64] and [63] respectively. The chemical concentration in water and sediment at steady state can be expressed as:

C_W (steady-state) (g/L) = M_W (at steady-state) (g) / volume of water (L) [62]

C_S (steady-state) (g/kg) = M_S (at steady-state) (g) / volume of sediment (kg) [63]

The chemical concentration in aquatic organisms at steady state can be calculated by setting $dC_B/dt = 0$ in the mass balance equation describing the change in chemical concentration in biota over change in time. The derivation of the chemical concentration in aquatic organism at steady-state is shown below:

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

$$0 = k_1 \bullet [m_O \bullet \Phi \bullet C_{WT.O} + m_P \bullet C_{WD.S}] + k_D \bullet \Sigma(P_{.i} \bullet C_{D.i})) - (k_2 + k_E + k_M + k_G) \bullet C_B$$

$$k_1 \bullet [m_O \bullet \Phi \bullet C_{WT.O} + m_P \bullet C_{WD.S}] + k_D \bullet \Sigma(P_{.i} \bullet C_{D.i})) = (k_2 + k_E + k_M + k_G) \bullet C_B$$

$$C_B = [k_1 \bullet [m_O \bullet \Phi \bullet C_{WT.O} + m_P \bullet C_{WD.S}] + k_D \bullet \Sigma(P_{.i} \bullet C_{D.i}))] / (k_2 + k_E + k_M + k_G)$$

[64]

The rate constants, k_1, k_2, k_D, k_E, k_M and k_G, are calculated as described earlier.

2.4 Model assumptions

The time-dependent food web bioaccumulation model was developed based on several key assumptions: First, to simplify the complex nature of the environment, the model assumes that the sediment and water compositions remain constant in the modelled aquatic ecosystem. Secondly, after the chemical is released into the water, the model assumes that the chemical will be homogeneously distributed in each environmental compartment including water, sediment and key aquatic organisms. Since the purpose of this model is to obtain an estimation of total chemical concentration in different environmental compartments, the model is not designed to estimate chemical concentrations in specific organs of the organism. Therefore, the model is best applied in situations in which the mass or concentration of the chemical in the whole organism is of interest. Another assumption of the model concerns chemical elimination via growth dilution. When an organism grows, the chemical concentration inside the organism is diluted due to an increase in organism's volume. Growth dilution is therefore considered an elimination process although no loss of chemical mass occurs. Because growth is associated with an increase in dietary consumption, growth dilution effect is counteracted by uptake of chemical from diet. The balance of these processes controls the ultimate concentration in the organism.

CHAPTER 3: METHODS

3.1 Modeling tools

The time-dependent food web bioaccumulation model was developed using Microsoft EXCEL spreadsheets. The EXCEL spreadsheet not only allows model users to enter the model parameters with ease but also provides a convenient viewing display of model outputs. 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 (model validation) and model application studies.

3.2 Model parameterization

3.2.1 Default model parameters

To perform simulations using the time-dependent food web bioaccumulation model, the model input parameters have to be parameterized according to the simulation conditions. The EPA had previously suggested a range of default model parameters that can be used to simulate pesticide applications and to estimate the pesticide concentrations in water, sediment and different aquatic organisms in the water bodies (i.e. ponds) near the pesticide application area. These values were evaluated by EFED (Environmental Fate and Effect Division of U.S. EPA) for review. After the evaluation, EFED suggested another set of

model parameter values that could be used for general usages for water quality models for pesticide applications. The EFED recommended parameter values (Table 3-1) were used as the default values for the ecosystem-specific parameters.

The default values for the organism-specific parameters were developed according to the parameters used by the food-web bioaccumulation model addition to the EPA PRZM model used by EFED of the EPA to assess the behaviour of organic pesticides.

The parameterization is summarized in Table 3-1, 3-2 and 3-3.

Table 3-1 EFED recommended model input parameters for water quality models

Model Input Parameters	Unit	Symbol	Value
water body surface area	m^2	Saw	1.00E+04
sediment surface area	m^2	Sas	1.00E+04
average water depth	m	Dw	2
depth of active sediment layer	m	Ds	0.05
water in- and out-flow	L/day	F	9.60E+04
Concentration of particles in water	Kg/L	Cpw	3.00E-05
Concentration of DOC in water	Kg/L	Cdoc	1.20E-06
concentration of solids in sediment	Kg/L	Css	1.51
density of suspended solids	Kg/L	dpw	2.40
density of sediment solids	Kg/L	dss	2.40
organic carbon content of suspended solids	Unitless	Ocpw	4.00E-02
organic carbon content of bottom sediment	Unitless	Ocss	4.00E-02
density of organic carbon	Kg/L	doc	1.00
water-side evaporation mass transfer coefficient	m/day	vew	0.24
air-side evaporation mass transfer coefficient	m/day	vea	24.0
water-to-sediment diffusion mass transfer coefficient	m/day	vd	9.60E-03
solids settling rate	$g/m^2/day$	vss	80
sediment burial mass transfer coefficient	$g/m^2/day$	vb	40
sediment resuspension rate	$g/m^2/day$	vrs	40

Table 3-2 Organism-specific model parameters used by the EPA's food-web bioaccumulation model addition to the PRZM model

Organism-Specific Parameters							
Parameter	**Symbol**	**Phytoplankton**	**Zooplankton**	**Benthos (Diporeia)**	**Forage Fish A**	**Forage Fish B**	**Piscivorous Fish**
Weight (g)	Wb	------	1E-7	0.00001	0.01	0.01	1
Lipid fraction in biota (%)	Vlb	0.50	2	2	4	6	4
Nonlipid organic matter fraction in biota (%)	Vnb	20	20	20	22	22	20
Water fraction in biota (%)	Vwb	79.5	78.0	78.0	74.0	72.0	76.0
Nonlipid organic matter-octanol proportionality constant	Beta	0.35	0.035	0.035	0.035	0.035	0.035
Dietary absorption efficiency of lipid (%)	El	75	72	75	92	92	92
Dietary absorption efficiency of nonlipid organic matter (%)	En	75	72	25	55	55	55
Dietary absorption efficiency of water (%)	Eww	25	25	25	25	25	25
Fraction of the respiratory ventilation that involves overlying water (%)	mo	95	95	95	100	100	100
Fraction of the respiratory ventilation that involves sediment associated pore water (%)	Mp	5	5	5	0	0	0
Particle scavenging efficiency (%)	Sigma	100	100	100	------	------	------
Resistance to chemical uptake through the aqueous phase	A	0.00006	------	------	------	------	------
Resistance to chemical uptake through the organic phase	B	5.5	------	------	------	------	------
Invertebrate growth rate coefficient (T < 17.5 deg C)	Igr	------	5.02E-4	5.02E-4	5.02E-4	5.02E-4	5.02E-4
Invertebrate growth rate coefficient (T > 17.5 deg C)	Fgr	------	0.00251	0.00251	0.00251	0.00251	0.00251
Constant Aew	Aew	1.85	1.85	1.85	1.85	1.85	1.85
Constant Bew	Bew	155	155	155	155	155	155
Constant Aed	Aed	------	3E-7	3E-7	3E-7	3E-7	3E-7
Constant Bed	Bed	------	2	2	2	2	2

Table 3-3 Aquatic food-web structure used by the EPA's food-web bioaccumulation model addition to the PRZM model

Food Web Structure (percent dietary composition)						
Species	**Phytoplankton**	**Zooplankton**	**Benthos**	**Forage Fish A**	**Forage Fish B**	**Piscivorous Fish**
Sediment	0%	0%	100%	0%	0%	0%
Phytoplankton	0%	100%	0%	0%	0%	0%
Zooplankton		0%	0%	50%	50%	0%
Benthos			0%	50%	50%	0%
Forage Fish A				0%	0%	50%
Forage Fish B					0%	50%
Piscivorous Fish						0%

3.2.2 Model parameterizations for model performance analyses and model applications

Several performance analyses were conducted. They include:

- Evaluation of the model performance by simulating a bioconcentration study for metaflumizone to investigate the accuracy of the model in particular the chemical uptake rate (k_1), chemical depuration rate (k_2) and bioconcentration factor (BCF).
- Evaluation of the model performance by simulating microcosm studies for metaflumizone to determine the accuracy of the time-dependent food web bioaccumulation model. The predicted metaflumizone concentrations in water, sediment and in different aquatic organisms in the microcosm were compared with the empirical data.
- Evaluation of the model performance by simulating microcosm studies for two other pesticides, kresoxim-methyl (BAS 490 02F) and pyraclostrobin (BAS 500 00F), to test for the accuracy of the environmental fate sub-model.

In addition, the model was applied to evaluate:

- The recommended pulse loading amount for metaflumizone using external concentration
- The recommended pulse loading amount for metaflumizone using internal body burden
- The maximum allowable application rate for metaflumizone

- The difference in chemical concentration prediction between steady-state based food web bioaccumulation model and time-dependent food web bioaccumulation model for pesticide applications

The model parameterization for each model evaluation and application are discussed in the following sections.

3.2.3 Model parameterization for the evaluation of the model performance using a Bluegill bioconcentration study for metaflumizone

To investigate the accuracy of the model's ability to predict k_1, k_2 and the BCF, the model was used to simulate a bluegill sunfish BCF study for metaflumizone (BAS 320 I) performed by Afzal (unpublished report, 2004). The model predicted k_1, k_2, and BCF were compared with the empirical data from the Afzal' study.

In the Afzal' study, a 42-day exposure period was applied to evaluate the bioconcentration of metaflumizone by bluegill (*Lepomis macrochirus*). The treatment groups received a nominal concentration of 0.040 µg/L of metaflumizone. The chemical uptake rate constant (k_1), chemical depuration rate constant (k_2) and bioconcentration factor (BCF) of metaflumizone were determined. The time-dependent model was parameterized according to the metaflumizone BCF study (Afzal, 2004). For the parameters that were not available from the metaflumizone BCF study, the default model parameterization values were used to parameterize the model.

<u>Chemical-Specific parameterization</u>

Metaflumizone (CAS number: 139968-49-3) is a new insecticide for structural pest control. Metaflumizone has high activity against key insect pests. These pests include lepidoptera, coleopteran, hymenoptera, isopteran and diptera.

Metaflumizone has a molecular weight of 506.40 g/mol and its molecular formula is $C_{24}H_{16}F_6N_4O_2$. Metaflumizone has two isomers: E and Z. The structural formula for E and Z isomer of metaflumizone are shown in Figure 3-1. The log Kow values for E and Z isomers of metaflumizone are 5.1 and 4.4 respectively. According to EFED, it was assumed that both E and Z isomers of metaflumizone have a similar Henry's Law constant of 0.00351 Pa•m^3/mol. The degradation half-lifes of metaflumizone in water and sediment were suggested to be 4.2 and 208 days respectively (Paulick and Jackson, 2004). The detail list of model input parameters for this model application is shown in Table 3-4.

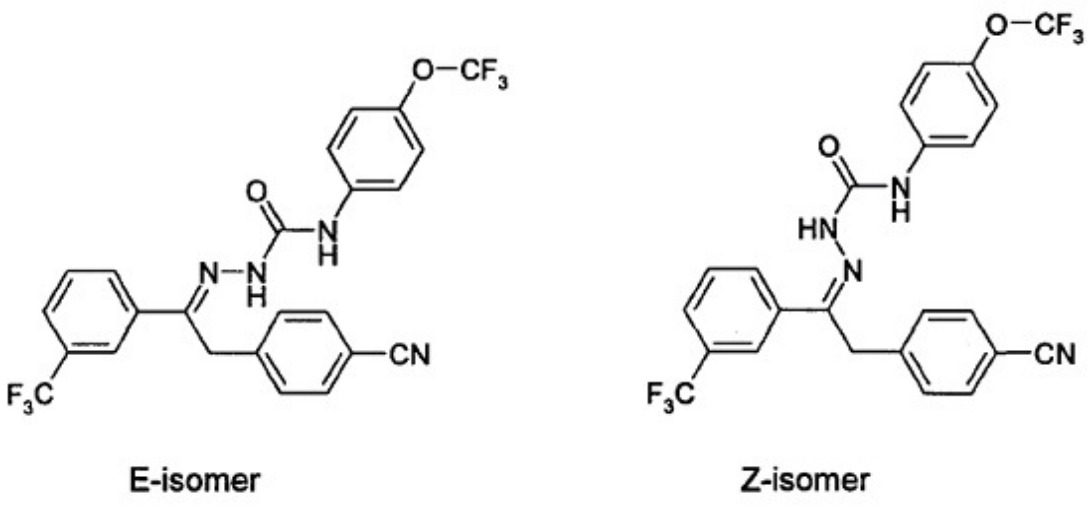

Figure 3-1 Structural formula for E and Z isomer of metaflumizone

Model simulations were performed for each isomer (E and Z) of metaflumizone independently. The model predicted values for k_1, k_2 and BCF were derived by combining the simulation results according to the ratio of E and Z isomer in metaflumizone (9:1).

Table 3-4 Model input parameters for the performance analysis of the time-dependent food web bioaccumulation model using metaflumizone BCF study

Chemical Name		**Metaflumizone**		
Chemical-Specific Properties	**Symbol**	**E-isomer**	**Z-isomer**	**Reference**
Molecular Weight (g/mol)	MolW	506.4	506.4	Paulick et al., 2004
Henry's Law Constant (Pa•m3/mol)	H	0.00351	0.00351	Paulick et al., 2004
log Kow of the chemical	log Kow	5.1	4.4	Paulick et al., 2004
chemical half life in water (day)	hlw	4.2	4.2	Paulick et al., 2004
chemical half life in sediment (day)	hls	208	208	Paulick et al., 2004

Ecosystem-Specific Properties	**Symbol**	**Value**	**Reference**
pH of water	pH	7.96	Afzal, 2004
water temperature (degC)	Tw	22.2	Afzal, 2004

Organism-Specific Parameters	Symbol	Bluegill Sunfish
Weight (g)	Wb	15
Lipid fraction in biota (%)	Vlb	6.76
Nonlipid organic matter fraction in biota (%)	Vnb	20
Water fraction in biota (%)	Vwb	73.24
Nonlipid organic matter-octanol proportionality constant	Beta	0.035
Dietary absorption efficiency of lipid (%)	El	92
Dietary absorption efficiency of nonlipid organic matter (%)	En	55
Dietary absorption efficiency of water (%)	Eww	25
Fraction of the respiratory ventilation that involves overlying water (%)	mo	100
Fraction of the respiratory ventilation that involves sediment associated pore water (%)	Mp	0
Invertebrate growth rate coefficient (T < 17.5 deg C)	Igr	5.02E-4
Invertebrate growth rate coefficient (T > 17.5 deg C)	Fgr	0.00251
Constant Aew	Aew	1.85
Constant Bew	Bew	155
Constant Aed	Aed	3E-7
Constant Bed	Bed	2

3.2.4 Model parameterization for the evaluation of the model performance using microcosm studies for metaflumizone

3.2.4.1 Overview

To evaluate the performance of the time-dependent food web bioaccumulation model in predicting chemical concentrations in the environmental compartments, model simulations were performed to mimic a field microcosm study (Funk, 2004, unpublished report) of metaflumizone. In the microcosm study, microcosms were set up to represent an aquatic ecosystem with water, sediment and key aquatic organisms. Metaflumizone was released into the water of the microcosms at specified application rates according to the experimental design. The metaflumizone concentrations in water, sediment and different aquatic organisms were determined on various sampling days. These data served as the empirical data for the model performance analyses. The simulation of the time-dependent food web bioaccumulation model calculates chemical concentrations in various environmental compartments. The predicted chemical concentrations are then compared to independent empirical concentrations, which are not used to calculate the environmental concentrations.

Two model parameterizations were done for the evaluation of the model performance of food web sub-model and the combined model respectively. The detail for each model parameterization is shown in the following sections.

3.2.4.2 Model parameterization for the evaluation of the performance of the food web bioaccumulation sub-model

Chemical application scenarios

To evaluate the performance of the food web sub-model, the observed metaflumizone concentrations in water and sediment from the metaflumizone bioaccumulation study (Funk, 2004), were used as input parameters. The observed water and sediment concentrations from the metaflumizone bioaccumulation study are listed in Table 6-1.

The time-dependent model was executed by solving the mass balance equations for chemical concentrations using a time-step increment value of 0.1 day. The observed water and sediment concentrations were only measured on the sampling days (Day 1, 7, 9, 12, 15, 22, 36, 64 and 78). To run the time-dependent food web bioaccumulation model, the water and sediment concentrations for all time points are required. A linear interpolation method was applied to the observed concentrations to calculate the water and sediment concentrations on the remaining time points.

Food-web structure parameterization

In the metaflumizone microcosm study, seven aquatic species were placed in the microcosm to represent an aquatic ecosystem. The aquatic species included periphyton, macrophyte (*Myriophyllum spicatum*), zooplankton, crustacean (*Asellus aquaticus*), zebra mussel (*Dreissena polymorpha*), aquatic snail (*Lymnea stagnalis*), and fish (*Pimephales promaelas*).

There was no information about dietary composition for these aquatic organisms in the microcosms. Therefore, assumptions were made to select the parameters for diet compositions. In Funk's study (2004), zooplankton was added in the microcosms every day as the major food source for the fishes. However, zooplankton was not included in the metaflumizone residue analysis. In order to mimic the food web structure in the microcosm aquatic ecosystem, zooplankton was included in the food web structure. It was assumed that zooplankton only ate periphyton. Crustaceans (*Asellus aquaticus*) are benthic organisms. It was assumed that they only ate detritus in the sediment. In addition, it was assumed that zebra mussel only ate periphyton; aquatic snail only ate macrophyte. It was assumed that diet of the fish included 70% of zooplankton, 10% of crustacean, 10% of zebra mussel and 10% of snail. The food web structure is shown in Figure 3.2.

Organism-Specific parameterization

The weight of each organism is required to parameterize the food web model. In the bioaccumulation study for metaflumizone (Funk, 2004), the weight of each aquatic organism in the microcosm was recorded on each sampling day. The average weight of organisms for each species on the initial sampling date was selected as the weight of the organism for the model input parameter value. The information of lipid, water and non-lipid organic matter contents for each organism was taken from Funk's study (2004). If this information was not available, the values were adopted from the Great Lakes Water Quality Initiative

(GLWQI) (U.S. EPA, 1995a). The growth (in body weight) of each aquatic organism is considered by the model's ability to calculate the growth rate constant, K_G, of zooplankton, aquatic invertebrate and fish (described in equation 57 and 58 in chapter 2-2).

For the parameters that could not be obtained from the metaflumizone microcosm study report, the EFED recommended parameter values (Table 3-1) were used to parameterize the model. The model input parameters used to evaluate the model performance of the time-dependent food web sub-model are listed in Table 3-5.

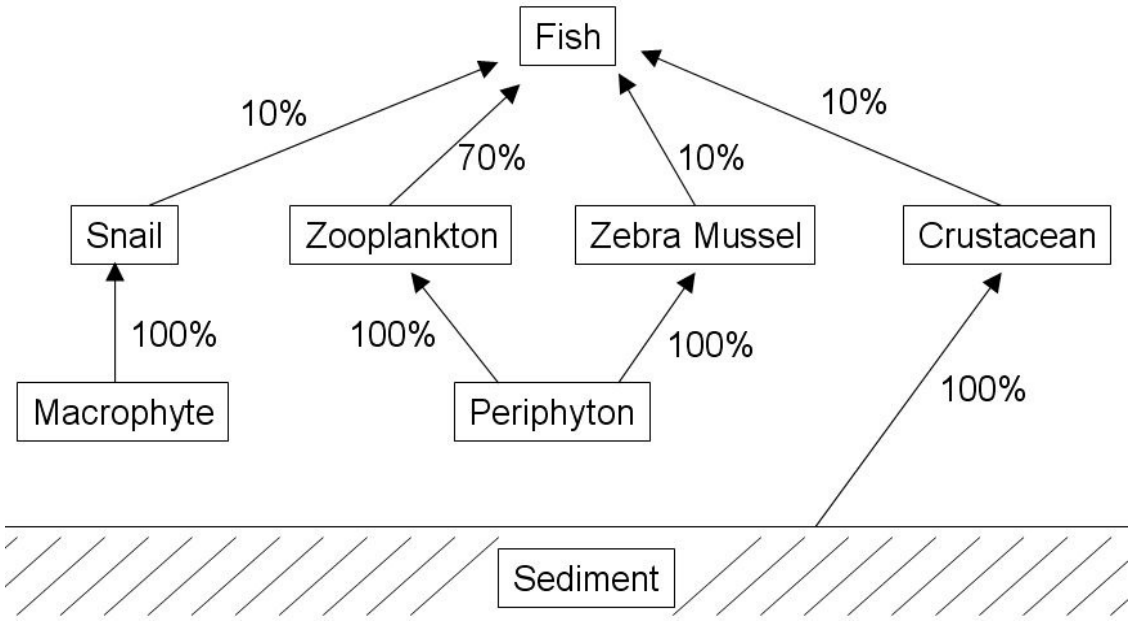

Figure 3-2 Food Web Structure for the validation of the food web bioaccumulation model using metaflumizone. Arrows represent feeding interactions and the corresponding number represents the contribution of each diet item to the total diet of the organism.

3.2.4.3 Model parameterization for the evaluation of the performance of the combined time-dependent environmental fate and food web bioaccumulation model

The evaluation of model performance of the combined time-dependent environmental fate and food web bioaccumulation model was done by performing model simulation mimicking the metaflumizone bioaccumulation study. Model simulations were performed for each isomer of metaflumizone (E and Z isomers) independently with the application scenario of two applications at 7-day intervals. The detail of chemical application scenarios are described in later section. The sum of E and Z isomer concentrations in water, sediment and different aquatic organisms were calculated.

The model parameterizations for chemical-specific and organism-specific parameters were the same as those described in chapter 3.2.4.2. The rationale for selecting the time-dependent environmental fate model parameters are summarized in the section below.

<u>Ecosystem-Specific parameterization</u>

In the metaflumizone bioaccumulation study (Funk, 2004), each microcosm was set up such that the surface area for both water and sediment was 0.92 m^2. The depth of water and sediment were 50 cm and 5 cm respectively.

Water and sediment characterization:

DOC and TOC:

The values for the dissolved organic carbon content (DOC) and total organic carbon content (TOC) of the water were obtained from the metaflumizone microcosm study (Funk, 2004). The total organic carbon content in sediment was reported to be 0.64%. The mean DOC concentration (5.07 ± 1.02 mg/L) and the mean TOC concentration (5.48 ± 1.26 mg/L) in water were used to parameterize the model.

Oxygen saturation level:

The reported oxygen saturation (%) values in water was ranged between 85.9 and 103.1%. An average value of 94.5% was calculated as the oxygen saturation level to be used in the model.

Water pH and temperature:

The physical-chemical water parameters such as pH values and water temperature were recorded throughout the experimental period. Mean values for pH and water temperature (8.60 ± 0.30 and 23.9 ± 2.61 ^{o}C respectively) were used as the model parameter values.

Concentration of solids in sediment:

According to EFED, the EXAMS (Exposure Analysis Modelling System) scenarios for ponds and lakes assume the sediment contains approximately 37%

of water and 63% of sediment. However, in the microcosm study, artificial sediment was used to mimic the natural aquatic ecosystem. There is no additional information about the volume fraction of solids in sediment. It is assumed that the artificial sediment contains mostly solids. The volume fraction of solids in sediment was assumed to be 95%. EFED suggested the bulk sediment density to be 1.85 kg/L. Assuming the water density is 1 kg/L, the density of sediment can be determined as: (1.85 kg/L – 1kg/L x 5%) / 95% = 1.895 kg/L. The concentration of solids in sediment can be calculated as 1.895 kg/L x 0.95 = 1.8 kg/L.

Time-step selection

The time-step was set to 0.1 day to capture changes in chemical concentrations in the environmental compartments over time.

The chemical loading rate in the mass balance equation has units of g/day. To adapt to this time-step of 0.1 day, when the chemical is released into the water as pulse loading, the total pulse-loading amount of chemical released into water is expressed in units of g/0.1 day.

Chemical application scenarios

In order to perform model simulations, the amount of chemical (pulse loading) that was released into the water has to be determined. The pulse-loading amount can be calculated by multiplying the nominal metaflumizone concentration in the

water by the water volume. According to the metaflumizone bioaccumulation study, metaflumizone was released twice into the water of the microcosms. The nominal content of metaflumizone is 22.6% (E+Z). Among the 22.6%, 21.2% is E isomer and 0.62% is Z isomer. The resulting metaflumizone concentration in water right after each application was 20 µg/L. Since the total water volume is 460L. We can calculate the pulse loading amount of metaflumizone released into the water for each application as 20 µg/L x 460L = 9200 µg. However, this amount included 97.16% (21.2 / 21.82) E isomer and 2.84% (0.62 / 21.82) Z isomer. Therefore, the amount of E isomer and Z isomer released into the water for each application were 8939 µg (97.16% x 9200 µg) and 261 µg (2.84% x 9200 µg) respectively. The unit for pulse loading amount in the model is in g/0.1day; since, the time-step was set to be 0.1 day. To adapt to this unit, the pulse-loading amount of metaflumizone for E and Z isomers that were calculated above have to be multiplied by 10 to have a nominal water concentration of 20 µg/L (Example: pulse loading for E-isomer = 8938.72 µg/day = 89387.2 µg/0.1 day x 10). The final pulse-loading rate for E and Z isomer of metaflumizone was 0.0893872g / 0.1day and 0.0026128g / 0.1day. (The number of pulses is two.)

Table 3-5 Model input parameters for the performance analysis of the food web bioaccumulation sub-model (chapter 3.2.4.2) and the combined time-dependent food web bioaccumulation model (chapter 3.2.4.3) in the metaflumizone microcosm study

Chemical Name		**Metaflumizone**		
Chemical-Specific Properties	**Symbol**	**E-isomer**	**Z-isomer**	**Reference**
Molecular Weight (g/mol)	MolW	506.4	506.4	Paulick et al., 2004
Henry's Law Constant ($Pa \bullet m^3/mol$)	H	0.00351	0.00351	Paulick et al., 2004
log Kow of the chemical	log Kow	5.1	4.4	Paulick et al., 2004
chemical half life in water (day)	hlw	4.2	4.2	Paulick et al., 2004
chemical half life in sediment (day)	hls	208	208	Paulick et al., 2004

Food Web Structure							
Species	**Periphyton**	**Macrophyte**	**Zooplankton**	**Crustacean**	**Zebra mussel**	**Snail**	**Fish**
Sediment	0%	0%	0%	100%	0%	0%	0%
Phytoplankton	0%	0%	100%	0%	100%	0%	0%
Macrophtye			0%	0%	0%	100%	0%
Zooplankton			0%	0%	0%	0%	70%
crustacean				0%	0%	0%	10%
Zebra mussel					0%	0%	10%
snail						0%	10%
fish							0%

Ecosystem-Specific Properties	Symbol	Value	Reference
water body surface area (m^2)	Saw	9.20E-01	Funk, 2004
sediment surface area (m^2)	Sas	9.20E-01	Funk, 2004
average water depth (m)	Dw	0.5	Funk, 2004
depth of active sediment layer (m)	Ds	0.05	Funk, 2004
water in- and out-flow (L/day)	F	0.00E+00	Estimated
Concentration of particles in water (kg/L)	Cpw	5.48E-05	Funk, 2004
Concentration of DOC in water (kg/L)	Cdoc	5.07E-06	Funk, 2004
concentration of solids in sediment (kg/L)	Css	1.80E-01	Estimated
density of suspended solids (kg/L)	dpw	2.40E+00	Estimated
density of sediment solids (kg/L)	dss	1.90E+00	Estimated
organic carbon content of suspended solids (unitless)	Ocpw	1.00E-01	Estimated
organic carbon content of bottom sediment (unitless)	Ocss	6.40E-03	Funk, 2004
density of organic carbon (kg/L)	doc	1.00E+00	EFED, 2007
water-side evaporation mass transfer coefficient (m/day)	vew	2.40E-01	EFED, 2007
air-side evaporation mass transfer coefficient (m/day)	vea	2.40E+01	EFED, 2007
water-to-sediment diffusion mass transfer coefficient (m/day)	vd	9.60E-03	EFED, 2007
solids settling rate (g/m^2/day)	vss	32	EFED, 2007
sediment burial mass transfer coefficient (g/m^2/day)	vb	16	EFED, 2007
sediment resuspension rate (g/m^2/day)	vrs	16	EFED, 2007
dissolved oxygen saturation (%)	S	95%	Funk, 2004
Disequilibrium factor POC (unitless)	Dpoc	1	Estimated
Disequilibrium factor DOC (unitless)	Ddoc	1	Estimated
POC-octanol proportionality constant (unitless)	αpoc	0.35	Estimated
DOC-octanol proportionality constant (unitless)	αdoc	0.08	Estimated
pH of water	pH	8.6	Funk, 2004
water temperature (^oC)	Tw	23.9	Funk, 2004
Sediment OC octanol proportionality constant (unitless)	αsoc	0.35	Estimated
Simulation Parameters	**Symbol**	**Value**	
Time increment	dt	0.1	

Organism-Specific Parameters								
Parameter	**Symbol**	**Periphyton**	**Macrophyte**	**Zooplankton**	**Crustacean**	**Zebra Mussel**	**Snail**	**Fish**
Weight (g)	Wb	0.3462	2.996	0.0001	0.19	0.702	1.338	1.35
Lipid fraction in biota (%)	Vlb	0.50	0.50	2	1	2	1.5	3
Nonlipid organic matter fraction in biota (%)	Vnb	20	20	20	20	20	16	20
Water fraction in biota (%)	Vwb	79.5	79.5	78	79	78	82.5	77
Nonlipid organic matter-octanol proportionality constant	Beta	0.35	0.35	0.035	0.035	0.035	0.035	0.035
Dietary absorption efficiency of lipid (%)	El	75	75	72	75	75	75	92
Dietary absorption efficiency of nonlipid organic matter (%)	En	75	75	72	5	75	75	55
Dietary absorption efficiency of water (%)	Eww	25	25	25	25	25	25	25
Fraction of the respiratory ventilation that involves overlying water (%)	mo	95	95	95	95	95	95	100
Fraction of the respiratory ventilation that involves sediment associated pore water (%)	Mp	5	5	5	5	5	5	0
Particle scavenging efficiency (%)	Sigma	100	100	100	100	100	100	------
Resistance to chemical uptake through the aqueous phase	A	6.0E-5	0.002	------	------	------	------	------
Resistance to chemical uptake through the organic phase	B	5.5	500	------	------	------	------	------
Invertebrate growth rate coefficient ($T < 17.5\ ^{o}C$)	Igr	------	------	5.02E-4	5.02E-4	5.02E-4	5.02E-4	5.02E-4
Invertebrate growth rate coefficient ($T > 17.5\ ^{o}C$)	Fgr	------	------	0.00251	0.00251	0.00251	0.00251	0.00251
Constant Aew	Aew	1.85	1.85	1.85	1.85	1.85	1.85	1.85
Constant Bew	Bew	155	155	155	155	155	155	155
Constant Aed	Aed	------	------	3E-7	3E-7	3E-7	3E-7	3E-7
Constant Bed	Bed	------	------	2	2	2	2	2

3.2.5 Model parameterization for the evaluation of model performance using microcosm studies for BAS 490 02F and BAS 500 00F

The time-dependent environmental fate sub-model was developed by modifying the time response PCB model by Gobas et al (1995). To test if the model is capable to be applied in pesticide applications, model simulations were performed to mimic two ecosystem studies (Dohmen, 1995 and 2000) for two pesticides, BAS 490 02F (kresoxim-methyl, CAS No:144167-04-4) and BAS 500 00F (pyraclostrobin, CAS No:175013-18-0) that were developed by BASF. The structural formula for kresoxim-methyl and pyraclostrobin are shown in Figure 3-3 and 3-4 respectively. The reported chemical properties and ecosystem characteristics from Dohmen's ecosystem studies (1995 and 2000) were used to parameterize the model required input parameters. The chemical and ecosystem specific parameters are summarized in Table 3-6.

Chemical application scenarios for BAS 490 02F

The application rate for BAS 490 02F in the ecosystem study was six applications of BAS 490 02F at 14-day intervals such that the resulting water concentration right after the release of BAS 490 02F would reach 13.3 µg/L. BAS 490 02F contains 50% of the active ingredient kresoxim-methyl. The total volume of the water is 6335L. The total amount of kresoxim-methyl released into the water for single application was 0.0421g. Model simulations were performed for the active ingredient kresoxim-methyl at the rate of six applications of 0.0421g kresoxim-methyl / application at 14-day intervals.

Chemical application scenarios for BAS 500 00F

The application rate for BAS 500 00F applied in the ecosystem study was eight applications in 14-day intervals at rates increasing from 60 to 160 g a.i./ha during the season. The application rates are listed in Table 3-5.

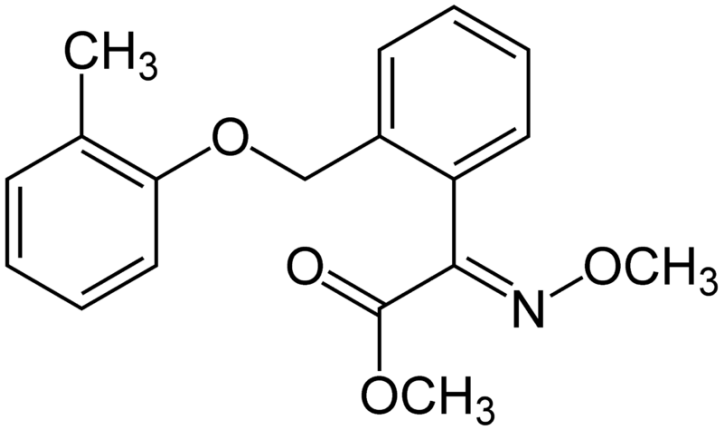

Figure 3-3 Structural formula of kresoxim-methyl

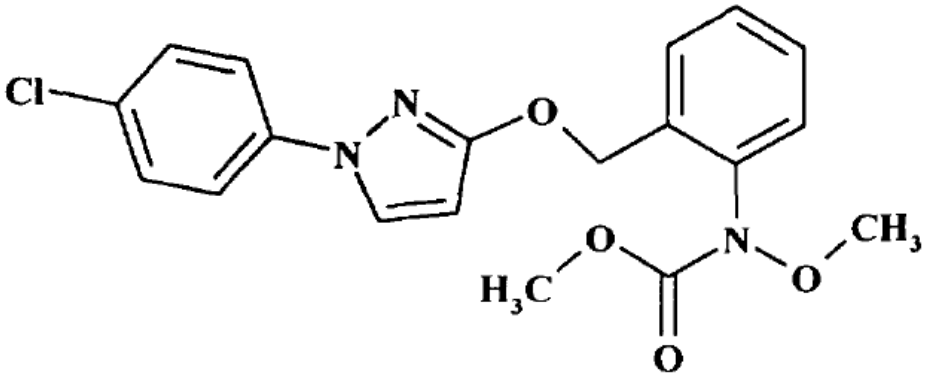

Figure 3-4 Structural formula of pyraclostrobin

Table 3-6 BAS 500 00F application rate in the ecosystem study (Dohmen, 2000)

Day	Application rate (g a.i./ha)	% drift	Concentration in water (µg/L)	Pulse loading amount (g/application)
1	60	1.6	2.171	0.018
15	60	1.6	2.611	0.018
29	60	5	8.999	0.057
43	60	5	7.789	0.057
57	100	5	13.245	0.095
71	120	5	16.055	0.114
85	160	5	26.06	0.152
99	160	5	24.702	0.152

Note: The volume of water is 6335L

Table 3-7 Model input parameters for the validation of time-dependent environmental fate sub-model using microcosm studies for BAS 490 02F and BAS 500 00F

Chemical Name: BAS 490 02F (kresoxim-methyl)			
Chemical-Specific Properties	**Symbol**	**Value**	**Reference**
Molecular Weight	MolW	313.3	Dohmen, 1995
Henry's Law Constant (Pa•m^3/mol)	H	3.60E-04	PMRA, 2003
log Kow of the chemical	log Kow	3.4	Dohmen, 1995
chemical half life in water (day)	hlw	1.6	PMRA, 2003
chemical half life in sediment (day)	hls	1.6	PMRA, 2003

Chemical Name: BAS 500 00F (pyraclostrobin)			
Chemical-Specific Properties	**Symbol**	**Value**	**Reference**
Molecular Weight	MolW	387.82	Dohmen, 2000
Henry's Law Constant (Pa•m^3/mol)	H	5.31E-06	Ohnsorge, 2000
log Kow of the chemical	log Kow	3.99	Dohmen, 2000
chemical half life in water (day)	hlw	5	APVMA, 2003
chemical half life in sediment (day)	hls	4	APVMA, 2003

BAS 490 02F (kresoxim-methyl)			
Ecosystem-Specific Properties	**Symbol**	**Value**	**Reference**
water body surface area (m^2)	Saw	6.33	Dohmen, 1995
sediment surface area (m^2)	Sas	6.33	Dohmen, 1995
average water depth (m)	Dw	1	Dohmen, 1995
depth of active sediment layer (m)	Ds	0.1	Dohmen, 1995
water in- and out-flow (L/day)	F	6.33E+03	Dohmen, 1995
Concentration of particles in water (kg/L)	Cpw	5.33E-05	Dohmen, 1995
Concentration of DOC in water (kg/L)	Cdoc	3.78E-06	Dohmen, 1995
concentration of solids in sediment (kg/L)	Css	1.51	EFED, 2007
density of suspended solids (kg/L)	dpw	2.40	EFED, 2007
density of sediment solids (kg/L)	dss	2.40	EFED, 2007
organic carbon content of suspended solids (unitless)	Ocpw	1.00E-01	Dohmen, 1995
organic carbon content of bottom sediment (unitless)	Ocss	2.00E-03	Dohmen, 1995
density of organic carbon (kg/L)	doc	1.00	EFED, 2007
water-side evaporation mass transfer coefficient (m/day)	vew	0.24	EFED, 2007
air-side evaporation mass transfer coefficient (m/day)	vea	24.0	EFED, 2007
water-to-sediment diffusion mass transfer coefficient (m/day)	vd	9.60E-03	EFED, 2007
solids settling rate (g/m^2/day)	vss	80	EFED, 2007
sediment burial mass transfer coefficient (g/m^2/day)	vb	40	EFED, 2007
sediment resuspension rate (g/m^2/day)	vrs	40	EFED, 2007
dissolved oxygen saturation (%)	S	131%	Dohmen, 1995
Disequilibrium factor POC (unitless)	Dpoc	1	Estimated
Disequilibrium factor DOC (unitless)	Ddoc	1	Estimated
POC-octanol proportionality constant (unitless)	αpoc	0.35	Estimated
DOC-octanol proportionality constant (unitless)	αdoc	0.08	Estimated
pH of water	pH	9.5	Dohmen, 1995
water temperature (^oC)	Tw	17.5	Dohmen, 1995
Sediment OC octanol proportionality constant (unitless)	αsoc	0.35	Estimated
Simulation Parameters	**Symbol**	**Value**	
Time increment	dt	0.1	

BAS 500 00F (pyraclostrobin)			
Ecosystem-Specific Properties	**Symbol**	**Value**	**Reference**
water body surface area (m^2)	Saw	6.33E+00	Dohmen, 2000
sediment surface area (m^2)	Sas	6.33E+00	Dohmen, 2000
average water depth (m)	Dw	1	Dohmen, 2000
depth of active sediment layer (m)	Ds	0.1	Dohmen, 2000
water in- and out-flow (L/day)	F	0	Estimated
Concentration of particles in water (kg/L)	Cpw	9.76E-05	Dohmen, 2000
Concentration of DOC in water (kg/L)	Cdoc	8.68E-06	Dohmen, 2000
concentration of solids in sediment (kg/L)	Css	1.51	EFED, 2007
density of suspended solids (kg/L)	dpw	2.40	EFED, 2007
density of sediment solids (kg/L)	dss	2.40	EFED, 2007
organic carbon content of suspended solids (unitless)	Ocpw	1.00E-01	Dohmen, 2000
organic carbon content of bottom sediment (unitless)	Ocss	5.00E-03	Dohmen, 2000
density of organic carbon (kg/L)	doc	1.00E+00	EFED, 2007
water-side evaporation mass transfer coefficient (m/day)	vew	2.40E-01	EFED, 2007
air-side evaporation mass transfer coefficient (m/day)	vea	2.40E+01	EFED, 2007
water-to-sediment diffusion mass transfer coefficient (m/day)	vd	9.60E-03	EFED, 2007
solids settling rate (g/m^2/day)	vss	80	EFED, 2007
sediment burial mass transfer coefficient (g/m^2/day)	vb	40	EFED, 2007
sediment resuspension rate (g/m^2/day)	vrs	40	EFED, 2007
dissolved oxygen saturation (%)	S	129%	Dohmen, 2000
Disequilibrium factor POC (unitless)	Dpoc	1	Estimated
Disequilibrium factor DOC (unitless)	Ddoc	1	Estimated
POC-octanol proportionality constant (unitless)	αpoc	0.35	Estimated
DOC-octanol proportionality constant (unitless)	αdoc	0.08	Estimated
pH of water	pH	9.5	Dohmen, 2000
water temperature (^oC)	Tw	20.5	Dohmen, 2000
Sediment OC octanol proportionality constant (unitless)	αsoc	0.35	Estimated
Simulation Parameters	**Symbol**	**Value**	
Time increment	dt	0.1	

3.2.6 Model parameterization for model application for the evaluation of the recommended pulse loading amount for metaflumizone

The manufacturer's suggested application rate for metaflumizone is four applications at 7-day intervals annually with each pulse loading amount of 280g of metaflumizone per hectare. Model simulations were performed using this application scenario to investigate the implications of long term (i.e. 10 years) annual metaflumizone application.

The EFED recommended parameters (Table 3-1) were used to parameterize the chemical-specific and ecosystem-specific parameters for the model application for the evaluation of the recommended pulse loading amount for metaflumizone. The ratio between E and Z isomer of metaflumizone was assumed to be 9 to 1. The organism-specific parameters were selected according to the metaflumizone toxicity studies for *Chironomus tentans* (Aufderheide, 2002), *Hyalella azteca* (Aufderheide, 2004) and *Leptocherius plumulosus* (Aufderheide, 2004). The model input parameters for the model application to evaluate the recommended pulse loading amount for metaflumizone are listed in Table 3-8.

Table 3-8 Model input parameters used to determine the recommended pulse loading application rate of metaflumizone

		Metaflumizone		
		E-isomer	Z-isomer	
Chemical-Specific Properties	**Symbol**	**Value**	**Value**	**Reference**
Molecular Weight	MolW	506.4	506.4	Paulick et al., 2004
Henry's Law Constant (Pa•m3/mol)	H	0.00351	0.00351	Paulick et al., 2004
log Kow of the chemical	log Kow	5.1	4.4	EFED, 2007
chemical half life in water (day)	hlw	378	378	EFED, 2007
chemical half life in sediment (day)	hls	208	208	Paulick et al., 2004

Food Web Structure (percent dietary composition)						
Species	**Phytoplankton**	**Zooplankton**	***Chironomus tentans***	***Hyalella azteca***	***Leptocheirus plumulosus***	**Zebra fish**
Sediment	0%	0%	100%	100%	100%	0%
Phytoplankton	0%	100%	0%	0%	0%	0%
Zooplankton		0%	0%	0%	0%	100%
Chironomus tentans			0%	0%	0%	0%
Hyalella azteca				0%	0%	0%
Leptocheirus plumulosus					0%	0%
Zebrafish						0%

Ecosystem-Specific Properties	Symbol	Value	Reference
water body surface area (m^2)	Saw	1.00E+04	EFED, 2007
sediment surface area (m^2)	Sas	1.00E+04	EFED, 2007
average water depth (m)	Dw	2	EFED, 2007
depth of active sediment layer (m)	Ds	0.05	EFED, 2007
water in- and out-flow (L/day)	F	9.60E+04	EFED, 2007
Concentration of particles in water (kg/L)	Cpw	3.00E-05	EFED, 2007
Concentration of DOC in water (kg/L)	Cdoc	1.20E-06	EFED, 2007
concentration of solids in sediment (kg/L)	Css	1.51E+00	EFED, 2007
density of suspended solids (kg/L)	dpw	2.40E+00	EFED, 2007
density of sediment solids (kg/L)	dss	2.40E+00	EFED, 2007
organic carbon content of suspended solids (unitless)	Ocpw	4.00E-02	EFED, 2007
organic carbon content of bottom sediment (unitless)	Ocss	4.00E-02	EFED, 2007
density of organic carbon (kg/L)	doc	1.00E+00	EFED, 2007
water-side evaporation mass transfer coefficient (m/day)	vew	2.40E-01	EFED, 2007
air-side evaporation mass transfer coefficient (m/day)	vea	2.40E+01	EFED, 2007
water-to-sediment diffusion mass transfer coefficient (m/day)	vd	9.60E-03	EFED, 2007
solids settling rate (g/m^2/day)	vss	80	EFED, 2007
sediment burial mass transfer coefficient (g/m^2/day)	vb	40	EFED, 2007
sediment resuspension rate (g/m^2/day)	vrs	40	EFED, 2007
dissolved oxygen saturation (%)	S	90%	Estimated
Disequilibrium factor POC (unitless)	Dpoc	1	Estimated
Disequilibrium factor DOC (unitless)	Ddoc	1	Estimated
POC-octanol proportionality constant (unitless)	αpoc	0.35	Estimated
DOC-octanol proportionality constant (unitless)	αdoc	0.08	Estimated
pH of water	pH	7.00	Estimated
water temperature (^oC)	Tw	17	Estimated
Sediment OC octanol proportionality constant (unitless)	αsoc	0.35	Estimated
Simulation Parameters	**Symbol**	**Value**	
Time increment	dt	0.1	

Organism-Specific Parameters

Parameter	Symbol	Phytoplankton	Zooplankton	*Chironomus tentans*	*Hyalella azteca*	*Locheirus plumulo*	Zebrafish
Weight (g)	Wb	------	0.0001	1.6E-6	8.0E-8	4.0E-07	2.53E-5
Lipid fraction in biota (%)	Vlb	0.50	2	2.5	7	10	4
Nonlipid organic matter fraction in biota (%)	Vnb	20	20	20	20	16	20
Water fraction in biota (%)	Vwb	79.5	78	77.5	73	74	76
Nonlipid organic matter-octanol proportionality constant	Beta	0.35	0.035	0.035	0.035	0.035	0.035
Dietary absorption efficiency of lipid (%)	El	75	72	75	75	75	92
Dietary absorption efficiency of nonlipid organic matter (%)	En	75	72	5	5	5	55
Dietary absorption efficiency of water (%)	Eww	25	25	25	25	25	25
Fraction of the respiratory ventilation that involves overlying water (%)	mo	95	95	95	95	95	100
Fraction of the respiratory ventilation that involves sediment associated pore water (%)	Mp	5	5	5	5	5	0
Particle scavenging efficiency (%)	Sigma	100	100	100	100	100	------
Resistance to chemical uptake through the aqueous phase	A	0.00006	------	------	------	------	------
Resistance to chemical uptake through the organic phase	B	5.5	------	------	------	------	------
Invertebrate growth rate coefficient ($T < 17.5\ ^{o}C$)	Igr	------	5.02E-4	5.02E-4	5.02E-4	5.02E-4	5.02E-4
Invertebrate growth rate coefficient ($T > 17.5\ ^{o}C$)	Fgr	------	0.00251	0.00251	0.00251	0.00251	0.00251
Constant Aew	Aew	1.85	1.85	1.85	1.85	1.85	1.85
Constant Bew	Bew	155	155	155	155	155	155
Constant Aed	Aed	------	3E-7	3E-7	3E-7	3E-7	3E-7
Constant Bed	Bed	------	2	2	2	2	2

3.2.7 Model parameterization for the evaluation of differences between the outcomes of the steady-state based food web bioaccumulation model and time-dependent food web bioaccumulation model for pesticide applications

Metaflumizone was used to illustrate the difference in prediction of chemical concentrations between the steady-state based food web bioaccumulation model and the time-dependent food web bioaccumulation model. EFED recommended model parameterization values (Table 3-1) were used for the parameterization of chemical and ecosystem-specific parameters. The food web structure and organism-specific parameters were parameterized using the default model parameter values (Table 3-2 and Table 3-3) used by EPA. The model input parameters for this application are listed in Table 3-9 and Table 3-10.

Table 3-9 Model input parameters for the evaluation of the difference between steady-state based bioaccumulation model and time-dependent bioaccumulation model

		Metaflumizone		
		E-isomer	Z-isomer	
Chemical-Specific Properties	**Symbol**	**Value**	**Value**	**Reference**
Molecular Weight (g/mol)	MolW	506.4	506.4	Paulick et al., 2004
Henry's Law Constant ($Pa.m^3/mol$)	H	0.00351	0.00351	Paulick et al., 2004
log Kow of the chemical	log Kow	100	100	EFED, 2007
chemical half life in water (day)	hlw	378	378	EFED, 2007
chemical half life in sediment (day)	hls	208	208	Paulick et al., 2004

2

Ecosystem-Specific Properties	Symbol	Value	Reference
water body surface area (m^2)	Saw	1.00E+04	EFED, 2007
sediment surface area (m^2)	Sas	1.00E+04	EFED, 2007
average water depth (m)	Dw	2	EFED, 2007
depth of active sediment layer (m)	Ds	0.05	EFED, 2007
water in- and out-flow (L/day)	F	9.60E+04	EFED, 2007
Concentration of particles in water (kg/L)	Cpw	3.00E-05	EFED, 2007
Concentration of DOC in water (kg/L)	Cdoc	1.20E-06	EFED, 2007
concentration of solids in sediment (kg/L)	Css	1.51E+00	EFED, 2007
density of suspended solids (kg/L)	dpw	2.40E+00	EFED, 2007
density of sediment solids (kg/L)	dss	2.40E+00	EFED, 2007
organic carbon content of suspended solids (unitless)	Ocpw	4.00E-02	EFED, 2007
organic carbon content of bottom sediment (unitless)	Ocss	4.00E-02	EFED, 2007
density of organic carbon (kg/L)	doc	1.00E+00	EFED, 2007
water-side evaporation mass transfer coefficient (m/day)	vew	2.40E-01	EFED, 2007
air-side evaporation mass transfer coefficient (m/day)	vea	2.40E+01	EFED, 2007
water-to-sediment diffusion mass transfer coefficient (m/day)	vd	9.60E-03	EFED, 2007
solids settling rate (g/m^2/day)	vss	80	EFED, 2007
sediment burial mass transfer coefficient (g/m^2/day)	vb	40	EFED, 2007
sediment resuspension rate (g/m^2/day)	vrs	40	EFED, 2007
dissolved oxygen saturation (%)	S	90%	Estimated
Disequilibrium factor POC (unitless)	Dpoc	1	Estimated
Disequilibrium factor DOC (unitless)	Ddoc	1	Estimated
POC-octanol proportionality constant (unitless)	αpoc	0.35	Estimated
DOC-octanol proportionality constant (unitless)	αdoc	0.08	Estimated
pH of water	pH	7.00	Estimated
water temperature (^oC)	Tw	17	Estimated
Sediment OC octanol proportionality constant (unitless)	αsoc	0.35	Estimated
Simulation Parameters	**Symbol**	**Value**	
Time increment	dt	0.1	

Organism-Specific Parameters

Parameter	Symbol	Phytoplankton	Zooplankton	Benthos (Diporeia)	Forage Fish A	Forage Fish B	Piscivorous Fish
Weight (g)	Wb	------	1E-7	0.00001	0.01	0.01	1
Lipid fraction in biota (%)	Vlb	0.50	2	2	4	6	4
Nonlipid organic matter fraction in biota (%)	Vnb	20	20	20	22	22	20
Water fraction in biota (%)	Vwb	79.5	78.0	78.0	74.0	72.0	76.0
Nonlipid organic matter-octanol proportionality constant	Beta	0.35	0.035	0.035	0.035	0.035	0.035
Dietary absorption efficiency of lipid (%)	El	75	72	75	92	92	92
Dietary absorption efficiency of nonlipid organic matter (%)	En	75	72	25	55	55	55
Dietary absorption efficiency of water (%)	Eww	25	25	25	25	25	25
Fraction of the respiratory ventilation that involves overlying water (%)	mo	95	95	95	100	100	100
Fraction of the respiratory ventilation that involves sediment associated pore water (%)	Mp	5	5	5	0	0	0
Particle scavenging efficiency (%)	Sigma	100	100	100	------	------	------
Resistance to chemical uptake through the aqueous phase	A	0.00006	------	------	------	------	------
Resistance to chemical uptake through the organic phase	B	5.5	------	------	------	------	------
Invertebrate growth rate coefficient (T < 17.5 deg C)	Igr	------	5.02E-4	5.02E-4	5.02E-4	5.02E-4	5.02E-4
Invertebrate growth rate coefficient (T > 17.5 deg C)	Fgr	------	0.00251	0.00251	0.00251	0.00251	0.00251
Constant Aew	Aew	1.85	1.85	1.85	1.85	1.85	1.85
Constant Bew	Bew	155	155	155	155	155	155
Constant Aed	Aed	------	3E-7	3E-7	3E-7	3E-7	3E-7
Constant Bed	Bed	------	2	2	2	2	2

Table 3-10 Food-web structure for the evaluation of the difference between steady-state based bioaccumulation model and time-dependent bioaccumulation model

Food Web Structure (percent dietary composition)						
Species	**Phytoplankton**	**Zooplankton**	**Benthos**	**Forage Fish A**	**Forage Fish B**	**Piscivorous Fish**
Sediment	0%	0%	100%	0%	0%	0%
Phytoplankton	0%	100%	0%	0%	0%	0%
Zooplankton		0%	0%	50%	50%	0%
Benthos			0%	50%	50%	0%
Forage Fish A				0%	0%	50%
Forage Fish B					0%	50%
Piscivorous Fish						0%

3.3 Model performance analysis

3.3.1 Overview

The model performance analysis is divided into three major parts:

1. Validation of the time-dependent food web bioaccumulation model using the metaflumizone BCF study
2. Validation of the time-dependent food web bioaccumulation model using the microcosm studies for metaflumizone
3. Validation of the time-dependent environmental fate sub-model using the ecosystem studies of BAS 490 02F and BAS 500 00F

The model performance was assessed by (1) comparing the model predicted chemical concentrations to observed chemical concentrations from laboratory and microcosm studies and (2) calculating the mean model bias (MB) and its 95% confidence interval to numerically express the accuracy of the model predictions.

3.3.2 Comparison between model predictions and empirical data

The model performance analyses were conducted to evaluate the accuracy of the food web sub-model, environmental fate sub-model, and combined model.

For the model performance analysis using BCF studies for metaflumizone, the model predicted chemical uptake rate (k_1), depuration rate (k_2) and BCF were compared to the empirical data.

For the model performance analysis using microcosm study for metaflumizone, the model predicted metaflumizone concentrations (total metaflumizone concentration, including both E and Z isomers) in water, sediment and in aquatic organisms in the microcosm were compared to those of the observed metaflumizone concentrations from the microcosm study report (Funk, 2004).

For the model performance analysis using microcosm studies for BAS 490 02F and BAS 500 00F, the concentrations of active ingredient of BAS 490 02F and BAS 500 00F in water were compared graphically with the corresponding empirical data from the microcosm study reports.

The model predicted pesticide concentrations and observed pesticide concentrations in water, sediment and different aquatic organisms were plotted against time on the same graph to illustrate the similarity and/or differences between the model predictions and observed values.

3.3.3 Model bias calculation

To quantitatively express model performance combining the results for all *n* time points in a single species, the mean model bias (MB) was calculated as:

$$MB_j = 10^{\sum_{i=1}^{n} \frac{[\log(Cpred,i / Cobs,i)]}{n}} \quad [65]$$

Where

MB_j = the mean model bias for all time points in a single species *j*

n = total number of time points

$C_{pred,i}$ = predicted 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:

$$MB_{tot} = 10^{\left[\sum_{j=1}^{m} \frac{(\sum_{i=1}^{n} \frac{[\log(Cpred,i,j / Cobs,i,j)]}{n}}{m} \right]} \quad [66]$$

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

$C_{pred,i,j}$ = predicted chemical concentration in species *j* at time point *i*

$C_{obs,i,j}$ = observed chemical concentration in species *j* at time point *i*

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

The 95% confidence intervals of the geometric mean were calculated to represent the range of MB values, which includes 95% of the predicted chemical concentrations in different environmental compartments. Therefore, the 95% confidence intervals of the geometric mean is an indication of the model's accuracy.

The merit of using the mean MB value and the associated 95% confidence intervals to express model performance is that by comparing the final model prediction directly with the empirical data, all sources of error including model parameterization errors, errors in model structure, analytical errors in the empirical data as well as variability in the empirical data used for the model performance are considered.

Mean model bias (MB) was calculated for 3 different applications to evaluate accuracy of model predictions: (1) model performance analysis of the food web sub-model using metaflumizone bioaccumulation study, (2) model performance analysis of the environmental fate sub-model using BAS 490 02F and BAS 500 00F ecosystem studies and (3) model performance analysis of the combined model (combined environmental fate and food web models) using metaflumizone bioaccumulation study.

3.4 Application of the model to determine pesticide application rate

3.4.1 Overview

Four model applications were performed to illustrate how the time-dependent food web bioaccumulation model can be used to aid the regulation of pesticide. The methods of each model applications are discussed in the following sections.

3.4.2 Methods for the evaluation of the recommended pulse loading amount for metaflumizone using external concentration

The targets for most pesticide applications are never the aquatic organisms. However, due to accidental spraying or water run-off, it is possible for the pesticide to be released into the water bodies and may pose hazards to aquatic organisms. Without conducting a detailed risk assessment or field study, the time-dependent model can be used to simulate the pesticide application at the recommended application rate to evaluate if the resulting pesticide concentrations in water and sediment will exceed the ambient water quality criteria values and/or toxic concentrations (e.g. LC50) over the specified period.

BASF has suggested the application rate for metaflumizone to be four times annually at 7-day intervals with each application amount of 280g / ha. Assuming there is 5% drift, the amount of metaflumizone released into a 1 ha water body is 14 g (5% of 280g). To evaluate if this recommended application rate will cause toxic effects to aquatic organisms in the ponds near the metaflumizone application site, the time-dependent food web bioaccumulation model was

simulated to mimic a long term (10 years) annual metaflumizone application at the recommended application rate in the field.

After model simulations, the model predicted metaflumizone concentrations in water and sediment are compared to toxicity data to determine whether the recommended metaflumizone application rate can be expected to cause toxic effects to the aquatic organisms. Because metaflumizone is a newly developed insecticide, there are no environmental guidelines that could be used for this analysis. Acute toxicity data were used for this evaluation.

The metaflumizone acute toxicity tests for *Chironomus tentans* (Aufderheide, 2002), *Hyalella azteca* (Aufderheide, 2004) and *Leptocherius plumulosus* (Aufderheide, 2004) are shown in Table 3-10. The lowest LC50 value among the three toxicity studies for metaflumizone is 1.8 mg a.i./kg sediment (for *Chironomus tentans*) and the lowest toxicity value among the available toxicity studies for all endpoints is 0.93 mg a.i./kg as the NOEC for survival (10-day survival test for *Chironomus tentans*). The predicted metaflumizone concentrations in sediment were compared with all toxicity data for metaflumizone to evaluate whether the recommended metaflumizone application rate will result in sediment concentrations that exceed the toxicity values for benthic organisms. The predicted water concentrations were compared with the NOEC of 0.015mg/L for reproduction and survival for zebrafish (*Danio rerio*) from the toxicity study by Schäfers (BASF unpublished report, 2004) to evaluate if the

recommended metaflumizone application rate will result in water concentrations that cause toxicity in fish.

Table 3-11 Toxicity data (LC50, NOEC and LOEC for growth and reproduction) for metaflumizone for *Chironomus tentans, Hyalella azteca, Leptocheirus plumulosus* and *Danio rerio* (Zebrafish)

Organism	***Chironomus tentans***	***Hyalella azteca***	***Leptocheirus plumulosus***	***Danio rerio* (Zebrafish)**
LC50	1.8 (mg/kg) [a]	> 995 (mg/kg) [b]	> 935 (mg/kg) [c]	N/A
NOEC	0.93 (mg/kg) [a]	105 (mg/kg) [b]	397 (mg/kg) [c]	0.015 (mg/L) [d]
LOEC	N/A	230 (mg/kg) [b]	935 (mg/kg) [c]	N/A

Reference: [a] Aufderheide, 2002. [b] Aufderheide, 2004. [c] Aufderheide, 2004. [d] Schäfers, 2004.

3.4.3 Methods for the evaluation of the recommended pulse loading amount for metaflumizone using internal body burden

The application rate for metaflumizone suggested by the manufacturer, BASF, is four applications per year at 7-day interval with the application amount of 280 g/ha. To evaluate whether this pulse loading amount for metaflumizone will cause metaflumizone concentrations in the aquatic organisms to exceed the toxicological endpoints, model simulations were performed to mimic the available metaflumizone toxicity studies. The metaflumizone toxicity data were available for four aquatic species: zebrafish (*Danio rerio*), *Chironomus tentans*, *Hyalella azteca* and *Leptocheirus plumulosus*. These aquatic organisms were incorporated into the model. These available metaflumizone toxicity data were expressed in term of external (i.e. water) concentrations; therefore, the internal whole body concentrations were calculated for the test organisms exposed to these external concentrations (LC50, NOEC and LOEC).

The internal whole body concentration of metaflumizone in zebrafish was calculated by multiplying the BCF of metaflumizone in zebrafish by the exposure concentration of metaflumizone in water. The equation used to calculate the internal whole body concentration was shown as:

Internal whole body concentration (C_F) = BCF x Cw [67]

Where

Internal whole body concentration (C_F) = whole organism concentration in fish (g/kg)

BCF = bioconcentration factor (L/kg)

C_w = chemical concentration in water (g/L)

The time-dependent model was used to calculate the BCF at the end of the duration of the toxicity test and the metaflumizone concentration in water was obtained from the zebrafish toxicity report (Schäfers, 2004).

For benthic organisms, the internal whole body concentration was calculated as:

Internal whole body concentration (C_B) = Cs x BSAF [68]

Where

Internal whole body concentration (C_B) = chemical concentration in benthic organisms (g/kg)

Cs = chemical concentration in sediment (g/kg)

BSAF = biota / sediment accumulation factor (kg/kg)

The BSAF values were estimated using the food web bioaccumulation model assuming that the chemical reaches steady state in the benthic organism. The BSAF values were calculated as concentration in benthic organism at steady-state divided by the concentration in sediment at steady-state. The calculated BSAF and internal metaflumizone concentrations for *Chironomus tentans, Hyalella azteca, Leptocheirus plumulosus* and zebrafish (*Danio rerio*) are shown in Table 3-11.

Model simulations were performed for metaflumizone using the model default parameters (Table 3-1) suggested by EFED. The organism-specific parameters

were parameterized according to the available metaflumizone toxicity study reports (Fuchsman et al., 1998; Volkman et al., 2004; Lotufo et al., 2001; McGee et al., 1998; Schäfers, 2004).

The model predicted chemical concentrations in biota were compared to the calculated whole organism toxicological concentration graphically to determine whether the recommended metaflumizone application rate can cause metaflumizone concentrations in the aquatic organisms that will exceed the toxicological endpoints.

Table 3-12 Organism specific characteristics and the calculated internal metaflumizone concentrations for different toxicity end points for *Chironomus tentans, Hyalella azteca, Leptocheirus plumulosus* and *Danio rerio* (Zebrafish)

Organism	***Chironomus tentans***	***Hyalella azteca***	***Leptocheirus plumulosus***	***Danio rerio* (Zebrafish)**
Organism weight (mg)	1.6 [a]	0.08 [a]	0.4[a]	25 [e]
Lipid content (%)	2.5 [b]	7 [c]	10 [d]	4 [f]
Calculated BSAF	4.74	11.47	15.64	N/A
Calculated internal body burden at LC50 (g/kg wwbw)	0.00854	> 11.4	> 14.6	N/A
Calculated internal body burden at LOEC (g/kg wwbw)	0.00948	2.64	14.6	N/A
Calculated internal body burden at NOEC (g/kg wwbw)	0.00441	1.20	6.21	0.034

Note: 1. Model default parameter for total organic carbon content of sediment is 4%
2. Reference: [a] Fuchsman et al., 1998; [b] Volkman et al., 2004; [c] Lotufo et al., 2001; [d] McGee et al., 1998; [e] Schäfers, 2004; [f] Estimated value

3.4.4 Methods for the derivation of the maximum allowable application rate for metaflumizone

The maximum allowable application rate for metaflumizone is the application rate which will not exceed the environmental guidelines or toxicity values for metaflumizone after prolonged application. The maximum allowable application rate for metaflumizone was determined by performing model simulations with different metaflumizone pulse loading rates. The default model parameters were used to parameterize the ecosystem-specific model parameters and the organism-specific parameters were the same as those described in chapter 3.4.3. The application rate that leads to the highest model predicted metaflumizone concentrations in water, sediment and biota and still below the available toxicity endpoint values for metaflumizone after long application period is referred to as the maximum allowable application rate.

3.4.5 Methods for the evaluation of the difference between steady-state based food web bioaccumulation model and the time-dependent food web bioaccumulation model for pesticide applications

To investigate the difference in chemical concentration predictions between steady-state based food web bioaccumulation model and the time-dependent food web bioaccumulation model, the time-dependent food web bioaccumulation model was simulated to mimic metaflumizone application for two scenarios. The first scenario assumes metaflumizone has reached steady-state in the aquatic organism and steady-state assumption was applied to the model. The second scenario assumes metaflumizone does not reach steady-state; therefore, a time-dependent estimation of metaflumizone concentration is applied.

<u>Steady-state food web bioaccumulation model application:</u>

The steady-state based bioaccumulation model was performed for 2 applications:

- Application 1: constant chemical emission with 12.6 g / day of E-isomer and 1.4 g / day Z-isomer.
- Application 2: According to the recommended metaflumizone application rate to the 1 ha pond, the total amount of E and Z isomers of metaflumizone were calculated over the 5 year application period. The average emission rates for E and Z isomer of metaflumizone were calculated. The calculation of chemical application rate is shown below:

E: 12.6 g / application x 4 application / year x 5 year = 252 g

Z: 1.4 g / application x 4 application / year x 5 year = 28 g

Average daily emission rate:

E: 252 g / 5 years x 1 year / 365 days = 252 g / 1825 days = 0.138 g / day

Z: 28 g / 5 years x 1 year / 365 days = 28 g / 1825 days = 0.01534 g / day

Model simulations were performed for the above application scenarios for 5 years. The time-dependent model predicted metaflumizone concentrations in water, sediment, and different aquatic organisms were compared to the steady-state model predicted values graphically to illustrate the difference between model predictions.

The metaflumizone concentrations at steady-state were obtained using the steady state initialization function of the time-dependent model. The chemical mass in water at steady state can be calculated by setting the change in chemical mass over change in time to be zero. The calculation of chemical mass in water and sediment were discussed earlier in the steady-state model theory (chapter 2.3).

Time-dependent food web bioaccumulation model application:

The recommended application rate for metaflumizone by BASF is four applications per year at 7-day interval with the application amount of 280 g/ha. With 5% wind drift, the amount of chemical released into the 1 ha pond for single metaflumizone application is 14 g. Assume that the isomer ratio for E and Z form of metaflumizone is 9 to 1. The amount of E form metaflumizone released into the water for single application at the recommended rate is 12.6 g. The amount

of Z form metaflumizone released into the water for single application at the recommended rate is 1.4 g.

Model simulations were performed for both E and Z isomer independently. The resulting concentrations for E and Z isomers were combined to calculate the total metaflumizone concentration at each time point. The detailed list of model input parameters is shown in Table 3-1 and Table 3-9.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Evaluation of the model performance using Bluegill bioconcentration studies for metaflumizone

The time-dependent model was used to simulate a Bluegill bioconcentration study for metaflumizone (Afzal, 2004, BASF unpublished reports). The model predicted uptake rate constant (day^{-1}), k_1, and depuration rate constant (day^{-1}), k_2, were 389 and 0.041 respectively (Table 4-1). The reported k_1 and k_2 were 380 ± 38 and 0.048 ± 0.0057 respectively. The reported BCF for metaflumizone in Bluegill was 7800 ± 1200. The predicted BCF was 7730. The predicted values are within one standard deviation of the reported values and the values are also closed to the mean observed values suggesting that the model predictions are in good agreement with the empirical data.

Table 4-1 Comparison between model predictions and empirical data for bluegill bioconcentration studies for metaflumizone

Treatment Group	Observed values (Afzal, 2004)	Model Prediction
k_1, uptake rate constant (day^{-1})	380 ± 38	389
k_2, depuration rate constant (day^{-1})	0.048 ± 0.0057	0.041
Bioconcentration Factor (BCF) (at steady-state)	7800 ± 1200	7730

From the results of the model performance analysis using metaflumizone BCF study, the developed time-dependent food web bioaccumulation model can estimate k_1, k_2 and BCF with good accuracy. The values of k_1 and k_2 can further be used in the equations of food web model.

4.2 Model performance analysis for the food web bioaccumulation sub-model

Figures 4-1 to 4-5 illustrate the comparison of the model predicted and observed metaflumizone concentrations in the aquatic organisms in the microcosm of the metaflumizone bioaccumulation study.

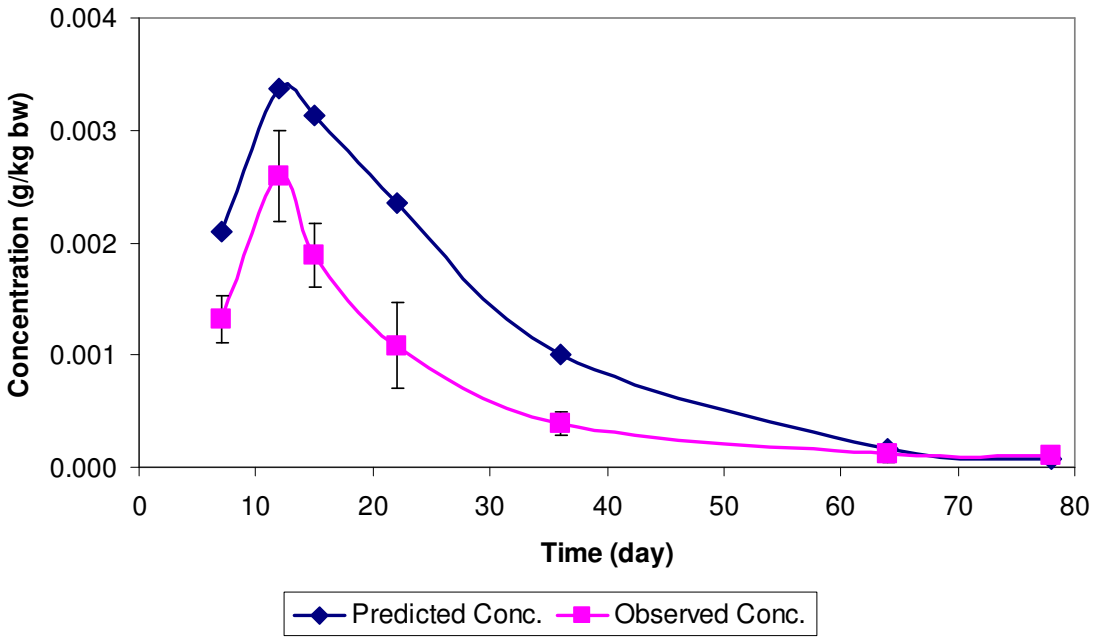

Figure 4-1 Model predicted and the mean of the observed metaflumizone concentrations (g/kg body weight) in macrophytes. Error bars represent one standard deviation of the observed mean metaflumizone concentration. (n = 3)

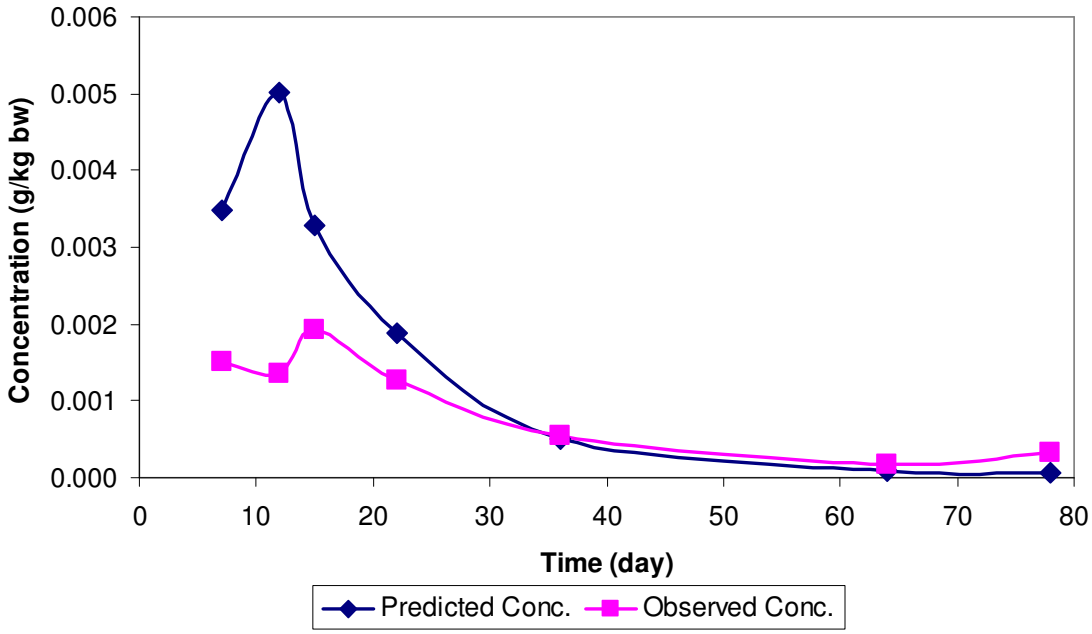

Figure 4-2 Model predicted and the mean of the observed metaflumizone concentrations (g/kg body weight) in crustaceans. (n = 1)

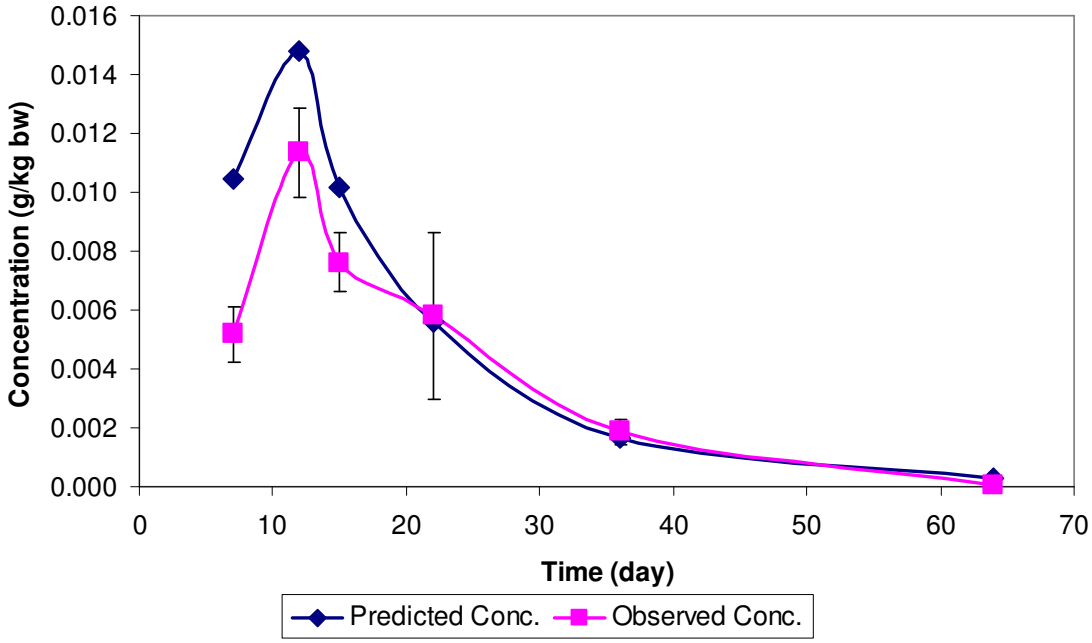

Figure 4-3 Model predicted and the mean of the observed metaflumizone concentrations (g/kg body weight) in zebra mussels. Error bars represent one standard deviation of the observed mean metaflumizone concentration. (n = 3)

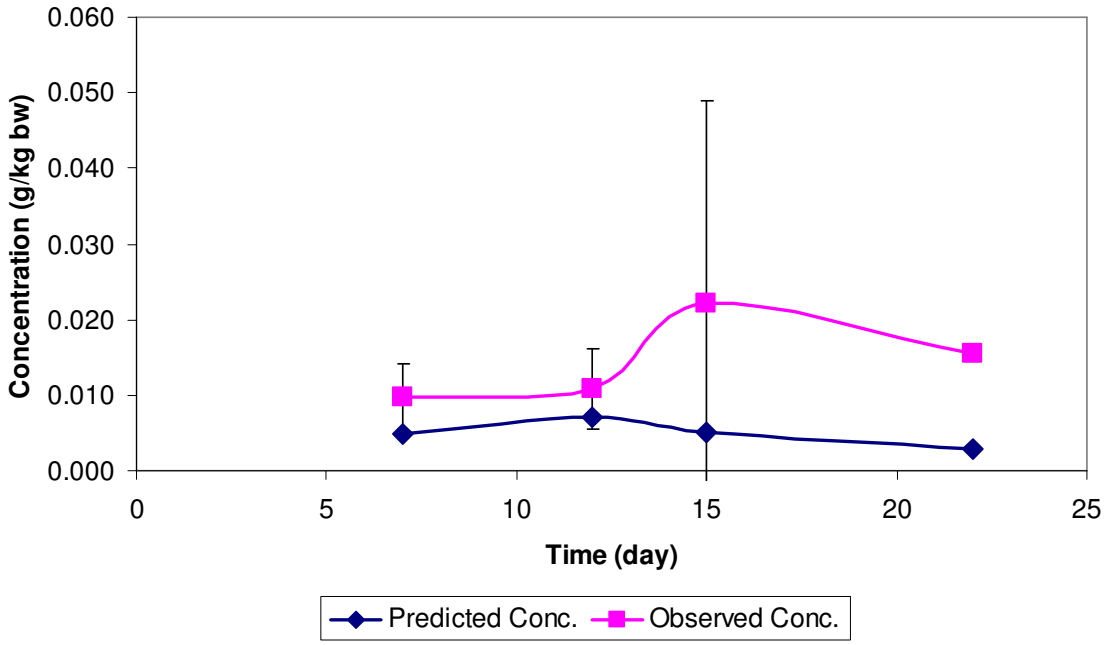

Figure 4-4 Model predicted and the mean of the observed metaflumizone concentrations (g/kg body weight) in snails. Error bars represent one standard deviation of the observed mean metaflumizone concentration. (n = 3 for the first 3 data points; n = 1 for the last data point)

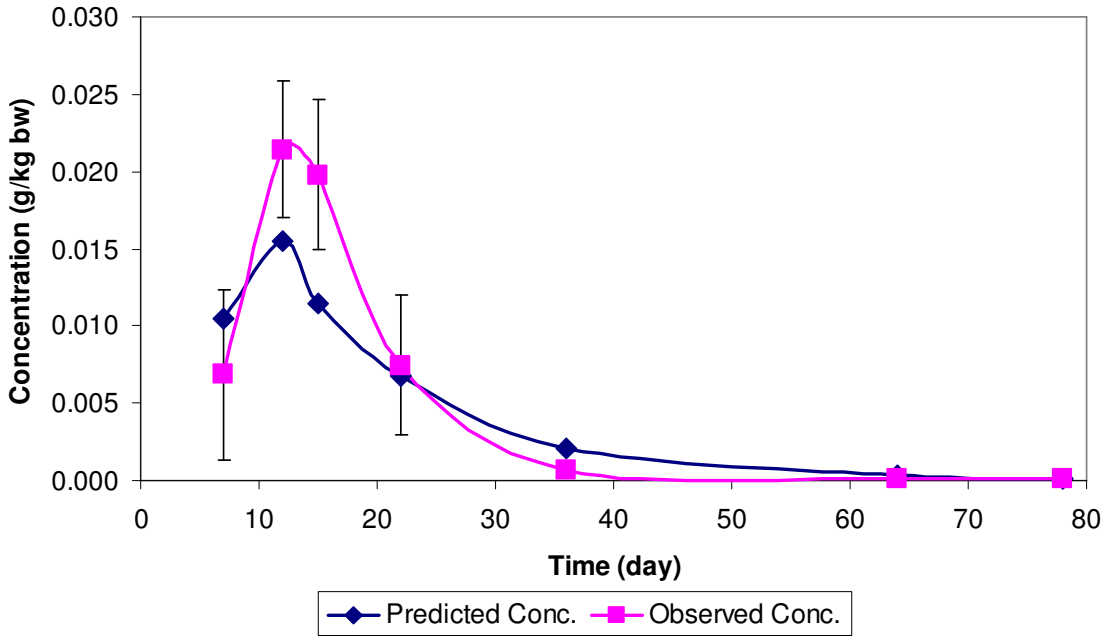

Figure 4-5 Model predicted and the mean of the observed metaflumizone concentrations (g/kg body weight) in fish. Error bars represent one standard deviation of the observed mean metaflumizone concentration. (n = 3)

The mean MB values calculated for each aquatic organism were shown in Table 4-2. Underestimation by the model was observed for snail. However, there was a large variation in the observed metaflumizone concentrations on the 3rd sampling day and there was only one sample taken on the 4th sampling day. The predicted metaflumizone concentrations in snails fall within one standard deviation of the mean of the observed concentration. Considering the variation level of observed data, the predicted metaflumizone concentrations in snails are acceptable.

The mean MB value for all organisms was calculated to be 1.04 with the 95% confidence interval from 0.30 to 3.52. This result suggests that the model as parameterized for this model performance analysis has a tendency to slightly overestimate the chemical concentrations in these aquatic organisms. The overestimation is most prevalent for zebra mussel.

Table 4-2 Calculated geometric mean model bias and its 95% confidence intervals for each test organisms in the model performance analysis of the time-dependent food web bioaccumulation sub-model

Organism	Model Bias		
	n	Mean	95% confidence interval
Macrophyte	7	1.48	0.60 - 3.66
Crustacean	7	1.09	0.14 – 7.91
Zebra Mussel	6	1.51	0.50 – 4.58
Snail	4	0.35	0.11 – 1.12
Fish	7	1.41	0.38 – 5.20

Note: n = number of time points used in the calculation of the MB

4.3 Model performance analysis for the time-dependent environmental fate sub-model

Figures 4-6 and 4-7 show that the predicted concentrations of BAS 490 02F and BAS 500 00F in water were in very good agreement with those of observed concentrations. The mean MB value for BAS 490 02F concentrations in water was calculated to be 1.19 with 95% confident intervals of 0.31 and 4.65. The mean MB value for concentrations of BAS 500 00F in water was calculated to be 1.00 with 95% confident intervals of 0.48 and 2.10. This suggests that the model is capable of estimating chemical concentrations for not only metaflumizone but also for other organic pesticides.

Table 4-3 Calculated mean MB and standard deviation for water for the environmental fate sub-model performance analysis

	Model Bias		
	n	**Mean**	**95% confidence interval**
BAS 490 02F	11	1.19	0.31 – 4.65
BAS 500 00F	21	1.00	0.48 – 2.10

Note: n = number of time points used in the calculation of the MB

There are only limited data points for sediment concentrations for BAS 490 02F and BAS 500 00F ecosystem studies. Therefore, the performance of the sediment portion of the environmental fate model was not evaluated for these substances. However, the performance of the sediment portion of the time-

dependent environmental fate sub-model will be evaluated when the performance of the combined model are evaluated using metaflumizone.

The results of the model performance analysis of the environmental fate sub-model show that the model predicted BAS 490 02F and BAS 500 00F concentrations in water are in good agreement with the observed concentrations from the microcosm studies. The results suggest that the environmental fate sub-model can be used to estimate chemical concentrations in water with good accuracy.

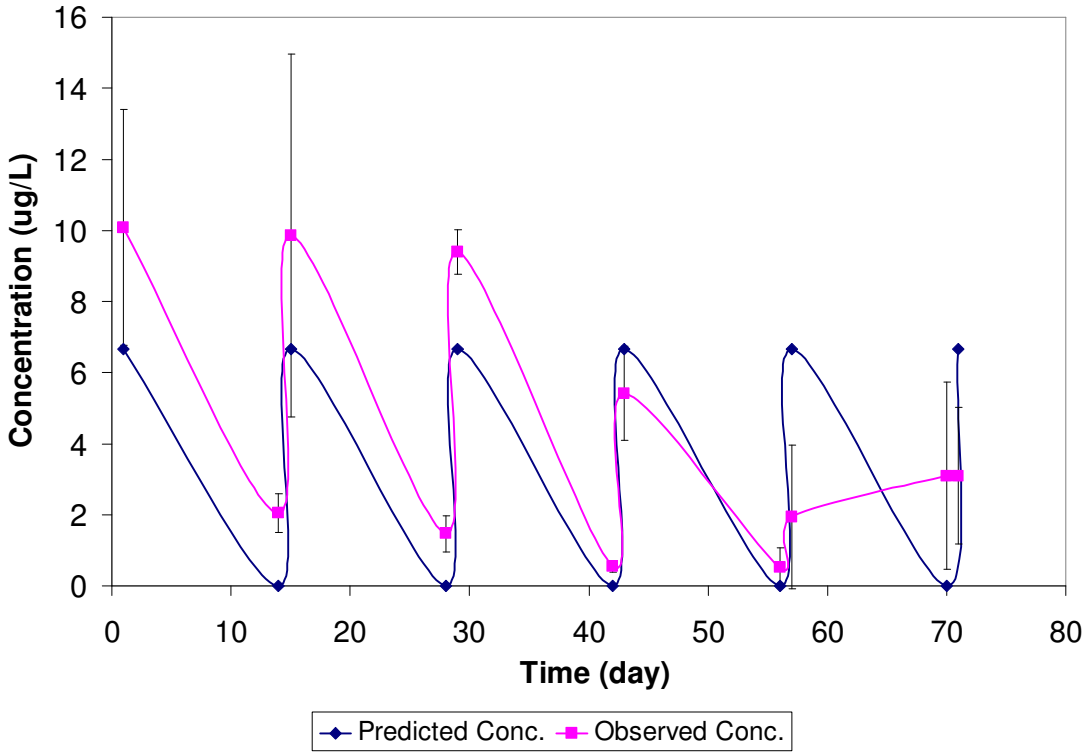

Figure 4-6 Comparison of model predicted and observed concentration for the active ingredient of BAS 490 02F in water of microcosms. Error bars represent one standard deviation of the mean of observed BAS 490 02F concentration in water.

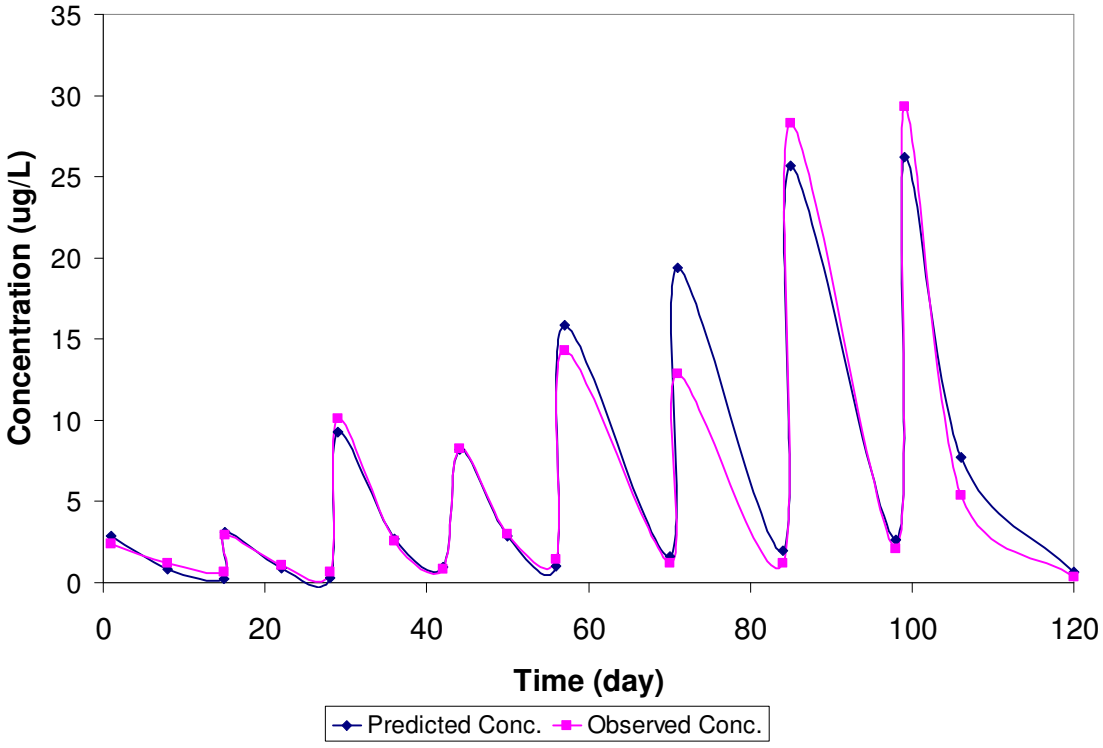

Figure 4-7 Comparison of model predicted and observed BAS 500 00F concentrations in water.

4.4 Model performance analysis for the combined model

Figures 4-8 and 4-9 illustrate the comparison of the model predicted and observed metaflumizone concentrations in water and sediments of the metaflumizone microcosm study. The mean MB values calculated for water and sediment (Table 4-4) were 0.62 and 2.17 respectively. The results indicate that the model slightly underestimates the concentrations of metaflumizone in water and overestimates the concentrations of metaflumizone in sediments.

While the model was parameterized to represent condition in the microcosm studies, EFED recommended parameters (Table 3-1) needed to be used for the density of organic carbon, water-side evaporation mass transfer coefficient, air-side evaporation mass transfer coefficient, water to sediment diffusion mass transfer coefficient because these empirical data were lacking. Assumptions were made to parameterize these parameters. It is possible that an even more realistic estimation of metaflumizone concentrations in water and sediment could have been obtained if these missing site-specific parameter values were available.

Table 4-4 Calculated mean model bias and its 95% confidence intervals for concentrations of metaflumizone in water and sediment in the combined model performance analysis using metaflumizone

	Model Bias		
	n	**Mean**	**95% confidence interval**
Water	12	0.62	0.05 – 7.24
Sediment	9	2.17	1.02 – 4.61

Note: n = number of time points used to calculate the MB

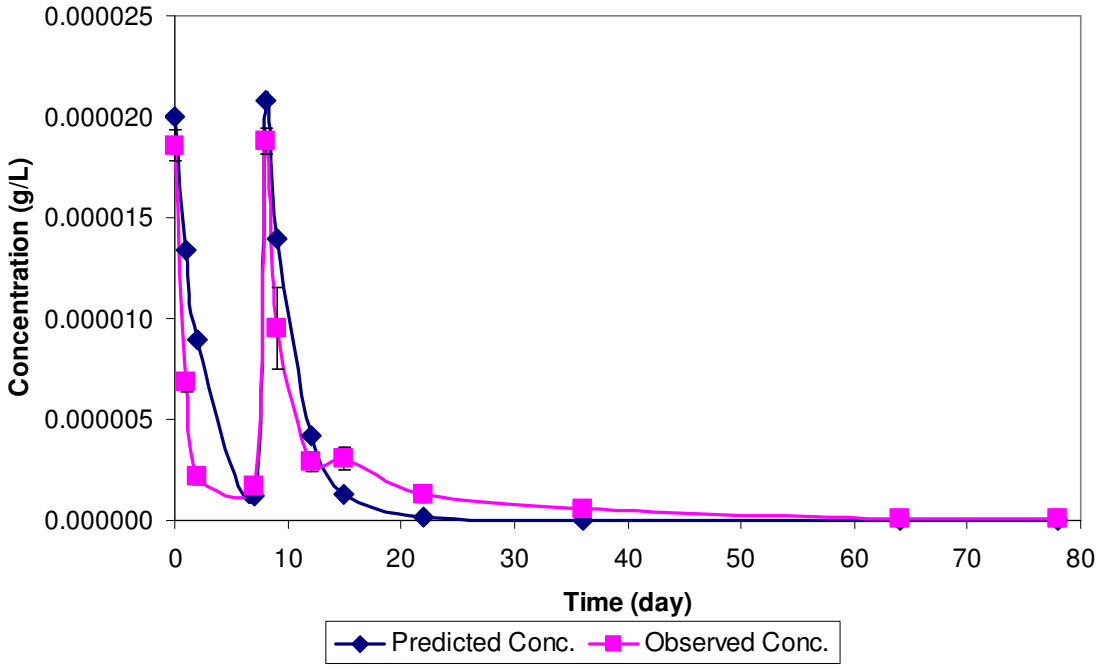

Figure 4-8 Comparison between predicted and observed concentrations of metaflumizone in water. Error bars represent the standard deviations of the mean of observed metaflumizone concentration. (n = 3)

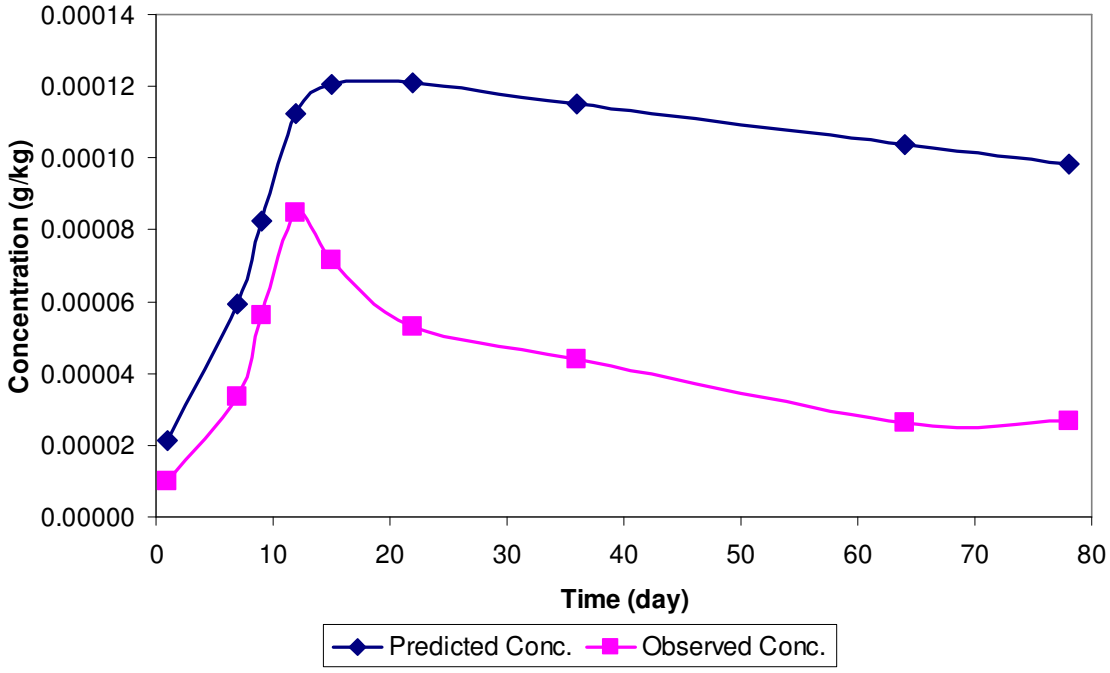

Figure 4-9 Comparison between predicted and observed concentrations of metaflumizone in sediment.

Figures 4-10 to 4-14 illustrate the comparison of the model predicted and observed metaflumizone concentrations in various organisms in the microcosm study. 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. The mean MB for all organisms was calculated to be 0.91 with 95% intervals of 0.44 and 1.88. With limited information available to parameterize the model to simulate the metaflumizone bioaccumulation study, the model generally underestimated the chemical concentrations. A better test of the model is possible if all model input parameters would have been available.

Table 4-5 Calculated mean model bias and its 95% confidence interval for test organisms in the combined model performance analysis using metaflumizone

Organism	Model Bias		
	n	Mean	95% confidence interval
Macrophyte	7	1.41	0.37 – 5.44
Crustacean	7	0.78	0.05 – 11.0
Zebra Mussel	6	0.72	0.04 – 11.8
Snail	4	0.61	0.10 – 3.90
Fish	7	1.29	0.44 – 3.77

Note: n = number of time points used to calculate MB

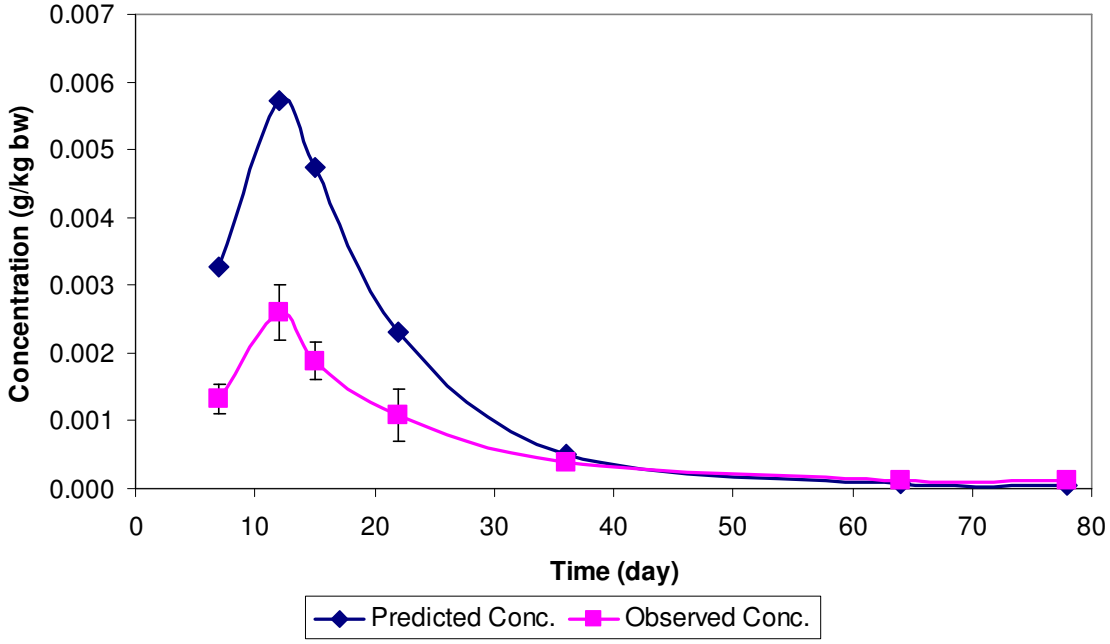

Figure 4-10 Model predicted and the mean of the observed metaflumizone concentrations (g/kg body weight) in macrophytes. Error bars represent one standard deviation of the mean metaflumizone concentration. (n = 3)

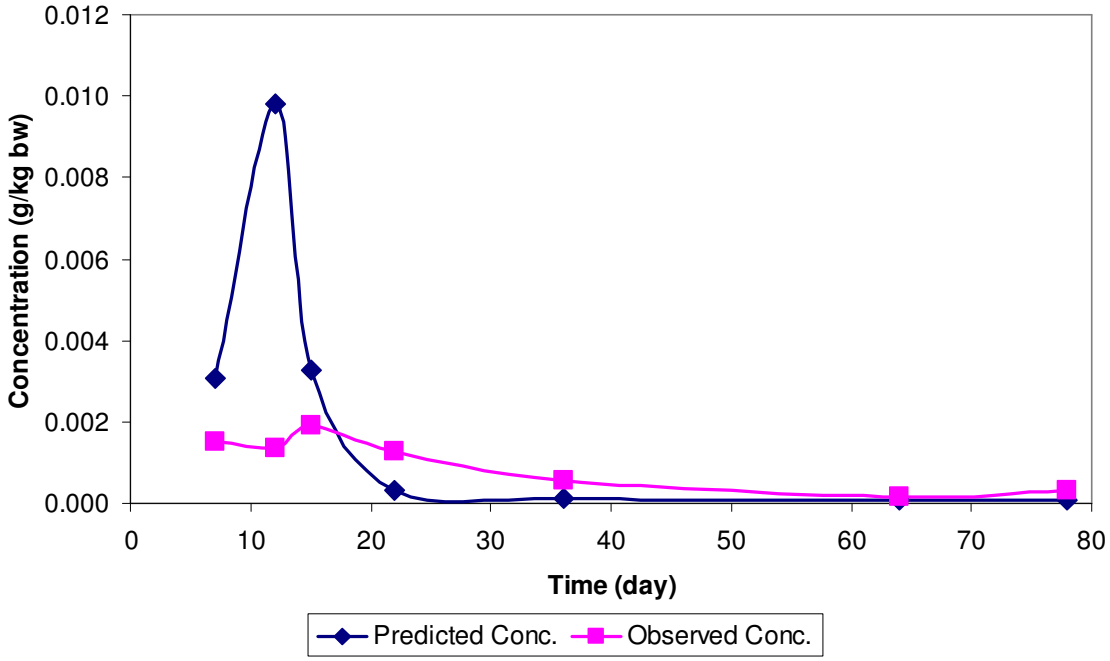

Figure 4-11 Comparison between predicted and observed metaflumizone concentrations in crustaceans. (n = 1)

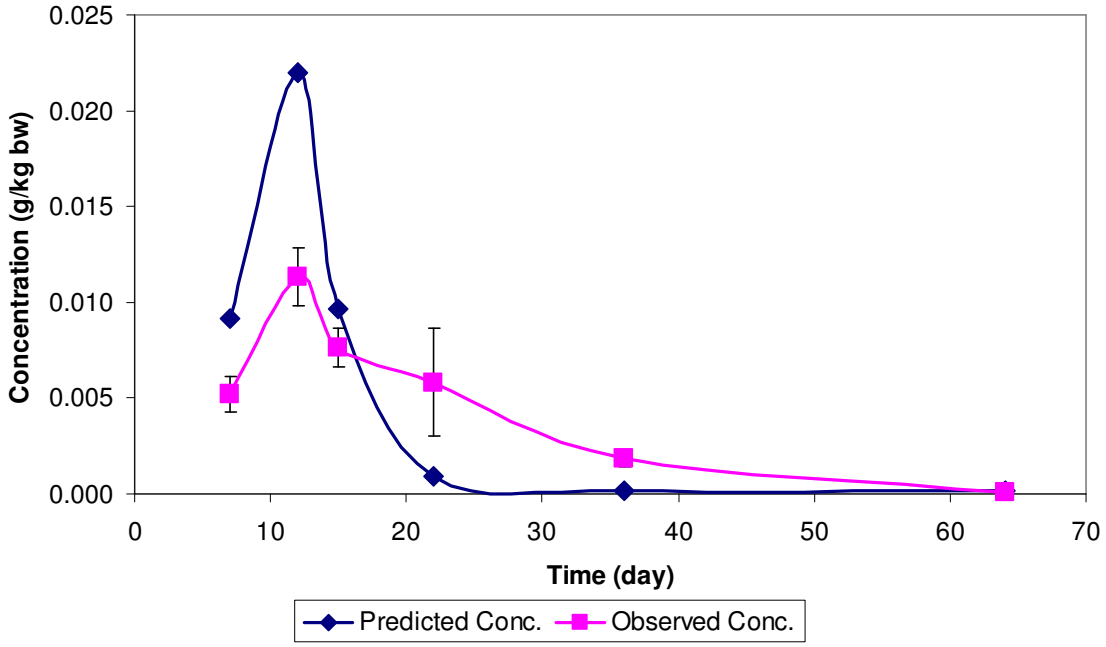

Figure 4-12 Model predicted and the mean of the observed metaflumizone concentrations (g/kg body weight) in Zebra mussels. Error bars represent one standard deviation of the mean metaflumizone concentration. (n = 3)

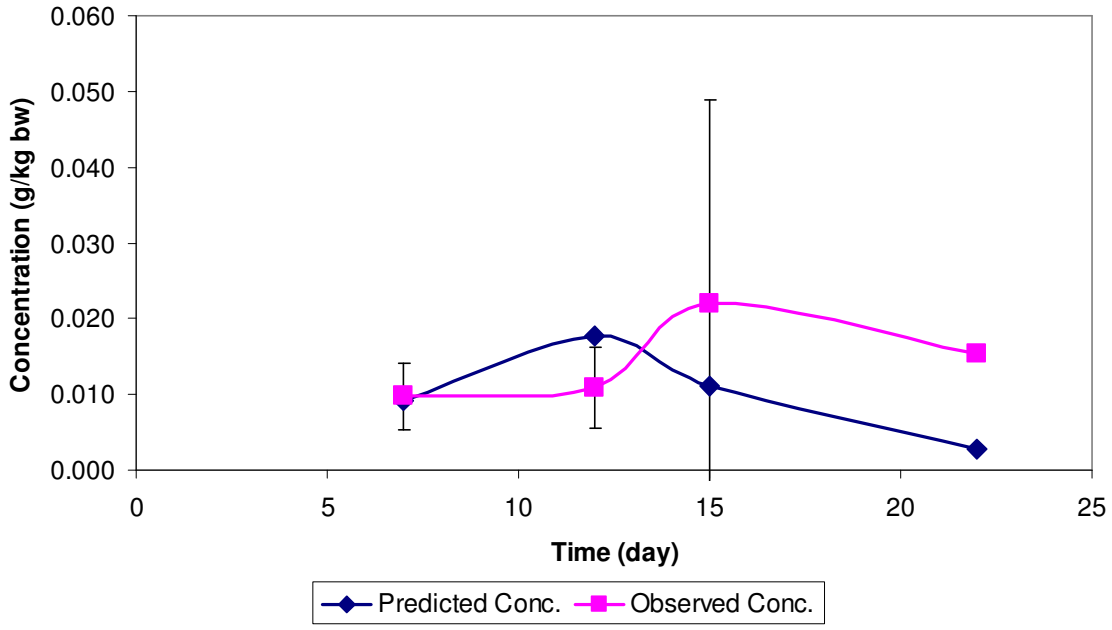

Figure 4-13 Model predicted and the mean of the observed metaflumizone concentrations (g/kg body weight) in snails. Error bars represent one standard deviation of the mean metaflumizone concentration. (n = 3 for the first 3 data points; n = 1 for the last data point)

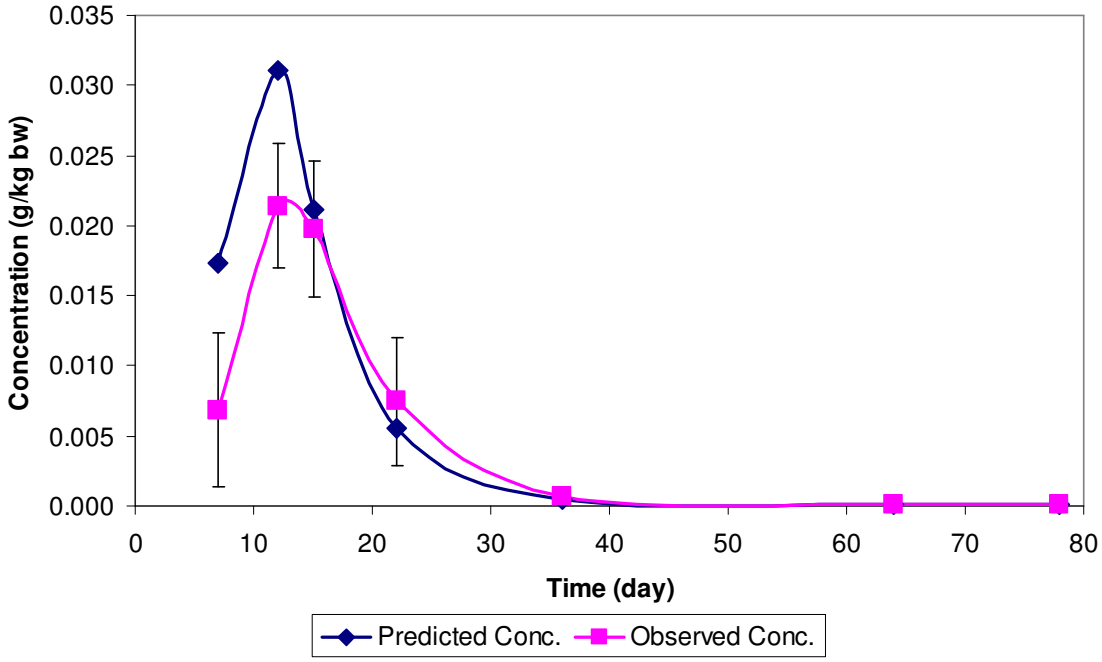

Figure 4-14 Model predicted and the mean of the observed metaflumizone concentrations (g/kg body weight) in fish. Error bars represent one standard deviation of the mean metaflumizone concentration. (n = 3)

4.5 Model application in pesticide applications

4.5.1 Evaluation of metaflumizone toxicity using external concentration

Model simulation results (Figure 4-15 and 4-16) show that the predicted metaflumizone concentrations in sediment and water can be expected not to exceed the toxicity threshold values of metaflumizone for *Chironomus tentans* (LC50 and NOEC) and Zebrafish (NOEC) after 10 years of annual metaflumizone application at the recommended application rate. Therefore, by applying metaflumizone following the BASF recommended application rate, these aquatic organisms will likely not be affected by metaflumizone.

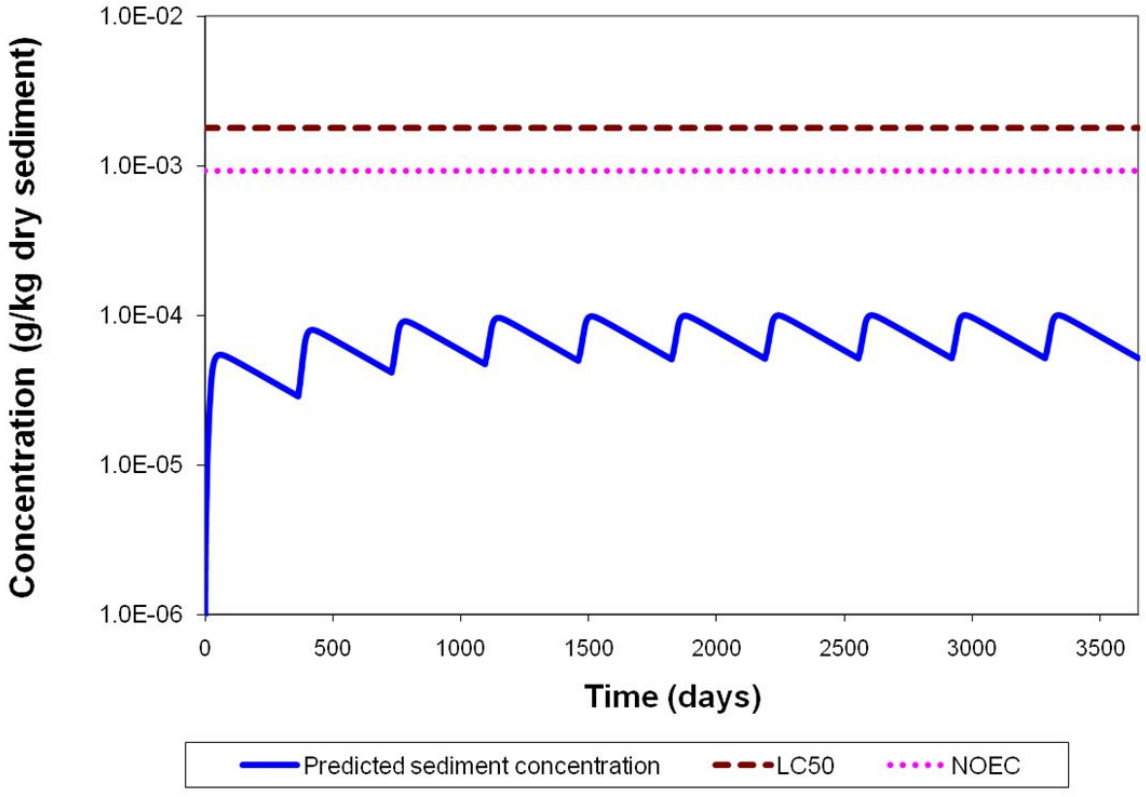

Figure 4-15 Comparison between the predicted metaflumizone concentration in sediment to the LC50 and NOEC of metaflumizone in *Chironomus tentans* (g/kg dry weight)

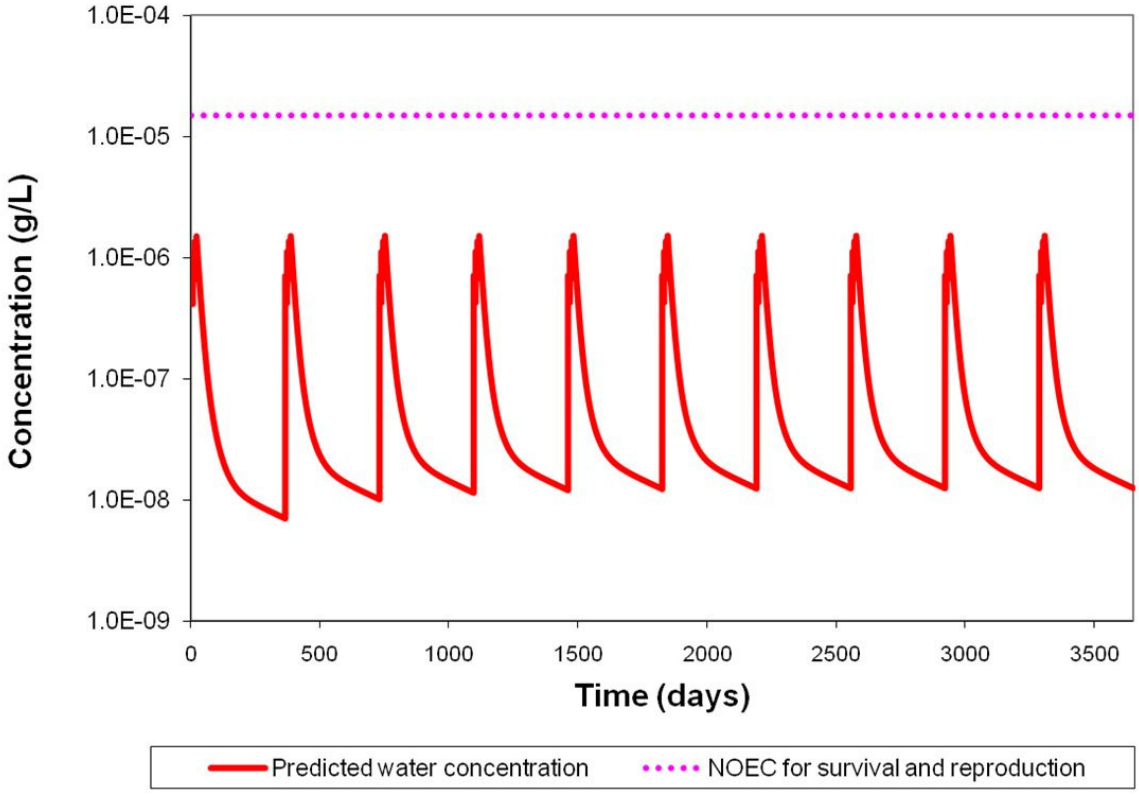

Figure 4-16 Comparison between the predicted metaflumizone concentration in water and NOEC of metaflumizone in Zebrafish (g/kg dry weight)

4.5.2 Evaluation of metaflumizone toxicity using internal body burden

The results comparing model predicted metaflumizone concentrations with the calculated internal concentration in organisms associated with different toxicity endpoints in different aquatic organisms are shown in Figures 4-17 to 4-20.

In the scenario where metaflumizone was applied to the field using the recommended application rate (four applications per year at 7-day interval with the application amount of 280 g/ha) with 5% wind drift, the predicted metaflumizone concentrations in all test organisms *are* expected not to exceed the internal body burden associated with the NOEC for reproduction and survival. Therefore, under this application scenario, metaflumizone is considered not harmful to these aquatic organisms. However, according to the model predictions, the highest metaflumizone concentration in *Chironomus tentans* is about 4.29 mg/kg, which is very close to the calculated body burden at NOEC of 4.41 mg/kg. Therefore, the BASF recommended metaflumizone application rate should be used with caution. For example, if the wind drift is higher than 5%, it is possible to cause lethality in *Chironomus tentans.* For the other three species that were evaluated, the internal concentration is expected not to cause toxic effects because the highest predicted internal metaflumizone concentration in each of these three species was significantly less than the associated no observable effect concentration (NOEC).

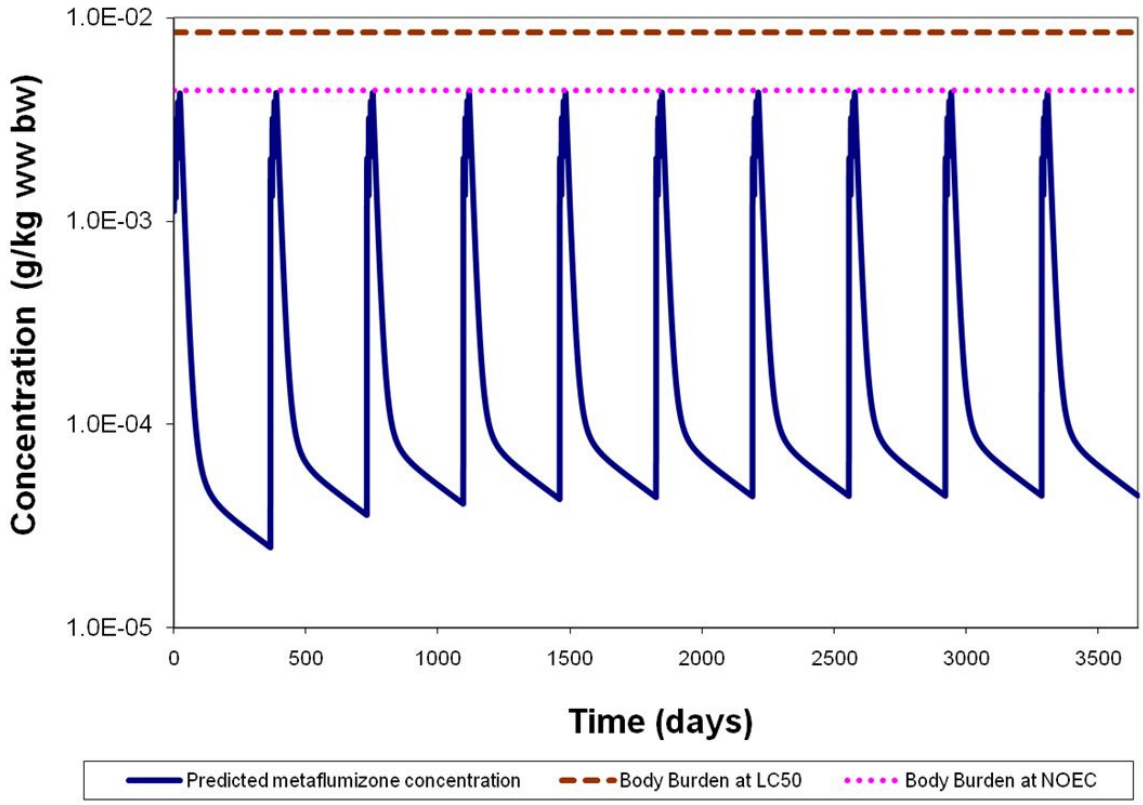

Figure 4-17 Comparison between the predicted metaflumizone concentration in *chironormus tentans* and the calculated internal body burden of metaflumizone in *chironormus tentans* associated with the LC50 and NOEC for survival and reproduction

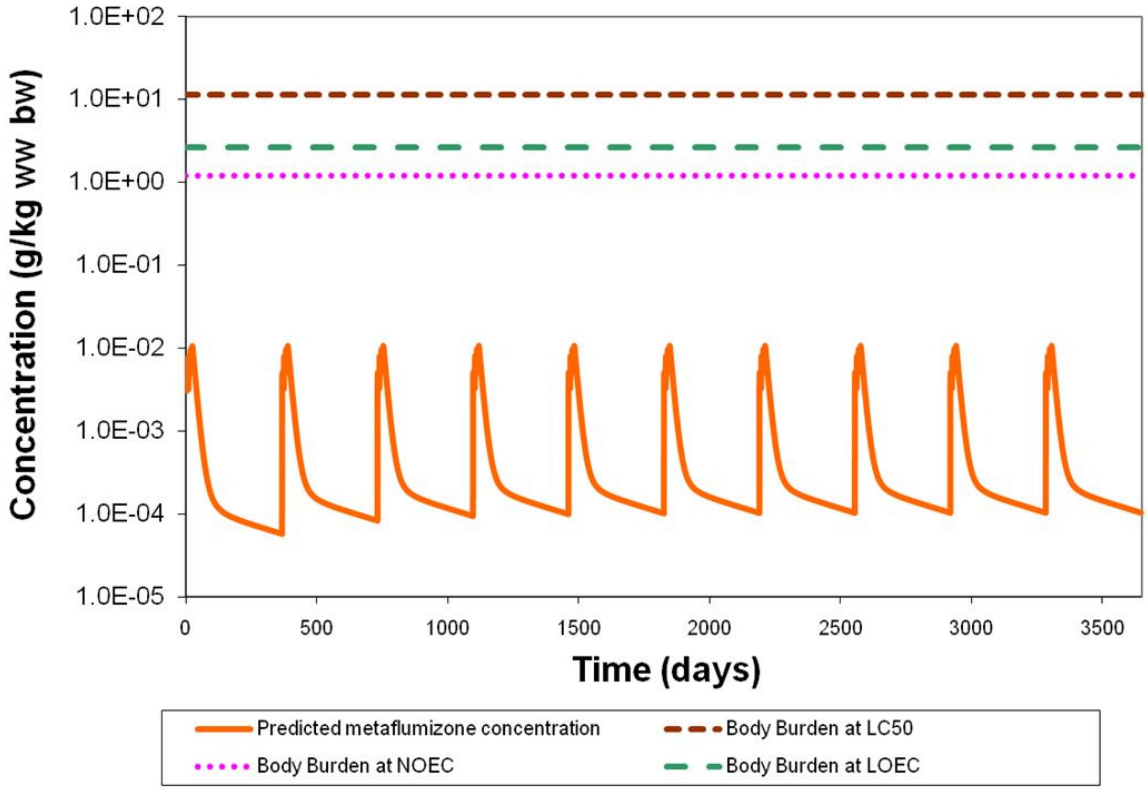

Figure 4-18 Comparison between the predicted metaflumizone concentration in *hyalella azteca* and the calculated internal body burden for *hyalella azteca* associated with the LOEC and NOEC for survival and reproduction and LC50

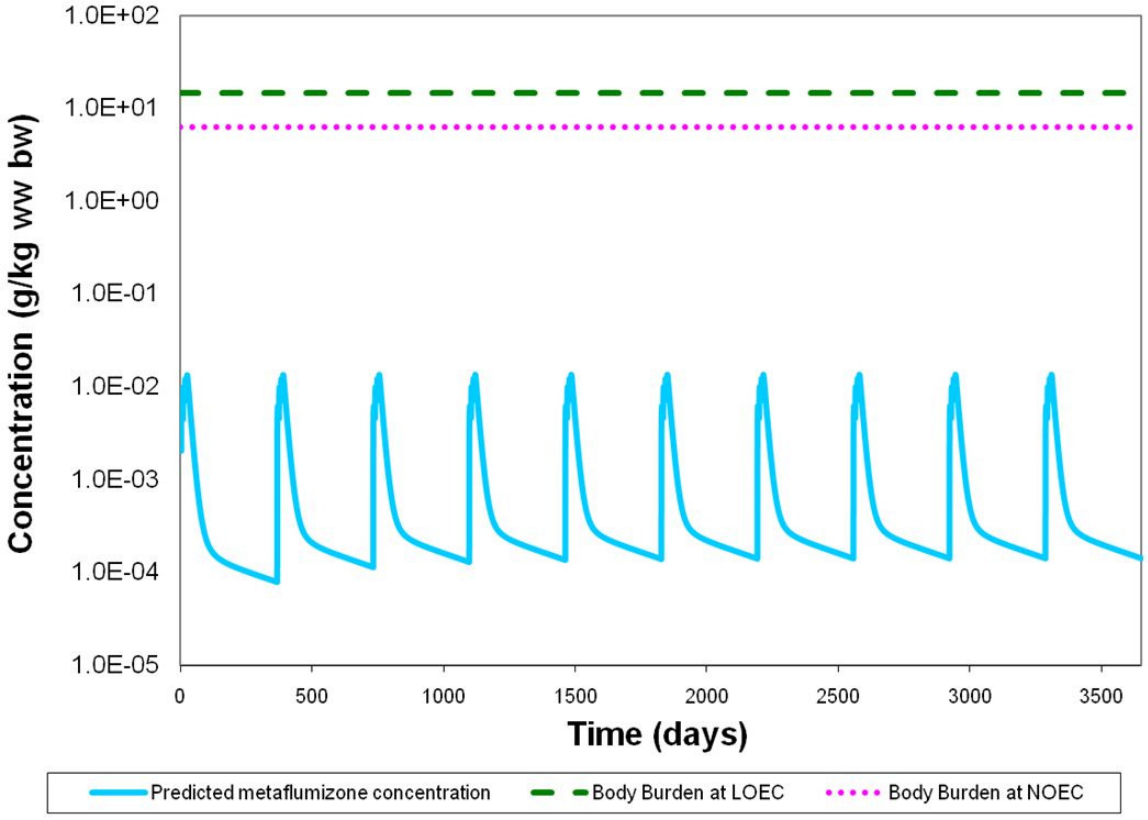

Figure 4-19 Comparison between predicted metaflumizone concentration in *leptocheirus plumulosus* and the calculated internal body burden for *leptocheirus plumulosus* associated with the LC50 and NOEC for survival and reproduction

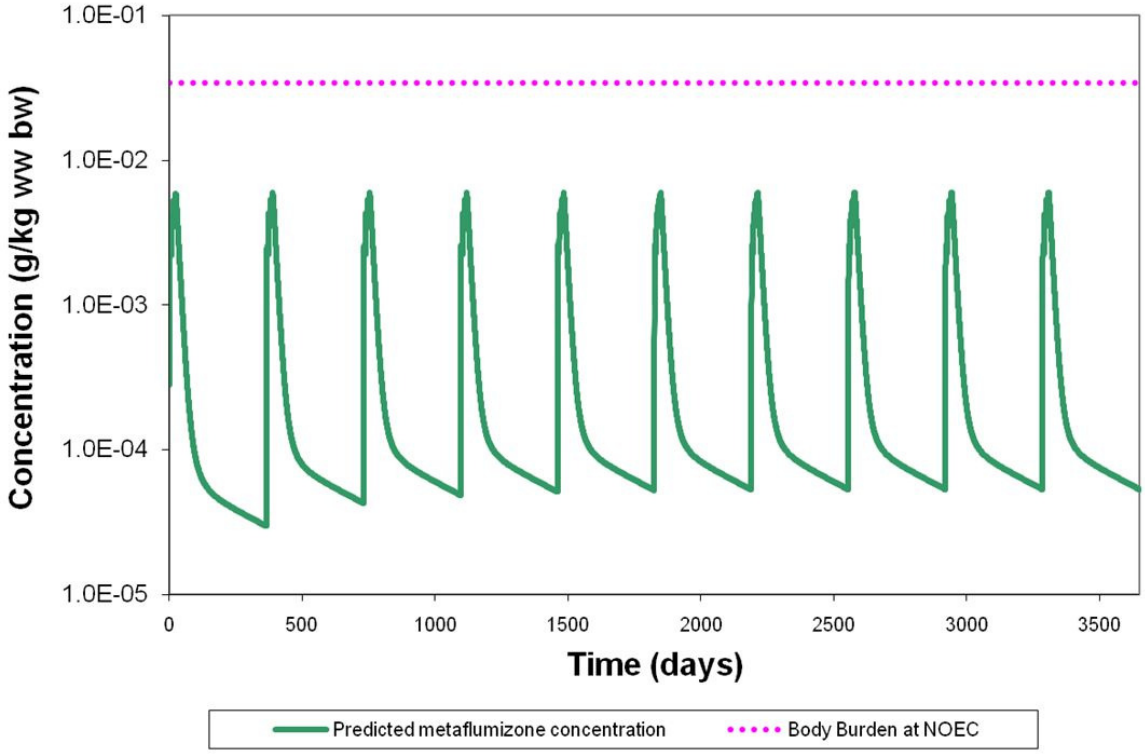

Figure 4-20 Comparison between predicted metaflumizone concentration in zebrafish and the calculated internal body burden for zebrafish associated with the NOEC for survival and reproduction

Currently, many environmental toxicity data (i.e. LC50 and EC50) are expressed as the concentration of the chemical in a medium (i.e. air, water, sediment and food) that is associated with a specific toxicity response in exposed organisms. Environmental quality regulations were also specified in terms of concentrations in the environmental media. The use of external concentration to represent chemical toxicity is supported by a finding that the magnitude of the biological response produced by a toxicant is a function of the amount of toxicant to which the organism is exposed (Filov et al., 1979). However, by using the external concentrations as toxicity effect concentration, the chemical's ability to bioaccumulate and biomagnify is not considered. It is necessary to evaluate chemical toxicity involving the bioaccumulation effect of the chemical especially for hydrophobic organic chemicals.

The critical body residue (CBR) approach (McCarty, 1990; McCarty et al. 1992a; Mackay et al., 1992; McCarty and Mackay, 1993) has been shown to indicate important relationships between internal chemical concentration in the organism and the associated toxicity responses. The time-dependent food web bioaccumulation model predicts chemical concentrations inside aquatic organisms. The predicted concentrations in the aquatic organisms represent the body burden of the chemical as a result of bioaccumulation including the effects of both chemical exposure and dietary uptake. Therefore, the time-dependent model can be used to simulate pesticide applications and the predicted

concentrations can be compared with the lethal body burden from the literature to evaluate if the pesticide application would cause toxic effects to aquatic organisms.

The accuracy of this approach to evaluate pesticide application can be improved when the toxicity data (i.e. body burden at various toxicity endpoints) for more organisms become available. The most sensitive species should be selected for the pesticide toxicity evaluation. By using the modelling approach, the time-dependent model is useful in pesticide regulation to evaluate if a pesticide application will have any potential to cause toxic effects to aquatic organisms.

4.5.3 Calculation of a recommended maximum allowable application amount for metaflumizone

According to the findings reported in chapter 4.5.1 and 4.5.2, the BASF recommended application rate for metaflumizone is shown not to be harmful to aquatic organisms as the predicted metaflumizone concentrations in water, sediment and aquatic organisms are below toxicity threshold values.

To derive a maximum allowable pulse loading rate for different pesticide applications, model simulations were performed using different pulse-loading amount under the same chemical application scenario with 5% wind drift. The maximum allowable rate of metaflumizone application resulting in body burden for all test organisms less than the body burden to cause toxic effects is about 287 g/ha (4 applications per year at 7 day intervals with 5% wind drift).

The same method can be used to derive the maximum allowable pulse loading amounts for other pesticide applications and other environmental systems. This approach is a useful tool to determine whether a specific pesticide application will cause toxic effects to aquatic organisms without conducting expensive and time consuming field studies. The modelling approach could potentially be used by the regulators for the regulation of pesticide usage in the protection of aquatic organisms from pesticide released.

4.6 Differences between steady-state and time-dependent food web bioaccumulation models for pesticide applications

Figure 4-21 illustrates the comparison between the steady-state and the time-dependent bioaccumulation model predictions of metaflumizone concentrations in water. It shows that the steady-state based bioaccumulation model predicts the concentration of metaflumizone in water to be about 9.8 µg/L after metaflumizone is released into the water at a rate of 14 g/day. According to the time-dependent model predictions, after four applications at 7-day intervals at 14 g/application annually for 5 years, the metaflumizone concentrations in water, fluctuate with time. The concentration will first rise to reach peaks corresponding to the pulse releases of metaflumizone directly into water. Due to the chemical clearance from water, metaflumizone concentrations in water decrease in time before the next release of metaflumizone to the water. Figure 4-21 shows that the magnitude of the fluctuation of the predicted metaflumizone concentrations in water is greater than 100 times comparing the maximum and minimum predicted values. The highest predicted metaflumizone concentration in water is about 1.45 µg/L, which is 6.76 times less compared with the steady-state model predictions. In addition, the steady-state based model predicted metaflumizone concentration is more than 1000 times greater than the lowest metaflumizone concentration in water predicted by the time-dependent model. The results show that when using steady-state based model to estimate pesticide concentrations, there is a potential to overestimate the chemical concentrations in the environmental compartments (i.e., water and sediment); since the metaflumizone concentration

never reaches steady state in the environmental compartments under the specified application rate.

Figure 4-21 further illustrates that when an average pesticide loading rate (calculated as the total amount of metaflumizone released into the water according to the pesticide application rate divided by the total time, 0.1534 g/day) is used in the steady-state model simulation, the predicted metaflumizone concentration in water fell in the middle range of the time-dependent model predicted water concentrations. This illustrates that the steady-state model will produce substantial underestimation and overestimation of metaflumizone concentrations if metaflumizone is applied in an episodic fashion.

Similar results were obtained for metaflumizone concentrations in sediment (Figure 4-22) and in different aquatic organisms (Figure 4-23 to 4-28).

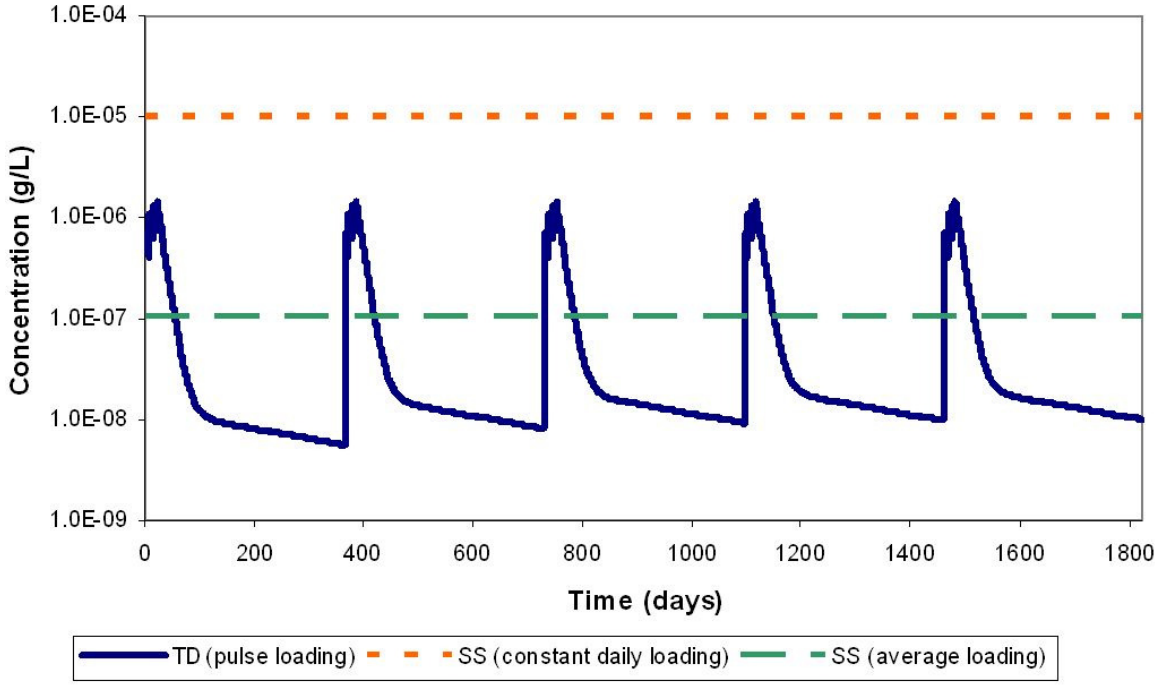

Figure 4-21 Comparison between steady-state and time-dependent bioaccumulation model predictions of metaflumizone concentrations in water. TD (pulse loading) represents time-dependent model predictions with application rate of 14g/application at 7-day intervals; SS(constant daily loading) represents steady-state model predictions with daily loading of 14g of metaflumizone; SS(average loading) represents steady-state model predictions with daily loading of 0.1534g of metaflumizone.

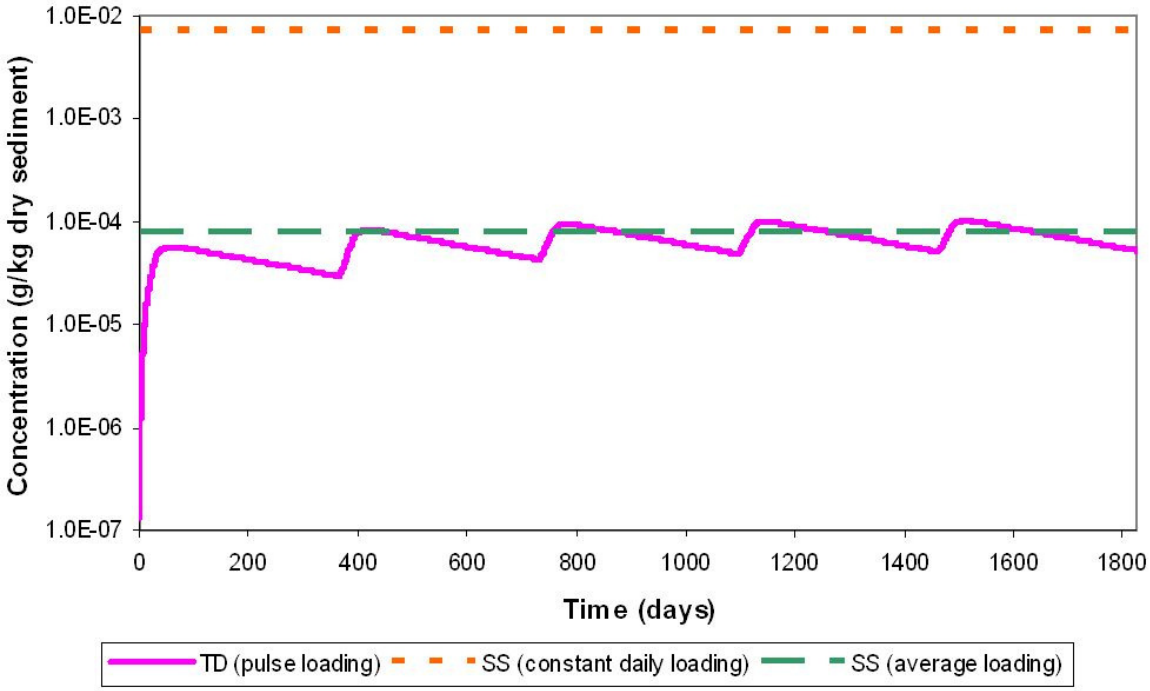

Figure 4-22 Comparison between steady-state and time-dependent bioaccumulation model predictions of metaflumizone concentrations in sediment. TD (pulse loading) represents time-dependent model predictions with application rate of 14g/application at 7-day intervals; SS(constant daily loading) represents steady-state model predictions with daily loading of 14g of metaflumizone; SS(average loading) represents steady-state model predictions with daily loading of 0.1534g of metaflumizone.

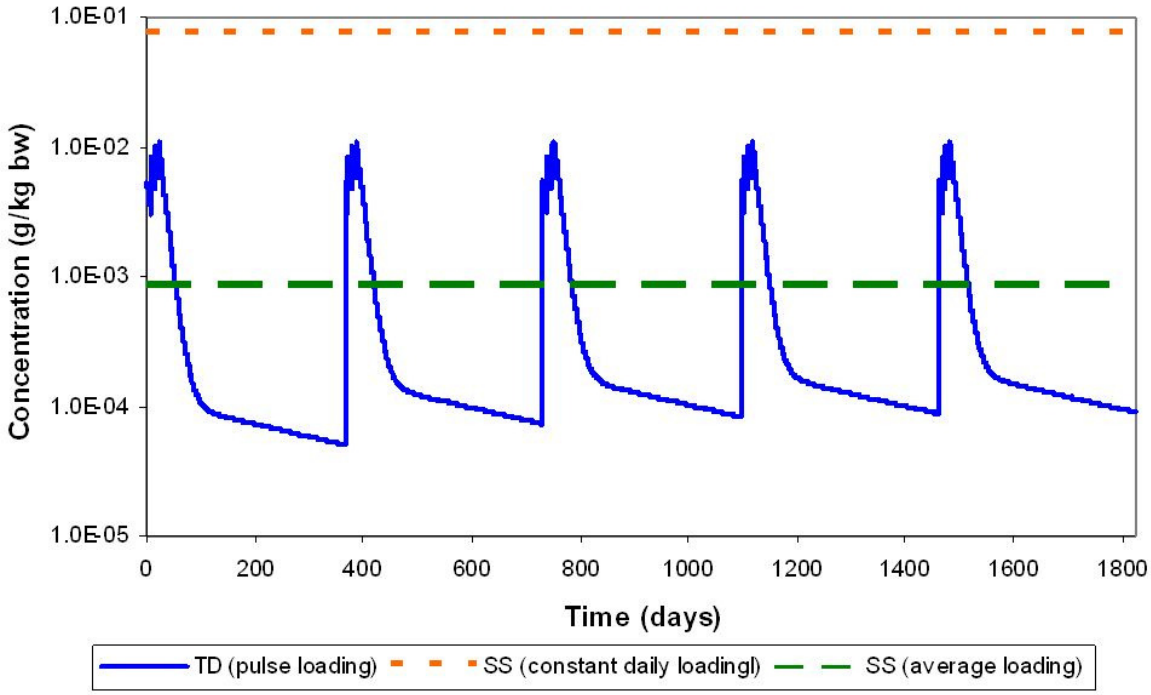

Figure 4-23 Comparison between steady-state and time-dependent bioaccumulation model predictions of metaflumizone concentrations in phytoplankton. TD (pulse loading) represents time-dependent model predictions with application rate of 14g/application at 7-day intervals; SS(constant daily loading) represents steady-state model predictions with daily loading of 14g of metaflumizone; SS(average loading) represents steady-state model predictions with daily loading of 0.1534g of metaflumizone.

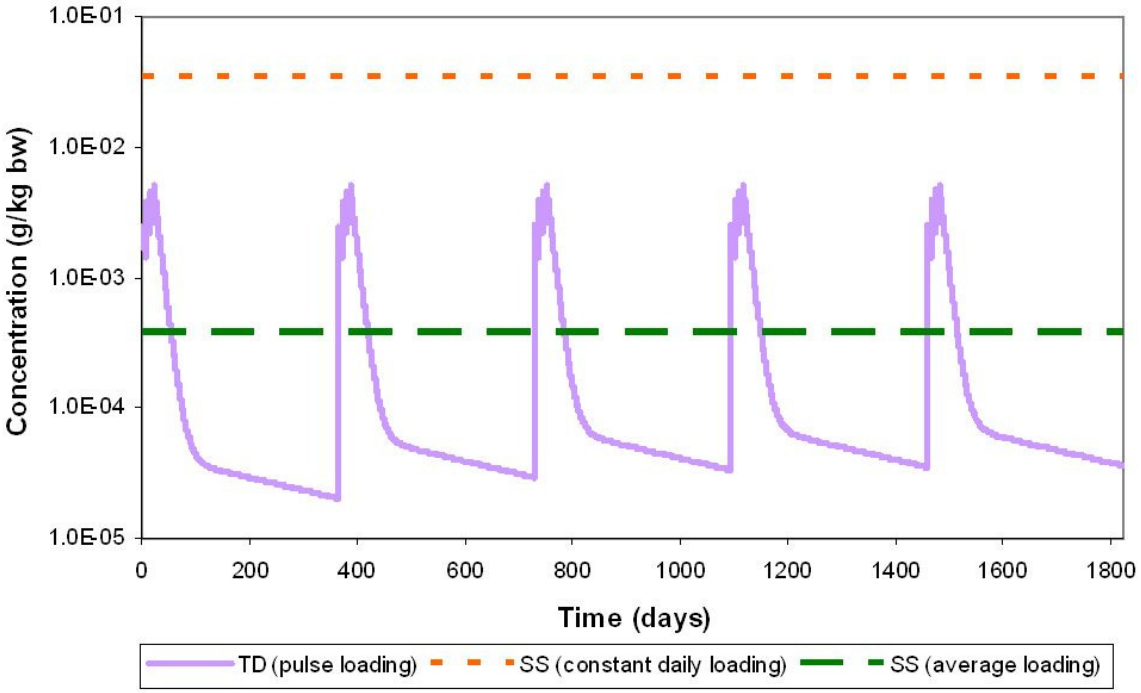

Figure 4-24 Comparison between steady-state and time-dependent bioaccumulation model predictions of metaflumizone concentrations in zooplankton. TD (pulse loading) represents time-dependent model predictions with application rate of 14g/application at 7-day intervals; SS(constant daily loading) represents steady-state model predictions with daily loading of 14g of metaflumizone; SS(average loading) represents steady-state model predictions with daily loading of 0.1534g of metaflumizone.

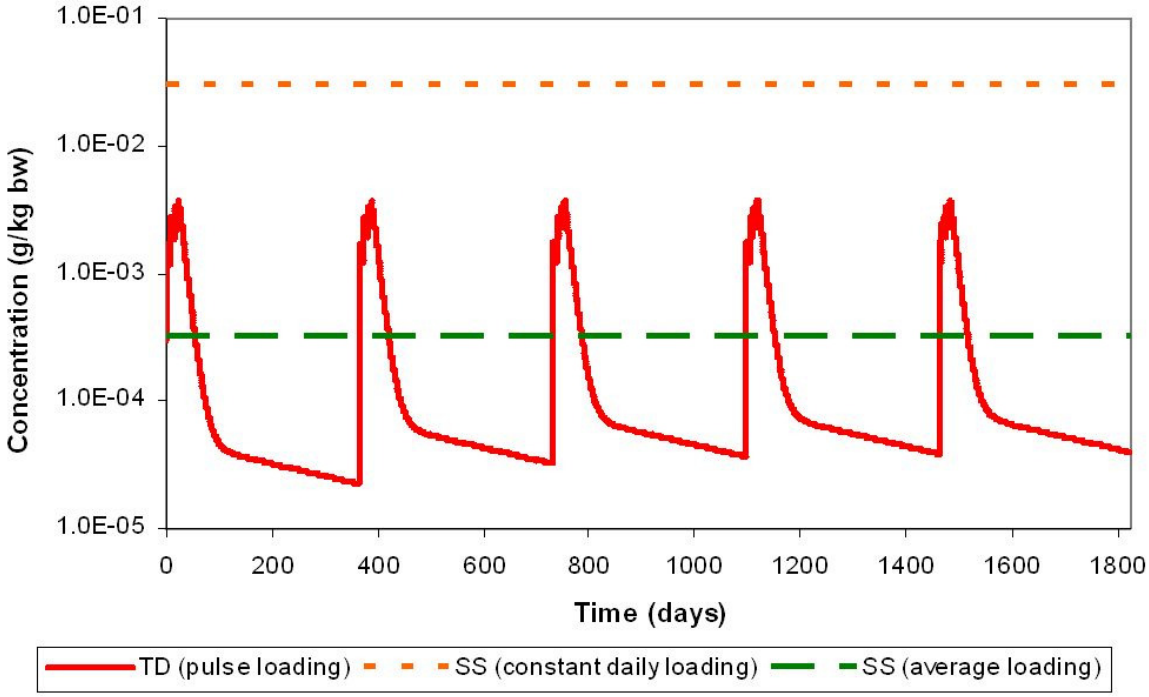

Figure 4-25 Comparison between steady-state and time-dependent bioaccumulation model predictions of metaflumizone concentrations in diporeia. TD (pulse loading) represents time-dependent model predictions with application rate of 14g/application at 7-day intervals; SS(constant daily loading) represents steady-state model predictions with daily loading of 14g of metaflumizone; SS(average loading) represents steady-state model predictions with daily loading of 0.1534g of metaflumizone.

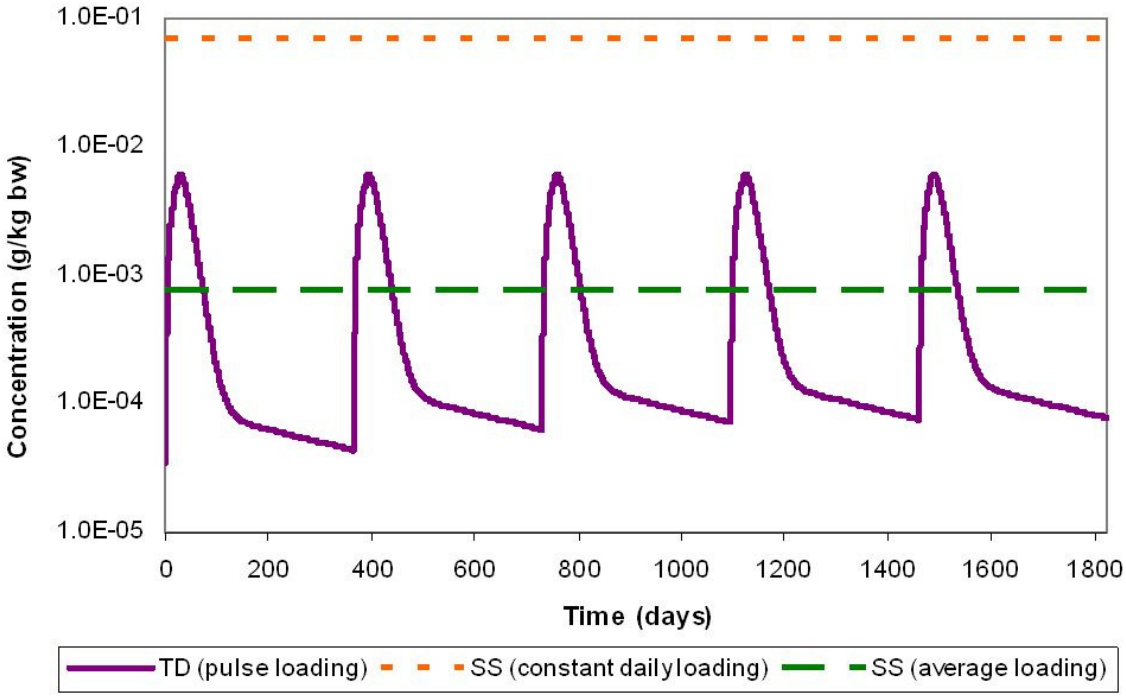

Figure 4-26 Comparison between steady-state and time-dependent bioaccumulation model predictions of metaflumizone concentrations in forage fish A**.** TD (pulse loading) represents time-dependent model predictions with application rate of 14g/application at 7-day intervals; SS(constant daily loading) represents steady-state model predictions with daily loading of 14g of metaflumizone; SS(average loading) represents steady-state model predictions with daily loading of 0.1534g of metaflumizone.

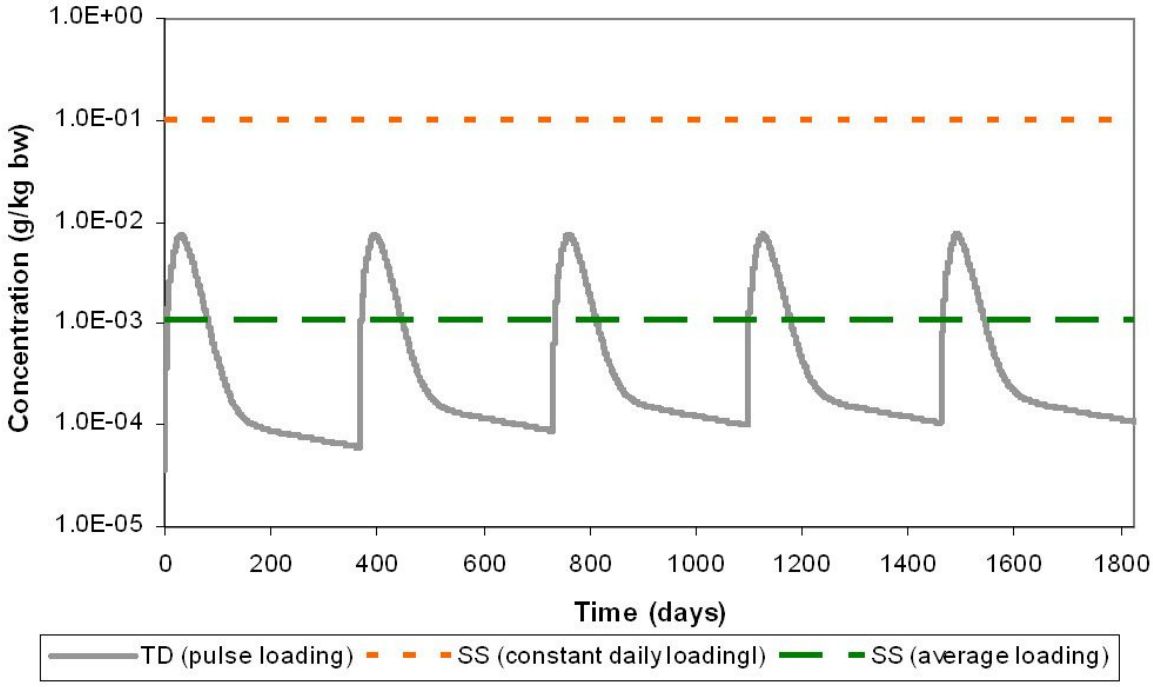

Figure 4-27 Comparison between steady-state and time-dependent bioaccumulation model predictions of metaflumizone concentrations in forage fish B. TD (pulse loading) represents time-dependent model predictions with application rate of 14g/application at 7-day intervals; SS(constant daily loading) represents steady-state model predictions with daily loading of 14g of metaflumizone; SS(average loading) represents steady-state model predictions with daily loading of 0.1534g of metaflumizone.

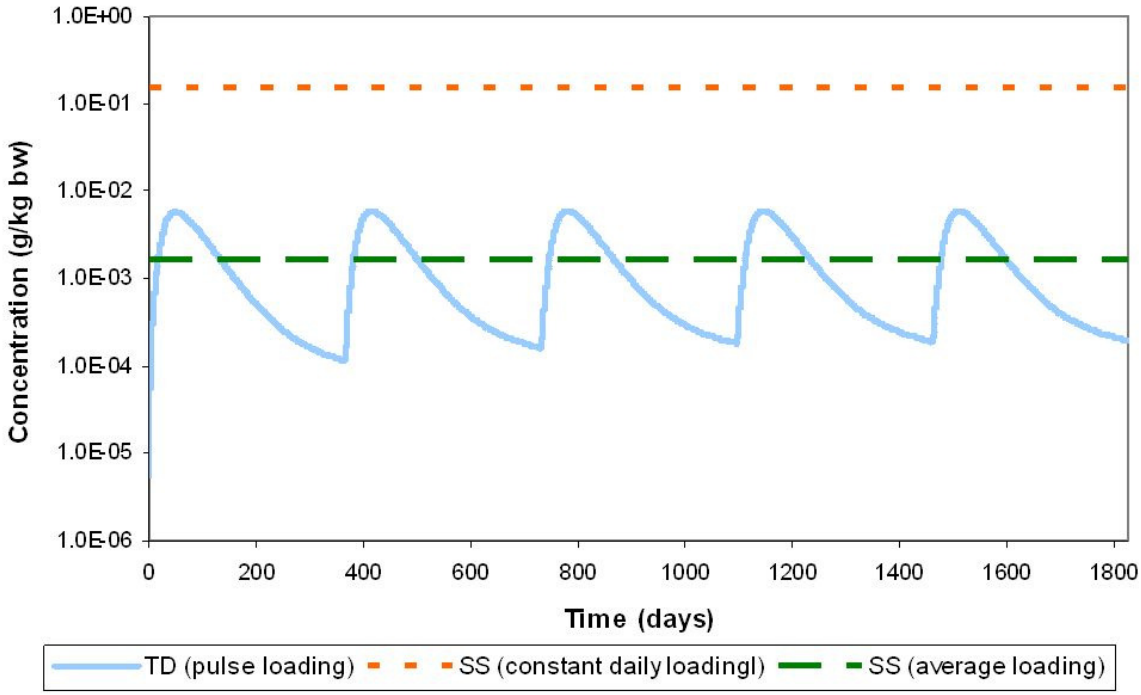

Figure 4-28 Comparison between steady-state and time-dependent bioaccumulation model predictions of metaflumizone concentrations in piscivorous fish. TD (pulse loading) represents time-dependent model predictions with application rate of 14g/application at 7-day intervals; SS(constant daily loading) represents steady-state model predictions with daily loading of 14g of metaflumizone; SS(average loading) represents steady-state model predictions with daily loading of 0.1534g of metaflumizone.

Currently, steady-state based models are the main tools used by the regulators to regulate pesticides. Steady-state based bioaccumulation model requires daily constant chemical emission for model simulations. These models assume the chemical reach steady states in different environmental compartments. However, in pesticide applications, chemicals are released into the environment at certain application rate. Different pesticides also have different chemical properties and therefore might accumulate or degrade in different environmental compartments at different rates. Because of these factors, some chemicals might never reach steady state under the specified application scenario. In the case of modeling pesticide applications, due to the dynamic characteristics of pesticide concentrations in the environmental compartments, the time-dependent bioaccumulation model can be used to provide a more realistic estimation of pesticide concentrations in each environmental compartment than that of a steady-state based model.

Instead, another approach should be considered, which is to use time-dependent models to estimate chemical concentrations in aquatic organisms. The internal chemical concentration in the aquatic organism can be compared with the lethal body burden of the chemical to access chemical toxicity. By comparing the lipid normalized chemical concentration in aquatic organisms on different level of food chain, we can evaluate whether chemical can biomagnify in the aquatic food web. To access the bioaccumulation potential of the chemical, we can evaluate the chemical concentration through time. If the chemical concentration in aquatic

organism increases as a function of time, the chemical have the ability to bioaccumulate in the aquatic organism.

The time-dependent food web bioaccumulation model is particularly applicable in pesticide regulation. Pesticides have been used in urban and agricultural areas for pest controls and agricultural productions for years. The primary targets for pesticide applications are in most cases not aquatic habitats. However, due to downwind drift or accidental pesticide spraying, aquatic habitats can be exposed to pesticides. Aerial spraying of pesticide is one of the major pesticide application methods. During the aerial pesticide application, there is a particular high risk of introducing pesticide in smaller water bodies since it is often impossible for a pilot in a low-flying spray aircraft to locate small water bodies in advance or to interrupt the spray treatment once the pilot has spotted them. The aerial spraying of pesticide has raised potential impacts to aquatic organisms. The model can be used to estimate pesticide concentrations in the aquatic organisms and their exposed environmental compartments in the small water bodies inside the agricultural area for pesticide regulation.

CHAPTER 5: CONCLUSIONS

Currently, steady state based bioaccumulation models are used by the US EPA for pesticide registration in the US. These steady state based models are used to estimate chemical concentrations in the environment and to derive BAFs and BCFs for the evaluation of the bioaccumulation potential of a chemical. Since, BAF and BCF are defined at steady state. However, it is justified that pesticide concentrations in the environmental compartments (i.e., water and sediment) and in biota can not be predicted accurately with steady-state based bioaccumulation model if pesticides were released into the environment as pulse loadings. Depending on the application rate and the chemical characteristics such as Kow, the pesticides may not reach steady-state in the environmental compartments.

As part of this study, a time-dependent food web bioaccumulation model was successfully developed. This model can be used to estimate hydrophobic organic pesticide concentrations in water, sediment and in key aquatic organisms.

The performance of the model was evaluated by conducting model performance analysis for the food web sub-model, environmental fate sub-model and the combined model. The results of model performance analysis show that the time dependent food-web bioaccumulation model is in reasonable agreement with the observed data from the microcosm studies. In particular, the calculated

concentrations in piscivorous fish are in good agreement with the observed concentrations in piscivorous fish in the microcosms. When the combined time-dependent environmental fate and food-web model is tested to the results from the microcosm studies, we observed good agreement between calculated and observed concentrations in the water. However, the metaflumizone concentrations in the sediments were over-predicted by about two folds. The model is anticipated to be able to accurately estimate the chemical concentrations in water, sediment and different aquatic organisms.

For chemicals that have high Kow values, it requires longer time to achieve steady-state in the aquatic organisms. Due to the chemical's bioaccumulation potential, the chemical with high Kow can be biomagnified up the aquatic food chain. If the chemical has not achieved steady-state in the aquatic organisms, it is possible for a steady-state based model to overestimate chemical concentrations. After using both steady-state and time-dependent model to simulate metaflumizone applications, it was found that with the time-dependent chemical concentration estimation ability, the time-dependent food web bioaccumulation can provide a more realistic estimation of chemical concentrations in different environmental compartments than those predicted by the steady-state based bioaccumulation models.

The results of model applications illustrate that the time-dependent food web bioaccumulation model can be used to derive the total maximum allowable chemical loading for metaflumizone so that the resulted metaflumizone concentrations in the environment will not exceed the toxicity threshold values

and the metaflumizone concentrations in the aquatic organisms will not exceed the lethal body burden in these organisms. This approach can be applied to other pesticides to facilitate pesticide regulations.

The time-dependent food web bioaccumulation model is a useful tool for pesticide regulations. When the model is used properly, it can provide useful information to assist environmental regulations.

CHAPTER 6: APPENDICES

6.1 Empirical data from the metaflumizone microcosm study for the performance analysis of the time-dependent food web submodel and the combined time-dependent model

Table 6-1 Observed metaflumizone (E + Z isomer) concentrations in water and sediment in the microcosms

Time (days) after first application	E isomer		Z isomer	
	Conc. in water (g/L)	Conc. in sediment (g/kg)	Conc. in water (g/L)	Conc. in sediment (g/kg)
1	3.29E-06	5.00E-06	8.59E-06	5.10E-06
7	1.07E-06	1.12E-05	2.99E-06	2.23E-05
9	3.72E-06	1.88E-05	1.05E-05	3.74E-05
12	1.27E-06	2.88E-05	4.33E-06	5.58E-05
15	1.14E-06	2.68E-05	3.49E-06	4.47E-05
22	6.11E-07	2.14E-05	2.01E-06	3.18E-05
36	1.47E-07	2.17E-05	5.30E-07	2.22E-05
64	2.50E-08	1.64E-05	7.10E-08	9.70E-06
78	2.50E-08	1.60E-05	2.50E-08	1.07E-05

Table 6-2 Predicted and average observed metaflumizone concentrations in macrophyte

Time (days) after first application	Average observed metaflumizone conc. (g/kg bw)	Standard deviation	Predicted metaflumizone conc. (g/kg bw)
7	1.32E-03	2.14E-04	2.10E-03
12	2.59E-03	4.10E-04	3.38E-03
15	1.89E-03	2.82E-04	3.13E-03
22	1.09E-03	3.87E-04	2.35E-03
36	3.89E-04	1.09E-04	1.00E-03
64	1.19E-04	7.88E-05	1.60E-04
78	1.11E-04	4.22E-05	6.78E-05

Table 6-3 Predicted and average observed metaflumizone concentrations in crustacean

Time (days)	Observed metaflumizone conc. (g/kg bw)	Predicted metaflumizone conc. (g/kg bw)
7	1.51E-03	3.47E-03
12	1.35E-03	5.00E-03
15	1.92E-03	3.27E-03
22	1.28E-03	1.87E-03
36	5.52E-04	5.13E-04
64	1.79E-04	8.72E-05
78	3.32E-04	6.14E-05

Table 6-4 Predicted and average observed metaflumizone concentrations in zebra mussel

Time (days) after first application	Average observed metaflumizone conc. (g/kg bw)	Standard deviation	Predicted metaflumizone conc. (g/kg bw)
7	5.18E-03	9.43E-04	1.05E-02
12	1.13E-02	1.53E-03	1.49E-02
15	7.61E-03	9.95E-04	1.02E-02
22	5.81E-03	2.81E-03	5.59E-03
36	1.87E-03	4.27E-04	1.63E-03
64	6.53E-05	4.33E-05	2.64E-04

Table 6-5 Predicted and average observed metaflumizone concentrations in snail

Time (days) after first application	Average observed metaflumizone conc. (g/kg bw)	Standard deviation	Predicted metaflumizone conc. (g/kg bw)
7	9.73E-03	4.44E-03	4.92E-03
12	1.09E-02	5.32E-03	7.15E-03
15	2.20E-02	2.69E-02	5.04E-03
22	1.54E-02	N/A	2.97E-03

Table 6-6 Predicted and average observed metaflumizone concentrations in fish

Time (days) after first application	Average observed metaflumizone conc. (g/kg bw)	Standard deviation	Predicted metaflumizone conc. (g/kg bw)
7	6.86E-03	5.50E-03	1.05E-02
12	2.14E-02	4.45E-03	1.56E-02
15	1.98E-02	4.87E-03	1.14E-02
22	7.47E-03	4.55E-03	6.75E-03
36	7.05E-04	3.78E-04	2.05E-03
64	1.11E-04	1.27E-04	3.01E-04
78	6.49E-05	2.32E-05	1.55E-04

6.2 Empirical data from the microcosm studies for BAS 490 02F and BAS 500 00F for the performance analysis of the time-dependent environmental fate submodel

Table 6-7 Comparison of model predicted and observed BAS 490 02F concentrations in water

Time (day)	Predicted Conc. (g/L)	Observed Conc. (g/L)
1	6.65E-06	1.01E-05
14	6.56E-12	2.05E-06
15	6.65E-06	9.86E-06
28	6.57E-12	1.47E-06
29	6.65E-06	9.40E-06
42	6.57E-12	5.48E-07
43	6.65E-06	5.41E-06
56	6.57E-12	5.18E-07
57	6.65E-06	1.94E-06
70	6.57E-12	3.09E-06
71	6.65E-06	3.10E-06

Table 6-8 Comparison of model predicted and observed BAS 500 00F concentrations in water

Time (day)	Predicted Conc. (g/L)	Observed Conc. (g/L)
1	2.88E-06	2.41E-06
8	8.45E-07	1.18E-06
14.9	2.54E-07	6.48E-07
15	3.13E-06	2.92E-06
22	9.19E-07	1.06E-06
28	3.23E-07	6.80E-07
29	9.27E-06	1.01E-05
36	2.72E-06	2.60E-06
42	9.56E-07	8.61E-07
44	8.23E-06	8.24E-06
50	2.88E-06	2.98E-06
56	1.01E-06	1.44E-06
57	1.59E-05	1.43E-05
70	1.63E-06	1.23E-06
71	1.94E-05	1.28E-05
84	2.00E-06	1.18E-06
85	2.57E-05	2.83E-05
98	2.65E-06	2.11E-06
99	2.62E-05	2.93E-05
106	7.70E-06	5.41E-06
120	6.77E-07	3.41E-07

6.3 Model parameter values for the performance analysis of the combined time-dependent food web bioaccumulation model

Table 6-9 Comparison between model predicted and observed metaflumizone concentrations in water

Time (days) after first application	Average observed metaflumizone conc. (g/kg bw)	Standard deviation	Predicted metaflumizone conc. (g/kg bw)
0	1.86E-05	7.68E-07	2.00E-05
1	6.84E-06	4.61E-07	1.34E-05
2	2.16E-06	3.44E-07	8.96E-06
7	1.67E-06	4.07E-07	1.24E-06
8	1.88E-05	6.42E-07	2.08E-05
9	9.51E-06	2.01E-06	1.40E-05
12	2.92E-06	5.00E-07	4.23E-06
15	3.06E-06	5.69E-07	1.32E-06
22	1.28E-06	3.89E-07	1.22E-07
36	5.34E-07	1.34E-07	3.18E-08
64	8.83E-08	2.19E-08	2.77E-08
78	8.77E-08	5.84E-08	2.62E-08

Table 6-10 Comparison between model predicted and observed metaflumizone concentrations in sediment

Time (days) after first application	Average observed metaflumizone conc. (g/kg bw)	Standard deviation
1	1.01E-05	2.13E-05
7	3.35E-05	5.93E-05
9	5.62E-05	8.22E-05
12	8.46E-05	1.12E-04
15	7.15E-05	1.20E-04
22	5.32E-05	1.21E-04
36	4.39E-05	1.15E-04
64	2.61E-05	1.04E-04
78	2.67E-05	9.83E-05

Table 6-11 Predicted and average observed metaflumizone concentrations in macrophyte

Time (days) after first application	Average observed metaflumizone conc. (g/kg bw)	Standard deviation	Predicted metaflumizone conc. (g/kg bw)
7	1.32E-03	2.14E-04	3.28E-03
12	2.59E-03	4.10E-04	5.72E-03
15	1.89E-03	2.82E-04	4.75E-03
22	1.09E-03	3.87E-04	2.31E-03
36	3.89E-04	1.09E-04	4.95E-04
64	1.19E-04	7.88E-05	7.10E-05
78	1.11E-04	4.22E-05	5.54E-05

Table 6-12 Predicted and average observed metaflumizone concentrations in crustacean

Time (days)	Observed metaflumizone conc. (g/kg bw)	Predicted metaflumizone conc. (g/kg bw)
7	1.51E-03	3.06E-03
12	1.35E-03	9.78E-03
15	1.92E-03	3.24E-03
22	1.28E-03	3.03E-04
36	5.52E-04	1.08E-04
64	1.79E-04	9.66E-05
78	3.32E-04	9.17E-05

Table 6-13 Predicted and average observed metaflumizone concentrations in zebra mussel

Time (days) after first application	Average observed metaflumizone conc. (g/kg bw)	Standard deviation	Predicted metaflumizone conc. (g/kg bw)
7	5.18E-03	9.43E-04	9.13E-03
12	1.13E-02	1.53E-03	2.21E-02
15	7.61E-03	9.95E-04	9.68E-03
22	5.81E-03	2.81E-03	8.89E-04
36	1.87E-03	4.27E-04	1.69E-04
64	6.53E-05	4.33E-05	1.49E-04

Table 6-14 Predicted and average observed metaflumizone concentrations in snail

Time (days) after first application	Average observed metaflumizone conc. (g/kg bw)	Standard deviation	Predicted metaflumizone conc. (g/kg bw)
7	9.73E-03	4.44E-03	9.18E-03
12	1.09E-02	5.32E-03	1.77E-02
15	2.20E-02	2.69E-02	1.10E-02
22	1.54E-02	N/A	2.76E-03

Table 6-15 Predicted and average observed metaflumizone concentrations in fish

Time (days) after first application	Average observed metaflumizone conc. (g/kg bw)	Standard deviation	Predicted metaflumizone conc. (g/kg bw)
7	6.86E-03	5.50E-03	1.74E-02
12	2.14E-02	4.45E-03	3.13E-02
15	1.98E-02	4.87E-03	2.12E-02
22	7.47E-03	4.55E-03	5.50E-03
36	7.05E-04	3.78E-04	4.15E-04
64	1.11E-04	1.27E-04	1.60E-04
78	6.49E-05	2.32E-05	1.51E-04

6.4 Calculated model parameters

Table 6-16 Methods for the calculation of model parameters in the environmental fate sub-model

Reaction Rate	Symbol	Equation
outflow (/day)	ko	=F/(1000Vw)
volatilization (/day)	kv	=(Saw*fDW*vE)/Vw
overall water-to-sediment transport (/day)	kws	=kws1+kws2
overall sediment-to-water transport (/day)	ksw	=ksw1+ksw2
solids settling (/day)	kws1	Saw*vs*(1-fDW)/Vw
water-to-sediment diffusion (/day)	kws2	=Sas*vD*fDW/Vw
solids resuspension (/day)	ksw1	=(ResFlux/Css)(1-fDS)/(1000Vs)
sediment-to-water diffusion (/day)	ksw2	=Sas*vD*fDS/Vs
burial (/day)	kB	=vB*Sas*(1-fDS)/dss*0.000001/Vs
degradation in water (/day)	kwr	=Ln(2)/hlw
degradation in sediment (/day)	ksr	=Ln(2)/hls

Calculated Parameters	Symbol	Equation
volatilization mass transfer coefficient (m/day)	ve	=1/(1/vEW+1/(Kaw*Vea))
partition coefficient of suspended particles in the water	Kpw	=0.35*Ocpw*Kow
partition coefficient of bottom sediment particles	Kps	=0.35*Ocss*Kow
air-water partition coefficient (unitless)	Kaw	H/(8.314*(273+Tw))
temperature dependence of Henry law constant (H)	ln H(Tw)	lnH(298)+20.18-(6013.6/Tw)
fraction of freely dissolved chemical in water (unitless)	fDW	1/(1+(Cpw*OCpw*Kow/dPW)
fraction of freely dissolved chemical in sediment (unitless)	fDS	1/(1+(Css*OCss*Kow/dss))
settling of sediment solids flux (kg/day)	SetFlux	= 1000*Cpw*kws1*Vw
burial flux of sediment solids (kg/day)	BurFlux	= 1000*Css*kB*Vs
temperature dependence of Henry law constant (H)	H(Tw)	=EXP(lnH(Tw))
sediment solids mass balance and resuspension flux (kg/day)	ResFlux	=SetFlux-BurFlux
water volume of lake (m^3)	Vw	=Saw*Dw
sediment volume (m^3)	Vs	=Sas*Ds
Octanol-water partition coefficient (unitless)	Kow	=10^ log Kow
organic carbon-water partition coefficient (L/Kg)	Koc	=10^ log Koc
Bioavailable solute fraction (unitless)	Φ	0.939001918
Concentration of particulate organic carbon (kg/L)	Xpoc	=Cpw*Ocpw
volume of sediment solids (kg)	Vss	=Css*(Vs*1000)
volume of sediment solids (L)	Vssl	=Vss*(1/dss)
volume of pore water in sediment (L)	Vws	=Vs*1000-Vssl

Table 6-17 Methods for the calculation of model parameters in the food web sub-model (Phytoplankton)

Definition	Units	Parameter	Equation
Gill uptake rate constant	L/kg.day	k1	$=(A+(B/Kow))^{-1}$
Dietary uptake rate constant	kg/kg.day	kd	= 0
Gill elimination rate constant	/day	k2	=k1/kpw
Fecal ejection rate constant	/day	ke	= 0
Growth dilution rate constant	/day	kg	= 0.1
Metabolic transformation rate constant	/day	km	= 0
total elimination rate constant	/day	ktotal	=k2+ke+kg+km
Phytoplankton-water partition coefficient	unitless	Kpw	=vlb*Kow+vnb*beta*Kow+vwb
Efficiency of chemical transfer via gill	%	Ew	$=(Aew+(Bew/Kow))^{-1}$
Dissolved oxygen concentration	mg O_2/L	Cox	=(-0.24*Tw+14.04)*S

Table 6-18 Calculations of model parameters in the food web sub-model (Zooplankton)

Definition	Units	Parameter	Equation
volume of lipid in organism	kg	Vl	=Wb*vlb
volume of NLOM in organism	kg	Vnlom	=Wb*vnb
volume of water in organism	kg	Vw	=Wb*vwb
Gill uptake rate constant	L/kg.day	k1	=Ew*Gv/Wb
Dietary uptake rate constant	kg/kg.day	kd	=Ed*Gd/Wb
Gill elimination rate constant	/day	k2	=k1/kbw
Fecal ejection rate constant	/day	ke	=Gf*Ed*Kgb/Wb
Growth dilution rate constant	/day	kg	$=lgr*Wb^{-0.2}$
Metabolic transformation rate constant	/day	km	= 0
total elimination rate constant	/day	ktotal	=k2+ke+kg+km
time to reach 95% of steady-state	day	t95	=3/ktotal
kd/ke (max theoretical BMF)	kg/kg	max BMF	=kd/ke
Biota-water partition coefficient	unitless	Kbw	=vlb*Kow+ vnb*beta*Kow+vwb
Gut-biota partition coefficient	unitless	Kgb	=(vlg*Kow+vng*αsoc*Kow+vwg)/(vlb*Kow+vnb*beta*Kow+vwb)
Gill ventilation rate	L/day	Gv	=1400*(Wb^0.65)/Cox
Feeding rate	kg/day	Gd	=0.022*(Wb^0.85)*EXP(0.06*Tw)
Fecal ejection rate	kg/day	Gf	=((1-el)*vld+(1-en)*vnd+(1-eww)*vwd)*Gd
Efficiency of chemical transfer via gill	%	Ew	$=(Aew+(Bew/Kow))^{-1}$
Efficiency of chemical transfer via intestinal tract	%	Ed	$=(Aed*Kow+Bed)^{-1}$
Lipid fraction in diet	kg/kg	vld	Sum(Fraction in diet (%) * lipid fraction in biota)
Lipid fraction in gut	kg/kg	vlg	=(1-el)*vld/((1-el)*vld+(1-en)*vnd+(1-eww)*vwd)
Nonlipid organic matter fraction in diet	kg/kg	vnd	Sum(Fraction in diet (%) * nonlipid organic matter fraction in biota)
Nonlipid organic matter fraction in gut	kg/kg	vng	=(1-en)*vnd/((1-el)*vld+(1-en)*vnd+(1-eww)*vwd)
Water fraction in diet	kg/kg	vwd	Sum(Fraction in diet (%) * water fraction in biota)
Water fraction in gut	kg/kg	vwg	=(1-ew)*vwd/((1-el)*vld+(1-en)*vnd+(1-eww)*vwd)
Dissolved oxygen concentration	mg O_2/L	Cox	=(-0.24*Tw+14.04)*S
Oxygen consumption	mg O_2/day	Vox	=980*Wb^0.65

Table 6-19 Calculations of model parameters in the food web sub-model (Benthos)

Definition	Units	Parameter	Equation
volume of lipid in organism	kg	Vl	=Wb*vlb
volume of NLOM in organism	kg	Vnlom	=Wb*vnb
volume of water in organism	kg	Vw	=Wb*vwb
Gill uptake rate constant	L/kg.day	k1	=Ew*Gv/Wb
Dietary uptake rate constant	kg/kg.day	kd	=Ed*Gd/Wb
Gill elimination rate constant	/day	k2	=k1/kbw
Fecal ejection rate constant	/day	ke	=Gf*Ed*Kgb/Wb
Growth dilution rate constant	/day	kg	$=lgr*Wb^{-0.2}$
Metabolic transformation rate constant	/day	km	= 0
total elimination rate constant	/day	ktotal	=k2+ke+kg+km
time to reach 95% of steady-state	day	t95	=3/ktotal
kd/ke (max theoretical BMF)	kg/kg	max BMF	=kd/ke
Biota-water partition coefficient	unitless	Kbw	=vlb*Kow+ vnb*beta*Kow+vwb
Gut-biota partition coefficient	unitless	Kgb	=(vlg*Kow+vng*αsoc*Kow+vwg)/(vlb*Kow+vnb*beta*Kow+vwb)
Gill ventilation rate	L/day	Gv	=1400*(Wb^0.65)/Cox
Feeding rate	kg/day	Gd	=0.022*(Wb^0.85)*EXP(0.06*Tw)
Fecal ejection rate	kg/day	Gf	=((1-el)*vld+(1-en)*vnd+(1-eww)*vwd)*Gd
Efficiency of chemical transfer via gill	%	Ew	$=(Aew+(Bew/Kow))^{-1}$
Efficiency of chemical transfer via intestinal tract	%	Ed	$=(Aed*Kow+Bed)^{-1}$
Lipid fraction in diet	kg/kg	vld	Sum(Fraction in diet (%) * lipid fraction in biota)
Lipid fraction in gut	kg/kg	vlg	=(1-el)*vld/((1-el)*vld+(1-en)*vnd+(1-eww)*vwd)
Nonlipid organic matter fraction in diet	kg/kg	vnd	Sum(Fraction in diet (%) * nonlipid organic matter fraction in biota)
Nonlipid organic matter fraction in gut	kg/kg	vng	=(1-en)*vnd/((1-el)*vld+(1-en)*vnd+(1-eww)*vwd)
Water fraction in diet	kg/kg	vwd	Sum(Fraction in diet (%) * water fraction in biota)
Water fraction in gut	kg/kg	vwg	=(1-ew)*vwd/((1-el)*vld+(1-en)*vnd+(1-eww)*vwd)
Dissolved oxygen concentration	mg O_2/L	Cox	=(-0.24*Tw+14.04)*S
Oxygen consumption	mg O_2/day	Vox	=980*Wb^0.65

Table 6-20 Calculations of model parameters in the food web sub-model (Fish)

Definition	Units	Parameter	Equation
volume of lipid in organism	kg	Vl	=Wb*vlb
volume of NLOM in organism	kg	Vnlom	=Wb*vnb
volume of water in organism	kg	Vw	=Wb*vwb
Gill uptake rate constant	L/kg.day	k1	=Ew*Gv/Wb
Dietary uptake rate constant	kg/kg.day	kd	=Ed*Gd/Wb
Gill elimination rate constant	/day	k2	=k1/kbw
Fecal ejection rate constant	/day	ke	=Gf*Ed*Kgb/Wb
Growth dilution rate constant	/day	kg	$=Fgr*Wb^{-0.2}$
Metabolic transformation rate constant	/day	km	= 0
total elimination rate constant	/day	ktotal	=k2+ke+kg+km
time to reach 95% of steady-state	day	t95	=3/ktotal
kd/ke (max theoretical BMF)	kg/kg	max BMF	=kd/ke
Biota-water partition coefficient	unitless	Kbw	=vlb*Kow+ vnb*beta*Kow+vwb
Gut-biota partition coefficient	unitless	Kgb	=(vlg*Kow+vng*beta*Kow+vwg)/(vlb*Kow+vnb*beta*Kow+vwb)
Gill ventilation rate	L/day	Gv	=1400*(Wb^0.65)/Cox
Feeding rate	kg/day	Gd	=0.022*(Wb^0.85)*EXP(0.06*Tw)
Fecal ejection rate	kg/day	Gf	=((1-el)*vld+(1-en)*vnd+(1-eww)*vwd)*Gd
Efficiency of chemical transfer via gill	%	Ew	$=(Aew+(Bew/Kow))^{-1}$
Efficiency of chemical transfer via intestinal tract	%	Ed	$=(Aed*Kow+Bed)^{-1}$
Lipid fraction in diet	kg/kg	vld	Sum(Fraction in diet (%) * lipid fraction in biota)
Lipid fraction in gut	kg/kg	vlg	=(1-el)*vld/((1-el)*vld+(1-en)*vnd+(1-eww)*vwd)
Nonlipid organic matter fraction in diet	kg/kg	vnd	Sum(Fraction in diet (%) * nonlipid organic matter fraction in biota)
Nonlipid organic matter fraction in gut	kg/kg	vng	=(1-en)*vnd/((1-el)*vld+(1-en)*vnd+(1-eww)*vwd)
Water fraction in diet	kg/kg	vwd	Sum(Fraction in diet (%) * water fraction in biota)
Water fraction in gut	kg/kg	vwg	=(1-ew)*vwd/((1-el)*vld+(1-en)*vnd+(1-eww)*vwd)
Dissolved oxygen concentration	mg O_2/L	Cox	=(-0.24*Tw+14.04)*S
Oxygen consumption	mg O_2/day	Vox	=980*Wb^0.65

6.5 CD-ROM data

Please find attached a CD containing an electronic copy of the food web bioaccumulation model for organic pesticide applications described in this document. Microsoft Excel software is required to run the model.

The CD-ROM attached forms a part of this work. Data file can be opened with Microsoft Excel or other spreadsheet program.

Data Files:

- Model performance analysis for the environmental fate submodel using BAS490 02F microcosm study 10.0 MB
- Model performance analysis for the environmental fate submodel using BAS500 00F microcosm study 8.3 MB
- Model performance analysis using Bluegill BCF study for metaflumizone 7.7 MB
- Model performance analysis for the food web submodel using metaflumizone microcosm study 21.3 MB
- Model performance analysis for the combined model using metaflumizone microcosm study 14.4 MB
- Comparison between model predictions between steady-state based bioaccumulation model and the time-dependent food web bioaccumulation model 65.4 MB
- Metaflumizone toxicity study 110.3 MB
- Time dependent food web bioaccumulation model for organic pesticides in aquatic ecosystems 6.8 MB

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