

Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, California 95812

**Report 293 – Part I:
Developing a California-Based Receiving Waterbody Model for Pesticide Product
Registration Evaluation: Review of Model Theory**

Yina Xie, Ph.D.

August 23, 2016

Executive summary

This is the first part of a two-part report for developing a California-based receiving waterbody model for pesticide product registration evaluation. A review of the existing regulatory receiving waterbody models establishes scientific basis for the development of a model appropriate for regulatory use by the California Department of Pesticide Regulation (DPR). Three regulatory receiving waterbody models are reviewed on their model theory. The models are 1) the Variable Volume Water Model (VVWM) developed by the U.S. Environmental Protection Agency Office of Pesticide Programs (USEPA/OPP), 2) the AGRO-2014 model developed by Stone Environmental, Inc., and 3) the Toxic Substances in Surface Waters (TOXSWA) model used by the European Forum for the Coordination of Pesticide Fate Models and Their Use (FOCUS) workgroup (FOCUS-TOXSWA). The models estimate pesticide concentrations in receiving waterbodies and predict pesticide exposure for aquatic risk assessment.

In these models, a receiving waterbody is conceptually represented by a compartmental system that consists of the water compartment and the sediment compartment. To describe pesticide behavior in the system, various processes are considered, including mass transfer between water and sediment (e.g., diffusion and exchange of sediment-sorbed pesticides via sediment settling/resuspension), sorption and desorption, degradation, volatilization, and sediment and sorbed pesticide burial. System inflow/outflow and environmental processes (e.g., precipitation and evaporation) are also included as influencing factors on pesticide transport and fate in the system.

By comparing the model theory of the three models, features and limitations of each model are summarized as follows:

- 1) VVWM is highlighted with three unique features that are promising to pesticide registration evaluation. First, VVWM is the only model making use of the data that are required by the USEPA per pesticide registration and readily submitted to and reviewed by DPR. The input data required by VVWM to simulate pesticide degradation, sorption, and volatilization completely match USEPA's data requirements. AGRO-2014 and FOCUS-TOXSWA, however, requires additional input data that are not readily available.

Second, VVWM considers the most complete list of pesticide fate and transport processes in a receiving waterbody. For example, it considers all individual pesticide degradation mechanisms (i.e., photolysis, hydrolysis, and biological metabolism), while AGRO-2014 and FOCUS-TOXSWA only model them as a bulk process. Moreover, VVWM includes a variety of all possible sorbing media, whereas AGRO-2014 and FOCUS-TOXSWA consider fewer media. Compared to the other models, therefore, VVWM better represents two key processes of particle-bound pesticides – pesticide sorption/desorption and pesticide removal by the outflow of sorbing media. Third, VVWM uses a versatile approach to simulate the mass transfer between water and sediment. It defines an overall mass transfer coefficient to include all means of pesticide exchange between water and sediment. AGRO-2014 and FOCUS-TOXSWA, in contrast, explicitly model the individual exchange mechanisms (e.g., diffusion and sediment settling/resuspension in AGRO-2014 and diffusion only in FOCUS-TOXSWA). They require model users having adequate knowledge to determine the transfer coefficients and to parameterize the model.

- 2) The unique feature of AGRO-2014 is the modeling capability that allows the concentration of suspended solids (SS) to elevate from a baseline/minimum level when excess sediments enter the system during runoff events. It defines a term – the 90% sediment clearance time – to describe the settling of the excess SS. The transfer coefficients for sediment burial, settling, and resuspension are also adjusted accordingly. The SS concentration comes back to the baseline level when the excess SS has settled. This feature mainly affects the simulation of hydrophobic organic pesticides as the partitioning of these chemicals is significantly affected by the SS concentration. However, it also requires model users to have adequate knowledge and field measurements to correctly parameterize the model. Alternatively, VVWM and FOCUS-TOXSWA simply assume an invariant concentration of SS during the simulation, but users can manually change the concentration value to reflect different field conditions.
- 3) The unique feature of FOCUS-TOXSWA is the capability of predicting a concentration gradient over space, i.e., in the direction of flow and in the direction of sediment depth. By considering the spatial variation in addition to the temporal variation, the results from FOCUS-TOXSWA have higher resolution than that from VVWM and AGRO-2014. The most important limitation of FOCUS-TOXSWA is that it distinctly excludes sediment settling and resuspension from the simulation of mass transfer between water and sediment. It also has no consideration of sediment burial, which is an important fate of pesticide in the sediment compartment.
- 4) Both VVWM and FOCUS-TOXSWA have two important modeling capabilities that are absent from AGRO-2014. First, the aqueous volume of the water compartment can vary as hydrologic conditions (e.g., precipitation, evaporation, runoff, and baseflow etc.) change. Second, they also have the capability to simulate the formation and transformation of degradates in water and sediment.

In addition, four standard receiving waterbody scenarios are pre-defined by the models for regulatory aquatic risk assessment. They are 1) the OPP standard farm pond, 2) the FOCUS

pond, 3) the FOCUS ditch, and 4) the FOCUS stream. The four scenarios are reviewed to inform the development of the California-relevant receiving waterbody scenarios, which will be conducted in the next stage of the study.

1. Introduction

A receiving waterbody model is a crucial component in evaluating the environmental risk of pesticides. The model accounts for different physical, chemical, and microbial processes associated with the transport and fate of pesticides in the receiving waterbody, and estimates environmental concentrations for pesticide exposure characterizations (Holvoet et al., 2007). An important category of the receiving waterbody model is the regulatory model, which is developed and configured to simulate the standard receiving waterbodies and provide conservative estimations of pesticide exposure. Currently, there are no systematic review and development of receiving waterbody models and associated modeling scenarios for pesticide assessments in California. Previous work conducted in DPR include a general review of the regulatory surface water models (Guo, 2002). Since the study was conducted prior to 2002, new models developed since then were not included. Moreover, the study only focuses on the general introduction of different models, and lacks further information of model theory and model development. More recently, DPR proposed a new study – Study 293, to develop a California-based receiving waterbody model (Xie, 2014). The study includes two parts. The first part is to review the existing regulatory receiving waterbody models and select the appropriate model(s) for regulatory use by DPR. In the second part of the study, the selected model(s) will be configured to represent receiving waterbodies that are consistent with California’s field conditions for aquatic risk assessments of pesticides. This report presents the results of the first part of the study, which is a review of model theory.

Currently, there are three receiving waterbody models specifically configured for regulatory pesticide risk assessments. They are:

- 1) The Variable Volume Water Model (VVWM) developed by the US Environmental Protection Agency Office of Pesticide Programs (USEPA/OPP) (Young, 2014). It is released as the successor to the Exposure Analysis Modeling System (EXAMS) model (Burns, 2000) and functions much like EXAMS but with greater efficiency and flexibility. It is coded in the FORTRAN programming language. Similar to the EXAMS model, VVWM is configured to be a regulatory model and usually used in conjunction with the Pesticide Root Zone Model (PRZM), which is a one-dimensional conceptual model that predicts pesticide loads from the treated field (Young and Fry, 2014). Linking the output of PRZM to VVWM produces a graphical user interface (GUI) – the Surface Water Concentration Calculator (SWCC) (Fry et al., 2014) or the later version – the Pesticide Water Calculator (PWC), which is the primary tool recommended by the USEPA for pesticide product registration evaluation and risk assessment in the US. The VVWM model (released on July 1, 2014) is reviewed here.
- 2) The AGRO-2014 model developed by Stone Environmental Inc. (Padilla et al., 2015). It was developed based on the modification of the Canadian Environmental Modelling Centre (CEMC)’s AGRO modeling system (Arnot et al., 2005; CEMC, 2007). The

AGRO model is a Microsoft Excel worksheet-based application that combines the Quantitative Water Air Sediment Interaction (QWASI) Fugacity model (Mackay, 2001; Mackay et al., 1983a; Mackay et al., 1983b) with the Food Web Model (Arnot and Gobas, 2004). The QWASI model describes the core processes in the system and has been used to assess chemical dynamics in rivers, lakes and reservoirs. AGRO was evaluated by the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Scientific Advisory Panel (SAP) in the 2008 meeting as part of their response to questions from USEPA related to risk assessment for pesticides with persistent, bioaccumulative and toxic characteristics (SAP, 2008). It was then refined into AGRO-2014 and specifically parameterized for predicting exposure of hydrophobic organic chemicals, such as pyrethroids. The PA5 shell (available at: <http://www.stone-nv.com/agchem/agres.php>) that combines PRZM with AGRO-2014 is provided as a GUI. AGRO-2014 version 1.2 (released on May 29, 2015) is reviewed here.

- 3) The Toxic Substances in Surface Waters (TOXSWA) model developed by Alterra, in cooperation with W!SL, the Wageningen Software Labs, in Wageningen, Netherlands (Adriaanse, 1996). It is a FORTRAN-coded application and has been used to simulate pesticide transport and fate in various receiving waterbodies. As recommended by the European Forum for the Coordination of Pesticide Fate Models and their Use (FOCUS) workgroup, TOXSWA is configured to a regulatory model and used in conjunction with PRZM as well as other field scale models (e.g., the spray drift calculator and the MACRO drainage model) for pesticide product registration evaluation in the European Union (FOCUS, 2015; Linders et al., 2003). The software interface is called the Surface Water Scenarios Help (SWASH) (Roller et al., 2003; Van den Berg et al., 2003; Van den Berg et al., 2008). TOXSWA version 4.4.3 (the current version linked with FOCUS, i.e., FOCUS-TOXSWA) (Adriaanse and Beltman, 2009) is reviewed here.

Although the three models describe pesticide behavior in receiving waterbodies, they differ from each other in the way the key processes are mathematically conceptualized, which further leads to difference in model output. It is critical to understand the features and limitations of each model, in order to select the most appropriate model(s) for regulatory use by DPR. Although VVWM is recommended by OPP as the standard procedure for pesticide risk assessment in the US, challenges on the limitations of VVWM have been raised by pesticide product registrants. For example, the Pyrethroid Working Group proposed AGRO and AGRO-2014 and asserted that these models outperformed VVWM on the simulation of hydrophobic organic pesticides (Padilla et al., 2015; SAP, 2008). Our thorough review of the existing regulatory receiving waterbody models will help provide the scientific basis to support and justify DPR's model selection and development.

When conducting aquatic risk assessments in support of a regulatory purpose, standard receiving waterbody scenarios are defined to represent common field conditions. To date, four standard receiving waterbody scenarios have been developed. They are 1) the OPP standard farm pond (Burns, 2000; Fry et al., 2014; Young, 2014), 2) the FOCUS pond, 3) the FOCUS ditch, and 4) the FOCUS stream (FOCUS, 2015; Linders et al., 2003). However, none of these scenarios are configured based on conditions commonly found in California. Moreover, there is no distinction between the urban setting (e.g., receiving waterbody that receives urban runoff, storm drains, and

wastewater treatment plant discharges) and the agricultural setting. Existing scenarios tend to be more agriculturally focused. A review of the existing standard receiving waterbody scenarios is included in this report. Parameters required defining the scenarios as well as the corresponding values are identified. The review informs the next stage of the study, which is to develop the California-relevant receiving waterbody scenarios.

2. Conceptual model

A typical receiving waterbody consists of two compartments – the water compartment and the sediment compartment. The water compartment contains several sub-compartments – pure water, suspended solids (SS), dissolved organic carbon (DOC) and biota. The sediment compartment contains pore water, benthic particles, benthic DOC, and benthic biota. Pore water, or sediment interstitial water, is defined as the water occupying the spaces between sediment particles (USEPA, 2001). It takes about 50% of the volume of a depositional (silt-clay) sediment and is in contact with sediment surfaces for relatively long periods of time and can be contaminated by chemical partitioning from the surrounding sediments (USEPA, 2001).

Key processes associated with the pesticide behavior in the water-sediment system are illustrated in the diagram of the conceptual model (Figure 1). These processes include pesticide sorption and desorption, mass transfer between water and sediment (e.g., diffusion and exchange of sediment-sorbed pesticide via sediment settling and resuspension), degradation, volatilization, and sediment/sorbed-pesticide burial. System inflow and outflow (including pesticides, water, SS and other sorbing media) as well as environmental processes (e.g., precipitation and evaporation) are included as they are important factors affecting the transport and fate of pesticides in the system.

In addition to the aforementioned processes, FOCUS-TOXSWA also considers pesticides transport with water flows. In FOCUS-TOXSWA, pesticides are transported in two directions – in the water compartment, they are transported horizontally in the direction of water flow via advection and dispersion while in the sediment compartment they are transported vertically downwards in the pore water via advection, dispersion and diffusion. FOCUS-TOXSWA uses a coordinate system, as shown in Figure 2 to quantify the transport process and presents a concentration gradient over the x and the z direction. For each computational segment (i.e., each Δx in Figure 2), the conceptual model for pesticide processes in **Error! Reference source not found.** still applies to FOCUS-TOXSWA. In the later description of this report, therefore, “water compartment” and “sediment compartment” for FOCUS-TOXSWA actually refer to the compartments in each modeling segment. VVWM and AGRO-2014 do not account for pesticide concentration gradients within the system. They assume that pesticides are uniformly distributed within the pure water and the pore water.

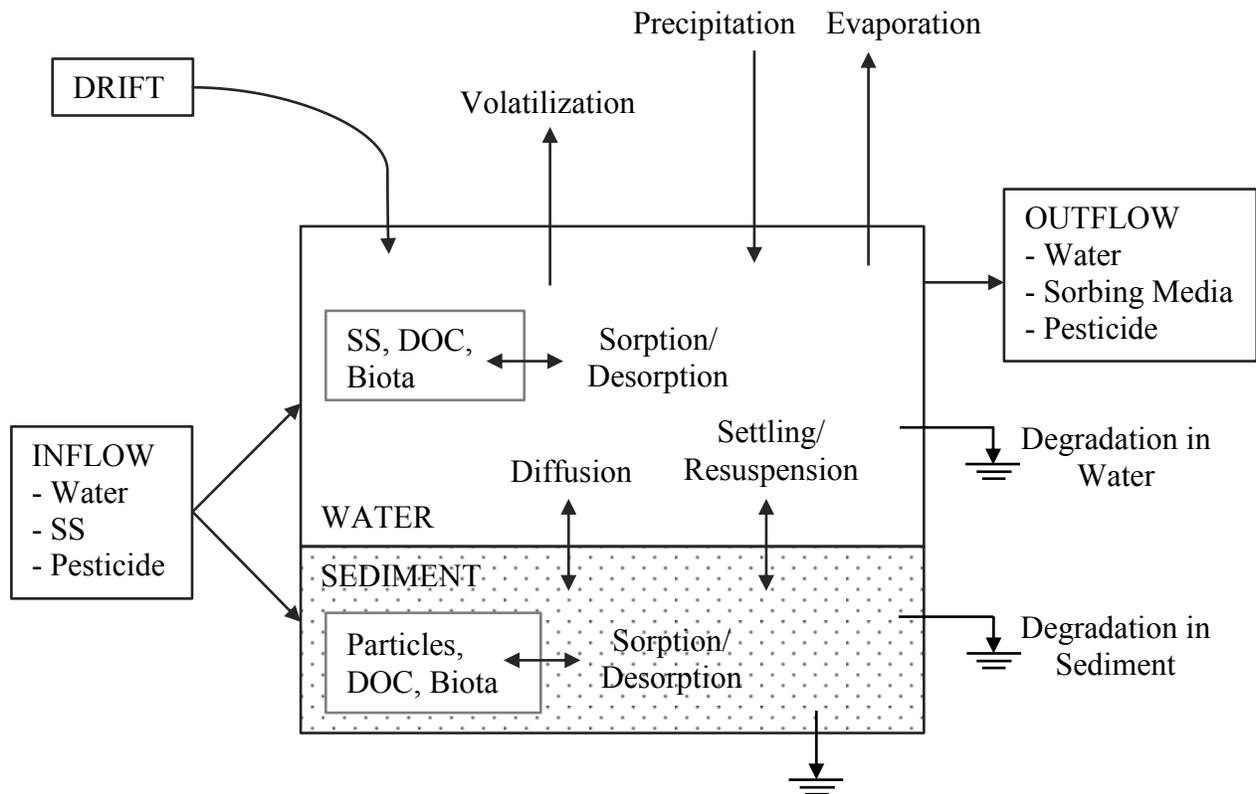


Figure 1: Schematic diagram of the conceptual model for pesticide fate and transport in a water body

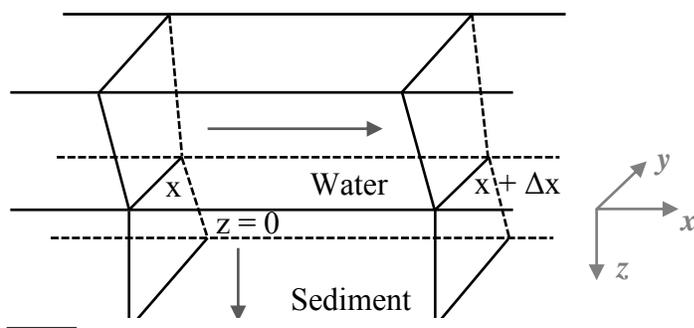


Figure 2: Structure of the FOCUS-TOXSWA waterbody system, adapted from Adriaanse (1996)

To simulate processes in the system, the three models commonly assumed that instantaneous equilibrium of pesticide is established within the water compartment and the sediment compartment (but not between the compartments), i.e., all material in each compartment is at thermodynamic equilibrium. This assumption is usually justified since chemical partitioning

within a compartment is a relatively rapid process compared to mass transfer between compartments (Mackay et al., 1983a). For FOCUS-TOXSWA, since it allows a concentration gradient in the direction of flow, it is assumed that the water layer is ideally mixed in any wetted surface perpendicular to the direction of flow.

Mass balance is the fundamental principle of the receiving waterbody modeling. Similar to each other, the three models impose mass balance on pesticide fluxes in the water compartment as well as in the sediment compartment. The mechanisms that are associated with the pesticide input and output are depicted in Figure 1 and Table 1. The rates of pesticide transfer via these mechanisms are discussed in Section 3. Equating the input and output gives the mass conservation equation for the water compartment and the sediment compartment, respectively. Solving the two equations gives pesticide concentrations in each (sub-) compartment. For the unsteady state conditions (i.e., pesticide concentrations are time-dependent), VVWM and AGRO-2014 retain an analytical solution to the group of differential equations, whereas FOCUS-TOXSWA retains a numerical solution.

Table 1 presents a schematic comparison of the key processes involved in the three models. VVWM considers all the processes that are necessary to describe pesticide transport and fate in the system, whereas AGRO-2014 and FOCUS-TOXSWA only simulate a part of them. For those processes that are commonly considered by the models, the way in which they are conceptually and mathematically formulated could be different. The particulars of the model theory comparison and contrast are presented in Section 3.

Table 2 elaborates on the key input parameters required by the three models to simulate the processes depicted above. The availability of the required input data is an important aspect for model selection. A model would be practical and favorable if the required input data are readily available to DPR. The required input parameters basically fall into two categories. One is variables related to the physiochemical properties and environmental fate of a pesticide. The USEPA has data requirements for new AI registration, which is defined in 40 Code of Federal Regulations (CFR), Part 158. DPR's data requirements are substantially similar to USEPA's and can be found in the DPR Registration Branch Desk Manual (CDPR, 2013). It is critical to ensure that the input data required by a model are also required by USEPA and readily submitted to and reviewed by DPR. Note that the data availability depicted in Table 2 is based on USEPA's data requirements for the registration of new AIs for agricultural uses. Among the three models, VVWM is the only model that precisely uses the USEPA-required data.

Table 1: Key processes considered in the three models

Process	VVWM	AGRO-2014	FOCUS-TOXSWA
<i>System Input Process</i> ^a			
Water inflow	X	X	X
SS inflow	X	X	X
Dissolved and sorbed pesticide inflow to water compartment	X	X	X
Direct delivery of sorbed pesticide to sediment compartment	X		
Pesticide drift	X	X	X
Precipitation	X	X ^b	X
<i>Water-Sediment Mass Transfer Process</i>			
Water-sediment diffusion	X ^c	X	X
Sediment settling	X	X	
Sediment resuspension	X	X	
<i>Sorption and Desorption Process (Sorbing Media)</i>			
SS in water compartment	X	X	X
DOC in water compartment	X		
Biota in water compartment	X		X
Benthic particles	X	X	X
Benthic DOC	X		
Benthic biota	X		
<i>Degradation Process</i>			
Photolysis	X	X ^d	X ^d
Aqueous hydrolysis	X		
Aqueous metabolism	X		
Benthic hydrolysis	X		
Benthic metabolism	X		
Formation of degradates in water and sediment	X		X
Temperature-adjusted degradation rate constant	X ^e	X	X
<i>System Output Process</i>			
Water outflow	X	X	X
Sorbing media outflow	X	X	X
Dissolved and sorbed pesticide outflow	X	X	X
Pesticide volatilization	X	X	X
Evaporation	X		X
Sediment/sorbed pesticide burial	X	X	
<i>Capability for varying water volume and flowthrough</i>			
	X		X

Notes:

^a: When used for pesticide registration evaluation, the models are commonly linked to the PRZM model. Therefore, system input of water, SS and pesticides is read from the PRZM output.

^b: In VVWM and FOCUS-TOXSWA, if variable water volume is enabled, precipitation affects the aqueous volume of the water compartment and thus affecting the pesticide concentration. In AGRO-2014, precipitation is considered only for rain dissolution of pesticides. It, however, doesn't affect the water volume.

^c: VVWM models the mass transfer as a bulk process that includes all means of chemical exchange between water and sediment. It is governed by an overall mass transfer coefficient. Please refer to Section 3.2 for details.

^d: AGRO-2014 and FOCUS-TOXSWA simulate the degradation mechanisms as a bulk process and use an overall degradation rate coefficient to cover the combined effects of all means of degradation in a compartment.

^e: In VVWM, temperature-adjustment is performed for the metabolism rate constant only.

A second category of the input parameter is the variables associated with the mechanistic processes being modeled, mainly those required in the simulation of mass transfer. The value of these parameters is usually suggested by the model developers. Model users are also allowed to specify a different value if it is available. Compared to the other two models, VVWM uses a relatively simplified way to represent the mass transfer process. It uses a generic mass transfer coefficient to include all means of pesticide exchange between water and sediment. The term is suggested to be on the order of 10^{-8} m s^{-1} by model developers based on a variety of existing sources. AGRO-2014 requires several variables to simulate the mass transfer and sedimentation process. The value of the variables is suggested by model developers, but should be verified by model users. It requires model users having adequate knowledge and field information to parameterize the model. FOCUS-TOXSWA only simulates the diffusion process and thus requires users to specify the value of the diffusion coefficient. It has the shortcoming that the process of sediment settling and resuspension is not modeled.

Table 2: Key input parameters required by the three models and data availability

Input Parameter (required in different processes)	Availability ^a	VVWM	AGRO-2014	FOCUS-TOXSWA
<i>Volatilization</i>				
Molecular weight	R by USEPA	X	X	X
Vapor pressure	R by USEPA	X	X	X ^b
Enthalpy of vaporization	NA			X
Water solubility	R by USEPA	X	X	X ^b
Enthalpy of dissolution	NA			X
Volatilization coefficients (liquid- and gas-phase resistance)	NA		X	
Henry's Law constant	R by USEPA		X	
<i>Sorption and desorption</i>				
<i>K_{om}</i>	NA			X
<i>K_{oc}</i> or <i>K_d</i>	R by USEPA	X	X	X
<i>K_{ow}</i>	NA		X	
Freundlich exponent	NA			X
Reference concentration in liquid phase	NA			X
<i>Degradation</i>				
Hydrolysis HL	R by USEPA	X		
Aqueous photolysis HL and reference latitude	R by USEPA	X		
Water metabolism HL	R by USEPA	X ^c		
Sediment metabolism HL	R by USEPA	X ^c		
Water overall degradation HL ^d	NA		X	X
Sediment overall degradation HL ^d	NA		X	X
Water and sediment Q10 (temperature scaling factor)	S by developers (default value = 2)	X	X	
Molar activation energy in water and in sediment	NA			X
<i>Formation of Degradates^e</i>				

Molar conversion factors	NA	X		X
Physiochemical properties and environmental fate of degradates	NA	X		X
<i>Mass Transfer</i>	S by developers (with default values showing below)			
Water-sediment overall mass transfer coefficient	On the order of 10^{-8} m s ⁻¹	X		
Water-sediment diffusion velocity	Varies ^f		X	
Initial sediment resuspension rate	1.16×10^{-8} kg m ⁻² s ⁻¹		X	
Initial sediment settling rate	2.32×10^{-8} kg m ⁻² s ⁻¹		X	
PRBEN ^g	50%	X		
90% sediment clearance time	3.4 days ^h		X	
Resuspension percentage	50%		X	
Reference diffusion coefficient in water	4.98×10^{-10} m s ⁻¹			X

Notes:

^a: Keys for data availability: R by USEPA = the data is required by the USEPA per pesticide registration and reviewed by DPR, and S by developers = the value of the parameter is suggested by model developers and the default value is also provided.

^b: FOCUS-TOXSWA also requires the reference temperatures at which the vapor pressure and solubility are measured.

^c: VVWM also requires the reference temperatures at which the half-lives are measured. The reference temperatures are available in the required data.

^d: FOCUS-TOXSWA also requires the reference temperature at which the half-lives are measured. AGRO-2014 presumes that the reference temperature is 25 °C.

^e: The data required for the simulation of formation and transformation of degradates is not required by USEPA. But DPR is currently working on a degradate module for pesticide registration evaluation. Further information of data requirements for degradate will be available.

^f: The suggested value varies depending on the type of waterbody being modeled. For example, the default value is suggested to be 1.39×10^{-5} m s⁻¹ and 1.11×10^{-7} m s⁻¹ for OPP farm pond and index reservoir, respectively.

^g: The term PRBEN in VVWM describes the percentage of sediment-sorbed pesticides in the inflow that is directly delivered to the sediment compartment. By default, it is suggested to be 50%, but the value can be changed by the model users based on field conditions and chemical properties. According to personal communication with model developer, Dirk Young, the OPP modeling team is working on modifying the setup of PRBEN. It is likely to be removed from the future version of the model.

^h: The default value of the 90% sediment clearance time is suggested to be 3.4 days by AGRO-2014 for the simulation of hydrophobic organic pesticides. It is suggested to be 7 days by AGRO for general use. The value of 3.4 days is determined based on the calibration by using pyrethroid mesocosm data from three different studies (Padilla et al., 2015).

3. Key processes

Generally a receiving waterbody model is composed of seven modules that simulate processes of: 1) pesticide input and loss, 2) mass transfer between water and sediment, 3) sorption and desorption, 4) pesticide degradation and volatilization, 5) formation and transformation of degradates in water and sediment, 6) variation of water volume, and 7) variation of SS concentration.

3.1 Pesticide input and loss

Pesticides are delivered to the receiving waterbody via overland runoff or spray drift. The runoff inflow consists of water and pesticides in the dissolved phase, and SS and pesticides in the

sorbed phase. The three models differ in the initial distribution of the inflow substances between the water compartment and the sediment compartment. In AGRO-2014 and FOCUS-TOXSWA, all substances in the runoff inflow are delivered to the water compartment. In VVWM, pesticides in the dissolved phase are delivered to the water compartment while the sorbed species are partitioned into two parts – 50% is delivered to the water compartment whereas the remaining 50% is directly delivered to the sediment compartment. This process is governed by the parameter PRBEN with a default value of 50%, and the value of PRBEN can be adjusted by users. In addition, pesticides may also be delivered to the waterbody via spray drift. All the three models assume that pesticides in spray drift are solely delivered to the water compartment.

Pesticides can be removed from the system through outflow, sediment burial, volatilization and degradation. The discussion on volatilization and degradation is presented in Section 3.4. Here we only focus on outflow and sediment burial.

Pesticides are removed by the outflow via two mechanisms – the loss of dissolved pesticides with outflow of pure water and the loss of sorbed pesticides with outflow of SS and other sorbing media. The former is determined by the volumetric water outflow rate and the concentration of dissolved pesticide. The latter is a function of the water outflow rate, the concentration of sorbing media in the water compartment, and the content of pesticide sorbed to the sorbing media. The three models differ in the way in which the water outflow rate is determined. In VVWM, the aqueous volume of the water compartment is updated daily. It is computed as a function of the water volume in the previous day and the daily runoff, precipitation, evaporation and seepage in the simulation day. The rate of water outflow (or washout) is calculated only if the flowthrough option is selected and the newly calculated water volume exceeds the pre-defined constant volume or maximum volume. In FOCUS-TOXSWA, a minimum water depth is maintained by a weir installed at the outflow end of the waterbodies. Outflow occurs across the weir. Similar to VVWM, in FOCUS-TOXSWA, the aqueous volume of the water compartment is updated every simulation time step and the change in water volume in the simulation time step (can achieve an hourly resolution) is computed as a function of the inflow from upstream, runoff from the adjacent contributing area, precipitation, evaporation, seepage, and outflow (if applicable). Unlike VVWM and FOCUS-TOXSWA, in AGRO-2014, the outflow rate is simply set to be the same as the inflow rate, which can either be a constant or a dynamic variable. The way in which the outflow rate is determined substantially affects the computation of the water volume. More details are provided in Section 3.6.

Another major difference among the models lies in the way in which the concentration of sorbing media in water (note that it is the same as that in outflow) is determined. In AGRO-2014, the concentration of SS is defined as a dynamic variable that maintains a baseline/minimum level but will increase when excess sediments enter the system. The settling of the excess SS, as well as the inflow and outflow of SS and sediment settling/resuspension, affect the mass of SS. The concentration of SS is computed as the sum of the concentration of the excess SS and the baseline concentration. It returns back to the baseline level when the excess SS have settled. In VVWM and FOCUS-TOXSWA, the concentration of sorbing media is assumed to be invariant over the simulation, i.e., the concentration of sorbing media in outflow is a constant. More details of the difference are described in Section 3.7.

Pesticides sorbed to the benthic particles can be removed via sediment burial. Both VVWM and AGRO-2014 include this process as one of the fates of pesticide in the sediment compartment. The sediment burial component, however, is not accounted for in FOCUS-TOXSWA.

3.2 Mass transfer between water and sediment

Pesticide mass transfer between the water compartment and the sediment compartment is one of the fundamental processes in the system. It governs pesticide partitioning between the two compartments. The main mechanisms associated with mass transfer include the diffusive pesticide exchange between pure water and pore water, and the exchange of sediment-sorbed pesticides via sediment settling and resuspension.

In general, there are two approaches to model the water-sediment mass transfer. One approach is to explicitly model each exchange mechanism, i.e., define the mass transfer coefficient for an individual mechanism and compute the mass flux accordingly. This approach is employed by the AGRO-2014 and the FOCUS-TOXSWA model. One difference between the two models is that AGRO-2014 mimics both the diffusion and the sediment settling/resuspension processes whereas FOCUS-TOXSWA assumes the sediment settling/resuspension process is negligible and only considers diffusion. However, the documentation of FOCUS-TOXSWA also indicates that this assumption is only acceptable if the sediment settling/resuspension flux is indeed negligibly small, which could be the case, for example, for sheltered and very slowly flowing ditches (Adriaanse, 1997). Otherwise, this assumption would be problematic due to the disregard for an essential process. The other approach is to model the mass transfer as a bulk process that includes all means of chemical exchange between water and sediment. This approach is adopted by the VVWM model. The model assumes that diffusion and sediment settling/resuspension occur at the velocity on the same order of magnitude and they are generically regulated by an overall mass transfer coefficient. The particular algorithm employed by the three models for computing mass transfer between water and sediment is demonstrated below. Symbols of key variables and subscripts are depicted in Table 3.

Table 3: Key variables and subscripts for pesticide partitioning between water and sediment

Symbol	Unit	Description
Variables		
f	Pa	Fugacity of a substance in a (sub-) compartment
Z	$\text{kg m}^{-3} \text{Pa}^{-1}$	Fugacity capacity of a substance in a (sub-) compartment
C	kg L^{-1}	Aqueous concentration of pesticide, C_{ww} and C_{dw}
	kg kg^{-1}	Sorbed concentration of pesticide, C_{wp} and C_{dp}
M	kg	Pesticide mass in a (sub-) compartment
m	kg	Mass of a (sub-) compartment
A	m^2	Area of interfacial surface between water and sediment
V	L	Total volume of a (sub-) compartment
v	dimensionless	Volume fraction of a sub-compartment in a compartment
$\rho_{particle}$	kg L^{-1} [particle]	Density of particle grains
θ	dimensionless	Porosity of bottom sediment ($= v_{dw}$)

ρ_b	kg L ⁻¹	Bulk density of bottom sediment $\rho_b = v_{dp}\rho_{particle} = (1 - v_{dw})\rho_{particle} = (1 - \theta)\rho_{particle}$
K_d	L kg ⁻¹	Sorption coefficient (the ratio of pesticide in solution (nmole/ml) to pesticide sorbed to soil (nmole/g))
Subscripts		
w		Water compartment
ww		Pure water in the water compartment
wp		SS in the water compartment
d		Sediment compartment
dw		Pore water in the sediment compartment
dp		Sediment particles in the sediment compartment

Since it is assumed that the water compartment and the sediment compartment are individually well-mixed, all sub-compartments within each compartment are at thermodynamic equilibrium, i.e., they have the same fugacity:

$$f_w = \frac{C_w}{Z_w} = \frac{C_{ww}}{Z_{ww}} = \frac{C_{wp}}{Z_{wp}} = \frac{M_w}{Z_w V_w} = \frac{M_{ww}}{Z_{ww} V_{ww}} = \frac{M_{wp}}{Z_{wp} V_{wp}} \quad (1)$$

$$f_d = \frac{C_d}{Z_d} = \frac{C_{dw}}{Z_{dw}} = \frac{C_{dp}}{Z_{dp}} = \frac{M_d}{Z_d V_d} = \frac{M_{dw}}{Z_{dw} V_{dw}} = \frac{M_{dp}}{Z_{dp} V_{dp}} \quad (2)$$

where f_w and f_d (Pa) is the fugacity of the water compartment and the sediment compartment, respectively, C_i (kg L⁻¹ for the aqueous phase and kg kg⁻¹ for the sorbed phase) is the pesticide concentration in (sub-) compartment i , M_i (kg) is the pesticide mass in (sub-) compartment i , Z_i (kg m⁻³ Pa⁻¹) is the fugacity capacity of (sub-) compartment i , V_i (L) is the volume of (sub-) compartment i . The concept of fugacity (f), is defined under the laws of thermodynamics to describe equilibrium of a system in which chemical migrates from phase to phase. Fugacity is linearly or nearly linearly related to the concentration of chemical in one phase. The proportional constant, termed as fugacity capacity (Z), is defined to relate the fugacity to the concentration, i.e., $f_i = Z_i C_i$. Fugacity capacity of water and particle are measurable quantities which are expressed as (Mackay, 2001; Mackay et al., 1983a; Mackay et al., 1983b):

$$Z_{water} = \frac{1}{H} \quad \text{and} \quad Z_{ww} = Z_{dw} = Z_{water} \quad (3)$$

$$Z_{particle} = \rho_{particle} K_d Z_{water} = \rho_{particle} K_{OC} f_{OC} Z_{water} \quad \text{and} \quad Z_{wp} = Z_{dp} = Z_{particle} \quad (4)$$

where H (Pa m³ mol⁻¹) is the Henry's law constant, $\rho_{particle}$ (kg L⁻¹ [particle]) is the density of particle grains, K_d (L kg⁻¹) is the sorption coefficient and can be computed as: $K_d = K_{OC} f_{OC}$, with K_{OC} (L kg⁻¹[OC]) is the organic carbon (OC)-normalized sorption coefficient and f_{OC} (dimensionless) is the OC content in particles.

The mass flux between water and sediment is computed as the difference between mass flux from sediment to water and that from water to sediment:

$$F_{dw} = \vec{F}_{dw} - \vec{F}_{wd} = M_d \vec{K}_{dw} - M_w \vec{K}_{wd} \quad (5)$$

where F_{dw} (kg s^{-1}) is the pesticide mass flux from sediment to water, \vec{F}_{ij} (kg s^{-1}) is the pesticide mass flux from compartment i to j , \vec{K}_{ij} (s^{-1}) is the transfer rate constant from compartment i to j . Ideally, if the rate of mass transfer due to each individual exchange mechanism is known, \vec{K}_{ij} can be computed as:

$$\vec{K}_{dw} = \frac{G_{diff} Z_{dw} + G_{resusp} Z_{resusp}}{Z_d V_d} \quad (6)$$

$$\vec{K}_{wd} = \frac{G_{diff} Z_{ww} + G_{settl} Z_{wp}}{Z_w V_w} \quad (7)$$

where G_{diff} , G_{resusp} , and G_{settl} ($\text{m}^3 \text{s}^{-1}$) are the transfer coefficients for water-sediment diffusion, sediment resuspension, and sediment settling, respectively, and they can be further computed in Eq. (8)-(10), Z_{dw} and Z_{ww} ($\text{kg m}^{-3} \text{Pa}^{-1}$) are the fugacity capacities of pore water and pure water, respectively, and they are the reciprocal of the Henry's law constant, as shown in Eq. (3), and Z_{resusp} and Z_{wp} ($\text{kg m}^{-3} \text{Pa}^{-1}$) are the fugacity capacities of resuspended sediment and SS in the water compartment, respectively, and they can be computed as Eq. (4).

$$G_{diff} = u_{diff} A \quad (8)$$

$$G_{resusp} = \left(\frac{J_{resusp}}{\rho_{particle}} \times 10^{-3} \right) A \quad (9)$$

$$G_{settl} = \left(\frac{J_{settl}}{\rho_{particle}} \times 10^{-3} \right) A \quad (10)$$

where u_{diff} (m s^{-1}) is the velocity of chemical diffusion between water and sediment, J_{resusp} and J_{settl} ($\text{kg m}^{-2} \text{s}^{-1}$) are the area-weighted (or areic) mass flux of sediment resuspension and settling, respectively, $\rho_{particle}$ (kg L^{-1}) is the density of particle grains, and A (m^2) is the area of the water-sediment interface.

In AGRO-2014, the value of u_{diff} is suggested to be $1.39 \times 10^{-5} \text{ m s}^{-1}$ and $1.11 \times 10^{-7} \text{ m s}^{-1}$ for index reservoir and for OPP farm pond, respectively. The initial values of J_{resusp} and J_{settl} are suggested to be $1.16 \times 10^{-8} \text{ kg m}^{-2} \text{ s}^{-1}$ (i.e., $1 \text{ g m}^{-2} \text{ day}^{-1}$) and $2.32 \times 10^{-8} \text{ kg m}^{-2} \text{ s}^{-1}$ (i.e., $2 \text{ g m}^{-2} \text{ day}^{-1}$).

¹), respectively. Note that when excess sediments enter the system (e.g., during runoff events), the model will elevate the SS concentration from a pre-defined baseline/minimum level, and adjust the sedimentation rate for the part of SS that exceeds the baseline/minimum level based on the user-defined sediment settling time. The values of J_{resus} and J_{settl} are updated accordingly. This process is called “dynamic sedimentation” in the AGRO-2014 documentation, and the details for the dynamic sedimentation are described in section 3.7.

By substituting Eq. (6)-(10) into Eq. (5), the mass flux between water and sediment can be computed as:

$$F_{dw} = \frac{M_d}{Z_d V_d} \left[u_{diff} AZ_{dw} + \left(\frac{J_{resus}}{\rho_{particle}} \times 10^{-3} \right) AZ_{resusp} \right] - \frac{M_w}{Z_w V_w} \left[u_{diff} AZ_{ww} + \left(\frac{J_{settl}}{\rho_{particle}} \times 10^{-3} \right) AZ_{wp} \right]$$

$$= f_d \left[u_{diff} AZ_{dw} + \left(\frac{J_{resus}}{\rho_{particle}} \times 10^{-3} \right) AZ_{resusp} \right] - f_w \left[u_{diff} AZ_{ww} + \left(\frac{J_{settl}}{\rho_{particle}} \times 10^{-3} \right) AZ_{wp} \right] \quad (11)$$

where the fugacity of the sediment compartment (f_d , Pa) and the water compartment (f_w , Pa) are computed by analytically solving the mass balance equations for the two compartments. With all these known information, the sediment-water mass transfer flux can be determined.

Similar to AGRO-2014, the exchange mechanisms are modeled individually in FOCUS-TOXSWA. While sediment settling and resuspension is absent, pesticide is exchanged between water and sediment through diffusion at the following rate:

$$J_{wd,diff} = -(v_{dw} D \frac{\partial C_{dw}}{\partial z})_{z=0} \quad (12)$$

where $J_{wd,diff}$ ($\text{kg m}^{-2} \text{s}^{-1}$) is the areal water-to-sediment mass flux by diffusion at the water-sediment interface ($z = 0$), v_{dw} (dimensionless) is the volume fraction of pore water in the sediment compartment, D ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient of the pesticide in pore water, which is the product of the tortuosity factor (i.e., the ratio of surface area of bottom material to liquid phase, dimensionless) and the diffusion coefficient of the pesticide in water ($\text{m}^2 \text{s}^{-1}$), and C_{dw} (kg L^{-1}) is the aqueous concentration of pesticide in the sediment compartment.

In many cases, however, the information regarding the transfer coefficient of each exchange mechanism is not readily available. Instead of simulating the individual mechanisms explicitly, the VVWM model mimics them as a bulk process. The physical process of this combined mixing is assumed to be completely governed by a first-order mass transfer coefficient. The mass flux of pesticide between water and sediment is therefore formulated as:

$$F_{dw} = -\omega(C_{ww} - C_{dw}) \quad (13)$$

where ω ($\text{m}^3 \text{s}^{-1}$) is the first-order water-to-sediment mass transfer coefficient, and C_{ww} and C_{dw} (kg m^{-3}) are aqueous concentrations of pesticide in the water compartment and the sediment compartment, respectively. Although Eq. (13) is referenced to the aqueous phase, i.e., the mass flux is proportional to the difference in aqueous concentration between water and sediment, it implicitly includes all means of pesticide exchange between the two compartments. A brief justification is given in the documentation of VVWM, which reads “*in compartment modeling, it is unnecessary to explicitly model the individual exchange mechanisms since all phases of pesticide within a compartment are at equilibrium, and therefore the concentration of a pesticide in any given form (aqueous or sorbed) dictates the concentration of the other forms of the pesticide*” (Young, 2014) (pp. 12). A more detailed deduction of Eq. (13) is presented in Luo (2011) and briefly summarized below.

According to Luo et al. (2007), Eq. (8)-(10) can be alternatively formulated as:

$$G_{diff} = \frac{D_{Dwd}}{Z_{ww}} = \frac{D_{Dwd}}{Z_{dw}} \quad (14)$$

$$G_{resus} = v_{dp} u_{resus} A \quad (15)$$

$$G_{settl} = v_{wp} u_{settl} A \quad (16)$$

where D_{Dwd} ($\text{kg Pa}^{-1} \text{s}^{-1}$) is Mackay-type D value for water-sediment diffusion (Mackay, 2001), u_{resus} and u_{settl} (m s^{-1}) are velocities of particle resuspension and settling, respectively, and v_{dp} and v_{wp} (dimensionless) are the volume fraction of particles in the sediment compartment and in the water compartment, respectively. By substituting Eq. (14)-(16) into Eq. (6)-(7) and substituting the new expressions into Eq. (5), the water-sediment mass flux can be written as:

$$F_{dw} = \frac{M_d}{Z_d V_d} (D_{Dwd} + A v_{dp} u_{resus} Z_{resusp}) - \frac{M_w}{Z_w V_w} (D_{Dwd} + A v_{wp} u_{settl} Z_{wp}) \quad (17)$$

Considering Eq. (1) and (2), Eq. (17) can be rewritten as:

$$\begin{aligned} F_{dw} &= \frac{M_{dw}}{Z_{dw} V_{dw}} (D_{Dwd} + A v_{dp} u_{resus} Z_{resusp}) - \frac{M_{ww}}{Z_{ww} V_{ww}} (D_{Dwd} + A v_{wp} u_{settl} Z_{wp}) \\ &= \frac{C_{dw}}{Z_{dw}} (D_{Dwd} + A v_{dp} u_{resus} Z_{resusp}) - \frac{C_{ww}}{Z_{ww}} (D_{Dwd} + A v_{wp} u_{settl} Z_{wp}) \end{aligned} \quad (18)$$

It is noted that AGRO-2014 separates resuspended sediment from SS and assign it with a different fugacity capacity than SS. In VVWM, in contrast, resuspended sediment is modeled as a part of SS and has a same fugacity capacity with SS, i.e., $Z_{resusp} = Z_{wp} = Z_{dp} = Z_{particle}$. By considering this and Eq. (3) and (4), Eq. (18) is rewritten as:

$$\begin{aligned}
F_{dw} &= \frac{C_{dw}}{Z_{water}}(D_{Dwd} + Av_{dp}u_{resus}Z_{particle}) - \frac{C_{ww}}{Z_{water}}(D_{Dwd} + Av_{wp}u_{settl}Z_{particle}) \\
&= \frac{D_{Dwd}}{Z_{water}}(C_{dw} - C_{ww}) + \frac{AZ_{particle}}{Z_{water}}(C_{dw}v_{dp}u_{resus} - C_{ww}v_{wp}u_{settl})
\end{aligned} \tag{19}$$

Substituting Eq. (4) into Eq. (19) results in:

$$\begin{aligned}
F_{dw} &= \frac{D_{Dwd}}{Z_{water}}(C_{dw} - C_{ww}) + AK_d\rho_{particle}(C_{dw}v_{dp}u_{resus} - C_{ww}v_{wp}u_{settl}) \\
&= \frac{D_{Dwd}}{Z_{water}}(C_{dw} - C_{ww}) + AK_d(C_{dw}\rho_b u_{resus} - C_{ww}c_{ss}u_{settl})
\end{aligned} \tag{20}$$

where ρ_b (kg L^{-1}) is the bulk density of the bottom sediment, and c_{ss} (kg L^{-1}) is the concentration of SS in the water compartment.

To simplify Eq. (20), two assumptions are made. First, it is assumed that there is a dynamic equilibrium between the mass of SS and that of bed sediment, i.e., $\rho_b u_{resus} = c_{ss} u_{settl}$. This assumption is usually justified for lakes and ponds (Luo, 2011). With this assumption, Eq. (20) can be rewritten as (by replacing the term $c_{ss} u_{settl}$ with $\rho_b u_{resus}$):

$$F_{dw} = \left(\frac{D_{Dwd}}{Z_{water}} + AK_d\rho_b u_{resus} \right) (C_{dw} - C_{ww}) \tag{21}$$

Compared to Eq. (13), ω can be written as:

$$\omega = \frac{D_{Dwd}}{Z_{water}} + AK_d\rho_b u_{resus} \tag{22}$$

Based on the two-film theory, the Mackay-type D value of interfacial diffusion is formulated as (Luo et al., 2007):

$$D_{Dwd} = A\theta \left(\frac{\delta_{dw-d}}{Z_d D_{td}} + \frac{\delta_{dw-w}}{Z_w D_{tw}} \right)^{-1} \tag{23}$$

Where θ (dimensionless) is the porosity of bottom sediment ($= v_{dw}$), δ_{dw-d} and δ_{dw-w} (m) are the boundary layer depths, and D_{td} and D_{tw} ($\text{m}^2 \text{s}^{-1}$) are the chemical diffusivities. Apparently, ω is a function of chemical diffusivity as well as velocities of particle settling and resuspension. As such, it is further assumed that the mass transfer velocities for diffusion, settling, and resuspension are in the same order of magnitude. With the second assumption, Eq. (22) can be simplified as:

$$\omega = k_{xfer}A(\theta + K_d\rho_b) \quad (24)$$

Considering all sorbing media in the sediment compartment (i.e., benthic particles, benthic DOC, and benthic biota), Eq. (24) can be generalized as:

$$\omega = k_{xfer}A\left[\theta + \frac{\sum(m_dK_d)}{V_d}\right] \quad (25)$$

where the term $\sum(m_dK_d)$ (L) is short-hand notation for the sum of all solid masses and the respective sorption coefficients for each sorbing media in the sediment compartment. In VVWM, the term k_{xfer} is empirically set on the order of 10^{-8} m s⁻¹ for lakes, ponds, and other standing waterbodies according to several sources (Luo, 2011; Young, 2014).

3.3 Sorption and desorption

Pesticides are sorbed to and desorbed from various sorbing media (sub-compartment) in the water compartment (e.g., SS, DOC, and biota) and the sediment compartment (e.g., benthic particles, benthic DOC, and benthic biota). VVWM includes a variety of sorbing media, whereas AGRO-2014 only considers SS and benthic particles, and FOCUS-TOXSWA only considers SS, aquatic biota, and benthic particles.

In VVWM and AGRO-2014, the sorption and desorption process is described using a linear isotherm, i.e., K_d in Eq. (26). Unlike the two other models, FOCUS-TOXSWA uses the Freundlich equation (Eq. 27), which is a non-linear relationship to describe pesticide sorption to SS and benthic particles. It, however, uses the linear isotherm to describe sorption to biota.

$$C_{sorb} = C_{solute}K_d \quad (26)$$

$$C_{sorb} = K_F C_e \left(\frac{C_{solute}}{C_e} \right)^n \quad (27)$$

where C_{sorb} (kg kg⁻¹) is the content of pesticide sorbed to the sorbing media of interest, C_{solute} (kg L⁻¹) is the mass concentration of pesticide in the solute phase, and K_d (L kg⁻¹) is the linear sorption coefficient, K_F (L kg⁻¹) is the Freundlich coefficient for sorption to the sorbing media, C_e (kg L⁻¹) is the solute concentration C_{solute} at which K_F is estimated, and n (dimensionless) is the Freundlich exponent for sorption to the sorbing media.

3.4 Pesticide degradation and volatilization

Pesticides dissipate in field via a variety of degradation processes, including photolysis, aqueous hydrolysis, aqueous metabolism, benthic hydrolysis, and benthic metabolism. In VVWM, all

these processes are considered individually. The degradation rate constants are all assumed to be first order.

The photolysis rate constant is derived from standard laboratory tests following USEPA-approved protocols and can be determined from the following equation:

$$\mu_{\text{photolysis}} = f_{\text{lat}} f_{\text{cloud}} f_{\text{atten}} \mu_{\text{measured}} \quad (28)$$

where $\mu_{\text{photolysis}}$ (s^{-1}) is the photolysis rate constant, f_{lat} (dimensionless) is the latitude adjustment factor, f_{cloud} (dimensionless) is the cloudiness adjustment factor, f_{atten} (dimensionless) is the attenuation factor to absorption, and μ_{measured} (s^{-1}) is the measured near-surface photolysis rate constant at reference latitude and clear atmospheric conditions, which is determined as a function of the measured hydrolysis half-life from the equation:

$$\mu_{\text{measured}} = \frac{\ln(2) / HL_{\text{photolysis}}}{86400} \text{ with } \ln(2) \text{ is the natural logarithm of 2 and } HL_{\text{photolysis}} \text{ (days) is the}$$

measured photolysis half-life. Full details of the reasoning behind the parameters can be found in Young (2014), only the input parameters required by VVWM are described here. To calculate the photolysis rate constant, two input parameters are required. They are (a) the reference latitude at which the measured photolysis rate was determinate (degrees) and (b) the measured photolysis half-life (days). The values of the parameters can be directly obtained from the registrant-submitted data.

For hydrolysis, VVWM assumes that benthic hydrolysis occurs at the same rate as hydrolysis in the water compartment. The hydrolysis rate constant is the experimentally-determined overall hydrolysis rate from tests conducted at the pH of interest and expressed as:

$$\mu_{\text{hydrolysis}} = \mu_{\text{overall,pH}} \quad (29)$$

where $\mu_{\text{hydrolysis}}$ (s^{-1}) is the hydrolysis rate constant and $\mu_{\text{overall,pH}}$ (s^{-1}) is the laboratory-measured overall hydrolysis rate constant at pH of interest. Similar to μ_{measured} in Eq. (28),

$\mu_{\text{overall,pH}}$ is a function of the measured hydrolysis half-life and can be calculated from the equation: $\mu_{\text{overall,pH}} = \frac{\ln(2) / HL_{\text{hydrolysis}}}{86400}$ with $HL_{\text{hydrolysis}}$ (days) is the measured hydrolysis half-

life and reported in the registrant-submitted data. The model also assumes that hydrolysis acts only on dissolved species; therefore the effective hydrolysis rate constant is reduced by the fraction of total pesticide that is present in the dissolved phase.

For the biological metabolism reactions, VVWM assumes that within a single compartment, the sorbed-phase metabolism occurs at the same rate as the aqueous-phase metabolism. The overall metabolism rate constants for the water compartment and the sediment compartment are expressed as:

$$\mu_{metabolism(w)} = \mu_{25} \times 2^{\left(\frac{T - T_{ref_aerobic}}{10}\right)} \quad (30)$$

$$\mu_{metabolism(d)} = \mu_{measured} \times 2^{\left(\frac{T - T_{ref_anaerobic}}{10}\right)} \quad (31)$$

where $\mu_{metabolism(w)}$ and $\mu_{metabolism(d)}$ (s^{-1}) are the metabolism rate constants in the water compartment and the sediment compartment, respectively, μ_{25} and $\mu_{measured}$ (s^{-1}) are the laboratory measured aerobic metabolism rate constant at 25°C and the laboratory measured anaerobic metabolism rate constant at $T_{ref_anaerobic}$, respectively, which can be determined from

the equations: $\mu_{25} = \frac{\ln(2) / HL_{metabolism(w)}}{86400}$ and $\mu_{measured} = \frac{\ln(2) / HL_{metabolism(d)}}{86400}$ with

$HL_{metabolism(w)}$ and $HL_{metabolism(d)}$ (days) are the aerobic aquatic metabolism half-life and the anaerobic aquatic metabolism half-life, respectively, T ($^{\circ}C$) is the temperature of the modeled waterbody, and $T_{ref_aerobic}$ and $T_{ref_anaerobic}$ ($^{\circ}C$) are the temperatures at which the aerobic laboratory study and the anaerobic laboratory study were conducted, respectively. The values of four parameters need to be specified by model users: the aerobic aquatic metabolism half-life, the anaerobic aquatic metabolism half-life, and the corresponding reference temperatures. They can be found in the registrant-submitted data volume.

Unlike VVWM, AGRO-2014 and FOCUS-TOXSWA model the degradation mechanisms as a bulk process and use an overall rate coefficient to describe the combined effects of the degradation reactions in each compartment. Similar to VVWM, they assume the processes are first order. They also define the degradation rate constant as a function of the temperature of the modeled waterbody. For example, in AGRO-2014, the degradation rate constant in a compartment is expressed as:

$$\mu_{adj_degradation} = \mu_{degradation} \times Q10^{\left(\frac{T-25}{10}\right)} \quad (32)$$

where $\mu_{adj_degradation}$ (s^{-1}) is the overall degradation rate constant in a compartment, $\mu_{degradation}$ (s^{-1}) is the laboratory measured degradation rate constant at 25 $^{\circ}C$, which is determined from the

equation: $\mu_{degradation} = \frac{\ln(2) / HL_{degradation}}{86400}$ with $HL_{degradation}$ (days) is the measured overall

degradation half-life in a compartment, $Q10$ (dimensionless) is the temperature scaling factor, which is 2 by default in AGRO-2014, and T ($^{\circ}C$) is the temperature of the modeled waterbody. The overall degradation half-life $HL_{degradation}$ is a user-specified value; however, it is usually not readily available from the registrant-submitted data. Instead of using the temperature scaling factor ($Q10$), FOCUS-TOXSWA uses the molar activation enthalpy/energy (in water and in sediment) to adapt the degradation rate constant from the reference temperature at which the half-life is measured to the temperature of the modeled waterbody.

Similar to each other, the temperature of the modeled waterbody is derived from the meteorological data that corresponds to the crop/location scenario being simulated. VVWM and AGRO-2014 take the air temperature while FOCUS-TOXSWA takes the water temperature. VVWM and AGRO-2014 use the previous 30-day average temperature and adjusts the temperature daily, whereas FOCUS-TOXSWA uses the average temperatures of 12 months or of a typical season to adjust the degradation rate for each scenario.

Volatilization is commonly considered in the three models and is modeled as a first-order process. The overall volatilization rate coefficient is described as follows:

$$\mu_{vol} = \frac{Ak_{vol}}{V_{ww}} \quad (33)$$

where A (m^2) is the surface area of the water compartment, k_{vol} ($m\ s^{-1}$) is the volatilization exchange coefficient, and V_{ww} (m^3) is the aqueous volume of the water compartment. Typically the volatilization exchange coefficient comprises the liquid-phase and the gas-phase resistances, representing the partitioning between water and air. For example, in VVWM, it is expressed as:

$$\frac{1}{k_{vol}} = \frac{1}{k_{liquid}} + \frac{1}{(H/RT)k_{air}} \quad (34)$$

where k_{vol} ($m\ s^{-1}$) is the volatilization exchange coefficient, k_{liquid} ($m\ s^{-1}$) is the liquid-phase resistance, which is a function of the molecular weight of the pesticide ($g\ mol^{-1}$), the wind speed at 10 m above the water surface ($m\ s^{-1}$) and the temperature of the modeled waterbody ($^{\circ}C$), k_{air} ($m\ s^{-1}$) is the gas-phase resistance, which is a function of the molecular weight of the pesticide ($g\ mol^{-1}$) and the wind speed at 0.1 m above the water surface ($m\ s^{-1}$), H ($m^3\ atm\ mol^{-1}$) is the Henry's law constant and can be computed from the equation: $H = \frac{vp/760}{Sol/MW}$ with vp (torr) is the vapor pressure of the pesticide, Sol ($mg\ L^{-1}$) is the solubility of the pesticide, and MW ($g\ mol^{-1}$) is the molecular weight of the pesticide, R ($= 8.026 \times 10^{-5}\ m^3\ atm\ mol^{-1}\ K^{-1}$) is the universal gas constant, and T (K) is the temperature of the modeled waterbody. The value of the wind velocities are automatically read in from the meteorological files. The value of the temperature of the modeled waterbody is derived in the same way as that used in the adjustment of metabolism rates. Parameters associated with the chemical properties of the pesticide, e.g., molecular weight, vapor pressure and solubility, are available from the registrant-submitted data.

The approach employed by FOCUS-TOXSWA and AGRO-2014 to determine the volatilization exchange coefficient is slightly different from that in VVWM. In FOCUS-TOXSWA, the Henry's coefficient is defined as a function of the temperature of the waterbody. The effect of temperature on vapor pressure and on solubility of the pesticide is derived from the Van't Hoff equation (Beltman et al., 2006). To compute the Henry's coefficient, the model requires the following input parameters, including the saturated vapor pressure and the temperature at which

it is measured, and the molar enthalpy of vaporization, which is needed to calculate the vapor pressure at the system temperature; and likewise, the solubility and the temperature at which it is measured, and the molar enthalpy of solubility.

The approach employed by AGRO-2014 is slightly different from that by VVWM as well. AGRO-2014 defines the liquid-phase resistance and the gas-phase resistance as a constant, and the default values are set to be 0.01 m h^{-1} and 1 m h^{-1} , respectively. It also uses the term k_{aw} (dimensionless) to replace the term (H / RT) in Eq. (34). It is expressed as:

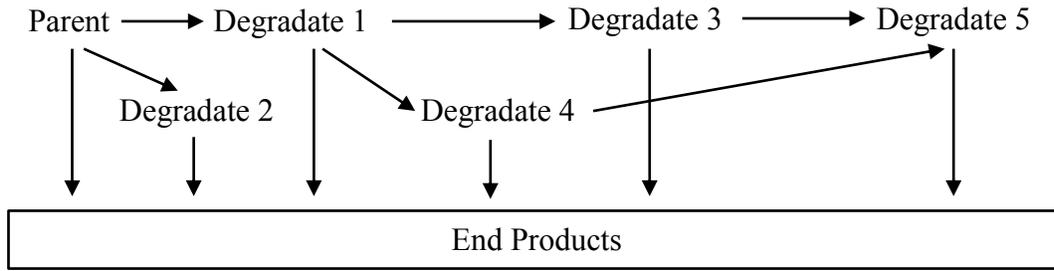
$k_{aw} = H / (R \times \text{Chem PropTemp})$ with H ($\text{m}^3\text{atm mol}^{-1}$) is the Henry's law constant, R ($= 8.026 \times 10^{-5} \text{ m}^3\text{atm mol}^{-1} \text{K}^{-1}$) is the universal gas constant, and Chem PropTemp (K) is the chemical property temperature, which is by default set to be 298.15 K (25 °C).

3.5 Formation and transformation of degradates in water and sediment

The formation and transformation of degradates is an important process occurring in the system. The simulation of this process is critical especially when the degradates are more toxic than the parent compound. Both VVWM and FOCUS-TOXSWA have the capability of simulating the formation and transformation of degradates in water and in sediment of the waterbody. For FOCUS-TOXSWA, this feature was incorporated since version 4.4.2 (Beltman et al., 2014). This feature, however, is not available in AGRO-2014. Without this modeling capability, AGRO-2014 is only able to handle the transport and fate of a degradate that enters the waterbody via inflow.

The degradate formation scheme supported by FOCUS-TOXSWA is flexible and can consist of degradates formed in parallel or formed in sequence or by a combination of both, while the scheme supported by VVWM only consists of degradates formed in sequence. Figure 3 describes the example reaction scheme of parent decomposed into various degradates simulated by (a) FOCUS-TOXSWA and (b) VVWM. Note that the VVWM only allows the sequential formation of up to two degradates. The theoretical background of the degradate simulation in FOCUS-TOXSWA and in VVWM can be found in Adriaanse et al. (2014) and Young (2014), respectively.

(a) FOCUS-TOXSWA, adapted from Figure 1 of Adriaanse et al. (2014)



(b) VVWM

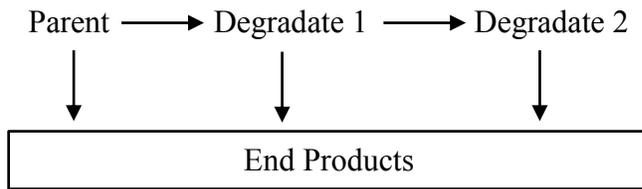


Figure 3: Example reaction scheme of parent decomposed into various degradates simulated in (a) FOCUS-TOXSWA and in (b) VVWM

Both models assume that the transformation and formation of degradates follows first-order kinetics. Transformation of the parent compound is described as follows:

$$R_{trfm,p} = \mu_p C_p \quad (35)$$

where $(\text{kg L}^{-1} \text{ s}^{-1} \text{ or } \text{kg kg}^{-1} \text{ s}^{-1})$ is the rate of transformation of the parent compound in the water or sediment compartment, (s^{-1}) is the rate constant for the transformation of the parent compound, and $(\text{kg L}^{-1} \text{ or } \text{kg kg}^{-1})$ is the concentration of parent compound in water or in sediment. The rate of formation of degradation products is described by first-order kinetics. For example, the formation of degradate 1, which is formed from the parent compound, is described as:

$$R_{form,dgt1} = \chi_{dgt1} \frac{M_{dgt1}}{M_p} R_{trfm,p} \quad (36)$$

where $(\text{kg L}^{-1} \text{ s}^{-1} \text{ or } \text{kg kg}^{-1} \text{ s}^{-1})$ is the rate of formation of degradate 1 from the parent compound in the water or sediment compartment, (dimensionless) is the molar fraction of parent transformed to degradate 1, and (g mol^{-1}) is the molar mass of degradate 1 and parent compound, respectively. The transformation of degradate 1 is described as:

$$(37)$$

where $R_{trfm,dgt1}$ ($\text{kg L}^{-1} \text{s}^{-1}$ or $\text{kg kg}^{-1} \text{s}^{-1}$) is the rate of transformation of degradate 1 in the water or sediment compartment, μ_{dgt1} (s^{-1}) is the rate constant for the transformation of degradate 1, and C_{dgt1} (kg L^{-1} or kg kg^{-1}) is the concentration of degradate 1 in water or sediment.

Similar rate equations are used for each degradation product. Note that since VVWM simulates each individual degradation mechanism (i.e., hydrolysis, photolysis, and biological metabolism) separately, the rate constant for the transformation of the parent compound and the degradation products (e.g., μ_{dgt1}) is defined separately for each mechanism. In FOCUS-TOXSWA, in contrast, since the degradation is modeled as a bulk process, there is only one overall rate constant for all degradation reactions in a compartment.

3.6 Variation of water volume in the water compartment

Water volume in the water compartment is an important factor affecting the partitioning of pesticide between pure water and the sorbing media. In VVWM, the aqueous volume of the water compartment can either be set as a constant or a dynamic variable that is updated as hydrologic conditions change by each simulation time step. Moreover, in VVWM, whether or not there is a water outflow (also called flowthrough or washout in VVWM) present is optional. In general, VVWM provides three options: 1) constant volume with no flowthrough, 2) constant volume with flowthrough, and 3) varying volume and flowthrough. The change in water volume is calculated from daily runoff, precipitation, evaporation, and seepage for any day. The model also defines a maximum and minimum level that the water volume can reach, denoted as V_{ww_max} and V_{ww_min} (m^3 , $0 < V_{ww_min} < V_{ww_max}$), respectively. For $V_{ww_min} < V_{ww(t)} < V_{ww_max}$, the water volume is expressed as:

$$V_{ww(t)} = V_{ww(t-1)} + \text{Runoff}_t + \text{Precip}_t - \text{Evap}_t - \text{Seep}_t \quad (38)$$

where $V_{ww(t)}$ and $V_{ww(t-1)}$ (m^3) is the aqueous volume of the water compartment at time t and at the previous simulation time step $t-1$, respectively, Runoff_t (m^3) is the runoff into waterbody at time t , Precip_t (m^3) is the direct precipitation on waterbody at time t , Evap_t (m^3) is the evaporation at time t , and Seep_t (m^3) is the seepage at time t , which is by default assumed to be negligible. If $V_{ww(t)} > V_{ww_max}$, the volume for the simulation day is set to V_{ww_max} , and the excess water is used in the calculation of washout. If the option of constant volume is selected, the water volume for the simulation day will be set to the user-specified constant, and the washout will be calculated if the flowthrough option is selected and the newly calculated water volume exceeds the pre-defined constant volume.

Similar to VVWM, in FOCUS-TOXSWA, the aqueous volume of the water compartment is updated every simulation time step and the change in water volume is computed as a function of the inflow from upstream, runoff from the adjacent contributing area, incoming lateral flow (for watercourse only), precipitation, evaporation, seepage, and outflow (if any). A constant

seepage/infiltration flow from the adjacent field into the waterbody (negative value) or out of the waterbody (positive value) can be entered. If the seepage/infiltration flow is not zero, the dispersion length should be given for each sediment horizon. Moreover, the model maintains a minimum water level by installing a weir at the outflow end of the waterbody. Outflow occurs across the weir. For every simulation time step, the model also updates the water depth based on the water conservation equations combined with the water depth-discharge relations with considerations of impacts of weirs on flow (Adriaanse and Beltman, 2009).

In AGRO-2014, the aqueous volume of the water compartment is simply assumed to be constant. The impacts of precipitation and evaporation on water volume are not accounted. It is also assumed that the outflow rate equals the inflow rate, and the inflow rate can either be a constant or a dynamic variable.

3.7 Variation of SS concentration in the water compartment

The concentration of SS in the water compartment is a critical factor affecting the pesticide partitioning between pure water and sorbing media. The relationship between SS and pesticide partitioning can be described as follows (Neitsch et al., 2005):

$$Frt_{dissolved} = \frac{1}{1 + K_d c_{ss}} = \frac{1}{1 + K_{OC} f_{OC} c_{ss}} \quad (39)$$

$$Frt_{sorbed} = \frac{K_d c_{ss}}{1 + K_d c_{ss}} = \frac{K_{OC} f_{OC} c_{ss}}{1 + K_{OC} f_{OC} c_{ss}} = 1 - Frt_{dissolved} \quad (40)$$

where $Frt_{dissolved}$ and Frt_{sorbed} (dimensionless) is the fraction of total pesticide in the dissolved phase and in the particulate phase, respectively, K_d ($= K_{OC} f_{OC}$, $L\ kg^{-1}$) is the sorption coefficient of SS, K_{OC} ($L\ kg^{-1}[OC]$) is the organic carbon (OC)-normalized sorption coefficient and f_{OC} (dimensionless) is the OC content in particles, and c_{ss} ($kg\ L^{-1}$) is the concentration of SS in the water compartment.

The three models differ in the way they calculate the SS concentration in the water compartment. In VVWM and FOCUS-TOXSWA, the concentration of SS is assumed to be constant. Since the water volume in the water compartment is adjusted due to hydrologic conditions (e.g., water inflow and outflow, precipitation, and evaporation), the mass of SS changes accordingly. Although the models do not explicitly model sediment inflow, the use of constant SS concentration actually artificially adds SS to the system as water volume increases. This portion of SS does not contain pesticides, but will become available for sorption and immediately afterwards result in redistribution of the total mass of pesticides in the water compartment. As a consequence, the concentration of pesticides dissolved in pure water will decrease as a portion of the pesticides will sorb to the additional SS.

In AGRO-2014, in contrast, the concentration of SS in the water compartment is described as a dynamic variable that varies as a function of sediment inflow, outflow and sedimentation. The

model explicitly tracks sediment inflow and outflow. Let $G_{pIn(t)}$ and $G_{pOut(t)}$ ($m^3 s^{-1}$) be the rates of sediment inflow and outflow at time t , respectively. The model maintains a baseline/minimum level of SS concentration at 30 mg L^{-1} (or other user-specified values) in the water compartment. When there are excess sediments entering the system, i.e., $G_{pIn(t)} > 0$ and $G_{pIn(t)} > G_{pOut(t)}$, the concentration of SS elevates. The portion of the SS that exceeds the baseline/minimum level settles gradually until the SS concentration comes back to the baseline. In AGRO-2014, this process is described by a variable called “the 90% sediment clearance time,” which is an indicator of the residency time of the excess SS in the water compartment. Note that the model doesn’t explicitly account for the impact of particle size and sedimentation velocity on the sedimentation rate. When there are excess SS present in the water compartment (i.e., the SS concentration is greater than the baseline level), the sedimentation of the excess SS is expressed as:

$$k_{sedloss} = \frac{\log(10)}{t_{settl} \times 86400} \quad (41)$$

where $k_{sedloss}$ (s^{-1}) is the rate constant for sediment loss, and t_{settl} (day) is the 90% sediment clearance time. AGRO-2014 suggests parameterizing the 90% sediment clearance time to be 3.4 days for the modeling of the highly hydrophobic organic pesticides (Padilla et al., 2015). It was set to be 7 days for general use in the AGRO model. The change in the mass of the excess SS due to sedimentation is expressed as:

$$\Delta m_{wp(t)} = m_{wp(t)} [1 - \exp(-k_{sedloss})] \quad (42)$$

where $\Delta m_{wp(t)}$ ($kg s^{-1}$) is the loss of the excess SS mass in the water compartment due to sedimentation at time t , and $m_{wp(t)}$ (kg) is the mass of the excess SS at time t .

If excess SS exits, the sediment burial rate is adjusted as:

$$G_{burial}^* = \frac{\Delta m_{wp(t)} + AJ_{burial}}{\rho_{particle}} \times 10^{-3} \quad (43)$$

where G_{burial}^* ($m^3 s^{-1}$) is the adjusted transfer coefficient for sediment burial when excess SS is present, J_{burial} ($kg m^{-2} s^{-1}$) is the baseline areal mass flux of sediment burial, and $\rho_{particle}$ ($kg L^{-1}$ [particle]) is the density of particle grains. The first part of Eq. (43) $\frac{\Delta m_{wp}}{\rho_{particle}}$ computes the rate of

sedimentation due to the presence of excess SS and the second part of the equation $\frac{AJ_{burial}}{\rho_{particle}}$

computes the baseline sediment burial rate when the SS concentration is at the baseline/minimum level. In AGRO-2014, the total sediment settling rate is partitioned between burial and resuspension, i.e.,

$$G_{settl} = G_{resus} + G_{burial} \quad (44)$$

$$Pct_{resus} = \frac{G_{resus}}{G_{settl}} \times 100\% \quad (45)$$

where Pct_{resus} (%) is the percentage of sediment deposition that resuspends. It is suggested to be 50% by the model developers. As the burial rate is adjusted when excess SS exists, mass transfer coefficients for sediment settling and resuspension are updated accordingly:

$$G_{settl}^* = G_{burial}^* \times \frac{100}{100 - Pct_{resus}} \quad (46)$$

$$G_{resus}^* = G_{settl}^* \times \frac{Pct_{resus}}{100} \quad (47)$$

where G_{settl}^* and G_{resus}^* ($m^3 s^{-1}$) are the adjusted transfer coefficients for sediment settling and resuspension, respectively. As such, when there is excess SS present in the water compartment, the transfer coefficients for sediment burial, settling, and resuspension are adjusted as a function of the 90% sediment clearance time. The adjustment continues until the excess SS has settled. Afterwards, the SS concentration is set back to the baseline level and the transfer coefficients are back to the baseline level as well.

4. Standard receiving waterbody scenarios

The properties of receiving waterbodies vary from site to site. Standard receiving waterbody scenarios are defined to conceptually represent the common field conditions for risk assessment. In VVWM, the USEPA/OPP standard farm pond scenario is pre-defined for aquatic risk assessment. This scenario was derived from a Georgian farm pond and is recommended by the USEPA/OPP as a national standard for evaluating the risk of pesticide products to aquatic organisms (Young, 2014). AGRO-2014 uses the same scenario with VVWM for aquatic risk characterization. In FOCUS-TOXSWA, three different receiving waterbody scenarios – the FOCUS pond, the FOCUS ditch, and the FOCUS stream – were defined (FOCUS, 2015; Linders et al., 2003). These scenarios were extracted from a reality check of the pre-selected geographical areas and represented the common characteristics shared by various receiving waterbodies on those sites. The schematic layout of the four standard receiving waterbody scenarios is demonstrated in Figure 4.

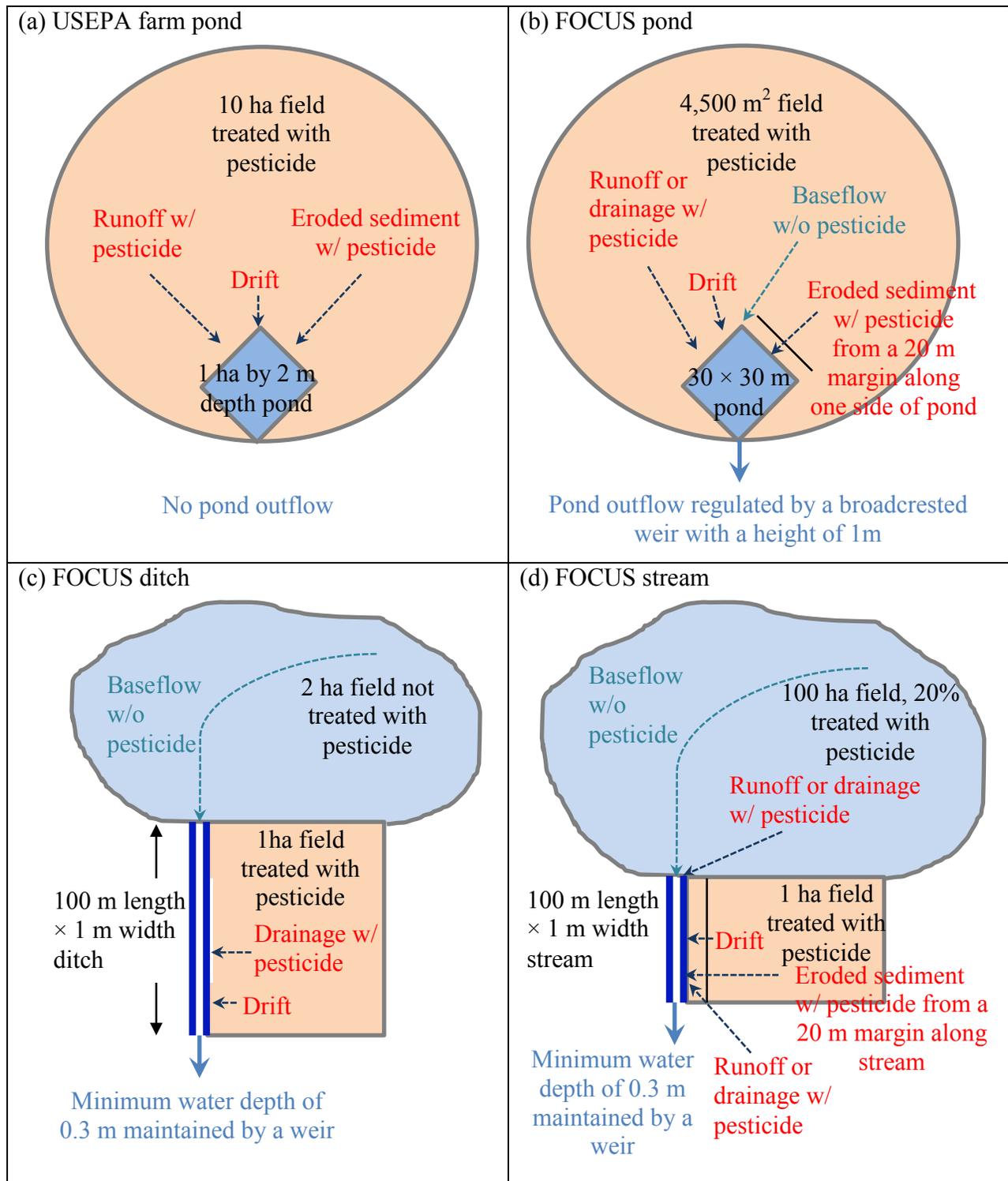


Figure 4: Schematic layout of the four standard receiving waterbodies parameterized for pesticide registration evaluation

Table 4 depicts the general setup of the four standard receiving waterbody scenarios. Similar to each other, each scenario consists of a draining area and a receiving waterbody. For example, the USEPA OPP standard farm pond scenario assumes a circular 10 ha field treated with pesticides emptying into a 1 ha farm pond. Similarly, the FOCUS pond scenario assumes a circular 4,500 m² field treated with pesticides draining into a 900 m² pond. In addition to the treated field adjacent to the receiving waterbody, the FOCUS ditch scenario and the FOCUS stream scenario also involve an upstream catchment which contributes baseflow, runoff, drainage and pesticides (if treated) to the receiving waterbody. The size of the upstream catchment is 2 ha (not treated) and 100 ha (20% of which is treated with pesticides) for the FOCUS ditch and the FOCUS stream, respectively. The surface area of the waterbody is assumed to be 100 m² in these two scenarios. The four scenarios differ in the water depth of the water compartment. The water depth is set to be a constant of 2 m for the OPP farm pond, while it retains a minimum level of 1, 0.3 and 0.3-0.5 m for the FOCUS pond, the FOCUS ditch, and the FOCUS stream, respectively. The minimum water level in the FOCUS scenarios is maintained by a weir that was installed at the outflow of the pond or at the downstream of the ditch and stream. It meets the need of FOCUS' aquatic risk assessment procedures for pesticide registration, which do not consider temporary waterbodies (Adriaanse and Beltman, 2009). Note that although VVWM and FOCUS-TOXSWA both allow users to enter constant seepage/infiltration flow, this component is assumed to be negligible in all the standard receiving waterbody scenarios.

Table 4: Parameterization of the four standard receiving waterbody scenarios

Parameter	Unit	OPP Farm Pond	FOCUS Pond	FOCUS Ditch	FOCUS Stream
1 Area of the treated field adjacent to the receiving waterbody	m ²	100,000	4,500	10,000	10,000
2 Area of the upstream catchment	m ²	0	0	20,000 (not treated)	1,000,000 w/ 20% treated
3 Surface area of the waterbody (width by length)	m ²	10,000	30 × 30	1 × 100	1 × 100
4 Depth of the water compartment ^a	m	2	1	0.3	0.3 to 0.5
5 Average vertical depth of the sediment compartment	m	0.05	0.05	0.05	0.05
6 Concentration of SS in the water compartment	mg L ⁻¹	30	15	15	15
7 Concentration of DOC in the water compartment	mg L ⁻¹	5	NA	NA	NA
8 Concentration of planktonic biomass in the water compartment	mg L ⁻¹	0.4	NA	NA	NA
9 Porosity of bottom sediment	-	0.5	0.6	0.6	0.6
10 Bulk density of bottom sediment	kg L ⁻¹	1.35	0.8	0.8	0.8
11 Concentration of DOC in the sediment compartment	mg L ⁻¹	5	NA	NA	NA
12 Concentration of benthos in the sediment compartment	g m ⁻²	0.006	NA	NA	NA
13 Fraction of organic carbon	-	0.04	0.05	0.05	0.05

Notes:

^a: The water depth in the FOCUS scenarios is the minimum water depth maintained by a weir located at the outflow end of the waterbody. It is also considered the average water depth of the waterbodies.

With regard to the average vertical depth of the sediment compartment, the four scenarios share the same value, which is 0.05 m. In addition, all the waterbodies in the four scenarios have a rectangular internal cross-section. Within the water compartment, the concentration of SS is assumed to be 30 mg L⁻¹ in the OPP farm pond, whereas it is set to be 15 mg L⁻¹ in the FOCUS receiving waterbodies. The OPP farm pond scenario also specifies the concentrations of DOC and biota in the water compartment, whereas the FOCUS receiving waterbodies are defined as containing neither DOC nor biota in the water compartment. It is noted that the FOCUS-TOXSWA model only considers SS and biomass as the sorbing media in the water compartment and does not account for DOC. The documentation of FOCUS-TOXSWA also states that the waterbodies are assumed to contain no biota in order to minimize the mass of pesticides sorbed to the sorbing media and retain a conservative estimation of the aqueous concentration (Linders et al., 2003). For the sediment compartment, the porosity of the OPP farm pond is slightly less than that of the FOCUS receiving waterbodies, whereas the bulk density is greater. Concentrations of DOC and biota in the sediment compartment are explicitly defined in the OPP farm pond scenarios while they are not applicable in the FOCUS scenarios. Benthic particle is the only sorbing media considered in the FOCUS-TOXSWA model. The fraction of organic carbon in particles (including both the SS and the benthic particles) is assumed to be 0.04 in the OPP farm pond, which is slightly less than in the FOCUS receiving waterbodies.

In addition, it is also important to note that although AGRO-2014 basically uses the OPP farm pond scenario, it parameterizes the pond in a slightly different way from VVWM. Since the concentration of SS is modeled as a dynamic variable in AGRO-2014, it maintains a baseline/minimum level of 30 mg L⁻¹ but can elevate as excess sediments enter the system. The residence time of the excess SS is governed by the settling-time parameters, in particular, the 90% sediment clearance time. Once the excess SS has settled, the SS concentration returns back to the baseline level. The fraction of organic carbon in SS is parametrized to be 0.067 in AGRO-2014 versus 0.04 in VVWM's OPP farm pond. The fraction of organic carbon in benthic particles and resuspended particles is set to be 0.04 in AGRO-2014, which is the same as VVWM.

5. Summary

VVWM, AGRO-2014, and FOCUS-TOXSWA are primary receiving waterbody models that are configured for the aquatic risk assessment of pesticide products. This report compares the model theory of the three models. In these models, the receiving waterbody is conceptually formulated into a compartmental system comprised of two compartments – the water compartment, which consists of pure water, SS and other sorbing media (e.g., DOC and biota), and the sediment compartment, which consists of pore water, benthic particles and other benthic sorbing media (e.g., benthic DOC and benthic biota). The three models commonly assume that each compartment is individually well-mixed, i.e., all materials in each compartment are at thermodynamic equilibrium. To describe the pesticide behavior in the system, three major processes are considered in the models. They are: [1] mass transfer between the water compartment and the sediment compartment, [2] pesticide sorption and desorption, and [3] pesticide degradation (e.g., photolysis, hydrolysis, and biological metabolism). Processes

associated with system input and system loss are also considered. They are inflow and outflow of water, SS and pesticides (in dissolved and sorbed phases), precipitation and evaporation, pesticide volatilization, and sediment/sorbed pesticide burial. To compare the way the three models simulate these processes, seven modules were considered. Key differences among the models are summarized as follows:

- 1) Initial distribution of pesticide inflow. In AGRO-2014 and FOCUS-TOXSWA, all pesticides (in dissolved and sorbed phases) in inflow are delivered to the water compartment whereas in VVWM pesticides in dissolved phase and 50% pesticides in sorbed phase are delivered to the water compartment and the remaining 50% of the sorbed pesticides are directly allocated to the sediment compartment.

Pesticide transport and loss. In FOCUS-TOXSWA, pesticides are transported by advection and dispersion in the direction of flow, which produces a concentration gradient along the flow direction, while in VVWM and AGRO-2014 pesticides are evenly distributed along the direction of flow. Commonly in the three models, pesticides are removed from the system through outflow. In VVWM and AGRO-2014, pesticides can also be removed from the system via sediment burial, which is not, however, considered in FOCUS-TOXSWA. In addition, the three models commonly include volatilization as a fate of pesticides in the water compartment.

- 2) Pesticide mass transfer between the water compartment and the sediment compartment. AGRO-2014 explicitly mimics individual mechanism of pesticide exchange between water and sediment, including the diffusive exchange between pure water and pore water, and the exchange of sediment-sorbed pesticide via sediment settling and resuspension. FOCUS-TOXSWA handles mass transfer in a similar manner, but it merely considers diffusion and assumes sediment settling and resuspension are negligible. In the two models, the processes are individually governed by the corresponding mass transfer coefficients. VVWM, in contrast, uses a bulk process to include all means of water-sediment pesticide exchange. This process is regulated by a first-order overall mass transfer coefficient.
- 3) Pesticide sorption and desorption. Sorbing media considered in VVWM include SS, DOC, and biota in the water compartment as well as benthic particles, benthic DOC, and benthic biota in the sediment compartment, whereas in FOCUS-TOXSWA only SS, biota in the water compartment and benthic particles are considered, and in AGRO-2014 only SS and benthic particles are considered. Moreover, in VVWM and AGRO-2014, the sorption process is described using a linear isotherm, whereas in FOCUS-TOXSWA it is described using the Freundlich equation (a non-linear relationship) except the sorption to biota in the water compartment, which is described using a linear isotherm.
- 4) Pesticide degradation. VVWM considers various means of pesticide degradation in the receiving waterbody, including photolysis, aqueous hydrolysis, aqueous metabolism, benthic hydrolysis, and benthic metabolism, and uses individual degradation rate constant to describe each mechanism. AGRO-2014 and FOCUS-TOXSWA, in contrast, model the degradation reactions as a bulk process. In each compartment, the two models use an

overall degradation rate constant to describe all means of pesticide degradation. The metabolism degradation rate constant in VVWM and the degradation rate constant in AGRO-2014 and FOCUS-TOXSWA are all adjusted with the temperature of the modeled waterbody.

- 5) Formation and transformation of degradates. Both VVWM and FOCUS-TOXSWA have the capability of simulating the formation and transformation of degradates in water and in sediment of the waterbody. The degrade formation scheme supported by FOCUS-TOXSWA is flexible and can consist of degradates formed in parallel or formed in sequence or by a combination of both, while the scheme supported by VVWM only consists of degradates formed in sequence and allows simulation of up to two degradates. AGRO-2014, in contrast, is only able to handle the transport and fate of a degrade that enters the waterbody via inflow.
- 6) Variation of water volume in the water compartment. Both VVWM and FOCUS-TOXSWA are able to update the aqueous volume of the water compartment by every simulation time step as hydrologic conditions change. VVWM has three general options – variable volume and flowthrough, constant volume with flowthrough, and constant volume without flowthrough. Outflow/washout is calculated if the flowthrough option is selected and the newly calculated water volume exceeds the pre-defined maximum level or constant level. FOCUS-TOXSWA is able to maintain a minimum water depth by installing a weir at the outflow end of the waterbody and update the water depth based on water conservation equations and water depth-discharge relationships with considerations of impacts of weirs on flow. In AGRO-2014, in contrast, the aqueous volume of the water compartment is simply assumed to be constant regardless of the changes in hydrologic conditions. It is also assumed that the outflow rate is the same as the inflow rate.
- 7) Variation of SS concentration in the water compartment. In VVWM and FOCUS-TOXSWA, SS concentration in the water compartment is assumed to be constant, whereas in AGRO-2014 it is formulated as a dynamic variable that maintains a baseline/minimum level but will elevate if excess sediments enter the system during runoff events. The portion of the SS that exceeds the baseline will settle until the SS concentration comes back to the baseline level. The settling of the excess SS is governed by the 90% sediment clearance time, a variable defined by AGRO-2014 to indicate the residency time of excess SS in the water compartment. Transfer coefficients for sediment burial, settling and resuspension are also adjusted accordingly during the sedimentation process.

Based on the compare and contrast of the model theory, key features and limitations of the three models are highlighted as follows:

- 1) VVWM is highlighted with three unique and promising features. First, as a regulatory model, VVWM precisely makes use of the data that are required by the USEPA for pesticide registration and readily submitted to and reviewed by DPR. The input data required by VVWM to simulate pesticide degradation, sorption, and volatilization completely match USEPA's data requirements. AGRO-2014 and FOCUS-TOXSWA, in

contrast, require additional input data that are not required by the USEPA. Second, VVWM considers the most complete list of pesticide fate and transport pathways in a receiving waterbody. For example, it considers all individual pesticide degradation mechanisms (i.e., photolysis, hydrolysis, and biological metabolism), while AGRO-2014 and FOCUS-TOXSWA only model them as a bulk process. Moreover, VVWM includes all possible sorbing media, whereas AGRO-2014 and FOCUS-TOXSWA only have SS and benthic particles (FOCUS-TOXSWA also considers biota in the water compartment). As a result, VVWM better represents two key processes of particle-bound pesticides – pesticide sorption/desorption and pesticide removal by the outflow of sorbing media. Third, VVWM uses a versatile approach to simulate the mass transfer between water and sediment. It defines an overall mass transfer coefficient to include all means of pesticide exchange between water and sediment. AGRO-2014 and FOCUS-TOXSWA, in contrast, explicitly model the individual exchange mechanisms (e.g., diffusion and sediment settling/resuspension in AGRO-2014 and diffusion only in FOCUS-TOXSWA). They require that model users have adequate knowledge and field information to determine the exact value of the transfer coefficients and precisely parameterize the model.

- 2) The unique feature of AGRO-2014 is the dynamic sedimentation. It allows the concentration of SS to elevate from the baseline/minimum level when excess sediments enter the system during runoff events. It defines a term – the 90% sediment clearance time – to describe the residency time of the excess SS. Accordingly, it adjusts the rates of sediment burial, settling, and resuspension that in turn affect the mass of SS and also affect the water-sediment mass transfer. The adjustment stops, and the SS concentration comes back to the baseline level when the excess SS has settled. This feature mainly affects the simulation of the highly hydrophobic organic pesticides as the partitioning of these chemicals is significantly affected by the SS concentration (Padilla et al., 2015). Alternatively, VVWM and FOCUS-TOXSWA simply assume the concentration of SS to be a constant, but users can change the concentration values to reflect different field conditions. This setup is reasonable for regulatory purpose because [1] for evaluation of pesticides with low to intermediate partitioning coefficient, the assumption of constant SS concentration has little impact on the model output since the partitioning to SS and other sorbing media is usually insignificant (Young, 2014), and [2] for evaluation of those with extremely high partitioning coefficient, it is possible to improve the prediction of partitioning by varying the SS concentration and other relevant parameters (e.g., PRBEN in VVWM) without revising the model structure (USEPA, 2008). Further study may be needed to achieve the optimal parameterization.

As claimed by the developers of AGRO-2014, the dynamic sedimentation also allows model users to explicitly tackle each individual mechanism associated with sedimentation and mass transfer. To take advantage of this feature, however, it also requires that model users have adequate knowledge and field information to parameterize the model. For example, users have to specify the mass transfer rates for diffusion, sediment settling and resuspension. They also have to estimate the 90% sediment clearance time and the percentage of resuspension to enable the dynamic sedimentation. Usually the value of these parameters is not readily available. Users have to estimate them from calibration of measured data. Again, this is subject to data availability and can be highly case-specific.

Errors may also arise if the model is not parameterized correctly to match real-world conditions. In VVWM, as stated in the above bullet, the mass transfer mechanisms are governed by one generic parameter – the overall mass transfer coefficient. Model developers suggest that this coefficient be parameterized at the order of 10^{-8} m s^{-1} based on various existing sources (Luo, 2011; Young, 2014). This setup helps to reduce the uncertainty in model parameterization. However, it is important to note that the simplification of the mass transfer process in VVWM is subject to two assumptions: [1] the mass of SS is at dynamic equilibrium with that of the bed sediment, and [2] the mass transfer velocities for diffusion, settling, and resuspension are on the same order of magnitude. As indicated by the modeling documentation, the assumptions are usually justified in typical receiving waterbodies (Luo, 2011; Young, 2014).

- 3) The unique feature of FOCUS-TOXSWA is the capability of predicting a concentration gradient over space, i.e., in the direction of flow and in the direction of sediment depth. By incorporating the spatial dimension to the temporal dimension, FOCUS-TOXSWA has higher resolution than the other two models. The most important limitation of FOCUS-TOXSWA is that it distinctly excludes sediment settling and resuspension from the simulation of mass transfer. The documentation of FOCUS-TOXSWA admits “*this approach is acceptable for sheltered, very slowly flowing field ditches, but whether it also is acceptable for large, full ditches in open polders or for included ditches is less clear*” (Adriaanse, 1996). Moreover, sediment burial, an important fate of pesticides in the sediment compartment, is not accounted in FOCUS-TOXSWA.
- 4) VVWM and FOCUS-TOXSWA commonly have two important modeling capabilities that are however absent in AGRO-2014. First, in both models, the aqueous volume of the water compartment can be varied as hydrologic conditions change. Meteorological data (e.g., precipitation and evaporation) as well as hydrology data (e.g., overland runoff derived from PRZM and baseflow etc.) are incorporated to specify the hydrologic conditions. Second, they also have the capability for simulating the formation and transformation of degradates in water and sediment.

In addition, there are four standard receiving waterbody scenarios formulated for aquatic risk assessments in support of regulatory decision making. They are the OPP standard farm pond, the FOCUS pond, the FOCUS ditch, and the FOCUS stream. The parameterization of these scenarios is also compared. Key variables required for defining a customized modeling scenario in the models are also identified.

6. Future work

The theoretical review shows that each of the three models has advantages and limitations. How these features affect the model output will be tested in the next stage of the study. Recommendations for model use will be given based on the theoretical review and the testing of model capabilities. Field conditions of receiving waterbodies in urban and agricultural settings in California will also be examined. The final goal of the study is to develop California-relevant receiving waterbody scenarios and parameterize the appropriate model(s) accordingly. A well-configured model is expected to provide conservative estimations of aquatic exposure for

pesticide product registration evaluation by DPR. Monitoring data and other field measurements will be used for model calibration and validation.

Acknowledgements

The author would like to acknowledge Kean S. Goh, Nan Singhasemanon and Yuzhou Luo for valuable discussions and comments in the initialization and development of this study.

References

- Adriaanse, P. (1996). Fate of Pesticides in Field Ditches: the TOXSWA Simulation Model. Report 90. DLO Winand Staring Centre for Integrate Land. *Soil and Water Research, Wageningen, The Netherlands*.
- Adriaanse, P., and Beltman, W. (2009). Transient water flow in the TOXSWA model (FOCUS) versions: concepts and mathematical description: Wettelijke Onderzoekstaken Natuur & Milieu.
- Adriaanse, P., Beltman, W., and van den Berg, F. (2014). Metabolite formation in water and in sediment in the TOXSWA model: theory and procedure for the upstream catchment of FOCUS streams: Alterra Wageningen UR.
- Adriaanse, P. I. (1997). Extended Summary SCI Pesticides Group Meeting Ecotoxicology of Organic Compounds in the Aquatic Environment. *Pesticide Science*, 49(2), 210-212.
- Arnot, J., Gouin, T., and Mackay, D. (2005). Development and application of models of chemical fate in Canada. *Practical Methods for Estimating Environmental Biodegradation Rates, Canadian Environmental Modelling Network, Trent University, Peterborough, Ontario, Canada*.
- Arnot, J. A., and Gobas, F. A. (2004). A food web bioaccumulation model for organic chemicals in aquatic ecosystems. *Environmental Toxicology and Chemistry*, 23(10), 2343-2355.
- Beltman, W., Ter Horst, M., Adriaanse, P., and De Jong, A. (2006). Manual of FOCUS TOXSWA version 2.2.
- Beltman, W., ter Horst, M., Adriaanse, P., de Jong, A., and Deneer, J. W. (2014). FOCUS_TOXSWA manual 4.4. 2: User's Guide version 4: Wettelijke Onderzoekstaken Natuur & Milieu.
- Burns, L. A. (2000). *Exposure Analysis Modeling System (EXMAS): User Manual and System Documentation*. US EPA/600/R-00/081.
- CDPR. (2013). *California Department of Pesticide Regulation The Pesticide Registration Branch Desk Manual*. (http://www.cdpr.ca.gov/docs/registration/manual/entire_manual.pdf). California Department of Pesticide Regulation, Sacramento, CA.
- CEMC. (2007). *User's Guide for CEMC_SFU_AGRO v1.2: The Combined Canadian Environmental Modelling Centre Water Quality Model and the Simon Fraser University Food Web Model*. http://www.trentu.ca/academic/aminss/envmodel/models/ftp/CEMC_SFU_AGRO_v1.2_Users_Guide.pdf. The Canadian Environmental Modelling Centre.
- FOCUS. (2015). *Generic guidance for FOCUS surface water Scenarios Version 1.4*. http://esdac.jrc.ec.europa.eu/public_path/projects_data/focus/sw/docs/Generic%20FOCUS_SWS_1.2.pdf.

- Fry, M., Milians, K., Young, D., and Zhong, H. (2014). *Surface Water Concentration Calculator User Manual*. USEPA/OPP 734f14001.
- Guo, L. (2002). *Evaluation of Environmental Models for Assessing Surface Water Contamination by Pesticides* (<http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/m041802.pdf>). California Department of Pesticide Regulation, Sacramento, CA.
- Holvoet, K. M., Seuntjens, P., and Vanrolleghem, P. A. (2007). Monitoring and modeling pesticide fate in surface waters at the catchment scale. *Ecological modelling*, 209(1), 53-64.
- Linders, J., Adriaanse, P., Allen, R., Capri, E., Gouy, V., Hollis, J., . . . Maier, W. (2003). FOCUS surface water scenarios in the EU evaluation process under 91/414/EEC. *Sanco/4802/2001-rev, 2*.
- Luo, Y. (2011). *Report 263: Review and Evaluation of Pesticide Modeling Approaches in Rice Paddies* (http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/report_263.pdf). California Department of Pesticide Regulation, Sacramento, CA.
- Luo, Y., Gao, Q., and Yang, X. (2007). Dynamic modeling of chemical fate and transport in multimedia environments at watershed scale—I: Theoretical considerations and model implementation. *Journal of environmental management*, 83(1), 44-55.
- Mackay, D. (2001). *Multimedia environmental models: the fugacity approach*: CRC press.
- Mackay, D., Joy, M., and Paterson, S. (1983a). A quantitative water, air, sediment interaction (QWASI) fugacity model for describing the fate of chemicals in lakes. *Chemosphere*, 12(7), 981-997.
- Mackay, D., Paterson, S., and Joy, M. (1983b). A quantitative water, air, sediment interaction (QWASI) fugacity model for describing the fate of chemicals in rivers. *Chemosphere*, 12(9), 1193-1208.
- Neitsch, S., Arnold, J., Kiniry, J., Williams, J., and King, K. (2005). SWAT theoretical documentation version 2005. *Soil and Water Research Laboratory, ARS, Temple Texas, USA*.
- Padilla, L. E., Winchell, M. F., and Jackson, S. H. (2015). Evaluation of AGRO-2014 for Predicting Hydrophobic Organic Chemical Concentrations in Ponds. *Journal of environmental quality*, 44(5), 1568-1578.
- Roller, J. A. t., Van den Berg, F., and Adriaanse, P. I. (2003). *Surface Water Scenarios Help (SWASH). Version 2.0. Technical Documentation version 1.3*. Alterra-rapport 508. Wageningen, Alterra Green World Research, the Netherlands. .
- SAP. (2008). *A Set of Scientific Issues Being Considered by the Environmental Protection Agency Regarding: Selected Issues Associated with the Risk Assessment Process for Pesticides with Persistent, Bioaccumulative, and Toxic Characteristics*. SAP Minutes No. 2009-01.
- USEPA. (2001). *Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual* (<http://water.epa.gov/polwaste/sediments/cs/upload/collectionmanual.pdf>). (EPA-823-B-01-002). U.S. Environmental Protection Agency, Office of Water.
- USEPA. (2008). *White Paper on Methods for Assessing Ecological Risks of Pesticides with Persistent, Bioaccumulative and Toxic Characteristics Submitted to the FIFRA Scientific Advisory Panel For Review and Comment*. Rep. EPA-HQ-OPP-2008-0550-0003,

- Environmental Fate and Effects Division, Office of Pesticide Programs, USEPA, Washington, DC.
- Van den Berg, F., Adriaanse, P. I., and Roller, J. A. t. (2003). *Surface Water Scenarios Help (SWASH). Version 2.0. User's Guide version 1.3*. Alterra-rapport 507. Wageningen, Alterra Green World Research, the Netherlands.
- Van den Berg, F., Adriaanse, P. I., Roller, J. A. t., Vulto, V. C., and Groenwold, J. G. (2008). *Surface Water Scenarios Help (SWASH) Manual 2.1. User's Guide version 2*. Werkdocument 83. Wageningen, The Netherlands.
- Xie, Y. (2014). *Study 293: Protocol to Develop a California-Based Water Quality Model for Pesticide Registration Evaluation*. (http://www.cdpr.ca.gov/docs/emon/pubs/protocol/study293protocol_final.pdf), California Department of Pesticide Regulation, Sacramento, CA).
- Young, D. F. (2014). *The Variable Volume Water Model*. (USEPA/OPP 734f14003). USEPA Office of Pesticide Programs, Washington, D.C.
- Young, D. F., and Fry, M. M. (2014). *PRZM5 A Model for Predicting Pesticide in Runoff, Erosion, and Leachate: User Manual*. (USEPA/OPP 734F14002). USEPA Office of Pesticide Programs, Washington, D.C.