

# Evaluation of AGRO-2014 for Predicting Hydrophobic Organic Chemical Concentrations in Ponds

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## Abstract

Highly hydrophobic organic chemicals (HOCs), like pyrethroids, adsorb strongly to eroded soil and suspended sediment. Therefore, total suspended solids (TSS) concentration in the water column of receiving waters is important for determining the proportion of chemical in the sediment-sorbed vs. the dissolved (bioavailable) state. However, most current regulatory exposure models, such as the Exposure Analysis Modeling System (EXAMS) and Variable Volume Water Model (VVWM), do not include dynamic modeling of TSS. The objective of this study is to compare the performance of those models for simulating observed pesticide concentrations in small water bodies with an updated version of the AGRO model, called AGRO-2014, which includes dynamic sediment processes. The paper also evaluates the importance of explicitly modeling sediment dynamics for HOCs. We calibrated AGRO-2014 for small, static, water bodies using published pyrethroid mesocosm data. To improve the basis for intermodel comparison, AGRO-2014 includes the same algorithm for temperature-dependent degradation found in EXAMS and VVWM, direct acceptance of organic C partition coefficient ( $K_{oc}$ ) inputs, and acceptance of user-defined pesticide loading durations. Differences in sediment processes in AGRO-2014, EXAMS, and VVWM significantly affected predicted concentrations of high- $K_{oc}$  compounds for standardized loading scenarios, whereas differences between the models were less evident for compounds with lower sorption to sediments. AGRO-2014 simulations of drift and slurry pyrethroid applications to ponds closely matched observed concentrations, while EXAMS and VVWM simulations underestimated the observations. The publicly available AGRO-2014 model offers improvements over other models for predicting concentrations of HOC compounds in small water bodies.

## Core Ideas

- Novel comparison of three receiving-water models for predicting pesticide exposure.
- Comparison of model predictions to mesocosm observed pyrethroid concentrations.
- Evaluates importance of explicitly modeling sediment dynamics for hydrophobic organic chemicals.
- Dynamic sediment processes significantly affected model results of high- $K_{oc}$  chemicals.
- Introduction of the refined AGRO-2014 model for pesticide exposure modeling.

THE EXCEPTIONALLY HIGH adsorption characteristics and corresponding low water solubilities of highly hydrophobic organic chemicals (HOCs), such as synthetic pyrethroids, dominate their mobility and effects in the environment. These molecules adsorb extensively to the organic C (OC) of eroded soil as well as the OC in receiving waters including suspended sediment and bed sediment OC, phytoplankton and plant biomass, and freely dissolved OC (DOC) in the water column. Therefore, the off-target transport of pyrethroid insecticides to small receiving waters is sensitive to erosion. In addition, the effect of erosion on concentrations of total suspended solids (TSS) influences HOC concentrations in runoff and receiving waters. Prediction of the concentrations of HOCs in receiving waters and especially the proportion of HOCs in sediment-sorbed vs. water-dissolved states is critical to understanding bioavailability of chemicals regulated under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). However, FIFRA regulatory aquatic exposure models, such as the Exposure Analysis Modeling System (EXAMS, version 2.98.04; Burns, 2004) and Variable Volume Water Model (VVWM, from version 1.106 of the Surface Water Concentration Calculator; Young, 2014) currently do not account for the effect of varying TSS levels on HOC sediment–water partitioning.

The AGRO model, developed at the Canadian Environmental Modeling Centre (CEMC, 2007), is a well-established water quality model with a dynamic sediment mass balance algorithm capable of simulating the effect of daily fluctuations in TSS on HOC concentrations. It combines the CEMC Quantitative Water, Air, Sediment Interaction (QWASI) fugacity model (Mackay, et al., 1983a; Mackay, 2001) with the Simon Fraser University bioaccumulation food web model (Campfens and Mackay, 1997; Arnot and Gobas, 2004). The QWASI model, which defines AGRO's core water, air, and sediment processes, has been used to assess chemical dynamics in lakes and rivers (Mackay et al., 1983b; Mackay and Diamond, 1989; Mackay and Hickie, 2000; Arnot and Gobas, 2004; Webster et al., 2006). The AGRO model was

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**Abbreviations:** CEMC, Canadian Environmental Modeling Centre; DOC, dissolved organic C; EXAMS, Exposure Analysis Modeling System; FIFRA, Federal Insecticide, Fungicide, and Rodenticide Act; HOC, hydrophobic organic chemical;  $K_{ow}$ , organic C partition coefficient;  $K_{ow}$ , octanol-water partition coefficient; OC, organic C; PRZM, Pesticide Root Zone Model; QWASI, Quantitative Water, Air, Sediment Interaction; SAP, Scientific Advisory Panel; TSS, total suspended solids; VVWM, Variable Volume Water Model.

evaluated by a 2008 Scientific Advisory Panel (SAP) as part of their response to questions from the USEPA Office of Pesticide Programs related to risk assessment for pesticides with persistent, bioaccumulative and toxic characteristics (SAP, 2008; USEPA, 2008). The SAP made recommendations for exposure modeling to include sediment burial either implicitly or explicitly as a mechanism for system pesticide losses and to avoid lumped parameter modeling of benthic-limnetic pesticide mixing (SAP, 2008, p. 32), both of which are satisfied by AGRO. The SAP also commented that AGRO's conceptual model for the formation of a pure chemical reservoir when solubility is exceeded and its redissolution once chemical concentrations fall below saturation is correct (SAP, 2008, p. 35). Before the SAP, a sensitivity analysis of AGRO model parameters (A. Wadley, personal communication, 2007) and two reviews of AGRO model code (T. Estes, personal communication, 2007) were conducted and submitted to USEPA. AGRO has also been evaluated by the Canadian Environmental Modeling Network (Webster et al., 2005).

Key water, sediment, and pesticide transport processes included in the EXAMS and VVWM models, as they have been conceptualized for regulatory modeling, and the AGRO conceptual model are depicted in the schematic of Fig. 1 with constituent tables comparing and contrasting model features. Each of the models is a two-compartment box model with constant-volume limnetic (i.e., water column) and benthic compartments. It is possible to configure EXAMS with multiple limnetic and benthic boxes; however, the two-box configuration used in regulatory modeling is the basis for comparison in this study. Along similar lines, VVWM may be run in a varying-volume mode, but for the purposes of comparing sediment processes only constant volume simulations were conducted in this study. All three models also apply equilibrium partitioning of chemical mass into subcompartments. Benthic subcompartments in all models include sediment-sorbed and pore-water dissolved chemical. Limnetic subcompartments include dissolved and TSS-sorbed chemical. The EXAMS and VVWM models also have plant or phytoplankton biomass and DOC

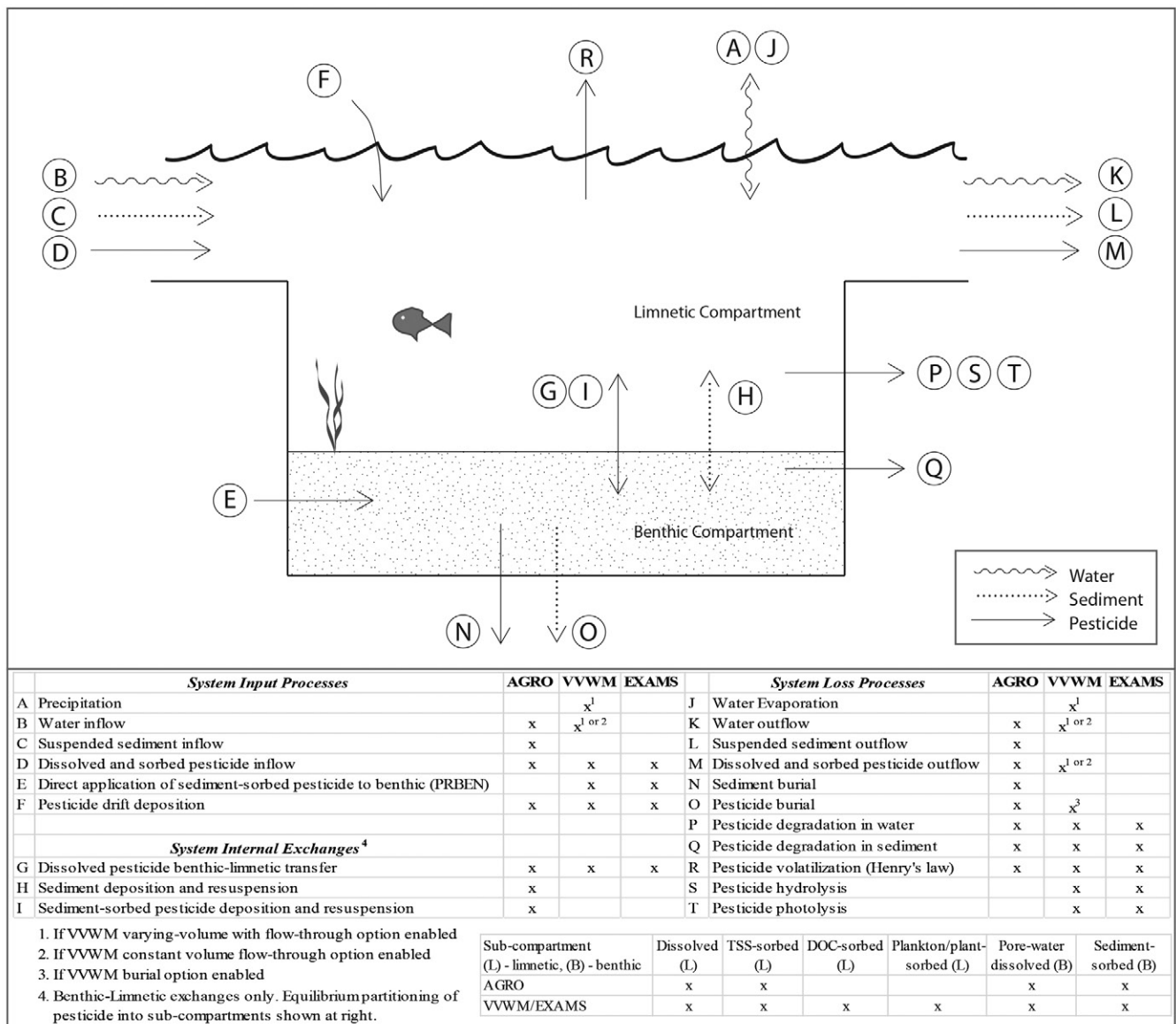


Fig. 1. Overview of AGRO, Variable Volume Water Model (VVWM), and Exposure Analysis Modeling System (EXAMS) conceptual models and comparison of key processes as they are configured for regulatory modeling.

subcompartments. AGRO, on the other hand, simulates TSS and DOC-sorbed chemical as one lumped subcompartment and does not simulate partitioning to plants or plankton.

AGRO is the only model of the three that explicitly simulates the time-varying sediment stream including inflow of eroded soil suspended in runoff, outflow, internal deposition and resuspension, and burial. As such, it is the only model in which the benthic–limnetic exchange of pesticide adsorbed to suspended sediment can be explicitly simulated. Details on the equations governing AGRO’s sediment dynamics are provided in the online supplemental material. The differences in key processes between the models are summarized in Table 1. As highlighted in the table, the concentration of TSS is held static at 30 mg L<sup>-1</sup> in EXAMS and VVWM (a FIFRA regulatory modeling parameter setting), while the AGRO concentration varies from a user-specified baseline TSS concentration depending on erosion inputs. In EXAMS and VVWM, lumped dissolved and sediment-sorbed chemical is exchanged implicitly between limnetic and benthic zones by a bulk diffusive mass transfer process, and direct transfer of a constant fraction of the sediment-sorbed pesticide inflow into the benthic compartment (set at 50% for regulatory modeling). AGRO, on the other hand, maintains separate diffusive and sediment-sorbed internal mixing processes. AGRO makes use of a sediment settling-time parameter not used in the other models because they do not simulate sediment deposition and resuspension. AGRO also simulates chemical in excess of the solubility limit as a separate reserve in the water column. As the dissolved limnetic concentration declines below saturation, chemical redissolves from this phase into the water column. In

contrast, EXAMS and VVWM allow dissolved concentrations to exceed solubility limits.

While AGRO’s dynamic sediment processes and model for chemical in excess of solubility provide a strong foundation for the prediction of HOC concentrations and partitioning, several modifications to the model were necessary to give it a better basis for comparison with the regulatory models. This resulted in a refined version of AGRO, called AGRO-2014, calibrated to observed data for the small, static water bodies used in regulatory modeling scenarios and updated to include the same algorithm for temperature dependent degradation found in EXAMS and VVWM, accept the organic C partition coefficient ( $K_{oc}$ ) as a direct input, and accept a user-defined duration of pesticide loading events. Changes made in developing AGRO-2014 only impacted the QWASI water quality part of the model. The food-web model component remained unmodified and retained all of the original functionality.

The objective of this paper is to compare the performance of EXAMS and VVWM with AGRO-2014 for simulating observed pesticide concentrations in small water bodies and to evaluate the importance of explicitly modeling sediment dynamics for HOCs. To accomplish this objective, intermodel comparisons were made for pyrethroid mesocosm experiments with different exposure pathways and for hypothetical agricultural field loadings with varied environmental conditions and chemical properties including both high and low  $K_{oc}$  compounds.

**Table 1. Comparison of significant model features as they are configured for regulatory modeling.**

Model attribute	EXAMS†	VVWM‡	AGRO	AGRO-2014
Suspended sediment concentration in water column	30 mg L <sup>-1</sup>	30 mg L <sup>-1</sup>	Varies with erosion inputs (baseline or minimum 30 mg L <sup>-1</sup> )	Same as AGRO
Chemical burial in deep bed sediment	None	Optional dynamic process varying with erosion inputs	Dynamic process varying with erosion inputs	Same as AGRO
Sediment or sorbed-chemical deposition to active bed	Chemical only modeled by PRBEN parameter, typically 50% of incoming sorbed chemical	Chemical only modeled by PRBEN parameter, typically 50% of incoming sorbed chemical	Chemical and Sediment together at rate determined by erosion inputs and settling time	Same as AGRO
Sediment settling time	N/A	N/A	7 d (90%)	3.4 d (90%)
Sediment, water, and chemical overflow	None	Depends on inflow rate and pond depth	Equal to inflow rate with chemical overflow at limnetic concentrations	Same as AGRO
Benthic–limnetic diffusive chemical exchange	Bulk process representing dissolved plus sediment-sorbed exchange	Bulk process representing dissolved plus sediment-sorbed exchange	Dissolved exchange only (0.0004 m h <sup>-1</sup> diffusion velocity)	Dissolved exchange only (0.05 m h <sup>-1</sup> diffusion velocity)
Concentration over solubility threshold	Dissolved concentrations permitted to exceed solubility	Dissolved concentrations permitted to exceed solubility	Excess chemical is stored in a separate reservoir until dissolved concentrations decrease	Same as AGRO
Chemical degradation rates as function of temperature	Yes	Yes	No	Yes
$K_{oc}$ parameter§	$K_{oc}$	$K_{oc}$	Derived from log( $K_{ow}$ )¶	$K_{oc}$ or derived from log( $K_{ow}$ )
Spray drift and runoff entry time	First time step of the simulation day	First time step of the simulation day	Over 24 simulation hours	Drift over two simulation hours; runoff over six simulation hours

† EXAMS, Exposure Analysis Modeling System.

‡ VVWM, Variable Volume Water Model.

§  $K_{oc}$  organic C partition coefficient.

¶  $K_{ow}$  octanol-water partition coefficient.

# Materials and Methods

## AGRO-2014

The EXAMS and VVWM models were compared with AGRO-2014, a refined version of the original AGRO model in which parameter calibration and programming changes were made to improve the fit to observed data and to improve the basis for comparison of the three models. The modified features of AGRO-2014 are highlighted and compared with the original AGRO, EXAMS, and VVWM in Table 1. As summarized in the table, the sediment processes in AGRO and AGRO-2014 are largely the same with the exception of the sediment settling time. The process for forming a separate reservoir of pure chemical when the dissolved pesticide concentration exceeds the solubility in water also remains unchanged. Two parameters, sediment settling time and benthic–limnetic diffusive exchange coefficient (diffusion velocity), were updated through calibration. Additional modifications to the degradation routine and pesticide and  $K_{oc}$  input options were made to improve physical realism and make AGRO more comparable with EXAMS and VVWM.

The settling-time parameter determines the residence time of excess suspended sediment (TSS above the baseline) in the water body after erosion events. Based on the average of observed settling velocities for fine clays ( $0.3 \text{ m d}^{-1}$ ) and coarse silt ( $30 \text{ m d}^{-1}$ ) reported by Chapra (1997, Table 17.3) and a 2-m pond depth, the settling-time parameter was lowered from 7 to 3.4 d to better represent settling in small water bodies. Once any excess suspended sediment has settled, AGRO-2014 maintains the same baseline TSS concentration as EXAMS and VVWM of  $30 \text{ mg L}^{-1}$  for regulatory scenarios, although this constant may be set to other values as determined by the user.

The diffusive exchange coefficient determines the dissipation of dissolved pesticide from the limnetic compartment to the benthic at times when the presence of TSS is low and pesticide mixing, as a result of sediment deposition and resuspension, is minimal. These conditions often apply when spray drift rather than runoff or erosion is the mechanism for chemical entry to the pond. Therefore, calibration of this coefficient was based on a pyrethroid spray drift mesocosm study with high-quality time-series data and multiple replicates conducted by Leistra et al. (2004). The Leistra experiment simulated spray drift events with the active ingredient lambda-cyhalothrin in replicate  $0.43 \text{ m}^3$  aquatic mesocosms with varying densities of plant material. The AGRO-2014, EXAMS, and VVWM model parameters were configured to match the chemical and environmental properties of the experiment as summarized in Table 2. The bulk limnetic concentrations (i.e., the water column including both dissolved and sediment-sorbed lambda-cyhalothrin) were compared for all models and experimental results. As shown in Fig. 2, the uncalibrated AGRO-2014, with a diffusive exchange coefficient based on molecular diffusion ( $0.0004 \text{ m h}^{-1}$  effective diffusion velocity), exhibited much slower than measured dissipation from the limnetic compartment; chemical persisted longer than all experiments and all other models. The poor fit of the uncalibrated coefficient indicated that an exchange coefficient with a magnitude representative of mixing by molecular diffusion was too low. The

magnitude of the exchange coefficient needed to be increased, effectively parameterizing additional sources of mixing. There was variability in the TSS concentration among the replicate mesocosms, so AGRO-2014 simulations were conducted for a range of TSS and exchange coefficients. Concentrations are shown in Fig. 2 for the calibrated AGRO-2014 with an effective diffusion velocity of  $0.05 \text{ m h}^{-1}$  at upper ( $15 \text{ mg L}^{-1}$ ) and lower ( $5 \text{ mg L}^{-1}$ ) TSS concentrations compared with the other models and observations. The calibrated fit at both TSS concentrations slightly overpredicted most of the measured concentrations in the first 20 h after the dose. The AGRO-2014 response curve for the higher TSS concentration predicted slightly higher concentrations than the maximum measured water column concentrations at 24 and 72 h while the AGRO-2014 response corresponding to the lower TSS concentration fell below the 24- and 72-h minimum measured concentrations and thus represented a considerable improvement over both EXAMS and VVWM. The EXAMS and VVWM responses were fairly insensitive to variation in TSS concentration and, at both 15 and  $5 \text{ mg L}^{-1}$  TSS, underestimated the observed minimum concentrations at all times. Under the spray drift conditions of this experiment, with constant TSS concentration in each simulation, the main difference in the models is the magnitude of the diffusion velocity. The greater diffusion velocity of AGRO-2014 leads to greater sensitivity to changes in the gradient of dissolved chemical at the benthic–limnetic interface and, therefore, greater sensitivity to TSS concentration (TSS concentration affects the dissolved chemical gradient because it is a factor in equilibrium partitioning of dissolved and adsorbed chemical in the water column.).

Besides calibration of the settling time and exchange coefficient, several modifications were made to improve physical realism and make AGRO-2014 more comparable with EXAMS and VVWM. The model for degradation rates in AGRO-2014 was improved to include adjustment of the rates for differences between the environmental and laboratory experimental temperatures. The temperature adjustment equations used currently in EXAMS and VVWM were incorporated into the AGRO-2014 code to account for the effects of seasonal and year-to-year variation in environmental temperatures on degradation.

Additionally, the period of time over which chemical and sediment inputs due to spray drift and runoff enter the system was made more physically realistic in AGRO-2014. Chemical inputs were originally distributed evenly throughout the day, resulting in smaller subdaily peak concentrations than if the chemical input arrived in just a few hours or minutes as occurs with spray drift events, for example. The AGRO-2014 code was modified to allow users to specify chemical and sediment input event durations to appropriately match storm events, field applications, or experimental input durations, resulting in more accurate simulation of peak concentrations. This also allowed AGRO-2014 to be configured with durations more consistent with the instantaneous runoff inputs applied during the first 1-h time step of the simulation day in EXAMS and VVWM.

The organic C partition coefficient was also added as a direct user input to AGRO-2014 to allow the user to take advantage of compound-specific experimental measurements of  $K_{oc}$ , such as those available for pesticide active ingredients. AGRO previously

only permitted user input of the logarithm of the octanol-water partition coefficient ( $K_{ow}$ ), an important input to the food web model. The  $K_{oc}$  used in QWASI was then calculated from a regression relationship with  $\log(K_{ow})$ . AGRO-2014 allows for the best use of available data by letting the user specify  $K_{oc}$  and  $\log(K_{ow})$  independently for the two different components of the model.

To accommodate the model improvements described above, additional changes were made to the AGRO-2014 user interface, such as the addition of inputs (e.g.,  $K_{oc}$ , drift, and runoff duration) and options to apply or omit certain modifications. For improved tracking of the chemical mass balance in the system, several additional variables were added to the reported outputs. The AGRO-2014 model has been documented in two technical reports (Padilla and Winchell, 2014; Desmarteau and Ritter,

2014) and is publically available at <http://www.stone-env.com/agchem/agers.php#agdownload>.

## Pyrethroid Mesocosm Validation Experiments

To examine the impact of the different sediment processes, AGRO-2014, EXAMS, and VVWM were parameterized to simulate the experimental conditions in aquatic mesocosms investigating the ecological impacts of pyrethroid entry by drift and runoff or erosion and results were compared with observed data. The goal of this comparison was to show how well the models simulated the different processes that are active for different input sources. This comparison also targeted one of the SAP long-term recommendations for improving USEPA's current modeling approach, that is, to conduct better validation of model predictions against field measurements (SAP, 2008, p. 35). The Springer et al. (1996) pond mesocosm with active ingredient

**Table 2. Chemical and environmental properties used in model simulations.**

Simulation	Leistra et al. (2004)	Springer et al. (1996)	Springer et al. (1996)	USEPA standard scenarios
Purpose	Observed data calibration	Observed data validation	Observed data validation	Standardized agricultural field loadings
Exposure pathways	Drift	Drift	Slurry (erosion)	PRZM† simulated drift and runoff
Chemical	Lambda-cyhalothrin	Fenpropathrin	Fenpropathrin	Hypothetical test chemical
Water degradation half-life (d)	56.2‡	34.1‡	34.1‡	12
Sediment degradation half-life (d)	100‡	169‡	169‡	70
$K_{oc}$ (ml g <sup>-1</sup> )	2,941,300§	1,029,873¶	1,029,873¶	50; 5,000; 500,000; or 5 million
Solubility (g m <sup>-3</sup> )	0.005#	0.0103††	0.0103††	0.05
Molar mass (g mol <sup>-1</sup> )	449.9#	349.4††	349.4††	420
Henry's Law constant (atm-m <sup>3</sup> mol <sup>-1</sup> )	$1.90 \times 10^{-7}$ #	$6.20 \times 10^{-7}$ ††	$6.20 \times 10^{-7}$ ††	$4.80 \times 10^{-7}$
Vapor pressure (pa)	$2.08 \times 10^{-7}$ #	$1.87 \times 10^{-6}$ ††	$1.87 \times 10^{-6}$ ††	$2.00 \times 10^{-6}$
Dose or application mass	$1.08 \times 10^{-5}$ g	1.061 g	1.82 g fenpropathrin, 30 L water, 118 kg sediment	1.12 g via drift entry six times per year‡‡, plus varied mass via runoff or erosion dependent on weather
Surface area (m <sup>2</sup> )	0.865	960	960	10,000
Volume (m <sup>3</sup> )	0.43	870	870	20,000
Baseline TSS concentration (mg L <sup>-1</sup> )§§	5 to 16	no data, defaults assumed	no data, defaults assumed	30
Atmospheric temperature (°C)	15.1	20	20	Varied daily with weather
Inflow or outflow	negligible	negligible	negligible	Varied daily with runoff, min. 5 m s <sup>-1</sup> (AGRO-2014); none (VVWM, EXAMS)
Organic C fraction of solids in bed sediment	0.04	0.04	0.04	0.04
Organic C fraction of solids in TSS	0.067 (AGRO-2014)¶¶ 0.04 (EXAMS, VVWM)	0.067 (AGRO-2014)¶¶ 0.04 (EXAMS, VVWM)	0.067 (AGRO-2014)¶¶ 0.04 (EXAMS, VVWM)	0.067 (AGRO-2014)¶¶ 0.04 (EXAMS, VVWM)

† PRZM, pesticide root zone model.

‡ Average of values from Meyer et al. (2013) as recalculated by Melendez (2013).

§ Mean corrected solid-phase microextraction (SPME) value (B.J. Mason, personal communication, March 2014).

¶ Based on Mackay regression equation:  $K_{oc} = 0.41 \times (10^{\log(K_{ow})})$  (Mackay, 2001) with  $\log(K_{ow})$  from Dix (2014).

# Values from Melendez (2010a).

†† Values from Melendez (2010b).

‡‡ Drift mass was calculated as 2% of 0.056 kg ha<sup>-1</sup> application rate. Applications began 26 Feb. 1961 with a 7 d interval for California onion and 11 May 1961 with a 5 d interval for Mississippi cotton. Applications were repeated annually for 30 yr. Properties not listed were unchanged from their regulatory default settings.

§§ TSS, total suspended solids.

¶¶ Organic C fraction of TSS was slightly higher in AGRO-2014 than EXAMS and VVWM to account for the effect of dissolved organic C and plant compartments that are simulated in EXAMS and VVWM but are not included in AGRO-2014.

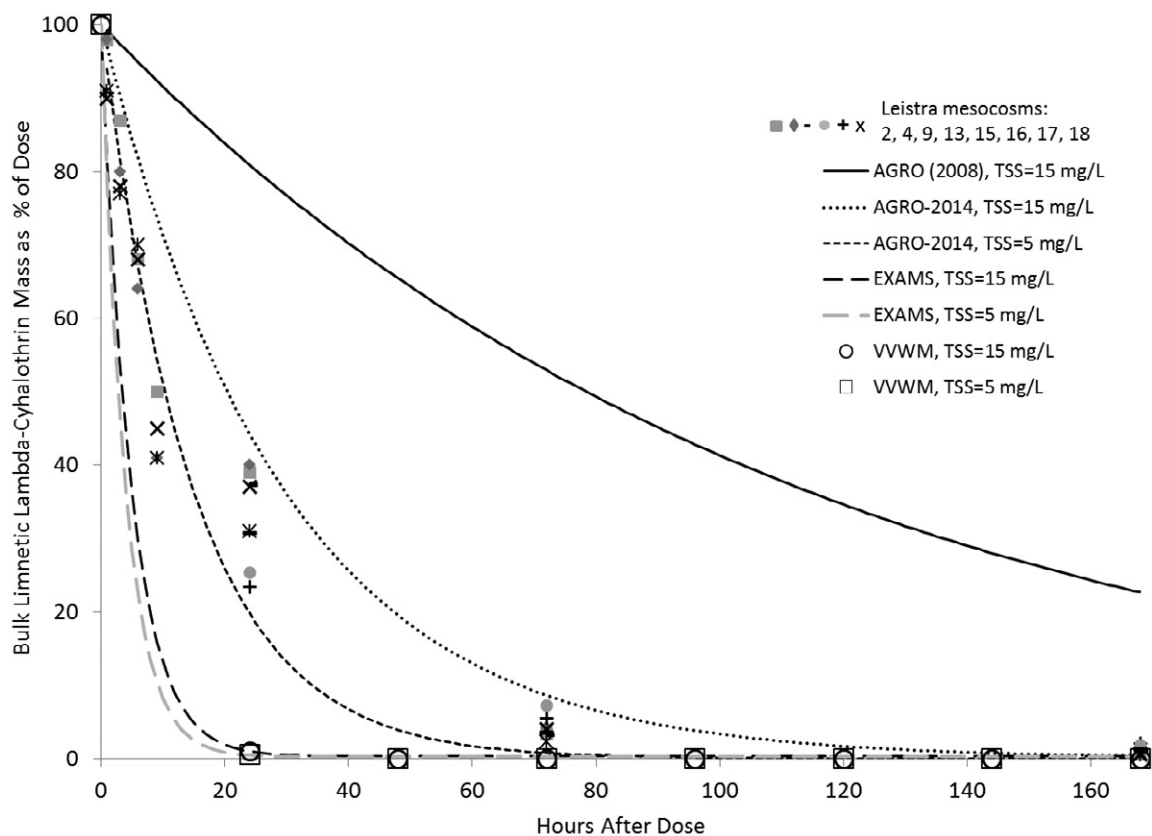


Fig. 2. Comparison of model simulated bulk limnetic (i.e., water column) pyrethroid mass to Leistra et al. (2004) measurements for AGRO-2014 benthic-limnetic exchange coefficient calibration.

fenpropathrin was selected for comparison because time-series concentration data was available for both drift and runoff or erosion input events. Spray drift events were simulated by adding a solution of fenpropathrin and water to the mesocosm water column. Runoff or erosion events were simulated by adding a slurry of sediment, water, and fenpropathrin to the water column. The first drift event and the final slurry event were selected for evaluation because chemical concentration measurements were collected daily for at least 1 wk following these events. Chemical and environmental parameters used in the model simulations are provided in Table 2, including degradation rates,  $K_{oc}$ , solubility, application mass and method, pond size, TSS concentration, and temperature. When no experimental information was available, model parameters were unchanged from regulatory modeling default values. No further model calibration was conducted. The model-predicted concentrations were compared with the available observed bulk limnetic concentrations. Differences in water-sediment partitioning and losses due to degradation were also compared among the three models.

### Model Comparison for Standardized Loadings

AGRO, EXAMS, and VVWM simulations were also compared in response to spray drift and runoff loadings generated by applications of hypothetical compounds to theoretical agricultural fields. The objective of this work was to compare model behavior for a range of chemical loadings resulting from different off-site transport mechanisms and temporal patterns and for a range of  $K_{oc}$  values, including the high values typical of pyrethroids but also for more typical compounds with much

lower  $K_{oc}$ . Simulations were conducted for two pesticide loading scenarios associated with high-vulnerability field conditions for onion (*Allium cepa* L.) and cotton (*Gossypium hirsutum* L.) crops grown in California and Mississippi, respectively. Pesticide loadings to the receiving waters via storm-induced runoff and erosion were simulated by the Pesticide Root Zone Model (PRZM, version 3.12.2) (Suarez, 2005), which may be coupled to each of the three aquatic models. PRZM provides runoff, eroded soil, and chemical loads (soluble and sorbed) as inputs to the receiving water models. Spray drift chemical loadings were calculated assuming that 2% of the chemical application rate was deposited directly on the receiving water. The hypothetical 2% spray drift loading was selected to approximate the aerial drift deposition load used in recent pyrethroid risk assessments (1.97%). The weather, crop, and soil parameter inputs required to run PRZM for the comparisons of this study were those specified in the USEPA's standard Mississippi cotton and California onion PRZM regulatory scenarios (available online at [http://www.epa.gov/oppefed1/models/water/water\\_models\\_archive.htm](http://www.epa.gov/oppefed1/models/water/water_models_archive.htm)). These two scenarios were selected because they have significantly different weather and runoff patterns. Loadings in the California onion scenario are largely driven by spray drift because of the relatively dry weather conditions and corresponding minimal runoff simulated for the San Joaquin Valley. In comparison, the wet weather conditions typical in central Mississippi lead to significant runoff and erosion events as the primary pathway for chemical off-target transport. Simulations were conducted for both scenarios for four hypothetical chemicals with  $K_{oc}$  values of 50, 5000, 500,000, and 5 million mL  $g^{-1}$  and other chemical and

environmental properties as summarized in Table 2. Predictions of aquatic concentrations following field applications of these hypothetical chemicals and subsequent storm events were compared to evaluate differences in the exchanges and transport of the chemical within the receiving water.

## Results

### Pyrethroid Mesocosm Validation Experiments

Model results compared with the fenpropathrin pond mesocosm data are shown in Fig. 3 for the drift experiment (panel A) and the slurry experiment (panel B). Results are compared for the decline of total fenpropathrin mass in the limnetic zone as a percentage of the initial dose over a 1-wk period. The observed limnetic dissipation rate in the slurry experiment was calculated to be twice as fast as in the drift experiment. Based on fitting a linear, first-order, exponential model to both data-sets, the half-life of the limnetic zone dissipation for the slurry experiment was estimated to be 0.7 d, while the half-life for the drift experiment was 1.4 d. Although there were differences in the initial observed and predicted concentrations within a few hours of the dose, with AGRO-2014 over predicting the measured maximum concentration, AGRO-2014 simulated the two different observed dissipation rates very well. The observed half-lives were in excellent agreement with half-lives calculated from the AGRO-2014 predictions for each respective experiment. In contrast, the dissipation rates predicted by EXAMS and VVWM were faster than the measured values in both experiments. The half-lives calculated for EXAMS (0.3 d) and VVWM (0.22 d) were the same for the two experiments; there was no differentiation in the rates for slurry compared with drift. The only component of the model response that

changed was the initial concentration due to the instantaneous transfer of 50% of the incoming sediment-sorbed chemical to the benthic zone.

To further evaluate the effect of the dynamic TSS in AGRO-2014, the slurry experiment was repeated while ignoring the measured values and holding the TSS levels constant at the default 30 mg L<sup>-1</sup> as in EXAMS and VVWM. The response is compared with the dynamic run, in which TSS concentrations initially became elevated over 135 mg L<sup>-1</sup> in response to simulating the addition of 118 kg of sediment in the slurry (Fig. 3B). The AGRO-2014 run with constant TSS had the same slower limnetic dissipation half-life as the drift experiment of 1.4 d and was not in good agreement with the observed data, indicating the importance of including dynamic sediment algorithms.

A snapshot of the mass balance 1 d after the dose shows how differences in the models' sediment processes translate to differences in fenpropathrin partitioning in each experiment (Fig. 4). In both experiments, AGRO-2014 retained more fenpropathrin in the limnetic zone than the other models, which is consistent with the time-series comparison (Fig. 3) that showed the other models overestimated the limnetic dissipation rate. This higher proportion of chemical in the limnetic zone had a small but noticeable effect on overall system losses due to degradation as seen by column total masses slightly less than 100% in Fig. 4. Degradation was generally minimal in all models just 1 d after application; however, AGRO-2014, with the most limnetic-zone chemical, predicted the greatest degradation due to the faster degradation rate of fenpropathrin in water (34.1 d half-life) compared with sediment (169 d half-life).

After 24 h, in all of the models, there was less fenpropathrin in the limnetic zone and more in the benthic zone for the slurry application than the drift application. The mechanisms

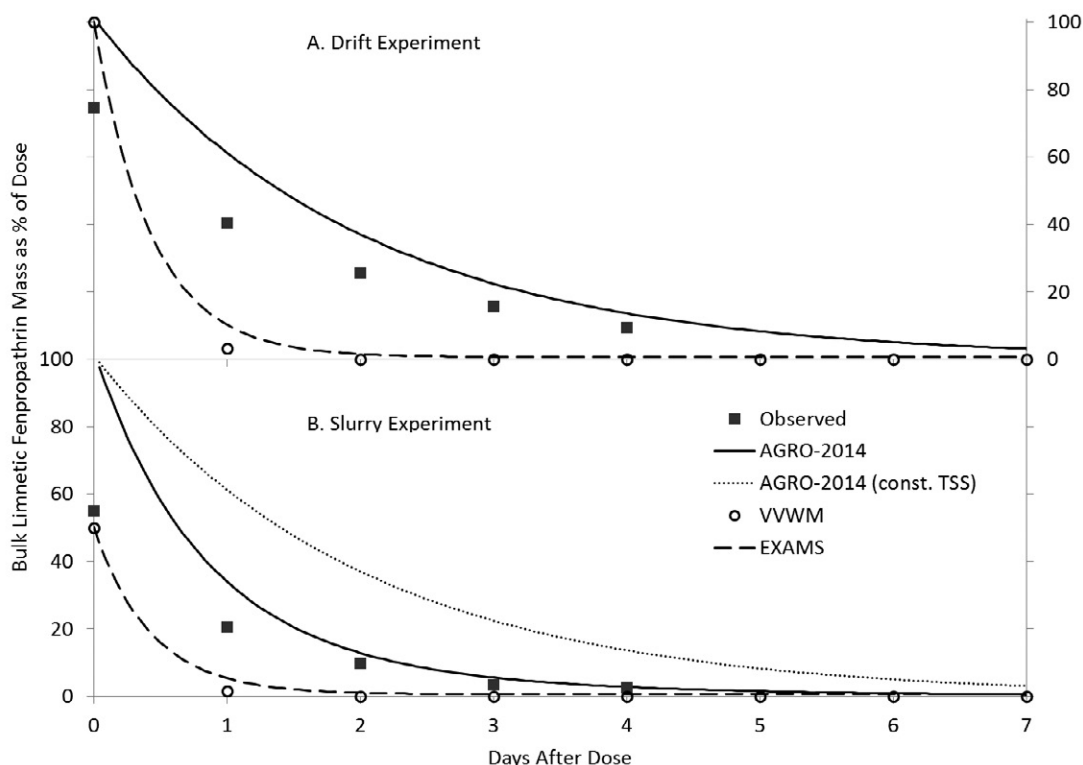


Fig. 3. Comparison of model predicted bulk limnetic pyrethroid mass to Springer et al. (1996) measurements for drift and slurry mesocosm exposure experiments.

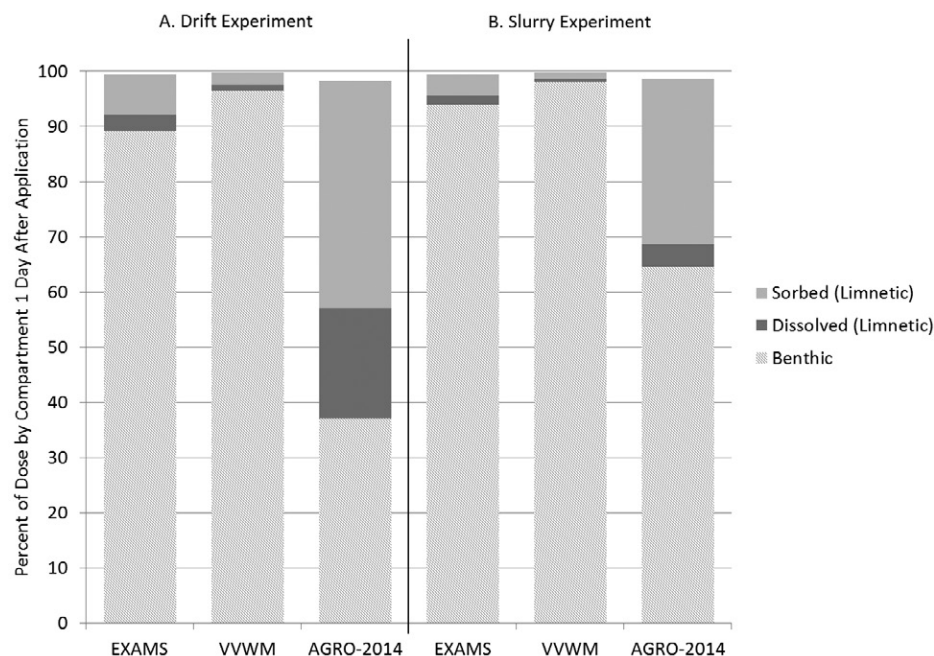


Fig. 4. Comparison of model-predicted mass balances 1 d after fenpropathrin drift or slurry applications.

responsible for this difference were the instantaneous fraction (PRBEN) delivered to the benthic compartment in EXAMS and VVWM and the dynamic settling of sediment and associated adsorbed chemical in AGRO-2014. In the drift experiment, those mechanisms were inactive, so fenpropathrin remained in the limnetic compartment longer in all models, dissipating at the rate of the models' respective fixed, lumped, diffusive, benthic–limnetic exchange processes. In all of the models, and both slurry and drift experiments, there was more fenpropathrin adsorbed to dissolved and particulate organic C and suspended sediments than there was freely dissolved fenpropathrin as a result of the very high  $K_{oc}$  and hydrophobic nature of the chemical. The ratio of dissolved to sorbed chemical was constant for EXAMS and VVWM but varied proportional to the concentration of TSS above the nominal 30 mg L<sup>-1</sup> for AGRO-2014.

### Model Comparison for Standardized Loadings

Similar to the different responses seen for the mesocosm spray drift and slurry modeling, the models exhibited different responses to those inputs in the simulations with standardized loadings with a high- $K_{oc}$  hypothetical compound. Depending on the amount of eroded sediment simulated as leaving the agricultural fields during runoff events, the model-predicted concentrations in the receiving waters varied widely because of differences in the sediment processes. A series of drift and erosion events from the Mississippi cotton scenario illustrates how the models' different behaviors impacted predictions of the freely dissolved, bioavailable chemical concentrations for the hypothetical HOC with  $K_{oc}$  of 5 million mL g<sup>-1</sup> (Fig. 5).

Initially, the modeled receiving waters were exposed to spray drift beginning 11 May and repeated for six pesticide applications every 5 d (Fig. 5, top panel). With the same baseline TSS concentration of 30 mg L<sup>-1</sup>, all models exhibited a similar response to the first event (Fig. 5, bottom panel, Event A), where AGRO-2014 was the most conservative, followed by EXAMS. Between the first and second pesticide application, the models

received an eroded sediment load of 144 t, carrying adsorbed pesticide, from a significant runoff event (Event B). The mass of pesticide present in the system increased in all models, and the TSS concentration increased with the eroded sediment entry in AGRO-2014 only. The elevated amount of TSS resulted in increased pesticide adsorption to suspended sediment and lowered the concentration of freely-dissolved pesticide in AGRO-2014 compared with EXAMS and VVWM. Similar behavior was seen several days later when significant runoff events on three consecutive days introduced additional pesticide and 341 t of eroded sediment into the AGRO-2014 receiving water. In AGRO-2014, the dissolved pesticide concentration decreased even more in response to the bigger sediment load, as both chemical already in the water body from the previous drift event and new chemical that arrived in the runoff adsorbed to elevated levels of TSS. After several dry weather days, the excess TSS and adsorbed pesticide in AGRO-2014 settled to the sediment bed, and the TSS concentration returned to the base 30 mg L<sup>-1</sup> concentration by 4 June. Therefore, with TSS concentration equal to the constant baseline concentrations of EXAMS and VVWM again, subsequent spray drift exposures resulted in similar dissolved pesticide concentrations in AGRO-2014 relative to the other models (Fig. 5, bottom panel, Event C).

The impacts of sediment loads on chemical concentrations described above diminished as the  $K_{oc}$  of the hypothetical chemical was decreased. As the  $K_{oc}$  in the Mississippi cotton and California onion scenarios approached 50 mL g<sup>-1</sup> (the smallest value evaluated), the concentrations of sediment-sorbed chemical approached zero. Nearly all chemical partitioned to the freely dissolved state in all models. The diminishing effect of sediment dynamics for low  $K_{oc}$  compounds is seen in Fig. 6, which shows the 90th percentile annual maximum dissolved limnetic concentration for each model and scenario diverging as a function of increasing  $K_{oc}$ . These 90th percentile expected environmental concentrations were less divergent in the California onion scenario compared with the Mississippi cotton scenario. The relatively drier California scenario



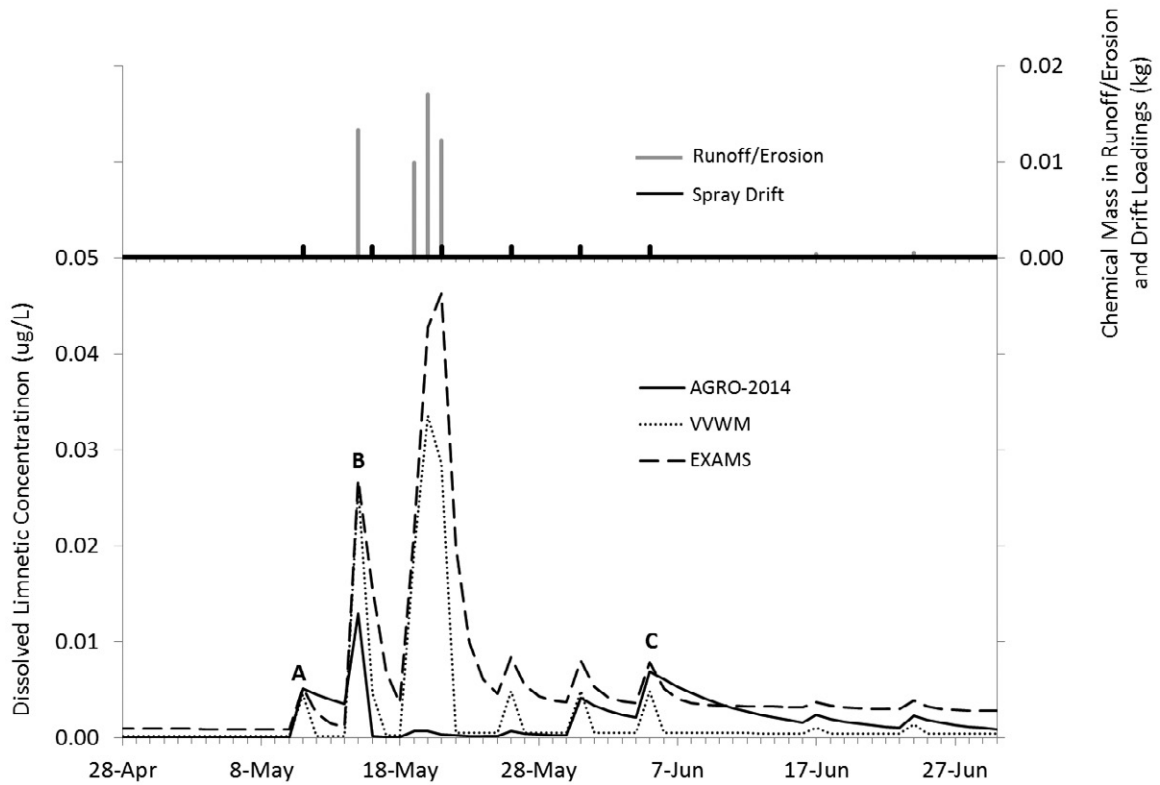


Fig. 5. Comparison of model predicted dissolved limnetic concentrations of a hypothetical hydrophobic organic chemical (bottom) after a series of chemical loadings to the receiving water via drift and runoff or erosion (top) in the standard Mississippi cotton (USEPA) scenario.

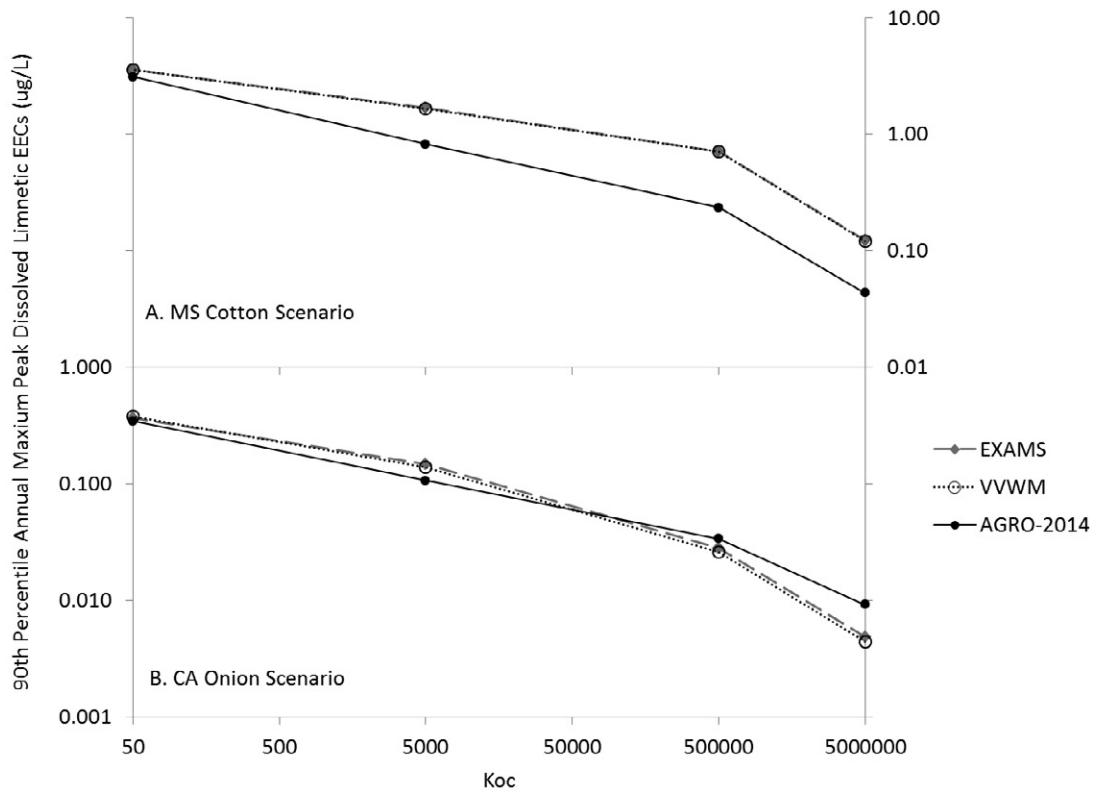


Fig. 6. Comparison of 90th percentile expected environmental concentrations as a function of organic C partition coefficient ( $K_{oc}$ ) for the Mississippi cotton and California onion standard (USEPA) scenarios.

weather resulted in fewer major runoff events with associated amounts of eroded sediment so the expected annual maximum dissolved concentrations were more likely to occur as a result of spray drift exposure unmitigated by adsorption to sediment. Although the effects of the different sediment processes were more pronounced in the wetter-weather Mississippi cotton scenario for high  $K_{oc}$  compounds, all three models performed alike in both scenarios at low  $K_{oc}$ .

## Discussion

This work compared the prediction of chemical concentrations by three aquatic exposure models in simulating actual mesocosm experiments and hypothetical standardized agricultural pesticide applications. The mesocosm comparison highlighted the differences in the ability of each model to capture the different pyrethroid dissipation rates for the spray drift and slurry inputs.

The instantaneous bed sediment loading (PRBEN fraction approach) used by the EXAMS and VVWM models was limited to instantaneously changing the initial chemical concentration in the limnetic and benthic zones; it had no impact on the rate of benthic–limnetic chemical exchange. In contrast, accounting for eroded sediment loading as TSS in the limnetic zone in AGRO-2014 allowed for a variable rate of exchange that was consistent with observations. The standardized scenario simulations further illustrated the impact of differences in the sediment processes for a range of weather and runoff patterns and chemical properties. The importance of the dynamic sediment algorithm in AGRO-2014 became increasingly evident as  $K_{oc}$  increased, while for more typical compounds, results were not distinguishable from the current regulatory models.

The bulk, dissolved, and sediment-sorbed limnetic concentrations were the focus of model comparisons. However, chemical concentrations in the bed sediment and pore water are also important for predicting exposure for benthic organisms. The different sediment processes of the three models had equally significant impact on benthic concentrations. Just as in the limnetic compartment, the bulk benthic chemical was divided into bioavailable pore-water and bed sediment-sorbed fractions by equilibrium partitioning. The high- $K_{oc}$  chemicals primarily adsorbed to bed sediment, resulting in low bioavailable pore water concentrations in all models. For HOCs in AGRO-2014, the amount of eroded sediment (as TSS) in the limnetic zone determined whether diffusive exchange or sediment settling was the dominant pathway for chemical arriving in the benthic zone during runoff events. For EXAMS and VVWM, however, the pathways for incoming benthic chemical were the instantaneous addition of 50% of incoming adsorbed chemical and the constant bulk diffusive exchange process. Differences in the benthic exposure pathways led to differences in the models' predictions of total benthic chemical mass. This resulted in different pore water concentrations among the models even though the pore-water/sediment partitioning ratios were the same. For more typical lower- $K_{oc}$  compounds, in all models and for both drift and runoff exposure, the primary pathway for chemical transfer to benthic was the constant diffusive exchange process. Under this mechanism, the models result in

the same predictions of bulk chemical mass in the benthic and, therefore, the same pore-water and sediment concentrations.

## Uncertainty

As with all modeling studies attempting to simulate observed behavior, results in this study were subject to inherent uncertainties in model assumptions and observations. There were few experimental datasets with enough high-quality observations over time that could be used in a comparison of suspended sediment effects. Of the limited available datasets examined here, some uncertainties existed in the experimental setups. For example, in the Springer (1996) slurry and drift mesocosms, the exact pond geometries were unknown, so reasonable assumptions about variations in the depth had to be made. In both the Springer (1996) and Leistra (2004) studies, there was insufficient information about the volume and density of the benthic zone and the total pesticide uptake by plants and fish to accurately calculate the mass balance. Many of the benthic pesticide concentration measurements were below detection limits. In addition, in the Springer (1996) experiments, there were just a few weeks between applications, so accumulation of pesticide in the benthic zone was possible, making it difficult to attribute benthic concentrations to a single application. For these reasons, direct comparisons of model results to benthic concentrations were not possible.

Modeling uncertainties in all three models included the use of spatially zero-dimensional box models with linearly parameterized physical processes. The assumed equilibrium within each box or compartment prohibited resolution of varying concentrations with depth. One of the long-term recommendations for exposure modeling from the 2008 SAP was to move away from the box-model approach (SAP, 2008). The SAP proposed using existing box models as a starting point for developing a one-dimensional model with several layers in the benthic region to improve representation of benthic–limnetic flux processes. In future work, AGRO-2014 would make a strong basis for building this kind of a higher-resolution model.

## Conclusions

Despite uncertainties, comparison of three aquatic exposure models, AGRO-2014, EXAMS and VVWM, showed that inclusion of dynamic sediment processes significantly impacted modeling results for high- $K_{oc}$  HOCs. The AGRO-2014 model was the best available model for predicting observed pyrethroid concentrations in drift and slurry mesocosm experiments. Standardized loading simulations showed that AGRO-2014 offered improvements over other models for predicting aquatic concentrations of HOCs in small agricultural ponds while returning results similar to the existing FIFRA regulatory models for more typical compounds with lower sorption to sediments.

AGRO-2014 includes the same sediment processes as AGRO (2008) but is calibrated for small ponds based on observed data and has been updated to improve physical realism and make certain processes more comparable with VVWM and EXAMS. The latest version of the improved AGRO-2014 (version 1.2) is publicly available for download at the Stone Environmental website: <http://www.stone-env.com/agchem/agres.php#agdownload>.

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