Development and Testing of an Updated AGRO Model (AGRO-2014) for Predicting Aquatic and Benthic Pesticide Concentrations in Ponds

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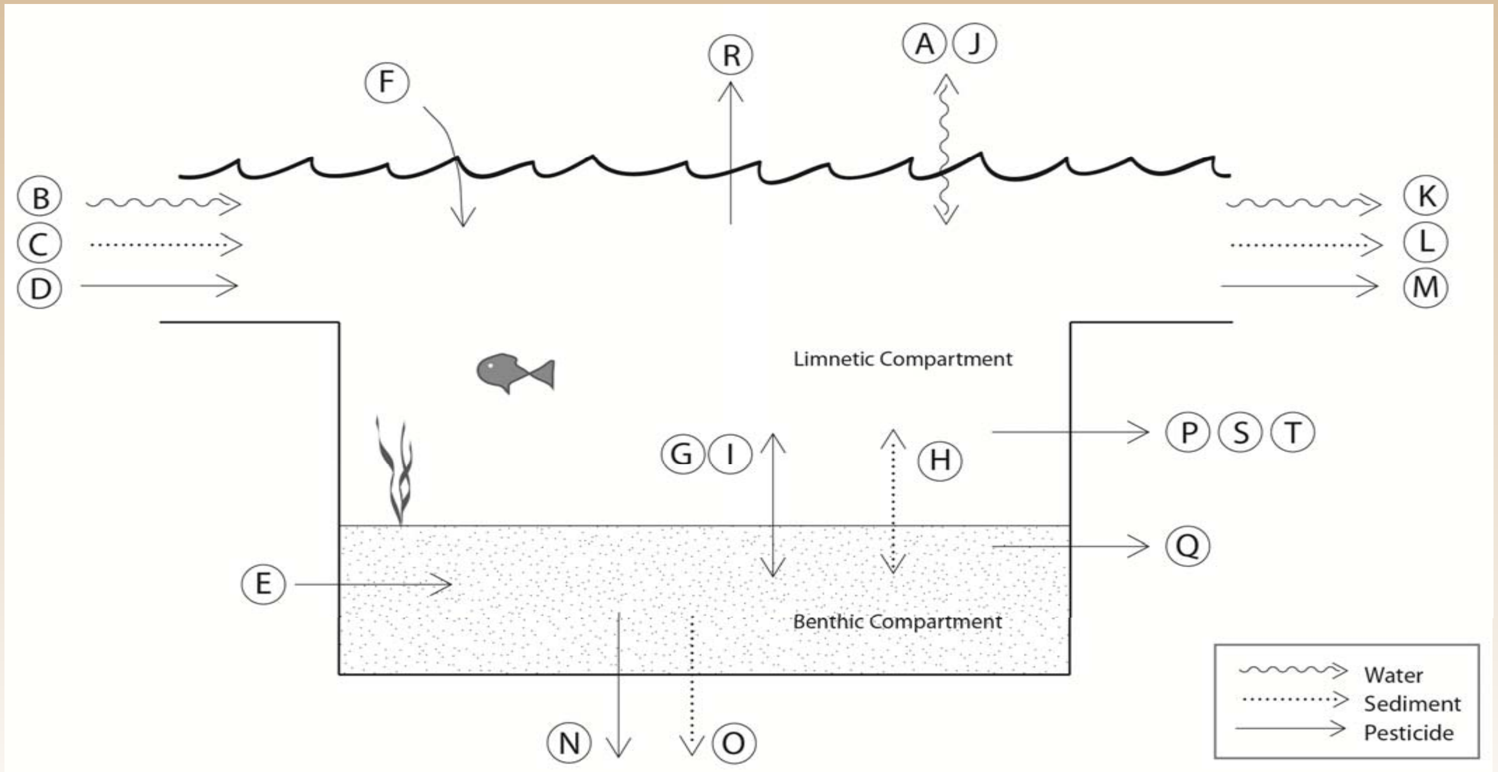
Background

- Historically, Exposure Analysis Modeling System (EXAMS) used to predict aquatic exposure concentrations in regulatory assessments
- Recently, Variable Volume Water Model (VVWM) replacing EXAMS to include important new features like varying volume, flow-through, burial
- A third model called AGRO, has additional dynamic features useful for exposure modeling, not included in EXAMS and VVWM, particularly for hydrophobic organic chemicals
- We will present a version of AGRO – AGRO-2014 – that has been calibrated for small ponds and modified for better comparison to EXAMS and VVWM

AGRO Model

- Developed by Canadian Environmental Modelling Centre (CEMC)/Trent University
- Used to assess chemical dynamics in lakes and rivers
  - Mackay, Paterson & Joy, 1983; Mackay & Diamond, 1989; Mackay & Hickie, 2000; Arnot & Gobas, 2004; Webster et al., 2006
- Evaluated by 2008 Scientific Advisory Panel (SAP)
  - Includes sediment burial as mechanism for system pesticide losses
  - Limits lumped parameter modeling of benthic-limnetic pesticide mixing
  - Formation of pure chemical reservoir when solubility exceeded and re-dissolution when concentrations fall below saturation recognized as conceptually correct
- Includes dynamic sediment mass algorithm for simulating fluctuations in suspended sediment concentration
  - Important for predicting concentrations for hydrophobic organic chemicals (HOCs)

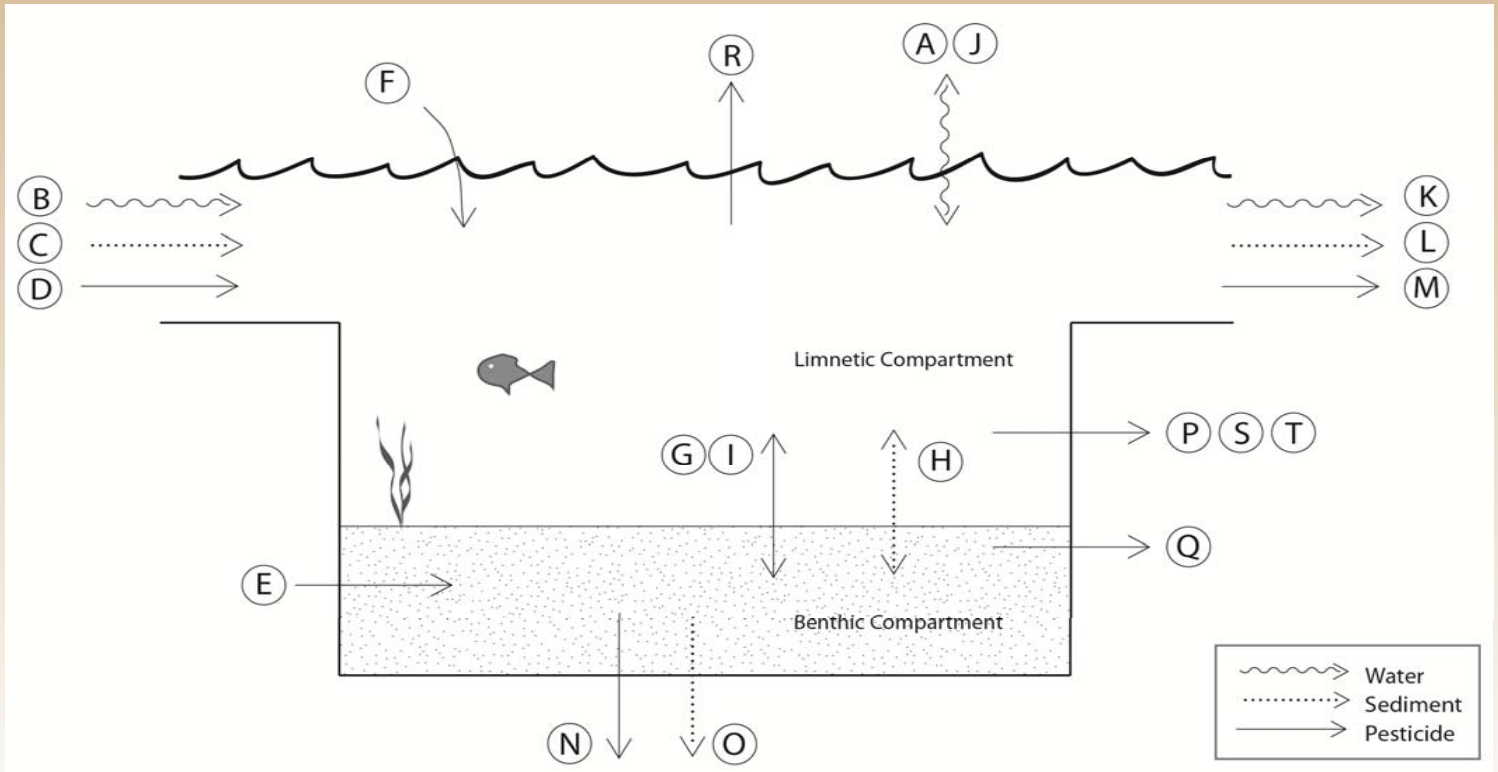
Comparison of Conceptual Models: System Inflows/Sources



	System Input Processes	AGRO	VVWM	EXAMS
A	Precipitation		x^{1}	
B	Water inflow	x	$x^{1\text{ or }2}$	
C	Suspended sediment inflow	x		
D	Dissolved and sorbed pesticide inflow	x	x	x
E	Direct application of sediment-sorbed pesticide to benthic (PRBEN)		x	x
F	Pesticide drift deposition	x	x	x

1. If VVWM varying-volume with flow-through option enabled
2. If VVWM constant volume flow-through option enabled

Comparison of Conceptual Models: System Outflows/Losses

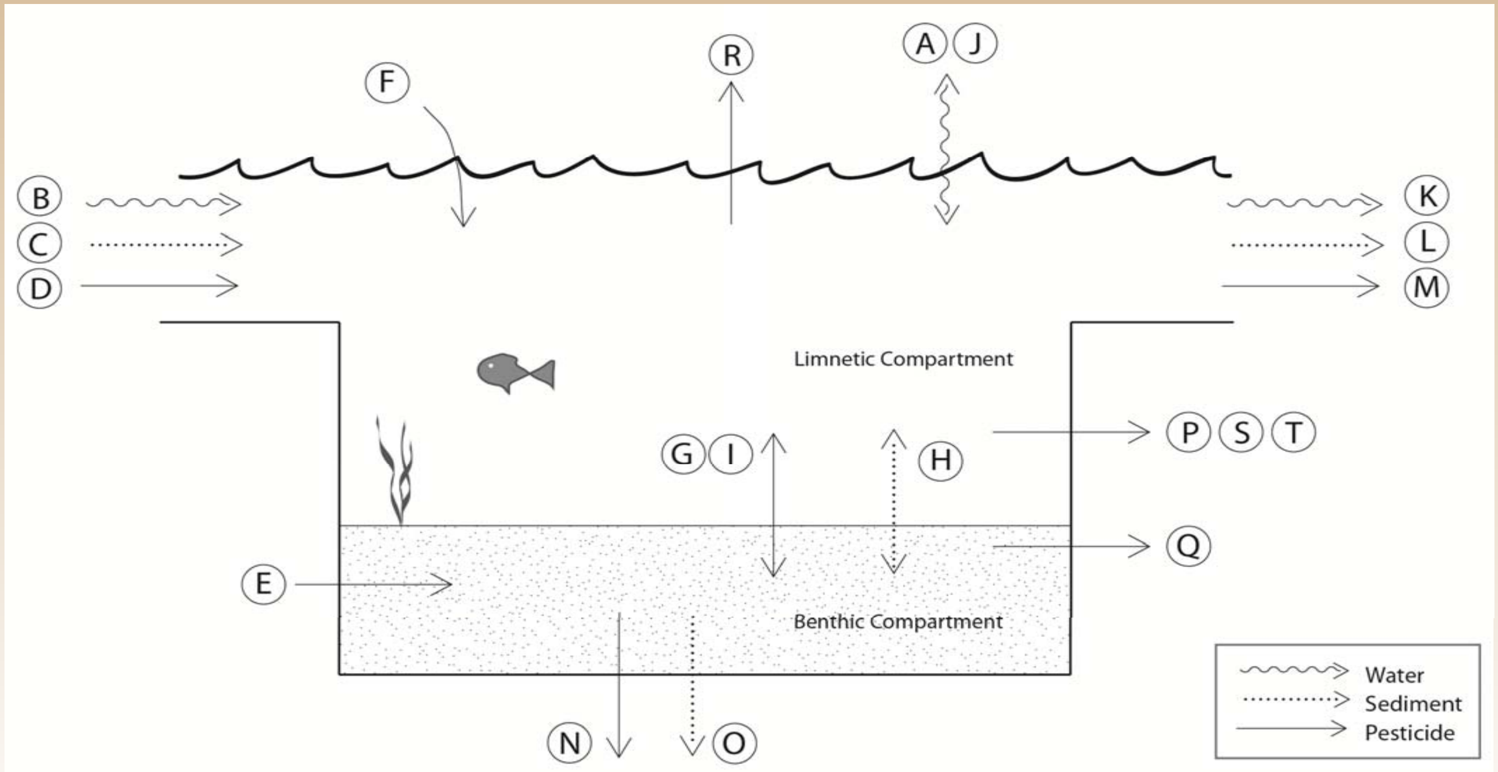


	System Loss Processes	AGRO	VVWM	EXAMS
J	Water Evaporation		x^1	
K	Water outflow	x	$x^{1\text{ or }2}$	
L	Suspended sediment outflow	x		
M	Dissolved and sorbed pesticide outflow	x	$x^{1\text{ or }2}$	
N	Sediment burial	x		
O	Pesticide burial	x	x^3	

	System Loss Processes	AGRO	VVWM	EXAMS
P	Pesticide degradation in water	x	x	x
Q	Pesticide degradation in sediment	x	x	x
R	Pesticide volatilization (Henry's law)	x	x	x
S	Pesticide hydrolysis		x	x
T	Pesticide photolysis		x	x

1. If VVWM varying-volume with flow-through option enabled
2. If VVWM constant volume flow-through option enabled
3. If VVWM burial option enabled

Comparison of Conceptual Models: System Internal Exchanges



	Benthic-Limnetic Exchanges	AGRO	VVWM	EXAMS
G	Dissolved pesticide benthic-limnetic transfer	x	x	x
H	Sediment deposition and resuspension	x		
I	Sediment-sorbed pesticide deposition and resuspension	x		

Equilibrium Partitioning Into Sub-compartments			
Sub-compartment (L) - limnetic, (B) - benthic	AGRO	VVWM	EXAMS
Dissolved (L)	x	x	x
TSS-sorbed (L)	x	x	x
DOC-sorbed (L)		x	x
Plankton/plant-sorbed (L)		x	x
Pore-water dissolved (B)	x	x	x
Sediment-sorbed (B)	x	x	x

AGRO-2014 – An updated version of AGRO

- Same sediment and pure chemical reservoir algorithms as AGRO

Model Attribute	EXAMS	VVWM	AGRO	AGRO-2014
Suspended sediment concentration in water column	30 mg/L	30 mg/L	Varies with erosion inputs (baseline/minimum 30 mg/L)	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/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, 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
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

AGRO-2014 – An updated version of AGRO

- Calibrated for small ponds to observed data
  - Settling time based on observed settling velocities (Chapra, 1997)
  - Diffusive exchange coefficient based on pyrethroid drift mesocosm
- Added features to improve basis for comparison to EXAMS/VVWM

Model Attribute	EXAMS	VVWM	AGRO	AGRO-2014
Sediment settling time	N/A	N/A	7 days (90%)	3.4 days (90%)
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 diffusion coefficient)	Dissolved exchange only (0.05 m/h diffusion coefficient)
Chemical degradation rates as function of temperature	Yes	Yes	No	Yes
Koc parameter	Koc	Koc	Derived from log(Kow)	Koc or derived from log(Kow)
Spray drift and runoff entry time	First time-step of the simulation day	First time-step of the simulation day	Over 24 simulation hours	User-specified

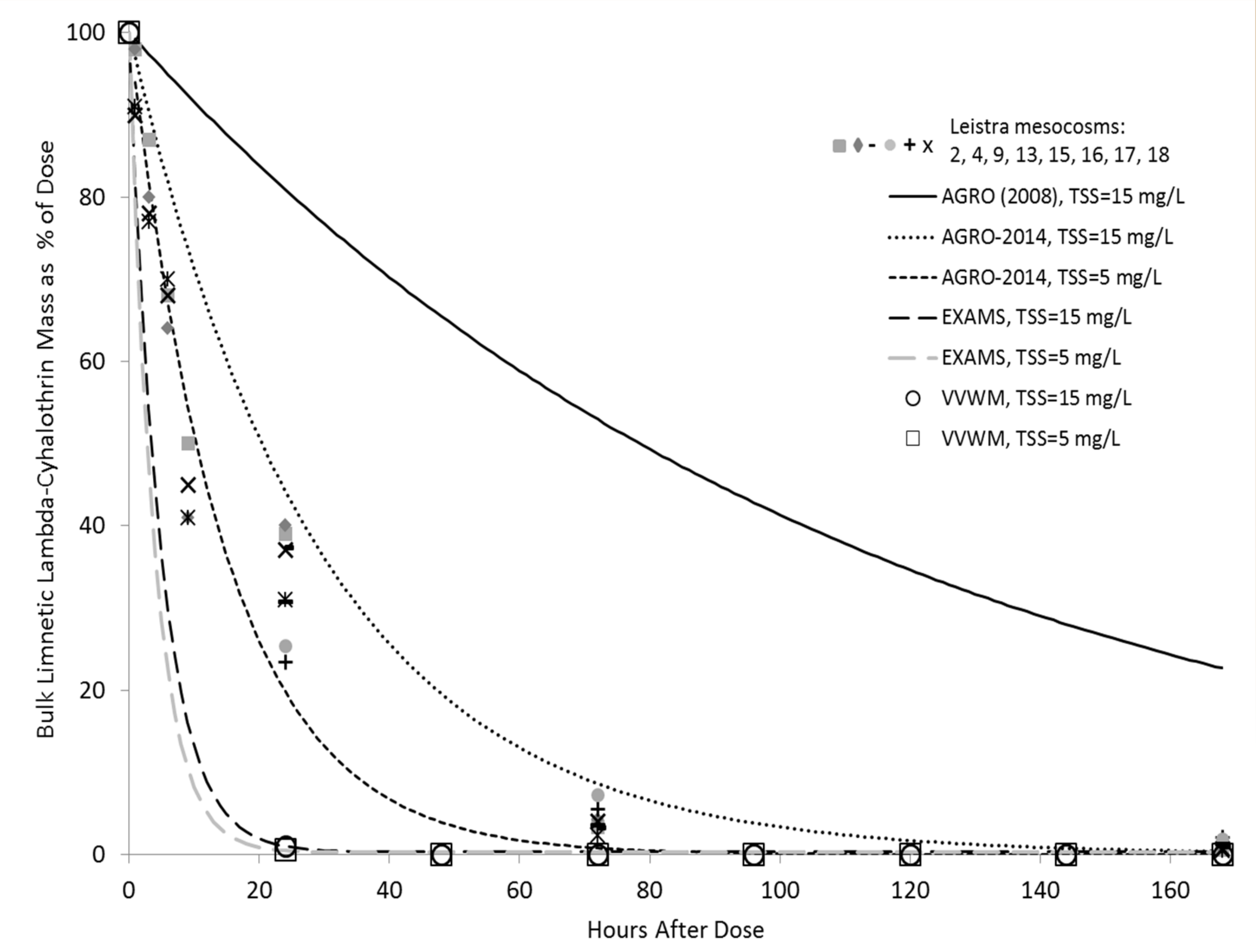
AGRO-2014 Calibration of Diffusive Exchange Coefficient

- Spray drift mesocosm study (Leistra et al. 2003) with water column concentration time-series and multiple replicates
- Suspended sediment concentration approximately constant
- Lambda-cyhalothrin in 0.43 m^3 aquatic mesocosms
- Chemical and environmental parameters set to match experimental setup

Simulation	Leistra et al. 2003
Purpose	observed data calibration
Exposure Pathways	Drift
Chemical	lambda-cyhalothrin
Water Degradation Half-life (days)	56.2[1]
Sediment Degradation Half-life (days)	100[1]
Koc (mL/g)	2,941,300[2]
Solubility (g/m3)	0.005[3]
Molar Mass (g/mol)	449.9[3]
Henry's Law Constant (atm-m3/mol)	1.90E-07[3]
Vapor Pressure (Pa)	2.08E-07[3]
Dose/Application mass	1.08E-5 g
Surface Area (m2)	0.865
Volume (m3)	0.43
Baseline TSS Concentration (mg/L)	5 to 16
Atmospheric Temperature (°C)	15.1
Inflow/Outflow	negligible

1. Average of values from Meyer et al., 2012 as recalculated by Melendez, 2013
2. Mean corrected Solid Phase Micro-Extraction (SPME) value, B.J. Mason, personal communication, March 2014
3. Values from Melendez, 2010a

AGRO-2014 Calibration of Diffusive Exchange Coefficient



- Exchange coefficient based on molecular diffusion velocity was too low
- Increasing coefficient to 0.05 m/h better represents benthic-limnetic exchange
- AGRO-2014 response more closely matches observations than EXAMS/VVWM

Model Comparison – Validation with Pyrethroid Mesocosm Observations

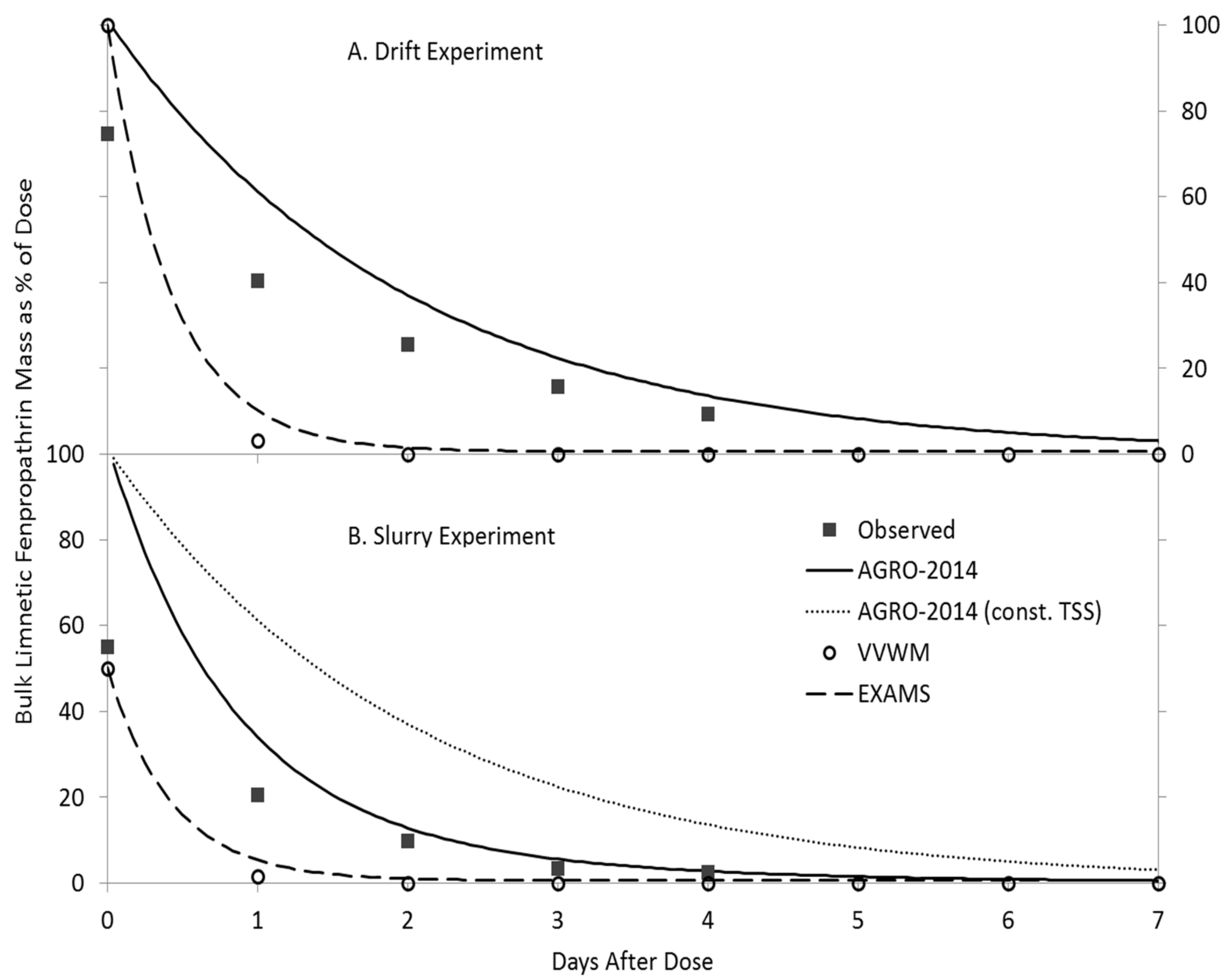
- Springer et al. 1996 simulated drift and erosion (slurry) mesocosms with water column concentration time-series and multiple replicates
- Environmental and chemical inputs were set to match experimental setup but no calibration was conducted

Simulation	Springer et al. 1996	Springer et al. 1996
Exposure Pathways	Drift	Slurry (Erosion)
Chemical	fenpropathrin	fenpropathrin
Water Degradation Half-life (days)	34.1[1]	34.1[1]
Sediment Degradation Half-life (days)	169[1]	169[1]
Koc (mL/g)	1,029,873[4]	1,029,873[4]
Solubility (g/m3)	0.0103[5]	0.0103[5]
Molar Mass (g/mol)	349.4[5]	349.4[5]
Henry's Law Constant (atm-m3/mol)	6.20E-07[5]	6.20E-07[5]
Vapor Pressure (Pa)	1.87E-06[5]	1.87E-06[5]
Dose/Application mass	1.061 g	1.82 g fenpropathrin, 30 L water, 118 kg sediment
Surface Area (m2)	960	960
Volume (m3)	870	870
Baseline TSS Concentration (mg/L)	no data, defaults assumed	no data, defaults assumed
Atmospheric Temperature (°C)	20	20
Inflow/Outflow	negligible	negligible

1. Average of values from Meyer et al., 2012 as recalculated by Melendez, 2013
4. Based on Mackay regression equation: Koc = 0.41*(10^log(Kow)) Mackay, 2001 with log(Kow) from Dix, 2014
5. Values from Melendez, 2010b

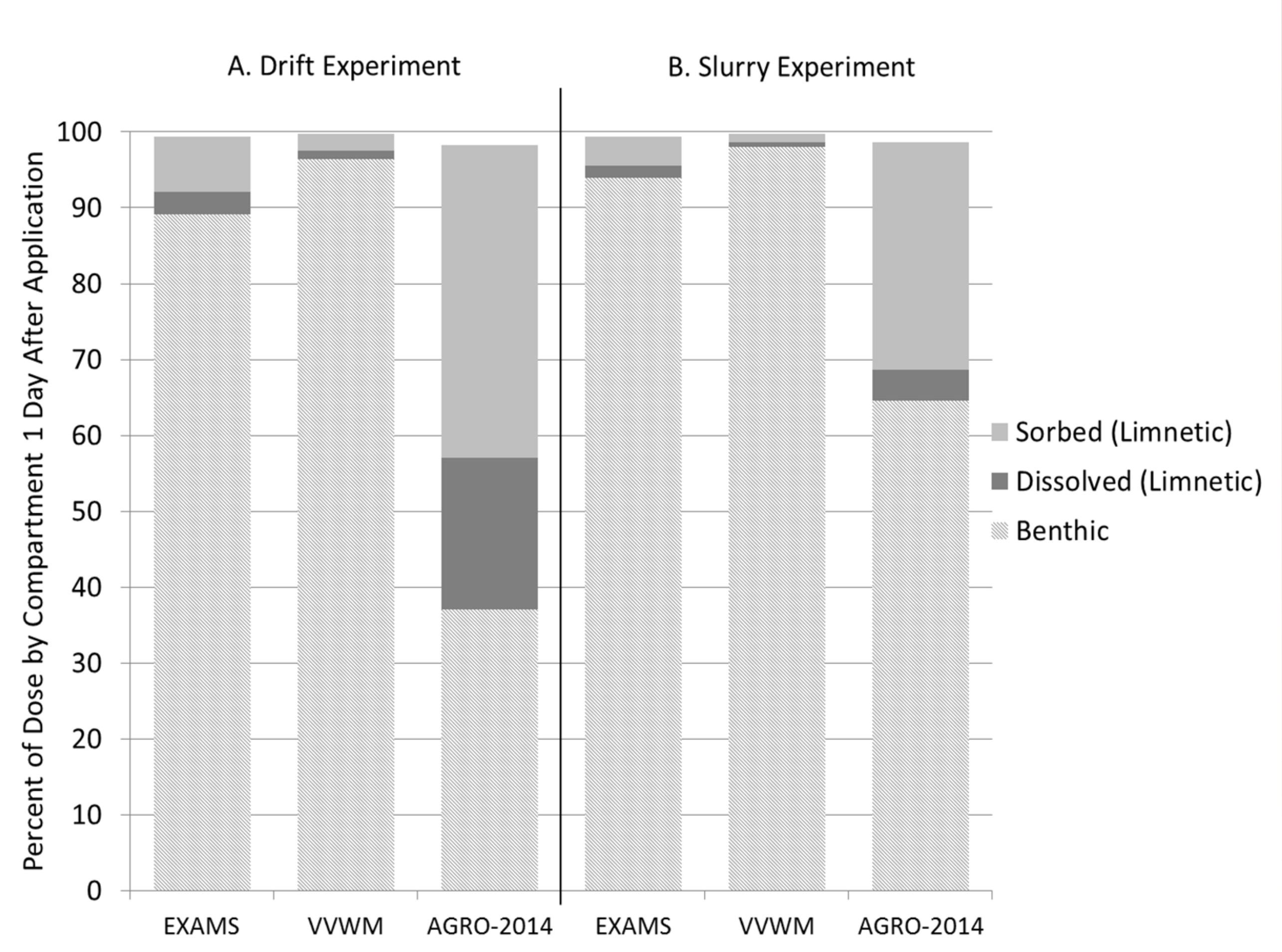
Model Comparison – Validation with Pyrethroid Mesocosm Observations

- The observed dissipation rate in the slurry experiment (0.7 day half-life) was twice the rate of the drift experiment (1.4 day half-life)
- AGRO-2014 slightly overestimated observed maximum concentrations, simulated different dissipation rates well
- EXAMS and VVWM underestimated rates and predicted same rates for both experiments, PRBEN fraction lowered initial concentration



- AGRO-2014 run without allowing TSS to fluctuate was not in good agreement with observations

Model Comparison – Validation with Pyrethroid Mesocosm Observations



- Total system losses by degradation were greatest in AGRO-2014 – more chemical in water, faster degradation rate in water than sediment

- Differences in sediment algorithms led to differences in partitioning between the two experiments
- Within the water column, the fraction adsorbed/dissolved chemical (determined by Koc) was the same for all models but there was more chemical in the water column overall in AGRO-2014
- All models had more chemical in the water column than the benthic in the drift experiment compared to the corresponding slurry experiment

Model Comparison – Standard Scenarios

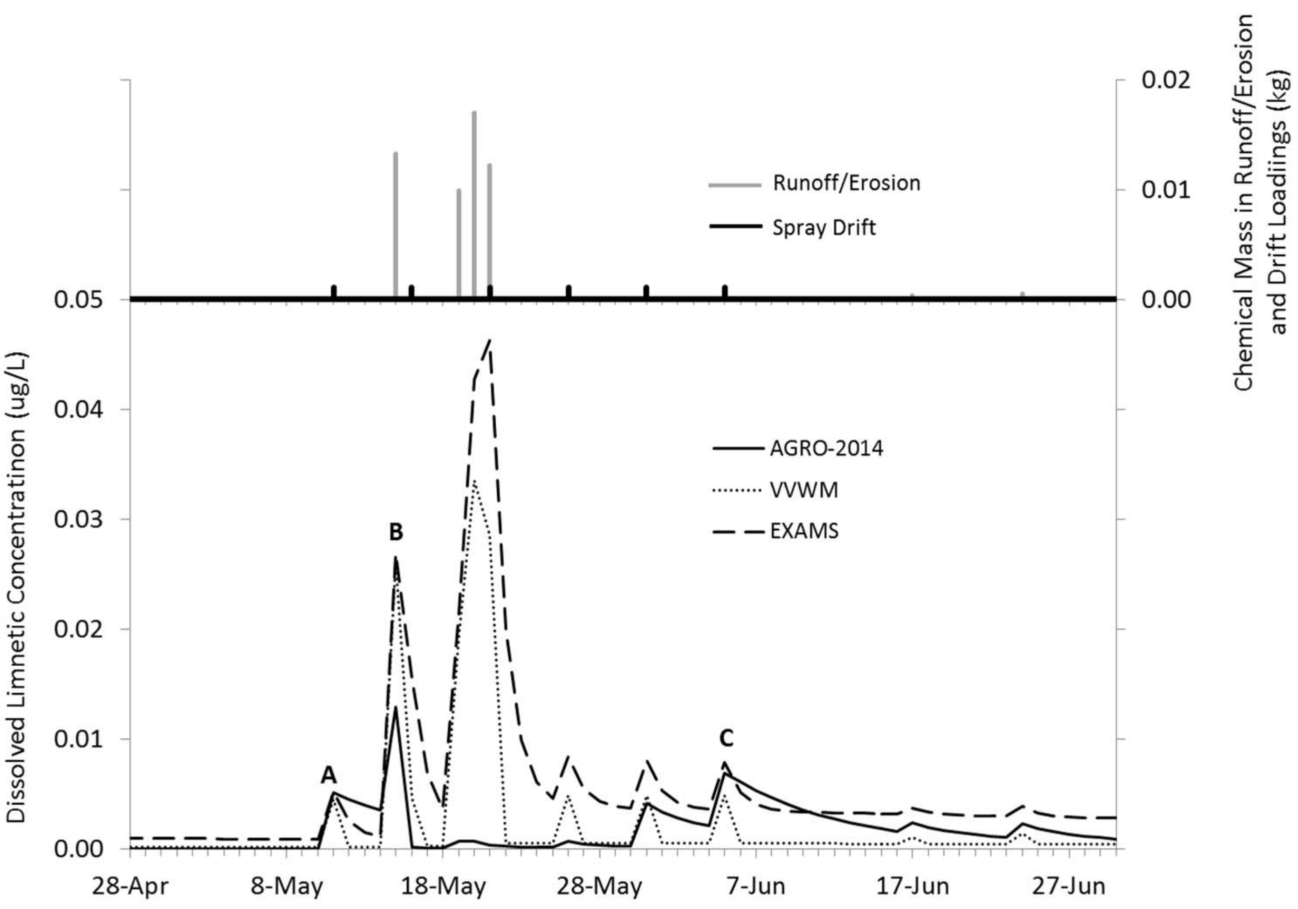
- Comparison of model predictions in response to drift and runoff inputs simulated by PRZM 3 for MS Cotton and CA Onion scenarios
- Assumed a hypothetical test chemical with a wide range of Koc values

Simulation	EPA Standard Scenarios
Purpose	standardized agricultural field loadings
Exposure Pathways	PRZM simulated drift and runoff
Chemical	hypothetical test chemical
Water Degradation Half-life (days)	12
Sediment Degradation Half-life (days)	70
Koc (mL/g)	50, 5000, 500000, or 5 million
Solubility (g/m3)	0.05
Molar Mass (g/mol)	420
Henry's Law Constant (atm-m3/mol)	4.80E-07
Vapor Pressure (Pa)	2.00E-06
Dose/Application mass	1.12 g via drift entry 6 times per year[6], plus varied mass via runoff/erosion dependent on weather
Surface Area (m2)	10000
Volume (m3)	20000
Baseline TSS Concentration (mg/L)	30
Atmospheric Temperature (°C)	varied daily with weather
Inflow/Outflow	varied daily with runoff, min 5 m/s (AGRO-2014); none (VVWM, EXAMS)

Model Comparison – Standard Scenarios

- Series of drift and erosion events for MS Cotton scenario, hypothetical chemical Koc = 5 million ml/g

- A. Models had same peak concentration after first drift event, AGRO-2014 response most conservative
- B. Large eroded sediment load carrying adsorbed pesticide increased chemical mass in all models and increased TSS in AGRO-2014
- Majority of chemical in AGRO-2014 water column adsorbed to increased TSS, reducing dissolved concentration

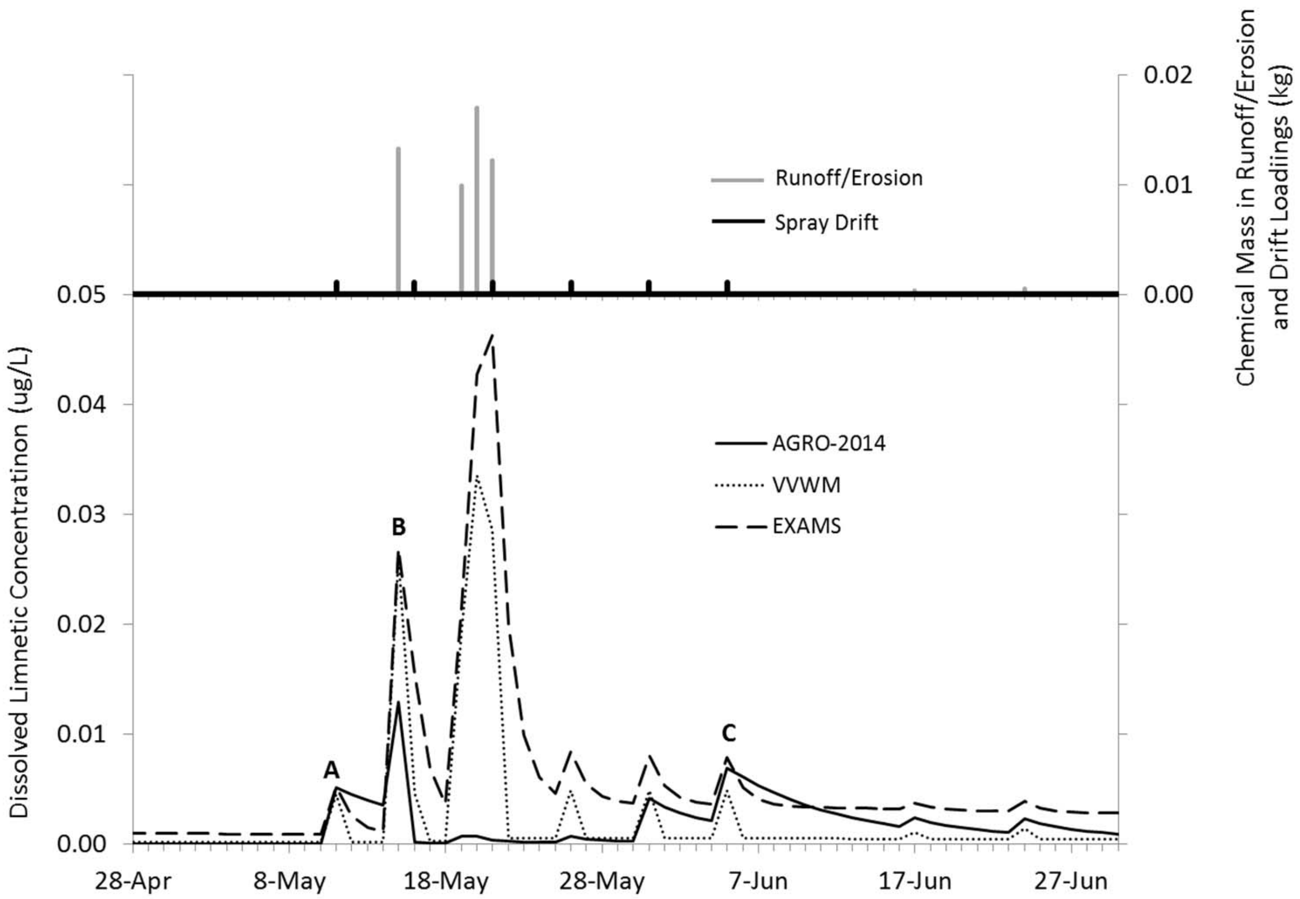


Model Comparison – Standard Scenarios

- Series of drift and erosion events for MS Cotton scenario, hypothetical chemical Koc = 5 million ml/g

- C. After several days without additional runoff/erosion, TSS concentration in AGRO-2014 decreased to base 30 mg/L

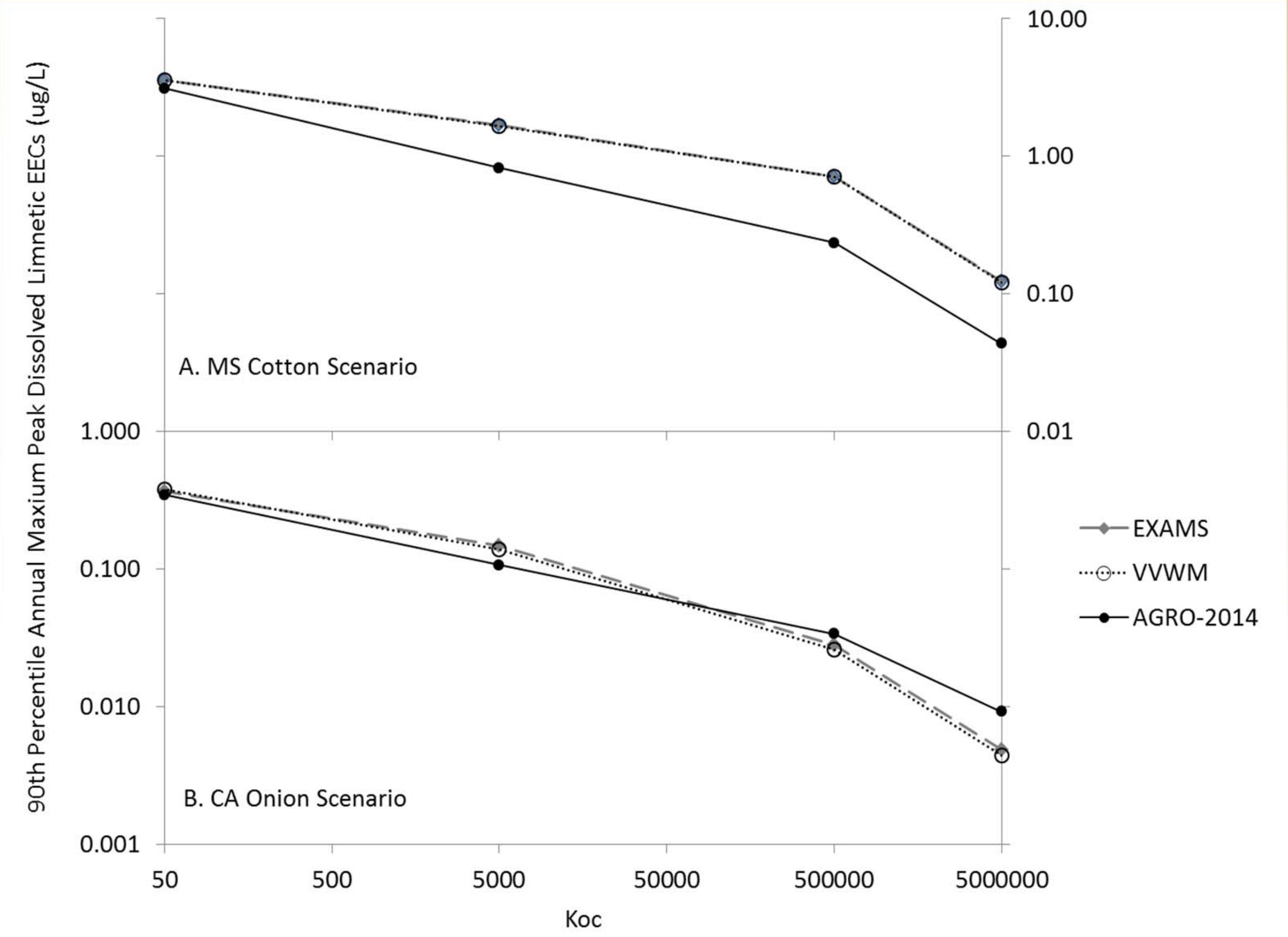
- AGRO-2014 response to subsequent drift event had similar peak dissolved pesticide concentration and more conservative dissipation rate compared to other models



Model Comparison – Standard Scenarios

- Comparison of 90th percentile annual maximum EECs for hypothetical chemical with Koc = 50, 5000, 500,000, 5 million for MS Cotton and CA Onion scenarios

- Similar results in all models and scenarios at low Koc
- Koc had a more pronounced effect in the wetter-weather MS Cotton scenario
- EECs in relatively drier CA scenario more likely to be driven by spray drift, in which case AGRO-2014 is more conservative for higher Koc chemicals



Discussion

- Mesocosm comparison highlighted the differences in ability of each model to capture different dissipation rates for spray drift and slurry inputs
- The effect of instantaneous bed sediment loading (PRBEN fraction) in EXAMS/VVWM was limited to changing initial chemical concentrations immediately after dose, no impact on rate of benthic-limnetic chemical exchange
- Accounting for eroded sediment loading as TSS in AGRO-2014 allowed for variable rate of exchange consistent with observations
- Standard scenario simulations showed dynamic sediment algorithms of AGRO-2014 became increasingly important as Koc increased
- For low-Koc compounds, AGRO-2014, VVWM, and EXAMS results were very similar

Summary/Conclusions

- AGRO-2014 which includes the same sediment dynamics as AGRO (2008) was calibrated for small ponds and updated to improve physical realism and make certain processes more comparable to VVWM and EXAMS
- Inclusion of dynamic sediment processes significantly impacted modeling results for high-Koc, hydrophobic organic compounds
- AGRO-2014 was the best model for predicting observed pyrethroid concentrations in drift and slurry mesocosm experiments
- All three models returned similar results for chemicals with low sorption to sediments

Questions?

- The latest version of AGRO-2014 (version 1.2) is publically available at http://www.stone-env.com/docs/PA5_v1.5b_Install_Beta_23.exe
- AGRO-2014 has been documented in the following technical reports submitted to EPA
  - Padilla & Winchell 2014, PWG-ERA-03b, Development and Testing of an Improved AGRO Model (AGRO-2014) for use in Predicting Aquatic and Benthic Pesticide Concentrations in Ponds
  - Desmarteau & Ritter 2014, PWG-ERA-07a, Sensitivity Analysis of Individual Parameters for Synthetic Pyrethroid Exposure Assessments to Runoff, Erosion and Drift Entry Routes for the PRZM, EXAMS and AGRO-2014 Models
- The following manuscript submitted to the Journal of Environmental Quality is currently in review
  - Padilla, Winchell, & Jackson, Evaluation of AGRO-2014 for predicting hydrophobic organic chemical concentrations in ponds

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