Evaluation of Three Models for Simulating Pesticide Runoff from Agricultural Fields in Semi-arid Regions

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INTRODUCTION

Mathematical models have been increasingly used to assist regulatory agencies and researchers in exposure assessments. In California, the Department of Pesticide Regulation (DPR) is required by law to evaluate pesticides not only during registration process but also when they are in use. Simulation models are helpful tools for this evaluation. Predicting pesticide loss at the edge of a field is fundamental to exposure assessment both at local and watershed scales. Current water quality regulations in California are often based on instantaneous water sampling designed to reflect the peak concentrations. These concentrations are compared to aquatic life benchmarks or water quality criteria to determine if a violation has occurred. Therefore, a model must be able to predict peak pesticide concentrations at field edge that occur soon after rainfall or irrigation events. In addition, wide-spread use of irrigation presents another challenge for exposure modeling. Many models do not have valid mechanisms for simulating irrigation water applications and subsequent runoff from a field. After a preliminary model search, three models with the above mentioned capabilities were selected to determine their accuracy in predicting pesticide runoff from agricultural fields: The Pesticide Root Zone Model (PRZM) developed by U.S. EPA (Carsel et al., 1998), the Root Zone Water Quality Model (RZWQM) developed by USDA ARS (Ahuja et al., 1999) and the Opus model also developed by USDA ARS (Smith, 1992). Although the three models have been used by governmental agencies and researchers worldwide, literature on validation of the three models for simulating irrigation runoff are limited. To address the unique regulatory and agricultural conditions, this study attempts to evaluate RZWQM and Opus in addition to the PRZM model for pesticide exposure modeling in California.

MATERIALS AND METHODS

Evaluation on model theory: models were evaluated qualitatively for their abilities to:

1) Simulate common crops in California mainly trees, vegetables, field crops, and alfalfa hay
2) Consider pesticide application method: ground, aerial spray and soil incorporation
3) Simulate runoff generated by different irrigation methods including gravity (e.g. flood, furrow) and sprinkler irrigation
4) Simulate pesticide partitioning in dissolved and adsorbed phases
5) Simulate pesticide degradation in soil, plant and water, ideally with consideration of temperature and soil moisture effects
6) Simulate pesticide volatilization into air
7) Simulate soil erosion and associated pesticide losses
8) Generate time series outputs on runoff flow, pesticide concentration, plant growth and crop evapotranspiration
9) Operate at hourly or finer time step
10) Simulate effects of management practices
11) Have strong and active technical support

Table 1: Main settings of the three field studies

	Fresno study	Winters study	Davis study
Location	38.836, -119.853	38.503, -121.977	38.532, -121.799
Crop	citrus row middle	peach	alfalfa
Soil	Hanford sandy loam	Yolo silty loam	Brent wood silty clay loam
Size	0.00187 ha / plot	0.033 ha / plot	0.281 ha (block A) 0.295 ha (block B)
Slope	2%	2%	0.14%
Water input	simulated rainfall; two events of 32 mm	natural rainfall; two events of 38 mm and 15mm	flood irrigation, 12 events ranged from 130-260 mm
Management practices	mechanical incorporation of pesticides	cover crop with oats and clover	alfalfa cut and harvest
Pesticides	simazine	chlorpyrifos, diazinon, methidathion	chlorpyrifos, diuron
Pesticide spray date	8/22/1995	1/4/1996	4/9/2012 chlorpyrifos 1/17/2013 diuron
Pesticide spray method	Ground, soil incorporation	Foliar	Ground
Application rate	2.0 kg/ha	1.2 kg/ha	0.53 kg/ha (chlorpyrifos) 2.28 kg/ha (diuron)
Weather station (hourly and daily)	CIMIS weather station at Fresno State	CIMIS weather station at Davis, CA	CIMIS weather station at Davis, CA

Sensitivity analysis

- ◊ Based on Fresno study (Troiano, 1998) (see Table 1)
- ◊ 57 parameters; randomly sample from parameter range
- ◊ 5000 run for each model
- ◊ Target output: water runoff, pesticide loss (dissolved, adsorbed), sediment erosion
- ◊ Calculate Spearman's rank coefficient to compare relative significance
- ◊ Versions of model used: PRZM3.12.3, RZWQM 2.5 science version, OpusCZ December 2013 version

Evaluation using Field studies

- ◊ Three field runoff studies were used as testing cases: Fresno study (Troiano, 1998), Winters study (Ross, 1997) and Davis study (Zhang, 2012) (Table 1).
- ◊ Fresno study: first event as calibration, second event as validation
- ◊ Winters study: bare soil plots as calibration, cover crop plots as validation
- ◊ Davis study: cold runs, no calibration
- ◊ Manual calibration: objective function: Mean Absolute Percent E rror (MAPE) (equation 3)

Statistics for model evaluation: Root Mean Square Error (RMSE), Percent of Difference (%D), and MAPE as bellows:

$$RMSE = \sqrt{\frac{\sum(P_i - O_i)^2}{n}} \quad (1)$$

$$\%D_i = \frac{P_i - O_i}{O_i} \times 100 \quad (2)$$

$$MAPE = \frac{100}{n} \times \sum_i^n \frac{|P_i - O_i|}{O_i} \quad (3)$$

P_i is the i th predicted value, O_i is the i th observed value, $\bar{O}$ is the average of the observed values, and n is the number of observations

RESULTS AND DISCUSSION

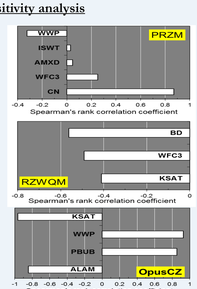
Theory evaluation results (Table 2)

- ◊ OpusCZ: more ideal compared to RZWQM and PRZM (most complete in representing hydrological and pesticide processes, sub-daily time step, options to model management practices)
- ◊ RZWQM: most user-friendly however lacks sediment erosion component
- ◊ PRZM: the most simple among the three: curve number for surface runoff not ideal; cannot simulate flood irrigation and subsurface drainage through drain tiles
- ◊ None of models has components for simulating spray drift.

Table 2: Comparison of the three models for hydrological processes, pesticide processes and other model components

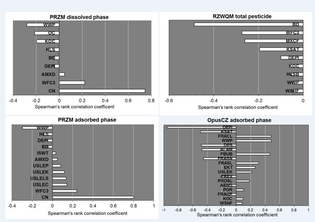
	PRZM	RZWQM	OpusCZ
Hydrology Processes			
Evapotranspiration	As input/ Hamon's	Modified Penman-Monteith	Ritchie's equation
Surface runoff	SCS curve number	Infiltration access	Infiltration access
Infiltration	Runoff excess	Green-Ampt	Darcy's law
Irrigation setting	relative dates, sprinkler, others as rainfall	Sprinkler, user rates and dates	Sprinkler, flood, user rates and dates
Sub-surface flow via tile drainage	No	Yes	Yes
Erosion	MUSLE/USLE	No	KINEROS
Pesticide Processes			
Application method	Yes	Yes	Yes
Metabolites	Yes	Yes	Yes
Sorption	Equilibrium; Linear	Equilibrium or kinetics; Linear/ Freundlich	Equilibrium or kinetics; Linear/ Freundlich/ Langmuir
Plant wash-off	Yes	Yes	Yes
Volatilization	Yes	Yes	Yes
Plant uptake	Yes	Yes	Yes
Degradation	First-order	Pseudo first-order	First-order sigmoidal
Degradation rate change in soil	Temperature	Moisture, temperature, soil depth	Moisture, temperature, soil depth
Other Components			
Input preparation	Fixed FORTRAN format	User GUI, users can prepare all inputs using GUI	User GUI, users need to prepare three input files with free format
Time step	Daily	Hourly	Continuous
Management practices	No specific modules	Reflect tillage, harvest	Reflect tillage, harvest, pond

Sensitivity analysis



↑ Fig 1. Parameters with significant sensitivity to surface water runoff. volume WWP: wilting point of soil; ISWT: initial soil water content; AMXD: maximum rooting depth; WFC3: field capacity of soil; CN: SCS runoff curve number; BD: soil bulk density; Ksat: soil saturated hydraulic conductivity; PBUB: Bubbling pressure of soil; ALAM: Log slope of retention curve at low water contents.

For PRZM, determination of the curve number is the most influential process to estimate volume of surface runoff water. In contrast, RZWQM and OpusCZ models emphasize soil hydraulic properties as significant influences.



↑ Fig 2. Parameters with significant sensitivity to pesticide runoff..

The three models show similar lists of sensitive parameters for pesticide runoff. The significant ones include those associated with soil adsorption (soil adsorption coefficient (Koc), Freundlich constant (FREQ)), degradation (soil half-life (HLS), foliar half-life (HLF)) and application depth (depth of soil incorporation (DEPI)).

Parameters associated with sediment erosion and transport show significance to runoff of adsorbed pesticides, for example, the universal soil loss equation parameters USLEP, USLEK, USLELS and USLEC in PRZM; FRACL(fraction of clay particle in sediment erosion), FRASN (fraction of sand particle in sediment erosion), FRASL(fraction of silt particle in sediment erosion), USLEK, EKT (relative erodibility factor for splash erosion), DPS (mean effective particle diameters for soil particle class), and PROSL (proportion of total sediment with certain particle sizes) in OpusCZ.

Simulation of field studies

1.Fresno study

↓ Table 3: Simulation results of the Fresno case run; Tillage was performed up to 7.6 cm of soil using a rototiller after pesticide application

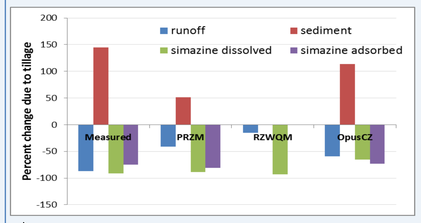
Event	Treatment		PRZM	%D	RZWQM	%D	OpusCZ	%D	Measured
Event 1 Calibration	No till	runoff (cm)	1.0	-7.7	1.6	-43.9	1.2	13.6	1.1
		sediment (g)	157.7	-3.8			134.5	-18.0	164.0
		simazine dissolved (mg)	118.2	-15.6	128.2	-30.3	143.4	2.4	140.0
		simazine adsorbed (mg)	5.5	-87.5			1.0	-97.6	44.0
		MAPE (%)	**38.2**		**58.0**		**43.9**		
	Tillage	runoff (cm)	0.6	9.1	1.0	76.1	0.5	-8.3	0.5
		sediment (g)	227.6	-0.6			285.2	-24.5	229.0
		simazine dissolved (mg)	12.7	27.0	6.8	-64.2	28.2	182.4	10.0
		simazine adsorbed (mg)	1.0	-89.1			0.3	-96.1	9.0
		MAPE (%)	**41.9**		**77.2**		**103.8**		
Event 2 Validation	No till	runoff (cm)	1.1	16.8	1.5	69.0	1.2	36.0	0.9
		sediment (g)	169.6	26.6			133.1	-0.6	134.0
		simazine dissolved (mg)	92.0	109.1	97.6	50.2	16.7	-62.1	44.0
		simazine adsorbed (mg)	4.3	-79.5			0.5	-97.7	21.0
		MAPE (%)	**77.3**		**66.6**		**65.5**		
	Tillage	runoff (cm)	0.6	-48.2	1.3	8.1	0.5	-57.7	1.2
		sediment (g)	256.9	-21.7			284.6	-13.2	328.0
		simazine dissolved (mg)	10.1	158.4	7.0	-23.9	5.8	48.2	3.9
		simazine adsorbed (mg)	0.8	-84.7			0.1	-97.6	5.3
		MAPE (%)	**110.2**		**16.0**		**72.2**		

All three models simulated simazine runoff with good accuracy (Table 3). The simulated results on amount of water runoff, sediment erosion, and simazine in runoff were all within twice of the observed values (MAPE between 16-110%).

For PRZM, there was greater deviation of predicted values from measured values compared to the calibration period .

For OpusCZ, simulation results for the tillage during validation had the smallest error compared to those for calibration.

RZWQM could not simulate sediment erosion, but the results on surface runoff and total pesticide runoff were close to those measured.



↑ Fig 3. Measured and simulated tillage effects for the second runoff event (validation period) in the Fresno case study

All three models simulated the tillage effects well, even though they were using different approaches (Fig. 3). Both RZWQM and OpusCZ have specific modules for simulating tillage effects, while PRZM does not. Therefore, to mimic effects of tillage practices in PRZM, one has to modify parameters such as the curve number and the C factors of universal soil loss equation (USLEC). This may have affected PRZM's performance during the validation event.

2.Winters study

The three models simulated runoff and sediment erosion with high accuracy (Table 6). All simulated values were within twice of the measured values with highest deviation error being 71% (Table 6). Although RZWQM did not simulate sediment erosion, its simulated results on runoff water from all land cover types were closest to the measurements.

Table 4: Simulated runoff and sediment results for the Winters study

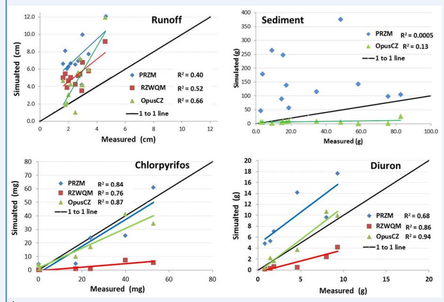
Treatment	Type	PRZM Simulated	PRZM %D	RZWQM Simulated	RZWQM %D	OpusCZ Simulated	OpusCZ %D	Measured
Bare	Runoff (mm)	1.5	-11.8	1.7	-1.2	1.7	-2.4	1.7
Clover	Runoff (mm)	0.6	-15.7	0.7	1.3	0.8	12.9	0.7
Oat	Runoff (mm)	0.9	5.4	0.9	-2.2	1.2	27.8	0.9
	MAPE (%)	11.0		1.6		14.3		
RMSE		0.1		0.0		0.2		
Bare	Sediment (g)	356.8	1.7			564	60.9	350.7
Clover	Sediment (g)	136.5	-27.9	--	--	215	13.3	189.3
Oat	Sediment (g)	188.5	-2.4			330	70.9	193.1
	MAPE (%)	10.7		--	--	48.4		--
RMSE		30.8				147.2		

The attenuation effects of cover crops were also successfully realized by the three models, with runoff water volume, sediment and pesticide significantly reduced by using the cover crops of clover and oat. For PRZM, this was accomplished by adjusting the curve number and the USLE C factor. For RZWQM and OpusCZ model, the effects were realized by setting up the crop growth parameters for oat and clover.

Table 5: Simulated pesticides in runoff for the Winters study. Units: mg ; Note: for RZWQM, the simulated results were for the total of adsorbed and dissolved pesticides

	Treatment	Chemical	Type	PRZM Simulated	PRZM %D	RZWQM Simulated	RZWQM %D	OpusCZ Simulated	OpusCZ %D	Measured
Calibration	Bare	Chlorpyrifos	Adsorbed	2.3	-42.7	4.7	3.1	3.8	-7.3	4.1
	Bare	Diazinon	Adsorbed	1.3	-85.0	15.4	22.6	2.2	-74.9	8.8
	Bare	Methidathion	Adsorbed	2.4	-83.7	30.6	4.1	2.8	-80.7	14.7
		MAPE (%)		**70.5**		**9.9**		**54.3**		
		RMSE		**8.4**		**1.8**		**7.8**		
	Bare	Chlorpyrifos	Dissolved	0.6	19.8	--		0.2	-52.6	0.5
	Bare	Diazinon	Dissolved	4.0	6.3	--		4.3	13.4	3.8
	Bare	Methidathion	Dissolved	11.2	-23.5	--		14.3	-3.0	14.7
		MAPE (%)		**16.5**		--		**23.0**		
		RMSE		**2.0**		--		**0.4**		
Validation	Clover	Chlorpyrifos	Adsorbed	0.9	-29.3	1.3	0.9	1.4	16.3	1.2
	Clover	Diazinon	Adsorbed	0.5	-76.6	4.1	24.0	0.8	-59.9	2.1
	Clover	Methidathion	Adsorbed	0.9	-80.3	10.4	33.9	1.1	-76.0	4.5
	Oat	Chlorpyrifos	Adsorbed	1.4	-36.5	2.4	-0.9	2.2	0.0	2.2
	Oat	Diazinon	Adsorbed	0.8	-91.3	12.3	1.0	1.3	-85.8	9.1
	Oat	Methidathion	Adsorbed	1.4	-71.9	18.3	46.3	1.7	-67.3	5.2
		MAPE (%)		**64.3**		**17.8**		**50.9**		
		RMSE		**4.1**		**2.6**		**3.8**		
	Clover	Chlorpyrifos	Dissolved	0.2	805.6	--		0.1	110.7	0.03
	Clover	Diazinon	Dissolved	1.6	37.9	--		0.2	-82.4	1.2
	Clover	Methidathion	Dissolved	4.6	38.6	--		3.4	3.5	3.3
	Oat	Chlorpyrifos	Dissolved	0.4	68.5	--		0.2	-29.8	0.2
	Oat	Diazinon	Dissolved	2.7	-14.5	--		3.0	-4.5	3.1
	Oat	Methidathion	Dissolved	7.4	0.7	--		9.9	33.9	7.4
		MAPE (%)		**161.0**		--		**44.1**		
		RMSE		**0.6**		--		**1.1**		

3. Davis study



↑ Fig 4. simulated and measured runoff for the Davis studies ; The error statistics MAPE and RMSE were calculated based on 12 runoff events. All results were from cold runs with no manipulations on the model parameters.

Simulated results by OpusCZ were the most accurate with the smallest errors for all measures including runoff, sediment erosion, and pesticides loss. For runoff flow, R^2 values were 0.40, 0.52 and 0.66 for PRZM, RZWQM and OpusCZ, respectively, indicating acceptable ability for all models in explaining variations of water volume among the 12 events.

For pesticide runoff, the three models captured the variances very well with R^2 ranged from 0.68 to 0.94. OpusCZ had highest R^2 values across all the measurements.

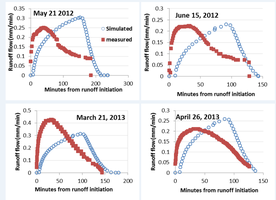
Table 6: Simulation performance of the Davis study by the three models (n = 12).

Note: units of RMSE is different for each measurement: runoff (cm), sediment (g), chlorpyrifos (mg), diuron (mg)

	MAPE (%) PRZM	MAPE (%) RZWQM	MAPE (%) OpusCZ	RMSE PRZM	RMSE RZWQM	RMSE OpusCZ
Runoff	195.3	113.4	82.9	5.0	2.9	3.0
Sediment	1064.4	--	74.9	156.3	--	35.0
Chlorpyrifos	411.3	78.4	384.1	8.7	26.1	8.7
Diuron	192.0	72.3	27.5	4661.9	3581.4	1229.3

The largest simulation errors were associated with the simulation of the sediment erosion due to a few reasons:

- ◊ Large uncertainty in measuring sediment erosion from field. The measured values tend to be over-estimates because the ditch from which samples were obtained was not concrete
- ◊ Alfalfa has a high ability to filter sediments, so concentrations of suspended sediment were low.
- ◊ Simulated results from OpusCZ were constantly lower than those measured. OpusCZ might have performed better considering measurement uncertainty
- ◊ PRZM consistently over-estimated sediment erosion by one order of magnitude. The errors could be even larger considering the uncertainty in origin of the sediment.
- ◊ Compared to chlorpyrifos, the MAPE for simulating diuron was smaller for all models. This could be partly associated with the poor sediment simulation by the models.



↑ Fig 5: OpusCZ simulated and measured event hydrograph

During the course of a runoff event, highest pesticide concentrations were one to six times of the average concentration. This suggests the importance of capturing the peak runoff rather than the daily average. Models such as RZWQM and OpusCZ run at sub-daily time steps and thus are better able to capture the peak pesticide concentrations. Given the short time duration and uncertainties in flow measurement, OpusCZ was effective at reproducing the shape, duration, and peak of the runoff hydrographs.

CONCLUSIONS

- ◊ **All three models simulate water and pesticide runoff with good accuracy for events generated by natural rainfall or sprinkler irrigation. However, for events generated by flood irrigation, OpusCZ stands out as the best performer due to inclusion of a specific modeling component followed by RZWQM.**
- ◊ The PRZM model is relatively simple and therefore easy to calibrate. It is also the "standard" model used by USEPA and the Europe Union for pesticide registration evaluation. However, the model did not perform as well as the other two models when used to simulate flood irrigation and on farm management practices. PRZM provides predictions of daily averages for pesticide runoff and thus it is not able to capture peak values that occur within a runoff event.
- ◊ The RZWQM model has the capabilities of simulating both types of runoff events with good accuracy. It is also the most user-friendly among the three with a GUI and strong technical support. However, the lack of sediment erosion limits its application for hydrophobic pesticides when sediment erosion is the target problem. The model may produce more realistic results with the addition of a reliable sub-model for sediment erosion.
- ◊ OpusCZ is the most reliable model among the three models with the great ability of simulating flood irrigation at two dimensions. It also has capacities to simulate various management practices such as on-farm pond, tillage practices, and cover crops. Therefore, it is the most suitable model to use for simulating pesticide runoff in semi-arid areas in California where agricultural is heavily dependent on irrigation.
- ◊ This evaluation study was limited by the availability of field studies with reliable measurements that are needed for model evaluation. More field studies covering a variety of crops and management practices are needed in the future for a more complete evaluation of the models.

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