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Evaluation of Three Models for Simulating Pesticide Runoff from Irrigated Agricultural Fields

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Abstract

Three models were evaluated for their accuracy in simulating pesticide runoff at the edge of agricultural fields: Pesticide Root Zone Model (PRZM), Root Zone Water Quality Model (RZWQM), and OpusCZ. Modeling results on runoff volume, sediment erosion, and pesticide loss were compared with measurements taken from field studies. Models were also compared on their theoretical foundations and ease of use. For runoff events generated by sprinkler irrigation and rainfall, all models performed equally well with small errors in simulating water, sediment, and pesticide runoff. The mean absolute percentage errors (MAPEs) were between 3 and 161%. For flood irrigation, OpusCZ simulated runoff and pesticide mass with the highest accuracy, followed by RZWQM and PRZM, likely owning to its unique hydrological algorithm for runoff simulations during flood irrigation. Simulation results from cold model runs by OpusCZ and RZWQM using measured values for model inputs matched closely to the observed values. The MAPE ranged from 28 to 384 and 42 to 168% for OpusCZ and RZWQM, respectively. These satisfactory model outputs showed the models' abilities in mimicking reality. Theoretical evaluations indicated that OpusCZ and RZWQM use mechanistic approaches for hydrology simulation, output data on a subdaily time-step, and were able to simulate management practices and subsurface flow via tile drainage. In contrast, PRZM operates at daily time-step and simulates surface runoff using the USDA Soil Conservation Service's curve number method. Among the three models, OpusCZ and RZWQM were suitable for simulating pesticide runoff in semiarid areas where agriculture is heavily dependent on irrigation.

Core Ideas

- We evaluate the models for simulation of pesticide runoff generated by irrigation and rainfall.
- PRZM, RZWQM, and OpusCZ were evaluated for accuracy in simulating pesticide runoff at edge of fields.
- Models were compared using data from three field studies conducted in California.
- For runoff generated by sprinkler irrigation and rainfall, all models were equally accurate.
- For runoff generated by flood irrigation, OpusCZ and RZWQM were more accurate.

Off-site movement of pesticides from applied agricultural areas has been recognized as one of the major contributors to the contamination of surface waters worldwide (Schulz, 2004; Gangbazo, 1999; Humenik et al., 1987; Line et al., 1997; Loague, 1998). Pesticides move into surface water via drift, surface runoff, or subsurface flow. Among these routes, surface runoff generated by rainfall events has attracted the most attention (Schulz, 2004). In semiarid regions, such as California, pesticide runoff occurs not only during the rainy season but also during the dry growing season between March and October when the crops are irrigated and pesticides are applied. Surface runoff generated by irrigation events has been identified as a major cause for the detection of pesticides in agricultural areas of California during the dry season (Starner et al. 2005; Starner, 2009; Foe, 1995).

To assess the ecological risks of pesticides in surface water, mathematical models that predict exposure to pesticides have been increasingly used in addition to water quality monitoring. Prediction of pesticide loss at the edge of a field is fundamental to exposure assessment both at local and watershed scales. In agricultural lands, field application of pesticides is the main source of pesticides found in nearby waters. Edge-of-field losses of pesticides range from less than 0.1% of total amount applied to 10% or more with the greatest loss being associated with storm events occurring shortly after application (Schulz, 2004). Desirable field-scale models should account for key hydrologic processes, crop growth, pesticide application, transformation processes, and field management practices within the application field. For use in semiarid regions where irrigation is widely applied, models should be capable of simulating pesticide runoff generated by rainfall and irrigation events.

A few field-scale models have been developed since the 1980s. 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 USEPA (Carsel et al., 1998), the Root Zone Water Quality Model

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Abbreviations: %D, percentage of difference; CDPR, California Department of Pesticide Regulation; CIMIS, California Irrigation Management Information System; GLEAMS, Groundwater Loading Effects of Agricultural Management System; GUI, graphical user interface; MAPE, mean absolute percentage error; MAPE, mean absolute percentage error; PRZM, Pesticide Root Zone Model; RZWQM, Root Zone Water Quality Model; SSURGO, Soil Survey Geographic database; USLEC, C factors of universal soil loss equation.

(RZWQM) developed by USDA–ARS (Ahuja et al., 1999), and the OpusCZ model, also developed by USDA–ARS (Smith, 1992). The PRZM is a one-dimensional model developed for predicting pesticide movement in unsaturated soils. The model was developed for the purpose of pesticide registration evaluation. The RZWQM and OpusCZ are mechanistic models. The RZWQM simulates water quality and the effects of management practices on crop growth, hydrology, nutrient cycling, organic matter, and chemical losses. Opus is a model designed for assessing the effects of land use and climatic factors on the movement of water, sediment, nitrogen, phosphorus, and pesticides at the field scale. OpusCZ is an updated version of the original Opus model with enhanced capabilities for chemical transport, soil water movement, and soil–surface water interactions. The modeling of plant growth, soil and plant evaporation, and the erosion processes were unchanged. 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.

Ma et al. (1999) compared the Groundwater Loading Effects of Agricultural Management System (GLEAMS), Opus, PRZM2β, and PRZM3 models using a 2-yr field study with simulated rainfall events. They found that GLEAMS, Opus, PRZM2β, and PRZM3 adequately predicted water runoff amounts, with normalized root mean square errors of 29, 29, 31, and 31%, respectively (Ma et al. 1999). The GLEAMS, Opus (with an equilibrium adsorption submodel), and PRZM3 models predicted atrazine concentrations in runoff within a factor of two of observed concentrations. Mottes et al. (2014) reviewed pesticide transfer models including RZWQM and PRZM, but not Opus, for their capabilities of simulating management practices. They found that RZWQM computes the effects of many field management practices such as tillage, pesticide interception by mulch, and slow-release pesticide formulation, while other models do not. The PRZM considers the effects of tillage on pesticide distribution in soil only if tillage is performed on the same day as pesticide application. Subsequent tillage operations have no effect in the model on pesticide distribution in soil layers (Mottes et al., 2014). Although Mottes et al. (2014) mentioned irrigation as one of the main field practices that affect the environmental characteristics associated with pesticide transfer, they did not evaluate models for the effects of irrigation. Very few papers in the open literature focus on evaluating these models for simulating runoff events generated by irrigation. Chang et al. (2008) investigated three models including PRZM3: the Pesticide Analytical Model and Integrated Pesticide Transport Modeling for simazine transport and fate under irrigated conditions. They concluded that "with the aid of the fuzzy multiattribute decision making method, PRZM3 is deemed as the most promising one for such precision farming applications." However, they did not show how the models perform when compared with measured data nor did they describe how PRZM3 was set up for simulating flood irrigation. In summary, there is a lack of data in evaluating the three preselected models (PRZM3, RZWQM, and OpusCZ) for their abilities in simulating pesticides in irrigation runoff.

In California, the Department of Pesticide Regulation (CDPR) 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. Current water quality regulations in California are often based on instantaneous water sampling designed to reflect the peak concentrations. These concentrations are compared with water quality criteria to determine if a violation has occurred. Therefore, a model should be able to predict peak pesticide concentrations at field edge that occur soon after rainfall or irrigation events. In addition, widespread 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.

To address the data gap in modeling irrigation runoff and the unique regulatory needs in California, this study evaluates PRZM, RZWQM, and OpusCZ models for simulating pesticide runoff generated by irrigation and rainfall events in California. The models will be evaluated on their accuracy in predicting pesticide runoff using measurements from field studies as well as their theoretical foundations.

Materials and Methods

The models were evaluated using three field studies conducted at agricultural fields in California. Simulated results were compared with measured data on runoff volume, sediment erosion, and pesticide mass in runoff. In addition, the models were differentiated by their mathematical representations of key environmental processes such as surface runoff, infiltration, and pesticide adsorption. Finally, the models were compared based on the following criteria: (i) output accuracy in simulating pesticides in runoff; (ii) representation of the key processes governing pesticide runoff in California's agricultural settings; and (iii) ease of use including data preparation, documentation of model, ability to retrieve, and display outputs.

Model Versions

For this study, we used the most current versions of the three models available at the time of investigation: PRZM version 3.12.3 released May 2006; RZWQM version 2.94 obtained from model developers in June 2015; and Opus version CZ (OpusCZ) obtained from the model developer in December 2013. During the revision of the paper, the newest version of PRZM (PRZM5) had become available via personal requests. Since there was little change in the sciences of the model, the results presented in this paper should also hold for PRZM5. The most current release of RZWQM (version 2.94, used here) included a newly added sediment erosion module, which was not available in previous versions. This paper is one of the earliest studies examining the sediment erosion component of the RZWQM model.

Evaluation Using Field Studies

Three field-runoff studies were used as testing cases (Table 1). The first study was conducted in a citrus grove located at Fresno, CA, in 1995. The experimental plots were bare grounds among citrus (*Citrus* spp.) trees (row middles). Each plot was a rectangular area of 3.4 by 5.5 m bounded by four trees. The soil was Hanford sandy loam (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents) with 73% sand, 19% silt, 8% clay, and an organic C content of 0.4%. The average bulk density was 1.71 g cm^{-3}, and the average infiltration rate was 0.864 cm h^{-1}.

The soil is of low permeability and prone to compaction, suggesting a high runoff potential. Simazine was applied at a rate of 2 kg ha^{-1} (a.i.) via a hand-held sprayer. Six of the total 12 blocks were randomly selected where simazine was mechanically incorporated into soil immediately after application. This treatment was to test the impacts of tillage on pesticide runoff. Two rainfall events were simulated using macro-sprinklers: the first occurred on the day of pesticide application, and the second occurred 7 d later. The following were measured: runoff volume, sediment in runoff water, and pesticide concentration in filtered and nonfiltered water samples. More details of this study can be found in Troiano and Garretson (1998).

The second study was conducted in a peach orchard located at Winters, CA, in 1996 (Table 1). Experimental plots were row middles among peach [*Prunus persica* (L.) Batsch] trees that were of three different surface covers: bare soil, clover, and, oat (*Avena sativa* L.). The plots were 4.73 by 69.9 m. The soil was classified as Yolo silty loam (fine-silty, mixed, superactive, nonacid, thermic Mollic Xerofluvents) with 37% sand, 38% silt, and 25% clay with an organic C content of 1.2%. The bulk density was 1.42 g cm^{-3}. Three insecticides (chlorpyrifos, diazinon, and methidathion) were applied together using a mini-air-blast sprayer at a nominal rate of 1.12 kg ha^{-1}. Two rain events occurred 12 and 14 d after application with the amount of 38 and 15 mm, respectively. Measurements from the second rain events were used for model simulation. The following were measured and used for model simulation: runoff volume, sediment in runoff water, and pesticide concentration in filtered and nonfiltered water samples (Table 1). More details of this study were documented in Ross et al. (1997).

The third study was conducted in an alfalfa (*Medicago sativa* L.) field located at Davis, CA, during 2012 and 2013 (Table 1). The field contained rows of alfalfa plants separated by levees. At the head of each row was a flood irrigation check, which delivered water from the head of the field to the other end. A tailwater ditch collected runoff water at the edge of the field. Two rows of the field were used for the study: one was 15.9 m in width and 176.2 m in length (block A), and the other was 16.7 m in width and 176.8 m in length (block B). The soil was classified as Brentwood silty clay (fine, smectitic, thermic Typic Haploxerepts) with 36.5% sand, 42.8% silt, and 20.7% clay and an organic C content of 1% (Table 1). The bulk density for the top layer (0–6 inch) was measured as 1.42 ± 0.067 g cm^{-3}. The saturated hydraulic conductivity for the top layers was measured as 0.93 ± 0.959 cm h^{-1} for block A and 2.11 ± 1.475 cm h^{-1} for block B. In addition, soil moisture contents at saturation, 1/3 bar and 15 bar, were also measured in both blocks.

Chlorpyrifos was applied on 9 Apr. 2012 at a nominal rate of 0.53 kg ha^{-1} using a HAGIE 8250 tractor sprayer (Hagie, Inc.). Diuron was applied on 17 Jan. 2013 at a nominal rate of 2.28 kg ha^{-1} via a handheld sprayer. The first irrigation occurred on block B on 21 May 2012, which was 42 d after chlorpyrifos application. Five additional irrigations were applied on block B on 15 June 2012, 28 Aug. 2012, 26 Feb. 2013, 21 Mar. 2013, and 26 Apr. 2013. Block A was also irrigated six times, each occurring 1 d after those on block B. The water input ranged from 13 to 20 cm per irrigation event. More details of the study can be found at Zhang (2012).

The three studies were chosen to represent variations in water input methods (simulated rainfall using macro-sprinkler, natural rainfall, and flood irrigation), pesticide application methods (ground, foliar, and soil incorporation), land cover (bare, tree crop, alfalfa), and pesticide groups (herbicides and insecticides). Main features of the studies are summarized in Table 1. The physiochemical properties of the five chemicals were listed on Table 2. The soil adsorption coefficients (K_{OC}) ranged from 400 for methidathion to 8151 for chlorpyrifos and the soil half-lives ranged from 6.4 d for diazinon to 90 d for simazine and diuron. Diazinon is the most volatile among the four, while simazine, diuron, and methidathion are nonvolatile (Table 2).

Simulation Design

Values for model inputs were set by three approaches: field measured values, public databases, and parameter estimates via model calibration. For the parameters with field measurements, the measured values were used. These parameters include field size, soil texture, pesticide application rates, rainfall or irrigation amount, and soil hydraulics measured in the Davis study. For the

Table 1. Main settings of the three field studies.

	Fresno study	Winters study	Davis study
Location	38.836° N, −119.853° W	38.503° N, −121.977° W	38.532° N, −121.799° W
Crop	Citrus row middle (bare ground)	Peach	Alfalfa
Soil	Hanford sandy loam	Yolo silty loam	Brentwood silty clay loam
Size	0.00187 ha plot^{-1}	0.033 ha plot^{-1}	0.281 ha (block A) 0.295 ha (block B)
Slope	2%	2%	0.14%
Water input	Simulated rainfall; two events of 32 mm each	Natural rainfall of 15 mm	Flood irrigation, 12 events ranged from 130–260 mm
Management practices	Mechanical incorporation of pesticides	Cover crop with oat and clover	Alfalfa cut and harvest
Pesticides	Simazine	Chlorpyrifos, diazinon, methidathion	Chlorpyrifos, diuron
Pesticide spray date	22 Aug. 1995	4 Jan. 1996	9 Apr. 2012 (chlorpyrifos) 17 Jan. 2013 (diuron)
Pesticide spray method	Ground, soil incorporation	Foliar	Ground
Application rate	2.0 kg ha^{-1}	1.2 kg ha^{-1}	0.53 kg ha^{-1} (chlorpyrifos) 2.28 kg ha^{-1} (diuron)
Weather station (hourly and daily)	CIMIS† weather station at California State University, Fresno	CIMIS weather station at Davis, CA	CIMIS weather station at Davis, CA

† CIMIS, California Irrigation Management Information System.

Table 2. Physiochemical properties of the pesticides applied in the case studies.

	Simazine	Chlorpyrifos	Diazinon	Diuron	Methidathion
Molecular weight (g mol^{-1})	201.7	350.6	304.4	233.1	302.3
Solubility (mg L^{-1})	5	1.05	60	35.6	240
Soil adsorption coefficient (K_{OC})	420	8151	643	813	400
Soil half-life (d)	90	15	6.4	90	9.6
Foliar half-life (d)	–	8.5	5.7	9	4.4
Henry's Law constant	1.30×10^{-8}	2.80×10^{-4}	0.061	2.06×10^{-8}	7.51×10^{-8}
Vapor pressure (mPa)	0.00081	1.43	11.97	0.00115	0.25

parameters without field measurements, data from public databases were used. For example, the weather data were from the California Irrigation Management Information System (CIMIS) stations (Table 1). Soil hydraulic properties of the Fresno and Winters studies were obtained from the Soil Survey Geographic (SSURGO) database (USDA–NRCS, 2011). For the parameters that could not be measured, default values were used for base simulation and may later have been modified during model calibration.

Calibration and Validation

Model calibration was conducted manually by modifying the parameters with the greatest effect on model output, such as the curve number for the PRZM and the saturated soil hydraulic conductivity for OpusCZ and RZWQM models. Model calibration takes two steps. First, the models were run with parameters that were measured in the field or obtained from literature. Second, parameters were adjusted based on comparing simulated results on runoff flow, sediment, and pesticide concentration with measured data from the field experiments. The objective function used to aid calibration is the mean absolute percentage error (MAPE), discussed in the next section. The calibration was completed when the best set of values was found so that the MAPE for all measurements, including runoff, sediment erosion, and pesticide loss, was minimized. Model validation was conducted by running the models on other events or conditions using the best set of parameters that resulted from the calibration. For the Fresno study, models were calibrated using data from the first runoff event. The second runoff event was used as model validation. For the Winters study, data from chlorpyrifos-treated plots were used as calibration, while the data from the other plots were used for validation.

Since most of the key input variables were measured in the Davis study, no manipulation of the parameters was done during model simulation, and all simulations were cold runs with parameter values set at the average values of measurements.

Statistics for Model Evaluation

For event-based simulations with small sample sizes, statistics commonly used for long-term simulation, such as regression-based terms, were not suitable. Instead, statistics based on difference measures were used (Moriasi et al., 2007). These statistics include RMSE, percentage of difference (%D), and MAPE, as expressed in Eq. [1–3], respectively:

$$\text{RMSE} = \sqrt{\frac{\sum \left(P_i - O_i\right)^2}{n}} \quad [1]$$

$$\%D_i = \left(\frac{P_i - O_i}{O_i}\right)100 \quad [2]$$

$$\text{MAPE} = \left(\frac{100}{n}\right)\sum_i^n \frac{\left|P_i - O_i\right|}{O_i} \quad [3]$$

where P_i is the ith predicted value, O_i is the ith observed value, and n is the number of observations.

These statistics are among the most commonly used for evaluating model performance (Willmott, 1982; Loague and Green, 1991; Legates and McCabe, 1999). The RMSE value is the square root of the mean of the squared differences between observations and predicted values. The RMSE assesses the quality of an estimator in terms of its variation and unbiasedness and provides information on the absolute error in units of the variable. The MAPE and percentage of difference (%D) express the absolute error in generic percentage terms. As such, %D and MAPE are not scale dependent and can be used to compare across different datasets. The RMSE is more sensitive than other measures to the occasional large errors because the squaring process gives disproportionate weight to very large errors.

For the Davis study, it was possible to use statistical criteria based on regression because of a larger number of simulated events. Linear regressions between measured and simulated values were conducted and the coefficient of determination (R^2), as shown in Eq. [4], was used as one of the evaluation criteria:

$$R^2 = 1 - \frac{\sum \left(O_i - P_i\right)^2}{\sum \left(O_i - \bar{O}\right)^2} \quad [4]$$

where $\bar{O}$ is the average of the observed values. In addition, graphs of observation versus prediction were used to qualitatively demonstrate model performance.

Results and Discussion

Simulation of the Fresno Study

The Fresno study represented scenarios where pre-emergent herbicides were applied on compact soils that are prone to runoff. All three models were able to simulate the amount of water runoff, sediment erosion, and simazine in runoff with good accuracy. The MAPE ranged from 29 to 87%. In general, the simulation results for the calibration event were better than the results for the validation event. There was no significant difference in prediction accuracies among the three models. The models tended to underestimate simazine runoff in adsorbed phase with the %D ranged from −80 to −98% (Table 3). Among the three models, PRZM was the easiest to calibrate with the curve number dominating the runoff process. However, the validation results indicated that there was greater deviation of predicted values from measured values than the calibration period (MAPE of 58 and 83 for validation compared with MAPE of 29 and 31 for calibration). In contrast, for the OpusCZ model, simulation results for the tillage scenario during the validation event had a smaller error than the calibration event (Table 3).

The Fresno study also examined the effects of tillage by mechanically incorporating the applied herbicide within the top 7.6 cm of soil. The tillage practices reduced the amount of runoff while increasing soil erosion (Fig. 1). Since pesticide residues were redistributed within the 7.6 cm of top soil instead of staying on the surface, less simazine mass was measured in runoff water. All three models simulated these effects well, even though they were using different approaches (Fig. 1). 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 compared with the other two models.

Simulation of the Winters Study

Table 4 shows the calibrated results for water and sediment runoff. Compared with the Fresno study, the Winters site had lower runoff potential with about 11% of the rainfall going to surface runoff (Table 4). Simulated runoff and sediment erosion by all three models were well within 1.5-folds of the measured value with MAPE less than 50%.

For pesticide simulation, the three models also showed good accuracy with the highest MAPE of 167% and the highest RMSE as small as 6.8 mg (Table 5). Unlike the Fresno study, model errors for validation simulations were smaller than those for calibration. Although there were no significant difference in simulation accuracies among the three models, OpusCZ simulated pesticide runoff with smaller errors compared with the other two models and the smallest RMSE in all simulations.

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	−8	1.6	47	1.2	14	1.1
		sediment (g)	157.7	−4	176	7	134.5	−18	164.0
		simazine dissolved (mg)	118.2	−16	112.8	−19	143.4	2	140.0
		simazine adsorbed (mg)	5.5	−88	1.74	−96	1.0	−98	44.0
		MAPE‡ (%)	28.7		42.5		32.9		
	Tillage	runoff (cm)	0.6	9	0.5	−17	0.5	−8	0.5
		sediment (g)	227.6	−1	240.0	5	285.2	25	229.0
		simazine dissolved (mg)	12.7	27	3.3	−67	28.2	182	10.0
		simazine adsorbed (mg)	1.0	−89	0.4	−95	0.3	−96	9.0
		MAPE (%)	31.4		45.9		77.8		
Event 2 validation	No till	runoff (cm)	1.1	17	1.6	78	1.2	36	0.9
		sediment (g)	169.6	27	176	31	133.1	−1	134.0
		simazine dissolved (mg)	92.0	109	108.7	147	16.7	−62	44.0
		simazine adsorbed (mg)	4.3	−80	1.66	−92	0.5	−98	21.0
		MAPE (%)	58.0		87.0		49.1		
	Tillage	runoff (cm)	0.6	−48	1.0	−13	0.5	−58	1.2
		sediment (g)	256.9	−22	257.0	−22	284.6	−13	328.0
		simazine dissolved (mg)	10.8	176	7.3	86	5.8	48	3.9
		simazine adsorbed (mg)	0.8	−85	0.4	−92	0.1	−98	5.3
		MAPE (%)	82.7		53.3		54.2		

† %D, percentage of diference.

‡ MAPE, mean absolute percentage error.

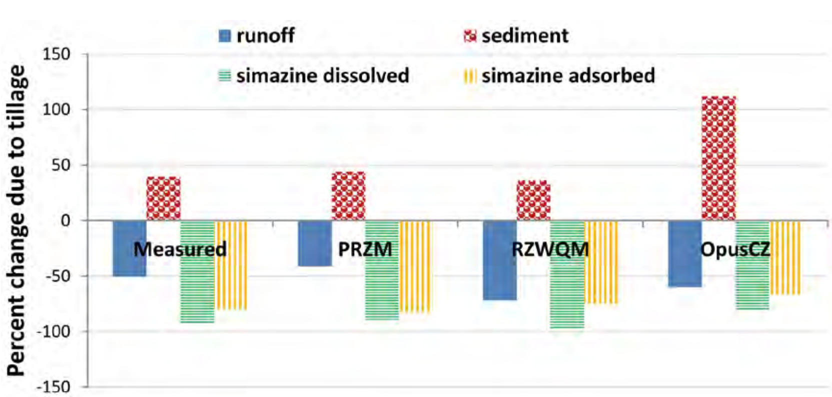

Fig. 1. Measured and simulated tillage effects for the second runoff event (validation period) in the Fresno case study.

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

Treatment	Type	PRZM		RZWQM		OpusCZ		Measured
		Simulated	%D†	Simulated	%D	Simulated	%D	
Bare	Runoff (mm)	1.5	−12	1.7	1	1.7	−2	1.7
Clover	Runoff (mm)	0.6	−16	0.8	11	0.8	13	0.7
Oat	Runoff (mm)	0.9	5	1.0	6	1.2	28	0.9
MAPE‡ (%)		11.0		5.9		14.3		
RMSE		0.1		0.1		0.2		
Bare	Sediment (g)	356.8	2	352.9	1	564.3	61	350.7
Clover	Sediment (g)	136.5	−28	189.8	0	214.5	13	189.3
Oat	Sediment (g)	188.5	−2	207.4	7	330.0	71	193.1
MAPE (%)		10.7		2.8		48.4		
RMSE		30.8		8.4		147.2		

† %D, percentage of difference.

‡MAPE, mean absolute percentage error.

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 USLEC. For RZWQM and OpusCZ model, the effects were realized by setting up the crop growth parameters for oat and clover.

Similar to the Fresno study, the three models tended to underestimate pesticide runoff in adsorbed phase regardless of land cover type and pesticide properties. This could be due to two possible reasons: (i) the uncertainties in the measurements themselves and (ii) the models' algorithm for calculating pesticide loss associated with sediment erosion. In both studies, pesticides in adsorbed phase in runoff were low with measurements ranging from 1.2 to 44 mg per event. In addition, the models were first calibrated for runoff and sediment before the pesticide loss. If the measured sediment erosion were underestimates, the resulting pesticide loss as a result of sediment erosion would also be underestimated. Therefore, uncertainties in lab and field measurements could have contributed to the underestimation of adsorbed pesticides in runoff. However, the adsorbed pesticides were underestimated even though sediment erosion was not always underpredicted. This suggested a limitation in the models' algorithms for calculating adsorbed pesticides in runoff. In PRZM3, pesticide loss as a result of erosion is a function of total sediment erosion and the enrichment ratio for organic matter (Suárez, 2006). The total amount of pesticides available for erosion was determined by the total amount of pesticides existing

Table 5. Simulated pesticides in runoff for the Winters study. Units: mg.

	Chemical	Land cover	Type	PRZM	%D†	RZWQM	%D	OpusCZ	%D	Measured
Calibration	Chlorpyrifos	Bare	Adsorbed	2.3	−43	1.7	−58	3.8	−7	4.1
		Clover	Adsorbed	0.9	−29	0.5	−58	1.4	16	1.2
		Oat	Adsorbed	1.4	−36	0.6	−75	2.2	0	2.2
		Bare	Dissolved	0.6	20	0.6	25	0.2	−53	0.5
		Clover	Dissolved	0.2	806	0.1	346	0.1	111	0.0
		Oat	Dissolved	0.4	68	0.2	−19	0.2	−30	0.2
	MAPE‡ (%)			167.1		96.8		36.1		
	RMSE			0.8		1.2		0.2		
Validation	Diazinon	Bare	Adsorbed	1.3	−85	1.0	−88	2.2	−75	8.8
		Clover	Adsorbed	0.5	−77	0.5	−74	0.8	−60	2.1
		Oat	Adsorbed	0.8	−91	0.2	−98	1.3	−86	9.1
		Bare	Dissolved	4.0	6	5.7	51	4.3	13	3.8
		Clover	Dissolved	1.6	38	1.2	5	0.2	−82	1.2
		Oat	Dissolved	2.7	−15	1.7	−46	3.0	−5	3.1
	MAPE (%)			51.9		60.4		53.5		
	RMSE			4.6		5.0		4.2		
	Methidathion	Bare	Adsorbed	2.4	−84	0.9	−94	2.8	−81	14.7
		Clover	Adsorbed	0.9	−80	0.5	−89	1.1	−76	4.5
		Oat	Adsorbed	1.4	−72	0.5	−90	1.7	−67	5.2
		Bare	Dissolved	11.2	−23	9.0	−39	14.3	−3	14.7
		Clover	Dissolved	4.6	39	2.1	−37	3.4	3	3.3
		Oat	Dissolved	7.4	1	3.4	−54	9.9	34	7.4
	MAPE (%)			49.8		67.2		44.1		
	RMSE			5.6		6.8		5.3		

† %D, percentage of difference.

‡ MAPE, mean absolute percentage error.

in the topmost compartment. As a result, a small top compartment could result in the underestimation of adsorbed pesticides in runoff (Luo and Zhang, 2011). To avoid this artificial error, we tested the model by varying the depths for the top soil layers. However, even when the depths of the topmost soil layers were increased to 10 cm, the model still underestimated pesticide runoff associated with erosion. It is possible that PRZM's underestimation of adsorbed pesticide in runoff might be related to an underestimate of the enrichment ratio. The RZWQM used a similar approach but a different equation for the enrichment ratio, which was a function of specific surface areas of soil particles. OpusCZ took a more mechanistic approach by solving the pesticide mass balance equation for the top soil. It was unclear why OpusCZ underestimated adsorbed pesticides in runoff. Further studies were needed to investigate the reasons associated with the underestimation of pesticide loss as a result of sediment erosion. This investigation could leads to improvements in model algorithms for simulating hydrophobic pesticides.

Simulation of the Davis Study

Compared with the previous two studies, the Davis study was a better dataset with more measurements for soil hydraulic properties and more runoff events. The study field is representative of the flood-irrigated agricultural lands in California's Central Valley with the typical amount of irrigation water use and irrigation frequency. The performance of the three models in simulating the Davis study is shown in Table 6 and Fig. 2. 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.

The simulation accuracies were different among the three models. Simulated results by OpusCZ were the most accurate with small errors for all measures including runoff, sediment erosion, and pesticides loss (Table 6). Most of the MAPEs for OpusCZ results were below 100%, except for chlorpyrifos runoff, where MAPE was 384%. In this case, the measured value itself was very low (0.2 mg) and the RMSE was 8.7 mg.

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

	MAPE†			RMSE		
	PRZM	RZWQM	OpusCZ	PRZM	RZWQM	OpusCZ
	%			units‡		
Runoff	195.3	168.2	74.4	5.0	4.3	2.3
Sediment	1064.4	96.3	74.9	156.3	22.5	35.0
Chlorpyrifos	411.3	79.2	384.1	8.7	20.8	8.7
Diuron	192.0	41.8	27.5	4661.9	2443.0	1229.3

† MAPE, mean absolute percentage error.

‡ Units of RMSE is different for each measurement: runoff (cm), sediment (kg), chlorpyrifos (mg), diuron (mg).

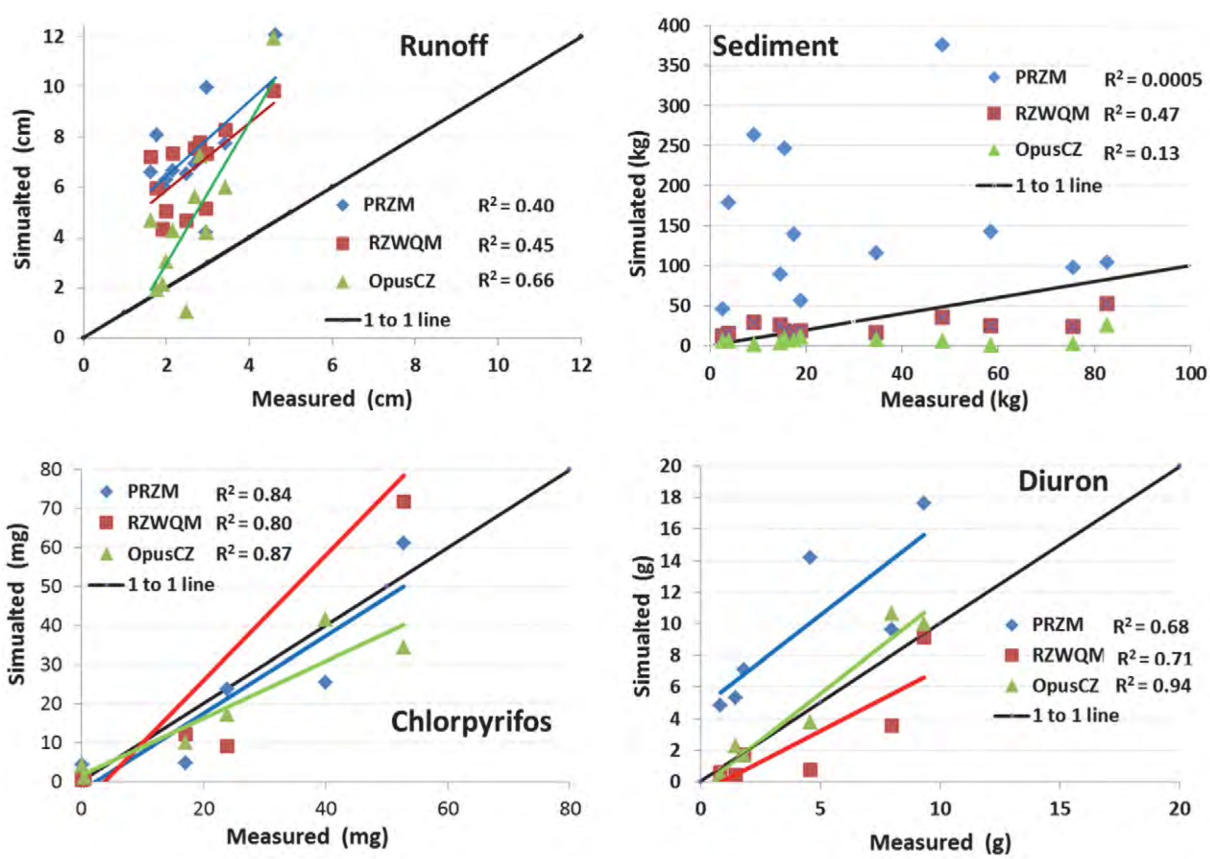

Fig. 2. Simulated and measured runoff for the Davis studies.

Compared with the calibrated results in the Fresno and Winters study, the errors in the cold-run results from OpusCZ were not much bigger. Since there were more measured events in the Davis study than the previous two studies, statistical measurements based on regression was possible. The coefficients of determination (R^2) were calculated for each model for runoff, sediment, and pesticide loss for scatter plots of simulated vs. measured data (Fig. 2). For OpusCZ, the regression lines were very close to the 1:1 line except for the sediment results, where sediment erosion was underestimated with a MAPE of 75% and RMSE of 35 mg. The R^2 for runoff, chlorpyrifos, and diuron were 0.66, 0.87, and 0.94, respectively. These results show that OpusCZ has strong abilities in mimicking reality and capturing variations in water and pesticide runoff.

The results from the RZMQM simulations were not as good as OpusCZ but also fairy accurate with MAPE ranging from 42 to 168%. The soil erosion results were the most accurate compared with PRZM and OpusCZ with a small RMSE of 22.5 mg (Table 6). The RZWQM tended to overestimate runoff volume, but the results on chlorpyrifos and diuron runoff were very close to the 1:1 line (Fig. 2). The R^2 for runoff, sediment, chlorpyrifos, and diuron were 0.45, 0.47, 0.80, and 0.71, respectively.

The simulation results from PRZM were not as accurate as the other two models. The PRZM tends to overestimate runoff volume, sediment, and diuron. The largest error was from the sediment erosion simulation with a MAPE of 1064% and a RMSE of 156 kg.

The significant differences among model performances could be due to the fact that the Davis study was conducted with flood irrigation and the models different abilities in simulating runoff generated by flood irrigation. The runoff-generating mechanisms in flood irrigations are different from those in natural rainfall or sprinkler irrigation. In natural rainfall or macro sprinkler, water enters into the field vertically and runoff occurs shortly after the rainfall starts. In flood irrigation, water enters the field at the top of the field slope—termed the head of the field—and advances down along the slope to the end of the field. The amount of runoff water produced is a complicated process based on the amount of time water is exposed to infiltration down the length of the run, the rate of water moving from the head to the end of the field, and the changes in infiltration rates of the soil over time. This process was modeled only in the OpusCZ model. This may explain why the three models perform equally well for the Fresno and Winters study, but the OpusCZ model performed much better than the other two for the Davis study.

It is clear that all three models were able to simulate natural rainfall, but they vary with respect to simulating specific irrigation methods. The PRZM did not simulate flood irrigation and treated sprinkler irrigation exactly the same as natural rainfall. As a result, users cannot set the water input rates for sprinkler irrigation in PRZM. The RZWQM considered sprinkler irrigation and allows users to define water input rates and application dates, yet did not have algorithms for flood irrigation. OpusCZ simulated both sprinkler and flood irrigation and allowed users to specify the date and rate of water input. Two methods were used in OpusCZ for infiltration depending on the surface condition. The first is an imposed ponding condition such as with flood irrigation. The model imposes a fixed soil water head at the surface, and Eq. [5] describes infiltration rate under this condition (Smith, 1992):

$$I = \int_{\theta_i}^{\theta_s} (\theta - \theta_i) \frac{D(\theta)}{f - K_s} \mathrm{d}\theta \quad [5]$$

where D is diffusivity, defined as K dψ/dθ (mm^2 min^{-1}); I is depth of infiltration from start of irrigation (mm); f is rate of infiltration (mm min^{-1}); θ is volumetric water content of soil (mm mm^{-1}); θ_i is initial water content (mm mm^{-1}); and K_s is effective saturated soil water conductivity (mm mm^{-1}).

The other surface condition is the common rainfall or sprinkler irrigation. For this case, water depth I increases at first because of rainfall:

$$I = \int_0^t r(t) \mathrm{d}t \quad [6]$$

until the surface becomes saturated, and the boundary condition changes to a fixed head of 0. Consequently, beyond that time, the infiltration capacity is controlled by the conditions near the soil surface. This point of control change is called the time of ponding, t_p, after which f is described by Eq. [5]. These features of the OpusCZ model allows it to accommodate various water inputs especially flood and furrow irrigation.

In general, the largest simulation errors were associated with the simulation of the sediment erosion. This could be explained by a few reasons. First, there was a large uncertainty in measuring sediment erosion from field. The measured values tend to be overestimates because the ditch from which samples were obtained was not concrete so part of the sediment may have originated from the bottom of the ditch and not the field. In addition, the field was covered by alfalfa, which is known for a high ability to filter sediments. So, runoff water exiting the field contains low concentrations of suspended sediment. Simulated results from OpusCZ were constantly lower than those measured. Considering this uncertainty in field measurement, the OpusCZ might have performed better in simulating sediment erosion than shown in Table 6 and Fig. 2. In contrast, PRZM consistently overestimated sediment erosion by one order of magnitude. The errors could be even larger considering the uncertainty in origin of the sediment.

Compared with chlorpyrifos, the MAPEs for simulating diuron were smaller for all models (Table 6). This could also be related to the uncertainty associated with sediment simulation because diuron is water soluble and travels mostly with water. Chlorpyrifos has a higher K_{OC} value resulting in higher tendency to attach to suspended sediments. As a result of the low concentration of suspended sediment leaving alfalfa field, the Davis study did not filter the sampled water and consequently did not have separate measurements for dissolved and adsorbed phases. Therefore, it was unclear whether the models would underestimate pesticides associated with sediment erosion as they did in the Fresno and Winters cases. However, the relative larger errors in chlorpyrifos simulation could be partly associated with the models' limited simulation algorithms for sediment erosion and associated pesticide loss.

The cutting and harvest processes were modeled in the RZWQM and OpusCZ model by the crop growth component. While in PRZM, the effect of cutting is mimicked by setting up different values of USLEC on dates of cutting. Simulated soil moisture content by the RZWQM and OpusCZ model mirrored the dynamics of field measurement, suggesting that the crop growth model did a good job in simulating alfalfa growth. For PRZM, the simulated soil moisture curve fluctuated between soil field capacity and wilting point and can hardly capture the measured variations.

In the Davis study, pesticide concentrations were measured during the course of runoff. Ten samples were taken per runoff event. The highest concentrations were one to six times of the average concentration (Fig. 3). This suggests the importance of capturing the peak runoff rather than the daily average. Models such as RZWQM and OpusCZ run at subdaily time-steps during storms and thus are better able to capture the peak pesticide concentrations. Figure 3 shows the event hydrograph output by OpusCZ for four of the runoff events. Given the short time duration and uncertainties in flow measurement, OpusCZ was effective at reproducing the shape, duration, and peak of the runoff hydrographs (Fig. 3).

Evaluation on the Model Components

In addition to the case studies, the models were also compared regarding their methods in representing the key environmental processes that govern surface runoff and pesticide movement in the environment. The major differences are highlighted in Table 7.

Surface Runoff

Most of the agricultural land in California is flat with very small slopes. The main mechanisms for runoff generation in flat agricultural fields are infiltration excess overland flow (Hortonian overland flow) and shallow subsurface flow. The three models are different in how they simulate Hortonian overland flow and shallow subsurface flow. The PRZM simulates surface runoff using the Soil Conservation Service curve number that was developed by USDA in 1954 (USDA, 1972; Table 7). The curve number method is an empirical watershed-scale-event model that was designed to compute streamflow volume for a storm (Garen and Moore, 2005). Garen and Moore (2005) indicate how the curve number can be misused to predict surface runoff at field or plot scale when the time-step is daily. A mechanistic approach based on infiltration excess is more appropriate. The RZWQM and OpusCZ use such an approach. As the other main mechanisms for runoff generation, subsurface flow through underground tile drain is computed in RZWQM and OpusCZ but not PRZM (Table 7). Tile-drain systems commonly exist in agricultural fields with shallow groundwater and have been found to transport agrochemicals from the field to the surface water in California (Domogalski, 1997; Letey et al., 1977). To simulate pesticide transport in these regions, models should have the ability to simulate water movement through tile drains.

Soil Erosion

Soil erosion is a common phenomenon and an important route for the transport of hydrophobic pesticides. Both PRZM and RZWQM simulate soil erosion using methods based on the USLE (Table 7). OpusCZ simulates soil erosion using methods based on a kinematic runoff and erosion model (KINEROS; Woolhiser et al., 1990) and the transport is spatially distributed within a field. Among the three models, OpusCZ is the most complete in representing the key hydrological processes. The RZWQM resides in between OpusCZ and PRZM regarding the complexity of represented processes. The PRZM is the most simple among the three; its use of curve number for computing surface runoff is not ideal, and it is not capable of simulating flood irrigation and subsurface drainage through drain tiles. Based on the curve number method, PRZM operates at a daily

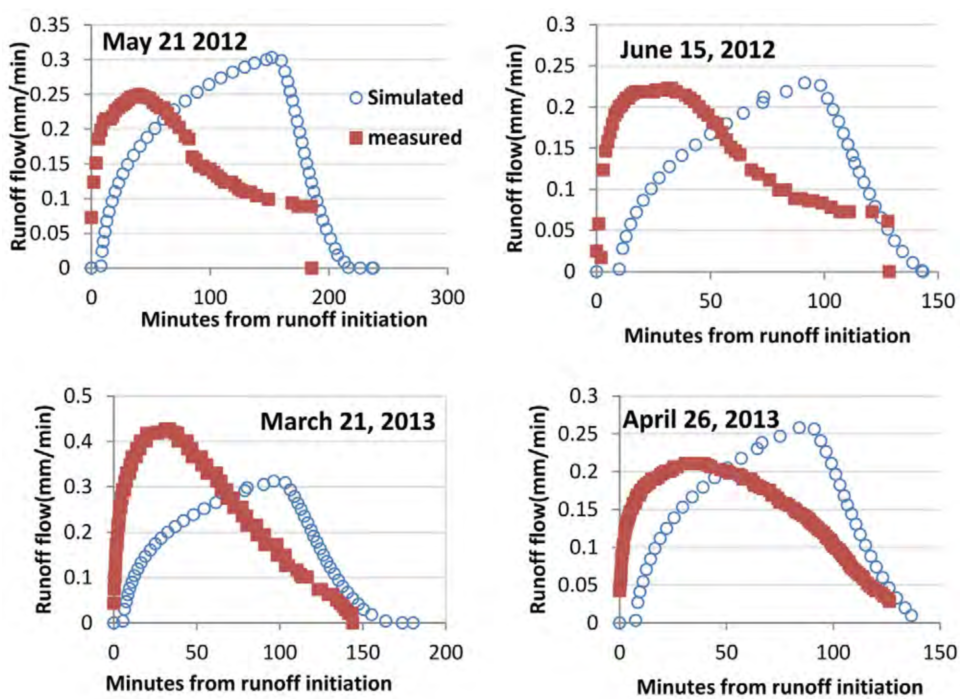

Fig. 3. OpusCZ simulated and measured event hydrograph.

time-step, whereas RZWQM and OpusCZ run at a finer time-step with breakpoint rainfall data input.

Pesticide Processes

For pesticide fate and transport within an agricultural field, the most important processes are application method, sorption, degradation, volatilization, plant wash-off (if applied over canopy), and plant uptake. The three models are similar with some differences in sorption method and degradation rate adjustment in soil (Table 7). For sorption, PRZM took the simplest approach assuming equilibrium status and linear sorption isotherm. RZWQM considered nonequilibrium kinetics with a linear sortion isotherm. And OpusCZ simulated both nonequilibrium kinetics and nonlinear sorption isotherm (Langmuir). For pesticide degradation, the three models use first-order or a slightly modified version of first-order degradation. They allow users to adjust degradation rate in soil according to the changes in temperature, soil moisture (except PRZM), and soil depth (except PRZM).

In addition to the above processes, spray drift can be a major pathway for pesticides movement offsite. All three models use a simple coefficient to account for fraction of pesticides lost to spray drift during application. None of the models have the capability of simulating the amount of spray drift based on key factors such as droplet size (nozzle type) and local field and weather conditions. Therefore, a spray drift model may be used in addition to these hydrological models to provide a better estimate on fraction of pesticides lost to spray drift.

Modeling Management Practices

Regarding management practices, PRZM does not have specific modules for any on-farm management (Table 7). The RZWQM has modules for simulating tillage and harvest operations. OpusCZ has specific modules for tillage, harvest, and on-farm water ponds.

Ease of Use

The RZWQM is the most user friendly because of a well-designed graphical user interface (GUI), through which users prepare all input files with help documents available for each step. The RZWQM also has the most detailed theoretical documentation and the strongest technical support. The newly added parameter estimation module has greatly facilitated sensitivity analysis and model calibration. OpusCZ has a Windows-based GUI. Users need to prepare contents of all input files beforehand and use the GUI to locate the input files and set output options. The theoretical documentation is not as detailed as for RZWQM. The PRZM is the most difficult to use among the three. All input files are FORTRAN fixed-format files and users need to follow the manual closely to prepare each input files. The theoretical document and the user manual provide good help. The newly developed PRZM5 has switched to a free-format input, which would improve user experiences.

Historically, research models such as RZWQM and Opus were criticized for having high input requirements (Engel et al., 1993; Luo et al., 2011). As environmental data are becoming more accessible to the public, it has become easier to obtain data for many of parameters in these models. This analysis showed that for simulating surface runoff, the major uncertainties are associated with the measurements of key soil variables, especially hydraulic conductivity and soil moisture content at 1/3 and 15 bars. The USDA–NRCS has made great advances in making the soil survey data available for public access. Data for these variables can be obtained from the SSURGO and State Soil Geographic databases that are available for download for most

Table 7. 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	Soil Conservation Service 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
Subsurface flow via tile drainage	No	Yes	Yes
Erosion†	MUSLE, USLE	USLE	KINEROS
		Pesticide processes	
Application method	Yes	Yes	Yes
Metabolites	Yes	Yes	Yes
Sorption	Equilibrium; linear	Equilibrium or kinetics; linear	Equilibrium or kinetics; linear, 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, PRZM5 is in free 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 during storm	Continuous
Management practices	No specific modules	Reflect tillage, harvest	Reflect tillage, harvest, pond

† MUSLE, modified universal soil loss equation; USLE, universal soil loss equation; KINEROS, kinematic runoff and erosion model.

agricultural areas in California. In addition, many institutes, including CDPR, have labs capable of measuring soil texture and hydraulic properties at reasonable cost. Another source of uncertainty is weather data. The RZWQM and OpusCZ require hourly weather and breakpoint rainfall data for simulations with hourly or finer time-step. The CIMIS, along with other weather monitoring systems, provides hourly weather data for many stations near agricultural production areas of California. As many of the soil and environmental data become more readily available, it is feasible to use the more data intensive RZWQM and OpusCZ models for simulating agriculture lands in California.

Overall Evaluation

The strength of the PRZM model is that it is relatively simple and, therefore, easy to calibrate. It is also the standard model currently used by USEPA and the European 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. Since PRZM operates only at a daily time-step, it can only provide predictions of daily averages for pesticide runoff and thus it is not able to capture peak values that occur within a runoff event. The findings here are consistent with previous studies. For PRZM, because of its limited abilities in simulating irrigation, few studies were found in the open literature that focused on its application for simulating irrigation runoff. Most of its applications were for simulating storm runoff generated by natural or simulated rainfall. Miao et al. (2004) evaluated PRZM for simulating effects of tillage on herbicide runoff using a 2-yr field dataset in northern Italy. The runoff events were generated by sprinkler irrigation and treated as natural rainfall in the model. They found that the model failed to correctly simulate event-based herbicide concentration, water runoff, and soil erosion, and they related this failure to the empirical equations used in the model for runoff and erosion process. Chang et al. (2008) evaluated three models, including PRZM3, for simulating flood irrigation; however, their focus was on pesticide transport at the subsurface. Since surface runoff in PRZM is calculated using the curve number method and is not related to subsurface processes, even though the paper gave high score ratings to PRZM3, it was not clear whether runoff was generated in their study, and it was unknown how PRZM performed compared with the other two models in simulating surface runoff.

The RZWQM was the most user friendly among the three models, with strong and active technical supports. The model was able to produce satisfactory results for the three case studies. As a mechanistic model, RZWQM accounted for many processes that were important for California agricultural scenarios such as surface cracks, macropores, subsurface flow, and tile drainage. The model has strong crop growth modules that allow for simulation of various management practices such as tillage, cover crops, and alfalfa cutting. One drawback of the model is its lack of algorithms for flood irrigation. In the literature, a few studies have been conducted to simulate irrigation runoff but mostly focused on pesticide concentration in soil profile. Bandaranayake et al. (1998) simulated bromide transport within soil profile in fields irrigated by sprinkler and flood irrigation. They found that RZWQM can simulate bromide concentration in soil very well for sprinkler irrigation, but the model faltered for flood irrigation. Azevedo et al. (2000) used RZWQM to simulate atrazine transport in flood irrigated corn fields in Portugal. They found that with proper calibration, RZWQM can simulate water and atrazine movement within soil profile with good accuracy. These papers have demonstrated RZWQM's abilities in simulating pesticide fate and transport within soil profiles under irrigation conditions. Our study confirmed that the RZWQM model has the capabilities of simulating both rainfall and irrigation runoff events with good accuracy. The model can be further improved with an addition of a flood irrigation component.

OpusCZ is the most complex model among the three, with mechanistic representations of the key processes such as infiltration and soil erosion. The special algorithms used in OpusCZ, as shown in Eq. [5] and Eq. [6], grant it the ability to simulate flood irrigation. It also has capacities to simulate various management practices such as on-farm pond, tillage practices, and cover crops. Santos et al. (1997) used the Opus model to simulate NO_3–N concentration in a flood irrigated corn (*Zea mays* L.) field in Portugal and found that with proper calibration the model produced satisfactory results. The demand of accurate soil and weather inputs may pose challenges in some areas. However, this can be overcome in California with the availability of hourly weather data and high quality soil data. The major drawback of the model is that it took relatively longer computational time compared with the other two models. This is typical for mechanistic models. Nonetheless, OpusCZ is a suitable model for simulating pesticide runoff in semiarid areas in California where agriculture is heavily dependent on irrigation.

Conclusions

Although the three models were all capable of predicting pesticide concentrations at field-edge, they differed in many aspects when comparing the hydrological component. The PRZM simulates soil water movement based on a tipping-bucket approach and predicts a daily time-step of water runoff based on the curve number method. The RZWQM solves the Green–Ampt equation to simulate soil water movement and predicts runoff as the part of rainfall or irrigation exceeding soil infiltration capacity (Ahuja et al., 1999). The OpusCZ simulates water movement both vertically and horizontally. The vertical movement is based on Darcey's Law while the horizontal movement is based on a diffusive-wave approach. 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 because of the inclusion of a specific modeling component for various surface conditions under rainfall and irrigation. The RZWQM is also a desirable model given its accuracy in predicting pesticide runoff, strong technique support, and user-friendliness.

This evaluation study was limited by the availability of field studies with reliable measurements that are needed for model evaluation. Some aspects of the models may have been left untested. More field studies covering a variety of crops and management practices are needed in the future for a more complete evaluation of the models. Studies should be conducted in estimating the contribution of spray drift relative to surface and subsurface runoff. Rather than coarsely estimating the fraction of pesticides lost to spray drift during pesticide application, spray drift models should be used to provide better estimations.

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