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RESEARCH ARTICLE

Numerical simulation of agricultural sediment and pesticide runoff: RZWQM and PRZM comparison

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Abstract

Agricultural sediment and pesticide runoff is a widespread ecological and human health concern. Numerical simulation models, such as Root Zone Water Quality Model (RZWQM) and Pesticide Root Zone Model (PRZM), have been increasingly used to quantify off-site agricultural pollutant movement. However, RZWQM has been criticized for its inability to simulate sedimentation processes. The recent incorporation of the sedimentation module of Groundwater Loading Effects of Agricultural Management Systems has enabled RZWQM to simulate sediment and sediment-associated pesticides. This study compares the sediment and pesticide transport simulation performance of the newly released RZWQM and PRZM using runoff data from 2 alfalfa fields in Davis, California. A composite metric (based on coefficient of determination, Nash–Sutcliffe efficiency, index of agreement, and percent bias) was developed and employed to ensure robust, comprehensive assessment of model performance. Results showed that surface water runoff was predicted reasonably well (absolute percent bias <31%) by RZWQM and PRZM after adjusting important hydrologic parameters. Even after calibration, underestimation bias ($-89\% \le PBIAS \le -36\%$) for sediment yield was observed in both models. This might be attributed to PRZM's incorrect distribution of input water and uncertainty in RZWQM's runoff erosivity coefficient. Moreover, the underestimation of sediment might be less if the origin of measured sediment was considered. Chlorpyrifos losses were simulated with reasonable accuracy especially for Field A (absolute $PBIAS \le 22\%$), whereas diuron losses were underestimated to a great extent ($-98\% \le PBIAS \le -65\%$) in both models. This could be attributed to the underprediction of herbicide concentration in the top soil due to the limitations of the instantaneous equilibrium sorption model as well as the high runoff potential of herbicide formulated as water-dispersible granules. RZWQM and PRZM partitioned pesticides into the water and sediment phases similarly. According to model predictions, the majority of pesticide loads were carried via the water phase. On the basis of this study, both RZWQM and PRZM performed well in predicting runoff that carried highly adsorptive pesticides on an event basis, although the more physically based RZWQM is recommended when field-measured soil hydraulic properties are available.

KEYWORDS

model evaluation, numerical modeling, pesticide, sediment, surface runoff

1 | INTRODUCTION

Runoff of sediment and pesticides is a widespread ecological and human health concern, as it degrades surface water quality and affects aquatic organisms (Starner & Zhang, 2011). Agriculture is one of the leading sources of sediment and pesticide contamination in surface waters (Liu, Mang, & Zhang, 2008; Schulz, 2004; Wauchope, 1978; M. Zhang & Goodhue, 2010). In order to ensure surface water quality, growers and regulators must evaluate the risk of surface water contamination caused by agricultural pesticide residues and develop mitigation plans when needed. Risk evaluation and mitigation rely heavily on the quantification of sediment and pesticide loss from croplands. Although many field experiments have focused on the topic, estimating the amount of sediment and pesticides in edge-of-field runoff still remains challenging due to the complexity of the factors and processes involved in the fate and transport of these pollutants across agricultural fields.

In recent decades, computational models have become valuable tools to investigate the off-site movement of agrochemical pollutants. Computational models are much more cost-effective than field measurements and can be used to quantitatively predict pollutant fate and transport across a wide range of field conditions. Numerous models have been developed to simulate edge-of-field sediment and pesticide runoff (Mottes, Lesueur-Jannoyer, Bail, & Malézieux, 2014). Two of the most widely used, extensively validated simulation models are the Pesticide Root Zone Model (PRZM; Carsel, Mulkey, Lorber, & Baskin, 1985) and the Root Zone Water Quality Model (RZWQM; Ahuja, Rojas, Hanson, Shaffer, & Ma, 2000).

PRZM is a one-dimensional, finite-difference model that simulates fate and transport of sediment and pesticide over, within, and below the crop root zone at a daily time step (Carsel et al., 1985). Most validation of PRZM focused on pesticide leaching and/or persistence in the soil (Burkart, Gassman, Moorman, & Singh, 1999; Chang, Srilakshmi, & Parvathinathan, 2008; Cogger, Bristow, Stark, Getzin, & Montgomery, 1998; Durborow, Barnes, Cohen, Horst, & Smith, 2000; Fox, Sabbagh, Chen, & Russell, 2006; Garratt, Capri, Trevisan, Errera, & Wilkins, 2003; Jmones & Mangels, 2002; Loague, Bernknopf, Green, & Giambelluca, 1996; Q. L. Ma, Hook, et al., 2000b; Q. L. Ma, Rahman, Holland, James, & McNaughton, 2014; Malone, Warner, Workman, & Byers, 1999; Mamy, Gabrielle, & Barriuso, 2008; Marín-Benito et al., 2014; Marín-Benito, Rodríguez-Cruz, Sánchez-Martín, & Mamy, 2015; Mueller, Bush, Banks, & Jones, 1992; Noshadi, Amin, & Maleki, 2002; Russell & Jones, 2002; Trevisan, Errera, Goerlitz, Remy, & Sweeney, 2000; Zacharias & Heatwole, 1994). For pesticide runoff simulation, PRZM (Versions 2.0 and 3.0) predicted runoff water amounts with good accuracy (Q. Ma, Holland, James, McNaughton, & Rahman, 2000a; Q. L. Ma, Smith, Hook, & Bridges, 1999), whereas PRZM (Beta Version 3.0) underestimated pesticide concentration in runoff flow (Malone et al., 1999). In a diclosulam runoff study, PRZM (Version 3.12) predicted water-phase pesticide loadings within 4% of the observed values, although it underpredicted sediment-bound pesticide mass by 97% (van Wesenbeeck, Peacock, & Havens, 2001). The evaluation of PRZM (Versions 3.0 and 3.12) by two studies produced less favorable results, which might be attributed to the irregularities of the field (Durborow et al., 2000) or the model's empirical description of runoff and erosion processes (Miao et al., 2004). In addition, PRZM (Version 3.12) was upscaled to predict basin-level, daily streamflow rates (R^2 = .83) and monthly flow-weighted concentrations of diazinon and chlorpyrifos (R^2 ≥ .69) using a spatially distributed flow-routing model (Luo & Zhang, 2009).

Similar to PRZM, RZWQM is a one-dimensional, field-based model developed for assessing the environmental impact of agricultural systems. However, RZWQM adopts more mechanistic algorithms to simulate soil water movement and pesticide transport and supports a variety of agricultural management practices. Previous studies showed that RZWQM was able to predict pesticide runoff within factors of 3 (Version 3.2; Ghidey, Alberts, & Kitchen, 1999) and 2 (Version 1.0; Q. L. Ma, Rahman, et al., 2004b) and with coefficient of determination values of at least .92 (Version 1; Q. L. Ma, Ahuja, Rojas, Ferreira, & Decoursey, 1995) and .52 (RZWQM98 Version 1.0; Chinkuyu, Meixner, Gish, & Daughtry, 2005). Model performance may be improved by accurate parameterization of restricting soil layers, accounting for pesticide sorption kinetics and calibrating pesticide half-life data (L. Ma, Ahuja, & Malone, 2007; Malone, Ahuja, et al., 2004a).

Although RZWQM has undergone extensive verification and refinement, it lacks a soil erosion and sediment transport component, which limits its ability to simulate the fate and transport of sediment and sediment-bound pollutants (Q. Ma, Wauchope, et al., 2004a; Q. L. Ma et al., 1995). Recently, the sedimentation module of Groundwater Loading Effects of Agricultural Management Systems (GLEAMS; Leonard, Knisel, & Still, 1987) was integrated into RZWQM (M. Zhang, DeMars, & Ahuja, 2014). This effort extends the application of RZWQM to sediment and sediment-bound pesticide simulation, allowing for a better characterization of the pesticide transport processes. However, the performance of the newly integrated RZWQM relative to field observations and PRZM remains largely unknown. It is critical to evaluate these numerical models in terms of model structure, scientific foundation, and predictive ability so that we could apply them for research and practical use in a proper manner.

Therefore, the goal of this study is to validate and compare RZWQM and PRZM in their abilities to predict sediment and pesticide runoff. Experimental data were obtained from two alfalfa fields applied with chlorpyrifos and diuron Alfalfa was selected as the target crop because it is widely grown throughout the world and is typically flood irrigated, therefore significantly contributing to pesticide contamination of surface water bodies (Prichard, 2010). We focused on chlorpyrifos and diuron given their extensive usage as well as broad-spectrum toxicity (Luo, Deng, Budd, Starner, & Ensminger, 2013). A composite metric (based on coefficient of determination, Nash–Sutcliffe efficiency, index of agreement, and percent bias) was developed and employed to ensure robust, comprehensive assessment of model performance. Qualitative evaluation of model structure, scientific foundation, and input requirements was also performed. Empowered by the enhancement in model algorithms, this study not only is valuable in facilitating a deeper understanding of hydrologic processes occurring in agricultural fields but also helps improve confidence in predictions of agricultural pesticide runoff, potentially facilitating model selection for scientific inquiry and water quality management.

2 | MATERIALS AND METHODS

2.1 | Site description and field measurements

The sediment and pesticide runoff data for evaluation of RZWQM and PRZM were obtained from two adjacent alfalfa fields (Fields A and B) at the University of California, Davis, California (X. Zhang, 2012). Fields A (0.281 ha) and B (0.295 ha) were separated by levees, with a slope of 0.14%. The soil is Brentwood silty loam with 35% sand, 40% silt, and 25% clay (Table 1). A flood irrigation check was located at the head of the fields, which delivered water from the head to the end. From 2012 to 2013, both fields were sprayed with chlorpyrifos and diuron, each followed by six flood irrigation events (Table 2). Negligible rainfall was observed during the study period. Therefore, irrigation water was the major driving force for runoff generation, as is the case for most semiarid regions during the dry season. Samples were collected from a tailwater ditch located at the downstream end of each field. Outflow

TABLE 1 Selected soil characteristics of the two alfalfa fields

	Depth (cm)	% sand	% silt	% clay	% organic matter	Bulk density (g/cm^3)
Field A	0–15	36.3	39.4	24.3	1.08	1.42
	15–66	35.0	39.4	25.6	0.92	1.42
	66–150	11.3	67.7	21.0	0.92	1.55
Field B	0–15	33.4	40.0	26.7	0.95	1.42
	15–66	28.4	42.9	28.7	0.84	1.51
	66–150	11.3	67.7	21.0	0.84	1.55

TABLE 2 Summary of pesticide application and irrigation events

	Date (month/day/year)		Event	Input amount (pesticide: kg/ha; irrigation water: cm)	
Event	Field A	Field B	number	Field A	Field B
Chlorpyrifos spray	4/9/2012		n/a	0.12	
Flood irrigation	5/22/2012	5/21/2012	1	16.8	20.1
	6/16/2012	6/15/2012	2	15.4	17.7
	8/29/2012	8/28/2012	3	15.3	15.7
diuron spray	1/17/2013		n/a	1.2	
Flood irrigation	n/a	2/25/2013	4	n/a	19.54
	2/27/2013	2/26/2013		16	7.43
	3/22/2013	3/21/2013	5	11.3	13.8
	4/29/2013	4/26/2013	6	15.7	15

n/a: not applicable.

was measured at 2-min intervals, and water samples were collected manually approximately every 30 min to quantify the concentration of suspended sediment and pesticides. A flume with known cross-sectional area was installed in the ditch to measure runoff flow. Water samples were analyzed at the University of California Davis Aquatic Toxicology laboratory using commercial enzyme-linked immunosorbent assay kits. Due to the low concentration of suspended sediment, it was not possible to quantify the amount of sediment-bound pesticides. Hence, only the total pesticide concentration was recorded.

2.2 | Model description

PRZM was developed by the U.S. Environmental Protection Agency in the 1980s to facilitate environmental quality management. It is now the standard model for the Environmental Protection Agency's pesticide aquatic environmental exposure assessment (Sabbagh, Fox, Muñoz-Carpena, & Lenz, 2010). The newest version, PRZM5, has been recently released (Young & Fry, 2014). In this update, problematic bugs in the degradation, erosion, and application routines have been fixed, and the new input file is in a free-format style, allowing for easier data preparation. PRZM models surface water runoff based on the empirical curve number (CN) method developed by the Soil Conservation Service (Natural Resources Conservation Service [NRCS], 2003). The daily CN depends on soil type, crop cover, and management practices. PRZM also relates daily CN to soil moisture in the top 10 cm of the soil. The runoff excess is first used to satisfy canopy water holdup capacity and then routed downward in the profile by a capacity model. PRZM does not distinguish evaporation from transpiration. Evapotranspiration (ET) is modeled as an integrated process that first consumes intercepted water on the plant canopy and then depletes soil moisture.

Soil loss by erosion is simulated by the empirical Modified Universal Soil Loss Equation (MUSLE; Williams, 1975) or MUSLE small watershed version (MUSS; currently lacks published documentation). Both MUSLE and MUSS estimate the event soil loss on the basis of seven variables: volume of daily runoff, field size, soil erodibility factor (Universal Soil Loss Equation [*USLE*] *K*), length slope factor (*USLE LS*), cover and management factor (*USLE C*), support practice factor (*P*), and peak storm runoff (q_p). PRZM calculates q_p using the Graphical Peak Discharge Method (NRCS, 1986). This method considers runoff hydrograph to be mainly determined by daily rainfall volume, rainfall distribution type (geographically defined), Manning's roughness coefficient, hydraulic flow length, and slope. The pesticide fate and transport is governed by an advection–dispersion–reaction equation that takes into account foliar wash-off, plant uptake, runoff and erosion extraction, soil sorption, decay, and volatilization of pesticides. A detailed description of the components in PRZM is listed in Table 3.

RZWQM was developed in the 1990s by the U.S. Department of Agriculture (USDA) Agricultural Research Service (ARS) scientists (Ahuja et al., 2000). It operates at a subhourly timescale for water flow, heat and solute transport, and chemical uptake. The water flow process is divided into two phases: (1) infiltration during a rainfall and/or an irrigation event, described by the Green–Ampt equation and (2) redistribution between two events, governed by the Richards equation. Preferential flow in macropores is treated separately from transport in the soil matrix, which has been subdivided into micropore (immobile) and mesopore (mobile) zones. Compared to PRZM, RZWQM contains much more detailed algorithms that describe pesticide processes within and across the root zone (Table 3). The newly released version, RZWQM2 3.00, was obtained from USDA ARS software website (http://arsagsoftware.ars.usda.gov/). In this update, RZWQM has been integrated with the sedimentation module of GLEAMS, which simulates daily sediment yield using an erosion/transport model. The soil erosion component employs the MUSLE, which treats soil detachment by rainfall (interrill erosion) and by overland flow (rill erosion) separately (Foster, Meyer, & Onstad, 1977). The sediment transport component simulates the transport capacity of flow based on the Yalin (1963) equation. If the sediment transport capacity is exceeded by the sediment load within any segment, a first-order equation is used to represent sediment deposition. The sediment yield predicted by GLEAMS is then used within RZWQM to partition the mass of pesticides into dissolved and sediment-bound phases according to user-specified sorption models and parameters.

2.3 | Model setup and parameterization

PRZM simulation was conducted for a 17-month period from January 1, 2012, to May 20, 2013. For RZWQM, simulation started earlier on January 1, 2005, to allow for the establishment of steady-state values for the soil nutrient pools (Ghidey et al., 1999). Meteorological data were obtained from the California Irrigation Management Information System, Station 6 (Davis, California). Potential ET was calculated by multiplying the crop coefficient for alfalfa by the ET rate of the reference crop, which was estimated using the California Irrigation Management Information System Penman equation based on meteorological data (Snyder, 1992). Because there is no option to apply date-specific

TABLE 3 Comparison of Pesticide Root Zone Model (PRZM) and Root Zone Water Quality Model (RZWQM) for simulation of agricultural pesticide runoff

	PRZM	RZWQM
	Temporal and spatial scale	
Time step	Daily time step	Subhourly time step for water flow and transport processes, daily time step for the rest
Spatial scale	1-D field	1-D field
Vertical resolution	User defined	For infiltration, 1-cm layer; for redistribution, model-generated numerical layers to achieve convergence for Richards equation
	Hydrological processes	
Evapotranspiration (ET)	User-defined potential ET, allocated by canopy interception and soil moisture	Determined by Richards equation with upper limits defined by potential ET, which is either user specified or calculated from the modified Shuttleworth–Wallace ET model
Surface runoff	Soil Conservation Service curve number	Infiltration excess
Subsurface water flow	Runoff and interception excess, governed by capacity model	Green–Ampt for infiltration, Richards equation for redistribution; allow preferential flow
Irrigation setting	Sprinkler; use-specified amounts	Sprinkler; user-specified rates and dates
Subsurface drainage	No	Yes
	Sedimentation processes	
Erosion	Modified Universal Soil Loss Equation (MUSLE)/MUSLE small watershed version	Foster's MUSLE; Yalin's sediment transport equation
	Pesticide processes	
Application method	Yes	Yes
Metabolites	Yes	Yes
Sorption	Equilibrium; linear	Equilibrium or kinetics; linear
Plant wash-off	Yes	Yes
Volatilization	Yes	Yes
Plant uptake	Yes	Yes
Degradation	First order	Pseudo first order
Degradation rate affected by	Temperature	Temperature, moisture, soil depth
	Other components	
Input requirement	Fortran 2003 free-format style	User graphical user interface
Management practices	No specified modules	Reflect tillage, harvest

irrigation in PRZM, irrigation inputs were added to the meteorological file as precipitation. Due to the inability of RZWQM to simulate flood irrigation, sprinkler irrigation was selected, which allowed user-specified rates and dates.

The major hydrologic parameter for PRZM is the CN. A CN of 71 was selected from tabulated values for meadow with Hydrologic Soil Group C (NRCS, 1986). For RZWQM, major hydrologic inputs are soil horizon hydraulic properties of water content–matric potential relationship described by Brooks–Corey parameters (Brooks & Corey, 1964) and hydraulic conductivity–matric potential relationships, which are obtained by the approximate capillary bundle approach (Campbell, 1974). Saturated hydraulic conductivity (K_{sat}), water content at saturation, 1/3 bar, 15 bar, and residual water content were measured on-site and used to estimate the Brooks–Corey parameters, using a scaling method provided in RZWQM (Ahuja et al., 2000). Other default hydrologic parameters were obtained from field measurements, model manuals, and the published literature.

The focus of this study was to assess and compare the abilities of RZWQM and PRZM to simulate sediment and pesticide transport processes. Therefore, hydrologic parameters were calibrated in an attempt to minimize the effect of incorrect hydrologic simulation on the resulting pollutant transport prediction (Malone, Ma, et al., 2004b). For PRZM, CN was calibrated due to its high sensitivity and uncertainty as an empirical parameter. Field capacity is another sensitive parameter that could affect runoff generation by changing antecedent soil moisture. Therefore, it was also calibrated to improve the fit between the simulated and observed runoff volumes for each event. For RZWQM, the macropore component was enabled to accommodate the field conditions, as preferential flow is more likely to happen in soils that are not tilled frequently, such as alfalfa fields. Because there was no measurement for macropore parameters, they were estimated by matching observed runoff with measured data. Calibrated macropore parameters were adsorption correction factor (*SFCT*), total macroporosity as fraction of soil volume (P_{mac}), and average radius of cylindrical holes (r_p). The calibration ranges were limited to those reported for no-till silty loam in the literature (Malone, Shipitalo, Ma, Ahuja, & Rojas, 2001; Malone, Ma et al., 2004b). No further calibration was carried out, as this study aimed to represent the field in a way that minimized the distortion of parameter values through calibration, therefore facilitating the generalization of simulation results to areas with similar environmental conditions (Knisel, 1980; Solomon et al., 1996). Calibration was performed using a nonlinear parameter estimation algorithm supported in software PEST (Doherty, 2010) with the objective function defined as the sum of squared deviations between model-generated and experimental observations.

In this study, MUSLE was adopted to simulate soil erosion in PRZM. For a given amount of runoff input, the most critical erosion parameters in PRZM and RZWQM are *USLE K*, *USLE LS*, *USLE C*, *P*, and Manning's *n*. These parameters were obtained from the USDA handbook for predicting rainfall erosion loss (Wischmeier & Smith, 1978) and look-up tables in the PRZM manual (Suarez, 2005). No calibration was performed for the simulation of sediment and pesticide loads (presented below).

The pesticide properties used in the simulations are listed in Table 4. Degradation of pesticides in both PRZM and RZWQM was simulated using the first-order decay function. The values of organic carbon–water partition coefficient (K_{oc}) and half-lives for chlorpyrifos and diuron were obtained from public databases (National Center for Biotechnology Information, 2009; National Institutes of Health, 2015; USDA, 2009). Linear equilibrium adsorption isotherm was assumed, and the linear adsorption distribution coefficient (K_d) was calculated as the product of K_{oc} and organic carbon fraction. It should be noted that the kinetic sorption model is a valid option in RZWQM, and in many cases, it provides a better description of pesticide long-term behavior in the field (Boesten, Van Der Pas, & Smelt, 1989; Q. L. Ma et al., 1995). Because kinetic sorption parameters need to be obtained through calibration (L. Ma et al., 2012), it was not performed in this study as our intention was to predict off-site pesticide loads using pesticide parameters obtained from model manuals, field and laboratory measurements, and literature searches.

2.4 | Evaluation criteria

A composite metric based on a combination of evaluation metrics was adopted to overcome the potential bias of individual metrics and to provide a comprehensive, quantitative measure of model performance, as has been recommended (Bennett et al., 2013; Harmel, Smith, & Migliaccio, 2010; Moriasi et al., 2007). These metrics are as follows (Table 5). (1) coefficient of determination, (2) Nash–Sutcliffe efficiency, (3) index of agreement, and (4) percent bias. In general, a coefficient of determination more than .5 is considered acceptable (Chinkuyu, Meixner, Gish, & Daughtry, 2004), so this benchmark was selected. A negative Nash–Sutcliffe efficiency is generally viewed as unacceptable as it indicates that the observed mean is a better estimator than the predicted value, so a benchmark of $NSE \geq 0$ was selected. In this study, we selected 0.5 as the benchmark for the index of agreement. In the literature, percent bias values of less than 25% and 70% have been considered as satisfactory for watershed-scale prediction of streamflow and associated pollutants, respectively (Harmel, Cooper, Slade, Haney, & Arnold, 2006; Moriasi et al., 2007). In this study, however, we were not able to apply constituent-specific performance ratings due to the difficulty in estimating the uncertainty in field-scale pesticide runoff data. Therefore, a benchmark of 50% was applied to all constituents (i.e., water flow and sediment and pesticide loads).

TABLE 4 Physiochemical properties of chlorpyrifos and diuron

Property	Chlorpyrifos	diuron
Water solubility (mg/L)	1.05	35.6
Henry's *K*	0.00028	2.06E−08
Enthalpy of vaporization of the pesticide (kcal/mol)	20[a]	20[a]
Organic carbon–water partition coefficient K_{oc} (ml/g)	8151	813
Linear adsorption distribution coefficient K_d (ml/g)	51.09/43.7/43.5[b]	4.5/3.95/3.95[b]
Foliar half-life (day)	4.97	9
Dissolved phase half-life (day)	29.6	43
Adsorbed phase half-life (day)	50	75.5
Vapor phase half-life (day)	0.25[c]	5.8[c]
Field dissipation half-life (day)	21	89

Note: Values are from public pesticide databases, unless stated otherwise.

[a]Value from the pesticide Root Zone Model manual.

[b]$K_d = K_{oc} \cdot F_{oc}$ (F_{oc}: organic carbon fraction).

[c]Value from Howard (1991).

2.4.1 | Composite metric

The quantitative, composite model comparison metric was defined as follows: For individual validation metric *i*, the model gets a score S_i, which equals to 1 if the scoring criterion (Table 5) is met and equals to 0 if not. A composite metric S_c was calculated as the sum of S_i a model gets for predicting one of the four individual processes (surface water runoff, sediment loss, chlorpyrifos runoff, and diuron runoff) for a specific field (Field A or B):

$$S_c = \sum_{i=1}^{4} S_i.$$

The model with a higher S_c (ranging from 0 to 4) was considered superior to the other. The final recommendation for model adoption also depended on qualitative evaluation of model structure, scientific foundation, and input requirements.

TABLE 5 Evaluation metrics for model comparison

i	Validation metrics	Scoring criteria
1	$R^2 = \left(\frac{\sum_{i=1}^{n} (y_i - \overline{y}) \left(\widehat{y}_i - \overline{\widehat{y}} \right)}{\sqrt{\sum_{i=1}^{n} (y_i - \overline{y})^2} \sqrt{\sum_{i=1}^{n} \left(\widehat{y}_i - \overline{\widehat{y}} \right)^2}} \right)^2$	$R^2 \geq 0.5$
2	$NSE = 1 - \frac{\sum_{i=1}^{n} (y_i - \widehat{y}_i)^2}{\sum_{i=1}^{n} (y_i - \overline{y})^2}$	$NSE \geq 0$
3	$d = 1 - \frac{\sum_{i=1}^{n} (y_i - \widehat{y}_i)^2}{\sum_{i=1}^{n} (\lvert y_i - \overline{y} \rvert + \lvert \widehat{y}_i - \overline{y} \rvert)^2}$	$d \geq 0.5$
4	$PBIAS = \frac{\sum_{i=1}^{n} (\widehat{y}_i - y_i)}{\sum_{i=1}^{n} y_i} \times 100$	$\lvert PBIAS \rvert \leq 50\%$

Note: y_i and $\hat{y}_i$ are the *i*th observed and predicted values, respectively; $\overline{y}$ and $\overline{\widehat{y}}$ are the average of the observed and predicted values, respectively; and *n* is the sample size.

3 | RESULTS

3.1 | Surface water runoff

3.1.1 | Simulation with default parameters

All measured runoff events from Fields A and B were of relatively similar magnitudes, except for the notably high runoff event on February 26, 2013, in Field B (Figure 1). corresponding to two consecutive irrigation events with a total volume of 27 cm (Table 2). PRZM and RZWQM overestimated runoff to a great extent, with a coefficient of determination less than .43, and Nash–Sutcliffe efficiency ranging from −12 to −154, an index of agreement less than 0.2, and a percent bias higher than 100% (Table 6). Both models received scores of 0 for surface runoff simulation. Although in our study, irrigation water was the major trigger for runoff generation, water runoff volume and irrigation water amounts were not strongly correlated (Spearman ρ = .45).

3.1.2 | Simulation with calibrated parameters

Limited calibration was performed to fit the predicted runoff volume with field measurements. The calibrated hydrologic parameters for PRZM and RZWQM are listed in Table 7. Measured and simulated surface water runoff after calibration along with evaluation metrics are presented in Figure 1 and Table 6. Prediction accuracy was improved for both PRZM and RZWQM after calibration (total score greater than one). For both models, the Nash–Sutcliffe efficiency values decreased by 1 to 2 orders of magnitude, the index of agreement increased by onefold to twofold, and percent bias decreased from over 100% to less than 30%, although there was no considerable increase in the coefficient of determination. Compared with RZWQM, PRZM predicted runoff from Field A slightly better in terms of the total composite metric (two vs. one).

As the measured hydrographs were similar across all events, only the hydrograph generated from Field A during Event 6 was presented (Figure 2). Runoff occurred 4 to 4.5 hr after irrigation started. All hydrographs had fairly steep rising and falling limbs and reached peak flow of around 1.6 cm/hr, half an hour after the beginning of runoff. The average duration of runoff events was 2.8 hr. The calibrated RZWQM was able to simulate the cumulative runoff volume with reasonable accuracy (Table 6). but the shape of the hydrograph was not well captured (Figure 2). The subdaily runoff output of RZWQM gradually increased with decreasing soil infiltration capacity and ceased as soon as irrigation ended.

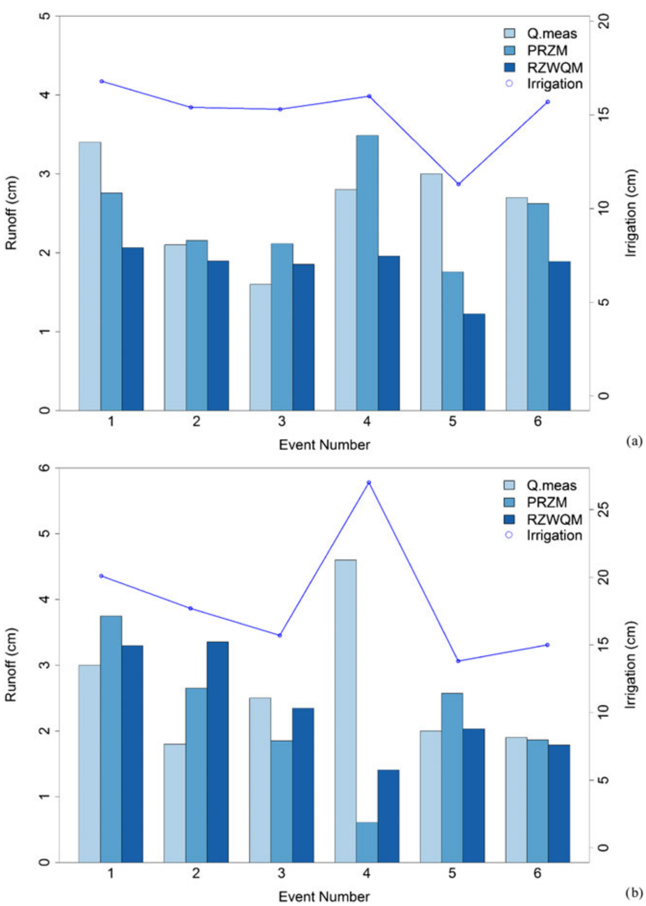

FIGURE 1 Irrigation water and measured (Q.meas) and simulated surface water runoff using Pesticide Root Zone Model (PRZM) and Root Zone Water Quality Model (RZWQM) for (a) Field A and (b) Field B, with calibrated hydrologic parameters

3.2 | Sediment loss

Large variation was observed in sediment loss from both fields (Figure 3). Given the similar amounts of irrigation input across the study period, those events with a high sediment yield were likely due to measurement error rather than physical processes. This is discussed further in Section 4.2. PRZM and RZWQM underestimated sediment yield, with a coefficient of determination of less than .3, an index of agreement less than 0.5, negative Nash–Sutcliffe efficiency ranging from −2.4 to −0.2, and percent bias ranging from −89% to −36% (Table 6). Both models got scores of 1 for predicting sediment loss from Field A but 0 scores for sediment loss from Field B. RZWQM performed slightly better than PRZM in terms of all the evaluation metrics under consideration.

3.3 | Pesticide loss

Figure 4 shows the measured concentration of chlorpyrifos and diuron in runoff flow generated from both fields. For each runoff event, nonfiltered water samples were collected and analyzed for pesticide concentration. Diuron concentration was 200 times higher than chlorpyrifos concentration in runoff water. Both chlorpyrifos and diuron concentration in runoff decreased with time, with chlorpyrifos concentration being almost zero for the last event. Pesticide mass was then calculated as the product of pesticide concentration, flow rate, and time interval. The results were presented in Figure 5. On average, losses of the total amount applied to the study sites were more than 0.19% for chlorpyrifos and 3.77% for diuron. The average chlorpyrifos loss from the first posttreatment event was 0.13% of the amount applied, or 69% of the total chlorpyrifos runoff during the investigation period. For diuron, the average pesticide loss from the first posttreatment event was 2.5% of the amount applied, or 67% of the total diuron runoff during the study period.

The chlorpyrifos loss predictions generated by PRZM and RZWQM matched well with the observed data, with a coefficient of

TABLE 6 Summary of model evaluation results

		R^2		NSE		d		PBIAS (%)		Total	
		A	B	A	B	A	B	A	B	A	B
Surface water runoff											
Def.	PRZM	0.08	0.43	−45.35	−23.82	0.20	0.07	149.1	148.8	0	0
	RZWQM	0.00	0.17	−153.78	−11.67	0.12	0.14	278.0	104.8	0	0
Cal.	PRZM	0.12	0.27	−0.28	−2.18	0.60	0.20	−4.5	−15.9	2	1
	RZWQM	0.01	0.16	−2.05	−1.25	0.41	0.29	−30.2	−10.0	1	1
Soil erosion											
PRZM		0.27	0.32	−0.60	−2.45	0.50	0.43	−60.6	−88.7	1	0
RZWQM		0.09	0.09	−0.20	−1.49	0.43	0.40	−35.9	−65.6	1	0
Pesticide loss											
Chlorpyrifos	PRZM	0.99	0.99	0.96	0.16	0.99	0.89	−11.9	54.3	4	3
	RZWQM	0.99	0.99	0.89	0.73	0.97	0.95	22.4	31.5	4	4
diuron	PRZM	0.83	0.53	−1.15	−1.06	0.57	0.49	−76.9	−98.4	2	1
	RZWQM	0.83	0.53	−1.87	−0.29	0.48	0.53	−84.4	−65.2	1	2

Note. Six events for each field and each process (water runoff, soil erosion, and pesticide loss). Cal. = calibrated model; Def. = default model with input parameters based on site-specific data, user manuals, and values from literature; PRZM = Pesticide Root Zone Model; RZWQM = Root Zone Water Quality Model.

TABLE 7 Calibrated hydrologic parameters for the Pesticide Root Zone Model (PRZM) and Root Zone Water Quality Model (RZWQM)

	PRZM		RZWQM		
	Curve number	Field capacity (0–66 cm)	Adsorption correction factor, *SFCT*	Total macroporosity, P_{mac}	Average radius of cylindrical holes, r_p (cm)
Field A	54	0.43	0.02	0.00004	0.04
Field B	50	0.42	0.2	0.000053	0.033

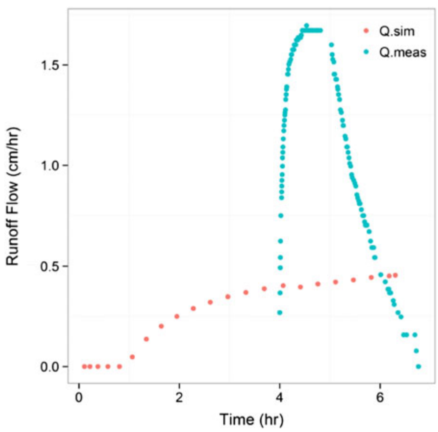

FIGURE 2 Measured (Q.meas) and simulated (Q.sim) surface water runoff at subdaily timescales using Root Zone Water Quality Model for Event 6 at Field A

determination and index of agreement above .99 and 0.89, respectively; positive Nash–Sutcliffe efficiency; and absolute percent bias less than 54% (Figure 5 and Table 6). However, both models underestimated diuron loss, resulting in a .16 to .46 decrease in the coefficient of determination, at least a 0.4 decrease in the index of agreement, negative Nash–Sutcliffe efficiency, and 34% to 65% increase in absolute percent bias. Both models predicted pesticide loads from Field A equally well with composite scores of 4. RZWQM performed slightly better than PRZM in predicting off-site pesticide movement from Field B, with a total score of 4 versus 3. PRZM and RZWQM partitioned pesticide mass in water and sediment-bound phases similarly. Both chlorpyrifos and diuron were predicted to transport mainly via surface water runoff (Table 8). The proportions of chlorpyrifos and diuron lost in the water phase were more than 93% and 99%, respectively.

4 | DISCUSSION

4.1 | Surface water runoff

About one sixth of the irrigation water exited the field as surface runoff. The variation in water runoff volume generally followed the change of irrigation water amounts (Figure 1). as irrigation was the major driver for runoff generation. However, the relationship between water runoff and irrigation was complicated by the varying infiltration rate, which is governed by water retention and conductivity functions of soil. Therefore, water runoff volume and irrigation water amounts were not strongly correlated. For runoff hydrograph, the high gradient of rising and falling limbs could be attributed to the uniformity of study fields. Uniform fields had approximately equal flow path and similar soil hydraulic properties from the head ditch to the drainage outlet. These conditions enabled runoff flow to progress roughly at the same speed across the cross section of the field so that runoff reached the drainage ditch at the same time, resulting in steep rising and falling limbs of runoff hydrographs. After calibration, both PRZM and RZWQM were able

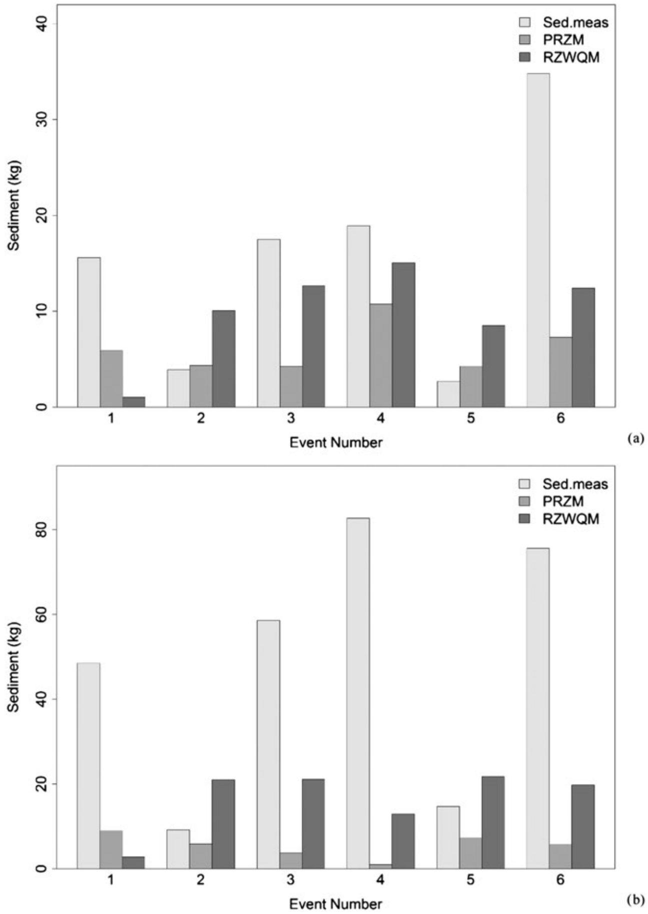

FIGURE 3 Measured (Sed.meas) and simulated sediment loss using Pesticide Root Zone Model (PRZM) and Root Zone Water Quality Model (RZWQM) for (a) Field A and (b) Field B, with default erosion parameters

to capture the overall trends in runoff volume (Figure 1). Runoff prediction of the calibrated models was not satisfactory, however, especially for the coefficient of determination, Nash–Sutcliffe efficiency, and index of agreement, resulting in total scores of not more than 2 (Table 6). This is likely due to the lack of linearity between the observed and predicted data and the relatively small variation in the observations. Therefore, a combination of evaluation metrics together with graphical comparison is necessary to assess model performance in simulating field-scale runoff events.

With default CN and field capacity, PRZM significantly overpredicted surface runoff (Table 6, percent bias). After calibration, the performance of PRZM improved (Figure 1). One exception was the notably high runoff on February 26, 2013, from Field B, which was underestimated beyond a factor of 2. This could be ascribed to the large irrigation event on the previous day (Table 2). On February 25, 2013, Field B was irrigated with 19.54-cm water. However, the field was so dry that there was no runoff by the end of the day. Therefore, an additional irrigation of 7.43 cm was applied the second day, which generated the high runoff event of 4.63 cm. PRZM did not adequately represent the runoff response of a field with high antecedent moisture. It is likely that the capacity model (which is essentially a storage-routing technique) employed in PRZM is not capable of simulating the proper infiltration and redistribution of soil water (Malone et al., 1999; Zacharias & Heatwole, 1994). Inaccurate simulations of antecedent soil water content could affect the CN value because it is adjusted according to the daily average soil moisture in the top 10 cm of the soil. Moreover, the CN method itself is also a possible source of error, as it is based on empirical rather than theoretically derived equations and operates on a daily time step. Surface runoff, among many other processes, needs to be simulated on a finer temporal scale to ensure greater accuracy (Suarez, 2005). Therefore, the CN method is more suitable for describing longer-term average trends, rather than for individual events (Ponce & Hawkins, 1996).

RZWQM also overestimated surface runoff when using default parameters. The preferential flow through macropore is a reasonable explanation for the measured runoff to be significantly less than the simulated runoff, especially in alfalfa fields with no tillage practice. After the macropore component is enabled, model performance improved (Figure 1 and Table 6). Compared to PRZM, RZWQM performed slightly better in capturing the peak runoff event on February 25, 2013, from Field B, partially due to the representation of the infiltration and redistribution processes using the physically based Green–Ampt and Richards equations. In addition, RZWQM divides the soil matrix into mesopore and macropore, allowing for a more realistic characterization of field conditions (Malone et al., 2001).

Figure 2 shows that the calibrated RZWQM was not able to capture the general shape of runoff hydrographs. This result was not surprising, as RZWQM is a point source model that does not account for routing of runoff flow. At each infiltration time step, RZWQM simulates runoff as infiltration excess but does not simulate the storage of runoff water. The generated runoff water is considered as an instantaneous loss to the system (Ahuja et al., 2000). Therefore, although RZWQM is able to output runoff at subdaily timescales, it is not capable of simulating runoff hydrograph without a valid flow-routing algorithm. Similar to RZWQM, PRZM also does not account for flow routing. Future model development should consider extending both models to two dimensions for better representation of runoff processes.

4.2 | Sediment loss

In this study, the event-based, average sediment loss from the fields was 112 kg/ha. For previous runoff studies conducted on silty loam, sediment loss ranged from 60 to 6,270 kg/ha, depending on the type of crop planted and the agricultural management practices employed (Malone et al., 1999; Wienhold & Gilley, 2010). The results of this study fall towards the lower end of the range, primarily due to alfalfa's ability to intercept sediment, its vigorous root system that increased soil stability, and the no-till operation that maintained soil integrity.

Both PRZM and RZWQM drastically underpredicted sediment yield, especially for the peak events (Figure 3 and Table 6). For PRZM, the underestimation of sediment might be attributed to its inability to realistically distribute the irrigation inputs (van Wesenbeeck et al., 2001). As shown in Figure 6, the NRCS Type IA hyetograph distributes rainfall over a 24-hr period, whereas in this study, irrigation events on average only lasted for 6.6 hr. Because peak runoff is largely determined by NRCS rainfall distribution, the attenuation of input water intensity would decrease peak runoff values, leading to less sediment

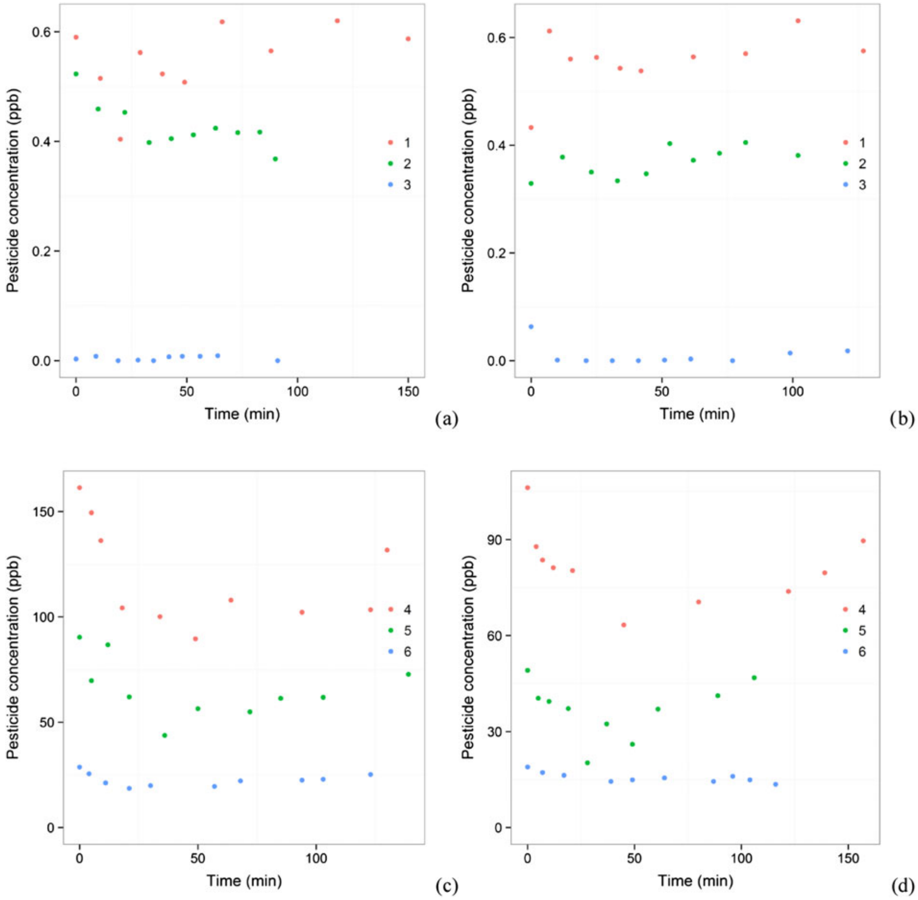

FIGURE 4 Measured pesticide concentration for chlorpyrifos at (a) Field A and (b) Field B and for diuron for (c) Field A and (d) Field B (colored by event number)

yield as predicted by PRZM. For RZWQM, modeling error might be the result of the uncertainty in the coefficient α used in the rill erosion equation. In RZWQM, runoff-driven soil detachment is directly proportional to the runoff erosivity factor, calculated as

$$\text{Runoff erosivity factor} = \alpha \cdot V_u \cdot \sigma_p^{1/3},$$

where V_u is the runoff volume per unit area and σ_p is the peak runoff rate (Foster et al., 1977). The coefficient α is an empirical parameter and a higher value of α infers the greater erosion capacity of runoff. Previous studies have found that increasing α to two to four times its original value improved the sediment simulations (Rudra, Dickinson, & Wall, 1985). Adjustment of α was not performed as part of these analyses as our intention was to evaluate the erosion modules using default parameters.

Another factor that might contribute to the underestimation of sediment yield is the errors involved in sediment measurements (X. Zhang, 2013). Sediment from the ditch walls and floor, not only sediment originating from the fields, was captured in the water quality samples, which very likely contributed to the drastic underprediction of erosion.

4.3 | Pesticide loss

Posttreatment chlorpyrifos and diuron losses from both fields followed the same temporal patterns (Figures 4 and 5). The quantity of pesticides transported via surface runoff decreased rapidly over time, with the first posttreatment events accounting for more than 67% of the total pesticide runoff. This finding is consistent with previous research (Q. L. Ma et al., 1999; Wauchope, 1978) and emphasizes the significance of these critical events in determining potential impacts of pesticide runoff on water quality. A less amount of chlorpyrifos (0.6% of the total loss) was transported off the field for the last event compared with diuron (8.6% of the total loss; Figure 5). This could be attributed to the following: (1) chlorpyrifos has a shorter field dissipation half-life than diuron (Table 4), and (2) the time intervals from pesticide application to the third runoff event were longer for chlorpyrifos (~142 days) than for diuron (~100 days), providing more time for pesticide degradation. A higher proportion of applied diuron (3.77%) was lost from the field in comparison with chlorpyrifos (0.19%), a result of the higher water solubility and lower adsorptivity of diuron.

PRZM and RZWQM were able to simulate chlorpyrifos runoff with reasonable accuracy (Figure 5 and Table 6). Diuron runoff events were, however, underestimated by both models. This might be attributed to the underprediction of diuron concentration in the top soil due to the overprediction of its movement, as observed in previous studies (Ahuja, Ma, Rojas, Boesten, & Farahani, 1996; Q. L. Ma et al., 1995; Malone et al., 1999; Zacharias & Heatwole, 1994). Observations showed that pesticide adsorptivity increased with time, and the desorption isotherm differed from the adsorption isotherm,

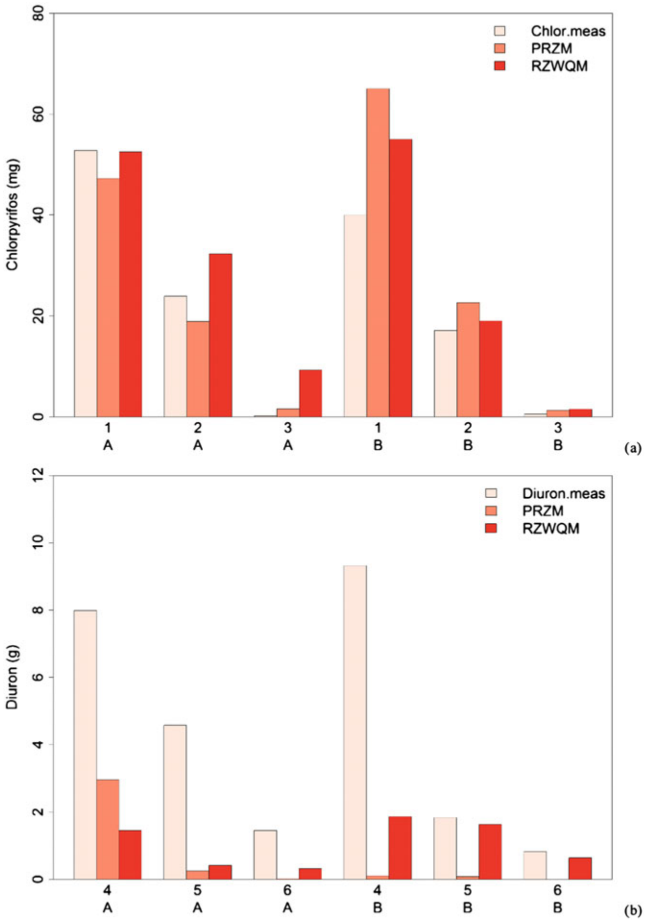

FIGURE 5 Measured (Chlor.meas and diuron.meas) and simulated pesticide loss using Pesticide Root Zone Model (PRZM) and Root Zone Water Quality Model (RZWQM) for (a) chlorpyrifos and (b) diuron, with default pesticide parameters, where 1 to 6 represent event number and A and B represent Field A and Field B, respectively

often in the direction of higher pesticide retention (Boesten et al., 1989; Koskinen, O'Connor, & Cheng, 1979). The existence of a slow sorption–desorption process and an adsorption–desorption hysteresis cannot be characterized by the instantaneous equilibrium sorption model (Ahuja et al., 1996; Q. L. Ma et al., 1995; Q. L. Ma, Rahman, et al., 2004b; Malone et al., 1999; Mueller et al., 1992). Therefore, more of the pesticides are likely to migrate from the mixing zone according to model simulation, leaving less pesticides available for subsequent runoff events. These effects would be expected to be more prominent for diuron as it has higher mobility in water flow. RZWQM does allow for equilibrium–kinetic sorption simulation. However, calibration of kinetic sorption parameters is needed for accurate predictions (L. Ma et al., 2012), and this would contradict our intention of using default or field-measured pesticide parameters. In addition, kinetic sorption is not available for pesticide transport in macropore, therefore complicating the interpretation of results (Malone et al., 2001). The underprediction of diuron losses might also result from a formulation effect, as the herbicide used was formulated as water-dispersible granules and is highly vulnerable to runoff events (Q. Ma, Wauchope, et al., 2004a). Neither PRZM nor RZWQM supports explicit modifier factors for formulation effects due to the general lack of experimental data for these parameters.

PRZM's and RZWQM's partitions of pesticides into the water and sediment phases were quite close (Table 8). Water flow was predicted as the dominant medium for off-site pesticide transport, even for strongly sorbed pesticides like chlorpyrifos. Such results, however, were not surprising. Although chlorpyrifos concentration in the sediment phase was high, the quantity of water was much greater than the quantity of sediment; therefore, water was able to transport the majority of pesticides off the field.

4.4 | Recommendations

In this study, both PRZM and RZWQM were able to reasonably simulate strongly adsorbed pesticide runoff after limited calibration of hydrologic components. However, the good performance of PRZM is probably due to the fact that it is highly sensitive to CN, so that it would be easier to calibrate this parameter to match the field data. RZWQM adopts more mechanistic approaches for hydrologic simulation. It might be possible that if field-measured macropore information were available, it would have outperformed PRZM without calibration. Therefore, we recommended both PRZM and RZWQM for event-based pesticide runoff simulation at the field scale, with preference

TABLE 8 Predicted pesticide loss composition via water runoff and sediment erosion by the Pesticide Root Zone Model (PRZM) and Root Zone Water Quality Model (RZWQM)

			PRZM				RZWQM			
	Date	Field	Total mass (mg)	Mass in water phase (mg)	Mass in sediment phase (mg)	% in water phase	Total mass (mg)	Mass in water phase (mg)	Mass in sediment phase (mg)	% in water phase
Chlorpyrifos	5/22/2012	A	47.2	46.2	1.1	97.7	52.4	52.4	0.04	99.9
	6/16/2012	A	18.9	18.6	0.3	98.6	32.4	32.2	0.2	99.4
	8/29/2012	A	1.6	1.6	0.004	99.7	9.3	9.3	0.1	99.4
	5/21/2012	B	65.0	63.6	1.4	97.8	54.1	53.6	0.5	99.1
	6/15/2012	B	22.6	22.4	0.3	98.7	20.1	18.6	1.5	92.6
	8/28/2012	B	1.3	1.3	0.003	99.7	1.6	1.5	0.1	93.1
diuron	2/27/2013	A	2,962.7	2,960.0	2.7	99.9	1,453.0	1,446.8	6.3	99.6
	3/22/2013	A	250.9	250.8	0.08	100	414.7	412.9	1.8	99.6
	4/29/2013	A	20.1	20.1	0.002	100	324.7	323.7	1.0	99.7
	2/26/2013	B	103.0	102.9	0.06	99.9	1,877.8	1858.6	19.3	99.0
	3/21/2013	B	84.3	84.2	0.03	100	1,646.4	1,630.9	15.5	99.1
	4/26/2013	B	3.8	3.8	0.0004	100	646.2	639.5	6.7	99.0

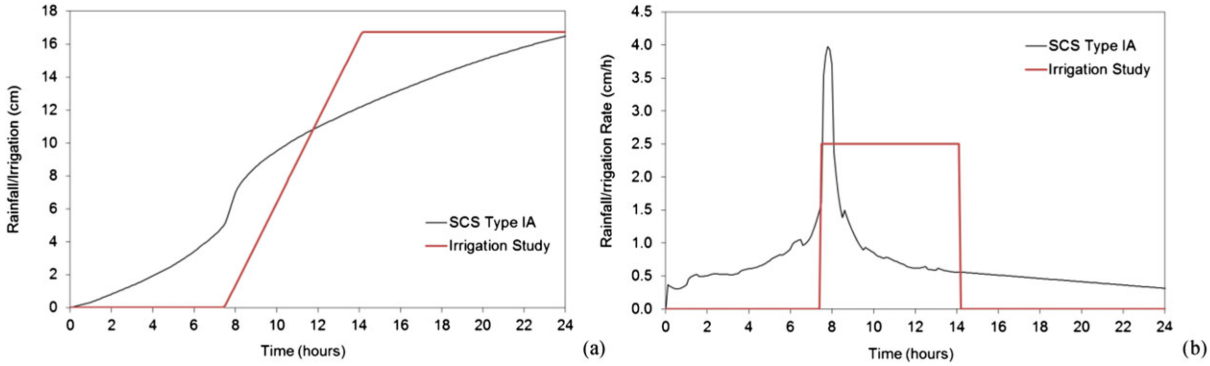

FIGURE 6 Distribution comparison of National Resource Conservation Service (Soil Conservation Service [SCS]) Type IA rainfall and irrigation water applied in this study (a: cumulative water input; b: water input rate).

given to RZWQM if field-measured soil hydraulic properties (including macropore parameters) are available.

5 | CONCLUSIONS

The newly integrated RZWQM was compared with PRZM in terms of their abilities to predict sediment and pesticide runoff from alfalfa fields. Limited hydrologic calibration was employed to minimize the effect of incorrect hydrologic simulation on pollutant transport. Results showed that both models performed reasonably well in simulating surface water runoff after calibration (absolute *PBIAS* < 31%), except for the peak event, which was underestimated. RZWQM is able to simulate preferential flow in macropore, allowing for a more realistic characterization of no-till alfalfa fields. Sediment yield was underestimated by both models (−89% ≤ *PBIAS* ≤ −36%), which can be partially attributed to the incorrect distribution of input water in PRZM and the uncertainty in the runoff erosivity coefficient used in RZWQM. However, the underestimation bias might be less considering the origin of sediment in a ditch without a concrete lining. Posttreatment chlorpyrifos losses were simulated with reasonable accuracy by both models, especially for Field A (absolute *PBIAS* ≤ 22%). Diuron losses, on the other hand, were underestimated to a great extent (−98% ≤ *PBIAS* ≤ −65%). This could be explained by the underprediction of diuron in the top soil due to the limitations of instantaneous equilibrium sorption model, along with the high runoff potential of the diuron used, which was formulated as water-dispersible granules. Both RZWQM and PRZM partitioned more than 93% of chlorpyrifos and 99% of diuron loads into the water phase, as the quantity of water was higher than the quantity of sediment in runoff by several orders of magnitude. On the basis of this study, RZWQM and PRZM performed well in predicting runoff and highly adsorptive pesticides, but RZWQM is recommended when field-measured soil hydraulic properties (including macropore parameters) are available. Future research needs include extending both models to two dimensions to account for flow-routing processes, as well as further studies on runoff erosivity coefficient of RZWQM, input water distribution of PRZM, and pesticide migration processes in the root zone. The results from this research are applicable to other arid or semiarid agricultural areas where irrigation is the major driver for runoff. Field-scale model comparison can also provide valuable information for pesticide runoff simulation at the watershed level, as many watershed models are based on field-level pesticide simulation models.

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