

Test of the Root Zone Water Quality Model (RZWQM) for predicting runoff of atrazine, alachlor and fenamiphos species from conventional-tillage corn mesoplots[†]

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Abstract: The Root Zone Water Quality Model (RZWQM) is a comprehensive, integrated physical, biological and chemical process model that simulates plant growth and movement of water, nutrients and pesticides in a representative area of an agricultural system. We tested the ability of RZWQM to predict surface runoff losses of atrazine, alachlor, fenamiphos and two fenamiphos oxidative degradates against results from a 2-year mesoplot rainfall simulation experiment. Model inputs included site-specific soil properties and weather, but default values were used for most other parameters, including pesticide properties. No attempts were made to calibrate the model except for soil crust/seal hydraulic conductivity and an adjustment of pesticide persistence in near-surface soil. Approximately 2.5 (± 0.9), 3.0 (± 0.8) and 0.3 (± 0.2)% of the applied alachlor, atrazine and fenamiphos were lost in surface water runoff, respectively. Runoff losses in the 'critical' events—those occurring 24 h after pesticide application—were respectively 91 (± 5), 86 (± 6) and 96 (± 3)% of total runoff losses for these pesticides. RZWQM adequately predicted runoff water volumes, giving a predicted/observed ratio of 1.2 (± 0.5) for all events. Predicted pesticide concentrations and loads from the 'critical' events were generally within a factor of 2, but atrazine losses from these events were underestimated, which was probably a formulation effect, and fenamiphos losses were overestimated due to rapid oxidation. The ratios of predicted to measured pesticide concentrations in all runoff events varied between 0.2 and 147, with an average of 7. Large over-predictions of pesticide runoff occurred in runoff events later in the season when both loads and concentrations were small. The normalized root mean square error for pesticide runoff concentration predictions varied between 42 and 122%, with an average of 84%. Pesticide runoff loads were predicted with a similar accuracy. These results indicate that the soil-water mixing model used in RZWQM is a robust predictor of pesticide entrainment and runoff.

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1 INTRODUCTION

Agricultural non-point source pollution is costly and difficult to control, and efficient management and analytical tools are needed. Comprehensive agrochemical fate and transport models integrate the major processes operating on agricultural ecosystems to simulate movement, persistence, transformation and potential impacts of agrochemicals. Once adequately verified and tested, these models can be used to explore the interactions and effects of agricultural management

practices on surface- and ground-water quality. They can provide valuable information for decision-makers and registration agencies regarding pesticide use. They can also be used to explore system behavior under a variety of scenarios that may be economically or technically impossible to investigate by individual experiments. The Root Zone Water Quality Model (RZWQM) has been developed for such purposes.¹ RZWQM is an integrated physical, biological and chemical process model that simulates plant growth

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and movement of water, nutrients and pesticides in a representative area of an agricultural system. It is one-dimensional (vertical into the soil profile) and designed to simulate conditions on a unit-area basis primarily in the crop root zone, although the depth can be extended to the vadose zone. The model incorporates a Microsoft Windows™ user interface to facilitate data input and parameterization. In particular, the pesticide sub-model of RZWQM has been recently revised and includes detailed algorithms for describing the complex interactions between pesticides and the agricultural systems in which they reside.^{2,3} Some of the algorithms have been tested and shown to work properly,^{3–5} while others have not been as extensively tested.

Simulation models such as RZWQM have to be thoroughly tested before use as management and analytical tools. However, it has frequently not been possible to obtain suitably comprehensive data for validating all state variables, even though great detail may have been available on selected variables and processes. The site-specific nature of simulation models makes it even more difficult to validate models. An alternative, attainable step towards ultimate model validation may be to test part of the model at a time and progressively gain confidence by extending the tests with more data. There have been several evaluations of RZWQM performance for simulating pesticide fate and transport in a range of environmental and cropping conditions. Malone *et al*⁶ reviewed and summarized these studies. Their conclusion was that RZWQM can adequately simulate the processes involved with pesticide fate and transport, but some key input parameters are both sensitive and site-specific. This study tests for the first time the performance of the model for simulating a complex, full-season runoff experiment, including three pesticides and parent–daughter–granddaughter dissipation and formation. Specifically, we compare predictions by RZWQM (RZWQM 98-1.0-2001, October 2001) against two years of field data from a ‘mesoplot’ rainfall-runoff simulation experiment,^{7,8} which measured runoff of water and alachlor (2-chloro-2',6'-diethyl-*N*-methoxymethylacetanilide), atrazine (6-chloro-*N*²-ethyl-*N*⁴-isopropyl-1,3,5 triazine-2,4-diamine) and fenamiphos (ethyl 4-methylthio-*m*-tolyl isopropylphoramidate). Fenamiphos is rapidly oxidized in the field to fenamiphos sulfoxide which is further oxidized to fenamiphos sulfone.^{9–12} Runoff of these degradates was also measured, providing a test of RZWQM's metabolite-tracking feature.

Model performance is evaluated by graphical comparison and statistical analyses. An RZWQM simulation of the hydrology of this field was reported previously using an older version (v3.1a, July 1995) based on general soil survey data.¹³ In the present study we use the current version and soil hydraulic properties measured at the experimental site (Reference 8 and James Hook, pers comm, 1999).

2 MODEL DESCRIPTION

2.1 Hydrology sub-model

A thorough description of RZWQM has been given by Ahuja *et al*.¹ A review of the overall features of the model and major algorithms is given by Malone *et al*⁶ and Wauchope *et al*.² A two-domain, soil matrix/macropore water flow model is used. However, macropore flow is not simulated because there is little or no macropore formation in this soil under conventional tillage. Water infiltration into the soil matrix during rainfall or irrigation is described by a modification of the Green–Ampt equation.^{14–16} Surface water runoff is generated when rainfall rate exceeds infiltration rate. Redistribution of soil water following infiltration is modeled by a mass-conservative numerical solution of the Richards' equation:¹⁷

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K \frac{\partial h}{\partial z} - K \right] - S(z, t) \quad (1)$$

where θ is volumetric soil water content and K is hydraulic conductivity; both are functions of soil water suction head h , depth z , and time t . $S(z, t)$ is a sink term for plant root water uptake and tile drain. The $S(z, t)$ term is solved following the method of Nimah and Hanks.¹⁸ The θ and K functions follow those of the Brooks and Corey,¹⁹ with some modifications.¹

RZWQM uses a modification of the double-layer Penman–Monteith model^{20,21} to calculate potential soil evaporation and crop transpiration. A generic plant growth model is used to simulate plant growth and phenology.²²

2.2 Pesticide sub-model

To account for the distinctive behaviors of pesticides in different compartments of a typical agricultural system, the system is conceptually divided into four compartments:² crop foliage, crop residues, soil surface and soil sub-surface or root zone. Depending on the compartments, different dissipation processes may be simulated. All individual dissipation processes in each compartment are assumed to follow pseudo-first-order kinetics.^{2,3} The rate constants for soil surface and sub-surface compartments are further adjusted for temperature and soil water content according to Walker:^{23,24}

$$k(T, \theta) = k(T_{\text{ref}}, \theta_{\text{ref}}) \exp \left[\frac{E_a}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right] \left(\frac{\theta}{\theta_{\text{ref}}} \right)^{-\beta} \quad (2)$$

where $k(T, \theta)$ is the rate constant at temperature T (K) and soil water content θ ; $k(T_{\text{ref}}, \theta_{\text{ref}})$ is the value of the rate constant at reference temperature T_{ref} (K) and reference soil water content θ_{ref} ; E_a is the degradation activation energy; R is the universal gas constant; and β is Walker's constant.

Formation and degradation of daughter and granddaughter products can be simulated in plant foliage, plant residues, soil surface and the root zone.

Transformation parameters for each compartment are defined individually in the input; currently the transformation process cannot be simulated simultaneously in more than one compartment. One or two daughter products may be specified or a daughter–granddaughter succession. All these processes are first order.

Transfer of pesticides from soil to surface runoff is modeled by a non-uniform mixing model^{25,26} assuming the mixing occurs in top 2 cm of the soil. Mass transfer of pesticides between soil layers is modeled by a partial-piston displacement and partial-mixing approach for each 1-cm depth increment. Pesticide displacement and mixing occur only in mesopores and macropores (mobile phase). Pesticide diffusion is allowed between micropores (immobile phase) and mesopores according to Fick's first law, and pesticide concentrations in both micropores and mesopores are updated at the end of each time step.

Soil sorption of pesticides may be modeled by a linear instantaneous equilibrium, a Freundlich isotherm or a two-site, equilibrium–kinetic sorption model.^{2,3,5,27–29} For partially ionized pesticides whose degree of ionization is determined by soil pH, RZWQM calculates the degree of ionization using an ionization equilibrium constant, K_a or K_b (for acids and bases, respectively), and calculates an apparent soil sorption coefficient which is a combination of neutral and ionized species coefficients. For example, for a basic pesticide such as atrazine, the apparent sorption equilibrium constant (K_d) is calculated by:²

$$K_d = \frac{K_w \cdot K_{ads}^0 + K_{base} \cdot C_{ns}^{H+} \cdot K_{ads}^+}{K_w + K_{base} \cdot C_{ns}^{H+}} \quad (3)$$

where K_{ads}^0 and K_{ads}^+ are the soil sorption constants for the neutral and cationic species (the latter usually assumed to be $10^5 \times$ soil organic carbon fraction³⁰), K_w and K_{base} are the dissociation constants for water and the pesticide, and C_{ns}^{H+} is the hydrogen ion concentration near the soil particle surface, calculated by:

$$C_{ns}^{H+} = 10^{-pH+1.8} \quad (4)$$

C_{ns}^{H+} is used instead of C^{H+} to correct for the lower pH near soil particle surfaces;^{31,32} the value of -1.8 is an approximation of surface acidity.^{2,33} Likewise, an equation has been developed for acidic pesticides. This method for calculating the sorption coefficient for charged pesticides may be applied to any of the sorption models.

2.3 Limitations of RZWQM

RZWQM is a one-dimensional model for simulating the vertical movement of water and solutes. Thus, RZWQM best describes areas where rainfall, soil and crop conditions are uniform. In heterogeneous situations the model may have to be run for different

conditions in order to characterize the combination, as demonstrated by Ma *et al.*¹³

RZWQM neglects vapor-phase flux of water and pesticides, but simple first-order vapor dissipation from soil or plant surfaces may be specified. Although pesticide volatilization is sensitive to temperature and soil moisture,³⁴ these effects are not explicitly coupled.

Field observations of pesticide disappearance in soils often indicate that dissipation slows more as time elapses than is predicted by a simple exponential function.^{35–38} A two-rate, biexponential dissipation model can sometimes better describe pesticide dissipation in the field,³⁹ and the USEPA has added a two-rate, biexponential dissipation model in the latest version of the Pesticide Root Zone Model, PRZM3.⁴⁰ It is possible, however, that accounting for simultaneous individual dissipation processes, as can be done in detail by RZWQM, will allow simple exponentials to adequately describe such complex field observations, provided that parameters for defining these individual dissipation processes are available.

RZWQM overcomes many of the difficulties encountered in daily time-step models by updating soil moisture distribution and solute transport in much smaller time steps. However, other processes which also can change during rainfall are currently changed only daily, eg reconsolidation of soils when rain falls on freshly tilled soil.¹³ Since changes in some soil properties affected by rainfall are only changed in the model at the end of the rainfall event (at the end of the day on which no rainfall occurs) this can lead to a significant under-prediction of runoff in some cases.

Although there are exceptions to the theory that it is only soil organic carbon that absorbs pesticides,^{2,41–43} RZWQM takes the value of K_{oc} , the soil organic carbon sorption coefficient, as an input and then determines the corresponding K_d value for each soil horizon based on the single K_{oc} value and soil organic carbon content of the horizon. This is inconvenient in the case where a user has site-specific values for K_d for the soil horizons to begin with. A future version of RZWQM should allow the user to input such data.

Plant uptake of pesticides has been activated in the current version of RZWQM and an irreversible binding of pesticides to soils has also been added. However, neither process worked properly in our test, and these algorithms are being revised. Finally, RZWQM currently does not simulate erosion—a serious limitation for pesticides with strong sediment/soil sorption. This sub-routine is currently under development.

3 MATERIALS AND METHODS

3.1 Field experiment and data collection

The field studies were conducted in Tifton, GA on a Tifton loamy sand (fine-loamy, kaolinitic, thermic Plinthic Kandiudults). The experiment was designed to collect data for evaluating model performance: details are given elsewhere.^{7,8,44} Two replicate maize plots 14.5 m wide (eight 1.5-m wide 2-row beds) by

42.9 m long with rows parallel to the slope were managed under conventional tillage practice. Six almost identical (*ca* 5 cm in 2 h) rainfall events, intense enough to generate significant runoff, were applied to each plot in each of the two growing seasons. The rainfall simulator and rainfall monitoring system are described in detail by Sumner *et al.*⁷

Rainfall events were applied after specific tillage operations or chemical applications each year. Event 1 occurred 1 day after moldboard plowing when the planting beds were rough (but not cloddy) and the tractor wheel tracks were freshly packed. Event 2 occurred 1 day after maize planting and chemical applications. Fenamiphos (0.36 kg liter⁻¹ EC formulation applied in 187 liter ha⁻¹ water carrier) was applied surface broadcast to bare soil at a rate of 6.7 kg AI ha⁻¹ and then incorporated into the soil to approximately 12 cm depth with a rototiller. Maize (*Zea mays* L) was then planted, followed by broadcast applications of alachlor (0.48 kg liter⁻¹ EC) and atrazine (900 g kg⁻¹ WG) in 187 liter ha⁻¹ carrier water at 2.8 and 1.6 kg AI ha⁻¹, respectively. After these operations the beds had a smooth and uncrusted surface. Event 3 was applied at the 3-leaf maize stage; the bed surface was very smooth and crusted from the previous rainfall. Event 4 occurred at the 10-leaf stage (0.3-m tall), Event 5 at the 14-leaf stage (1.2-m tall) and Event 6 occurred on mature corn prior to senescence. Runoff, channeled by wheel tracks, was monitored with a flow meter and sampled at 5- or 10-min intervals. Pesticide concentration for each event was obtained by integrating all sample concentrations for that event. We compared runoff predictions for all six events; however, pesticide concentrations in Events 5 and 6 were below analytical detection levels of approximately 0.1 µg liter⁻¹.

3.2 Model parameterization

3.2.1 Soil parameters

The measured soil and soil hydraulic properties (Table 1) were input, including particle-size distribution, soil bulk density, soil pH, saturated hydraulic conductivity (K_s) and soil water retention across a range of suction heads (only soil water retention at 33 kPa and 1500 kPa suction heads were included in Table 1). Parameters for the Brooks–Corey equations were obtained by a conversion method based

on measured soil water retention data.⁴⁵ The fitted parameters included air-entry pressure, pore size distribution index, saturated soil water content, and residual soil water content. These fitted parameters and the measured K_s were used to estimate parameters for the hydraulic conductivity curve using the capillary-bundle model according to Campbell.⁴⁶

One of the characteristics of Tifton loamy sand is to develop surface crusts/seals when exposed to high-intensity rainfall.^{47,48} Surface crusts/seals can dramatically reduce infiltration rate and thus increase runoff potential. This effect was not measured in the experiment, and the input parameter for the crust/seal saturated hydraulic conductivity was calibrated by minimizing runoff prediction errors using the 1992 data from plot A. The resulting value of 0.015 cm h⁻¹ is within the range of measured values for this soil.^{47,48} This optimized value is approximately twice that obtained when parameters for the θ and K functions [eqn (1)] were estimated using the extended similar-media scaling technique based on soil texture, soil bulk density and soil water content at 33 kPa suction head,^{1,3,49} a second option for estimating parameters for the θ and K functions when detailed, site-specific data are not available.¹

3.2.2 Pesticide parameters

Pesticide sorption coefficient K_{oc} , half-life in soil surface (0–1 cm) and sub-surface layers (>1 cm), degradation activation energy, soil moisture correction factor (Walker's constant) and base protonation constant (pK_b) are given in Table 2. Soil surface layer (1 cm) half-life was arbitrarily assumed to be one-third of the soil sub-surface layer half-life to account for the rapid loss of these semi-volatile pesticides at the soil surface by volatilization and other dissipation processes observed in the field.^{34–38} Atrazine base protonation constant ($pK_b = 12.3$) was obtained from the pesticide properties database included in the model.

We used the instantaneous equilibrium adsorption model for pesticide sorption, and did not simulate irreversible binding. Default parameter values for the non-uniform mixing model for chemical runoff were used.^{25,26}

Table 1. Means ($n = 24$) of selected soil and soil hydraulic properties of Tifton loamy sand^a

Depth (m)	Sand (%)	Silt (%)	Clay (%)	OC (%)	θ_{33} (m ³ m ⁻³)	θ_{1500} (m ³ m ⁻³)	pH	BD (mg m ⁻³)	K_s^g (cm h ⁻¹)
0.0–0.29	84.6	9.3	6.1	0.79	0.141	0.047	4.8	1.64	12.05
0.29–0.62	63.4	11.4	25.2	0.34	0.215	0.149	4.6	1.69	4.54
0.62–0.92	62.9	11.0	26.1	0.24	0.257	0.162	5.0	1.66	3.52
0.92–1.11	62.3	10.6	27.1	0.12	0.259	0.177	5.5	1.68	3.35
1.11–1.43	60.4	11.8	27.8	0.02	0.281	0.187	5.1	1.69	0.49
1.43–1.60	48.3	15.8	35.9	0.01	0.291	0.224	4.3	1.65	0.19

^a OC is soil organic carbon content; θ_{33} and θ_{1500} are volumetric soil water contents at 33 kPa and 1500 kPa suction heads, respectively; BD is soil bulk density; and K_s^g is the geometric mean of the saturated hydraulic conductivity. Soil pH was measured using 0.01 M CaCl₂ solution.

Table 2. Selected properties of the tested pesticides and degradation products^a

Pesticide/degradation product	K_{oc}^n (litre kg ⁻¹)	K_{oc}^b (litre kg ⁻¹)	$T_{1/2}^{sf}$ (day)	$T_{1/2}^{rz}$ (day)	pK _b	E_a (kJ mol ⁻¹)	β	FP (%)
Alachlor	170		5.0	15.0		54.0	0.8	
Atrazine	100.0	10 ⁵	20.0	60.0	12.3	54.0	0.8	
Fenamiphos	370.0		1.67	5.0		54.0	0.8	
Fenamiphos sulfoxide	90.0		9.33	28.0		54.0	0.8	75
Fenamiphos sulfone	103.0		4.67	14.0		54.0	0.8	50

^a K_{oc}^n and K_{oc}^b are adsorption coefficients for neutral and cationic pesticide species, respectively. $T_{1/2}^{sf}$ and $T_{1/2}^{rz}$ are pesticide dissipation half-life in the soil surface layer (0–1 cm) and root zone, respectively. pK_b is the negative logarithm of the base pesticide dissociation constant. FP is daughter or granddaughter formation percentage. The K_{oc} values for fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone were obtained from Lee *et al.*¹⁰ Soil half-lives for fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone were obtained from Truman *et al.*¹² The K_{oc} values and root zone half-lives for alachlor and atrazine were obtained from the pesticide database included in RZWQM.^{43,44}

3.2.3 Plant and weather parameters and statistics

Default parameter values in the model for Iowa maize growth and phenology were used. Measured weather data input included daily maximum and minimum air temperature, radiation, wind speed, relative humidity and hourly rainfall for 1992 and 1993.

The statistical method for evaluating the model performance was the ratio of the simulated value to the measured value and the normalized root mean square error (NRMSE). The ratio criterion has been used for goodness-of-fit tests for storm runoff simulations.^{50–52} The NRMSE is selected because it accounts for errors of overestimation and underestimation. The NRMSE is calculated by:

$$\text{NRMSE} = \frac{100}{\hat{O}} \sqrt{\frac{\sum_{i=1}^n (P_i - O_i)^2}{n}} \quad (5)$$

where O_i is the measured value and P_i is the corresponding predicted value; \hat{O} is the mean of the measured values, and n is the number of measurements. For a perfect fit, the NRMSE would be equal to zero. All statistical analyses were performed at 0.05 significance level unless specified otherwise.

4 RESULTS AND DISCUSSION

4.1 Surface water runoff

The surface crust hydraulic conductivity (0.015 cm h⁻¹), obtained by minimizing the root mean square errors between measured and simulated water runoff from plot A in 1992, was applied to other plot-years. Figure 1 shows that RZWQM reasonably simulated the pattern of surface water runoff, but discrepancies of 0.6 to 2.3 times the observed values occurred for individual plot/event combinations. The ratios were randomly distributed and the average ratio was 1.2 (±0.5). The NRMSE for runoff predictions, calculated for each plot-year (six runoff events), varied between 20.5% and 41.7%, with an average of 32.9%. Calibrating the surface crust hydraulic conductivity was the key to obtaining good predictions of water runoff in this soil. Without this calibration, the model predicted no runoff for Events 1 and 2. We also had

to manipulate the timing of rainfall relative to tillage and pesticide applications for Events 1 and 2 to have the model reform crusts/seals before these simulated rainfall events, as detailed by Ma *et al.*³

4.2 Alachlor losses in runoff

Measured alachlor runoff varied among plot-years as a result of soil spatial variability and environmental conditions. On average, 2.5 (±0.9)% of the applied alachlor was lost in surface water runoff over 4 plot-years, with 91 (±5)% of the runoff occurring in the first runoff event after alachlor application ('critical' runoff event). The coefficient of variation for the 4 plot-years was 39%. This is an overall measurement error including errors in soil spatial variability, environmental conditions and instrumental analysis errors. RZWQM gave adequate predictions of alachlor concentrations and loads in surface runoff (Fig 2), especially for the four largest-loss runoff events that occurred 24 h after alachlor application. The ratio of predicted to measured concentration for all runoff events varied between 0.7 and 6.3, with an average of 2.2. The ratio for the first runoff events after alachlor application (Event 2 in each plot-year) varied between 0.7 and 1.2, with an average of 0.9. Thus, RZWQM accurately predicted alachlor runoff in these 'critical' highest-load runoff events.⁵³ According to Parrish and Smith,⁵¹ predictions within a factor of 2 of the corresponding measured value may be considered as reasonably accurate. The NRMSE of the concentration predictions for all twelve runoff events was 41.5%.

RZWQM generally over-predicted alachlor concentrations for later runoff Events 3 and 4 (Fig 2). The over-predictions could result from the lack of a sediment transport component of the model. The measured sediment yields for Events 1 to 6, averaged for plots A and B in 1992 and 1993, were 788 (±68), 1085 (±11), 1395 (±148), 1551 (±284), 788 (±318) and 157 (±11) kg ha⁻¹,⁵⁴ respectively. Thus, sediment loss increased from Event 1 to Event 4 and decreased thereafter. A calculation for plot A in 1992 based on these sediment losses and a linear equilibrium adsorption model² indicated that approximately 8, 7 and 11% more alachlor would have been lost with sediment for Events 2, 3 and 4, respectively. If these losses were not

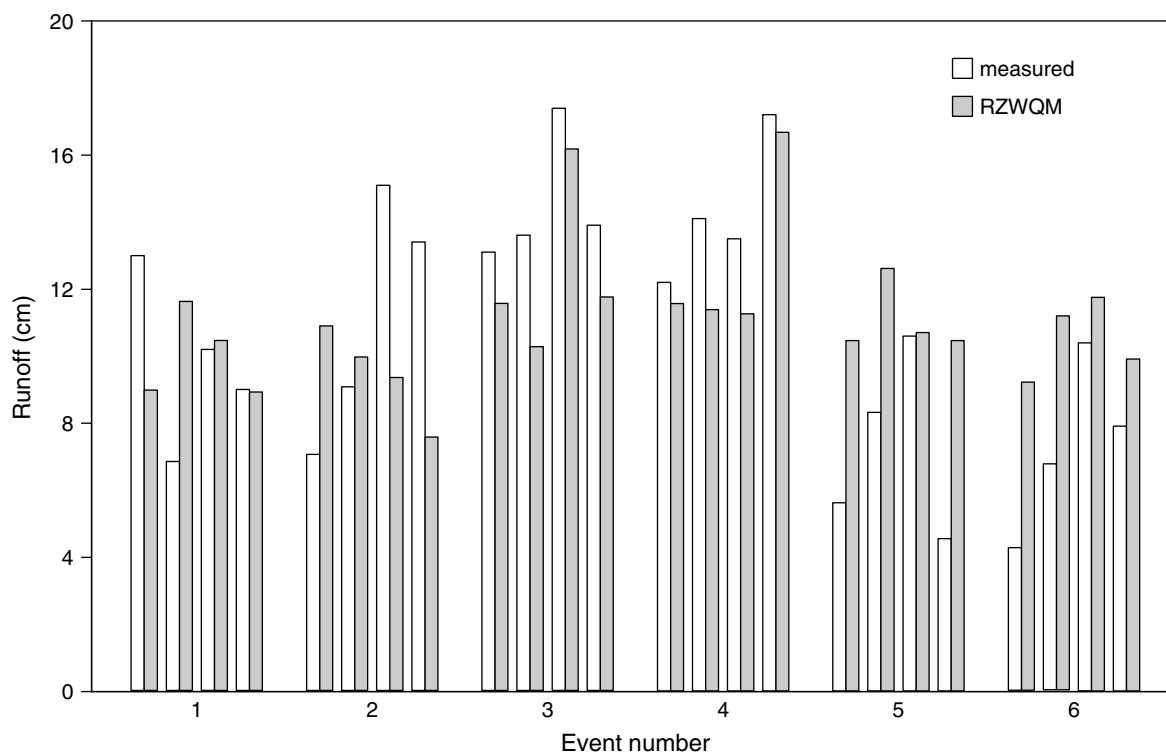


Figure 1. Measured and RZWQM-simulated surface water runoff from mesoplots. Within each event, bars represent, from left to right, 1992 plots A and B and 1993 plots A and B.

properly subtracted from the system, as they are for RZWQM simulations, more alachlor in the soil than actually should have presented would equilibrate with alachlor in soil solution and be available for runoff. As a result, alachlor in runoff was over-predicted. This process would influence pesticide runoff even more for pesticides with higher apparent K_{oc} .

Even when errors in predicted runoff volume and alachlor concentration are combined in the calculation of total runoff load, the resulting errors for 'critical' events are within the '2×' criterion. For all event runoff loads the predicted/measured ratios varied between 0.5 and 5.9, with an average of 2.0. The NRMSE of the load predictions for all 12 runoff events was 75.9%. The errors of alachlor runoff concentration and load predictions (41.5% and 75.9%, respectively) are about twice as large as that of surface water runoff prediction (32.9%).

4.3 Atrazine losses in runoff

On average, 3.0 (± 0.8)% of the applied atrazine was lost in surface water runoff over 4 plot-years and 86 (± 6)% of the runoff occurred in the 'critical' runoff event. The coefficient of variation for the 4 plot-years was 26%. RZWQM prediction errors for atrazine concentrations in Events 3 and 4 were quite similar to those of alachlor (Fig 3), but concentrations in the 'critical' events (Event 2) were largely under-predicted as compared to alachlor. This result is most likely due to the exceptionally high runoff capability of atrazine formulated as water-dispersible granules.^{11,53,55,56}

Another contributor to the under-predictions for atrazine runoff in Event 2 may be errors in the model

assumptions leading to the calculated K_d . With a pK_b of 12.3, RZWQM calculates that approximately 5% of atrazine would be protonated at a soil pH of 4.8 (near soil particle surface pH of 3). Thus, protonation of atrazine would increase the apparent K_d from 0.79 to 39 liter kg^{-1} (calculated using eqn (3) assuming a cation K_{oc} of 10^5 liter kg^{-1} and an organic carbon content of 0.79% as in Table 1). A model default value of $K_{oc} = 10^5$ liter kg^{-1} may be too large for protonated atrazine, which causes significant over-estimation of atrazine apparent adsorption constant and under-predictions of atrazine runoff. To explore the sensitivity of this effect, we ran the model with the ionization equilibrium option turned off (assume atrazine is neutral), forcing K_d to be equal to 0.79 liter kg^{-1} . This resulted in a triple increase in predicted atrazine runoff losses and overestimation of atrazine runoff. We then ran the model by gradually reducing the model default value of K_{oc} for cations and the atrazine runoff predictions were significantly improved overall (not shown). Thus, protonation of atrazine in the soil (pH ~ 5) must have occurred, but might not have proceeded as fast or as strongly as eqn (3) predicts. Atrazine is a weak base ($pK_b = 12.3$), sorption of the protonated ions to soil particle surfaces is typically a slow, diffusion-controlled process based on the Guoy–Chapman diffuse-layer theory. Furthermore, eqn (3) was originally developed based on the chemical thermodynamics theory for describing chemical reaction potentials in 'ideal' solutions. When applied to soils, discrepancies may occur. RZWQM assumes that the protonation is instantaneous in calculating the apparent equilibrium

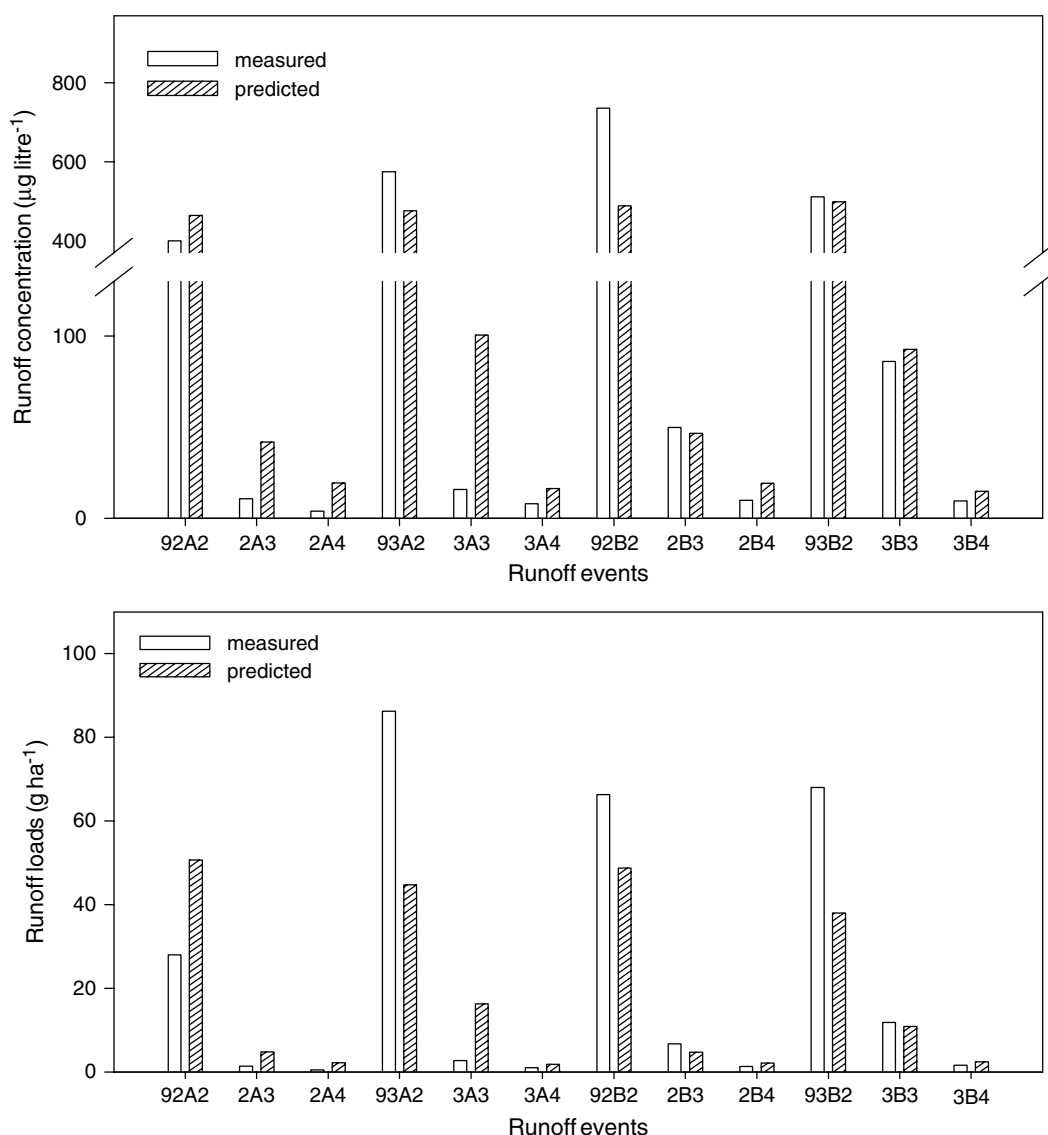


Figure 2. Measured and predicted alachlor concentrations and loads in surface runoff, plots A and B, 1992–1993.

adsorption constant. Therefore, it may overestimate this adsorption constant. This also could lead to under-predictions of atrazine concentrations in runoff shortly after atrazine application.

For later runoff Events 3 and 4, RZWQM significantly over-predicted atrazine concentrations in runoff (Fig 3), which may be caused, as for alachlor, by the lack of a sediment transport component of the model. Because atrazine has a much higher apparent adsorption constant than alachlor as a result of protonation, the sediment loss weighs even more on atrazine runoff (Fig 3). Ratios of predicted to measured concentrations for all events varied between 0.5 and 24.9, with an average of 5.5. The NRMSE for all 12 runoff events was 79.5%. Similar agreements were obtained for loads: ratios varied between 0.4 and 24.4, with an average of 5.0. NRMSE was 88.9%.

4.4 Runoff losses of fenamiphos and its degradates

Measured fenamiphos concentrations and loads in the 'critical' runoff events after applications in 1993

were less than half of those measured in 1992, while the oxidative daughter product concentrations were greater in 1993 (Table 3), indicating that degradation of the parent compound was faster in 1993. A similar result was observed in another study,¹¹ also indicating that the oxidative process is fast and that the kinetics is sensitive to environmental conditions—most likely soil moisture and temperature. The coefficient of variation for the 4 plot-years was 54%. Measured fenamiphos runoff was 0.3 (± 0.2)% of that applied, with 96 (± 3)% of runoff occurring in the 'critical' events. RZWQM, using single values for both plots and years for mother–daughter and daughter–granddaughter kinetic rate constants, can be expected to have difficulty as errors in individual species concentration predictions cascade exponentially in time. Still, RZWQM accurately predicted total fenamiphos species runoff from the 'critical' Event 2, with about the same level of accuracy as for the other emulsion formulation, alachlor. For total loads of all species, ratios averaged 0.8 for Event 2, 3.7 for Event 3, and 12.7 for Event 4 (Table 3)—again our predictions

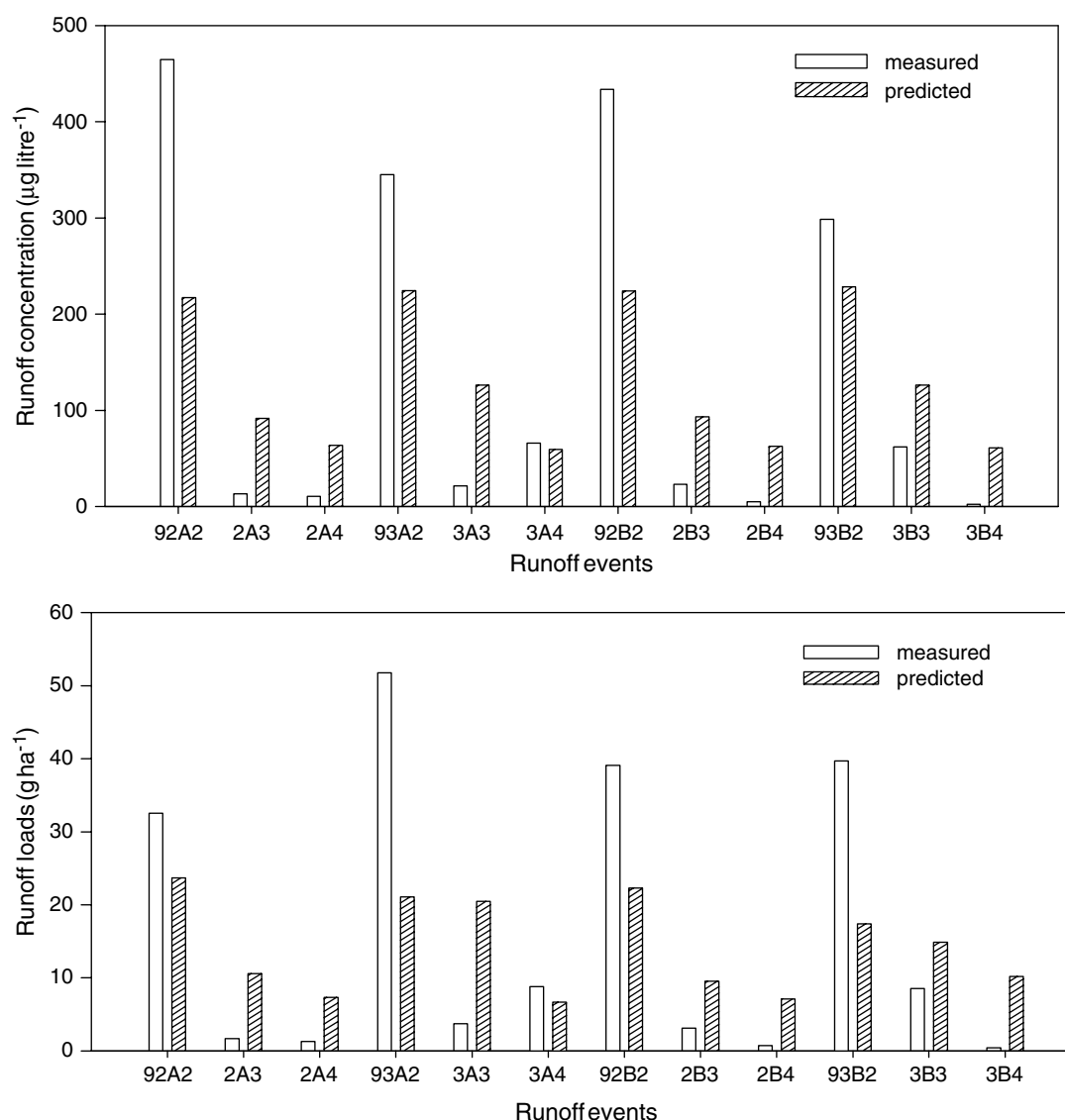


Figure 3. Measured and predicted atrazine concentrations and loads in surface runoff, plots A and B, 1992–1993.

are too high for the later events. The NRMSE values for individual species concentrations and loads were typically of the order of 100% or more for all events

5 CONCLUSIONS

This study provided a test of the ability of RZWQM to predict pesticide runoff from soil applications (surface broadcast and incorporation) with minimum adjustment of input variables. Rainfall conditions in the experiment, which were designed to simulate ‘reasonable worst case’ conditions, were rather extreme and field conditions changed drastically during the experiment. The model was run with site-specific soil properties—the hydrology is very sensitive to these, and crust/seal hydraulic conductivity had to be calibrated. Under these conditions the hydrology performed very well: the average predicted/measured runoff ratio for individual events was 1.2 and the average NRMSE was 32.9%.

Pesticide processes received essentially no calibration except for a rough adjustment for persistence in

the surface soil, yet RZWQM adequately simulated pesticide runoff losses for the ‘critical’ events—those events that contributed to the vast majority (86–96% in this study) of surface chemical transport. For the ‘critical’ events the average ratio of predicted to measured pesticide concentrations was 1.0. For all events RZWQM generally over-predicted pesticide concentrations and loads, giving an average ratio of predicted to measured pesticide concentrations in all runoff events near 7. One could easily improve the pesticide simulation results with a few reasonable adjustments such as (a) distributing the Event 2 rainfall occurring on the day after tillage so that reconsolidation can take place before runoff begins; (b) adjusting the rapidly oxidizing fenamiphos half-life between years; (c) allowing for increasing soil sorption of the chemicals in time, thus decreasing their availability for runoff and (d) accounting for pesticide losses through sediment transport. Thus, the RZWQM runoff mixing model appears to provide excellent predictions of chemical entrainment into runoff water, at least when the chemicals are in the soil in dissolved/adsorbed

Table 3. Fenamiphos runoff loads: observed vs RZWQM-predicted

Year/plot	Fenamiphos species loads in runoff events (g ha ⁻¹)					
	Event 2		Event 3		Event 4	
	Measured	Predicted	Measured	Predicted	Measured	Predicted
Fenamiphos						
1992-A	20.6	34.2	0.5	1.5	0.1	0.3
1992-B	35.0	34.0	3.0	1.6	0.2	0.3
1993-A	14.4	32.0	0.1	5.4	<dl ^b	0.1
1993-B	12.4	25.5	0.5	4.0	0.3	0.2
Fenamiphos sulfoxide						
1992-A	22.6	12.5	19.4	11.2	6.6	7.3
1992-B	ns ^a	9.4	35.0	11.5	13.7	7.3
1993-A	64.0	9.8	3.7	36.0	0.6	7.8
1993-B	35.8	9.3	12.1	22.5	0.1	10.5
Fenamiphos sulfone						
1992-A	0.2	0.2	1.7	1.1	0.8	1.0
1992-B	ns ^a	0.2	2.5	1.6	1.7	1.5
1993-A	0.6	0.1	0.0	3.3	<dl ^b	1.3
1993-B	0.5	0.2	0.5	3.0	<dl ^b	2.8
Total fenamiphos species ^c						
1992-A	43.5	46.9	21.6	13.8	7.5	8.6
1992-B		34.6	40.5	14.7	15.6	9.1
1993-A	79.0	41.9	3.8	44.7	0.6	9.2
1993-B	48.7	35.0	13.1	29.5	0.4	13.5
Ratios of predicted to measured load						
1992-A		1.1		0.6		1.1
1992-B				0.4		0.6
1993-A		0.5		11.8		15.3
1993-B		0.7		2.3		33.7
Average		0.8		3.7		12.7

^a Not sampled.

^b <dl = less than experimental analytical detection limit.

^c Degradation corrected to parent molecular weight.

forms and not present in residual granules or ionized forms, as was the case with atrazine.

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