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Modeling hydrology, metribuzin degradation and metribuzin transport in macroporous tilled and no-till silt loam soil using RZWQM[†]

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Abstract: Due to the complex nature of pesticide transport, process-based models can be difficult to use. For example, pesticide transport can be effected by macropore flow, and can be further complicated by sorption, desorption and degradation occurring at different rates in different soil compartments. We have used the Root Zone Water Quality Model (RZWQM) to investigate these phenomena with field data that included two management conditions (till and no-till) and metribuzin concentrations in percolate, runoff and soil. Metribuzin degradation and transport were simulated using three pesticide sorption models available in RZWQM: (a) instantaneous equilibrium-only (EO); (b) equilibrium-kinetic (EK, includes sites with slow desorption and no degradation); (c) equilibrium-bound (EB, includes irreversibly bound sites with relatively slow degradation). Site-specific RZWQM input included water retention curves from four soil depths, saturated hydraulic conductivity from four soil depths and the metribuzin partition coefficient. The calibrated parameters were macropore radius, surface crust saturated hydraulic conductivity, kinetic parameters, irreversible binding parameters and metribuzin half-life. The results indicate that (1) simulated metribuzin persistence was more accurate using the EK (root mean square error, RMSE = $0.03\,\mathrm{kg\,ha^{-1}}$) and EB (RMSE = $0.03\,\mathrm{kg\,ha^{-1}}$) sorption models compared to the EO (RMSE = $0.08\,\mathrm{kg\,ha^{-1}}$) model because of slowing metribuzin degradation rate with time and (2) simulating macropore flow resulted in prediction of metribuzin transport in percolate over the simulation period within a factor of two of that observed using all three pesticide sorption models. Moreover, little difference in simulated daily transport was observed between the three pesticide sorption models, except that the EB model substantially under-predicted metribuzin transport in runoff and percolate >30 days after application when transported concentrations were relatively low. This suggests that when macropore flow and hydrology are accurately simulated, metribuzin transport in the field may be adequately simulated using a relatively simple, equilibrium-only pesticide model.
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Keywords: preferential flow; model validation; pesticide degradation; kinetic sorption

1 INTRODUCTION

Malone *et al*[1] tested the pesticide transport models PRZM-3 and GLEAMS against field data and observed that total metribuzin transport in percolate over the simulation period (70 + days) was under-predicted by a factor of more than ten. Possible model-related (not user-related) reasons for the under-predicted transport are the lack of a macropore flow component in the models or the pesticide sorption components of the models being too simple. The Root Zone Water Quality Model (RZWQM) simulates macropore flow and 'kinetic' sorption, where a fraction of a pesticide is strongly held and undergoes slow (on the order of days or weeks instead of instantaneous) sorption–desorption, with the remaining fraction in instantaneous equilibrium.[2,3] Kumar *et al*[4] found that macropore flow was important to accurately simulate atrazine transport on Floyd, Readlyn and Kenyon soils to subsurface drains using RZWQM. The combined effect of these two factors (macropore flow and

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sorption kinetics) on RZWQM-simulated pesticide transport has not been assessed to date.

Pesticide degradation with increasing half-life as time elapses[5,6] will also affect pesticide transport. The pesticide module of RZWQM can simulate the formation of irreversibly bound pesticide,[7] where bound pesticide is assumed to degrade slower than unbound pesticide. This algorithm has not been assessed to date. When kinetic sorption is activated during RZWQM simulations, degradation also slows because degradation is not simulated on kinetic sites.

A thorough model assessment should include a complete data-set consisting of pesticide concentration in runoff, percolate and soil. Measurements of pesticide concentrations in soil are necessary to investigate total dissipation (degradation and transport), but using subsurface soil samples to estimate leaching may suggest less pesticide transport than percolate samples when macropores are present.[8,9] Furthermore, management effects are a major focus of RZWQM[2] and a thorough assessment should include two or more management scenarios (eg, different tillage).

We used RZWQM (version 1.0.2000.929) and the same field data as Malone *et al*[1] to investigate the effects of macropore flow, two-compartment pesticide sorption–desorption, and two-compartment pesticide degradation on metribuzin transport. The data set included two management conditions (till and no-till), and metribuzin concentrations in percolate, runoff and soil. Metribuzin fate and transport were simulated using three pesticide sorption models: (a) equilibrium-only; (b) equilibrium-kinetic (includes sites with slow desorption and no degradation); and (c) equilibrium-bound (includes irreversibly bound sites with relatively slow degradation). This study enabled us to investigate complex processes involved with pesticide transport (macropore flow, two-compartment pesticide degradation, and two-compartment pesticide sorption–desorption), and to thoroughly test the modified RZWQM pesticide component using a complete data set.

2 RZWQM DESCRIPTION

RZWQM simulates water and pesticide movement during a rainfall event as follows:

- rainfall, irrigation and chemicals are received by the soil surface, plant foliage and residue
- rainfall (or irrigation) exceeding the infiltration rate becomes overland flow and enters macropores
- overland flow exceeding both the maximum macropore flow capacity and infiltration rate becomes edge-of-field runoff
- a portion of the chemicals in the top 2 cm of the surface soil, plant foliage, and crop residue are transferred to overland flow
- as the solution moves through the macropores it mixes with the soil surrounding macropore walls, and a portion of the water and chemicals radially infiltrate into the soil matrix.

2.1 Pesticide processes

Chemicals are transferred from soil to overland flow by rainfall impact mixing with the top 2 cm of soil (contribution decreases exponentially with depth), and by chemical washoff from foliage and crop residue (mulch). Chemical transfer from soil to overland flow is expressed by

$$M_{\text{ave}} = \mathrm{e}^{-B1z} \tag{1}$$

where M_{ave} is the average degree of mixing between rainfall and soil solution for each depth increment, $B1$ is the non-uniform mixing parameter, and z is the center of each depth increment (0.5 or 1.5 cm). The chemical is transferred from soil to rainwater each time increment and may be determined using a mass balance approach.[10] RZWQM simulates chemical washoff from plant foliage and mulch as

$$C_{\text{f}} = 0.01\,C_{\text{o}}(100 - F) + 0.01\,C_{\text{o}}F(\mathrm{e}^{-Pti}) \tag{2}$$

where C_{f} is the chemical concentration remaining on mulch or foliage (μg ha^{-1}) after an incremental rainfall amount with intensity i (cm h^{-1}) and time t (h), C_{o} is the initial concentration on mulch or foliage at the beginning of each time increment, and P and F are washoff parameters.

Figure 1 summarizes the pesticide sorption, desorption and degradation paths that were simulated. The three possible metribuzin adsorption sites consist of equilibrium ($P_{\text{e}} = (1-f)K_{\text{d}}C_{\text{w}}$), kinetic ($\mathrm{d}P_{\text{k}}/\mathrm{d}t = RK2[(1-f)K_{\text{d}}C_{\text{w}} - P_{\text{k}})$, and irreversibly bound ($\mathrm{d}P_{\text{b}}/\mathrm{d}t = K_{\text{b}}C_{\text{w}}$). When $f = 0$, all pesticide not irreversibly bound are in equilibrium with water ($P_{\text{e}} = K_{\text{d}}C_{\text{w}}$). Where, P_{e} is the pesticide on the equilibrium sites (μg g^{-1}); f is the fraction of sorption sites that are kinetic (dimensionless); K_{d} is the partition coefficient (ml g^{-1}); C_{w} is the pesticide in water (μg ml^{-1}); P_{k} is the pesticide on kinetic sites (μg g^{-1}); t is time (day); $RK2$ is the desorption rate constant from

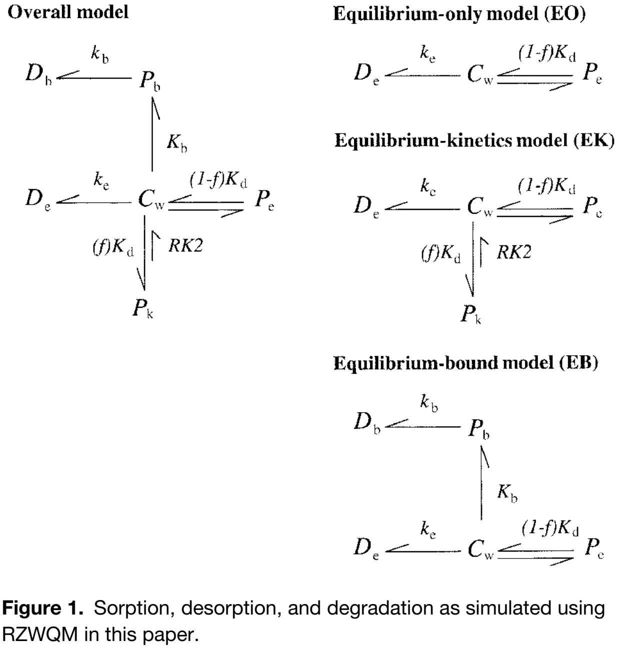

Figure 1. Sorption, desorption, and degradation as simulated using RZWQM in this paper.

kinetic sites (day^{-1}); P_b is the pesticide on irreversibly bound sites (μg g^{-1}); and K_b is the bound pesticide formation coefficient (ml g^{-1} day^{-1}).

Pesticide degradation is simulated as a first order process in RZWQM and the degradation rates are assumed to be different for the three sorption sites (kinetic, bound, equilibrium). Under our simulation scenarios, metribuzin in equilibrium with water degrades to an unspecified daughter product (D_e) according to $dC_w/dt = k_e C_w$. RZWQM assumes no degradation on kinetic sites and assumes a relatively slow degradation rate of irreversibly bound pesticide ($dP_b/dt = k_b P_b$) to an unspecified daughter product (D_b). The metribuzin half lives are then $H_e = \ln 2/k_e$ and $H_b = \ln 2/k_b$. Where k_e is the degradation coefficient of pesticide in equilibrium with water (day^{-1}); k_b is the degradation coefficient of pesticide on irreversibly bound sites (day^{-1}); H_e is the half life of pesticide in equilibrium with water (day) and H_b is the half life of irreversibly bound pesticide (day).

Pesticide half-life is affected by soil water content and temperature[11] and these processes are simulated in RZWQM by

$$H = H_{\mathrm{ref}} e^{(E_a/R)(1/T - 1/T_{\mathrm{ref}})} \tag{3}$$

$$H = H_{\mathrm{ref}} (\theta/\theta_{\mathrm{ref}})^{-B2} \tag{4}$$

where H is pesticide half-life in soil adjusted for soil temperature and/or soil water content (day); H_{ref} is pesticide half-life in soil at reference temperature and/or reference soil water content (day); E_a is activation energy (kJ mol^{-1}); R is the gas constant (8.314 J mol^{-1}K^{-1}); T is the field temperature of soil (K); T_{ref} is the reference temperature at which pesticide half-life input into RZWQM was measured (K); θ is field soil water content (cm^3 cm^{-3}); θ_{ref} is reference soil water content at which pesticide half-life input into RZWQM was measured (cm^3 cm^{-3}); and $B2$ is an adjustable constant (dimensionless). Pesticide half-life is only adjusted for equilibrium sites, degradation on bound sites remains constant and degradation is never simulated on kinetic sites.

2.2 Soil matrix water processes

RZWQM simulates water infiltration using a modification of the Green–Ampt equation and water redistribution is simulated using Richards' equation. Soil hydraulic properties are described with a modification of the Brooks–Corey equation

$$\theta(\tau) = \theta_s \qquad 0 \le \tau \le \tau_b \tag{5}$$

$$\theta(\tau) = \theta_r + B\tau^{-\lambda} \qquad \tau \ge \tau_b \tag{6}$$

where θ is volumetric soil water content (cm^3 cm^{-3}); τ is matric suction (cm water, $\tau = -h$, where h is the soil water pressure head); θ_s and θ_r are saturated and residual soil water contents, respectively (cm^3 cm^{-3}); τ_b is the air-entry or bubbling suction (cm); λ is a pore size distribution index (dimensionless); and B is a dimensionless constant calculated from:

$$B = (\theta_s - \theta_r)\tau_b \tag{7}$$

The hydraulic conductivity (K, cm h^{-1}) versus matric suction (τ, cm) relationship is expressed as:

$$K(\tau) = K_S \qquad 0 \le \tau \le \tau_{bk} \tag{8}$$

$$K(\tau) = C2\tau^{-N2}; \qquad \tau \ge \tau_{bk} \tag{9}$$

where K_s is the saturated hydraulic conductivity (cm h^{-1}); τ_{bk} is the air-entry or bubbling suction (cm) for the hydraulic conductivity relationship; and $N2$ and $C2$ are constants.

Furthermore, a crust on the soil surface may be input into RZWQM to reduce the saturated hydraulic conductivity of the surface soil (K_c, cm h^{-1}).

2.3 Macropore processes

When the rainfall rate exceeds the infiltration rate as determined by the vertical Green–Ampt equation, excess water is routed into macropores to the limit of flow-rate capacity of macropores determined by Poiseuille's law. For each time step (determined as the time to vertically saturate each 1-cm increment), the flow is sequentially routed downward through the continuous macropores in 1-cm increments. In each depth increment, the macropore flow is allowed to infiltrate laterally into the soil if saturation has not occurred according to the lateral (radial) Green–Ampt equation.

The radial infiltration rate in macropores (V_r) may be impeded by compaction of macropore walls or an organic coating surrounding macropore walls. To account for this, V_r multiplied by a lateral sorptivity reduction factor ($V_r = V_r \times$ lateral sorptivity reduction factor).

The water entering macropores is evenly distributed among macropores, and the number of macropores per unit area most effective in transmitting water ($nmacro^*$) is computed as a function of effective macroporosity ($macro^*$, cm^3 cm^{-3}) and average macropore radius (rp)

$$nmacro^* = macro^*(\pi \times rp^2)^{-1} \tag{10}$$

We use effective macroporosity because only a fraction of total macroporosity transmits water[12–14] and most percolate is from a relatively small percentage of percolate-producing macropores.[15] The water and chemicals moving through macropores mix with a portion of the soil surrounding the macropore walls (effective soil radius), and react with soil according to chemical partitioning.

3 MATERIALS AND METHODS

To accomplish our objectives the following were needed: a complete data-set (field measurements of pesticide in percolate, runoff and soil); field measurements of soil temperature and soil water content because they influence pesticide degradation and transport; detailed climate information (eg breakpoint rainfall, air temperature, solar radiation); detailed soil analysis (eg water retention curves, saturated hydraulic conductivity, bulk density, soil carbon); and the partition coefficient for the site specific soil and pesticide.

3.1 Field study

Two field plots ($22.0 \times 7.3\,m^2$; 10% slope) were installed at the Kentucky State University (KSU) research farm near Frankfort, KY in May 1994 to study the fate of metribuzin under two field conditions: no-till and tilled bare soil. The soil was a Lowell silt loam (fine, mixed, active, mesic Typic Hapludalf). The no-till plot was last tilled in 1994, then glyphosate was applied to kill the rye cover in April 1995. The tilled plot was rototilled 15 cm deep in April 1995. Although the no-till plot was tilled in 1994, the field observations (runoff, percolate, soil water content, metribuzin concentration in percolate) suggest obvious management differences between the two plots.

Two zero-tension pan lysimeters ($61 \times 61\,cm^2$) were installed at 75 cm below the soil surface in horizontal tunnels near the down gradient edge of both plots in 1994 to collect percolating water. Pre-calibrated tipping buckets were installed to measure total runoff and collect a flow-proportional runoff sample for pesticide and sediment analysis. Soil cores were taken immediately after pesticide application and then weekly thereafter to 75 cm, composited by horizon, and frozen until analyzed.

Tensiometers and thermocouples were installed at approximately 12, 28, 46 and 66 cm depths to measure capillary pressure and soil temperature. Soil pressure was converted to soil water content using water retention curves (Fig 2). Water retention curves were developed by obtaining three soil cores from each depth, saturating the cores in Tempe cells and drying the cells by applying increasing amounts of pressure in the 0–80 kPa range. Field tensiometer measurements below −80 kPa were removed from analysis because of tensiometer limitations.

Metribuzin was extracted from soil and sediment using supercritical fluid extraction and from water using solid phase extraction. Using $50\,\mu g\,kg^{-1}$ spiked soil, $2\,\mu g\,liter^{-1}$ spiked water, and $0.25\,\mu g\,liter^{-1}$ spiked water, recovery was 92 (±14)% ($n = 48$ replications), 91 (±1)% ($n = 2$ replications), and 115 (±3)% ($n = 2$ replications), respectively. Metribuzin analysis was

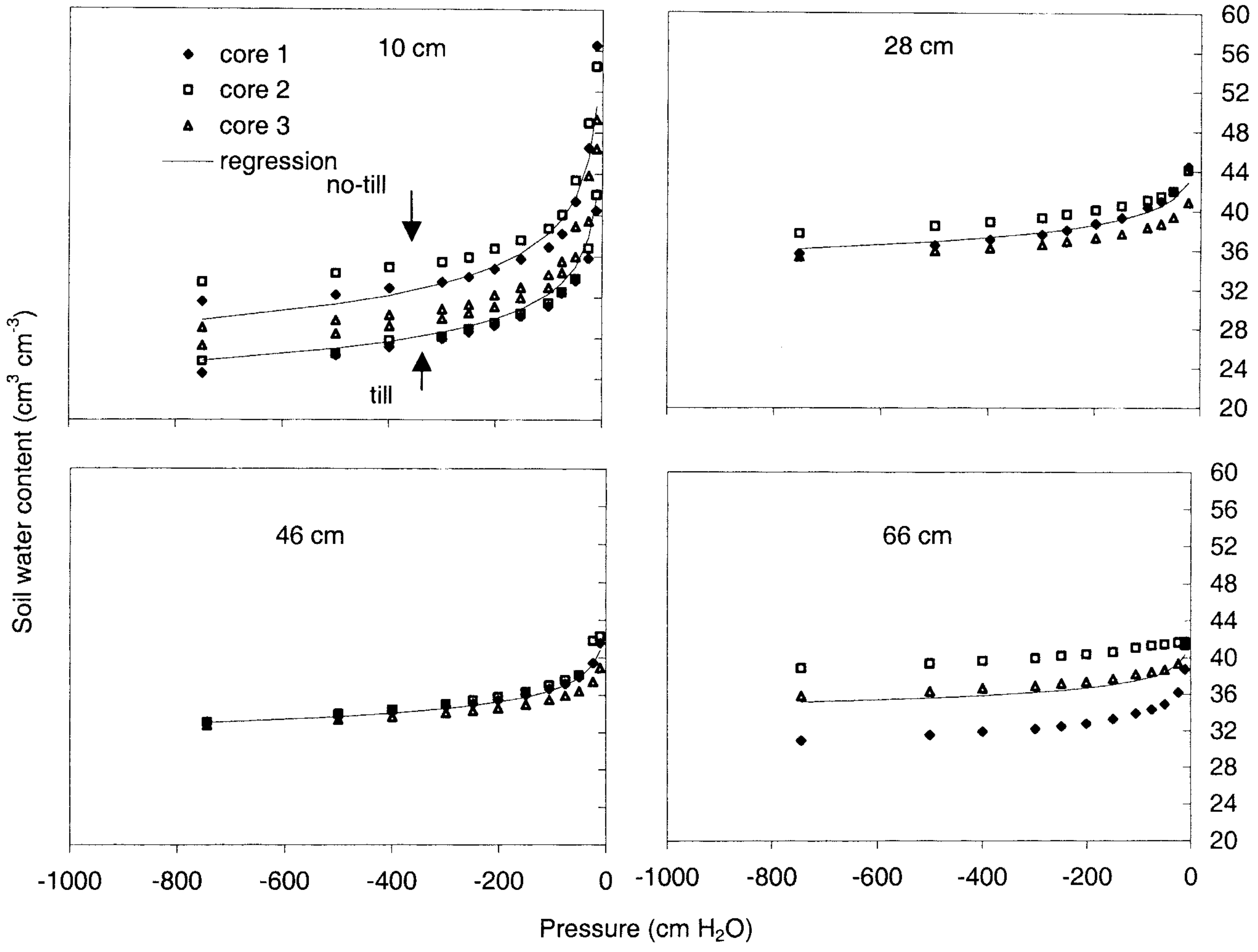

Figure 2. Water retention curves. Below 15 cm depth, no-till and till water retention curves were equal.

performed using gas liquid chromatography. Details of the extractions and analytical methods were discussed in Malone *et al.*[16] Sediment data is not included in this paper because RZWQM does not simulate sediment transport and over ten times more metribuzin was in the aqueous phase than in the sediment phase.[17,18]

3.2 Measured RZWQM input parameters

Metribuzin (2.64 g AI liter^{-1} water) was applied to the two plots using a carbon-dioxide-pressurized backpack sprayer on days 128 and 156. Two applications extended detectable soil concentrations from a little more than 20 days to about 70 days, which provided more field data for model evaluation. Exact metribuzin application to each plot was determined by measuring mixture volume before and after application (Table 1). Application was designed to minimize drift, but to account for this the measured soil metribuzin on the day of application was used as model input.

Climatic data were measured at the KSU research farm, with the exception of solar radiation data, which was obtained from a nearby weather station. Daily breakpoint rainfall was measured with an automated tipping bucket rain gauge. Missing data were estimated from nearby weather stations.

Several soil parameters (soil carbon, K_s, λ, τ_b, bulk density) in Table 1 were determined from triplicate core samples from four depths (12, 28, 46 and 66 cm). The partition coefficient was measured using batch-type procedures[19] on the surface soil (0–15 cm) and is described more fully by Malone *et al.*[1] The soil carbon was determined by dry combustion. The bubbling pressure and pore size distribution were estimated from the water retention curves (Fig 1) and Eqns (5)–(7). The soil characteristics were assumed to be equal for till and no-till soils at depths greater than 15 cm. The reference soil temperature and reference soil water were computed as the average of all field measurements after the second application on the tilled plot.

3.3 Estimated RZWQM input parameters

Several difficult-to-determine RZWQM parameters were estimated from the literature (Table 2). Most of the estimation techniques are explained in Table 2, but macroporosity needs further explanation. The effective

Table 1. Measured and calibrated soil and chemical RZWQM input parameters

Parameter	Value
Measured soil and chemical parameters	
Partition coefficient normalized for soil carbon ($K_{oc} = K_o$/oc, ml g^{-1})	46
Soil carbon (oc = mass carbon per mass soil)	0.013 (0–15 cm)
	0.003 (15–75 cm)
Saturated hydraulic conductivity (K_s, cm h^{-1})	144 (0–15 cm, till and no-till)
	12.6 (15–30 cm)
	3.7 (30–55 cm)
	1.2 (55–72 cm)
Pore size distribution index (λ, dimensionless)	0.118 (0–15 cm, till); 0.13 (0–15 cm, no-till)
	0.051 (15–30 cm)
	0.053 (30–55 cm)
	0.034 (55–72 cm)
Bubbling suction for water content (K_b, cm)	0.32 (0–15 cm, till); 3.66 (0–15 cm, no-till)
	7.88 (30 cm)
	7.96 (55 cm)
	4.66 (72 cm)
Bulk density	1.0 (0–15 cm, till); 1.1 (0–15 cm, no-till)
	1.45 (15–30 cm)
	1.55 (30–75 cm)
Applied metribuzin (kg ha^{-1})	0.79 (till, 1st application); 0.82 (no-till, 1st application)
	0.71 (till, 2nd application); 0.63 (no-till, 2nd application)
Measured soil metribuzin same day of application (kg/ha)	0.59 (till, 1st application); 0.39 (no-till, 1st application)
	0.47 (till, 2nd application); 0.25 (no-till, 2nd application)
Reference soil temperature (T_{ref}, °C)	25.6 (till, 2nd application)
Reference soil water (θ_{ref}, cm^3 cm^{-3})	0.283 (till, 2nd application)
Calibrated soil parameters	
Macropore radius (*rp*, cm)	0.03 (till); 0.06 (no-till)
Surface crust saturated hydraulic conductivity (K_c cm h^{-1})	0.01 (till); 0.02 (no-till)
Calibrated chemical parameters	
Fraction of sorption sites that are kinetic (*f*)	0.06
Desorption rate constant from kinetic sorption sites (*RK2*, day^{-1})	0.001
Bound pesticide formation coefficient (K_b, day^{-1})	0.007
Bound pesticide half life (H_b, day)	29
Equilibrium half life (H_e, day)[a]	4.6 (EO); 2.3 (EK); 2.4 (EB)

[a] EO is equilibrium-only; EK is equilibrium-kinetic; EB is equilibrium-bound pesticide sorption models.

Table 2. Estimated RZWQM input parameters

Parameter	Value	Estimation method[a]
Soil parameters		
Bubbling suction for hydraulic conductivity (τ_b, cm)	3.66 (15 cm, till and no-till) 7.88 (30 cm) 7.96 (55 cm) 4.66 (72 cm)	$\tau_{bk} = \tau_b$ (user manual). Note that till was input as the no-till value (3.66) because 0.32 resulted in substantially under predicted water loss after day 165.
Unsaturated hydraulic conductivity constant (*C2*)	2283 (15 cm, till and no-till) 867 (30 cm) 260 (55 cm) 27.3 (72 cm)	$C2 = K_s{}^*(\tau_{bk})^{N2}$ (user manual).
Unsaturated hydraulic conductivity constant (*N2*)	2.12 (15 cm, till) 2.13 (15 cm, no-till) 2.05 (30 cm) 2.05 (55 cm) 2.03 (72 cm)	$N2 = \lambda + 2$ (Russo and Bresler;[20] Kutilek and Nielsen[21]).
Effective macroporosity (*macro**)	0.0001 (no-till) 0.00003 (till)	macro* = nmacro* (πrp^2) (Malone *et al*[22]). rp = average radius of macropores (cm)
Effective number of percolate producing macropores (*nmacro**)	0.01/cm^2 (till and no-till)	nmacro* is 50% of percolate producing macropores and assumed constant at different soil depths (Malone *et al*[22]).
Sorptivity reduction factor	0.1	Ahuja *et al*[23]
Chemical parameters		
Effective soil radius (cm)	0.6	Malone *et al*[22]
Pesticide half life on mulch (day)	2.3	Assumed equal to half life for non-kinetic sites.
Non-uniform mixing factor (*B1*, cm^{-1})	4.4	User manual
Pesticide washoff parameters (no-till only)	0.033 (P) 100 (F)	User manual
Pesticide degradation adjustment constant for water content (*B2*)	0.8	User manual
Activation energy (E_a, kJ mol^{-1})	54 000	User manual

[a] The term 'user manual' indicates that the techniques described in the user manual and/or help screen (part of user interface) were used to determine this parameter, or that the parameter was the model default value.

number of percolate-producing macropores was input as 50% of percolate-producing macropores[22] and assumed to be equal for till and no-till.[24] The number of percolate-producing macropores were assumed to be 0.02 cm^{-2}.[12] The water and chemicals moving through macropores mix with a portion of the soil surrounding the macropore walls, and this is called effective soil radius as described above in Section 2.3. Although the macroporosity was not measured, macropores were suspected because matrix flow models (PRZM and GLEAMS) could not predict the high pesticide concentration in percolate soon after application.[1] Even if macroporosity were measured (eg tension infiltrometer data; counting the number of macropores in soil), assumptions would still be necessary because water may flow through only a fraction of macroporosity.[13,22]

3.4 Model calibration, testing and sensitivity

Some of the parameters in Table 1 were calibrated because they are difficult to measure and/or estimates can be uncertain. The soil parameters (macropore radius and surface crust saturated hydraulic conductivity) were calibrated using the entire data-set and both field conditions (till and no-till) because metribuzin transport was sensitive to these input parameters (see sensitivity analysis), and our goal was to minimize the affect of incorrect hydrology simulation on metribuzin transport. The soil parameter calibration consisted of adjusting soil parameters until simulated hydrology was reasonable compared to observed hydrology (eg runoff, soil water content). Using the entire data-set for soil parameter and hydrology calibration was acceptable because our objectives did not include testing the hydrology component.

The second application on the tilled plot was used for chemical parameter calibration because metribuzin was detected most frequently in soil samples collected in this trial. The chemical parameters were transferred to three other applications: an additional application on the tilled plot and two applications on the no-till plot. These three applications are called non-calibrated applications and were used to evaluate RZWQM simulated persistence. Model evaluation included comparing predicted persistence from the three pesticide models (equilibrium-only, equilibrium-kinetic, equilibrium-bound) to observed persistence. Persistence comparisons included observed and simulated: (1) metribuzin concentrations in soil for the three non-calibrated applications, and (2) computed metribuzin half-life from both plots and both applications.

Data from calibrated and uncalibrated applications were used to compare observed and simulated metribuzin transport. This was acceptable because the chemical parameters were calibrated using persistence data and an objective optimization technique; transport data were not used for pesticide parameter calibration. Comparisons included simulated and observed: total metribuzin transport over the experiment and daily metribuzin concentrations in percolate and runoff. RZWQM-simulated metribuzin transport in percolate was also compared to PRZM-3 and GLEAMS simulations.[1] Malone *et al*[1] compared PRZM-3- and GLEAMS-simulated metribuzin transport to the same observed data described in this paper.

A limited, single-variable sensitivity analysis was performed on the tilled plot to investigate the effect of selected input parameters on simulated metribuzin fate using the kinetic approach only. Soil input parameters analyzed were K_c, K_s, τ_{bk}, $N2$, rp, $nmacro^*$, sorptivity reduction factor. Chemical input parameters analyzed were f, $RK2$, H_e effective soil radius, $B1$, T_{ref}, θ_{ref}, $B2$, E_a. The effective soil radius was included with the chemical analysis because this parameter only affects chemical transport in percolate (water is not affected). The analysis included increasing or decreasing a single RZWQM input parameter from the original value. Changing K_s, τ_{bk}, $N2$, rp, $nmacro^*$, involved changing $C2$ or $macro^*$ proportionally, as required by Eqns (9) and (10). The change in simulated percolate volume, runoff volume, and metribuzin transport (percolate and runoff) are shown for soil parameter changes. The change in metribuzin transport (percolate and runoff) and metribuzin in soil (day 160 and day 206) are shown for chemical parameter changes. Changes are reported as the percentage difference from the original value.

4 MODEL CALIBRATION

4.1 Hydrology calibration

Hydrological calibration was performed using the complete simulation period (day 128–206) from both field conditions (till and no-till). The macropore radius (rp) and surface crust hydraulic conductivity (K_c) were adjusted until the following simulations were reasonable compared to field observations (Table 3 and Figs 3, 4 and 5): soil water content (surface, 15 cm and 75 cm profile), total percolate volume for simulation period, total runoff volume from simulation period, percolate volume on a rainfall event basis, and runoff volume on a rainfall event basis. The same macropore radius was input for all depths.[22] The higher-than-predicted observed percolate amounts for till and no-till (Fig 3) may be because of a high water table or lateral flow entering pan lysimeters and skewing observations. Calibrating macropore radius and crust saturated hydraulic conductivity differently can produce more accurate simulations of one hydrology component (total runoff, daily percolate, 15 cm soil water, etc), but another component will suffer.

As expected, the calibrated macropore radius was less for tilled (0.03 cm) than no-till (0.06 cm) soil. No-till soil was tilled the previous year, therefore the calibrated macropore radius was less than if the plot were in long-term no-till. Shipitalo and Edwards[12] found the average macropore radius on a long-term no-till soil was approximately 0.15 cm.

The surface crust saturated hydraulic conductivity was also reasonable for both the no-till ($0.02\,\mathrm{cm\,h^{-1}}$) and tilled ($0.01\,\mathrm{cm\,h^{-1}}$) plot. McIntyre[25] found the crust conductivities of the top 5 mm of long-term cultivated soils to be about $0.02\,\mathrm{cm\,h^{-1}}$ when excluding replicates with imperfections in the crust (small perforations or cracks). McIntyre[25] excluded more than half of the replicates because the aim

Table 3. Observed and simulated hydrology, metribuzin degradation, and metribuzin transport

			RZWQM[b]			
	PRZM[a]	GLEAMS[a]	EO	EK	EB	Obs
Till						
Runoff (cm)	2.5	3.0	5.8	5.8	5.8	4.5
Total percolate (cm)	6.9	3.8	5.2	5.2	5.2	7.2
Macropore percolate (cm)	NA[c]	NA	2.0	2.0	2.0	NM[c]
Metribuzin in runoff ($\mathrm{g\,ha^{-1}}$)	14.5	31.6	34.0	18.7	16.9	10.2
Metribuzin in percolate ($\mathrm{g\,ha^{-1}}$)	0.0	0.0	1.6	1.1	1.1	1.8
Metribuzin half-life for 1st application (H_e days)	NA	NA	9.3	5.8	5.5	4.2
Metribuzin half-life for 2nd application (H_e days)	NA	NA	6.6	7.0	6.9	6.7
No-till						
Total percolate (cm)	11.1	11.1	9.4	9.4	9.4	10.4
Macropore percolate (cm)	NA	NA	2.8	2.8	2.8	NM
Metribuzin in percolate ($\mathrm{g\,ha^{-1}}$)	0.1	0.5	7.5	6.4	6.3	9.0
Metribuzin half-life for 1st application (H_e days)	NA	NA	9.0	5.7	5.7	4.1
Metribuzin half-life for 2nd application (H_e days)	NA	NA	6.6	6.3	7.2	6.4

[a] Values from Malone *et al*.[1]

[b] EO is equilibrium-only; EK is equilibrium-kinetic; EB is equilibrium-bound pesticide sorption models.

[c] NA, NM indicate not applicable not measured.

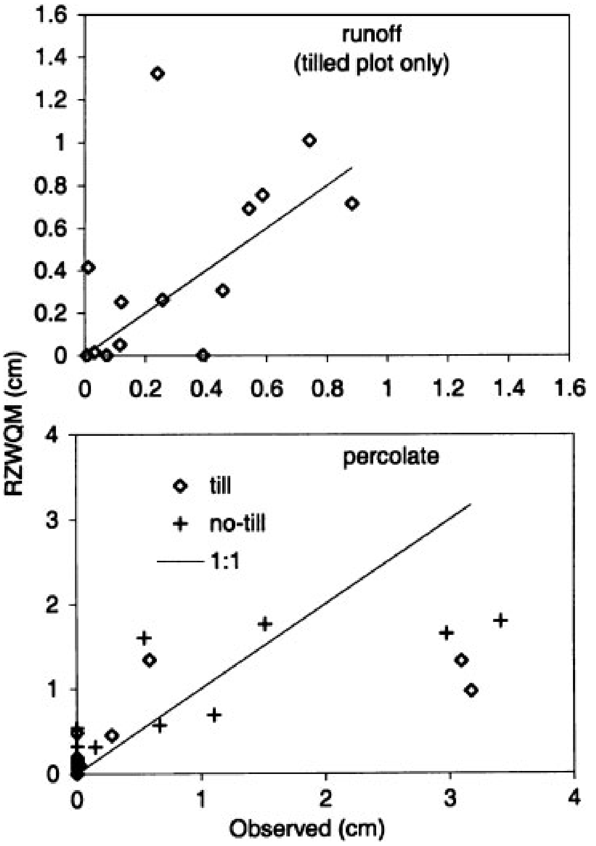

Figure 3. Simulated and observed runoff and percolate volume. Negligible runoff was observed on the no-till plot.

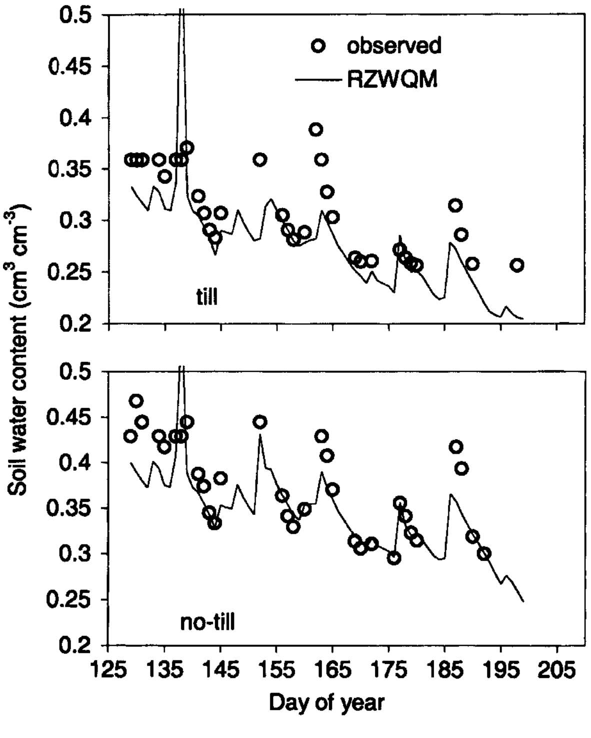

Figure 4. Daily volumetric soil water content at 10 cm.

was to determine the crust conductivity, not surface conductivity approximating field conditions. More recently Rawls *et al*[26] found the effective hydraulic

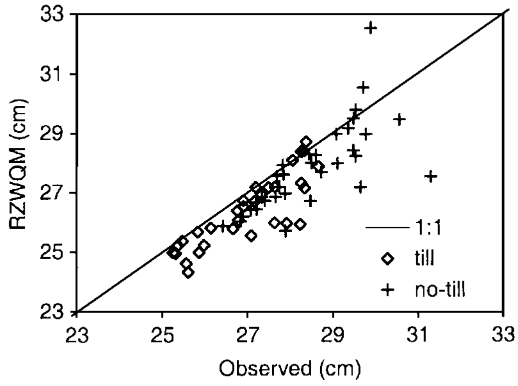

Figure 5. Simulated and observed soil water in 75 cm profile.

conductivity of the wetted depth of crusted silt loam soils ranged from 0.1 to $0.9\,\mathrm{cm\,h^{-1}}$ resulting in a 5-mm crust conductivity of about $0.05\,\mathrm{cm\,h^{-1}}$. However, $0.05\,\mathrm{cm\,h^{-1}}$ for crust hydraulic conductivity using the Rawls *et al* data may be high for input into RZWQM. Rawls *et al* determined effective hydraulic conductivity on initially uncrusted soil, therefore, more runoff may have occurred (less infiltration) if initially crusted soils were used. Furthermore, Rawls *et al* were investigating plot hydraulic conductivity and it is possible that imperfections in the crust (small cracks or perforations) were present unlike the McIntyre[25] data (WJ Rawls, pers comm). In our case, the crust conductivity input for RZWQM should exclude any crust imperfections and should be for an initially crusted soil. Therefore, a value 0.01 to $0.02\,\mathrm{cm\,h^{-1}}$ is reasonable.

The soil water content trends were accurately simulated: as observed soil water increased, simulated soil water increased and greater soil water content was simulated in no-till compared to till (Fig 5). Simulated percolate was less than observed (Table 3), however, partly because simulated evaporation was more than observed, as evidenced by lower simulated soil water content than observed (Fig 5). More accurate evaporation could have been simulated by adjusting the soil bubbling pressure and the soil unsaturated hydraulic conductivity constants (τ_{bk} *C2, and N2*) at the four depths, and adjusting the albedo for dry soil, wet soil and mulch. We decided not to do this, partly because our focus is mainly pesticide transport and persistence, not hydrology, and we wanted to limit the number of calibrated parameters. In addition, the saturated hydraulic conductivity of the soil matrix could have been less than measured because conductivity measured using soil cores in the laboratory includes preferential flow paths. RZWQM requires input of soil matrix conductivity, without preferential flow paths, but saturated hydraulic conductivity was measured and therefore we decided not to adjust it. Moreover, as discussed above, lateral flow or a high water table may have contributed to higher observed percolate than actual. It is promising that RZWQM simulates the hydrology differences between till and no-till (Fig 5,

Table 3) with minimal calibration because simulation of management practice effects is a major emphasis of RZWQM.[2]

The results of the runoff and percolate scatter plots (Fig 3) are not more accurate, partly because effective macroporosity changes with rainfall intensity and antecedent water content,[22] and because sorptivity reduction factor may change with antecedent water content.[23] Simulated percolate is somewhat sensitive to these two parameters, especially percolate movement through macropores (see Section 5.3 below). At this time RZWQM does not simulate changes in effective macroporosity and sorptivity reduction factor; an average value is assumed.

4.2 Chemical calibration

After the macropore radius and surface crust conductivity were calibrated, the chemical parameters were adjusted to obtain the most accurate degradation on the second metribuzin application for the tilled plot. This data set was used for calibration because it contained the most detectable metribuzin soil samples. Optimization of the chemical parameters were achieved by adjusting $RK2$, f, and H_e (equilibrium-kinetic); K_b, H_b, and H_e (equilibrium-bound); and H_e (equilibrium-only) to minimize the root mean square error (RMSE) between the natural log of predicted and observed soil metribuzin concentration in the tilled plot after the second application. The equilibrium soil half-life (H_e) was calibrated because degradation can vary considerably under different conditions (soils, management, climate, time period of study).

The root mean square error (RMSE) was computed by

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}(P_i - O_i)^2}{n}}$$

where P_i are predicted values, O_i are the observed values, i is the event (runoff, percolation, or soil sample event 1, 2, etc), and n is the number of observations (events). The equilibrium-kinetic and equilibrium-bound pesticide models, where a portion of the metribuzin is in kinetic or bound pools, resulted in more accurate simulations than the equilibrium-only model on the chemical calibration data set (RMSE is $0.01\,\mathrm{kg\,ha^{-1}}$ for equilibrium-bound and equilibrium-kinetic, and $0.06\,\mathrm{kg\,ha^{-1}}$ for equilibrium-only; Fig 6).

The calibrated equilibrium half-life (H_e) was 4.6 days for the equilibrium-only approach (Table 1), but the measured value was 6.7 days (Table 3, till). This is probably related to the fact that the simulated soil water content and temperature were under-predicted after day 157 on the tilled plot (Figs 4 and 7). At this time RZWQM assumes the surface boundary soil temperature (top 1 cm) is equal to the air temperature, whereas surface soil temperature is often greater than air temperature. A more complex RZWQM simulation approach for surface soil temperature is in development. Using the average simulated soil moisture and soil temperature ($0.252\,\mathrm{cm^3\,cm^{-3}}$ and 22.9 °C) as reference value RZWQM input rather than the measured values ($0.283\,\mathrm{cm^3\,cm^{-3}}$ and 25.6 °C, Table 1) results in a calibrated equilibrium half-life of nearly 6.7 days.

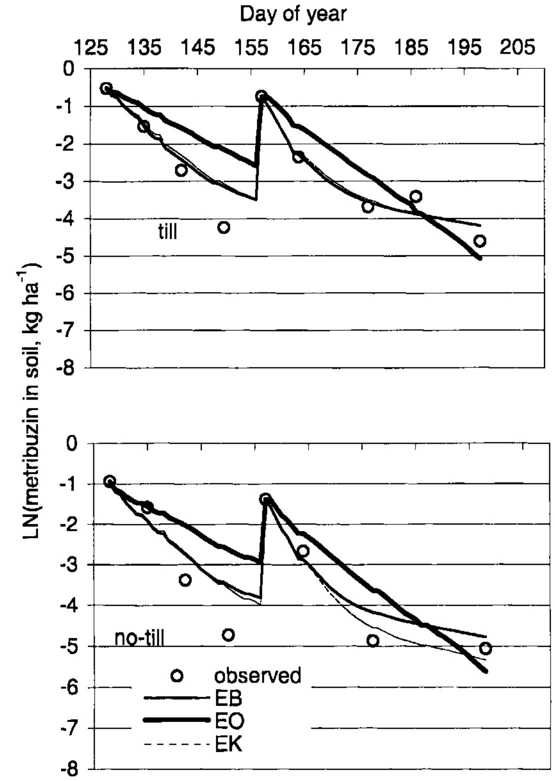

Figure 6. Daily metribuzin in soil profile. Three different modeling approaches are shown. The y-axis is the natural log of soil concentration.

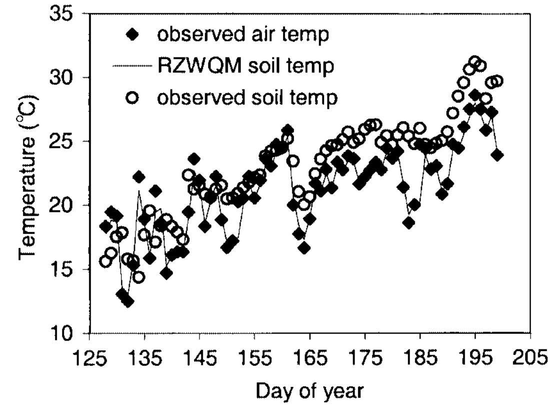

Figure 7. Daily soil temperature at 10 cm (tilled plot), and observed air temperature.

The calibrated equilibrium half-life (H_e) for the equilibrium-bound and equilibrium-kinetic approaches were about half the value of the equilibrium-only approach (Table 1). This is because the equilibrium-bound model simulates less degradation on bound sites and no degradation is simulated on kinetic sites. Figure 6 also illustrates that shortly after application when the vast majority of metribuzin is sorbed to equilibrium sites using the equilibrium-kinetic and equilibrium-bound models, simulated degradation is much faster than the equilibrium-only pesticide model.

5 RESULTS AND DISCUSSION

5.1 Metribuzin persistence

Transferring the calibrated chemical parameters to the three non-calibrated metribuzin applications resulted in good simulated soil metribuzin concentrations for the bound and kinetic approaches (Figs 6 and 8). The equilibrium-only (EO) approach resulted in over-predicted persistence for all sample dates except day 198 (no-till) and had a higher RMSE on the non-calibrated data than the equilibrium-bound (EB) and equilibrium-kinetic (EK) approaches (RMSE for equilibrium-kinetic, equilibrium-bound, and equilibrium-only are 0.03, 0.03, and 0.08 kg ha^{-1}, respectively). Moreover, the equilibrium-bound and equilibrium-kinetic approaches accurately simulated the trend of lower half-life for the first application compared to the second application on both the no-till and tilled plots, but the equilibrium-only approach failed to simulate this trend (Table 3). The EB and EK approaches simulate metribuzin degradation better than the EO approach because they simulate a slowing degradation rate with time.

5.2 Metribuzin transport

Total metribuzin transport (sum of first and second application) in runoff and percolate was reasonably simulated by RZWQM (Table 3). For both the no-till and tilled field conditions, metribuzin transport in percolate was simulated within a factor of two for the three modeling approaches. Metribuzin transport in runoff was simulated within a factor of two for the equilibrium-bound and equilibrium-kinetic modeling approaches and within a factor of 3.3 for the equilibrium-only modeling approach. These results are near or within a factor of two times that observed, which is often considered good model performance.[27] Part of the inaccuracy is due to simulated water inaccuracy: percolate amount was under-predicted, runoff amount was over-predicted predicted as discussed in Section 4. In contrast, PRZM and GLEAMS (no macropore flow component) under-predicted metribuzin transport in percolate by greater than an order of magnitude for both tilled and no-till field conditions (Table 3). The three RZWQM pesticide models (equilibrium-only, equilibrium-kinetic and equilibrium-bound) also under-predicted metribuzin transport in percolate by more than an order of magnitude when macropores were not simulated, while the soil water content, percolate and runoff were reasonably simulated (data not shown).

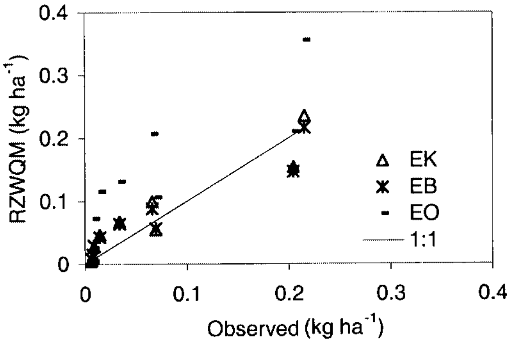

Figure 8. Simulated and observed metribuzin in soil profile using three modeling approaches. Note that only non-calibrated data is included. That is days 128 and 157 (till and no-till); and days 164, 177, 186, 198 (till) are not shown.

It is encouraging that the effective soil radius surrounding macropores was input as determined by Malone *et al*[22] and reasonable metribuzin transport in percolate was simulated. Malone *et al* determined the effective soil radius for input into RZWQM using long-term no-till soil and indicated that it may change with different conditions (soils, management, etc). The results from Malone *et al* and this paper indicate that the effective soil radius may remain constant (0.6 cm) for different management conditions (tilled, short-term no-till, long-term no-till) but more investigation is needed.

The equilibrium-kinetic and equilibrium-only pesticide modeling approaches resulted in simulated percolate and runoff metribuzin concentration within a factor of ten of observed for each event except the day 160 simulated percolate on the no-till (Fig 9). Simulating a dynamic sorptivity reduction factor and/or a dynamic effective macroporosity rather than using an average value would improve simulated daily percolate concentrations because these parameters affect metribuzin concentration in addition to affecting percolate volume, as discussed in Section 4.1. Day 160 (no-till) may be a measurement outlier because this was the first event after the second application and a higher concentration than measured was expected. The equilibrium-bound approach resulted in under-predicted percolate and runoff concentrations >30 days after metribuzin application (days 186, 204 and 206). RZWQM simulates bound metribuzin to be immobile in soil, yet the field results suggest that persistent metribuzin residue is more mobile than the equilibrium-bound method predicts (Fig 9). It should be noted, however, that rainfall events shortly after application are generally the most critical, and the equilibrium-bound model reasonably simulated metribuzin transport over the study period (Table 3). The equilibrium-only approach tended to over-predict metribuzin concentration in percolate and runoff compared to the equilibrium-bound approach, equilibrium-kinetic approach, and observed (Fig 9 and Table 3) partly because the equilibrium-only approach over-predicted metribuzin persistence (Fig 8).

A clearly superior pesticide transport modeling approach (equilibrium-bound, equilibrium-kinetic, equilibrium-only) cannot be determined from this data set when hydrology and macropore flow are accurately simulated. Comparing simulated metribuzin transport

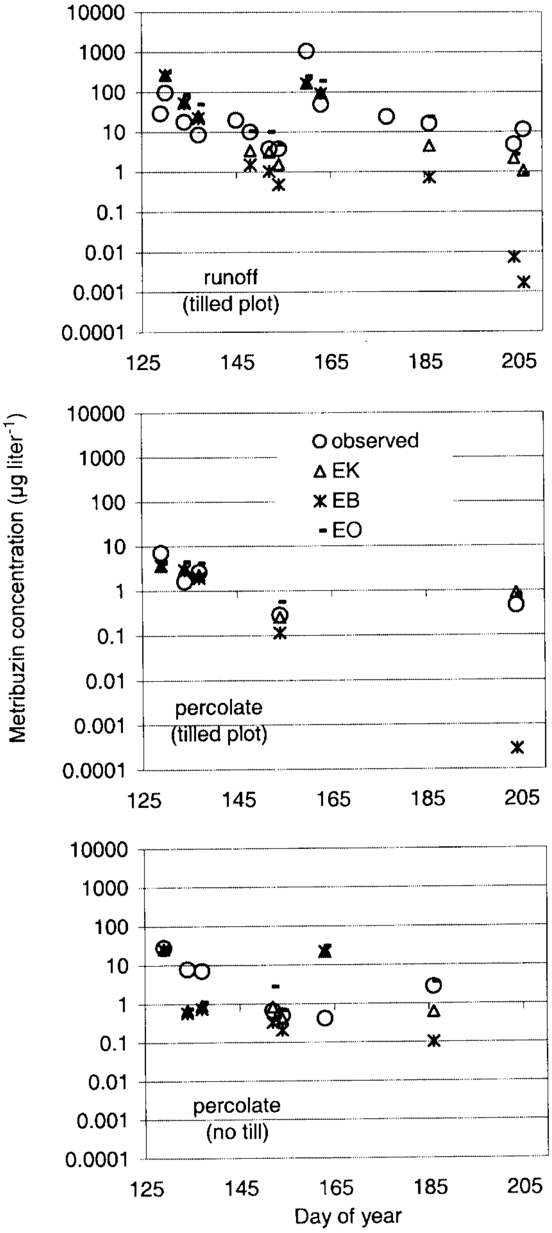

Figure 9. Daily metribuzin concentration in runoff and percolate.

in runoff and percolate to observed data for each event and both field conditions using the RMSE indicated little difference between pesticide modeling approaches (RMSE not shown). It should be noted that the equilibrium-only was slightly more accurate than the equilibrium-bound and equilibrium-kinetic approaches for runoff, but a little less accurate for percolate. The equilibrium-only pesticide modeling approach over-predicted transport compared to the other approaches (Table 3) but when different data were used for calibrating the half-life (eg the first metribuzin application on the tilled plot rather than the second application), the equilibrium-only approach predicted runoff and percolate transport within a factor of two (data not shown). The equilibrium-kinetic approach appeared to provide the best overall simulations for the complete data set (persistence, total transport, daily runoff and percolate concentrations) but the kinetic parameters (*f* and *RK2*) need to be calibrated, which limits its general use. The pesticide half-life (H_e), however, may also need to be calibrated because half-life is a sensitive parameter and RZWQM recommends 40 days for the metribuzin half-life while the measured half-life was less than 5 days. Although the equilibrium-bound approach did not accurately simulate transport long after application (>30 days), evidence for pesticide binding is documented[28] and this component needs explored further. Until the binding component of RZWQM is explored further and better guidance provided, it may be wise to avoid the equilibrium-bound option unless observed pesticide transport data are available for model comparison.

5.3 Model sensitivity

The model generally responded as expected to input parameter changes (Tables 4 and 5) and only a few observations will be discussed. Adjusting the soil parameters had a major influence on metribuzin transport in percolate (Table 4). For example, adjusting the following input parameters by 50% resulted in simulated metribuzin transport in percolate to change by over 100%: saturated hydraulic conductivity (K_s), soil crust conductivity (K_c), unsaturated hydraulic conductivity constant (*N2*), average macropore radius (*rp*), soil bubbling pressure (τ_{bk}), and effective number of percolate-producing macropore (*nmacro**). This is notable because the data of Rawls *et al*[26] shows soil crust conductivities on six silt loam soils had a coefficient of variation of 61% and Rawls *et al*[29] showed that the bubbling pressure of a variety of silt loam soils had a coefficient of variation of over 200%. Increasing K_s by 50% resulted in increased metribuzin transport in runoff because this resulted in runoff occurring on day 129 (the first rainfall event after application) when no runoff occurred on this day with the original K_s.

Adjusting the chemical parameters within the range listed generally affected metribuzin transport as expected (Table 5). Notably, the kinetic parameters (*f* and *RK2*) had little influence on transport because they had little influence on persistence shortly after application (day 160) when most transport occurred. The equilibrium half-life (H_e) did, however, affect transport by affecting persistence shortly after application.

6 SUMMARY AND CONCLUSIONS

Metribuzin fate (persistence, runoff, and percolate) was simulated for two field conditions (tilled and no-till) and two applications. A comprehensive data set was used to test RZWQM that included metribuzin in runoff, metribuzin in percolate, and metribuzin in soil. The data-set included several measured soil and chemical parameters (eg water retention curves, saturated hydraulic conductivity, metribuzin partition coefficient) so that RZWQM could be parameterized

Table 4. Sensitivity analysis of soil parameters on tilled plot

Parameter		Percolate and runoff volume			Metribuzin transport	
Description	Difference (%)[a]	Total percolate (%)[a],[b]	Macropore flow (%)[a],[b]	Runoff (%)[a]	Percolate (%)[a]	Runoff (%)[a]
Surface crust saturated hydraulic conductivity (K_c cm h^{-1})	50	1	−29	−19	−87	−7
	−50	−2	31	25	158	26
Saturated hydraulic conductivity (K_s cm h^{-1})	50	−4	−19	−6	−69	32
	−50	8	34	7	321	−9
Bubbling suction for hydraulic conductivity (τ_{bk} cm)	50	11	−51	−50	−61	−23
	−50	−2	31	40	321	−13
Unsaturated hydraulic conductivity constant (*N2*)	10	3	23	5	265	−11
	−5	−1	−14	−6	−59	33
Macropore radius (*rp*, cm)	46	79	184	−80	47	−81
	−40	−40	−95	51	−100	107
Effective number of percolate producing macropores (*nmacro**)	40	11	21	−13	−42	−13
	−65	−26	−55	34	203	55
Sorptivity reduction factor	50	−3	−14	0	−28	0
	−50	3	14	0	32	0

[a] The percentage difference from the original value (new-original) 100/original. The original values for simulated total percolate, macropore percolate, runoff, metribuzin transport in percolate, and metribuzin transport in runoff were 5.2 cm, 2.0 cm, 5.8 cm, 1.1 g ha^{-1}, 18.7 g ha^{-1}, respectively. The original parameter values were from Tables 1 and 2.

[b] Total percolate is soil matrix percolate plus macropore flow.

with minimal calibration. Several soil and chemical parameters were determined from the literature. Soil parameter calibration consisted of adjusting soil crust conductivity and macropore radius to optimize simulated percolate, runoff and soil water content compared to observed data. This calibration procedure resulted in reasonable hydrology simulation (runoff, percolation, soil water) and the observed trends between no-till and till soil were simulated.

Three approaches were used to simulate metribuzin fate in the field (equilibrium-bound, EB; equilibrium-kinetic, EK; and equilibrium-only, EO). Each approach required calibration of some chemical parameters: desorption rate constant, fraction of sorption sites that are kinetic, and equilibrium metribuzin half-life (EK); bound pesticide formation coefficient, bound pesticide half-life, and equilibrium metribuzin half-life (EB); and equilibrium metribuzin half-life (EO). Chemical parameters were adjusted to optimize simulated metribuzin persistence compared to field observations from the second metribuzin application on the tilled plot. These calibrated chemical parameters were transferred to three other metribuzin applications (another metribuzin application on the tilled plot and two applications on the no-till plot) to test simulated persistence. Simulated metribuzin transport (percolate and runoff) was then compared with observed data.

Little difference was observed between the EB and EK approaches (two-compartment approaches) to simulate metribuzin persistence, but the EO approach (single-compartment approach) over-predicted persistence. RZWQM predicted metribuzin concentrations in runoff and percolate fairly accurately using all three pesticide modeling approaches (EO, EK, and EB). The EB under-predicted metribuzin concentrations in percolate and runoff several weeks after application (>30 days), but this had little affect on total transport because the first few events after application contributed the most to total transport. When macropores were not simulated, however, all of RZWQM pesticide models (EO, EK, and EB) under-predicted metribuzin transport in percolate over the simulation period by more than an order of magnitude. Macroporosity is a complex process, but RZWQM only requires four input parameters: number of percolate producing macropores, average radius of percolate producing macropores, effective pesticide sorption radius surrounding macropore walls, and sorptivity reduction factor for macropore wall compaction. Sorptivity reduction factor, effective sorption radius and the number of percolate-producing macropores were estimated from the literature and macropore radius was calibrated.

It may be concluded that, when macropore flow and hydrology are accurately simulated, RZWQM can adequately simulate metribuzin transport in the field using a relatively simple pesticide model (equilibrium-only). This conclusion is especially true given the possible input range of other parameters and their effect on simulated transport. The more complex models more accurately simulated persistence but this had little affect on transport. For example, individually decreasing surface crust hydraulic conductivity and saturated hydraulic conductivity by 50% both increased metribuzin transport in percolate more than 100%,

Table 5. Sensitivity analysis of chemical parameters on tilled plot

Parameter		Metribuzin transport		Metribuzin in soil	
Description	Difference (%)[a]	Percolate (%)[a]	Runoff (%)[a]	Day 160 (%)[a]	Day 206 (%)[a]
Fraction of sorption sites that are kinetic (*f*)	50	0	1	7	50
	−50	0	−1	−7	−50
Desorption rate constant from kinetic sorption sites (*RK*2, day^{-1})	50	0	1	−1	−42
	−50	−1	−2	2	78
Equilibrium half life (H_e, day)	50	22	48	43	17
	−50	−38	−62	−56	−11
Effective soil radius (cm)	50	−86	0	0	0
	−50	290	0	0	0
Non-uniform mixing factor (*B1*, cm^{-1})	50	−63	−62	1	1
	−50	149	135	−4	−1
Reference soil temperature (T_{ref} °C)	10	10	21	19	6
	−10	−11	−19	−17	−4
Reference soil water (θ_{ref} $\text{cm}^3\ \text{cm}^{-3}$)	10	4	8	8	2
	−10	−5	−9	−8	−2
Pesticide degradation adjustment constant for water content (*B2*)	200	−9	−1	−1	3
	−99	4	1	1	−1
Activation energy (E_a, kJ mol^{-1})	50	16	13	10	3
	−50	−18	−12	−8	−3

[a] The percentage difference from the original value (new-original) 100/original. The original values for simulated metribuzin transport in percolate, metribuzin transport in runoff, metribuzin in soil on day 160, and metribuzin in soil on day 206 were 1.1 g ha^{-1}, 18.7 g ha^{-1}, 196 g ha^{-1}, 13 g ha^{-1}, respectively.

but changing the kinetic parameters by 50% changed transport over the simulation period by less than 2%.

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