MACROPORE COMPONENT ASSESSMENT OF THE ROOT ZONE WATER QUALITY MODEL (RZWQM) USING NO–TILL SOIL BLOCKS

R. W. Malone, M. J. Shipitalo, L. Ma, L. R. Ahuja, K. W. Rojas

ABSTRACT. *In structured soils, macropores can contribute to rapid movement of water and solutes through the profile. To provide insight into these processes, model assessments should be performed under a variety of conditions. We evaluated the macropore component of the RZWQM using undisturbed soil blocks with natural macropores. To accomplish this, atrazine, alachlor, and bromide were surface–applied to nine 30 × 30 × 30 cm blocks of undisturbed, no–till silt loam soil at three water contents (dry, intermediate, and wet). One hour later, we subjected the blocks to a 0.5–h, 30–mm simulated rain. Percolate was collected and analyzed from 64 uniform size cells at the base of the blocks. After percolation ceased, the soil was sectioned and analyzed to determine chemical distribution. We tested the chemical sub–component of macropore flow using these blocks following hydrologic calibration, while a separate set of blocks was used to calibrate selected chemical parameters. Parameterization of the macropore component included measuring the effective macroporosity (50% of percolate producing macropores) and calibrating the effective soil radius (0.6 cm). The effective soil radius represents the soil surrounding the macropores that interacts with macropore flow. This parameterization strategy resulted in accurate simulations of the composite chemical concentrations in percolate (i.e., all simulated chemical concentrations were within a factor of 2.0 of the average observed value). However, observed herbicide concentration in percolate decreased with cumulative percolate volume, while simulated concentrations increased. Model modifications, such as incorporating a dynamic effective macroporosity (effective macroporosity increase with increasing rainfall) and chemical kinetics in macropores, may improve simulations.*

Keywords. *Transport modeling, Pesticides, Leaching.*

Numerous models have been developed to study pesticide transport (e.g., LEACHMP, GLEAMS, PRZM–2, and RZWQM), but only a few simulate macropore flow. Macropores can allow water to bypass much of the soil matrix, and neglecting their contribution may result in under–predicted chemical loss in percolate (Kumar et al., 1998, Malone et al., 1999b; Smith et al., 1991).

The RZWQM simulates macropore flow. Furthermore, it is an integrated physical, biological, and chemical process model that simulates plant growth and movement of water, nutrients, and pesticides over and through the root zone of agricultural management systems (Ahuja et al., 1999).

The RZWQM has been evaluated under numerous conditions (e.g., Ahuja et al., 1999; Ma et al., 1998; Ma et al., 2000a; Malone et al., 1999a). However, the macropore component of the RZWQM has only been evaluated under very limited conditions. For instance, Ahuja et al. (1995) evaluated the RZWQM using soil columns with artificial macropores and a non–reactive tracer (bromide). Stehouwer et al. (1994) observed that the behavior of natural macropores may differ from that of artificial macropores. Ahuja et al. (1993) studied pesticide transport through macropores using the RZWQM, but they did not evaluate the model against field or lab data. Although Kumar et al. (1998) evaluated the model using field data, field evaluations generally lack the detail and control necessary for a rigorous evaluation of complex processes in a model such as the RZWQM. In addition, field studies concerning the macropore component of the RZWQM have used tension infiltrometers to determine macroporosity (Jaynes and Miller, 1999; Kumar et al., 1998), which can be a difficult procedure and has limitations (Close et al., 1998; Villholth et al., 1998).

Therefore, our objective was to evaluate the macropore component of the RZWQM (RZWQM98, version 1.0.2000.1129) using data collected from undisturbed, no–till soil blocks with natural macropores subjected to intense rainfall shortly after chemical application. The evaluation included model refinement and parameterization guidance (e.g., guidance concerning macroporosity and

---

Article was submitted for review in August 2000; approved for publication by the Soil & Water Division of ASAE in March 2001.

Contribution from the USDA Agricultural Research Service. The mention of trade or commercial names is made for information only and does not imply an endorsement, recommendation, or exclusion by the USDA Agricultural Research Service.

The authors are **Robert W. Malone,** ***ASAE Member Engineer,*** Research Agricultural Engineer, USDA Agricultural Research Service, National Soil Tilth Laboratory, Ames, Iowa; **Martin J. Shipitalo**, Research Soil Scientist, USDA Agricultural Research Service, North Appalachian Experimental Watershed (NAEW), Coshocton, Ohio; **Liwang Ma**, Research Soil Scientist, **Lajpat R. Ahuja**, Research Leader and Research Soil Scientist, and **Ken W. Rojas**, Computer Specialist, USDA Agricultural Research Service, Great Plains Systems Research (GPSR), Fort Collins, Colorado. **Corresponding author:** Robert W. Malone, USDA Agricultural Research Service, National Soil Tilth Laboratory, 2150 Pammel Drive, Ames, Iowa 50011; phone: 515–294–8327; fax: 515–294–8125; e–mail: malone@nstl.gov.

effective soil radius input, both described below), testing the chemical sub–component of macropore flow, determination of possible model improvements, and a limited sensitivity analysis.

RZWQM MACROPORE COMPONENT

Following is a brief description of the macropore component of the RZWQM. More complete descriptions are presented elsewhere (Ahuja et al., 1999; Ahuja et al., 1993; Ahuja et al., 1995; Kumar et al., 1998).

The RZWQM simulates water and chemical movement through macropores during a rainfall event as follows:

- Rainfall, irrigation, and chemicals are received by the soil surface, plant foliage, and mulch.
- Rainfall (or irrigation) exceeding the infiltration rate becomes overland flow and enters macropores.
- Overland flow exceeding the maximum macropore flow capacity and infiltration rate becomes runoff.
- A portion of the chemicals in surface soil (0–2 cm), plant foliage, and mulch 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.

WATER TRANSPORT

The RZWQM simulates vertical infiltration in soil and radial infiltration in macropores using an adaptation of the Green–Ampt equation. When the rainfall rate exceeds the infiltration rate, as determined by the vertical Green–Ampt equation, overland flow begins. Overland flow is routed into macropores to the limit of flow rate capacity 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 laterally infiltrate into the soil if saturation has not occurred, according to the lateral Green–Ampt equation.

The water entering the macropores is evenly distributed among the macropores, and the number of macropores per unit area (nmacro) is computed as a function of macroporosity (volume macropores per volume soil) and average macropore radius (rp):

$$\text{nmacro} = \frac{\text{macroporosity}}{\pi \times \text{rp}^2} \tag{1}$$

Macroporosity is a sensitive input parameter (see the Sensitivity Analysis section), and determining it can be difficult because research suggests that only a fraction of total macroporosity transmits water (Shipitalo and Edwards, 1996; Villholth et al., 1998; Trojan and Linden, 1992). In addition, research suggests that most percolate is from a relatively small percentage of percolate–producing macropores (Quisenberry et al., 1994). We call the macroporosity that is most effective in transmitting water the "effective macroporosity" and compute it as a function of the number of effective macropores per unit area (nmacro*). The method for determining nmacro* is discussed in the Model Parameterization section. This parameterization strategy is offered as an alternative to using tension infiltrometer data to determine macroporosity, as described by Jaynes and Miller (1999) and Kumar et al. (1998). Selection of a parameterization strategy will depend partly upon the information available.

The radial infiltration rate in macropores (Vr) may be impeded by compaction of macropore walls or by an organic coating surrounding macropore walls. To account for this, Ahuja et al. (1995) multiplied Vr by a lateral sorptivity reduction factor:

$$\text{Vr}^* = \text{Vr} \times \text{lateral sorptivity reduction factor} \tag{2}$$

CHEMICAL TRANSPORT

Chemicals are transferred from soil to overland flow by rainfall impact mixing with the top 2 cm of soil, and the contribution decreases exponentially with depth. The average degree of mixing between rainfall and soil solution for each depth increment (M_{ave}) is simulated by:

$$M_{ave} = e^{-Bz} \tag{3}$$

where B is the non–uniform mixing parameter, and z is the center of the depth increment (0.5 or 1.5 cm). The chemical is transferred from soil to rainwater in each time increment and may be determined using a mass balance approach (Heathman et al., 1986).

The RZWQM simulates chemical washoff from plant foliage and mulch as:

$$C_f = 0.01C_o(100 - F) + 0.01C_oF(e^{-Pti}) \tag{4}$$

where C_f is the chemical concentration remaining on mulch or foliage (μg/ha) after an incremental rainfall of intensity i (cm/hr) and time t (hr), C_o is the initial concentration on mulch and foliage at the beginning of each time increment, and P and F are chemical washoff parameters.

The water and chemicals moving through the macropores mix with a portion of the soil surrounding the macropore walls (i.e., the effective soil radius) and react with the soil according to chemical partitioning. The RZWQM assumes that the relationship between chemical adsorbed to soil (C_{ad}, μg/g) and chemical in solution (C_{sol}, μg/mL) is linear and instantaneous, and that it is a function of the partition coefficient ($C_{ad} = K_d \times C_{sol}$). Furthermore, K_d is related to soil carbon:

$$(K_{oc} = K_d/oc) \tag{5}$$

where oc is the fraction of organic carbon in soil (kg/kg). Determination of K_d is described in the Materials and Methods section.

In the course of this assessment, we found that it was necessary to adjust the effective soil radius to accurately simulate herbicide transport through natural macropores. Therefore, the macropore component of RZWQM98 (version 1.0.2000.1129) was modified to allow this. Previous RZWQM versions utilized an effective soil radius of either 0.1 mm or 0.5 mm (Ahuja et al., 1993; 1995).

MATERIAL AND METHODS

BLOCK EXPERIMENT

Data used to assess the RZWQM were from a study by Shipitalo and Edwards (1996), in which an intense simulated rainfall was applied shortly after chemical application. These conditions often result in high chemical concentrations in percolate (Malone et al., 1996; Kladivko et al., 1991; Shipitalo et al., 1990).

Twelve 30 × 30 × 30 cm blocks of undisturbed soil (Glenford silt loam: fine–silty, mixed, mesic Aquic Hapludalf) were collected from two fields that had been planted in long–term no–till corn (*Zea mays* L.). Nine blocks were collected in 1993 as part of the study by Shipitalo and Edwards (1996), and the data were used in the current study primarily to test the chemical sub–component of macropore flow (i.e., chemical transport through the macropores). These will be referred to as "test blocks" or TB. Three additional blocks were collected in 1999 from a nearby no–till field (watershed 188) because the field where the TB were obtained was no longer in no–till management. These three blocks will be referred to as "chemical calibration blocks" or CCB. They were used primarily to calibrate the chemical washoff parameters (F and P), the non–uniform mixing factor (B), and the effective soil radius. Data necessary to calibrate parameters F, P, and B were not collected from the TB.

The procedures performed on the TB were a little different from the CCB. These procedures will be briefly described below. More details are provided by Shipitalo and Edwards (1996).

Test Blocks (TB) — The size, number, and position of visible macropores at 30 cm were recorded. Three blocks were randomly assigned to each of three antecedent soil water contents: dry (approximately 17% cm^3/cm^3), intermediate (approximately 27%), and wet (approximately 33%). The intermediate and wet water contents, respectively, were attained by sprinkling 30 mm or 60 mm of distilled water on the blocks at a rate of 15 mm/h. The dry blocks did not receive additional water. After water was applied, the blocks were covered and allowed to equilibrate for 7 d. Atrazine, alachlor, and bromide were surface applied to the blocks at rates equivalent to 2.25, 4.5, and 428 kg a.i. per ha, respectively. Atrazine and alachlor were applied in 5 ml of water using a pipette; granular bromide was hand sprinkled. A 0.5–h, 30 mm rainfall was simulated approximately 1 h after chemical application. Percolate was collected from each cell of a 64–square grid at the bottom of the soil blocks (3.75 × 3.75 cm cells) in approximately 10 mL increments. Approximately 30 min after simulated rainfall ceased, the soil blocks were sliced into eight horizontal slabs (approximately 3.75 cm) that were subsequently weighed, mixed, and sampled for chemical and gravimetric moisture analysis. Soil samples were collected in 1999 from the TB field to determine soil carbon content and the alachlor and atrazine partition coefficients (K_d).

Chemical Calibration Blocks (CCB) — The size, number, and position of visible macropores at 30 cm were recorded. Atrazine and alachlor were applied to the three blocks at a rate equivalent to 2.25 kg a.i. per ha. A 0.5–h, 30 mm rainfall was simulated approximately 1 h after chemical application. During rainfall simulation, a pipette was used to collect water samples from surface depressions at approximately 10, 15, 20, 25, and 30 min after rainfall initiation, following a procedure similar to that of Edwards et al. (1997). These samples were analyzed for atrazine and alachlor and considered representative of overland flow (i.e., excess infiltration). Because little ponding was observed, a more descriptive term might be "water from saturated surface soil." One composite percolate sample was collected from each cell that produced percolate. For simplicity, samples were not collected in 10 ml increments as in the TB. Approximately 30 min after simulated rainfall ceased, the soil blocks were sliced into eight horizontal slabs (approximately 3.75 cm) that were subsequently weighed, mixed, and sampled for gravimetric moisture analysis.

MEASURED RZWQM INPUT

Measured input parameters are presented in table 1. The method used to determine effective macroporosity is discussed in the Model Parameterization section. The partition coefficient (K_d, fig. 1) and the carbon content of the 0–15 cm soil were determined to compute the K_{oc}. The 0–15 cm soil K_d was used because this layer likely contributes the most to chemical sorption, and the RZWQM does not allow K_{oc} to be input by soil layer. The K_d was determined by mixing 20 mL of alachlor– and atrazine–spiked solution and 10 grams of oven–dried soil for approximately 24 h in Teflon centrifuge tubes. Initial concentrations were 5, 3, 2, 1, 0.5 µg/mL for atrazine and 1.0, 0.6, 0.4, 0.2, 0.1 µg/mL for alachlor. To account for dissipation during mixing, alachlor and atrazine solution without soil was mixed in adjacent mixing tubes. The adsorption was fairly linear, and the K_d values were similar among the sites (fig. 1). The K_{oc} values were greater for the CCB than for the TB (table 1) primarily because of differences in organic carbon between the two sites.

RZWQM CALIBRATION, TESTING, AND SENSITIVITY

Model Calibration — Calibrated parameters are divided into soil parameters and chemical parameters. Calibrated soil parameters are lateral sorptivity reduction factor, saturated hydraulic conductivity, and field capacity of the surface layer (0–3 cm). Calibrated chemical parameters are the chemical washoff parameters (F and P), the non–uniform mixing parameter (B), and the effective soil radius. We calibrated soil parameters that directly affect simulated hydrology using the TB. Therefore, only the chemical sub–component of macropore flow was tested. Although the performance of the hydrology component was not actually tested, this component is discussed, and we gained insight into its performance. Only the CCB were used to calibrate chemical parameters. Details and discussion concerning model calibration is contained in the Model Parameterization section.

Testing the Chemical Sub–component of Macropore Flow — The calibrated chemical parameters (F, P, non–uniform mixing factor, and effective soil radius), determined using the CCB, were used to simulate chemical transport on the TB. Simulated and observed comparisons include: composite chemical concentrations, composite chemical transport (product of volume and concentration), the progression of herbicide concentration in percolate with time, and chemical distribution in soil. In addition, rainfall intensity and effective macroporosity were adjusted on the dry blocks (TB) to determine the effect on simulated

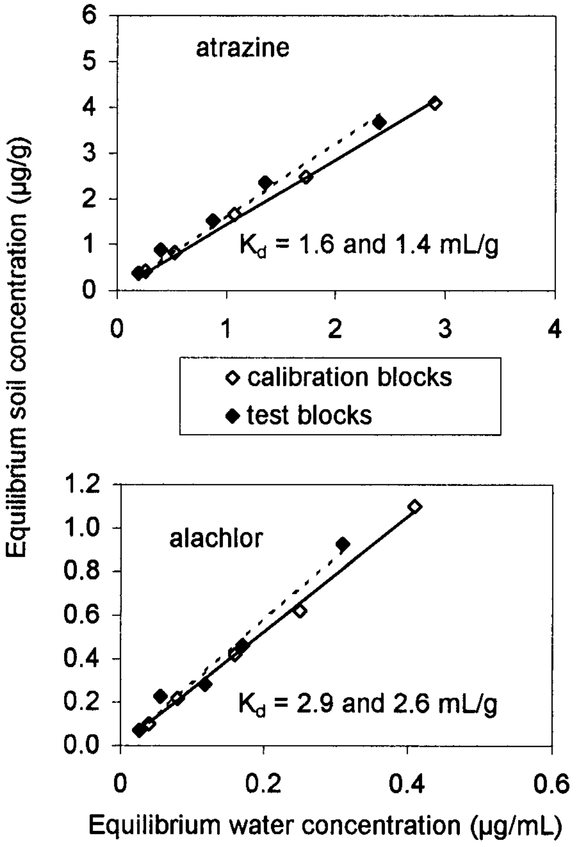

Figure 1. Determination of atrazine alachlor partition coefficients (K_d) for 0–15 cm CCB and TB soil (isotherm plots).

percolate volume and atrazine concentration, as compared to the study of Edwards et al. (1992).

Sensitivity Analysis — A limited, single–variable sensitivity analysis was performed on the TB (intermediate condition only) to investigate the effect of selected input parameters on macropore flow. Input parameters analyzed were: effective macroporosity, average macropore radius, lateral sorptivity reduction factor, K_{sat}, non–uniform mixing factor, chemical washoff parameters (F and P), K_{oc}, and effective soil radius. The analysis included increasing or decreasing a single RZWQM input parameter by 50% from the original value (table 1 or 2). Washoff parameter F was adjusted by 25% rather than 50% because the calibrated F was near its upper limit of 100 (table 2). The change in simulated percolate volume and chemical concentration in percolate are then reported as the percent difference from the original value.

Table 1. Measured RZWQM input parameters.

Parameter	Chem. Calib. Blocks (CCB)	Test Blocks (TB)
Effective macroporosity (cm/cm)	0.0011	0.00020 (dry) 0.00067 (inter.) 0.0013 (wet)
Bulk density (g/cm^3)		
0–3 cm	1.2	1.4
3–30 cm	1.6	1.6
Gravimetric soil carbon (%)		
0–3 cm	2.6	2.5
3–8 cm	1.2	2.1
8–15 cm	0.80	1.8
15–30 cm	0.55	1.1
Volumetric initial water (%)		
0–3 cm	30	19 (dry)
3–30 cm	28	17 (dry)
0–3 cm		29 (inter.)
3–30 cm		26 (inter.)
0–3 cm		35 (wet)
3–30 cm		32 (wet)
K_{oc} (ml/g)		
Alachlor	195	152
Atrazine	105	85

MODEL PARAMETERIZATION

EFFECTIVE MACROPOROSITY

The total number of percolate–producing cells in the TB increased with increasing initial water content (fig. 2). This suggests that the number of percolate–producing macropores increased with increasing initial soil water content. In addition, more than 90% of flow from both the TB and CCB was from less than 50% of the percolate–producing cells regardless of initial water content (fig. 3). Figure 3 was produced by ordering cells of a given set of blocks (dry, intermediate, etc.) from most productive to least productive. Based on this analysis, we assumed the number of effective macropores (nmacro*) to be 50% of percolate–producing macropores and that one average–size macropore (0.15 cm radius) from each active 3.75 × 3.75 cm cell was involved with transport from that cell.

HYDROLOGY CALIBRATION

The lateral sorptivity reduction factor, saturated hydraulic conductivity (K_{sat}), and field capacity of the surface layer were adjusted (table 2) until water content and cumulative percolate with time on the TB were reasonably simulated (figures 4 and 5). Data from the TB were used to calibrate the

Table 2. Calibrated RZWQM input parameters.

Parameter	Value
Soil Parameters[a]	
K_{sat} (cm/h)	
0–3 cm layer	1.0
3–8 cm	0.5
8–15 cm	0.3
15–30 cm	0.3
0.10 bar field capacity (cm/cm), 0–3 cm[b]	
CCB	0.5
TB	0.4
Lateral sorptivity reduction factor	0.2
Chemical Parameters[a]	
Non–uniform mixing parameter (1/cm)	6
Chemical washoff parameter F	80
Chemical washoff parameter P	
atrazine	0.15
alachlor	0.45
Effective soil radius (cm)	0.6

[a] The soil parameters were calibrated using data from both the CCB and TB, but the chemical parameters were calibrated using only the CCB.

[b] The 3–30 cm 0.10 bar field capacity for both the CCB and TB was input as the RZWQM default value for silt loam soil (0.364 cm/cm).

lateral sorptivity reduction factor because this data was not collected from the CCB. The calibrated lateral sorptivity reduction factor determined from the TB was transferred to the CCB. The surface soil field capacity and saturated hydraulic conductivity were then adjusted on the CCB (table 2) until soil water content by layer and total percolate were reasonable (fig 4, table 3).

The default RZWQM field capacity (0.364 cm/cm) was used for the 3–30 cm layer. The initially dry soil (TB) could have been more accurately simulated if field capacity were adjusted for all soil layers, but a criteria of the calibration was to calibrate the minimum number of soil parameters. In addition, there was little difference between the calibrated K_{sat} for the TB and the CCB. Therefore, we used the same value for both sets of blocks to minimize the number of calibrated parameters.

To reasonably simulate the cumulative percolate with time (fig. 5), the lateral sorptivity reduction factor was adjusted using data from the TB. This adjustment resulted in slight over–prediction of average total percolate volume, but the simulated values were within the range of observed values. The percolate rate may be simulated more accurately if the RZWQM is modified to account for increased effective macroporosity as the wetting front moves deeper into the soil during infiltration. As the time of rainfall increases and the wetting front deepens, the number of cells contributing to percolate increased (fig. 6). Modifying the RZWQM to account for a dynamic effective macroporosity during percolation would allow percolate to occur sooner because less macropores would be transporting the water. When simulated effective macroporosity was greater toward the end of the event, the simulated percolate rate would then be less because more macropores would be transporting the water. As effective macroporosity increases, simulated percolate volume decreases (see the Sensitivity Analysis section below). When more macropores are transmitting water, more soil is available for water to laterally sorb into soil matrix. But accurately simulating dynamic effective macroporosity would be difficult due to the limited understanding of how the wetting front (and/or other factors) affect effective macroporosity.

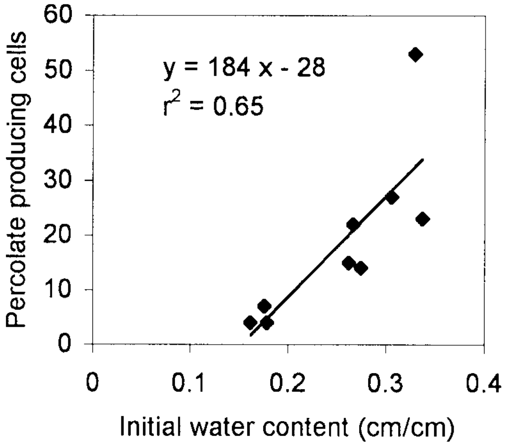

Figure 2. Number of cells out of 64 contributing to percolate versus initial water content after 30 mm of rainfall.

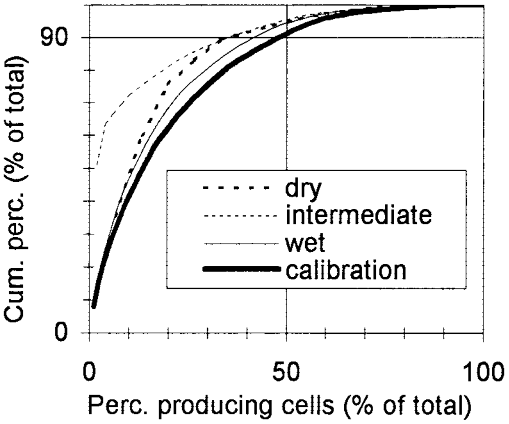

Figure 3. Relationship between cumulative cells producing percolate and cumulative percolate. The values are presented as a percent of total for each set of blocks (dry, intermediate, wet, and calibration).

CHEMICAL CALIBRATION

Chemical calibration was done after hydrology calibration using only data from the CCB. The washoff parameters (F and P) and the non–uniform mixing parameter (B) were adjusted (table 2) until simulated alachlor and atrazine concentrations in overland flow were reasonable (fig. 7). Finally, the effective soil radius was adjusted until simulated composite chemical concentration in percolate was reasonable (table 3, CCB).

The calibrated effective soil radius was 0.6 cm (table 2). It is unlikely that the water moving through macropores was mixing with a 0.6–cm radius of soil surrounding the macropores, but the calibrated effective soil radius takes into account greater partitioning between soil and pesticides in natural macropores compared to the soil matrix (Stehouwer et al., 1993 and 1994), and blockage and tortuosity of natural macropores. In addition, the water moving through the macropores may mix with a greater radius of soil at the soil surface than deeper in the profile, partially due to lateral movement of water into macropores rather than ponded water moving into macropores (Stehouwer et al., 1994). Under this scenario, the effective soil radius would be greater at the soil surface than deeper in the profile, but the RZWQM does not allow for different effective radii with depth.

RESULTS AND DISCUSSION

TESTING THE CHEMICAL SUB–COMPONENT OF MACROPORE FLOW

Transferring the chemical parameters determined using the CCB resulted in reasonable simulated chemical concentrations in percolate (table 3) on the TB. Simulated concentrations fell within the range of observed values in most instances and were within a factor of 2.0 of average observed concentrations. A constant value of effective soil radius produced reasonably accurate simulations on blocks of different water content, possibly indicating that effective soil radius is constant under different conditions (e.g., water contents, depth of wetting front) unlike effective macroporosity. Further research is needed to determine if an effective soil radius of 0.6 cm can be transferred to soil types and conditions other than those investigated.

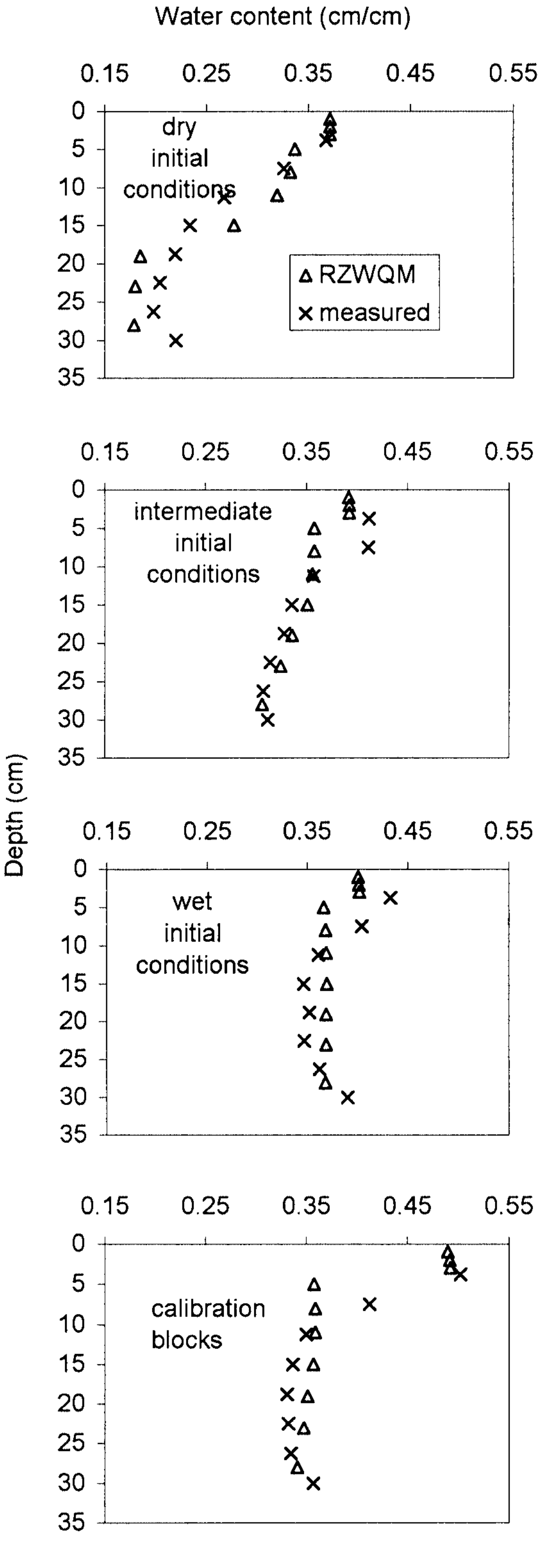

Figure 4. Average observed post–rain soil–water content and RZWQM–simulated water content versus depth for each block condition.

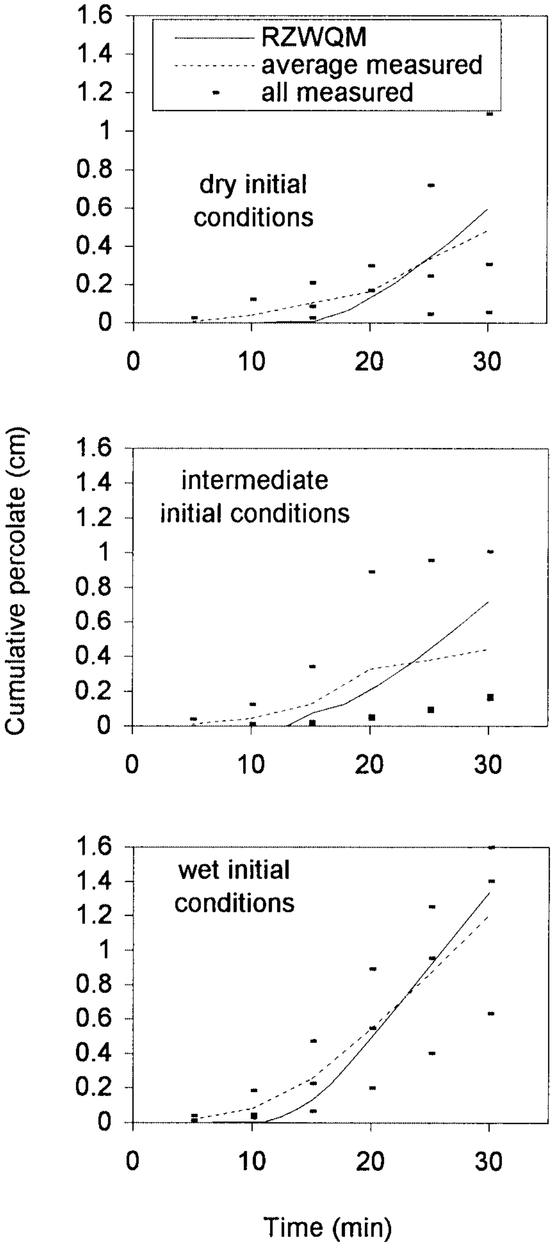

Figure 5. RZWQM–simulated and observed cumulative percolate versus time (test blocks only).

The change in atrazine concentration in percolate with time was not accurately simulated. The observed concentrations decreased with time, while the simulated concentrations generally increased (fig. 8). Similar results were observed with alachlor (results not shown). This may be due to the RZWQM's inability to simulate dynamic effective macroporosity, as previously discussed. As macroporosity increased, simulated herbicide concentration in percolate decreased (see the Sensitivity Analysis section below), partially because more soil was available to adsorb chemicals moving through macropores, given a constant macropore radius and a constant effective soil radius. In addition, equilibrium adsorption inside the macropores was assumed; a kinetic adsorption approach may improve predictions.

The RZWQM generally over–predicted the surface (0–4 cm) and under–predicted the subsurface (4–30 cm) alachlor and atrazine mean soil concentrations for the different block conditions (fig. 9). Simulating kinetic sorption in the soil matrix slightly improved the distributions (results not shown), but the RZWQM does not simulate kinetic sorption through macropores, complicating interpretation of results. Ma et al. (1995) suggested that kinetic

Table 3. Percolate amount (depth equivalent) and composite chemical concentrations.

Percolate and Chemical Concentration	Chemical. Calib. Blocks (CCB)		Test Blocks (TB)					
			Dry		Intermediate		Wet	
	Observed	RZWQM	Observed	RZWQM	Observed	RZWQM	Observed	RZWQM
Percolate (cm)	0.48[a] (0.11–0.95)[b]	0.69	0.49 (0.05–1.11)	0.54	0.46 (0.17–1.00)	0.74	1.43 (0.74–1.79)	1.61
Alachlor (ìg/mL)	0.11 (0.09–0.14)	0.09	0.27 (0.19–0.34)	0.38	0.20 (0.09–0.33)	0.20	0.14 (0.12–0.16)	0.25
Atrazine (µg/mL)	1.19 (0.87–1.64)	1.20	1.80 (1.08–2.41)	1.27	1.28 (1.03–1.49)	1.22	1.08 (0.77–1.26)	1.47
Bromide (µ/mL)	na	na	442 (345–610)	444	528 (422–650)	497	463 (359–574)	414

[a] The mean of three replications.

[b] The range of three replications.

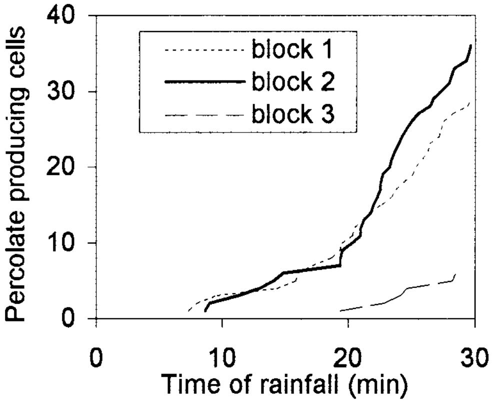

Figure 6. The number of cells out of 64 contributing to percolate versus time on the chemical calibration blocks (CCB).

sorption may improve RZWQM–simulated chemical distribution in soil. Because the RZWQM assumes water and chemicals entering macropores are derived from overland flow, chemical distribution in the soil has no direct effect on chemical transport in percolate at 30 cm if surface water concentrations are accurately simulated and the wetting front has not reached 30 cm. However, the alachlor and atrazine concentrations in simulated percolate subsequent to the first rainfall event may be over–predicted.

Chemical transport in percolate (alachlor, atrazine, and bromide) was simulated within a factor of 2 of the average observed transport for all block conditions, and most simulations were within the observed range. Chemical transport was generally over–predicted (fig. 9), partly because the total percolate volume at the end rainfall was over–predicted compared to observed (table 3 and fig. 5). Although simulated percolate volume was greater than observed, it was within the range of observed data (table 3 and fig. 5).

The above results include only one rainfall rate. Therefore, we investigated the effect of rainfall intensity on simulated percolate quantity and atrazine concentration from the dry blocks. Increasing the intensity by a factor of 2 resulted in little change in simulated concentration (1.32 µg/mL), but the percolate quantity increased to 0.785 cm, which is consistent with the undisturbed soil block study of Edwards et al. (1992). Decreasing the rainfall intensity by a factor of 4 resulted in no simulated percolate, which is within the range of Edwards et al. (1992). Because Edwards et al. (1992) observed increased effective macroporosity with increased rainfall intensity, the only adjusted RZWQM parameters were time of rainfall and the effective macroporosity. Macroporosity was adjusted to 0.0005 or 0.00012 cm/cm for a time of rainfall of 15 or 120 minutes, respectively. It should be noted that Edwards et al. (1992) used blocks obtained from the same field as the TB. Although these results are promising, more investigation is necessary to thoroughly assess the performance of the RZWQM under different rainfall intensities.

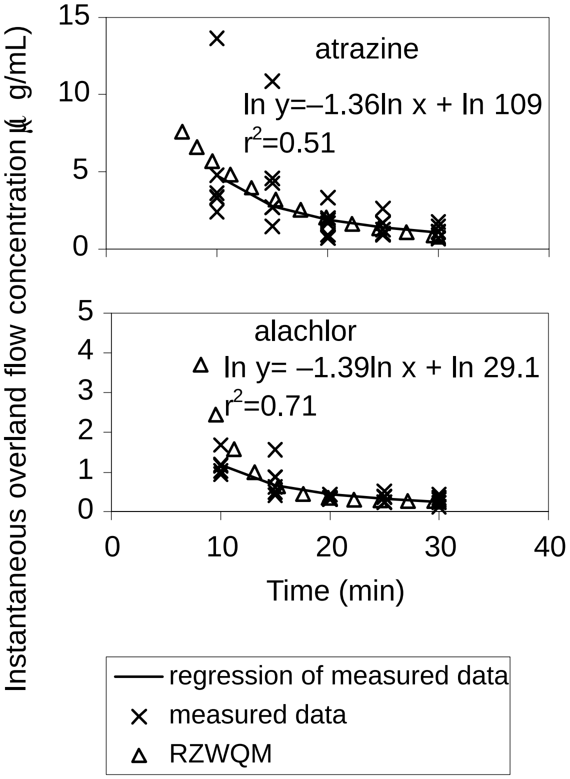

Figure 7. Herbicide concentration in surface water (CCB). Note that there are six measured data points at each time (10 min., 15 min., etc.)

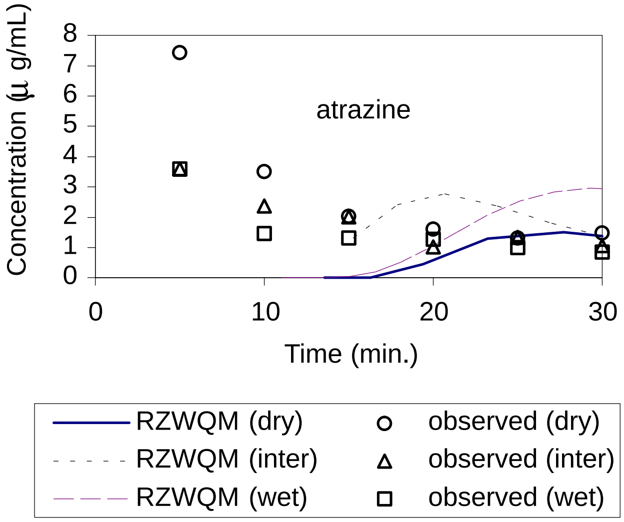

Figure 8. Simulated and measured atrazine concentration in percolate as a function of time.

SENSITIVITY ANALYSIS

The soil parameters affected percolate as expected (table 4). An increase in effective macroporosity results in more macropore surface area available for lateral water sorption and lower simulated percolate volume. An increase in the average macropore radius results in less surface area available for lateral water sorption and more simulated percolation, as observed by Ahuja et al. (1993).

Adjusting the soil parameters resulted in simulated bromide concentrations that remained within the range of values observed from the TB (tables 3 and 4). However, the alachlor and atrazine concentrations were significantly affected by adjustment of all soil parameters except the lateral sorptivity reduction factor. Both effective macroporosity and average macropore radius affected herbicide concentration in the percolate by affecting the surface area of soil available for chemical adsorption, as described above. An increase in K_{sat} resulted in less herbicide concentration in the percolate, partially because K_{sat} affected the quantity of chemical transported into the macropores, and thus the amount available for transport through the macropores. Kumar et al. (1998) also observed less atrazine loss with increased K_{sat}.

The chemical parameters affected chemical concentration in the percolate as expected (table 5). Simulated chemical movement into the macropores increased with a decreased mixing factor and washoff parameter F. Increasing alachlor and atrazine sorption to the soil (increased K_{oc}) resulted in less simulated chemical concentration in the percolate. In contrast to our observations, Kumar et al. (1998) observed that K_{oc} did not have much affect on atrazine loss (30% change in K_{oc} changed atrazine loss less than 5%). This may

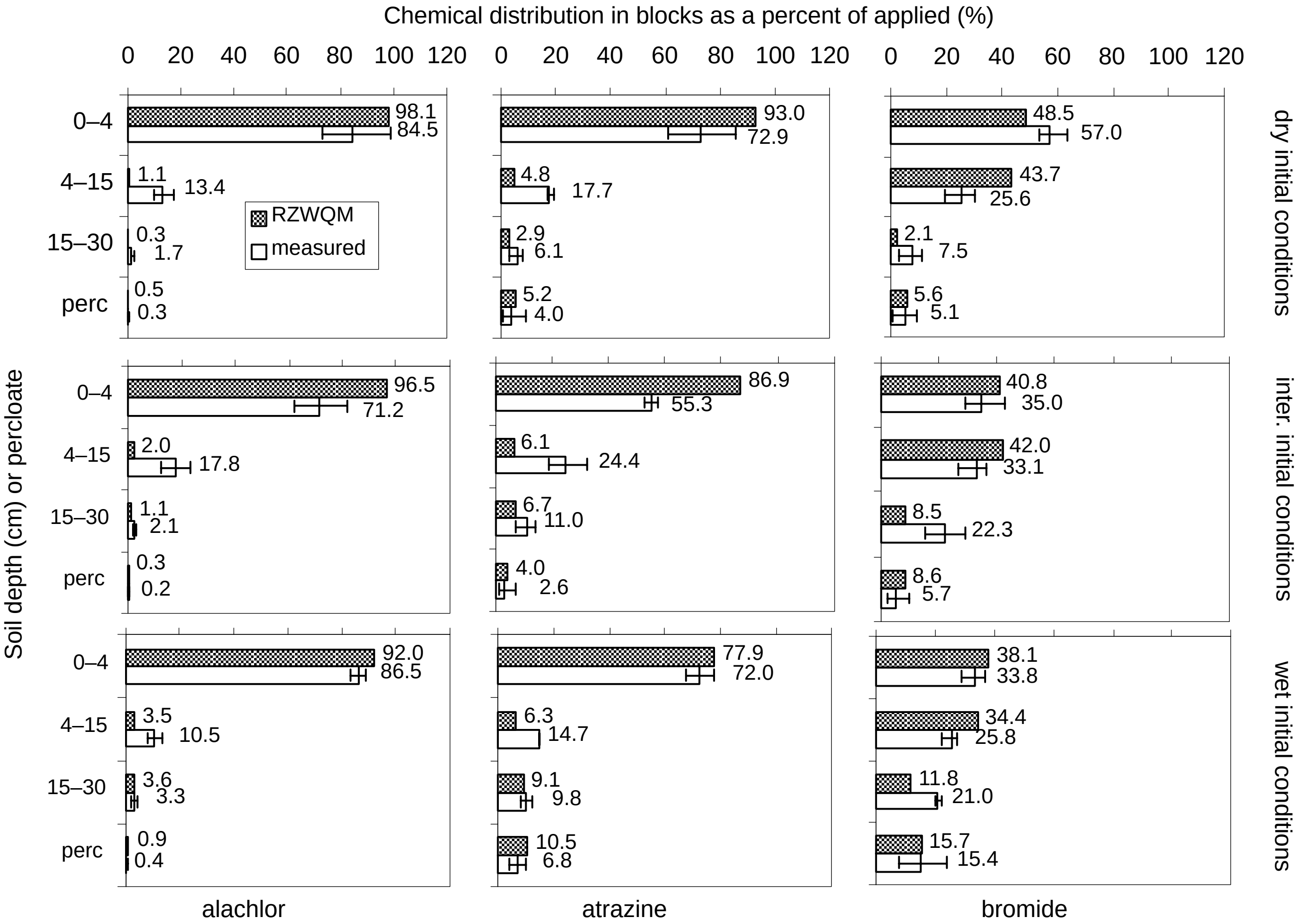

Figure 9. Chemical distribution in soil and percolate as a percent of applied. The bars represent the range of observed data.

Table 4. Sensitivity analysis on soil parameters for intermediate test blocks (TB).

Parameter	Parameter Difference from Table 1 or 2 Value (%)[a]	Difference from Table 3 Value[a]			
		Perc. Vol. (%)	Alachlor (%)	Atrazine (%)	Bromide (%)
Effective macroporosity	+50	–30	–85	–50	–3
	–50	+35	+268	+51	+5
Average macropore radius	+50	+35	+254	+50	+4
	–50	–55	–100	–98	–7
Sorptivity reduction factor	+50	–23	–6	+2	–2
	–50	+31	–5	–5	+9
K_{sat}	+50[b]	–34	–75	–38	–6
	–50[b]	+64	+234	+47	+19

[a] The percent difference from the original value was computed by (new–original)100/original. All parameter values were increased or decreased by 50% from the original values.

[b] The K_{sat} was adjusted by the indicated amount for each depth increment.

Table 5. Sensitivity analysis on chemical parameters for intermediate test blocks (TB).

Parameter	Difference in Parameter from Table 1 or 2 Value (%)[a]	Difference from Table 3 Value[a]		
		Alachlor (%)	Atrazine (%)	Bromide (%)
Non–uniform mixing factor	+50	–23	–10	–24
	–50	+103	+44	+34
Chemical washoff parameter F	+25	–39	–14	–10
	–25	+71	+10	+11
Chemical washoff parameter P	+50	–46	–25	–16
	–50	+147	+12	+18
K_{oc}	+50, +50, 0[b]	–85	–55	<1
	–50, –50, 0[b]	+370	+61	<1
Effective soil radius	+50	–98	–82	+11
	–50	+365	+55	–9

[a] The percent difference from the original value was computed by (new–original)100/original.

[b] The K_{oc} for alachlor, atrazine, and bromide, respectively.

be due to the effective soil radii differences (0.6 cm vs. less than 0.05 cm), illustrating the complex interaction between input parameters and the need for an in–depth sensitivity analysis considering parameter interaction. An increased effective soil radius resulted in lower percolate concentration because more soil was available to mix with the water transported through the macropores.

The sensitivity analysis illustrates some of the challenges in parameterizing and applying the RZWQM to simulate macropore flow. Several parameters are sensitive and difficult to determine, such as effective macroporosity, average macropore radius, and effective soil radius (tables 4 and 5). It is possible that average macropore radius and the effective soil radius are constant for different soils, as with the different blocks from this study, but further research is needed. However, the measured effective macroporosity changed with different antecedent water content and may be difficult to determine for different soils and management conditions. Therefore, further research is needed to provide guidance on applying the concept of effective macroporosity to different modeling scenarios (different soil types, management conditions, tillage, initial water content, etc.). This sensitivity analysis also indicates that a multiple–parameter sensitivity analysis to investigate parameter interaction on RZWQM–simulated macropore flow similar to Ma et al. (2000b) may be warranted.

SUMMARY AND CONCLUSIONS

The RZWQM was modified to allow effective soil radius as a model input, and a constant value of 0.6 cm was acceptable for the conditions of this study. Effective soil radius is defined as the soil surrounding macropores that interacts with macropore flow. An alternative method to measure macroporosity for input into the RZWQM used the concept of effective macroporosity, defined as 50% of the percolate–producing macropores. This parameterization strategy resulted in reasonable simulation of chemical transport in percolate for three chemicals and three initial soil water contents.

However, the model and this assessment have at least three limitations: 1) only the first percolate event after chemical application and only one soil type were studied, 2) the change in simulated herbicide concentration with time in percolate did not match observed data, and 3) the surface soil herbicide concentration was over–predicted and the subsurface soil herbicide concentration was under–predicted after rainfall. Despite these limitations, this assessment is beneficial, in part, because the macropore component of the RZWQM has not been previously assessed for pesticides at this level of detail (e.g., natural macropores, rigorous laboratory study). In addition, the first rainfall event after chemical application is generally the most important because this is when percolate concentrations are often highest.

Further research should address:

- The soils and conditions to which a 0.6–cm effective soil radius applies
- Application of the effective macroporosity parameterization strategy to other soils and management
- Performance of the RZWQM under multiple rainfall events, different rainfall intensities, soils, management, and climate
- The effect of kinetics on simulated macropore flow
- Parameter interaction on simulated macropore flow (e.g., Monte Carlo simulation).

Suggested model improvements are modifying the model to: 1) simulate dynamic effective macroporosity during an event, 2) allow effective soil radius and partition coefficient to vary with depth, and 3) simulate kinetics and physical non–equilibrium within macropores.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the team of individuals that assisted in obtaining the blocks, simulating rainfall, and chemical analysis (listed in alphabetical order): Greg Alloway, Joyce Alloway, Phyllis Dieter, Dan Hothem, Don Lightell, and Steve Storm. We also acknowledge the support of Dr. Lloyd Owens, Research Leader and Soil Scientist, North Appalachian Experimental Watershed (NAEW), USDA–ARS. We also thank Dr. Binayak Mohanty (U. S. Salinity Lab, Riverside, Calif.) for reviewing a draft of the manuscript.

REFERENCES

Ahuja, L. R., D. G. DeCoursey, B. B. Barnes, and K. W. Rojas. 1993. Characteristics of macropore transport studied with the ARS root zone water quality model. *Trans. ASAE* 36(2): 369–380.

Ahuja, L. R., K. E. Johnsen, and G. C. Heathman. 1995. Macropore transport of a surface–applied bromide tracer: Model evaluation and refinement. *Soil Sci. Soc. Am. J.* 59(5): 1234–1241.

Ahuja, L. R., K. W. Rojas, J. D. Hanson, J. J. Shaffer, and L. Ma. 1999. *The Root Zone Water Quality Model*. Highlands Ranch, Colo.: Water Resources Publications, LLC.

Close, K. R., G. Frasier, G. H. Dunn., and J. C. Loftis. 1998. Tension infiltrometer contact interface evaluation by use of a potassium iodide tracer. *Trans. ASAE* 41(4): 995–1004.

Edwards, W. M., M. J. Shipitalo, W. A. Dick, and L. B. Owens. 1992. Rainfall intensity affects transport of water and chemicals through macropores in no–till soil. *Soil Sci. Soc. Am. J.* 56(1): 52–58.

Edwards, W. M., M. J. Shipitalo, R. Lal, and L. B. Owens. 1997. Rapid changes in concentration of herbicides in corn field surface depressions. *J. Soil and Water Cons.* 52(4): 277–281.

Heathman, G. C., L. R. Ahuja, and J. L. Baker. 1986. Test of a non–uniform mixing model for transfer of herbicides to surface runoff. *Trans. ASAE* 29(2): 450–455, 461.

Jaynes, D. B., and J. G. Miller. 1999. Evaluation of the Root Zone Water Quality Model using data from the Iowa MSEA. *Agron. J.* 91(2): 192–200.

Kladivko, E. J., G. E. Van Scoyoc, E. J. Monke, K. M. Oates, and W. Pask. 1991. Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. *J. Environ. Qual.* 20(1): 264–270.

Kumar, A., R. S. Kanwar, and L. R. Ahuja. 1998. Evaluation of preferential flow component of RZWQM in simulating water and atrazine transport to subsurface drains. *Trans. ASAE* 41(3): 627–637.

Ma, Q. L., L. R. Ahuja, K. W. Rojas, V. F. Ferreira, and D. G. DeCoursey. 1995. Measured and RZWQM predicted atrazine dissipation and movement in a field soil. *Trans. ASAE* 38(2): 471–479.

Ma, L., L. R. Ahuja, M. J. Shaffer, J. D. Hanson, and K. W. Rojas. 1998. Parameterization, calibration, and sensitivity analysis of the RZWQM: A synthesis. Presented at theASAE annual international meeting, 12–16 July 1998, Orlando, Florida. Paper No. 98–2214. St. Joseph, Mich.: ASAE.

Ma, L., L. R. Ahuja, J. C. Ascough, M. J. Shaffer, K. W. Rojas, R. W. Malone, and M. R. Cameira. 2000a. Integrating system modeling with field research in agriculture: Applications of the Root Zone Water Quality Model (RZWQM). *Advances in Agronomy* 71: 233–292.

Ma, L., J. C. Ascough II, L. R. Ahuja, M. J. Shaffer, J. D. Hanson, and K. W. Rojas. 2000b. Root Zone Water Quality Model sensitivity analysis using the Monte Carlo simulations. *Trans. ASAE.* 43(4): 883–895.

Malone, R. W., R. C. Warner, and M. Byers. 1996. Subsurface losses of surface–applied metribuzin as influenced by yard waste compost amendments, no–tillage, and conventional–tillage. *Bull. Environ. Contam. Toxicol.* 57(5): 751–758.

Malone, R. W., L. Ma, L. R. Ahuja, and K. W. Rojas. 1999a. Validation of the Root Zone Water Quality Model (RZWQM): A review. Presented at the ASAE Annual International Meeting, 18–22 July 1999, Toronto, Ontario. Paper No. 99–2145. St. Joseph, Mich.: ASAE.

Malone, R. W., R. C. Warner, S. R. Workman, and M. E. Byers. 1999b. Modeling surface and subsurface pesticide transport under three field conditions using PRZM–3 and GLEAMS. *Trans. ASAE* 42(5): 1275–1287.

Quisenberry, V. L., R. E. Phillips, and J. M. Zeleznik. 1994. Spatial distribution of water and chloride macropore flow in a well–structured soil. *Soil Sci. Soc. Am. J.* 58(5): 1294–1300.

Shipitalo, M. J., W. M. Edwards, W. A. Dick, and L. B. Owens. 1990. Initial storm effects on macropore transport of surface applied chemicals in no–till soil. *Soil Sci. Soc. Am. J* 54(6): 1530–1536.

Shipitalo, M. J., and W. M. Edwards. 1996. Effects of initial water content on macropore/matrix flow and transport of surface–applied chemicals. *J. Environ. Qual.* 25(4): 662–670.

Smith, W. N., S. O. Prasher, and S. F. Barrington. 1991. Evaluation of PRZM and LEACHMP on intact soil columns. *Trans. ASAE* 34(6): 2413–2420.

Stehouwer, R. C., W. A. Dick, and S. J. Traina. 1993. Characteristics of earthworm burrow lining affecting atrazine sorption. *J. Environ. Qual.* 22(1): 181–185.

Stehouwer, R. C., W. A. Dick, and S. J. Traina. 1994. Sorption and retention of herbicides in vertically oriented earthworm and artificial burrows. *J. Environ. Qual.* 23(2): 286–292.

Trojan, M. D., and D. R. Linden. 1992. Microrelief and rainfall effects on water and solute movement in earthworm burrows. *Soil Sci. Soc. Am. J* 56(3): 727–733.

Villholth, K. G., K. H. Jensen, and J. Fredericia. 1998. Flow and transport processes in a macroporous subsurface–drained glacial till soils: Field investigations. *J. Hydrology* 207: 98–120.