Pest Management Science

Pest Manag Sci **60**:277–285 (online: 2004)
DOI: 10.1002/ps.791

Herbicide leaching as affected by macropore flow and within-storm rainfall intensity variation: a RZWQM simulation[†]

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Abstract: Within-event variability in rainfall intensity may affect pesticide leaching rates in soil, but most laboratory studies of pesticide leaching use a rainfall simulator operating at constant rainfall intensity, or cover the soil with ponded water. This is especially true in experiments where macropores are present—macroporous soils present experimental complexities enough without the added complexity of variable rainfall intensity. One way to get around this difficulty is to use a suitable pesticide transport model, calibrate it to describe accurately a fixed-intensity experiment, and then explore the affects of within-event rainfall intensity variation on pesticide leaching through macropores. We used the Root Zone Water Quality Model (RZWQM) to investigate the effect of variable rainfall intensity on alachlor and atrazine transport through macropores. Data were used from an experiment in which atrazine and alachlor were surface-applied to 30 x 30 x 30 cm undisturbed blocks of two macroporous silt loam soils from glacial till regions. One hour later the blocks were subjected to 30-mm simulated rain with constant intensity for 0.5 h. Percolate was collected and analyzed from 64 square cells at the base of the blocks. RZWQM was calibrated to describe accurately the atrazine and alachlor leaching data, and then a median Mid-west variable-intensity storm, in which the initial intensity was high, was simulated. The variable-intensity storm more than quadrupled alachlor losses and almost doubled atrazine losses in one soil over the constant-intensity storm of the same total depth. Also rainfall intensity may affect percolate-producing macroporosity and consequently pesticide transport through macropores. For example, under variable rainfall intensity RZWQM predicted the alachlor concentration to be 2.7 μg ml^{-1} with an effective macroporosity of 2.2 E^{-4} cm^3 cm^{-3} and 1.4 μg ml^{-1} with an effective macroporosity of 4.6 E^{-4} cm^3 cm^{-3}. Percolate-producing macroporosity and herbicide leaching under different rainfall intensity patterns, however, are not well understood. Clearly, further investigation of rainfall intensity variation on pesticide leaching through macropores is needed.

Keywords: modeling; preferential flow; water quality; infiltration and seepage; agricultural hydrology

1 INTRODUCTION

Water quality models are tools policy-makers can use to help make decisions and scientists can use to investigate water quality issues.[1,2] To describe or predict adequately the water quality impacts of chemical transport in soils, two effects are clearly important, inadequately investigated and likely to be interacting: the contribution of macropores to leaching, and the effect of rainfall intensity variation during events.

Fractures and macropores in the root zone can lead to rapid transport of water and chemicals to ground water.[3,4] This may be especially important in areas of fractured glacial till where ground water can be subject to rapid recharge and contamination.[5,6] Studying macropore flow, however, can be difficult and expensive, and models offer an efficient approach for this type of research. The Root Zone Water Quality Model (RZWQM) shows promise in accurately

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(*Received 3 September 2002; revised version received 7 January 2003; accepted 24 July 2003*)

simulating chemical transport through macropores,[7,8] including through fractured glacial till soil.[9] The RZWQM simulates macropore flow by routing rainfall in excess of infiltration (overland flow) into macropores, and then any rainfall excess remaining after infiltration and macropore flow is routed to runoff.[10]

Variable rainfall intensity within a storm significantly affects transport of pesticides in runoff[11] and may affect transport in macropore flow and fractures. For storms in the US Midwest, the rainfall intensity is generally higher at the beginning of the storm than at the end of the storm.[12] Several studies suggest that rainfall intensity, timing, and amount affect water and chemical transport in macropore flow.[13–17] Most laboratory studies of pesticide leaching through macropores, however, use a rainfall simulator operating at constant rainfall intensity or cover the soil with ponded water.

The effect of variable rainfall intensity within a storm on macropore flow has not been studied—it is difficult enough to study pesticide transport through macropores under constant rainfall intensity or ponded conditions. One of the primary values of a water-quality model is to illuminate which aspects of a system are most in need of further study.[18] Therefore, our objectives were to investigate the effect of variable rainfall intensity within a storm on alachlor and atrazine transport through macropores in glacial till soil using the RZWQM results of Malone *et al*,[9] which used constant-intensity rainfall. Malone *et al*[9] calibrated RZWQM to describe accurately the atrazine and alachlor leaching data of Granovsky *et al*[19] under constant rainfall intensity.

2 MODEL DESCRIPTION

A brief description of how RZWQM simulates pesticide transport is provided. More complete model descriptions are presented elsewhere.[7,10,20,21]

The RZWQM simulates vertical infiltration into the soil surface and radial infiltration in macropores using an adaption of the Green–Ampt equation during rainfall or irrigation. When the rainfall rate exceeds the infiltration rate, overland flow begins which is routed into macropores to the limit of macropore flow rate capacity. The flow rate capacity of the macropores is determined by Poiseuille's law and the infiltration rate is determined by the vertical Green–Ampt equation. For each simulated time step, the flow is sequentially routed downward through continuous macropores in 1-cm increments. In each depth increment, the macropore flow laterally infiltrates into the soil if saturation has not occurred at a rate determined by the lateral Green–Ampt equation. Chemicals are transferred from the soil to overland flow using the non-uniform mixing model,[22] and washoff from mulch and plant foliage is simulated.[23] Partition theory is used to simulate chemicals sorbed to soil and in solution in both macropores and soil matrix.

Poiseuille's law and the Green–Ampt equation incorporated in RZWQM have been described elsewhere.[10,21] To understand the RZWQM parameterization, however, we briefly describe below: macropore flow, partition theory, chemical washoff from mulch and foliage to overland flow, and chemical transfer from surface soil to overland flow.

2.1 Water and chemical transport in macropores

If the rainfall rate exceeds the infiltration rate during a time increment, the excess is considered overland flow and transported into macropores. The water entering macropores is evenly distributed among macropores, and the number of macropores per unit area (*nmacro*) is computed as

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

where *macro* is macroporosity or volume macropores per volume soil ($\mathrm{cm^3\,cm^{-3}}$) and *rp* is average macropore radius (cm). Not all macropores produce percolate and some macropores produce only a very small amount.[24,25] Macroporosity is a sensitive parameter for RZWQM and Malone *et al*[8] recommended using the effective macroporosity (*macro*⋆), defined as 50% of percolate-producing macropores (*nmacro*⋆) for long-term no-till corn. This parameterization strategy has been successfully applied to several silt loam soils and tillage methods.[8,9]

Compaction along macropore walls may reduce lateral infiltration:[20]

$$Vr^* = \mathrm{SFCT} \times Vr \tag{2}$$

where $Vr^\star$ is the lateral infiltration rate with compaction ($\mathrm{cm\,h^{-1}}$), *Vr* is the lateral infiltration rate without compaction ($\mathrm{cm\,h^{-1}}$) and SFCT is lateral sorptivity reduction factor (dimensionless).

Chemicals in macropore flow react with the pore walls according to partition theory (see Section 2.2). Water and chemicals vertically moving through macropores mix with and react with a user-defined radial length of the macropore wall. Malone *et al*[8] called this effective soil radius and found that 0.6 cm produced good simulations for silt loam soil in long-term no-till corn. The effective soil radius of 0.6 cm takes into account greater partitioning between soil and pesticides in natural macropores compared with the soil matrix; blockage and tortuosity of natural macropores; and lateral water movement through soil into macropores rather than ponded water movement into macropores as simulated by RZWQM.[8,26,27]

2.2 Chemical partitioning and chemical transfer to overland flow

Kinetic sorption/desorption, irreversible sorption, and Freundlich (non-linear) sorption are available RZWQM options, but we assumed linear and instantaneous pesticide sorption to soil.[9] The amount adsorbed to soil (C_{ad}, $\mu g\,g^{-1}$) may be expressed as $C_{\mathrm{ad}} = K_{\mathrm{d}}C_{\mathrm{sol}}$, where $K_{\mathrm{d}}(\mathrm{ml\,g^{-1}})$ is the partition coefficient and $C_{\mathrm{sol}}(\mu g\,\mathrm{ml}^{-1})$ is the chemical concentration in solution. The partition coefficient for various chemicals and soils may be estimated from the literature[28] or directly measured using batch-type procedures as described by Roy *et al.*[29] Batch procedures combine water, chemical and soil, then the chemical in water and chemical adsorbed to soil after 24 h of continuous mixing is measured. The K_{d} value is often expressed relative to organic carbon ($K_{\mathrm{oc}} = K_{\mathrm{d}}\ \mathrm{oc}^{-1}$), where oc is the mass carbon per unit mass soil ($\mathrm{g\,g^{-1}}$).

Chemicals are transferred to overland flow from plant foliage and mulch by washoff[23]

$$C_{\mathrm{f}} = 0.01C_{\mathrm{o}}(100 - F) + 0.01C_{\mathrm{o}}F(e^{-Pti}) \qquad (3)$$

where C_{f} is the chemical concentration remaining on mulch or foliage ($\mu g\,\mathrm{ha}^{-1}$) after an incremental rainfall of intensity i ($\mathrm{cm\,h^{-1}}$) and time t (h), C_{o} is the initial concentration on mulch and foliage at the beginning of each time increment, and P and F are washoff parameters which Malone *et al*[8] calibrated for atrazine and alachlor washoff from no-till corn mulch.

Chemical is transferred to overland flow by rainfall impact, and the contribution by depth is assumed to decrease exponentially from 0–2 cm. This can be expressed as the non-uniform mixing model,[22]

$$M_{\mathrm{ave}} = e^{-\mathrm{B}Z} \qquad (4)$$

where M_{ave} = average degree of mixing for depth increment between rainfall and soil solution, B = constant (6.0 for no-till),[8] and Z = center of depth increment (0.5 or 1.5 cm).

3 MATERIALS AND METHODS

3.1 Experimental data

Data from Granovsky *et al*[19] were used as a base simulation of pesticide transport through macropores on no-till soil from a glacial till region under constant rainfall intensity. Previously, Malone *et al*[9] had concluded that the RZWQM accurately simulated pesticide transport through these soil blocks under constant rainfall intensity. These soil blocks were then used to investigate the effect of variable rainfall intensity on pesticide transport through macropores.

Granovsky *et al*[19] had applied simulated rainfall with constant intensity to undisturbed soil blocks shortly after pesticide application. These conditions often result in high pesticide concentrations in the percolate.[16,30,31] Granovsky *et al*[19] report that no-till soil transported more pesticide in percolate than moldboard plow soil. Therefore, investigating the effect of variable rainfall intensity on no-till soil, shortly after application is a worst-case scenario.

Granovsky *et al*[19] describe the block experiment in detail, but we will briefly describe it here. The soil blocks were a Crosby silt loam (fine, mixed, active, mesic Aeric Epiaqualfs) and Wooster silt loam (fine-loamy, mixed, mesic Oxyaquic Fragiudalfs). Three 30 × 30 × 30 cm blocks of each undisturbed no-till soil (Wooster and Crosby) were collected in 1990 from plots that had been planted in long-term no-till corn (*Zea mays* L) using procedures similar to Shipitalo *et al.*[16] The size, number and position of visible macropores at 30 cm were recorded. Atrazine and alachlor were surface applied at rates equivalent to 8.5 and 4.0 kg AI ha^{-1}. A 0.5-h, 30-mm simulated rainfall was applied approximately 1 h after chemical application (Fig 1). Percolate was collected from each cell of a 64-square grid at the bottom of the soil blocks (3.75 × 3.75 cm). Concentrations of atrazine and alachlor were determined using gas chromatography. Details on the rainfall simulator, 64-square grid percolate collection system and chemical analysis methods can be found in Shipitalo *et al*[16] and Shipitalo and Edwards.[32]

3.2 Chemical transport simulation under constant-rainfall intensity

3.2.1 Measured and estimated input parameters

Although the data of Granovsky *et al*[19] were used, some RZWQM input parameters had to be measured,

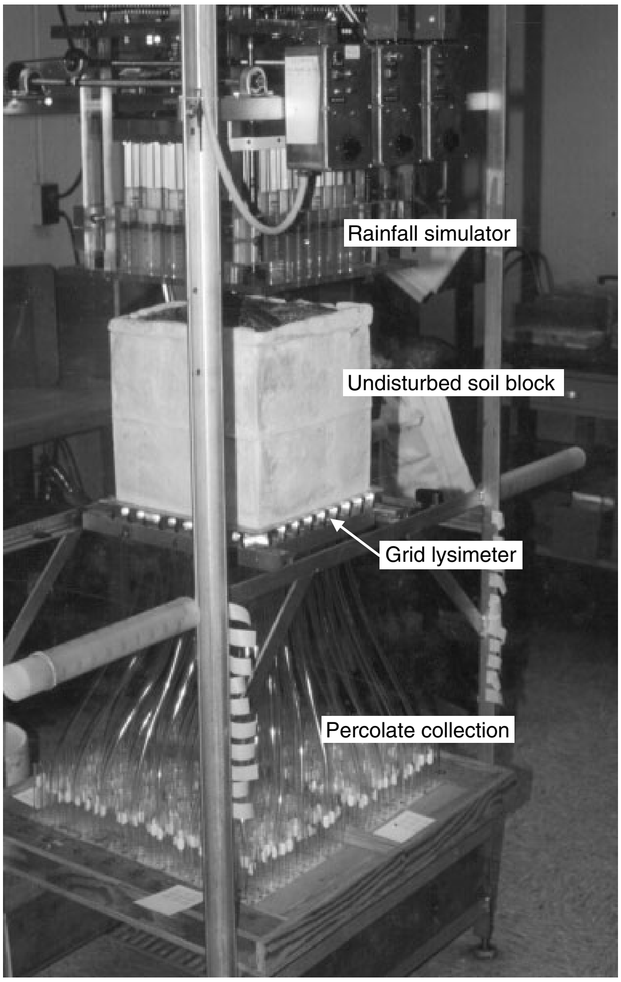

Figure 1. System used to simulate rainfall on the undisturbed soil blocks.

Table 1. Selected RZWQM input parameters

Parameter	Crosby silt loam	Wooster silt loam	Comments
Measured input parameters			
Number of percolate producing macropores (*nmacro*, cm^{-2})	0.0063 (0.0056–0.0078)[a]	0.031 (0.021–0.042)[a]	Derived from data of Granovsky *et al*[19]
Gravimetric soil carbon (%)	3.3 (0–3 cm) 1.4 (3–8 cm) 0.7 (8–30 cm)	3.3 (0–3 cm) 1.8 (3–8 cm) 0.8 (8–30 cm)	Unpublished 1993 data[b]
Partition coefficient (K_{oc}, ml g^{-1})	190 (alachlor) 124 (atrazine)	190[c] 124[c]	Measured using batch tests[8]
Estimated input parameters			
Non-uniform mixing parameter (*B*, cm^{-1})	6	6	Malone *et al*[8]
Effective macroporosity (*macro**, cm^3 cm^{-3})	2.2 E^{-4}	1.1 E^{-3}	Computed from eqn (1)
Chemical washoff parameters *F*	80	80	Malone *et al*[8]
P	0.45 (alachlor) 0.15 (atrazine)	0.45 0.15	
Particle density (g cm^{-3})	2.4 (0–3 cm) 2.5 (3–8 cm) 2.55 (8–30 cm)	2.4 (0–3 cm) 2.5 (3–8 cm) 2.55 (8–30 cm)	0–8 cm density derived from Mahboubi *et al*[33]; 2.65 g cm^{-3} is RZWQM default
Calibrated input parameters			
Bulk density (g cm^{-3})	1.20 (0–3 cm) 1.45 (3–8 cm) 1.50 (8–30 cm)	1.20 (0–3 cm) 1.30 (3–8 cm) 1.38 (8–30 cm)	Crosby values reasonable compared to Mahboubi *et al*,[33] Wooster values reasonable compared to data of Granovsky *et al*[19]
Pore size distribution index	0.12 (0–30 cm)	0.12 (0–30 cm)	Reasonable compared to observations of Malone *et al*[35] and Rawls *et al*[34] on silt loam soil
Soil matrix saturated hydraulic conductivity (K_{s}, cm h^{-1})	5.0 (0–8 cm) 2.5 (8–30 cm)	3.0 (0–8 cm) 1.2 (8–30 cm)	The lower K_{s} for subsurface soil may be because of more consolidation and lower soil carbon than the surface soil

[a] The range of three replicates.

[b] Jeanne Durkalski, School of Natural Resources, Ohio State University, Wooster, OH, personal communications (2000).

[c] The partition coefficients were not measured on the Wooster soil, but they were input as for Crosby soil because both silt loam soils were long-term continuous corn with similar carbon content.

estimated or calibrated. Therefore, 0–15-cm-deep cores of Crosby silt loam soil were collected in 2000 for partition coefficient determination (Table 1) from the same plots as sampled by Granovsky *et al*.[19]

Selected input parameters that were estimated are also listed in Table 1. The parameters affecting pesticide concentration in overland flow (non-uniform mixing parameter, *F*, *P*) were determined under conditions similar to those discussed above: undisturbed soil blocks (Glenford silt loam) taken from fields that were in long-term no-till corn and rain applied within 1 h of chemical application.[8] Five tonne ha^{-1} of dry mulch were assumed on the no-till blocks. The particle density of the surface soil was derived from Mahboubi *et al*[33] where the same no-till soil was investigated.

The RZWQM macropore parameterization strategy discussed in Malone *et al*[8] was utilized, including the measured number of percolate-producing macropores and an estimated effective soil radius of 0.6 cm (Table 1). To determine the effective macroporosity on the no-till blocks (50% of percolate-producing macropores), it was assumed that one average sized (0.15 cm), continuous macropore contributed to percolate from each square of the 64-square grid in which percolate was observed. Granovsky *et al*[19] observed that an average of 5.7 squares produced percolate from the three Crosby soil no-till blocks, therefore, the effective macroporosity was 2.85 macropores per 900 cm^2 block or 0.0032 effective macropores per cm^2. The effective soil radius was assigned to be 0.6 cm[8,9] because little guidance is available in the literature on estimating this parameter.

3.2.2 *Calibrated input parameters*

The bulk density, pore-size distribution index and saturated hydraulic conductivity (K_s) were calibrated on the no-till blocks to produce similar observed and simulated percolate (Fig 2; Table 2). There were insufficient data to plot the observed Wooster soil percolate, but the simulated breakthrough time (timing of percolate initiation) and total amount of simulated percolate (Table 2) were reasonable compared with observed values.[9] The calibrated subsurface soil K_s (8–30 cm) was lower than surface soil K_s possibly because of more consolidation than the surface soil. The calibrated pore-size distribution index (0.12) is within the range of Rawls *et al*[34] who found values between 0.1 and 0.4 for a variety of silt loam soils. The calibrated subsurface (15–30 cm) pore size distribution index (0.12) is also reasonable

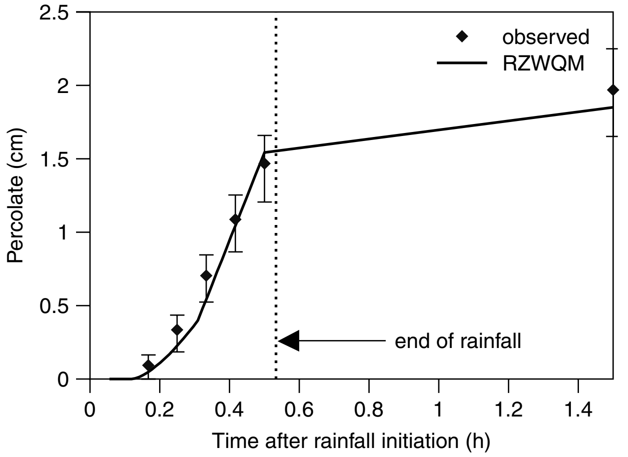

Figure 2. The average cumulative percolate observed from three Crosby soil blocks verses RZWQM simulated at 30 cm. The error bars represent the range of the three blocks.

compared to values measured (0.05) on Lowell silt loam soil.[35] Calibration procedures and justification of calibrated parameters are described in detail by Malone *et al.*[9] The meanings of calibrated parameters as related to RZWQM are described by Malone *et al.*[35]

3.3 Chemical transport simulation under variable-rainfall intensity

Two modeling scenarios were used to investigate the effect of variable rainfall intensity on pesticide transport. Scenario 'a' estimates the effect of the median rainfall intensity variation in the US Midwest[12] (Fig 3) on pesticide transport through macropores using the same effective macroporosity as the 'constant-intensity' scenario. Scenario 'b' is identical to 'a' except that the effective macroporosity was increased. The input parameters for scenarios 'a' and 'b' were the same as for the 'constant-intensity' scenario except rainfall intensity variation was added to both scenarios ('a' and 'b'). Figure 4 illustrates the effective macroporosity and total macroporosity of scenarios 'a' and 'b' on the no-till Crosby soil blocks. The RZWQM was used to simulate chemical transport through macropores under variable rainfall intensity because it had accurately responded to three different constant-rainfall intensity storms on Glenford silt loam soil,[8] and it accurately simulated chemical transport on the Crosby and Wooster silt loam soil blocks under constant rainfall intensity.[9]

Scenario 'b' was included because variable rainfall intensity during a storm may alter effective macroporosity. The data of Edwards *et al*[14] suggest that effective macroporosity increases with increasing rainfall intensity (Fig 5). The formula to compute absolute

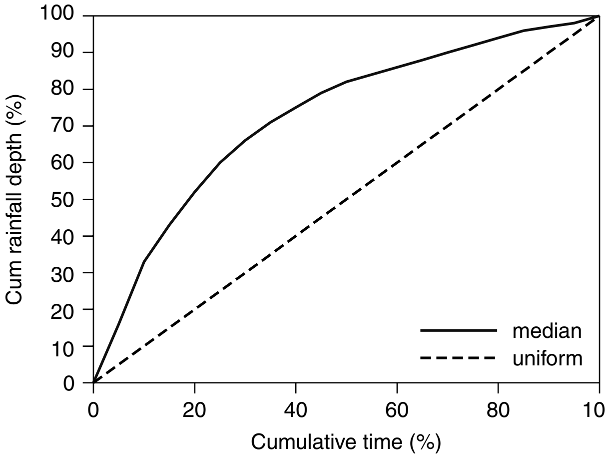

Figure 3. Time distribution of rainfall at a point. The median distribution is what can be expected in the US Midwest.[12] The uniform distribution has constant-intensity throughout the event.

Table 2. Chemical transport through no-till soil blocks at 30 cm with a 30-mm rainfall

		Modeling scenario using RZWQM		
	Observed	'Constant-intensity'[a]	'a'	'b'
Rainfall intensity distribution[b]	Uniform	Uniform	Median	Median
Crosby soil blocks				
Effective macroporosity (cm^3 cm^{-3})	2.2 E^{-4}	2.2 E^{-4}	2.2 E^{-4}	4.6 E^{-4c}
Percolate (mm)	20 (17–22)[d]	18.5	18.5	18.5
Initial percolate breakthrough time (min)	8.0 (5.5–11.4)	7.8	0.8	1.3
Alachlor concentration (μg ml^{-1})	0.42 (0.23–0.53)	0.60	2.7	1.4
Atrazine concentration (μg ml^{-1})	6.1 (4.2–7.5)	4.7	9.2	6.4
Wooster soil blocks				
Effective macroporosity (cm^3 cm^{-3})	1.1 E^{-3}	1.1 E^{-3}	1.1 E^{-3}	2.3 E^{-3c}
Percolate (mm)	17 (16–19)	19.7	19.7	19.7
Initial percolate breakthrough time (min)	8.1 (5.3–10.8)	6.8	0.23	2.4
Alachlor concentration (μg ml^{-1})	0.29 (0.27–0.29)	0.28	0.66	.003
Atrazine concentration (μg ml^{-1})	4.4 (3.9–4.8)	4.0	4.8	0.21

[a] The constant-intensity modeling scenario is from Malone *et al.*[9]

[b] See Fig 3.

[c] The effective macroporosity was estimated from eqn (5) assuming rainfall intensity of 114 mm h^{-1} was representative of the variable rainfall intensity (intensity varied from 23 to 192 mm h^{-1}).

[d] The values in parentheses indicate the range of the three replicates.

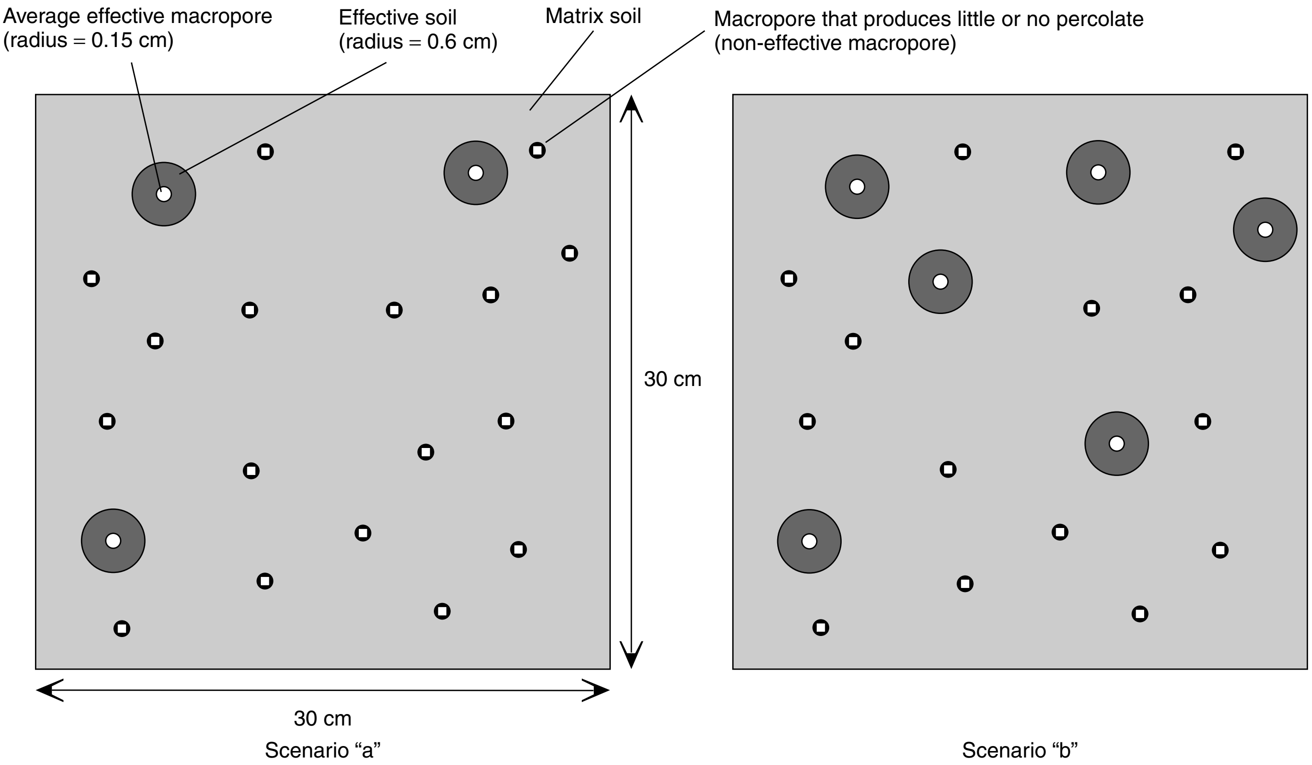

Figure 4. Illustration of the bottom of two Crosby soil blocks with the same total macroporosity and different effective macroporosity. Scenario 'a' has an effective macroporosity of 2 E^{-4} cm^3 cm^{-3}; scenario 'b' has an effective macroporosity of 5 E^{-2} cm^3 cm^{-3}. Not drawn to scale.

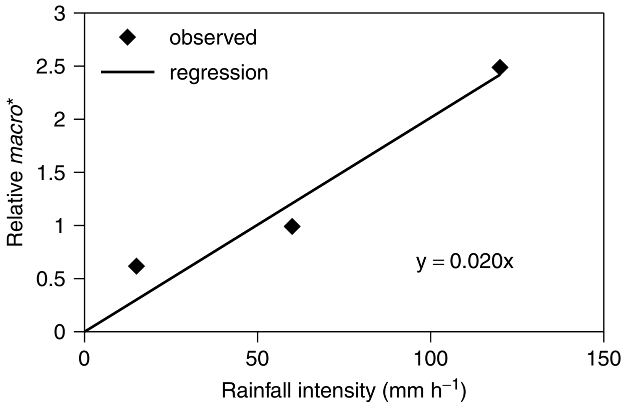

Figure 5. Effective macroporosity (*macro**) versus rainfall intensity. *macro** is relative to effective macroporosity at a rainfall intensity of 6 cm h^{-1} (2 E^{-4} cm^3 cm^{-3}). Data is from Edwards *et al.*[14]

effective macroporosity (*macro**) of Fig 5 is

$$macro^*(2) = [(\times 2 - \times 1)m + 1]macro^*(1) \qquad (5)$$

where *macro**(2) is effective macroporosity at ×2, ×2 and ×1 are different rainfall intensities, *m* is the slope of the regression (0.020 h mm^{-1}), and *macro**(1) is effective macroporosity at ×1. Reasonable chemical transport through macropores under different rainfall intensities can be simulated using RZWQM when rainfall intensity remains constant throughout the storm.[8] When the rainfall intensity changes during a storm, effective macroporosity can be based on the average rainfall intensity, the maximum value, or the minimum value. To help illustrate the problem, a median 0.5-h, 30-mm US Midwest storm yields rainfall intensities ranging from 10 to 200 mm h^{-1} and the average number of percolate-producing macropores can increase from 3.7E^{-3} cm^{-2} to 1.5E^{-2} cm^{-2} for rainfall intensities of 15 to 120 mm h^{-1}, respectively.[12,14]

4 RESULTS AND DISCUSSION

4.1 Constant-intensity simulation

The 'constant-intensity' modeling scenario resulted in good simulated chemical transport compared to the observed data in a complex system that included macropores (Table 2). Simulated values were within a factor of 1.5 of the average observed and within or nearly within the range of observations. This is evidence that, after calibration, the RZWQM-simulated chemical transport through macropores fits observed data well for no-till corn in glacial till regions with uniform rainfall. This is important because, in 2000, over 4 million ha in the US Midwest were in no-till corn.[36]

4.2 Variable-intensity simulation

The ratio of simulated alachlor and atrazine concentrations in Crosby soil block percolate were 4.5 and 2.0 times more, respectively, under median Midwest rainfall intensity variation compared with constant rainfall intensity (Table 2, 'constant-intensity' and 'a' modeling scenarios). Variable rainfall intensity was also predicted to increase percolate concentration on the Wooster soil blocks, but to a lesser degree than the Crosby soil blocks (Table 2). In comparison (to illustrate the importance of the rainfall intensity effect), Shipitalo and Edwards[32] found that the ratio of atrazine and alachlor concentrations in percolate between three initial soil water contents was less than 2.0. Also, Edwards *et al*[14] observed that the ratio between atrazine transport in percolate for a 30-mm, 0.5-h storm and a 30-mm, 0.25-h storm was less than 1.4.

More intense rainfall at the beginning of a storm affects pesticide transport through macropores because overland flow begins with less total rainfall and at a shorter time interval compared to constant rainfall intensity. This results in higher flow-weighted chemical concentrations in overland flow which becomes macropore flow. For example, during the first 10 mm of rainfall, the simulated water flow into macropores was 5.8 mm for the median rainfall distribution and only 1.1 mm for the constant distribution (Fig 6). The resulting average alachlor concentration in overland flow entering macropores after 1.0 mm of flow was then 17 μg ml^{-1} for the median distribution and 7.7 μg ml^{-1} for the uniform distribution. The average alachlor concentration in overland flow entering macropores after 2.0 mm of flow was 8.4 μg ml^{-1} for the median distribution and 3.3 μg ml^{-1} for the uniform distribution.

The modeling results under variable rainfall intensity need to be confirmed with field and laboratory studies, but the overland flow concentrations are consistent with other studies.[11] Zhang *et al*[11] showed that more intense rainfall early in a storm can result in overall flow-weighted concentration in overland flow being higher than in uniform intensity storms. They explained that, under high rainfall intensity early in the event, peak overland flow occurs with less cumulative rainfall compared with uniform intensity storms, and herbicide concentrations are higher with less cumulative rainfall, regardless of rainfall pattern.

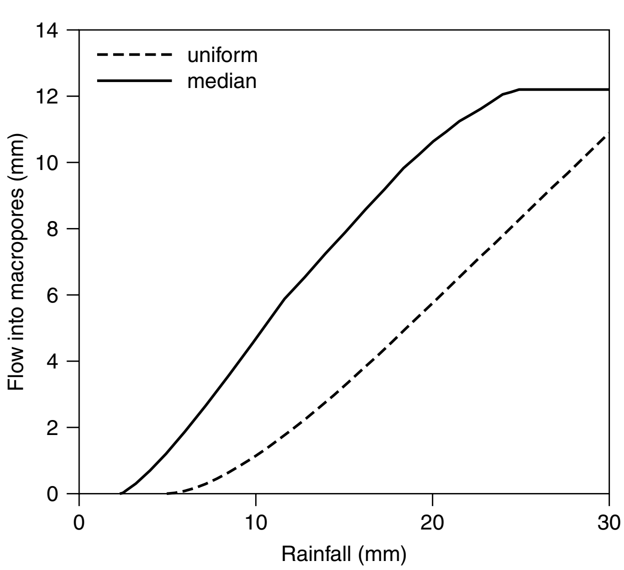

Figure 6. RZWQM simulated water flow into macropores for two rainfall intensity distributions. The uniform distribution is the 'constant-intensity' scenario; the median distribution is scenario 'a'.

4.3 Macroporosity effect on herbicide transport

As discussed above, rainfall intensity may affect effective macroporosity (Fig 5) and consequently herbicide transport through percolate may be affected. Table 2 shows that the ratio of simulated alachlor and atrazine concentrations on the Crosby soil blocks were 1.9 and 1.4 times less, respectively, for an effective macroporosity of 4.6E^{-4} compared to 2.2E^{-4} cm^3 cm^{-3} under variable rainfall intensity (Table 2, 'b' and 'a' modeling scenarios). The effect of increased effective macroporosity was greatly intensified for the Wooster soil (eg simulated alachlor concentration decreased from 0.66 to 0.003 μg ml^{-1}).

The increased effective macroporosity estimate for the Crosby soil may be reasonable because at a constant rainfall intensity of 60 mm h^{-1} the effective macroporosity was about 2.2E^{-4} cm^3 cm^{-3} for both the Edwards *et al*[14] (Fig 5) and the Crosby soil (Table 1). Figure 5 was developed from the data of Edwards *et al*.[14] The estimated effective macroporosity increase for the Wooster soil (1.1E^{-3} to 2.3E^{-3} cm^3 cm^{-3}) is less certain because measured effective macroporosity (*macro*⋆) was much higher than Edwards *et al*[14] soil under constant 60 mm h^{-1} rainfall (Table 1). That is, scenario 'b' (Table 2) assumes that *macro*⋆ increases at the same rate with increasing rainfall intensity for Wooster and Crosby initial *macro*⋆ (Fig 5), whereas the increase may be less for Wooster because of the larger initial *macro*⋆ (1.1E^{-3} cm^3 cm^{-3}).

The herbicide concentrations were less under scenario 'b' because water and chemicals transported into macropores are distributed between more macropores than in scenario 'a' (Fig 4). Therefore, more soil was available for chemical partitioning per mass of chemical for scenario 'b'. In fact, 'b' had 2.7 μg cm^{-2} simulated alachlor sorbed to macropore walls, 'a' had 0.39 μg cm^{-2}. It is uncertain which effective macroporosity estimate is more representative of natural conditions (estimated using average or extreme rainfall intensity), suggesting a need for more laboratory and/or field investigations.

As shown (Table 2, scenarios 'a' and 'b'), it is important to understand the role of effective macroporosity to understand pesticide transport through the root zone. The effect of different effective macroporosities under uniform rainfall intensity on RZWQM-simulated herbicide transport is illustrated in Fig 7. The only RZWQM input parameter change from the constant-intensity modeling scenario for Fig 7 was effective macroporosity. For the Crosby soil constant-intensity modeling scenario, effective macroporosity has little affect on chemical transport at relatively low effective macroporosity (Fig 7) because a relatively large quantity of the chemical transported into macropores was transported out of the macropores when effective macroporosity

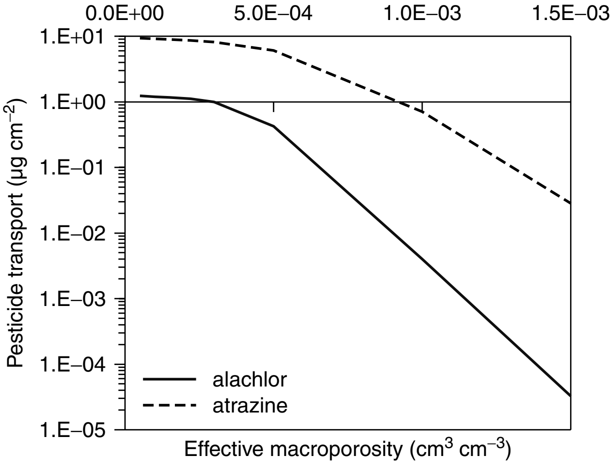

Figure 7. RZWQM simulated pesticide transport through macropores at 30 cm versus effective macroporosity during constant-intensity rainfall on the Crosby soil blocks. Simulated percolate remained constant (18.5 mm).

was $2.2\,\mathrm{E}^{-4}\,\mathrm{cm}^3\,\mathrm{cm}^{-3}$. As effective macroporosity increases (as *nmacro** increases), more of the soil matrix contributes to sorption (Fig 4) and simulated pesticide transport through macropores declines rapidly (Fig 7).

Increasing effective macroporosity on the Wooster soil (scenario 'a' and 'b') also illustrates the importance of effective macroporosity on pesticide transport through macropores (Table 2). Factors in addition to rainfall intensity may affect effective macroporosity. For example, Malone *et al*[8] and Shipitalo *et al*[32] show that antecedent soil water affects effective macroporosity (effective macroporosity for wet blocks 6.5 times more than for dry blocks). Because the effects of conditions such as soil, antecedent soil water, management and rainfall variation on effective macroporosity (0.5 × percolate producing macroporosity) are not well understood, more field/laboratory investigations are necessary.

ACKNOWLEDGMENTS

The authors appreciate the helpful comments provided by Sally Logsdon and Jim Bonta on an earlier version of the manuscript.

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