Tillage effect on macroporosity and herbicide transport in percolate

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Abstract

Research suggests that pesticide transport to tile drains and shallow groundwater may be greater for no-till than tilled soil. Also, most pesticide transport through soil can be from macropore flow, but the effect of tillage on macropore transport is uncertain. Our objective was to investigate the effect of tillage on herbicide leaching through hydraulically active macropores. The number of percolate-producing macropores at 30 cm (nmacro) and the timing of initial percolate were measured from an experiment where atrazine, alachlor and rainfall were applied to moldboard plowed (MP) and no-till (NT) undisturbed soil blocks from two different silt loam soils. Alachlor and atrazine transport through the undisturbed soil blocks was simulated using the Root Zone Water Quality Model (RZWQM). The time of initial percolate breakthrough at 30 cm was significantly less for NT than for MP (p < 0.001), but nmacro was not significantly different between MP and NT treatments. Additionally, nmacro was significantly different between the two silt loam soils (p < 0.001). Multiple linear regression revealed that flow-weighted herbicide concentration in percolate decreased with increasing nmacro (cm$^{-2}$) and increasing time for initial percolate breakthrough (min) ($R^2 = 0.87$ for alachlor and 0.85 for atrazine). Because a small fraction of nmacro produces the majority of percolate, we used half of measured nmacro for RZWQM input. Also, soil parameters were calibrated to accurately simulate the water flow component timing of percolate arrival and percolate amount through macropores. This parameterization strategy resulted in accurate predicted herbicide concentrations in percolate at 30 cm using RZWQM (within the range of observations). The modeling results suggest that differences in soil properties other than macroporosity such as a lower soil matrix saturated hydraulic conductivity and porosity in subsurface soil (8–30 cm) can cause percolate to occur sooner through macropores on NT than on

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MP and cause higher herbicide concentrations in percolate on NT, even when nmacro does not differ between till and no-till.

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Keywords: Preferential flow; RZWQM; Contaminant transport; Model validation; Macropores

1. Introduction

No-till soil often shows higher pesticide concentrations in percolate, shallow groundwater or drainage than tilled soil (Elliott et al., 2000; Masse et al., 1998; Kanwar et al., 1997; Isensee et al., 1990). The reason(s) for this, however, are uncertain. Possibly, tillage completely destroys macropores, changes macropore properties (more or less macropores, change in tortuosity, change in macropore continuity, etc.) and/or changes soil matrix soil properties (e.g., change in soil matrix hydraulic conductivity). Soil macroporosity is one of the most important factors affecting pesticide movement to tile drains and shallow groundwater (Shipitalo et al., 2000; Kladivko et al., 1991). Even in tilled soils, pesticide transport can occur through preferential flow paths (Levanon et al., 1993; Granovsky et al., 1993). Understanding the effect(s) of tillage on macroporosity and pesticide transport should help in the development and use of simulation models, and ultimately help design management strategies that reduce water quality problems associated with pesticide use.

Some studies show that tillage can significantly affect the number of active macropores (e.g., Petersen et al., 2001). Tillage may also disrupt macropore continuity, which can reduce solute movement (Vervoort et al., 2001). However, the tillage effect on macroporosity is uncertain because some studies show that the quantity of hydraulically active macropores are not significantly different between different management practices (Azevedo et al., 1998; Droogers et al., 1998). Re-analysis of tension infiltrometer studies on several soils and tillage methods also show no clear tillage effect on hydraulically active macropores (see Section 2). Hydraulically active macropores are important because only a fraction of total macroporosity produce percolate (e.g., Malone et al., 2001; Trojan and Linden, 1992; Villholth et al., 1998).

The uncertainty of the tillage effect on macroporosity adds complexity to simulating the effect of agricultural management on water quality. As a simplified approach, the Root Zone Water Quality Model (RZWQM) destroys the continuity of macropores in the tilled zone during tillage and the macropores are allowed to slowly reform during reconsolidation. As a result, RZWQM does not simulate macropore flow shortly after tillage possibly resulting in under predicted herbicide transport to drains or shallow groundwater. It is possible that tillage does not completely destroy macropore continuity, but affects macropore flow through changes in other soil and macropore properties such as soil matrix hydraulic conductivity and macropore tortuosity.

We first re-analyzed tension infiltrometer data from the literature that included several soil types and tillage methods to investigate the effect of tillage on active macropores. We then studied the effects of tillage on active macropores and herbicide leaching from moldboard plow (MP) and no-till (NT) soil blocks using the data of Granovsky et al.
(1993), and using RZWQM to simulate herbicide leaching through active macropores from the MP and NT soil blocks.

2. Re-analysis of tension infiltrometer data from the literature

Tension infiltrometer data from the studies of Logsdon and Kaspar (1995), Logsdon et al. (1993b,c), Kaspar et al. (1995) and unpublished data were re-analyzed to quantify surface and subsurface macropores. The soil descriptions and the number of observations for each soil-tillage group are summarized in Table 1. All soils described in Table 1 are structured soils (no sandy soils) from the Midwest, and include four drainage classes and five tillage methods. We sorted soils by drainage class because it was expected that drainage class has more influence on macroporosity than soil texture in structured soils. Surface tension infiltrometer measurements were taken at a soil depth of 0–1 cm. Subsurface measurements on chisel, disk, ridge-till and no-till were taken at 15 cm because soil disturbance from chisel tillage extends to about 15 cm (Logsdon et al., 1990). Measurements on moldboard plow were at 25 or 35 cm because moldboard plow can disturb soil to about 25 cm (Logsdon et al., 1990).

Macroporosity was determined by measuring steady-state infiltration rate from a tension infiltrometer at zero tension and at a tension \( h \) of 3 cm of water to exclude transport in pores greater than 0.05 cm radius. The minimum macropore radius (0.05 cm) not to conduct flow \( R_{\text{min}} \, \text{cm} \) under tension was calculated from the capillary equation

\[
R_{\text{min}} = \frac{2\gamma \cos \theta}{g(p_1 - p_g)h} = -0.15/h
\]

Where \( \gamma \) is surface tension, \( \theta \) is contact angle (assumed to be 0), \( g \) is acceleration due to gravity, \( p_1 \) is density of water and \( p_g \) is density of air (assumed to be 0). Total "hydraulically active" macroporosity \( M, \text{cm}^3 \text{ cm}^{-3} \) was computed using Poiseuille' law

\[
M = \frac{8\mu \Delta K}{(g \rho_1 R^2)}
\]

Where \( \mu \) is viscosity of water, \( \Delta K \) is the infiltration rate difference between ponded and 3 cm tension, and \( R \) is the assumed mean radius for percolate-producing macropores between 0 and 3 cm tension \( R=0.15 \, \text{cm} \). Eq. (2) assumes laminar flow (no turbulence), macropores are completely full and not interconnected, and tortuosity and pore necks are insignificant. Because of the assumptions, the resulting \( M \) is merely an equivalent value, not a true macropore volume fraction. This equivalent value, while not completely accurate, can provide a relative estimate (Logsdon et al., 1993b) for “hydraulically active” macropores (Watson and Luxmoore, 1986; Wilson and Luxmoore, 1988) over small depths (Logsdon, 1997). The number of macropores \( N \) was then calculated from

\[
N = M/(\pi R^2)
\]

Details of converting tension infiltrometer data into number of macropores is presented in Watson and Luxmoore (1986) and Wilson and Luxmoore (1988). Details concerning tension infiltrometer measurement depth, measurement date and management date (e.g.,
Table 1
Description of soils used for calculation of number of hydraulically active macropores from tension infiltrometer data (measurements were at 0 and 15 or 35 cm below soil surface)

<table>
<thead>
<tr>
<th>Soil</th>
<th>Soil classification</th>
<th>Tillage (number of observations) [publication]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Well-drained soils</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clarion silt loam</td>
<td>fine-loamy, mixed, superactive, mesic Typic Hapludoll</td>
<td>RT6(2); CT4(0); DK2(2) [a, d]⁠¹</td>
</tr>
<tr>
<td>Ida silt loam</td>
<td>fine-silty, mixed, superactive, calcareous, mesic Typic Udorthent</td>
<td>RT2; DK2 [a]</td>
</tr>
<tr>
<td>La Rose silt loam</td>
<td>fine-loamy, mixed, active, mesic Typic Argiudoll</td>
<td>NT2; CT2 [a]</td>
</tr>
<tr>
<td>Marshall silt loam</td>
<td>fine-silty, mixed, superactive, mesic Typic Argiudoll</td>
<td>RT2; DK2 [a]</td>
</tr>
<tr>
<td>Tama silt loam</td>
<td>fine-silty, mixed, superactive, mesic Typic Argiudoll</td>
<td>NT6; CT6; RT6 [a]</td>
</tr>
<tr>
<td>Waukegan silt loam</td>
<td>fine-silty over sandy, mixed mesic Typic Hapludoll</td>
<td>MP2, 6; NT2, 4 [b]²</td>
</tr>
<tr>
<td><strong>Moderately well-drained soils</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kennebec silt loam</td>
<td>fine-silty, mixed, superactive, mesic Cumulic Hapludoll</td>
<td>RT2; DK2 [a]</td>
</tr>
<tr>
<td>Kenyon loam</td>
<td>fine-loamy, mixed, superactive, mesic Typic Hapludoll</td>
<td>NT2; CT2; MP2; RT2 [c]</td>
</tr>
<tr>
<td>Napier silt loam</td>
<td>fine-silty, mixed, superactive, mesic Cumulic Hapludoll</td>
<td>RT2; DK2 [a]</td>
</tr>
<tr>
<td>Saybrook silt loam</td>
<td>fine-silty, mixed, superactive, mesic Oxyaquic Argiudoll</td>
<td>NT4; CT4 [a]</td>
</tr>
<tr>
<td><strong>Somewhat poorly drained</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flanagan silt loam</td>
<td>fine, smectitic, mesic Aquic Argiudoll</td>
<td>NT2; CT2 [a]</td>
</tr>
<tr>
<td>Floyd loam</td>
<td>fine-loamy, mixed, superactive, mesic Aquic Argiudoll</td>
<td>NT1; CT1; MP1; RT1 [c]</td>
</tr>
<tr>
<td>Lisbon silt loam</td>
<td>fine-silty, mixed, mesic Aquic Argiudoll</td>
<td>NT2; CT2 [a]</td>
</tr>
<tr>
<td>Nicollet clay loam</td>
<td>fine-loamy, mixed, mesic Aquic Hapludoll</td>
<td>NT3; CT3; RT5; MP3; DK2 [a, c]</td>
</tr>
<tr>
<td>Readlyn loam</td>
<td>fine-loamy, mixed, superactive, mesic Aquic Hapludoll</td>
<td>NT2; CT2; MP2; RT2 [c]</td>
</tr>
<tr>
<td><strong>Poorly and very poorly drained soils</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Canisteo silty clay loam</td>
<td>fine-loamy, mixed, superactive, calcareous, mesic Typic Endoquoll</td>
<td>NT4; CT4; RT6; DK2 [a]</td>
</tr>
<tr>
<td>Drummer silty clay loam</td>
<td>fine-silty, mixed, superactive, mesic Typic Endoquoll</td>
<td>CT2; NT2 [a]</td>
</tr>
<tr>
<td>Harps clay loam</td>
<td>fine-loamy, mixed, superactive, mesic Typic Calciaquoll</td>
<td>RT2; DK2 [a]</td>
</tr>
<tr>
<td>Okoboji silty clay loam</td>
<td>fine, smectitic, mesic Cumulic Vertic Endoquoll</td>
<td>RT2; DK2 [a]</td>
</tr>
<tr>
<td>Webster silty clay loam</td>
<td>fine-loamy, mixed, superactive, mesic Typic Endoquoll</td>
<td>NT38, 6; CT38, 6; RT38, 6 [a, c]</td>
</tr>
</tbody>
</table>
latest tillage/cultivation before measurement), and tension infiltrometer methods can be found in the publications listed in Table 1. The previously unpublished data for the Readlyn, Floyd and Kenyon loam soils are from the same fields as Logsdon et al. (1993a); the previously unpublished data for the Nicollet clay loam are from one of the same plots described in Logsdon and Kaspar (1995). The disk permeameters were either 23 or 7.6 cm, but base size has little affect on unsaturated hydraulic conductivity (Logsdon, 1993). Most measurements were made in undisturbed areas with little wheel traffic.

The time between tension infiltrometer measurement and the last cultivation/tillage ranged between 1 and 100 days. This time is important because rainfall can rapidly reconsolidate tilled soil to near its condition before tillage (Ahuja et al., 1998). The time range likely adds variability to the data, but the time range was probably random between tillage practices and drainage classes. If bias were present, it is unlikely that it was significant because of spatial variability and other factors (Logsdon, 1993; Logsdon et al., 1993a). Our goal was simply to determine if clear macroporosity differences between Midwest tillage practices or soils could be detected by reviewing several tension infiltrometer studies.

2.1. Discussion of tension infiltrometer data

There was no clear trend for the number of active macropores measured using tension infiltrometer data between tillage practices (Table 2). For example, the mean surface numbers of macropores were 0.055 cm\(^{-2}\) for MP and 0.039 cm\(^{-2}\) for NT; subsurface values were 0.021 (NT) and 0.019 cm\(^{-2}\) (MP). Other research found little relation between soil management practices and the number of hydraulically active macropores measured with tension infiltrometers (Azevedo et al., 1998) and dye staining techniques (Droogers et al., 1998). The overall average was 0.022 macropores cm\(^{-2}\) for subsurface soil and 0.032 cm\(^{-2}\) for surface soil (Table 2). The overall averages are within the range of percolate producing macropores at 30 cm (nmacro) as reported by Shipitalo and Edwards (1996) for silt loam soil at intermediate and wet antecedent soil water (nmacro of 0.016–0.059 cm\(^{-2}\)). This might suggest that percolate-producing macroporosity at a 30-cm depth (nmacro) for RZWQM input can be estimated from hydraulically active subsurface macroporosity determined by tension infiltrometers. This also suggests that 0.02 cm\(^{-2}\) may be a reasonable first estimate for nmacro when working with structured soils.

Surface soil macropore numbers were slightly greater (0.032 cm\(^{-2}\)) than subsurface soil (0.022 cm\(^{-2}\)). This trend was also observed for MP and NT soils (Table 2). Other research suggests that the number of hydraulically active macropores may decrease with depth (Droogers et al., 1998; Ghodrati and Jury, 1990; Trojan and Linden, 1998).

Notes to Table 1:

\(a\) The number of observations was the same for surface and subsurface measurements unless indicated (e.g., Clarion RT soil had six surface observations and two subsurface observations, while the Ida RT soil had two surface and two subsurface observations).
Our main goal in this section was to determine if a clear difference in the number of hydraulically active macropores could be detected under different tillage practices for a variety of Midwest soils. We investigated hydraulically active macropores because Malone et al. (2001) assessed the macropore component of RZWQM using data from Shipitalo and Edwards (1996) and concluded that using total visible macroporosity for model input could substantially under predict pesticide transport through macropores. Shipitalo and Edwards (1996) measured $n_{macro}$ of 0.019 cm$^{-2}$ on the intermediate soil water blocks but reported 0.08 cm$^{-2}$ visible macropores. Furthermore, using image analysis on similar MP and NT soils as in Table 1, Logsdon et al. (1990) determined mean subsurface (15 or 25 cm deep) macropore quantity of 0.054 cm$^{-2}$, compared with 0.020 cm$^{-2}$ determined from tension infiltrometers (Table 2, MP and NT soils only). Other research suggests that active macroporosity is a small fraction of total visible macroporosity (Trojan and Linden, 1992; Villholth et al., 1998). The sensitivity of RZWQM predicted herbicide concentration in percolate to $n_{macro}$ is briefly discussed below in Section 5.2.2.

There are limitations associated with using tension infiltrometers to characterize hydraulically active macroporosity (Cameira et al., 2000; Timlin et al., 1994; Close et al., 1998; Villholth et al., 1998; Trojan and Linden, 1998; Logsdon, 1995). For example, tension infiltrometer measurements include flow in dead-end macropores that are continuous through the depth of wetting. Because tension infiltrometers wet only a small and ill-defined soil depth (Logsdon, 1997), possibly 5–7 cm, tension infiltrometer measurements do not represent continuous macroporosity for soil profiles (Timlin et al., 1994). Also, Villholth et al. (1998) observed that tension infiltrometer measurements may under predict total active macroporosity compared to dye studies, possibly because water

### Table 2

<table>
<thead>
<tr>
<th>Tillage</th>
<th>WD</th>
<th>MWD</th>
<th>SPD</th>
<th>PD</th>
<th>Mean$^{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0–1 cm depth</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moldboard</td>
<td>0.003</td>
<td>0.066</td>
<td>0.097</td>
<td>na</td>
<td>0.055</td>
</tr>
<tr>
<td>Disk</td>
<td>0.016</td>
<td>0.003</td>
<td>0.020</td>
<td>0.007</td>
<td>0.011</td>
</tr>
<tr>
<td>Chisel</td>
<td>0.014</td>
<td>0.018</td>
<td>0.043</td>
<td>0.021</td>
<td>0.024</td>
</tr>
<tr>
<td>Ridge</td>
<td>0.022</td>
<td>0.026</td>
<td>0.046</td>
<td>0.018</td>
<td>0.028</td>
</tr>
<tr>
<td>No-till</td>
<td>0.033</td>
<td>0.036</td>
<td>0.070</td>
<td>0.016</td>
<td>0.039</td>
</tr>
<tr>
<td>Mean$^{b}$</td>
<td>0.018</td>
<td>0.030</td>
<td>0.055</td>
<td>0.015</td>
<td>0.032$^{c}$</td>
</tr>
</tbody>
</table>

|        | 15- or 35-cm depth |      |      |      |            |
| Moldboard | 0.001 | 0.037 | 0.020 | na  | 0.019 |
| Disk     | 0.028 | 0.018 | 0.007 | 0.003 | 0.014 |
| Chisel   | 0.046 | 0.016 | 0.035 | 0.031 | 0.032 |
| Ridge    | 0.009 | 0.040 | 0.029 | 0.012 | 0.023 |
| No-till  | 0.018 | 0.015 | 0.035 | 0.017 | 0.021 |
| Mean$^{b}$ | 0.020 | 0.025 | 0.025 | 0.016 | 0.022$^{c}$ |

WD is well drained, MWD is medium well drained, SPD is somewhat poorly drained and PD is poorly drained.

$^{a}$ Computed assuming each tillage-drainage value (e.g., 0.046 macropores cm$^{-2}$ for chisel, WD) is representative of that combination.

$^{b}$ Overall mean for 0–1 cm soil.

$^{c}$ Overall mean for 15 or 35 cm soil.
flux rate per macropore is overestimated. That is, macropore constrictions, tortuosity of flow and air entrapment may reduce flow rate of some active macropores, which leads to low calculations of total active macroporosity using Poiseuille’s equation and tension infiltrometer data.

Despite the limitations associated with using tension infiltrometers to estimate active macroporosity, the estimates in Table 2 are useful in a relative sense (Logsdon et al., 1993b) and they suggest no clear trend between tilled and no-till soils. It is counterintuitive that till and no-till soils have the same quantity of active macropores but the reason for this is unclear. It could be that tillage destroys some active macropores and creates some active macropores with no clear net loss or gain. Further research and new methods are needed to characterize hydraulically active continuous macropores in whole soil profiles, as well as noncontinuous and dead-end macropores in different soil horizons.

3. RZWQM description

A brief description of simulated chemical transport using the RZWQM is included so that the model parameterization and the discussion are understandable. More complete model descriptions are presented elsewhere (Ahuja et al., 2000). The RZWQM simulates water and pesticide movement during rainfall or irrigation as follows:

- rainfall, irrigation and chemicals are received by the soil surface, plant foliage and surface residue;
- rainfall or irrigation exceeding the soil matrix infiltration rate becomes overland flow and enters macropores;
- overland flow exceeding both the maximum macropore flow capacity and soil matrix infiltration rate becomes surface runoff;
- a portion of the chemicals on the top 2 cm of the surface soil, plant foliage, and crop residue are extracted and transferred to overland flow and macropore flow;
- as chemicals move through the macropores they interact with the soil surrounding the macropore walls, and a portion of the water and chemicals radially infiltrate into the soil matrix.

3.1. Soil matrix water processes

The RZWQM simulates water infiltration into the soil matrix using the Green-Ampt equation and water redistribution using the Richards’ equation. The modified Green-Ampt equation may be described by

\[
V = \frac{K_s(h_c + h_o + Z_{wf})}{Z_{wf}}
\]

where \( V \) = soil matrix infiltration rate during a time increment (cm h\(^{-1}\)); \( K_s \) = effective saturated hydraulic conductivity of the wetting zone (cm h\(^{-1}\)); \( h_c \) = capillary suction at the
wetting front (cm); \( h_0 \) = depth of ponding, if any (cm); \( Z_{wf} \) = depth of the wetting front (cm). The \( K_s \) is equal to the saturated hydraulic conductivity \( (K_s) \) for homogeneous soils or equal to the harmonic mean \( K_s \) of the wetting zone for nonhomogeneous soils. Thus, the \( K_s \) may change from time increment to time increment. At times, the infiltration rate will be higher than the rainfall rate and set equal to the rainfall rate.

One of the challenges of the Green-Ampt infiltration approach is determining the capillary suction, \( h_c \), which may be determined by

\[
h_c = \frac{-\int_0^{h_n} K(h) dh}{K_s}
\]

where \( h_n \) is the soil suction corresponding to the average initial soil water content of the soil horizon and \( K(h) \) is the unsaturated hydraulic conductivity as a function of suction (see Eqs. (9) and (10) below).

Soil hydraulic properties are described with a modification of the Brooks-Corey equation

\[
\theta(h) = \theta_s \quad 0 \leq h \leq h_b
\]

\[
\theta(h) = \theta_r + B h^{-\lambda} \quad h \geq h_b
\]

where \( \theta \) is volumetric soil water content \((\text{cm}^3 \text{ cm}^{-3})\); \( h \) is the soil water suction (cm); \( \theta_s \) and \( \theta_r \) are saturated and residual water contents, respectively \((\text{cm}^3 \text{ cm}^{-3})\); \( h_b \) is the air-entry or bubbling suction (cm); \( \lambda \) is the pore size distribution index (dimensionless); and \( B \) is a dimensionless constant calculated from:

\[
B = (\theta_s - \theta_r) h_b^{-\lambda}
\]

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

\[
K(h) = K_s; \quad 0 \leq h \leq h_{bk}
\]

\[
K(h) = C_2 h^{-N_2}; \quad h \geq h_{bk}
\]

where \( h_{bk} \) is the air-entry or bubbling suction (cm) for the hydraulic conductivity relationship; \( N_2 = 2 + 3 \lambda \) (Kutilek and Nielsen, 1994; Ahuja et al., 2000); and \( C_2 = K_s (h_{bk})^{N_2} \).

Eqs. (4)–(10) may be solved if reasonable estimates are available for \( K_s, \theta_s \) (soil porosity), \( h_b \) (e.g., Rawls et al., 1982), \( \lambda, \theta_r \) (e.g., Rawls et al., 1982), \( h_{bk} = h_b \) (Ahuja et al., 2000).

3.2. Macropore processes

If the rainfall rate exceeds the soil matrix infiltration rate during a time increment, the excess is considered overland flow and transported into macropores to the limit of
macropore flow determined by Poiseuille’s law described above. The water entering macropores is evenly distributed among macropores. It has been observed, however, that not all macropores produce percolate and some macropores produce only a very small amount (e.g., Quisenberry et al., 1994). Malone et al. (2001) concluded that percolate-producing macroporosity ($P_{mac}$, cm$^3$ cm$^{-3}$) was an important RZWQM parameter for long-term no-till corn and recommended using half of percolate-producing (hydraulically active) macroporosity at a 30-cm soil depth ($P_{mac}^*$)

$$P_{mac}^* = 0.5n_{macro}(\pi \times r_p^2)$$  \hspace{1cm} (11)

where $n_{macro}$ is the number of percolate-producing macropores per soil area (cm$^{-2}$) at 30-cm depth and $r_p$ is the average radius of percolate-producing macropores (cm). The parameter $n_{macro}$ affects both the maximum flow rate through macropores (Poiseuille’s law) and sorption to macropore walls (Eq. (13) below). Overland flow in excess of maximum macropore flow is routed to surface runoff, but in our modeling scenarios (described below) no runoff was observed or simulated. The $r_p$ mostly affects maximum flow rate through macropores and to a lesser extent chemical sorption to macropore walls (Poiseuille’s law and Eq. (13)).

Compaction along macropore walls may reduce lateral infiltration (Ahuja et al., 1995)

$$V_{r}^* = SFCT \times V_{r}$$  \hspace{1cm} (12)

where $V_{r}$ is the lateral infiltration rate without compaction (cm h$^{-1}$) determined using the lateral Green-Ampt equation (Ahuja et al., 1993) and SFCT is a dimensionless reduction factor. Ahuja et al. (1995) observed that an SFCT of 0.1 produced reasonable results.

Chemicals in macropore flow react with the soil walls according to partition theory (described below). Water and chemicals vertically moving through macropores mix and react with a user defined radial length of the macropore wall. Malone et al. (2001) called this the effective soil radius (ESR) and found that 0.6 cm produced good simulations for silt loam soil in long-term no-till corn. The ESR of 0.6 cm assumes (1) greater partitioning between soil and pesticides in natural macropores than in the total soil matrix, (2) blockage and tortuosity of natural macropores and (3) lateral water movement through soil into macropores rather than just ponded water movement into macropores as simulated by RZWQM (Malone et al., 2001; Stehouwer et al., 1993; Stehouwer et al., 1994). The soil volume, surrounding macropores available for sorption of chemicals per total soil volume at each 1-cm depth increment of soil, is then

$$W_{VOL} = \pi 0.5n_{macro}[(r_p + ESR)^2 - r_p^2]$$  \hspace{1cm} (13)

### 3.3. Chemical partitioning and chemical transfer to overland flow

Assuming that herbicide sorption to soil is linear and instantaneous, the amount adsorbed to soil ($C_{ad}$, $\mu$g g$^{-1}$) may be expressed as $C_{ad} = K_d C_{sol}$, where $K_d$ (ml g$^{-1}$) is the partition coefficient and $C_{sol}$ ($\mu$g ml$^{-1}$) is the chemical concentration in solution. The partition coefficient for various chemicals and soils may be estimated from the literature (e.g., Wauchope et al., 1992). Another technique is to directly measure $K_d$ using batch type procedures (e.g., Roy et al., 1992). 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 $K_d$ is often expressed relative to organic carbon ($K_{oc} = K_{doc}/C_{o1}$), where $C_{oc}$ is the mass of organic carbon per mass of soil (g g$^{-1}$).

Chemicals are transferred to overland flow from plant foliage and mulch (crop residue) by washoff (Wauchope et al., 2000)

$$C_f = 0.01C_o(100 - F) + 0.01C_oF(e^{-Pi})$$

where $C_f$ is the chemical concentration remaining on mulch or foliage ($\mu g$ ha$^{-1}$) after an incremental rainfall of intensity $i$ (cm h$^{-1}$) and time $t$ (h); $C_o$ is the initial concentration on mulch and foliage at the beginning of each time increment ($\mu g$ ha$^{-1}$); and $P$ and $F$ are dimensionless washoff parameters.

Chemical transferred from soil surface to overland flow and macropore flow by rainfall impact is assumed to occur within the top 2 cm of soil, and contribution decreases exponentially within this depth increment (0–2 cm). This can be expressed as the nonuniform mixing model (Ahuja, 1986),

$$M_{ave} = e^{-B1Z}$$

where $M_{ave}$ = average degree of mixing for depth increment between rainfall and soil solution; $B1$ = constant; $Z$ = center of depth increment (0.5 or 1.5 cm). The chemical is transferred to rainwater each time increment and may be determined using a mass balance approach (Heathman et al., 1986).

4. Materials and methods

4.1. Soil block data

Data from Granovsky et al. (1993) was used to investigate the effect of tillage on macroporosity and pesticide transport through soil. In this study, an intense simulated rainfall was applied shortly after chemical application. These conditions often result in high pesticide concentrations in percolate and the later rainfalls are generally less important because concentrations are lower (Kladivko et al., 1991; Shipitalo et al., 1990, 2000). The data set of Granovsky et al. (1993) was used for several reasons: (1) two pesticides with different soil adsorption properties were applied; (2) the areas at the base of the blocks that produced percolate were recorded; and (3) two tillage systems were included (till and no-till).

The soils investigated were a Crosby silt loam (fine, mixed, active, mesic Aeric Epiaqualf) and Wooster silt loam (fine-loamy mixed mesic Oxyaquic Fragiudalf). Twelve 30 × 30 × 30 cm blocks of undisturbed silt loam soil were collected in 1990 from plots that had been planted in long-term NT or MP corn (Zea mays L.) using procedures similar to Shipitalo et al. (1990). Three replicates of each soil-tillage combination were collected. The MP Wooster soil was plowed four weeks prior to sampling; the MP Crosby soil was plowed the previous fall and shallow disked before sampling. The size, number and
position of visible macropores at 30 cm were recorded for each block. Atrazine and alachlor were surface applied at rates equivalent to 8.5 and 4.0 kg ha\(^{-1}\) a.i. A 0.5-h, 3-cm simulated rainfall was applied approximately 1 h after herbicide application. Percolate was collected from each cell of a 64 square grid at the bottom of the soil blocks (3.75 × 3.75 cm). For each cell, collection bottles were changed if they filled during an experiment (about 130 ml increments) and the time to the first appearance of water in each bottle was recorded. Concentrations of atrazine and alachlor were determined using gas chromatography. Details on the rainfall simulator, 64 square grid percolate collection system and herbicide analysis methods can be found in Shipitalo et al. (1990) and Shipitalo and Edwards (1996).

4.2. Modeling experiment

The number of percolate-producing macropores (Table 3, \(n_{macro}\)) from the undisturbed soil blocks were determined assuming one continuous macropore (0.15–cm radius) per percolate-producing cell from the 64 square grid (Malone et al., 2001). Dead-end macropores were not simulated. Some of the percolate-producing cells did not have visible macropores, but Allaire-Leung et al. (2000a) concluded that macropores closed at the bottom of a soil column cannot be neglected in modeling chemical transport. Granovsky et al. (1993), however, only included visible macropores for computing percolate-conducting macropore area. We did not simulate tillage using the model because in the current version of the model, macropores are destroyed during tillage. That is, any tillage effects were simulated using directly input soil parameters (measured, estimated and calibrated parameters).

The partition coefficients (\(K_d\)) were determined for two MP and two NT Crosby soil plots by mixing 20 ml of alachlor and atrazine spiked solution and 10 g of oven dried soil for approximately 24 h in teflon centrifuge tubes. The 0–15-cm soil was obtained for \(K\_{oc}\) (\(K_d/\text{oc}\)) determination in year 2000 for the NT soil and in 2001 for the MP soil. Initial concentrations were 5, 3, 2, 1 and 0.5 \(\mu\)g ml\(^{-1}\) for atrazine and 1.0, 0.6, 0.4, 0.2 and 0.1 \(\mu\)g ml\(^{-1}\) 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 (\(R^2>0.90\)) and the \(K_d\) values were similar among plots (Fig. 1). The atrazine \(K_{oc}\) values were slightly greater for the NT plots than the MP plots (Table 3).

The nonuniform mixing parameter (\(B1\)) was estimated to be less for MP than NT. This has the effect of increasing the simulated mixing between the soil mixing zone (0–2 cm) and rainfall for MP soils, which then increases pesticide concentration in overland flow extracted from soil mixing zone (0–2 cm). Using a lower \(B1\) for MP simulates more soil mixing, which is reasonable because the NT surface mulch reduces rainfall mixing with the topsoil. The nonuniform mixing parameter for NT was input as determined by Malone et al. (2001) on long-term no-till soil.

The average macropore radius (\(r_p\)) was determined to be 0.15 cm (NT) from the observations of Granovsky et al. (1993). The \(r_p\) for MP was input as 0.05 cm because Malone et al. (in preparation) adjusted macropore radius to achieve accurate RZWQM simulated runoff and percolate volumes compared to field observations on soil tilled within 1 year, and the calibrated values were between 0.03 and 0.06 cm. Varying
Table 3
Selected RZWQM input parameters and measured data for the Crosby and Wooster soil

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Crosby silt loam</th>
<th>Wooster silt loam</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NT</td>
<td>MP</td>
<td>NT</td>
</tr>
<tr>
<td><strong>Measured data</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of percolate producing macropores (nmacro, cm⁻²)</td>
<td>0.0063 (0.0056 – 0.0078)a</td>
<td>0.01 (0.0044 – 0.016)a</td>
<td>0.031 (0.021 – 0.042)a</td>
</tr>
<tr>
<td>Time to percolate breakthrough (min)</td>
<td>7.9 (5.5 – 11.2)a</td>
<td>21.6 (19.4 – 25.1)a</td>
<td>8.1 (5.3 – 10.8)a</td>
</tr>
<tr>
<td>Gravimetric soil carbon (%)</td>
<td>3.3 (0 – 3 cm)</td>
<td>0.9 (0 – 30 cm)</td>
<td>3.3 (0 – 3 cm)</td>
</tr>
<tr>
<td></td>
<td>1.4 (3 – 8 cm)</td>
<td></td>
<td>1.8 (3 – 8 cm)</td>
</tr>
<tr>
<td></td>
<td>0.7 (8 – 30 cm)</td>
<td></td>
<td>0.8 (8 – 30 cm)</td>
</tr>
<tr>
<td>Gravimetric soil water content (g g⁻¹)</td>
<td>0.23 (0.21 – 0.25)a</td>
<td>0.22 (0.19 – 0.25)a</td>
<td>0.38 (0.36 – 0.40)a</td>
</tr>
<tr>
<td>Partition coefficient (Koc, ml g⁻¹)</td>
<td>190 (alachlor)</td>
<td>190</td>
<td>190c</td>
</tr>
<tr>
<td></td>
<td>124 (atrazine)</td>
<td>106</td>
<td>124c</td>
</tr>
<tr>
<td><strong>Estimated input parameters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-uniform mixing parameter (B1, cm⁻¹)</td>
<td>6</td>
<td>4.4</td>
<td>6</td>
</tr>
<tr>
<td>Effective macroporosity (Pmac*, cm³ cm⁻³)</td>
<td>2.2e – 4</td>
<td>3.9e – 5</td>
<td>1.1e – 3</td>
</tr>
<tr>
<td></td>
<td>2.4 (0 – 3 cm)</td>
<td>2.55 (0 – 25 cm)</td>
<td>2.4 (0 – 3 cm)</td>
</tr>
<tr>
<td></td>
<td>2.5 (3 – 8 cm)</td>
<td>2.6 (25 – 30 cm)</td>
<td>2.5 (3 – 8 cm)</td>
</tr>
<tr>
<td></td>
<td>2.55 (8 – 30 cm)</td>
<td></td>
<td>2.55 (8 – 30 cm)</td>
</tr>
</tbody>
</table>
Porosity ($\theta_s$, cm$^3$ cm$^{-3}$) & 0.42 (3–8 cm) & 0.45 (0–25 cm) & 0.48 (3–8 cm) & 0.51 (0–25 cm) & computed from estimated particle density and calibrated bulk density \\
& 0.41 (8–30 cm) & 0.44 (25–30 cm) & 0.46 (8–30 cm) & 0.50 (25–30 cm) & \\
Field capacity at a tension of 333 cm of water (cm$^3$ cm$^{-3}$) & 0.36 (0–3 cm) & 0.30 (0–25 cm) & 0.36 (0–3 cm) & 0.34 (0–25 cm) & soil >3 cm assumed to remain relatively constant between MP and NT (Ahuja et al., 1998) \\
& 0.30 (3–8 cm) & 0.30 (25–30 cm) & 0.35 (3–8 cm) & 0.33 (25–30 cm) & \\
& 0.30 (8–30 cm) & 0.33 (8–30 cm) & & & \\

| Calibrated input parameters | Bulk density (Mg m$^{-3}$) | 1.20 (0–3 cm) | 1.40 (0–25 cm) | 1.20 (0–3 cm) | 1.25 (0–25 cm) |
| | 1.45 (3–8 cm) | 1.45 (25–30 cm) | 1.30 (3–8 cm) | 1.30 (25–30 cm) & Crosby values reasonable compared to Mahboubi et al. (1993); Wooster values reasonable compared to data of Granovsky et al. (1993). 
| | 1.50 (8–30 cm) & 1.38 (8–30 cm) | & | |

Pore distribution index ($\lambda$) & 0.12 & 0.15 & 0.12 & 0.15 & trend of higher $\lambda$ for MP soil agrees with Ahuja et al. (1998); see Fig. 4 

Soil matrix saturated hydraulic conductivity ($K_s$, cm h$^{-1}$) & 5.0 (0–8 cm) & 4.0 (0–30 cm) & 3.0 (0–8 cm) & 2.0 (0–30 cm) & the lower $K_s$ for subsurface NT soil may be due to more consolidation and lower soil carbon compared to the surface soil 

| & 2.5 (8–30 cm) & 1.2 (8–30 cm) & | & |

---

*a Range of three replicates.

*b Jeanne Durkalski, School of Natural Resources, Ohio State University, Wooster, OH, personal communication (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.
A macropore radius between 0.05 and 0.15 cm has little affect on RZWQM simulated chemical transport through macropores when water transport is accurately simulated (see Eq. (13)). Using a smaller radius for tilled soil may account for constrictions and tortuosity in tilled macropores that reduce maximum macropore flow and increase surface runoff (Eqs. (2) and (3)).

Other input parameters that weren’t calibrated include 0.1 for SFCT (Ahuja et al., 1995); $h_b$ of 20 cm (Rawls et al., 1982); $\theta_i$ of 1.5% (Rawls et al., 1982); dimensionless pesticide washoff parameter ($F$) for NT corn mulch of 80 for alachlor and atrazine (Malone et al., 2001); dimensionless pesticide washoff parameter ($P$) for NT corn mulch of 0.45 for alachlor and 0.15 for atrazine (Malone et al., 2001); ESR of 0.6 cm (Malone et al., 2001); mulch at 5.0 Mg ha$^{-1}$ for Crosby and Wooster NT soil; and herbicide applications rates of 4 kg ha$^{-1}$ (alachlor) and 8.5 kg ha$^{-1}$ (atrazine). Estimated initial volumetric soil water content of the blocks were 0.34, 0.34, 0.38 and 0.40 cm$^3$ cm$^{-3}$ for Crosby MP, Crosby NT, Wooster MP and Wooster NT, respectively. The initial volumetric soil water content was estimated based on gravimetric soil water content (Table 3) as reported by Granovsky et al. (1993).

Three parameters were calibrated (bulk density, pore size distribution index and saturated hydraulic conductivity). These parameters were adjusted to reduce the difference between simulated and observed water transport-percolate breakthrough time and total percolate collected. The model was then tested for simulated pesticide concentration in percolate. This calibration and testing procedure was similar to Malone et al. (2001) and is acceptable because calibration and testing data are different. Herbicide concentration was used for testing, hydrology data was used for calibration.
5. Results and discussion

5.1. Soil block results

Analyzing nmacro of the undisturbed soil blocks (Table 3) using two-factor analysis of variance indicated no significant difference in the number of percolate-producing macropores between NT and MP \((p = 0.3)\), but a significant difference was detected between the Wooster and Crosby soils \((p < 0.001)\). Analyzing the time to first appearance of water in percolate for each soil block (time to breakthrough, min, Table 3) using two-factor analysis of variance reveals a significant difference between NT and MP \((p < 0.001)\) but no difference between Wooster and Crosby soil \((p = 0.5)\). Because of the significance of breakthrough time between tillage practices and the number of percolate-producing macropores between soils (nmacro), we investigated the effect of these variables on flow-weighted herbicide concentration using multiple linear regression (Fig. 2). The regression equations used to produce Fig. 2 are:

\[
\text{atrazine concentration} = 7.7 - 0.26\text{(time to breakthrough)} - 0.020\text{(nmacro)}
\]

\[
\text{alachlor concentration} = 0.58 - 0.020\text{(time to breakthrough)} - 0.0036\text{(nmacro)}
\]

Time to breakthrough \((p < 0.001)\) and nmacro \((p < 0.05)\) significantly affected alachlor concentration, and time to breakthrough significantly affected atrazine concentration \((p < 0.001)\). If nmacro were removed from the regression, \(R^2\) is reduced from 0.85 to 0.83 for atrazine and from 0.87 to 0.77 for alachlor. It is reasonable that nmacro has more

Fig. 2. Correlation between observed flow-weighted herbicide concentration and predicted concentration using multiple linear regression (Eqs. (16) and (17)). The independent variables for Eqs. (16) and (17) are percolate breakthrough time and nmacro. The concentrations are relative to average (average atrazine and alachlor are 3.7 and 0.23 \(\mu g \text{ ml}^{-1}\)).
effect on alachlor in percolate because alachlor is more strongly sorbed to soil (Table 3, \(K_{\text{oc}}\)), and higher nmacro indicates more soil available for chemical sorption given a constant ESR and \(r_p\) (Eq. (13)).

The undisturbed soil blocks suggest no clear trend between till and no-till for nmacro (Table 3) and this is consistent with the tension infiltrometer studies (Table 2). The nmacro difference between Crosby and Wooster soils (Table 3) may be partly because of the higher average antecedent water content in the Wooster soil (0.34 kg kg\(^{-1}\); Granovsky et al., 1993) compared to the Crosby soil (0.23 kg kg\(^{-1}\); Granovsky et al., 1993). Using similar undisturbed silt loam soil blocks and apparatus as Granovsky et al. (1993), Shipitalo and Edwards (1996) observed that the number of cells contributing to flow was significantly greater with increasing antecedent soil water content. Kung et al. (2000a,b) also suggested that hydraulically active macropores may increase with soil wetting. The Wooster soil may have been wetter because rainfall within 7 days prior to obtaining the undisturbed blocks was 3.0 cm compared to 0.3 cm for the Crosby soil.

The time to percolate breakthrough difference between till and no-till (Table 3) and the significance of the regression equations suggest that percolate breakthrough timing is a key reason higher pesticide concentrations in percolate are often observed on no-till soils. This is also consistent with the modeling results to follow.

5.2. Modeling results

5.2.1. Model calibration

Because of the correlation between flow weighted herbicide concentration in percolate and percolate breakthrough time discussed above, we adjusted bulk density, pore size distribution index (\(\lambda\)) and soil matrix saturated hydraulic conductivity \(K_s\) to reduce the difference between simulated and observed percolate breakthrough time and total percolate amount collected (Fig. 3). If this calibration procedure results in good pesticide

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![Fig. 3. Observed and RZWQM simulated percolate amount as a function of time after rainfall initiation. Moldboard plow is MP; no-till is NT. The y-axis error bars represent the range of observed percolate amount; the x-axis error bars represent the range of observed percolate breakthrough time.](image-url)
transport simulations, it would provide additional evidence that time to breakthrough is a key reason for pesticide transport differences between till and no-till soils.

The simulated percolate volume with time follows observed percolate volume for Crosby (NT). In the case of the moldboard plow Crosby soil blocks (MP) and the Wooster soil blocks (MP and NT), collected percolate volume with time data was insufficient to compare with predicted, but simulated percolate breakthrough time and total percolate amount were within or nearly within the range of observations (Fig. 3).

A constraint adhered to in the soil parameter calibration process was to maintain relatively constant field capacity and bubbling pressure between MP and NT subsurface soils (3–30 cm), and higher porosity and pore size distribution index on MP soils (Table 3). This follows the trends between NT and MP observed by Ahuja et al. (1998) and results in the soil water retention curves in Fig. 4.

Mahboubi et al. (1993) investigated several soil properties on the same plots as Granovsky et al. (1993). The calibrated bulk density of Crosby NT is reasonable compared to measurements at 0–15 cm Crosby soil (traffic zone of plots, 1.43 Mg m$^{-3}$) made by Mahboubi et al. (1993) and at 0–30 cm (1.46 Mg m$^{-3}$) by Granovsky et al. (1993). The calibrated Wooster values (NT and MP) are low compared to Mahboubi et al. (1993), but the values match the measured bulk density of unpublished Granovsky et al. (1993) data (1.35 and 1.25 Mg m$^{-3}$ for NT and MP, respectively). The calibrated Crosby MP bulk density is high compared to Granovsky et al. (1993) data (1.28 Mg m$^{-3}$), but 1.40 Mg m$^{-3}$ was necessary to reasonably simulate percolate timing and amount (Fig. 3) and 1.40 Mg m$^{-3}$ was reasonable compared to 1.46 Mg m$^{-3}$ measured by Mahboubi et al. (1993).

Calibration of soil parameters for agricultural systems models can be an iterative process (Ma et al., in preparation). After a few iterations to establish pore size distribution index and bulk density, the soil matrix saturated hydraulic conductivity ($K_s$) was calibrated. Several combinations of $K_s$ values result in good hydrology simulations. We decided to minimize the number of $K_s$ values with depth and using two depths for NT (0–8 and 8–30 cm) and one depth for MP worked well. The MP soil may be more homogenous than the NT soil because moldboard plow can disturb soil to about 25 cm

![Soil water retention curves from calibrated and estimated parameters (bubbling pressure, bulk density, soil particle density and pore size distribution index). MP is moldboard plow and NT is no-till.](image-url)
The lower Wooster MP than Crosby MP \( K_s \) values were consistent with the observations of Mahboubi et al. (1993). The lower calibrated \( K_s \) for subsurface (8–30 cm) no-till soil may be due to more consolidation and lower soil carbon compared to the surface soil.

### 5.2.2. Model testing

For the most part, simulated herbicide concentrations are within the range of observations (Table 4). Also, the observed trends were generally simulated. For example, observed and simulated alachlor and atrazine concentrations in percolate are less on MP than NT and less on Wooster NT than Crosby NT.

Because the simulations are reasonable, using the measured percolate-producing macropores at 30 cm (nmacro) for modeling herbicide transport through macropores may be necessary for tilled soil as it was for long-term no-till soil (Malone et al., 2001). Also, if average nmacro from Crosby MP and NT are used for RZWQM input (0.0081 cm\(^{-2}\)), the simulated alachlor concentration in percolate drops from 0.60 to 0.55 \( \mu \text{g ml}^{-1} \) on NT and increases from 0.060 to 0.15 kg ha\(^{-1}\) for MP. These simulated values are still within the range of observations (Table 4). If, however, nmacro is increased to 0.031 (as for Wooster NT), alachlor concentration in percolate decreases to 0.001 \( \mu \text{g ml}^{-1} \) (Crosby NT) and 0.01 \( \mu \text{g ml}^{-1} \) (Crosby MP). If macropores are not simulated and soil matrix \( K_s \) is raised to 6.0 cm h\(^{-1}\) to prevent surface runoff on the MP soil blocks, simulated alachlor concentration is reduced to 0.015 \( \mu \text{g ml}^{-1} \) on Crosby MP and to 0.00 \( \mu \text{g ml}^{-1} \) on Wooster MP. It is clear that nmacro within the range observed on the blocks is necessary for accurate simulations for both NT and MP soils.

Although using nmacro for model input can be a successful modeling strategy for till and no-till soil, measuring or estimating this parameter is difficult due to our lack of understanding of the processes involved. The data presented suggest that antecedent soil water content (see Section 5.1) may affect nmacro more than tillage. Also, Malone et al. (2001) suggest that rainfall intensity may affect nmacro. This indicates that further study might be useful to determine how different conditions (antecedent water content, rainfall intensity, etc.) affect nmacro.

### Table 4

<table>
<thead>
<tr>
<th></th>
<th>Crosby soil</th>
<th>Wooster soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No-till</td>
<td>Moldboard plow</td>
</tr>
<tr>
<td>Percolate (cm)</td>
<td>2.0 (1.7–2.2)(^a)</td>
<td>1.85 (1.7–2.2)</td>
</tr>
<tr>
<td>Alachlor (µg ml(^{-1}))</td>
<td>0.42 (0.23–0.53)</td>
<td>0.60 (0.23–0.53)</td>
</tr>
<tr>
<td>Atrazine (µg ml(^{-1}))</td>
<td>6.1 (4.2–7.5)</td>
<td>4.7 (4.2–7.5)</td>
</tr>
</tbody>
</table>

\(^a\) Range of three replicates.
These modeling results are further evidence that nmacro differs little between till and no-till. Furthermore, they are additional evidence that percolate breakthrough timing is a key reason for pesticide transport differences between till and no-till. On the other hand, the tension infiltrometer data (Table 2) did not add insight into higher pesticide concentrations often observed on NT than MP. Indeed, the tension infiltrometer data suggest an increase in surface soil macropores from more intensive disk tillage to less intensive no-till (Table 2). If surface runoff is not simulated, however, more macropores for no-till would result in more soil volume for pesticide sorption (Eq. (13)) and lower RZWQM simulated pesticide concentration in no-till percolate than in tilled soil.

5.2.3. Timing of macropore flow

The higher simulated herbicide concentrations in percolate on NT compared to MP are mostly because of simulated macropore flow occurring sooner on NT. Flow is simulated to enter pores sooner mostly because of the interaction between infiltration rate ($V$), capillary suction at the wetting front ($h_c$), soil matrix saturated hydraulic conductivity ($K_s$) and the related soil parameters (e.g., $\lambda$ and $\theta_s$) in 8–30-cm depth soil (Eqs. (4)–(10)). The saturated soil wetting front reaches greater than 8-cm depth before macropore flow begins. Because the simulations fit the measured data reasonably well (Table 4), we investigated the importance of percolate breakthrough timing on simulated alachlor transport through macropores (Fig. 5).

Simulated overland flow (which immediately enters macropores) begins on Crosby NT at 0.08 h and begins on the Crosby MP ($K_s = 4.0 \text{ cm h}^{-1}$) at 0.20 h (Fig. 5b). The higher $K_s$, porosity ($\theta_s$) and pore size distribution index ($\lambda$) of Crosby MP at 8–30-cm depth contribute to higher soil matrix infiltration rate ($V$) and longer elapsed time before overland flow begins (Eqs. (4)–(10)). A sensitivity analysis indicates that as soil matrix $K_s$ is decreased and as pore size distribution index and porosity are both decreased in the Crosby MP soil, RZWQM simulated percolate breakthrough time decreases and alachlor concentration in percolate increases. The resulting total alachlor transport into macropores is 1.3 $\mu g \text{ cm}^{-2}$ for Crosby NT and 0.82 $\mu g \text{ cm}^{-2}$ for Crosby MP ($K_s = 4.0 \text{ cm h}^{-1}$) (Fig. 5d).

Timing of macropore flow affects herbicide concentration partly because shorter breakthrough time results in more pesticide transport into macropores. Decreasing soil matrix $K_s$ of the Crosby MP to 3.0 cm h$^{-1}$ reduces the time before overland flow begins from 0.20 to 0.13 h (Fig. 5b) and the total alachlor transport into macropores increases from 0.82 to 1.6 $\mu g \text{ cm}^{-2}$ (Fig. 5d). The resulting flow weighted percolate concentration simulated on the Crosby MP then increases from 0.060 to 0.58 $\mu g \text{ ml}^{-1}$ (Fig. 5c), about the same as Crosby NT (Table 4).

More factors than simply higher alachlor transport into macropores cause the higher simulated alachlor concentrations in percolate from NT and MP ($K_s = 3.0 \text{ cm h}^{-1}$) compared to MP ($K_s = 4.0 \text{ cm h}^{-1}$). For example, increasing the applied alachlor from 4 to 8 kg ha$^{-1}$ increases alachlor transport into Crosby MP macropores from 0.8 to 1.6 $\mu g \text{ cm}^{-2}$ (Fig. 5d) but the flow weighted percolate concentration at 30 cm only increases from 0.060 to 0.11 $\mu g \text{ ml}^{-1}$ (Fig. 5c). This is because higher simulated sorption on macropore walls (Fig. 6) along with the higher simulated alachlor concentration in
overland flow for Crosby (MP = 8.0 kg ha\(^{-1}\)) (Fig. 5a). Fig. 6 also illustrates that less alachlor is sorbed to NT macropore walls compared to the other simulations because the low alachlor concentration in overland (macropore) flow at the end of rainfall on NT results in desorption (Fig. 5a). The simulated alachlor concentration in overland flow on Crosby NT began relatively high and decreased rapidly because of washoff from corn mulch. After the alachlor washed off the corn residue, less mixing was simulated between soil and rainfall on NT because of the mulch (refer to Section 4.2).

Fig. 5. Effect of timing of water transport into macropores on alachlor transport through macropores as simulated by RZWQM (Crosby silt loam soil). NT is no-till; MP (\(K_s = 3.0\) cm h\(^{-1}\)) is moldboard plow with low saturated hydraulic conductivity; MP (\(K_s = 4.0\) cm h\(^{-1}\)) is moldboard plow with calibrated \(K_s\) (Table 2); MP (8.0 kg ha\(^{-1}\) alachlor applied) is moldboard plow with high alachlor application.
This suggests that tillage affects timing of macropore flow (i.e., overland flow) which controls RZWQM simulated pesticide concentrations in percolate. Table 3 shows that nmacro was not significantly different between tillage practices (NT and MP), but the time to percolate breakthrough was significantly different between NT and MP (see Section 5.1). Therefore, tillage may affect timing of macropore flow more than nmacro and have more affect on pesticide transport in percolate. Timing of rainfall and amount of rainfall relative to herbicide application can affect herbicide concentration in percolate and overland flow (Shipitalo et al., 1990; Flury, 1996; Wauchope, 1978). Few studies, however, report on the effect of timing of macropore flow within a storm on pesticide transport through macropores.

5.2.4. Soil properties

The modeling results reveal that subsurface soil properties (8–30 cm) affected by tillage ($K_s$, porosity, pore size distribution index; Table 3) can affect the timing of macropore flow during a storm and ultimately pesticide concentrations in percolate. The RZWQM calibration strategy included adjusting pore size distribution index ($\lambda$), bulk density ($\theta_s$) and $K_s$ while keeping field capacity and bubbling pressure relatively constant between tillage practices (MP and NT). Several other parameterization strategies are possible and a range of parameter combinations can result in accurate simulated water and herbicide transport. But most combinations of calibrated soil parameters that result in accurate timing of percolate breakthrough result in accurate simulated pesticide concentrations. The main point is that using reasonable and well-justified soil parameters that result in accurate timing of percolate breakthrough result in accurate simulated pesticide concentrations. The main point is that using reasonable and well-justified soil parameters that result in accurate timing of percolate breakthrough result in accurate simulated pesticide concentrations. The main point is that using reasonable and well-justified soil parameters that result in accurate timing of percolate breakthrough result in accurate simulated pesticide concentrations.

Fig. 6. RZWQM simulated alachlor sorbed to macropore walls at the end of rainfall on Crosby silt loam soil. Meaning of curve labels described in Fig. 5.
parameters as model input (see Section 5.2.1) suggests that soil property changes due to tillage can result in change in macropore flow timing and herbicide concentrations in percolate.

In addition to $K_s$, bulk density and pore size distribution, macropore tortuosity may affect timing of percolate breakthrough and adsorbed chemical breakthrough concentrations. Allaire-Leung et al. (2000b) observed that increased macropore tortuosity decreased percolation rate and increased chemical sorption. It is conceivable that water moves through more tortuous macropores on the tilled blocks compared to the no-till.

6. Conclusions

Tension infiltrometer data from several soils and tillage methods did not provide clear evidence supporting different hydraulically active macropores between tilled and no-till soils. Applying rainfall to undisturbed soil blocks and collecting the percolate at 30 cm revealed that: (1) the number of percolate-producing macropores ($n_{\text{macro}}$) did not differ between MP and NT; (2) the timing of initial percolate breakthrough was less for NT compared to MP ($p < 0.001$); and (3) $n_{\text{macro}}$ was less for Crosby compared to Wooster soils ($p < 0.001$). Multiple linear regression on the undisturbed soil block data (Eqs. (16) and (17)) revealed that as time to percolate breakthrough increased, alachlor and atrazine concentration in percolate decreased, and as $n_{\text{macro}}$ increased alachlor concentration in percolate decreased.

The RZWQM results provide further evidence that $n_{\text{macro}}$ does not change between tilled and no-till soil and that time of percolate breakthrough is a key reason for higher pesticide transport on no-till than on tilled soil. The RZWQM results also suggest that soil property differences (e.g., lower calibrated soil matrix $K_s$ and porosity on 8–30 cm NT soil) may be a controlling factor for percolate to occur sooner on NT than on MP. Macropore tortuosity may also be greater in tilled systems resulting in lower pesticide concentrations in percolate, but tortuosity was beyond the scope of this research. The modeling results also suggest that using continuous macropores that are open at the soil surface as RZWQM input for till and no-till soils produce accurate simulations. In the current version of the model, however, RZWQM destroys the continuity of macropores in the tilled zone during tillage and the macropores are allowed to slowly reform. As a result, RZWQM may under predict pesticide transport through macropores shortly after tillage if macropore flow actually occurs. Therefore, modifications of the model may be necessary.

More research is necessary to confirm that soil property differences between till and no-till ($K_s$, bulk density and possibly macropore tortuosity) result in different pesticide transport. Also, estimating $n_{\text{macro}}$ under different conditions (e.g., soils, antecedent water contents and rainfall intensity) is difficult due to our lack of understanding of the processes involved and more study in this area may be useful. Oreskes et al. (1994) suggest that 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. Overall, the tension infiltrometer data, the undisturbed soil block data and the modeling suggest that $n_{\text{macro}}$ may not differ between till and no-till; the undisturbed soil block data and the modeling suggest that percolate breakthrough
time in macropores during a storm may be a key reason for pesticide transport differences between till and no-till.

Acknowledgements

The authors appreciate the helpful comments provided by D. Jaynes and E. McCoy on an earlier version of the manuscript.

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