A Simple Equation for Predicting Preferential Flow Solute Concentrations
Tammo S. Steenhuis,* Jan Boll, Gil Shalit, John S. Selker, and Ian A. Merwin

ABSTRACT
The transport of pesticides and other chemicals through macropores has been widely observed and predicting it is a challenge. This article considers a simplified two-layer model, similar to overland flow models in which the processes of adsorption and desorption are separated. For the layer near the surface, or the mixing layer, the solute concentration is equal to that in the percolating water (including preferentially moving water). In the lower profile, the flow is partitioned between matrix and preferential flow. The solute concentration of the matrix flow is characterized by the soil condition near the outlet point, whereas the preferential flow is represented by the solute concentration in the mixing layer. The closed form equation, exhibiting exponentially decreasing macropore flow solute concentrations, is tested against solute breakthrough curves using three independent sets of experimental data. The predicted depths of mixing between 5 and 25 cm are physically realistic and the closed form is shown to reproduce the form of experimental data, particularly under conditions of significant macropore flow. Although highly simplified, the physically based model yields a framework for predicting solute concentration for preferentially moving water.

MANY STUDIES have found high concentrations of pesticides in tile lines or shallow groundwater shortly after application (Kladivko et al., 1991; Gish et al., 1991; Smith et al., 1990). High concentrations are associated with preferential flow through cracks in structured soils (Lawes et al., 1882), unstable wetting fronts (Hill and Parlane, 1972), and funnel flow (Kung, 1990a,b). Models based on the convective–dispersive equation (CDE), are unable to predict fast transport to the groundwater (Sposito et al., 1986; Steenhuis et al., 1994). Recently, models have been developed that attempt to include preferential flow transport (Steenhuis et al., 1990; Chen and Wagenet, 1992; Ahuja, 1991; Workman and Skaggs, 1990). However, these models are complicated and provide little insight into the critical processes governing the transport of chemicals through preferential flow paths. In this article, we develop a simple model to predict the solute concentration in preferentially moving water. We apply the model to data recently published by Czapar et al. (1992), Edwards et al. (1992), and our own experimental data.

THEORY
The following theory is based on the observations by Lawes et al. (1882) that water collected in drains (or solute samplers) can be separated into two constituents: preferential flow (direct drainage) and matrix flow (general drainage). As shown schematically in Fig. 1, rainfall enters a mixing zone where it mixes with the water and solutes in this layer. Water and solute loss from the mixing layer is as matrix or preferential flow. The preferential flow passes with little modification through the soil channels to the deeper soil or groundwater. The chemical composition of this water reflects, thus, the concentration of chemicals in water near the surface. Matrix flow is water that flows slowly through the soil while sampling all pore spaces, obeying the convective–dispersive equation.

To calculate the solute concentration of preferentially moving water, we make the assumption that water enters the macropores at or near atmospheric pressure (Phillips et al., 1989). Thus, surface runoff and macropore flow starts at the same time and we can equate the concentration in surface runoff to that in macropores (Jarvis et al., 1991). Concentrations of agrichemicals in runoff water have been modeled by a number of researchers (Havis et al., 1992; Heathman et al., 1986; Snyder and Woolhiser, 1985; Haith, 1980; Steenhuis and Walter, 1980; Wallach and van Genuchten, 1990; Wallach, 1991). The most recent models, such as by Wallach and coworkers, are most precise but also require the most input data. In this paper, we will be using a simpler (and therefore, less precise) model requiring only minimal input data because we are interested in explaining solute breakthrough curves in soils with preferential flow paths for which, otherwise, only little other specific data is known. We selected our earlier simple surface runoff model (Steenhuis and Walter, 1980), which was consistent with the conceptual framework of Lawes and coworkers (1882) discussed above. The model assumed that free water at the surface and percolating water mix with all or part of the water in a so-called mixing layer and that the adsorption and desorption characteristics of the chemical were the same. However, as we will see later, this assumption of similar adsorption and desorption behavior is not valid for pesticides moving in macropores.

In the following section, equations are derived for the solute concentration in preferentially moving water where the adsorption and desorption partition coefficients are different. As shown in Fig. 2, during the time that the mixing layer becomes saturated (Fig. 2a), adsorption of surface-applied solutes takes place in the mixing zone. Once the mixing layer becomes saturated (Fig. 2b), water and solutes are desorbed and released to the subsoil as preferential and matrix flow (Fig. 2c). For


mathematical convenience, we take the time, $t$, to be zero when water flow out of the mixing zone and desorption starts.

**Adsorption.** To find the analytical solution, we use the approach of Steenhuis and Walter (1980) that, after application, the solute is evenly distributed in the mixing zone with the infiltrating water. The initial concentration of the solute in the mixing zone, $C_w^0$, is then calculated as:

$$ C_w^0 = M^0 / [h_{mix} (m_s + \rho k_d)] $$  \[1\]

where $M^0$ (M/L) is the mass of solute applied per unit of land surface, $h_{mix}$ (L) is the thickness of the mixing layer, $k_d$ (L/$\text{T}$) is the linear adsorption partition coefficient, $\rho$ (M/L$^3$) is the bulk density of the soil, and $m_s$ (L$^3$/L$^2$) is the saturated moisture content.

**Desorption and Release.** Once the mixing zone is filled with water, solutes are lost through percolation. The rate of change of the mass of solutes remaining in the mixing zone per unit area, $M$ (M/L$^2$), is given by:

$$ dM(t) / dt = -C_w(t) R $$  \[2\]

where

$$ C_w(t) = M(t) / [h_{mix} (m_s + \rho k_d)] $$  \[3\]

The desorption partition coefficient, $k_d$ (L/$\text{T}$), is used because this is a desorption–dilution process; $R$ (L/$\text{T}$) ($T =$ time) is the rainfall rate.

Substituting Eq. [3] into Eq. [2], assuming that the mixing depth is constant, we find, by separation of variables and integration with respect to $C_w$ and $t$, that:

$$ C_w = C_w^0 \exp \left( \frac{1}{R} R \text{d}t / W_d \right) $$  \[4\]

where $C_w^0$ (M/L$^3$) is the concentration of the solutes in the water at the end of the adsorption phase before desorption starts ($t = 0$) and can be expressed with Eq. [1] as:

$$ C_w^0 = M^0 / W_s $$  \[5\]

where $W_s$ and $W_d$ (L/L$^3$) are the apparent water contents per unit surface area in the mixing layer during adsorption and desorption phases and are equal to:

$$ W_s = h_{mix} (m_s + \rho k_d) $$  \[6\]

$$ W_d = h_{mix} (m_s + \rho k_d) $$  \[7\]

For nonadsorbed solutes, the apparent water contents per unit surface are, as expected, both equal to the amount of water in the mixing zone. For adsorbed solutes, the use of different $k$'s during sorption and desorption is obviously only approximate. Conceptually, the desorption $k_d$ value is the tangent to the desorption isotherm, while $k_d$ is an average over the whole range, as shown in Fig. 3. Taking $k_d$ as the tangent is a reasonable assumption since the amount of adsorbed solutes lost is usually only a small portion of the total amount. However, modeling hysteresis this way, while maintaining continuity in the water phase solute concentration in Eq. [2] and [3], causes a mathematical artifact such that $M(t)$ at time zero, $M(0)$, is less than $M^0$ (i.e., only a portion of the solutes is initially available for loss in macropore flow).

In the next section, we will determine the values of the apparent water contents of the mixing zones by linear regression from the observed breakthrough curves of dyes, pesticides, and nonadsorbed solutes. So far, we have only determined the concentration of water leaving the mixing zone. The theory needs to be extended to the solute concentration in the outflow water. We will use a modified, two-domain CDE in which water and solutes move through the macropores instantaneously as plug flow and in the matrix, more slowly, while obeying

**Fig. 3.** Adsorption and desorption isotherm and associated linear adsorption partition coefficients.
Fig. 4. Spatially averaged Br⁻ and blue dye concentrations in the outflow water of the wick pan sampler under the mowed sod cover in the orchard experiment.

the CDE. Thus, especially for adsorbed solutes, the travel time through the matrix is so slow that we can assume (although the concentration of the preferential and matrix flow was the same when leaving the mixing zone), the matrix flows free of solutes, initially, at the point where the water flows out of the column. Assuming steady state and no solutes in the matrix flow, the concentration of water flowing out of the column, \( C_w \), is equal to:

\[
C_w = \frac{M^0 r / W_0}{\exp(- \int R dt / W_0)} \tag{8}
\]

where \( r \) is the quotient of preferential outflow and total flow:

\[
r = \frac{V_p}{V_p + V_m} \tag{9}
\]

\( V_p \) is the volume of preferential flow and \( V_m \) is the volume of matrix flow. Expressions, when the matrix flow is not free of solutes, can easily be developed, but requires knowledge of the matrix flow concentration.

The linear regression consists of regressing the natural logarithm of the concentration, \( C_w, t \), water vs. the cumulative outflow, \( \int R dt \), of the preferentially moving water; \( W_e \) and \( W_s \) can then be found from Eq. [4] and [5] as:

\[
W_e = - \frac{1}{a} \tag{10}
\]

\[
W_s = r M^0 / \exp(b) \tag{11}
\]

where \( a \) is the slope of the regression line and \( b \) is the intercept with the y axis.

**MATERIALS AND METHODS**

Three sets of experiments (one carried out by us and two from the literature) are used as a test for the equations presented above. They are also used to find values for the apparent adsorption and desorption water contents for soils under several cultural practices.

**Orchard Experiment.** During the summer of 1991, we performed a tracer study in the Cornell Orchard on Hudson silty clay loam soil (Udic hapludalf), in which a study has been underway since 1985 to determine how soil management practices will affect the establishment of apple (Malus sylvestris Mill.) trees (Merwin et al., 1994). The first soil management treatment consisted of a mowed red fescue (Festuca rubra L.) sod cover with very fine roots in the upper 30 cm and no cracks larger than 1 mm. Below the 30-cm depth, the original structure of the soil was undisturbed and water could flow through structural cracks between the ped. The ped had a hexagonal shape and were approximately 20 to 30 cm in diam. Roots and wormholes had established themselves in the cracks, which were filled with sandy material, causing a much higher conductivity in the cracks than in the ped. The second treatment consisted of two applications of glyphosate herbicide in May and July of each year to kill the grass and other weeds. A glyphosate-resistant moss had established itself as ground cover, and large open surface connected cracks were visible (sometimes as large as 1–2 cm wide). Some of these cracks remained open to a depth of at least 1 m. Water was applied with two Rainbird sprinklers with a 15 SQ nozzle making a rectangular pattern to two 4 by 6 m plots (one for each treatment) daily at a rate of 1 cm/h for 3 to 4 h for up to 12 d. Two tracers were applied with the first irrigation, 0.1 M bromide, a nonadsorbed tracer, and 700 mg/L FD&C no. 1 blue dye, an adsorbed organic tracer. In each plot, the percolating water was collected withwick and gravity pan samplers installed at a depth of 60 cm. Each sampler had 25 cells arranged in a square pattern with five cells (measuring each 6 by 6 cm) on each site.

**Artificial Macropore Columns.** In experiments performed by Czapar et al. (1992), 18 cm high by 15 cm wide soil cores were used in which 6-mm artificial macropores were made to several depths to study pesticide movement. 3.3 μg/cm² cyanazine (2-[4-chloro-6(ethylamino)-1,3,5-triazin-2-yl] amino)-2-methylpropanenitrile), 12.7 μg/cm² alachlor (2-chloro-2',6'-diethyl-N- methoxymethylaniline), 6.6 μg/cm² pendimethalin (N-(1-Ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine), and 1.48 mg/cm² Cl⁻ were dripped with less than 0.5 mm of water on the soil. Twenty-four hours later, the columns were irrigated with 63 mm of a 0.0075 M calcium sulfate solution in a 2-h time period. The herbicides were detected only in the outflow of three columns (labeled A-1, B-1, and C-1), which had a continuous macropore. Chloride was detected in the outflow of all columns.

**Undisturbed No-Till Columns.** Edwards et al. (1992) investigated the effect of rainfall intensity on the movement of water and chemicals through a no-till soil containing earthworm burrows and other macropores. Cubes of soil with sides of 30 cm were collected from the surface of a no-till corn (Zea mays L.) field. The soil cubes received a surface application of 7.7 kg/ha atrazine (6-chloro-N-ethyl-1H-1-methylthio-1,3,5-triazine-2,4-diamine) and 428 kg Br⁻/ha, and were subjected to simulated rain of 30 mm at three intensities. Percola-
tion water was collected in 64 cells measuring 3.75 by 3.75 cm at the base of each block. A second 30-mm rain was applied 1 wk later to all blocks. The composite sample for each cell and rainfall event was analyzed for atrazine and Br\textsuperscript{−}.

**MODEL TESTING**

**Orchard Experiment**

The natural log of the spatially averaged solute concentrations (over the 25 cells) as a function of the cumulative outflow, observed with the wick and gravity pan samplers, are depicted in Fig. 4 and 5 for the mowed sod treatment and in Fig. 6 for the glyphosate treatment. A linear fit to the data would make the model expressed in Eq. [4] or [8] valid. In the grass-covered plots, the blue dye concentration fit a straight line over the whole concentration range. For all other treatments, two straight lines can be distinguished that fit the data. The Br\textsuperscript{−} concentration in the grass plots and both the Br\textsuperscript{−} and blue dye concentrations in the glyphosate-treated plots fit a two-stage linear plot. The initially sharp declining linear portions of Fig. 4 to 6 (representing up to 15–20 cm outflow and 90% loss) illustrate that most of the solutes moved preferentially down there. There was very little matrix flow due to the tight subsol (Steenhuis et al., 1994). Initially the matrix flow was Br\textsuperscript{−} free. Thus, \( r = 1 \) in Eq. [8]. Later both matrix and preferential flow contained bromide producing the more or less horizontal portions of the data in Fig. 4 to 6. We will now focus on the initial steep part of the line representing the first 90% of the solute loss.

To derive the apparent water contents from the data presented in Fig. 4 to 6, the initial mass of solutes, \( M_0 \), needs to be determined. This depends on the amount of water per unit area at saturation in the mixing zone and the depth of irrigation water in which the Br\textsuperscript{−} and blue dye were dissolved. When the irrigation water amount is smaller than the water in the mixing layer at saturation, the mass applied is simply that in the irrigation pulse (i.e., 2.75 kg/m\textsuperscript{2} Br\textsuperscript{−} and 70 g/m\textsuperscript{2} blue dye). However, when the depth of irrigation water is more than the water that can be stored in the mixing layer at saturation (as is the case for the glyphosate plots) the initial mass is equal to the water content in the mixing concentration times the concentration in the irrigation water. The excess water in the pulse is released directly to the macropores with the irrigation water concentration.

The apparent water contents obtained from a linear regression of the data in Fig. 4 to 6, using Eq. [10] and [11], are shown in Tables 1 and 2. For nonadsorbed Br\textsuperscript{−} outflow in the mowed sod plot (Table 1), the apparent water contents, \( W_1 \) and \( W_2 \) (between 9.3 and 10.1 cm), were approximately the same. This is in agreement with the assumption that, for nonadsorbed solutes, the apparent water contents during adsorption and desorption are equal \( (k_a \) and \( k_d \) are zero in Eq. [6] and [7]). These values are consistent with our field observations that the top 20 to 25 cm was uniformly dyed (i.e., the mixing zone) in grass plots. Below the mixing zone, the water flowed through cracks. The average moisture content of the mixing layer in the mowed sod plot was between 40 and 50%, resulting in an averaged apparent water content of 10 cm, which agrees closely with the values predicted by regression. For blue dye (with an adsorption partition coefficient of 2 to 3 according to Andreini and Steenhuis, 1990), in the same plots, we found that the apparent desorption water content, \( W_v \), was between 11 and 13 cm, similar to the nonadsorbed tracer and making \( k_d = 0 \). The apparent adsorption water content, \( W_v \), was approximately 50 cm (Table 1), indicating that the blue dye was adsorbed (a \( k_v \) value of approximately 1.5) in the mixing zone itself.

<table>
<thead>
<tr>
<th>Table 1. Apparent water contents for the mowed sod plots in the orchard experiment.</th>
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<tr>
<td><strong>Bromide</strong></td>
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<tr>
<td><strong>Sampler type</strong></td>
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<tr>
<td>----------------</td>
</tr>
<tr>
<td>Gravity sampler</td>
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<td>Wick sampler</td>
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</table>

For the glyphosate-treated plots, the apparent water content of the mixing zone during desorption–dilution was approximately 2 cm (Table 2) and was independent of the type of solute. As this water content is less than the pulse of 3.5 cm, the concentrations of the Br\textsuperscript{−} and blue dye were initially close to the input concentration, as explained above. Thus, \( W_v \) cannot be predicted by regression as it falls out in Eq. [8]. The 2-cm water content of the mixing zone agrees well with observations in the field, in which only the top 2 to 4 cm of the surface layer was uniformly blue in the glyphosate plots.

In summary, the results of our orchard experiments show that the equations for predicting the solute concentrations in the preferentially moving water are physically

<table>
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<tr>
<th>Table 2. Apparent water contents for the plots treated with glyphosate herbicide in the orchard experiment.</th>
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<tr>
<td><strong>Bromide</strong></td>
</tr>
<tr>
<td><strong>Sampler type</strong></td>
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<tr>
<td>----------------</td>
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<tr>
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correct, especially for the nonadsorbed solutes. For the adsorbed dye, the partition coefficient during desorption was close to zero, as $W_d$ was similar for both $Br^-$ and blue dye.

Artificial Macropore Columns

In Fig. 7 and 8, the pesticide concentrations of Czapar et al. (1992), for columns A-1 and B-1 with artificial macropores, are re-plotted on a logarithmic scale. In all cases, a straight line fits the data well with approximately the same slope, indicating the same apparent desorption water content in the mixing layer. To find the apparent water contents, unlike the orchard experiment, matrix flow cannot be neglected. The columns with the partial macropores can be used to find the matrix flow component. These columns had $Cl^-$ breakthrough after less than 0.4 pore volumes and no detectable pesticide outflow (Czapar et al., 1992). Thus, the assumption (in Eq. [8]) that matrix flow was free of solutes was met for the pesticides, but not for the $Cl^-$. Also, the data show that the preferential flow in column C-1 was extremely small. Thus, the regressions will only be performed on the pesticide data for columns A-1 and B-1.

The results of the regression (Fig. 7 and 8) are shown in Table 3. The mixing layer desorption water contents for each of the columns were, indeed, similar and independent of the pesticide compound, despite the widely varying partition coefficients: 2.6 cm for column A-1 and 5.2 cm for column B-1. The apparent adsorption water contents were much higher and depended on the amount of preferential flow assumed.

These experiments confirm that the desorption apparent water contents are independent of the degree of adsorption of the pesticide and are much smaller than the adsorption apparent water contents. The results are, therefore, in agreement with our findings in the orchard.

Undisturbed No-Till Columns

In the experiments of Edwards et al. (1992) with no-till soils, the total losses of atrazine and $Cl^-$, as well as the time at which the macropores started flowing during the two rainfall events, were measured in each of the 64 cells. The calculated concentrations are, thus, averages for each cell throughout the whole infiltration cycle during each rain. Each cell can be thought of as a separate path, having its own characteristic macropores that connect the mixing zone with the outlet. Because it was a no-till soil, most of the water flowed through macropores (consequently, $r = 1$ in Eq. [8]).

In this experiment, water was added to the columns after it was brought in from the field and it is likely that the infiltration rate decreased with time. Hence, the amount of excess water (i.e., the rainfall rate minus the infiltration into the matrix) increased and was carried downward through different macropores in other paths. This would result in more and more paths taking part in the transport process. Thus, the initial solute concentration when each cell started flowing would be equal to the concentration in the mixing zone at that time. With these assumptions, the average concentration during each rainfall event can be found as follows: Eq. [8] is integrated to obtain the mass of solutes per unit area in the mixing zone at the time when the outflow started from the cell, $t_o$, and the time when the flow ended, $t_e$. By subtracting the two masses and dividing by the amount of water that leaves the mixing zone during that time span (i.e., $R(t_e-t_o)$), the average concentration, $C_w$ is obtained, viz:

$$C_w = \frac{M^o W_d}{R W_e (t_e - t_o)} \left[ \exp\left(-\frac{R t_o}{W_d}\right) - \exp\left(-\frac{R t_e}{W_d}\right) \right]$$  \[12\]

Table 3. Regressed apparent water contents for three pesticides and two columns of Czapar et al. (1992).

<table>
<thead>
<tr>
<th>Column/pesticide</th>
<th>$w_o$</th>
<th>$w_d$</th>
<th>$r^2$</th>
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</thead>
<tbody>
<tr>
<td><strong>Column A-1</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyanazine</td>
<td>32.0</td>
<td>2.8</td>
<td>78.9</td>
</tr>
<tr>
<td>Alachlor</td>
<td>48.5</td>
<td>2.2</td>
<td>86.6</td>
</tr>
<tr>
<td>Pendimethalin</td>
<td>68.0</td>
<td>2.7</td>
<td>92.6</td>
</tr>
<tr>
<td><strong>Column B-1</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyanazine</td>
<td>168.3</td>
<td>4.9</td>
<td>84.1</td>
</tr>
<tr>
<td>Alachlor</td>
<td>210.7</td>
<td>4.1</td>
<td>77.5</td>
</tr>
<tr>
<td>Pendimethalin</td>
<td>443.3</td>
<td>6.7</td>
<td>81.5</td>
</tr>
</tbody>
</table>
where $t_o$ is the time that the outflow begins, and $t_e$ is the time that the outflow ends.

Equation [12] cannot be written in linear regression form. Therefore, we plotted the average concentration calculated using Eq. [12] vs. the average observed concentration for block B for the two rainfalls. The amounts applied (71.0 mg of atrazine and 3.89 g of Br$^-$) and the times when the outflow started were taken from Tables 4 and 6 of Edwards et al. (1992). The values for apparent desorption water content were, after some initial attempts, set equal to 4.5 cm, which was the same as the value found for no-till fields in northern New York (Shalit et al., 1992). Also, the apparent adsorption water content for the Br$^-$ and the apparent desorption water content for the blue dye (in accordance with the orchard and artificial macropore experiments) were set equal to the same 4.5 cm value. The apparent adsorption water content for atrazine was fitted to 9 cm and corresponded to an adsorption partition coefficient of approximately 1.5 L/kg (1.5 cm$^3$/g).

The observed and calculated concentrations are depicted for the Br$^-$ and atrazine in Fig. 9 and 10, respectively. It should be noted that this is only one realization of input parameters of possibly a large number of other realizations. Despite this, it is obvious that the simple exponential model does a reasonable job in explaining some of the variation in the observed concentrations, especially for Br$^-$ . The model does not predict very well the highest atrazine concentrations. There might be a number of reasons, such as the faster flowing region might have a smaller adsorption partition coefficient (as noted before by Andreini and Steenhuis, 1990) or the water contents during desorption were not the same for this experiment.

**CONCLUSIONS**

The equations for predicting preferentially moving solute concentrations, which are based on the assumption that water and solutes mix in a layer near the surface (expressed in its simplest form in Eq. [4]), seem to estimate very well the nonadsorbed solute concentrations in the macropores which account for 75 to 90% of the initial solute loss. For the adsorbed solutes, it is encouraging that, during the dissolution and desorption process, concentrations in the macropore water can be predicted reasonably well, using the same mixing zone water content as for the nonadsorbed solutes. However, our inability to predict the initial concentration in the mixing zone shortly after the solute application is of concern and requires more research. In short, the theory that is tested with three widely varying independent data sets gives good insight into some of the important factors in the loss of fertilizers and pesticides to groundwater shortly after application via preferential flow.

**ACKNOWLEDGMENTS**

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**REFERENCES**

USDA-ARS Nat. Agric. Water Qual. Lab., Durant, OK.