RELATIONSHIP BETWEEN HERBICIDE CONCENTRATION IN PERCOLATE, PERCOLATE BREAKTHROUGH TIME, AND NUMBER OF ACTIVE MACROPORES

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ABSTRACT. *Identification of the major factors affecting herbicide transport through macropores improves our understanding of preferential flow and aids in the development and use of macropore−flow models, such as the Root Zone Water Quality Model (RZWQM). Recent research suggests that macropore−flow breakthrough time (bt) and the number of percolate−producing macropores (nmacro) affect herbicide concentration in percolate (hc). Therefore, we investigated the effect of bt and nmacro on hc during the first storm after herbicide application using multiple regression and partial correlation. Observed data were from five different leaching experiments that included five soil series and two tillage types (no−till and moldboard plow). Multiple regression was used to develop a model to predict herbicide concentration (hc) in preferential flow at 30 cm during the first rainfall after application using data from the five studies. The ln(hc) in macropore flow at 30 cm was related to bt (min) at 30 cm, ln(nmacro) at 30 cm, herbicide type (alachlor or atrazine), and herbicide application rate (R^2 = 0.96). Partial correlation confirmed the relationship between ln(hc) and bt ($P < 0.0001$; $r = -0.77$) and ln(nmacro) ($P < 0.0001$; $r = -0.46$). A single−variable sensitivity analysis on the regression equation suggested that the observed range of bt (1.4 to 25 min) results in an eight−fold change in atrazine concentration (4.0 to 0.48 mg L^{-1}). Clearly, breakthrough time during the first storm after application affects herbicide transport.*

Keywords. *Alachlor, Atrazine, Herbicide leaching, Multiple parameter regression, Preferential flow, RZWQM.*

Soil macroporosity is one of the most important factors affecting pesticide movement to subsurface drains and shallow groundwater (Shipitalo et al., 2000; Kladivko et al., 1991; Kladivko et al., 2001). Even in tilled soils, pesticide transport can occur primarily through preferential flow paths (Levanon et al., 1993; Granovsky et al., 1993). Preferential flow is a complex process, and to add to the complexity, pesticide transport can be different through tilled and no−till soil (Gish et al., 1991; Donigian and Carsel, 1987; Elliott et al., 2000; Granovsky et al., 1993).

A physically based model that simulates pesticide transport through tilled and no−till soils, such as the Root Zone Water Quality Model (RZWQM), requires an understanding of how soil properties, including macroporosity, are affected by management such as tillage. Sensitive RZWQM input parameters that control simulated herbicide concentration in macropore flow include the number of percolate−producing macropores (*nmacro*) and soil matrix saturated hydraulic conductivity (Malone et al., 2001). A reduced soil matrix saturated hydraulic conductivity decreases RZWQM−simulated macropore flow breakthrough time (*bt*), which results in greater RZWQM−simulated herbicide concentration in percolate (Malone et al., 2003).

Malone et al. (2003) concluded that the number of percolate−producing macropores (*nmacro*) was similar between long−term no−till (NT) and moldboard plow (MP) soils, and that time of initial percolate breakthrough at 30 cm (*bt*) was less for NT than MP soils. Macropore flow breakthrough time (*bt*) was less for NT than MP possibly because NT had lower soil matrix saturated hydraulic conductivity. The objective of Malone et al. (2003), however, was to investigate the effect of tillage on herbicide leaching through macropores. Expanding the regression analysis of Malone et al. (2003) to include more sophisticated statistical techniques and more soils may confirm the effect of *nmacro* and *bt* on herbicide transport through macropores. Understanding the significance of *bt* and *nmacro* on herbicide transport can aid in the development and use of pesticide transport models and may improve our understanding of preferential flow.

Several studies suggest that the timing 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). Other studies have shown the importance of herbicide sorption to soil (partition coefficient), herbicide degradation rate (half−life), and soil organic matter on herbicide transport through soil (e.g., Soutter and Musy, 1999). Some studies suggest that preferential flow is not a uniform process during a leaching event, and hydraulically active macropores may increase with soil wetting (Jaynes et al., 2001; Malone et al., 2001; Kung et al., 2000a, 2000b). Few studies report on the effect of percolate

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breakthrough time within a storm on pesticide transport through macropores. The objective of this study was to investigate the effect of percolate breakthrough time (*bt*) and the number of percolate−producing macropores (*nmacro*) on alachlor and atrazine leaching using data from five different studies and five different soils.

MATERIALS AND METHODS

The data presented are from five separate laboratory studies where alachlor and/or atrazine movement was investigated using a total of 39 undisturbed soil blocks collected from no−till and tilled fields (table 1). These five data sets were used because the areas at the base of the blocks that produced percolate and the breakthrough times were recorded. The methods are described in the original publications, but all of the studies had several common aspects. Blocks of undisturbed soil (30 × 30 × 30 cm) were collected using procedures similar to Shipitalo et al. (1990), with at least three replicates of each soil−treatment combination. Each soil block was uniquely characterized by measurable macropore properties (*nmacro* and *bt*). Atrazine and/or alachlor were surface applied at rates listed in table 1 for a total of 69 herbicide observations. A 0.5 or 0.25 h, 3 cm simulated rainfall was applied approximately 1 h after herbicide application. Rainfall shortly after chemical application often results in high pesticide concentrations in percolate, and the later rainfalls are generally less important because concentrations are lower (Kladivko et al., 1991; Kladivko et al., 2001; Shipitalo et al., 1990; Shipitalo et al., 2000). Percolate was collected at atmospheric pressure from each 3.75 × 3.75 cm cell of a 64 square grid at the bottom of the soil blocks. Each cell had tubing that led to a separate collection vessel. The *nmacro* was determined by assuming one percolate−producing macropore per percolate−producing cell. The time of first appearance of water in each collection vessel was recorded. Concentrations of atrazine and alachlor were determined using gas chromatography. Details on the rainfall simulator, percolate collection system, and herbicide analysis methods can be found in Shipitalo et al. (1990) and Shipitalo and Edwards (1996).

Multivariate regression was used to evaluate the relationship between herbicide concentration in percolate (*hc*) and *bt* and *nmacro*. A stepwise procedure was used for variable selection ($P < 0.15$ for variable inclusion). The five studies, discussed above, applied different rates of herbicide to the blocks; therefore, application rate was added as a separate variable. Furthermore, two herbicides were included in the analysis (alachlor and atrazine), so a fourth indicator variable was added to the analysis (alachlor = 0; atrazine = 1). Through exploratory data analysis, we selected a second−order multivariate polynomial model (response surface form) for the stepwise procedure:

$$\begin{aligned}\ln(hc) &= a0 + a1(bt) + a2(bt)^2 + a3(bt \times lnmacro)\\ &+ a4(bt \times applied) + a5(type \times bt) + a6(type \times bt^2)\\ &+ a7(lnmacro) + a8(lnmacro)^2 + a9(type \times lnmacro)\\ &+ a10(type \times lnmacro^2) + a11(applied)\\ &+ a12(applied \times type) + a13(applied)^2\\ &+ a14(type \times applied^2) + a15(lnmacro \times applied)\\ &+ a16(type) + a17(typ \times bt \times lnmacro)\\ &+ a18(type \times bt \times applied)\\ &+ a19(type \times lnmacro \times applied) \qquad (1)\end{aligned}$$

where *bt* is initial breakthrough time (min), *lnmacro* is the ln−transformed *nmacro*, *type* is the herbicide type (alachlor = 0, atrazine = 1), and *applied* is the herbicide application rate (kg/ha).

Data splitting is often used for model validation (e.g., Montgomery and Peck, 1982). One method of data splitting is cross validation, which involves splitting the data set into two subsets, using the two subsets alternately as data sets for estimation and prediction, and examining the resulting regression equations (e.g., Kaspar et al., 2003; Montgomery and Peck, 1982).

Another data splitting technique is called PRESS (Montgomery and Peck, 1982). The PRESS technique involves omitting an observation (*i*) one at a time, fitting the regression model to the remaining $n - 1$ observations, and using this

Table 1. Description of soil blocks used for regression analysis and partial correlation.

Study	Soil	No. of Blocks	Treatment(s)	Average Break−through Time (min)	Average No. of Cells Producing Percolate (*nmacro*)	Average Atrazine Conc. in Percolate (mg L^{-1})	Atrazine Applic. Rate (kg ha^{-1})	Average Alachlor Conc. in Percolate (mg L^{-1})	Alachlor Applic. Rate (kg ha^{-1})
Shipitalo and Edwards (1996)	Glenford silt loam	9	No−till with dry, intermediate, and wet soil	8.6 ±4.5[a] (2.5−14.5)[b]	18.8 ±15.3 (4−53)	1.39 ±0.5 (0.77−2.41)	2.25	0.21 ±0.09 (0.09−0.34)	4.5
Edwards et al. (1992)	Glenford silt loam	6	No−till with 15 and 30 min rainfall (3 cm)	3.25 ±1.34 (1.4−5.1)	9.3 ±5.16 (4−17)	8.21 ±1.26 (6.7−9.5)	7.7	NA	NA
Granovsky et al. (1993)	Wooster silt loam; Crosby silt loam; Hoytville silt clay loam	18	No−till and moldboard plow	12.6 ±6.3 (3.5−25.1)	20 ±13.4 (4−42)	3.5 ±1.7 (0.6−7.5)	8.5	0.21 ±0.14 (0.02−0.53)	4.0
Shipitalo et al. (1990)	Rayne silt loam	3	No−till	2.50 ±0.30 (2.20−2.80)	8.67 ±1.15 (8−10)	6.97 ±3.51 (4.5−11.0)	7.7	NA	NA
Malone et al. (2001)	Glenford silt loam	3	No−till	11.73 ±6.59 (7.30−19.30)	28.33 ±16.80 (10−43)	1.19 ±0.40 (0.87−1.64)	2.25	0.11 ±0.03 (0.09−0.14)	4.5

[a] Mean value ±standard deviation.
[b] Minimum value − maximum value.

equation to predict the withheld observation (y_i). This is repeated for each observation for a set of n predictions. We selected the PRESS technique for model validation because of several reasons, including the limited number of observations in the dataset (n = 69). Partial correlation was used to evaluate the strength of the relationship between ln(hc) and bt and *lnmacro*. Partial correlations are correlations between two variables while adjusting for the effect of one or more of the other variables.

Results and Discussion

Applying stepwise regression to the five data sets (table 1) resulted in the following equation:

$$\begin{aligned} \ln(hc) &= 2.57 - 0.0742(bt) - 1.82(lnmacro) \\ &+ 0.0235(bt \times lnmacro) + 0.556(type \times applied) \\ &+ 0.0272(type \times lnmacro \times applied) - 0.00264(bt^2) \\ &+ 0.232(lnmacro)^2 - 0.0420(applied^2) \end{aligned} \quad (2)$$

The regression model suggests that ln(hc) is related to *lnmacro* and bt, because all variables contribute significantly using stepwise selection ($P < 0.06$ for each included variable; R^2 = 0.96; n = 69). The relationship between ln(hc) and *lnmacro* and bt was also confirmed with partial correlation ($P < 0.0001$ for both bt and *lnmacro*; r = −0.77 for bt; r = −0.47 for *lnmacro*; n = 69).

The alachlor and atrazine observations from an individual block may be correlated, which violates the independence assumption of multiple regression and artificially increases the degrees of freedom. Developing separate second−order response−surface equations, however, for alachlor and atrazine suggest that bt and *lnmacro* significantly affect hc ($P < 0.030$ for components of the variables *lnmacro* and bt for both alachlor and atrazine; R^2 = 0.94 and n = 39 for atrazine; R^2 = 0.97 and n = 30 for alachlor). First−order responses and simple non−linear models also suggest that the variables bt and *lnmacro* significantly affect hc. Therefore, percolate concentration is clearly related to bt and *lnmacro*, but determination of the best equation was beyond the scope of this research.

The sensitivity of equation 2 for predicting hc from bt and *nmacro* can be illustrated with an example. Assuming an atrazine application rate of 4.0 kg/ha and an *nmacro* of 10 (table 1), the atrazine concentration in percolate was predicted to be 4.0 mg/L with a bt of 1.4 min and 0.48 mg/L with a bt of 25 min. With an atrazine application rate of 4.0 kg/ha and a bt of 10 min, atrazine concentration in percolate was predicted to be 4.6 mg/L with an *nmacro* of 4 and 2.4 mg/L with an *nmacro* of 50. In comparison, with an *nmacro* of 10 and bt of 10 min, atrazine concentration in percolate is predicted to be 4.1 mg/L with an application rate of 8 kg/ha and 1.2 mg/L with an application rate of 2 kg/ha. Note that the predicted hc from equation 2 was more sensitive to bt than *nmacro*.

Equation 2 predicted that hc responds to changes in *nmacro* and bt as simulated by the Root Zone Water Quality Model (RZWQM). Malone et al. (2001) observed that RZWQM−simulated hc increased with decreasing *nmacro* and decreasing soil matrix saturated hydraulic conductivity (K_{sat}). A lower K_{sat} results in simulated macropore flow occurring with less rainfall. Therefore, decreased K_{sat} results in increased RZWQM−simulated hc, mostly because of decreased simulated bt (Malone et al., 2003). Decreasing *nmacro* results in increased RZWQM−simulated hc mostly because of decreased soil available for herbicide sorption (Malone et al., 2001). When *nmacro* is increased, an RZWQM−simulated amount of macropore flow (cm) is distributed among a greater number of macropores, which allows macropore flow to interact with more soil surrounding macropore walls.

The PRESS technique shows that equation 2 is reasonably stable, with a strong correlation between observations and PRESS predictions (fig. 1): R^2 = 0.95, y = 1.00 (±0.03) + 0.00 (±0.04). Splitting the PRESS predictions into alachlor and atrazine data also results in correlations between observations and PRESS predictions (R^2 = 0.66, n = 30 for alachlor; R^2 = 0.84, n = 39 for atrazine). The PRESS technique suggests little bias in equation 2 for the alachlor, atrazine, or complete dataset because the slope is not significantly different from one and the intercept is not significantly different from zero. Although the alachlor correlation was weaker than that for atrazine, predicted alachlor concentrations (inverse of ln−transformed data) were within or nearly within a factor of 2 of observed concentrations. A factor of 2 is sometimes used as an acceptability measure for process−based model predictions (Ma et al., 2000). Note that equation 2 is an empirical model, not a process−based model.

Knowledge of the relationship between pesticide concentration in macropore flow and breakthrough time and the number of percolate−producing macropores has practical application in process−based modeling. For example, Malone et al. (2003) reported that RZWQM−simulated herbicide transport is sensitive to simulated breakthrough time and that RZWQM−simulated macropore flow breakthrough time is controlled by soil parameters such as soil matrix saturated hydraulic conductivity and water retention variables (bulk density, pore size distribution index, and bubbling pressure).

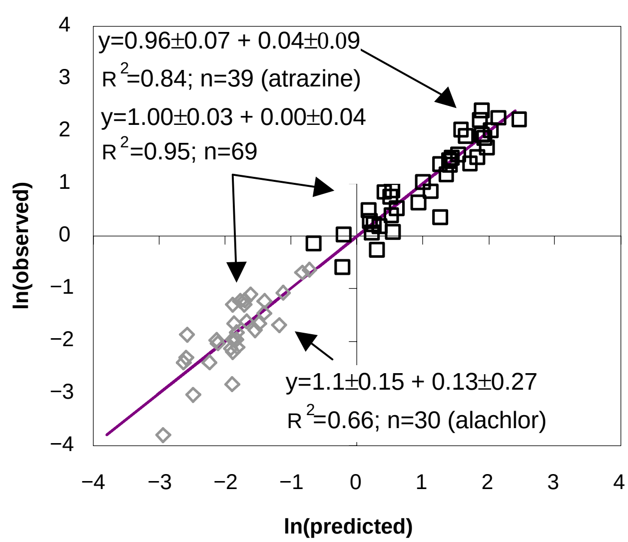

Figure 1. Observed and predicted alachlor and atrazine concentrations in percolate (mg/L) for the five studies described in table 1. The figure was developed using the PRESS technique, and the standard errors are presented with the slope and intercept values. The PRESS technique involved omitting an observation (*i*), fitting the regression model to the remaining *n* − 1 observations, and using this equation to predict the withheld observation (y_i).

Therefore, the multivariate regression analysis used here and the RZWQM analysis of Malone et al. (2003) suggest that carefully selecting soil parameters that control water transport is necessary to accurately predict pesticide concentration and transport through macropore flow. In contrast, Soutter and Musy (1999) concluded that the parameters controlling pesticide degradation and sorption are far more important to simulated pesticide leaching than those parameters controlling water transport processes, but the analysis did not include macropore flow.

Equation 2 should be improved and more thoroughly evaluated before being used as a predictive tool. Improvement may include validating equation 2 with other datasets and/or more thoroughly investigating other regression techniques (e.g., nonlinear, more mechanistic) to determine the best equation or approach. However, this research confirms the relationship between herbicide transport during the first storm after chemical application and breakthrough time and the number of percolate−producing macropores.

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