

Saturated Transport of Atrazine Under Two Tillage Systems

Alton B. Johnson*

ABSTRACT

Atrazine, 6-chloro-N-ethyl-N^o-(1-methylethyl)-1,3,5-triazine-2,4-diamine, is a pre-emergence herbicide used for weed control in corn (*Zea mays*). This herbicide is considered to be relatively mobile in soils. The objective of this study was to determine the transport characteristics of atrazine in a conventional tillage system (CT) with no winter cover and a no-till system (NT) with hairy vetch (*Vicia villosa* Roth ssp. *villosa*) as winter cover. Miscible displacement experiments were conducted on intact columns under saturated condition to quantify transport parameters of atrazine. The soil under study was Memphis silt loam (Fine-silty, mixed, thermic Typic Hapludalf). Atrazine adsorption was described by the Freundlich isotherm. Average K_d was higher ($1.272 \text{ cm}^3 \text{ kg}^{-1}$) in NT than CT ($1.021 \text{ cm}^3 \text{ kg}^{-1}$), but showed no significant difference. A nonlinear least-square program (CXTFIT) was used to fit the two-region physical non-equilibrium model to the experimental data. Average dispersion coefficient of non-reactive bromide for CT was 6 times lower than for NT. Average atrazine eluted in the NT columns was 1.2 times higher than in the CT columns. Average pulse duration (t_p) was 1.5 times higher for CT than NT. Atrazine breakthrough curves for the NT columns were more asymmetrical and longer tailing, indicating preferential flow in the no-till system.

INTRODUCTION

Pesticide contamination of ground water has become a major concern in recent years. The concern is due to the health hazards associated with the entry of these chemicals into the food chain of animals and humans (Gomaa and Faust, 1974; Kennedy, 1978). Farmers in the United States who are actively involved in row crop production use pesticides to sustain yields. One commonly used herbicide for corn (*Zea mays* L.) production in the Southern Mississippi Valley is atrazine [2-chloro-N-ethyl-N-(1-methylethyl)-1,3,5-triazine-2,4-diamine]. This herbicide is used to control most small-seeded annual weeds and grasses. The mobility of agriculturally-related chemicals in the vadose zone has been quantified in recent years (Andreini and Steenhuis, 1990; Czapar et al., 1992; Ghodati and Jury, 1992; Wilson et al., 1998).

Because conventional tillage (CT) practices have been associated with excessive soil erosion, nutrient loss by runoff and relatively high energy costs, many farmers have adopted conservation tillage practices as important methods of crop production. Conservation tillage systems allow crop residues to be left on the soil surface to conserve soil water and reduce soil erosion. One type of conservation tillage

with relatively minimum soil disturbance is the no-till (NT) system. Under NT crop production system, macropores develop as a result of channeling by plant roots, earthworms, or soil shrinkage cracks. Herbicides are usually applied under NT practices to control weeds or winter covers. When sufficient rainfall occurs, infiltration under NT condition is often higher than CT. This increases the potential for shallow ground water loading due to movement through preferential paths in the soil profile (Wagenet and Hutson, 1986; Isensee et al., 1988; Singh et al., 1989; Wilson et al., 1998).

Tillage practices at varied locations have shown different results based on local climate, soil water holding capacity, soil topography and drainage characteristics (Wehtje et al. 1984). Xue et al. (1997) observed longer tailing and earlier breakthrough of alachlor, 2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide, in NT soil columns than CT soil columns under saturated conditions. Thomas and Phillips (1979) observed greater leaching of NO_3^- with NT than CT.

The path in which solute is transported in soil is important when assessing potential shallow ground water loading of pesticides. Work done by Bruseau et al. (1989) separated non-equilibrium transport processes into two general classes: physical non-equilibrium and chemical sorption-related non-equilibrium. The presence of mobile and immobile regions within porous media results in physical equilibrium, which affects both sorbing and non-sorbing solutes. Chemical non-equilibrium and intrasorbent diffusion give rise to sorption-related non-equilibrium which involves only sorbing solutes.

Much of the drinking water in Mississippi comes from wells in shallow aquifers that may be affected by loading of pesticides from agricultural practices. Little information and understanding exist on tillage effects on atrazine transport in the Mississippi Valley and Silty Uplands. The objective of this study was to assess and model the movement of atrazine in a common soil in the Mississippi Valley and Silty Uplands under two tillage practices.

MATERIALS AND METHODS

The soil used in this study was a loessial Memphis silt loam (Typic Hapludalf) obtained from plots (NT and CT) during early spring near the main campus of Alcorn State University in Lorman, Mississippi. The CT plots had no winter cover whereas the NT plot was covered with vetch (*Vicia villosa* Roth) during the winter. They had undergone these tillage practices for at least 5 years. Disturbed soil samples from the plots were collected (0-15 cm) for batch experiment. The Memphis soil consisted of 30, 760, and 210 g kg^{-1} sand, silt and clay, respectively and 10.7 and 12.1 g kg^{-1} organic carbon (OC) for the CT and NT plots,

*Alton B. Johnson, Mississippi River Research Center, 1000 ASU Drive #852, Alcorn State, MS 39096; bjohnson@lorman.alcorn.edu

respectively.

Two undisturbed soil columns were extracted from each tillage practice from near surface (0-15 cm depth) for solute transport study. The pulse solution for miscible displacement experiments contained 10 mg L⁻¹ of atrazine in 50 mg L⁻¹ Br⁻ and 50 μM CaCl₂. Bromide was used as a conservative tracer to investigate hydrodynamic dispersion and near surface preferential flow characteristics of the two tillage systems.

Batch Sorption Experiments

Distribution coefficients, K_d (cm³ kg⁻¹), for atrazine were determined in triplicate. Atrazine (99.8% purity) was obtained from Ultra Scientific (North Kingstown, RI) and solutions with initial concentrations of 0, 2, 4, 6, 10, and 20 mg L⁻¹ were prepared in 50 μM CaCl₂ for the batch experiments. Five grams of soil (on oven dry soil basis) and 15 mL of herbicide solution at the different concentrations were added to 25-mL glass centrifuge vials and sealed with Teflon-lined screw caps. The soil-solution mixtures were continuously shaken on a reciprocating shaker for 24 h at room temperature (~23°C). The vials were centrifuged at 3500 rpm for 30 minutes. The supernatant was then filtered through a disposable 0.45-μm nylon filter and the filtrates injected into a High Performance Liquid Chromatography (HPLC) column for atrazine analysis. The adsorbed concentration, S , (g kg⁻¹) was calculated as the difference between the initial concentration and the concentration at equilibrium, C_e (mg L⁻¹). Atrazine adsorption was described by the Freundlich equation for the two tillage systems:

$$S = K_d C_e^N \quad [1]$$

where N is an empirical constant. The partition coefficient of atrazine, K_{oc} [= 100(K_d /%OC)], was determined for each tillage system.

Miscible Displacement Experiments

Undisturbed soil cores were extracted in two Plexiglass flow cell columns (8 cm dia.) per tillage treatment. Map of infiltration rate of the field containing both tillage practices (CT and NT) is shown in Figure 1.

The samples were carefully trimmed to the length of flow cells (15 cm) and allowed to saturate from the bottom by connecting each column to a mariotte tube containing 50 μM CaCl₂. A pulse of 1 pore volume (PV) of atrazine solution, as described above, was applied to each column from the top. The herbicide was then displaced with tracer-free 50 μM CaCl₂ solution and effluent from each column was collected in tubes with a fraction collector (Retriever II,

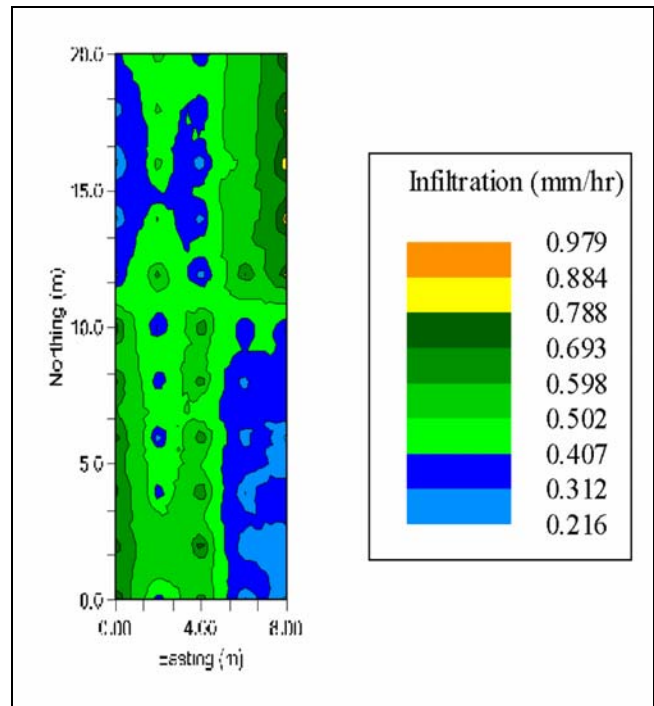


Figure 1. Map of infiltration rate of the field containing conventional till and no-till plot. Conventional till plots are located in the blue and light green shaded areas.

ISCO, Lincoln, NE) and analyzed or stored under 4°C until analyzed. To avoid change in hydraulic head, the liquid level in the mariotte tube was kept constant with a peristaltic pump. Experimental conditions for the transport experiment are presented in Table 1.

Chemical Analysis

Effluent samples were analyzed for atrazine with a DX 500 HPLC with an AD20 UV/Visible detector at a wavelength of 220 nm (Dionex Corp., Sunnyvale, CA). A Zorbax HPLC C-18 column (4.6 mm i.d x 25 cm) was used with 80:20 acetonitrile:water ratio as the mobile phase at a flow rate of 1 mL min⁻¹. The lower detection limit of these herbicides was 0.5 mg L⁻¹. Bromide was analyzed with a Dionex 500 Ion Chromatography (IC) system with an ED40 electrochemical detector. Bromide was injected into an IonPac AS4A-SC analytical column at a flow rate of 2 mL min⁻¹. The breakthrough curves (BTCs) for each column were expressed in relative concentration (C/C_0) vs. PV (V/V_0).

Table 1. Miscible displacement experimental conditions.

| Tillage system† | ρ | q | v | t_p | Θ_v | PV |
|-----------------|--------------------|--------------------|-------|--------|----------------------------------|-----------------|
| | g cm ⁻³ | cm h ⁻¹ | | h | cm ³ cm ⁻³ | cm ³ |
| CT1 | 1.34 | 0.0079 | 0.016 | 1118.8 | 0.494 | 388.3 |
| CT2 | 1.35 | 0.0083 | 0.017 | 1116.7 | 0.491 | 385.3 |
| NT1 | 1.43 | 0.0423 | 0.092 | 723.6 | 0.460 | 361.6 |
| NT2 | 1.39 | 0.0408 | 0.086 | 722.4 | 0.475 | 373.4 |

†CT1, conventional tillage - column #1; CT2, conventional tillage - column #2; NT1, no-till - column #1; NT2, no-till - column #2; ρ is bulk density; q is flux; v is pore water velocity; t_p is pulse duration; Θ_v is volumetric saturated water content; PV is pore volume.

Modeling Solute Transport

The experimental data (bromide and atrazine) were analyzed using the physical two-region non-equilibrium model of van Genuchten (1981) and Parker and van Genuchten (1984). The physical nature of each soil column was separated into two regions: a mobile region and an immobile region. It was assumed by van Genuchten (1981) that convective-dispersive transport of solute is restricted to the mobile phase with diffusion exchange with the immobile phase. The equations governing solute transport for the two-region model are:

$$(\Theta_m + f\rho K_d)\partial C_m/\partial t + [\Theta_{im} + (1-f)\rho K_d]\partial C_{im}/\partial t = \Theta_m D_m \partial^2 C_m / \partial z^2 - q \partial C_m / \partial z \quad [2]$$

$$[\Theta_{im} + (1-f)\rho K_d] \partial C_{im} / \partial t = \alpha (C_m - C_{im}) \quad [3]$$

where the subscripts m and im denote the mobile and immobile regions, respectively, Θ_v is volumetric water content ($\Theta_m + \Theta_{im} = \Theta_v$), f is the fraction of sorption sites that equilibrates with the mobile regions, C is the solution-phase solute concentration (mg L^{-1}), D is the dispersion coefficient ($\text{cm}^2 \text{h}^{-1}$), α is the mass-transfer coefficient between the mobile and immobile water regions (h^{-1}), t is time (h), q is the flux (cm h^{-1}) and z is distance from solute origin (cm). The initial and boundary conditions used were:

$$C_m = 0; \quad t = 0, \quad 0 \leq z < L \quad [4]$$

$$C_{im} = 0; \quad t = 0, \quad 0 \leq z < L \quad [5]$$

$$vC_m - D\partial C_m/\partial z = vC_o; \quad z = 0, \quad 0 < t \leq t_p \quad [6]$$

$$vC_m - D\partial C_m/\partial z = 0; \quad z = 0, \quad t > t_p \quad [7]$$

$$\partial C_m/\partial z = 0; \quad z = L, \quad t > 0 \quad [8]$$

where L is column length (cm), t_p is the pulse duration (h), and v is pore water velocity (cm h^{-1}). The dimensionless parameters associated with the model are:

$$\beta = (\Theta_m + \delta K_d)/(\Theta_v + \rho K_d) \quad [9]$$

$$\alpha = \omega q/L \quad [10]$$

where β is the fraction of mobile water content. Values of D , β , and α for Br^- in each soil column were computed using the program CXTFIT (Parker and van Genuchten, 1984). This computer program uses the nonlinear least-square inversion technique that can be used to optimize parameters for several theoretical one-dimensional solute transport models. Values of β and α for atrazine were also obtained using CXTFIT.

RESULTS AND DISCUSSION

Atrazine Adsorption

Adsorption of atrazine across the range of concentration used (0 to 20 mg L^{-1}) was described by the nonlinear Freundlich isotherm (Fig. 2). The average K_{oc} value for the NT system was $105.1 \text{ cm}^3 \text{ kg}^{-1}$ whereas K_{oc} for the CT system was $95.4 \text{ cm}^3 \text{ kg}^{-1}$. There was no significant difference in sorption between the two tillage systems.

Flow Characteristics

Atrazine transport in the soil columns from the two tillage practices were described by the physical non-equilibrium two-region model described in Eq. [2] to [10]. The model fitted the experimental atrazine data well and provided r^2 values ranging from 0.98 to 0.99 and low standard errors

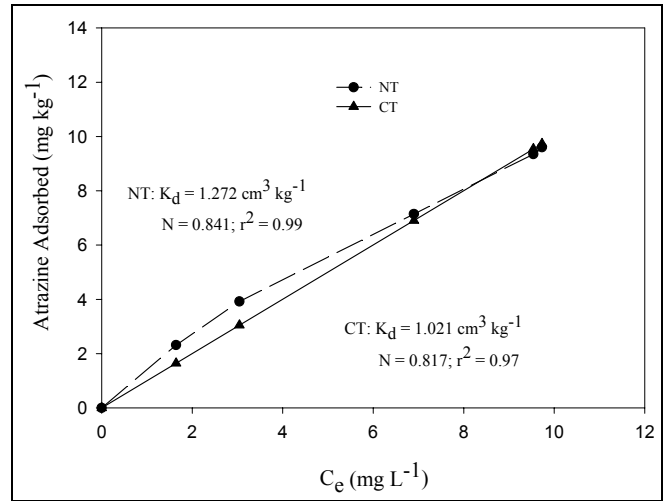


Figure 2. Adsorption isotherms of atrazine for conventional till (CT) and no-till (NT) plots.

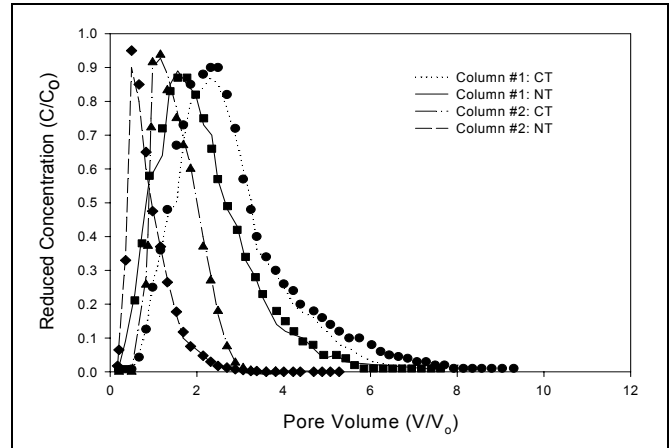


Figure 3. Bromide breakthrough curves for soil columns from conventional till (CT) and no-till (NT) plots.

(0.01 to 0.006). Estimated parameters for Br^- and atrazine are shown in Table 2. Average D_m value for the NT practice was 6 times higher than the average D_m value for CT (Table 2). Larger degree of dispersion was indicated by the higher D_m in the NT columns, which as a consequence suggests a wide distribution of v_m and preferential flow (Jardin et al 1988, 1989). This was consistent with the results from Singh and Kanwar (1991) and Xue et al., (1997) who found greater solute dispersion in no-till than conventional tillage soil columns. Bromide BTCs for the NT system were shifted to the left and exhibited more asymmetry compared to the BTCs for the CT system (Fig. 3). Average peak relative Br^- concentration was obtained at 0.97 PV for NT and 1.4 PV for CT.

Early atrazine breakthrough was observed in the NT columns than the CT columns (Fig. 4). This was probably due to the higher water velocity observed in the NT columns. Average atrazine peak concentration was 1.2 times higher in the NT columns than in the CT columns. The relatively more asymmetrical BTCs in the NT columns may be due to preferential flow (Brusseau et al. 1989). Assuming a wide range of pore-size distribution in the NT columns,

Table 2. Estimated β , α , Θ_m , and D_m obtained by fitting the two-region model to the experimental breakthrough curves.

| Tillage system† | Bromide | | | | | Atrazine | | |
|-----------------|-------------------|---------------------------------|------------|-------|-------|------------------|---------------------------------|-------|
| | β | α | Θ_m | D_m | r^2 | β | α | r^2 |
| CT1 | 0.332 (0.001) | 5.4×10^{-4} (0.001) | 0.180 | 0.014 | 0.99 | 0.365 (0.002) | 4.2×10^{-4} (0.010) | 0.99 |
| CT2 | 0.356 (0.001) | 1.3×10^{-3} (0.001) | 0.224 | 0.015 | 0.99 | 0.456 (0.006) | 1.5×10^{-4} (0.023) | 0.98 |
| Avg. | 0.334 | 9.1×10^{-3} | 0.170 | 0.014 | -- | 0.410 | 2.9×10^{-4} | -- |
| NT2 | 0.800 (0.004) | 0.061 (0.020) | 0.367 | 0.092 | 0.87 | 0.798 (0.008) | 4.3×10^{-4} (0.013) | 0.99 |
| NT2 | 0.0700 (0.004) | 0.024 (15.15) | 0.419 | 0.076 | 0.90 | 0.883 (0.006) | 7.5×10^{-4} (0.010) | 0.99 |
| Avg. | 0.750 | 0.042 | 0.393 | 0.084 | -- | 0.594 | 5.9×10^{-4} | -- |

†CT1, conventional tillage - column #1; CT2, conventional tillage - column #2; NT1, no-till - column #1; NT2, no-till - column #2.

‡Values in parentheses are standard errors.

atrazine BTC is more likely to be asymmetrical, coupled with larger dispersion and v_m when compared with CT columns (Xue et al., 1997). Average mobile water content for the NT columns was about 2 times that of CT columns. The lower α value of the CT columns indicates that atrazine in the immobile region was less likely to diffuse to the mobile region (Table 2). The longer tailing in the NT columns may have been the result of atrazine in the immobile region diffusing into the mobile region. This process occurred 1.5 times as fast in the NT columns with higher flow velocity as in the CT columns. In this study, increase in mass transfer with increased flow velocity agreed with other solute transport studies (van Genuchten and Wierenga, 1977; van Genuchten et al., 1977; De Smedit and Wierenga, 1984; De Smedit et al., 1986; Li and Ghodrati, 1994). Mobile dispersion coefficient linearly increased with mobile pore water velocity, v_m , ($D_m = 0.957v_m - 0.031$; $r^2 = 0.96$), suggesting that flow through the NT columns was heterogeneous as heterogeneity increases. In this study, the two-region transport model successfully described atrazine transport. Batch adsorption measurements and atrazine BTCs suggest that atrazine retention was not affected by either tillage system. Hence, preferential flow limited atrazine adsorption during transport. Solute-soil interaction is limited when preferential flow path exists, thereby leading to prevailing non-equilibrium conditions during movement. While in this study transport parameters were quantified near the soil surface (0-15 cm), similar studies containing both near surface and subsurface may provide better insight on flow path in the soil under study.

ACKNOWLEDGEMENT

I would like to thank Drs. David Radcliffe, H. Don Scott, and Glenn V. Wilson for their critical comments and many helpful suggestions on the manuscript. This work was partially supported by the USDA-CSREES Capacity Building Grant Program.

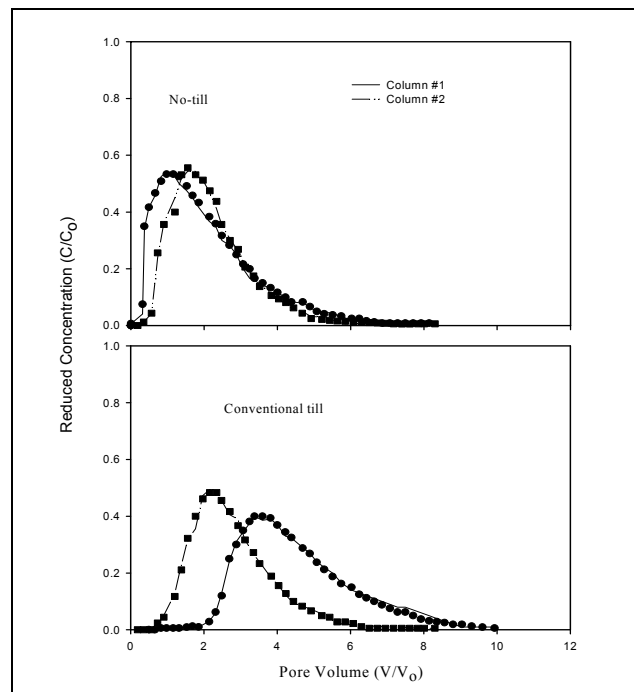


Figure 4. Atrazine breakthrough curves for soil columns from conventional till (CT) and no-till (NT) plots.

REFERENCES

- Andreini, M. S. and T.S. Steenhuis. 1990. Preferential paths of flow under conventional and conservation tillage. *Geoderma* 46:85-102.
- Brusseau, M.L., R.E. Jessup and P.S.C. Rao. 1989. Modeling the transport of solutes influenced by multi-processes nonequilibrium. *Water Resour. Res.* 25:1971-1988.
- Czapar, G.F., R. Horton and R S. Fawcett. 1992. Herbicide and tracer movement in soil columns containing an artificial macropore. *J. Environ. Qual.* 21:110-115.
- De Smedit, F, F. Wauters and J. Sevilla. 1986. Study of tracer movement through unsaturated sand. *J. Hydrol. (Amsterdam)* 85:169-181.

- De Smedt, F. and P.J. Wierenga. 1984. Solute transfer through columns of glass beads. *Water Resour. Res.* 20:225-232.
- Ghodrati, M. and W.A. Jury. 1992. A field study of the effects of soil structure and irrigation method on preferential flow of pesticides in unsaturated soil. *J. Contam. Hydrol.* 11:101-125.
- Gomaa, H.M. and S.D. Faust. 1974. removal of organic pesticides from water to improve quality. p. 413-450. In W. D. Guenzi (ed.) *Pesticide in soil and water*. SSSA, Madison, WI.
- Isensee, A. R., R.G. Nash and C. S. Helling. 1990. Effect of conventional vs. no-till on pesticide leaching to shallow ground water. *J. Environ. Qual.* 19:434-440.
- Isensee, A. R., and A. M. Sadeghi. 1994. Effects of tillage and rainfall on atrazine residue levels in soil. *Weed Sci.* 42:462-467.
- Jardin, P.M., G.V. Wilson and R.J. Luxmoore. 1988. Modeling the transport of inorganic ions through undisturbed soil columns from two contrasting watersheds. *Soil Sci. Soc. Am. J.* 52:1252-1259.
- Jardin, P.M., N.L. Weber and J.F. McCarthy. 1989. Mechanisms of dissolved organic carbon adsorption on soils. *Soil Sci. Soc. Am. J.* 53:1378-1385.
- Kennedy, M.V. 1978. Disposal and decontamination of pesticides. In R. F. Gould (ed.) *ACS Symp. Ser. 73*. Am. Chem. Soc. Washington, DC.
- Parker, J.C. van Genuchten, M.Th. 1984. Determining transport parameters from laboratory and field tracer experiments. Bulletin 84-3. Virginia Agric. Exp. Stn. Blacksburg, VA.
- Singh, P. and R.S. Kanwar. 1991. Preferential solute transport through macropore in large undisturbed soil columns. *J. Environ. Qual.* 20:295-300.
- van Genuchten, M.Th. and P.J. Wierenga. 1977. Mass transfer of sorbing porous media. II. Experiment evaluation with tritium. *Soil Sci. Soc. J.* 41:272-277.
- van Genuchten M.Th., P.J. Wierenga and G.A. O'Connor. 1977. Mass transfer of sorbing porous media. III. Experimental evaluation with 2,4,5-T. *Soil Sci. Soc. J.* 41: 278-284.
- van Genuchten, M.Th. 1981. Nonquilibrium transport parameters from miscible displacement experiments. Res. Rep. no. 119. U.S. Salinity Lab. Riverside, CA.
- Wilson, G.V., L. Yunsheng, H.M. Selim, M.E. Essington, and D.D. Tyler. 1998. Tillage and crop cover effects on saturated and unsaturated transport of floumeturon. *Soil Sci. Soc. Am. J.* 62:46-55.
- Xue, S. K., S. Cen and H.M. Selim. 1997. Modeling alachlor in saturated soils from no-till and conventional tillage systems. *J. Environ. Qual.* 26:1300-1307.