

MEASURED AND PREDICTED TRANSPORT OF TWO S-TRIAZINE HERBICIDES THROUGH SOIL COLUMNS *

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Abstract. Effluent concentration of chloride and two pesticides (prometon and atrazine) were measured during column displacement experiments at two water flow rates. A constant suction of approximately 1300 Pa was maintained in the packed soil columns which were positioned vertically on top of a vacuum chamber enclosing an automatic fraction collector. Measured breakthrough curves (BTC's) were analyzed in terms of two solute transport models: the standard two-parameter convection-dispersion equation (CDE), and a four-parameter two-site/two-region nonequilibrium model (TRM). Calculations obtained with the TRM model were found to be in better agreement with measured BTC's than predictions using the CDE model. Column retardation factors for prometon and atrazine calculated from equilibrium batch sorption coefficients were comparable to those estimated from the observed BTC's only when the nonequilibrium TRM model was used.

1. Introduction

Modern agricultural activities, industrial waste disposal, and landfills, provide potential sources for pesticides and other organics which, once released into the subsurface environment, may contaminate soil and groundwater systems, as well as surface water bodies. Mitigation of these pollution problems over the past several decades has been made easier because of an improved conceptual understanding of soil-solute interactions. Simultaneously, mathematical models have been developed which predict the migration of different contaminants in soil, groundwater, and air (Brusseau and Rao, 1989; Jury and Ghodrati, 1989; van Genuchten, 1991; Singh *et al.*, 1992).

Currently used solute transport models are generally based on the relatively standard one-dimensional convective-dispersion equation (CDE). Such models have helped to improve our understanding of the underlying mechanisms of subsurface solute movement. CDE-based models have been relatively successful for transport scenario's involving nonreactive chemical and relatively uniform soil profiles. However, they have generally been less accurate for reactive solutes, particularly for organics including pesticides. To improve predictions for organic solutes,

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the CDE has undergone a series of modifications and improvements, including the inclusion of linear (Green *et al.*, 1968; Davidson and Chang, 1972; Davidson and McDougal, 1973) and nonlinear (Swanson and Dutt, 1973; van Genuchten *et al.*, 1974) adsorption-desorption isotherms, as well as its coupling with relatively simple first-order type nonequilibrium sorption rate expressions. These modifications, however, have not materially improved the predictions, particularly the tailing and skewed (non-sigmoidal) nature of many observed concentration distributions. Tailing was subsequently explained on the basis of either physical (Skopp and Warrick, 1974; van Genuchten and Wierenga, 1976; Rao *et al.*, 1980; Nkedi-Kizza *et al.*, 1983; Seyfield and Rao, 1987) or chemical (Selim *et al.*, 1976; Cameron and Klute, 1977) nonequilibrium processes leading to two-region type (mobile-immobile) and two-site type chemical nonequilibrium transport models, respectively. Nkedi-Kizza *et al.* (1984), among others, showed that the underlying physical and chemical processes of these two conceptually different approaches are difficult to separate when studied by means of column displacement experiments. More involved multiple-process models incorporating different physical and chemical nonequilibrium processes were later developed by Brusseau and Rao (1989) and others.

Testing and validation of alternative equilibrium and nonequilibrium models has been limited by a lack of experimental data collected under both controlled laboratory and natural field conditions. Hence, the present study was designed to obtain additional information on pesticide transport in repacked soil columns. The experiments involve the transport of chloride and two s-triazine herbicides, prometon and atrazine, through 30-cm long soil columns at two flow rates. The data will be analyzed in terms of the classical two-parameter CDE and the three- or four-parameter two-site/two-region transport (TRM) model.

2. Experimental

2.1. SOILS AND HERBICIDES

A Hanford sandy loam, coarse loamy, mixed nonacid, them-tic typic xerorthents soil (0.43% organic carbon, 6.05 pH (1:1), 5.95 cmol kg⁻¹ CEC at 25 °C, 7.1% clay, 25.8% silt and 67.1% sand) was sampled in bulk from the Moreno Valley Research Farm of the University of California, Riverside, air dried at room temperature, and passed through 2-mm sieve.

Two s-triazine herbicides viz., prometon [2,4-bis-(isopropylamino)-6-methoxy-s-triazine], and atrazine [2-chloro-4-(ethylamino)-6-(iso propylamino)-s-triazine], were selected as representative organic species for our study. Prometon and atrazine have aqueous solubilities of 750 and 33 mg L⁻¹; and half-lives of 63 and 64 days, respectively (Singh *et al.*, 1990). They are used under different environmental conditions and for different purposes.

2.2. MISCIBLE DISPLACEMENT COLUMN EXPERIMENT

Plexiglass chromatographic columns (30 cm x 5.15 cm ID) fitted at both ends with detachable porous stainless steel plates, were hand-packed with air-dry soil to the desired bulk density by gently tapping on a rubber stopper. The porous plates (0.5 μm) had O-rings which closely fitted inside the columns. The plates helped to promote a radial distribution of the influent solution and reduced hydrodynamic dispersion of moving solution at or near the column exit. The soil was kept in close contact with the porous plates at both ends of the columns to avoid air pockets. The packed columns were positioned vertically on top of a vacuum chamber hosting an automatic fraction collector supported by a precise drop counter. A constant suction of approximately 1300 Pa was maintained in the vacuum chamber by means of a Nullmatic Regulator attached to a manometer.

A 0.01 N $\text{Ca}(\text{NO}_3)_2$ electrolyte solution was added to the columns until steady-state water flow conditions were established. Pesticide and non-pesticide solutions were injected at the top of the columns with the help of a very accurate multi-syringe pump. The column system was connected to the pump using teflon tubing, while separate syringes were used for the two types of input solutions. Pre-experimental calibration tests suggested that the soil used in this study can be maintained unsaturated under a optimal vacuum at a maximum flow rate of 48 cm day⁻¹, hence the two velocities, 40 (less than the highest rate) and 13 cm day⁻¹ (one third of the first) were selected to provide information on water flow effects on transport parameters. The actual inflow velocities observed during experimentation are given in Table I. Transport of the two herbicides was studied separately. Since prometon has higher aqueous solubility and K_{oc} (soil-water partitioning constant based on the organic carbon fraction of the soil) than atrazine and applied at much higher dosage in the fields (4-5 times than atrazine), was injected at higher concentrations (80 $\mu\text{g g}^{-1}$) than atrazine (12 $\mu\text{g g}^{-1}$). CaCl_2 (0.01 N) served as the background solution. After injecting approximately four pore volumes of herbicide solution, the columns were leached with 4-6 pore volumes of the initial $\text{Ca}(\text{NO}_3)_2$ solution to achieve desorption. Water contents in the columns were checked periodically during the experiments by weighing the columns. The experimental conditions for the four column experiments are summarized in Table I.

2.3. EXTRACTION AND ANALYSIS OF SAMPLES

All effluent samples, each weighing approximately 14 g, were weighed individually. Herbicides were extracted from the samples by liquid-liquid partitioning using analytical grade hexane for atrazine and dichloromethane for prometon. Each sample was extracted four times (4 x 25 mL) and the extract passed through a bed of anhydrous sodium sulfate. The extracts were analyzed with a Varian 3700 Gas Chromatograph equipped with NP Detector. Temperatures were maintained at 200, 180, 300 °C for the injection port, column and detector, respectively. The column

TABLE I
Experimental conditions for the four displacement experiments

Parameter	Experiment			
	PR SLOW	PR FAST	ATSLOW	ATFAST
Density, ρ_b (g cm ⁻³)	1.594	1.659	1.623	1.631
Water content θ (cm ² cm ⁻²)	0.220	0.216	0.219	0.221
Water flux q (cm day ⁻¹)	11.23	38.44	11.79	38.75
Pulse time, T_0 (pore vol.)	3.79	4.23	4.11	4.31
<i>Input conc. (C₀)</i>				
Herbicide ($\mu\text{g mL}^{-1}$)	80.09	80.45	12.16	12.40
Chloride (mg L ⁻¹)	16.30	11.30	10.15	10.19

was 90 cm x 2 mm ID packed with Ultrabond 20 M on Carbowax 100-120 mesh. The recovery of both herbicides from spiked water samples was 98-101%. Samples drawn from the inlet herbicide solutions at the beginning, middle, and end of the experiments were also analyzed, with the average concentration for each chemical being taken as the input concentration, C_0 . Relative effluent solute concentrations, C/C_0 , were used to plot the BTC's for each experiment. The measured curves are shown as circles in Figures 1-4.

2.4. BTC DATA ANALYSIS

The experimental effluent BTC data were analyzed in terms of two transport models frequently used for pesticide transport studies, i.e., the convection-dispersion equation (CDE) which assumes equilibrium transport, and the two-site/two-region model (TRM) which assumes nonequilibrium transport. The CDE equation is given by

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} + v \frac{\partial C}{\partial z} \quad (1)$$

where C is the solution concentration, D is the hydrodynamic dispersion coefficient, v is the average pore-water velocity, t is time, z is distance, and R is a retardation factor which accounts for linear equilibrium adsorption as follows:

$$R = 1 + \frac{\rho_b K_d}{\theta} \quad (2)$$

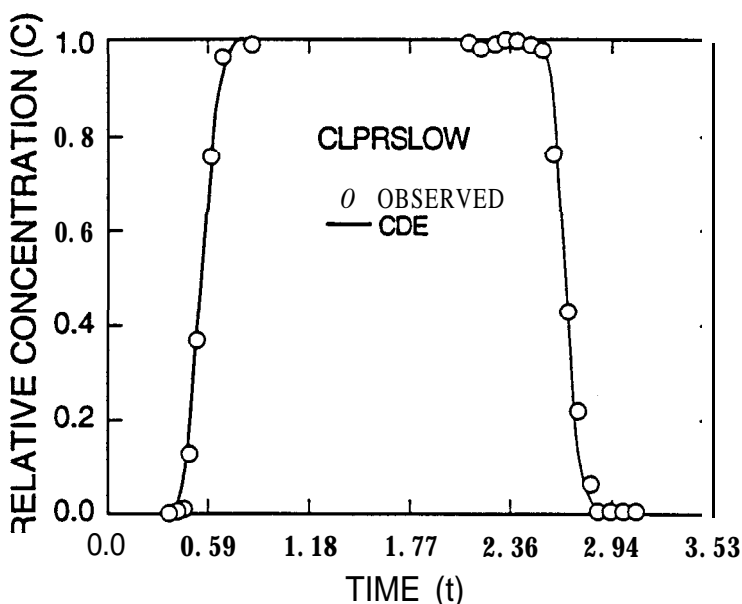


Fig. 1. Observed and CDE calculated BTC's for chloride (CLPRSLOW) slow velocity experiment.

in which θ is the volumetric water content ($\text{cm}^3 \text{cm}^{-3}$), ρ_b is the dry bulk density of the soil system (g cm^{-3}), and K_d is the soil water partitioning coefficient ($\text{cm}^3 \text{g}^{-1}$). Equation (1) may be expressed in dimensionless form as follows:

$$R \frac{\partial c}{\partial T} = \frac{1}{P} \frac{\partial^2 c}{\partial z^2} - \frac{\partial c}{\partial z} \quad (3)$$

$$T = \frac{vt}{L} \quad Z = \frac{z}{L} \quad (4a,b)$$

$$P = \frac{vL}{D} \quad c = \frac{C}{C_0} \quad (5a,b)$$

where z and T are dimensionless distance and time (or pore volume), respectively, L is the column length, P is known as the column Peclet number, c is the dimensionless concentration ($0 \leq c \leq 1$), and C_0 is the concentration of the applied solution at the inlet position $z=0$. Notice that the above model contains two independent parameters: P and R .

Equation (3) assumes equilibrium sorption of the herbicide onto the solid matrix of the soil. Results of many batch and solute transport experiments indicate that sorption reactions of pesticides generally do not proceed instantaneously. Several models have been proposed which invoke some type of nonequilibrium sorption process. The simplest formulation arises when first-order chemical kinetics between the herbicide and the soil matrix is assumed. More involved formulations occur

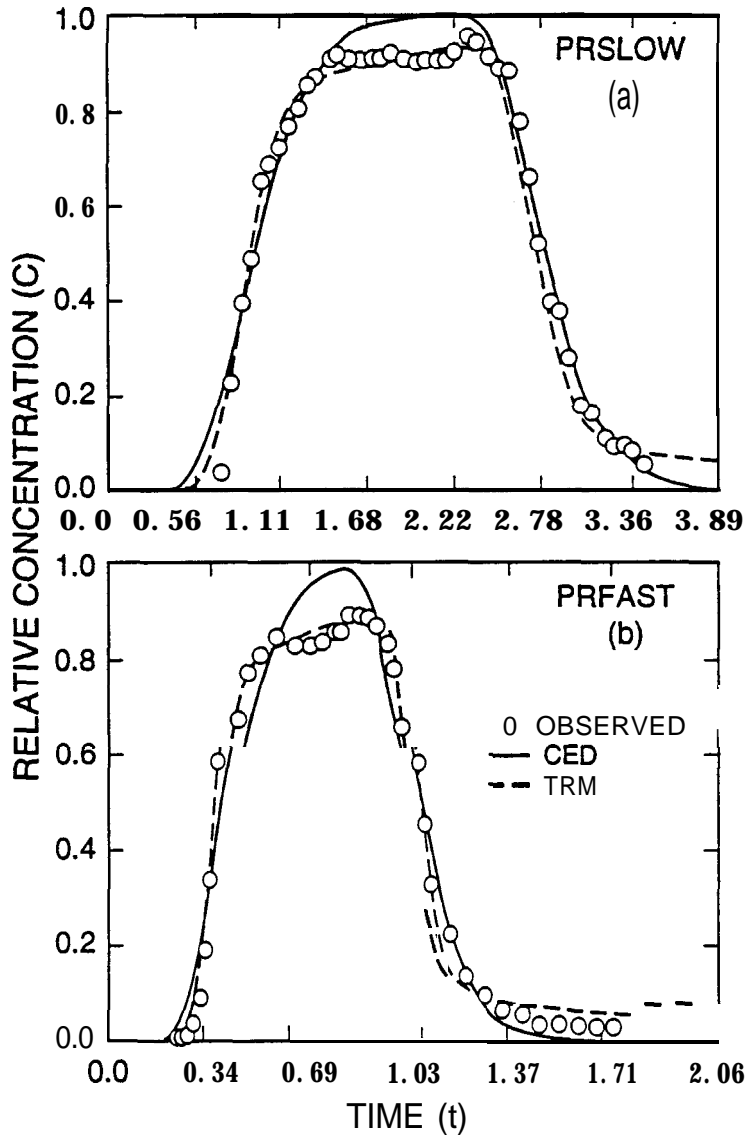


Fig. 2. Observed, CDE and TRM calculated BTC's for the prometon slow (a) and (b) fast velocity experiments.

when either a two-site chemical nonequilibrium process (Selim et al., 1976), or a two-region mobile-immobile type physical nonequilibrium model (van Genuchten and Wierenga, 1976) is hypothesized. While conceptually different, Nkedi-Kizza

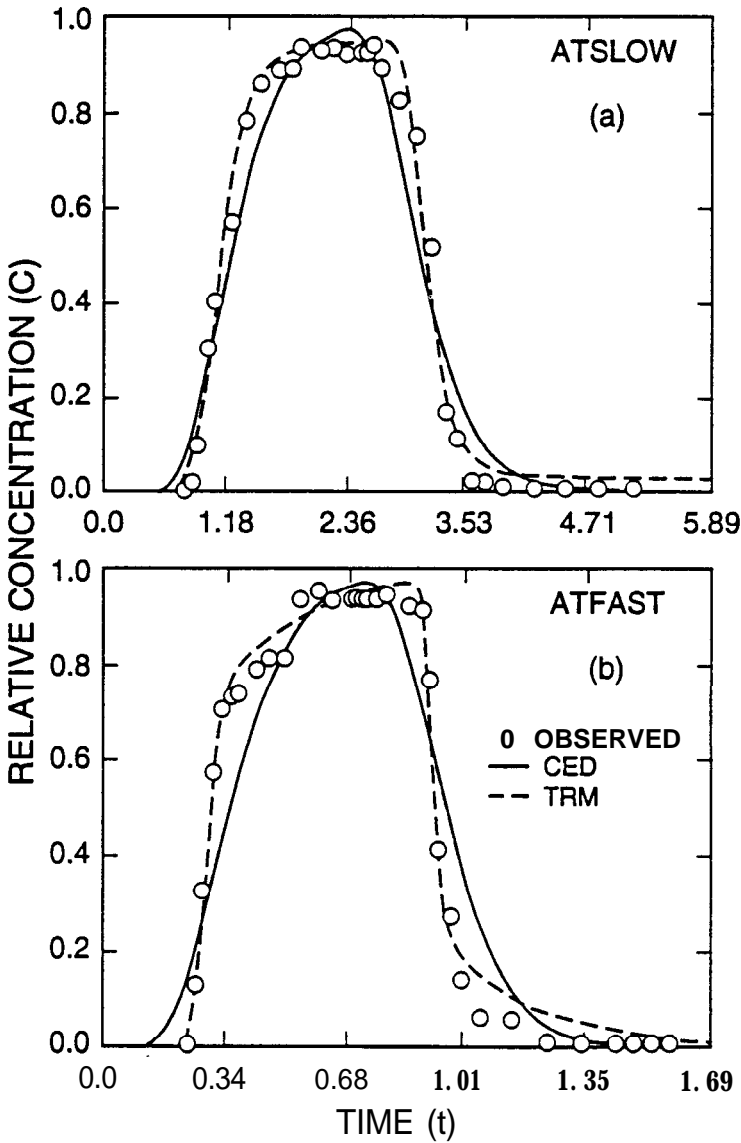


Fig. 3. Observed, CDE and TRM calculated BTC's for the atrazine slow (a) and (b) fast velocity experiments.

et al. (1984) showed that these two nonequilibrium formulations can be casted in the same dimensionless forms as follows:

$$\beta R \frac{\partial c_1}{\partial T} + (1 - \beta) R \frac{\partial c_2}{\partial T} = \frac{1}{P} \frac{\partial^2 c_1}{\partial Z^2} - \frac{\partial c_1}{\partial Z} \tag{6}$$

$$(1 - \beta) R \frac{\partial c_2}{\partial T} = \omega(c_1 - c_2), \tag{7}$$

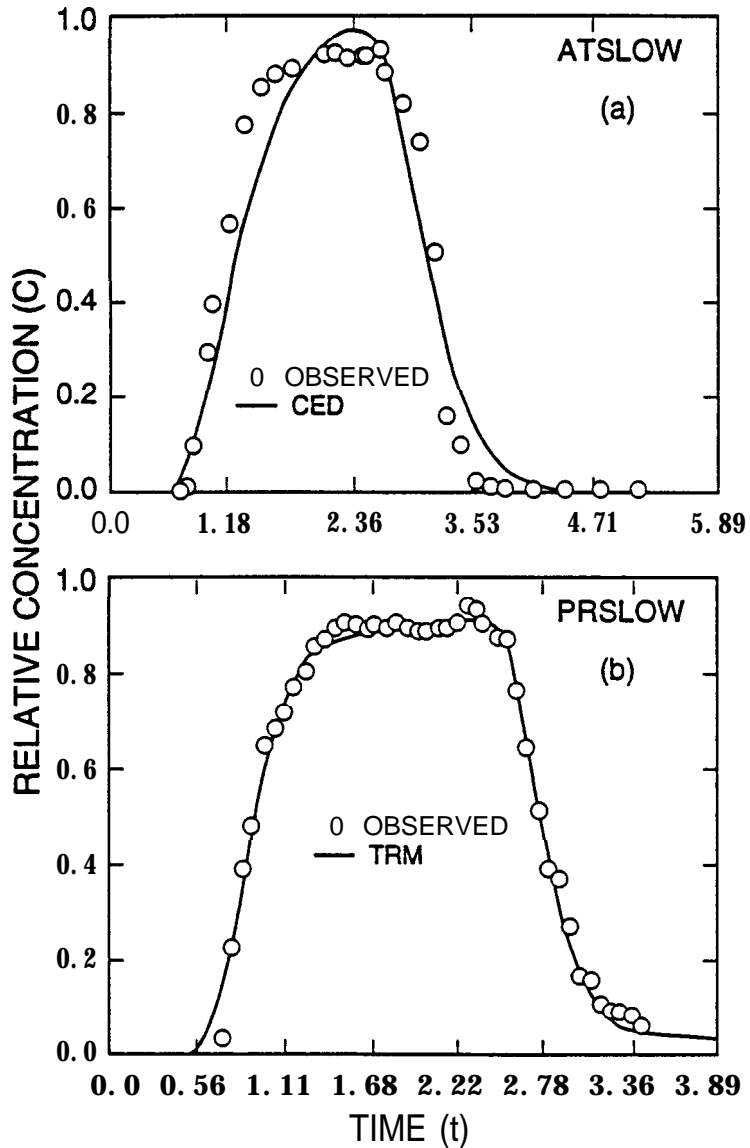


Fig. 4. (a) Observed atrazine movement at slow velocity and CDE calculated BTC's using batch-equilibrium R . (b) Observed prometon movement at slow velocity and TRM calculated BTC's using batch-equilibrium R .

in which the subscripts 1 and 2 refer to the equilibrium and nonequilibrium concentrations, respectively, Z and T represent dimensionless distance and time as before, P the column Peclet number, w is a dimensionless rate coefficient governing the rate of adsorption/desorption or mass transfer between region 1 and 2, and β is a dimensionless coefficient partitioning the system into equilibrium and nonequilib-

TABLE II

Fitted sorption parameters in the equilibrium CDE and nonequilibrium TRM models

Column	Parameters					
	CDE		TRM			
	R	P	R	P	β	ω
PR SLOW	1.757	20.48	2.129	40.87	0.757	0.180
PR FAST	2.530	21.00	3.301	85.37	0.676	0.244
AT SLOW	1.933	19.45	4.548	54.40	0.403	0.104
AT FAST	1.859	14.02	2.106	175.00	0.801	0.346

rium parts. Equations (6) and (7), further referred as the two-site/two-region model (TRM), contains four adjustable parameters: P , R , β and w .

Analytical solutions of the CDE and TRM models for an initially solute-free soil profile subject to a pulse of duration T_o and an effectively semi-infinite soil system, have been reported by Lindstrom et al. (1967) and van Genuchten and Wierenga (1976), respectively. Since the observed effluent concentrations are considered to be flux-averaged, solutions for a first- or concentration type inlet condition must be used. We refer to the report by Parker and van Genuchten (1984) for a compilation of these solutions.

The nonlinear least-square inversion program CFITIM (van Genuchten, 1981) was used to estimate the dimensionless parameters in the above two models. Results for the CDE and TRM models are listed in Table II. Notice that we also fitted the pulse input time T_o , which in some cases could not be determined accurately using the implemented experimental procedure. Values for the original model parameters, such as the partitioning coefficient, K_d and the dispersion coefficient D in the CDE model, can be calculated from the fitted dimensionless parameters using methods described by van Genuchten (1981).

3. Results and Discussion

A series of BTC's were obtained for different experimental conditions. Measured chloride tracer BTC's and the two herbicides viz., prometon and atrazine are shown in Figures 1-4.

3.1. CHLORIDE DISPLACEMENT EXPERIMENTS

Observed and calculated chloride effluent concentrations for the CLPR SLOW experiment when chloride (suffix CL) was applied simultaneously with Prometon

(PR) at the lower flow velocity (SLOW) are shown in Figure 1. The distributions indicate that the concentrations at the breakthrough (front) and elution (back) sides adjust rapidly to the changing input concentration without exhibiting any tailing. The chloride effluent curve in Figure 1 was found to be representative of all other chloride displacement experiments (results not further presented here). The measured chloride BTC data for all columns could be fitted well with solution of the CDE equation. Hence, the CDE model was found to be an appropriate model for simulating chloride transport through repacked soil columns of the type used in our experiments. Analysis of the BTC data in terms of the more elaborate TRM (with two additional adjustable parameters) did not improve the already excellent fit obtained with the CDE.

3.2. HERBICIDE DISPLACEMENT EXPERIMENTS

The observed, CDE, and TRM calculated prometon effluent concentrations for the relatively low (PR SLOW) and high (PR FAST) water flow rates are depicted in Figure 2. Notice that contrary to the Cl-data in Figure 1, the observed herbicide concentrations never reached a relative concentration of 1.0. In addition, the concentrations during elution after the solute pulses had passed never dropped below the detection limit ($0.05 \mu\text{g g}^{-1}$), even after leaching with many pore volumes of herbicide-free water. Slightly more tailing was observed for the higher velocity as compared to the lower velocity displacement experiment. The steeper prometon BTC during elution (desorption) for the fast flow rate (Figure 2b) as compared to the lower velocity (Figure 2a) is consistent with field results by Troiano et al. (1993) who achieved different percolation rates by implementing various types of irrigation. The CDE simulated curves in Figures 2a and b did not accurately match the measured BTC's at either flow velocity. They significantly overestimated the prometon peak concentrations, while tailing at the higher pore volumes is also described poorly, especially for the PR FAST example at the higher flow velocity.

The TRM model yielded a much better description of the effluent data than the CDE model particularly the tailing phenomena at both the lower and higher flow velocities. Some relatively small difference were still apparent at the higher pore volumes for the PR FAST experiment. The observed distributions in Figure 2 involving skewed (non-symmetric) curves and tailing are typical of nonequilibrium transport conditions observed for many organic chemicals, especially at - but not limited to -relatively high flow velocities (e.g., van Genuchten et al., 1974; Nkedi-Kizza et al., 1989; Brusseau and Rao, 1989; Karickhoff, 1980). Increased tailing at higher flow rates was also noticed by Gamerdinger et al. (1991) for atrazine transport using flow rates of 1.07 and 7.08 cm hr^{-1} .

A comparison of the observed atrazine displacement data with calculated curves obtained with the CDE equilibrium and TRM nonequilibrium models, respectively, is shown in Figure 3. Results are similar to those shown in Figures 2 for prometon,

except that tailing for atrazine at the higher flow velocity (Figure 3b) is less extensive than for prometon (Figure 2b) at approximately the same velocity. The CDE model again failed to describe the nonsigmoidal shape of the BTC's, especially for the ATFAST involving the higher water flow rate.

The calculated curves in Figures 2 and 3 were obtained by allowing the unknown parameters in the CDE (P and R) and TRM (P , R , β and ω) models to be adjustable. The fitted CDE and TRM sorption parameter values are listed in Table II. We also carried out the CFITIM parameter optimization by assuming a known retardation factor R as estimated from the measured batch equilibrium partitioning coefficient, K_d (Singh *et al.*, 1990) using Equation (2). Descriptions of the observed BTC's using the CDE model became worse when R was fixed, whereas those for the TRM model in most cases were far less affected. Two typical examples are shown in Figure 4 involving the ATSLow experiment as analyzed with the CDE model (a), and the PRSLow experiment in terms of the TRM model (b). Notice the increased dispersion in the CDE calculated atrazine distribution (Figure 4a) when R was fixed as compared to the curve in Figure 3a obtained with adjustable R . By comparison, the TRM model results for PRSLow were only minimally affected when the retardation factor was fixed at its batch-derived value (see Figures 4b and 2a). These results reflect the fact that herbicide sorption during batch equilibration can be quite different from that during transport. The major differences involve the degree of nonequilibrium and the invoked solution-sorbent ratios. When using the equilibrium CDE model, any nonequilibrium situation during herbicide transport can only be accounted for by artificially adjusting P and R , i.e., by perturbing the apparent dispersion and sorption parameters. The TRM model, on the other hand, includes specific terms to account for nonequilibrium. Hence, fixing R should not substantially affect the optimization results when the TRM model is used, provided that batch equilibration does not increase the overall K_d by exposing additional sorption sites. We note in this respect that batch studies normally involve unrealistically high solution-sorbent ratios and use shaking and centrifugation, conditions which may well change the surface properties of the sorbent particles (Kookana *et al.*, 1992).

The average K_d -values derived from the TRM model retardation factors (0.23 and 0.31 for prometon and atrazine, respectively) were reasonably close to the batch equilibrium values (0.36 and 0.27, respectively) as measured by Singh *et al.* (1990). However, the K_d values estimated with the CDE model (0.15 and 0.12, respectively) were less than half of the batch values. These differences between the batch and CDE column sorption coefficients were likely a result of the above-mentioned differences between batch-equilibration and column conditions, especially in view of the relatively low organic matter content of our soil which caused mineral sorption sites to become more significant. Batch-equilibrium sorption parameters, although useful for relative estimates, may not be appropriate for describing chemical transport in field soil profiles since they do not account for many of the time-dependent and other processes normally occurring under natural field situations. Hence, tran-

sient column sorption measurements should more accurately reflect actual field transport conditions, and therefore produce more reliable information.

4. Discussion

This study shows that the observed tailing in the herbicide BTC's could not be described adequately with the CDE model. The TRM nonequilibrium model on the other hand, predicted tailing during both breakthrough (sorption) and elution (desorption) for both organic chemicals. Nonequilibrium sorption of prometon and atrazine during the miscible displacement experiments were likely caused by diffusion-controlled sorption and diffusion within soil organic matter. Increased nonequilibrium (1-p) for atrazine at the higher flow rates (Figure 3b) must have been due to the decreased residence time of the solute in the columns. This trend of having increased non-equilibrium at higher flow rates was not as pronounced for prometon (Figure 2b). A plausible reason for the somewhat different behavior of prometon and atrazine could be the difference in physico-chemical properties particularly the solubilities of the two herbicides which may have caused the two compounds to behave somewhat differently at lower and higher flow rates. We tried to correlate the model parameters with solubility, half-life ($t_{1/2}$), soil carbon-water (K_{oc}), and octanal-water (K_{ow}) coefficient, but were not successful. As expected (e.g., van Genuchten, 1981), the w values were higher at the higher flow rates, but the degree varied for the two compounds probably because of their differences in solubility. Tailing during desorption could have been enhanced further by the formation of chemical precipitates, changes in desorption solution composition, some loss of chemical due to degradation, and irreversible binding of solutes to soil as reflected by possible hysteresis in the adsorption-desorption isotherms. Chemicals hysteresis has been reported for atrazine (Swanson and Dutt, 1973; Clay et al., 1988) as well as for other pesticides (van Genuchten et al., 1974). The parent molecular structures of prometon and atrazine involving different functional groups may lead to a variety of possible sorption mechanisms (Hayes, 1970). The two herbicides, hence, should not necessarily show sorption behavior during transport. The mechanisms of sorption and transport are numerous and complex, and cannot be explained in total by means of relatively simple column displacement experiments of the type discussed in this paper.

The column displacement data reported in this study were analyzed with the CDE and TRM models. While considerably more sophisticated than the more popular CDE model, the TRM model as used here still ignores a number of processes which might have improved the results. These processes include degradation (Gamerdinger et al., 1991; van Genuchten and Wagenet, 1989), metabolite formation (Adams and Thurman, 1991; Helling, 1971; Russel et al., 1968) and, most importantly, simultaneous leaching of dissolved organic matter and other macro- and colloidal molecules through the columns (Barriuso et al., 1992; Magee et al.,

1991; Schaefer *et al.*, 1991; and several others). Proper inclusion of these processes in the two models might have improved some of our calculations.

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