# Application of Two-Site/Two-Region Models for Studying Simultaneous Nonequilibrium Transport and Degradation of Pesticides

A. P. Gamerdinger, R. J. Wagenet,\* and M. Th. van Genuchten

# ABSTRACT

Quantitative laboratory study of pesticide sorption and degradation during transport can provide insight into the basic processes affecting pesticide fate in field soils. Accordingly, we demonstrate the application of analytical solutions of two-site/two-region transport models useful in studying simultaneous pesticide sorption and degradation. Soil-column displacement experiments involving <sup>3</sup>H<sub>2</sub>O, Cl, and atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) were conducted during steady-state water flow at two pore-water velocities and two pesticide concentrations. The soil used is a Valois silty loam (coarse-loamy, mixed, mesic Typic Dystrochrept). Effluent data from these experiments were used to demonstrate the application of these analytical solutions, as well as a parameter-estimation computer program based on these solutions. The ability to use laboratory-derived estimates of equilibrium sorption parameters to describe sorption under flowing conditions was evaluated at each flow velocity. Significant correlation between soil sorption partitioning and degradation prevents the simultaneous determination of both processes using these solutions. However, estimates of degradation obtained from mass balances of the column data were useful in identifying the equilibrium sorption parameters. Data collected elsewhere for 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) herbicide transport were used as an additional example of the application of the model with degradation. Strengths and weaknesses of the models, and suggestions for further study, are presented.

A SYMMETRIC BREAKTHROUGH CURVES for solutes leached through porous media have been observed for a variety of chemicals in a broad range of soils. Much of these data were obtained in laboratoryscale experiments and are reviewed elsewhere (Rao et al., 1979; van Genuchten and Wagenet, 1989; Brusseau and Rao, 1989a). Recently, Winters and Lee (1987) reported tailing of three trace organics during in situ experiments under field conditions. Similar observations have also been made for organic contaminant transport in groundwater systems (Goltz and Roberts, 1986). These results indicate a need for understanding the processes behind the tailing phenomenon as contaminant-transport models are being implemented in research and management.

Several models have been proposed to describe asymmetric breakthrough curves where tailing is attributed to either chemical or physical nonequilibrium processes. One-site or two-site chemical-process models assume that sorption is not at equilibrium and has a time-dependent or kinetic component. On the other hand, physical-process two-region models assume that sorption is always at equilibrium, but that transfer to some sorption sites is diffusion controlled. In these models, water is commonly divided into mobile and immobile regions. Brusseau and Rao (1989b) discussed intra-organic-matter diffusion as a third process that may contribute to the tailing of hydrophobic organic compounds.

The desire to distinguish physical and chemical processes that result in asymmetric breakthrough curves has led experimentalists to use several solutes in soilcolumn studies. Tritiated water  $({}^{3}H_{2}O)$  is often used to determine if immobile water is present in the system (Rao et al., 1980; Nkedi-Kizza et al., 1983). This tracer is probably the most suited for measuring the macroscopic average pore-water velocity, v, and the dispersion coefficient, D. The Cl ion is also often used as a tracer, the advantage being that this tracer is safer to handle than radioactive tritium. However, the use of Cl is only effective in so far as this tracer truly behaves as a noninteracting solute, thereby mimicking the flow of water. If this is true, then it may be possible to define a retardation factor, R, of unity. Unfortunately, Cl often undergoes anion exclusion, especially in relatively fine-textured soils (Biggar and Nielsen, 1962; Corey et al., 1963; Jacobs, 1964), resulting in R< 1.

Organic-chemical transport is simultaneously influenced by both sorption and degradation. Miscible-displacement techniques may be better suited to simultaneous study of sorption and degradation than are traditional batch techniques, as flowing conditions, even in the laboratory, may better represent dynamic, transient field conditions. Unfortunately, nonequilibrium sorption confounds the measurement of degradation in miscible-displacement studies. Likewise, chemically or biologically mediated transformations may complicate the measurement of sorption, particularly when sorption is time dependent. A survey of the literature reveals that, in most previous soil-column experiments, great efforts were taken to eliminate degradation during studies of sorption kinetics accomplished with pesticide-displacement experiments.

Detailed study of asymmetric breakthrough curves may be accomplished through a combination of analytical solutions of candidate transport models and properly designed experiments. The theoretical development of the two-site sorption (equilibrium and kinetic) and two-region (mobile-immobile water) transport models under conditions in which the solute is being transformed has been presented by van Genuchten and Wagenet (1989). We presented a generic analytical solution that allows implementation of different hypotheses about the relative rates of degradation in the liquid and solid phases of a soil. Here, we show how the generic model can be used to advantage in the analysis of observed column effluent data for Cl, <sup>3</sup>H<sub>2</sub>O, and atrazine, and for 2,4,5-T effluent data of van Genuchten (1974). We emphasize that the purpose of our study is not to provide a comprehensive analysis of atrazine movement, but rather to il-

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lustrate typical applications of the general two-site/ two-region model to both degradable and nondegradable chemicals.

# MATERIALS AND METHODS

Batch sorption studies and column displacement experiments were performed using a Valois silty loam soil. All soil was collected from the 5- to 30-cm depth of a field site previously used for alfalfa production. The soil was air dried and passed through a 2-mm sieve prior to use. The soil used in one displacement and in one sorption isotherm experiment was sterilized by gamma irradiation from a Co source. Selected physical and chemical properties are listed in Table 1. Aqueous stock solutions were prepared with analytical-grade atrazine (99.9% pure; USEPA Pesticides and Industrial Chemical Repository, Research Triangle Park, NC),  ${}^{3}H_{2}O$  (Amersham, Arlington Heights, IL), and Cl as KCl in 0.01 *M* CaSO<sub>4</sub>. A Hewlett-Packard HP1090A liquid chromatograph, Beckman LS 9800 liquid scintillation counter, and a Buchler-Cotlove chloridometer were used to analyze for atrazine,  ${}^{3}H_{2}O$ , and Cl, respectively.

### Sorption Isotherms

Equilibrium sorption isotherms were generated using standard sorption-isotherm batch techniques (Rao and Davidson, 1979). Duplicate samples of 5 g of soil and 10 mL of atrazine in solution at each of eight concentrations (0.06–21  $\mu$ g/mL) were shaken for 48 h in screw-cap test tubes. The samples were allowed to stand for an additional 15 to 30 min to separate the soil-water mixture from the supernatant solution. The supernatant was filtered through a 0.45- $\mu$ m nylon membrane. The resulting samples, and also those used for estimating the initial and input concentrations, were analyzed by direct injection into the HPLC.

#### Column Displacement Experiments

Six soil-column experiments were conducted, designated I through VI (Table 2). The method described by Zhong et al. (1986) was followed with some modifications. A pulse of aqueous solution containing either  ${}^{3}\text{H}_{2}\text{O}$  and Cl (Exp. I and II) or atrazine and Cl (Exp. III–VI) was applied to 21.3-cm-length glass soil columns under steady-state water flow at two different velocities. The experiments are further distinguished as Exp. Ia and IIa for  ${}^{3}\text{H}_{2}\text{O}$  (Table 3); Exp. IIIa, IVa,

Table 1. Unemical and physical properties of va
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Table 3. V	alues of the	retardation (	coefficient (R)	, the pore-w	ater
velocity	(v) and the a	pparent diffu	ision coefficie	nt (D) estim	ated
from the	soil-column	displacement	experiments	involving Cl	and
tritium.		-	-	-	

Experiment	Tracer	R	v	D	
		(dimensionless)	(cm/h)	(cm²/h)	
Ia	<sup>3</sup> H <sub>2</sub> O	1.000†	$6.07 \pm 0.07$	$1.01 \pm 0.20$	
Ib	CĹ	$0.910 \pm 0.008$	6.07†	$0.841 \pm 0.193$	
IIa	3H'O	1.000†	$0.907 \pm 0.013$	$0.251 \pm 0.046$	
ПЬ	CÎ	$0.916 \pm 0.008$	0.907†	$0.214 \pm 0.031$	
IIIb	Ċl	0.91†	$0.864 \pm 0.002$	$0.104 \pm 0.004$	
1Vb	Cl	0.91+	$0.933 \pm 0.063$	$1.66 \pm 0.63$	
Vb	Čl	0.91†	$0.877 \pm 0.014$	$0.533 \pm 0.078$	
VIb	Cl	0.91†	$6.27 \pm 0.13$	$13.80 \pm 1.62$	

† Parameter held constant during fitting procedure; fitted values include the 0.05 confidence interval.

Va, and VIa for atrazine (Table 4); and Exp. Ib to VIb for Cl, which was applied in all six cases (Table 3). Atrazine was applied at an input concentration,  $c_0$ , equal to approximately 1  $\mu$ g/mL in Exp. IIIa and IVa, and 10  $\mu$ g/mL in Exp. Va and VIa. Column-effluent data were collected and analyzed for each species.

In addition, on completion of each atrazine experiment, soil from the columns was extruded and then extracted with methanol to determine the total amount of atrazine remaining in the system. Mass balance was determined and degradation rates were estimated by applying a first-order kinetic-rate equation to the data. When the efficiency of the extraction procedure (92%) was considered, recovery of atrazine by this process was  $100 \pm 4\%$  in experiments with no degradation. Use of identical techniques in experiments with degradation, and considering only cases in which the mass-balance difference was  $\geq 10\%$ , provide estimates of pesticide degradation that could be compared with those obtained from the breakthrough curves of the same columns, but derived from use of the parameter-optimization program CXT4 as described below.

Soil-column effluent data were evaluated using a modified version of the parameter-optimization code CXTFIT of Parker and van Genuchten (1984). The code was modified to permit the optimization of the degradation parameters in the general two-site/two-region models as discussed in van Genuchten and Wagenet (1989). A series of numerical experiments with hypothetical data sets (not further discussed here) were conducted with the resulting code (called CXT4) for verification of the correct inversion on the two-site/two-

pH (1:1 H <sub>2</sub> O extract)	Cation		Exchangeable acidity	]	۱	
	-exchange capacity	Organic C		Sand	Silt	Clay
	mmol/100 g	%	mmol/100 g		%	
5.9	15.0	1.64	11.0	30.1	55.2	14.7

Table 2. Experimental conditions used in the six soil-column studies of tritium, Cl and atrazine displacement.

Experimental			Experime	nt no.			
parameters	I	II	III†	IV	v	VI	
Solutes included				atrazine, Cl			
Input concentration, $c_o$	462.5, 100 (Bg/mL, μg/mL)		0.968 (µg/mL)	0.985 (μg/mL)	9.443 (μg/mL)	9.969 (μg/mL)	
Approximate pore-water velocity (cm h <sup>-1</sup> )	6	1	1	1	1	6	
Bulk density, $\rho$ (g cm <sup>-3</sup> )	1.334	1.295	1.318	1.348	1.356	1.291	
Volumetric water content, $\theta$ (cm <sup>3</sup> cm <sup>-3</sup> )	0.450	0.471	0.443	0.454	0.448	0.490	
Percent saturation	90	92	88	89	92	96	
T (°C)	22	24.5	25	25	25	25	

† Sterilized soil; all other cases used nonsterile soil.

Table 4. Estimated and measured parameters of atrazine breakthrough curves in experiments IIIa to VIa. ND indicates that the loss of atrazine during the time period of this experiment was 2.5% and was within the limits of experimental error Parameters k,  $\alpha$ , and f are defined in Eq. [1] and [2], and  $\theta$  and  $\mu$  are defined in Eq. [5e].

Exp. no.	k†	α	f	Fitted ↓	Meas- ured ψ	Actual µ
		h-1				h-1
IIIa	2.46	0.0144‡ ± 0.0018	0.36‡ ± 0.02		0.0266§	0.00056
IVa	2.46	0.0144¶	0.36¶		0.0456§	0.0005
Va	1.82	0.0132‡ ± 0.0008	0.35‡ ± 0.01	_	0.0121	0.0005
IVa	2.46	0.0132¶	0.35¶	0.0441	0.0456§	0.0005
VIa	1.82	0.0132¶	0.35¶	0.0584	ND	ND

† Determined from the equilibrium sorption isotherm.

**‡** Fitted with the two-site model.

§ Corrected for noneluted atrazine.

I Determined independently in another experiment and fixed.

region model with degradation. These experiments also illustrated the sensitivity of the optimization to small changes in the parameters describing sorption, mobile-immobile water, and degradation in the solution and sorbed phases. Program CXT4 is available from the authors on request.

In previous displacement experiments conducted in our laboratory, Zhong et al. (1986) used Cl as a tracer for measuring  $\nu$  and D in similar column-displacement experiments using aldicarb [2-methyl-2(methylthio) propionaldehyde 0(methylcarbamoyl)oxime], a weakly sorbing pesticide, for the sandy soils used in their experiments. The experiments in our study were conducted using either <sup>3</sup>H<sub>2</sub>O and Cl, or Cl in combination with atrazine for the purpose of distinguishing between physical processes associated with mobile immobile water flow (<sup>3</sup>H<sub>2</sub>O), and chemical processes of anion exclusion (Cl) and nonequilibrium sorption (atrazine). Due to restrictions (specific to our laboratory and university policies) on the use of radioactive materials, experiments that combined both atrazine and <sup>3</sup>H<sub>2</sub>O as a tracer in the same soil column could not be conducted.

### Theoretical Model

Appropriate analytic solutions of the transport models describing both two-site sorption and two-region transport are discussed in detail in van Genuchten and Wagenet (1989). In short, the two models assume that pesticide transport under steady-state water flow can be represented as follows.

Two-Site Model

$$\left(1 + \frac{\rho f k}{\theta}\right) \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \frac{\alpha \rho}{\theta}$$

$$[(1 - f)kc - s_2] - \mu c - \frac{\mu_{s1} f \rho kc}{\theta}$$
[1]

$$\frac{\partial s_2}{\partial t} = \alpha[(1-f)kc - s_2] - \mu_{s_2}x_2 \qquad [2]$$

where f is the fraction of equilibrium-type sorption sites; k is the distribution coefficient for linear solute partitioning between the solution (c) and sorbed (s) phases;  $\alpha$  is a kinetic rate coefficient;  $\mu$  represents the degradation rate constant as applied to equilibrium sites ( $\mu_{s1}$ ) of the solid phase, to nonequilibrium sites ( $\mu_{s2}$ ) of the sorbed phase, and to the liquid phase ( $\mu_1$ ). Other symbols not yet defined are the volumetric water content ( $\theta$ ), the soil bulk density ( $\rho$ ), distance (x), and time (t). Two-Region Model

$$(\theta_{\rm m} + f\rho k) \frac{\partial c_{\rm m}}{\partial t} = \theta_{\rm m} D_{\rm m} \frac{\partial^2 c_{\rm m}}{\partial x^2} - q \frac{\partial c_{\rm m}}{\partial x} - \alpha (c_{\rm m} - c_{\rm im}) - (\theta_{\rm m} \mu_{\rm /m} + f\rho k \mu_{\rm sm}) c_{\rm m} \quad [3]$$

$$\begin{bmatrix} \theta_{\rm im} + (1 - f)\rho k \end{bmatrix} \frac{\partial c_{\rm im}}{\partial t} = \\ \alpha (c_{\rm m} - c_{\rm im}) - [\theta_{\rm im}\mu_{lim} + (1 - f)\rho k\mu_{\rm sim}]c_{\rm im} \qquad [4]$$

where all terms are as previously defined, except that the subscripts m and im now refer to mobile and immobile regions of soil water,  $q = \theta_m v_m$ , and  $\alpha$ , f and k are redefined to describe diffusion-type interactions between the two liquid regions of the soil, rather than chemical-kinetic processes.

Equations [1] and [2] show that, at least in theory, it is possible to have three different degradation coefficients if the two-site model is assumed to be applicable:  $\mu_1$  for degradation in the liquid phase,  $\mu_{s1}$  for degradation from the type-1 (equilibrium) sorbed phase, and  $\mu_{s2}$  for degradation from the type-2 (kinetically) sorbed phase. Similarly, Eq. [3] and [4] indicate four possible degradation-rate coefficients if the tworegion model holds:  $\mu_{lm}$  and  $\mu_{lim}$  for degradation in the mobile and immobile liquid phases, respectively, and  $\mu_{sm}$  and  $\mu_{sim}$  for degradation from the mobile and immobile sorbed phases, respectively. As shown by van Genuchten and Wagenet (1989), at most, two degradation coefficients in both the two-site and two-region models can be considered macroscopically as truly independent model parameters, thus illustrating the complexity of the measurement and parameter-estimation problem. Experimentally, we are only able to distinguish a single, "lumped" degradation-rate coeffi-cient. Two options are available in the CXT4 code as it is currently written: degradation in the liquid phase only, or a single degradation rate that applies over the entire soil-water system. Chemical hydrolysis of atrazine is catalyzed by contact with soil and a more rapid rate constant for the soilwater system has been reported (Armstrong et al., 1967; Armstrong and Chesters, 1968; Gamble and Khan, 1985). Although two distinct rate coefficients for the solution and sorbed phases have not been measured, there is evidence that degradation occurs in the sorbed phase. Therefore, we assume that all degradation coefficients are the same, regardless of whether the chemical is dissolved in the liquid phase or adsorbed onto the solid matrix, or whether the chemical is in the mobile or stagnant regions of the soil. Therefore,  $\mu_1 = \mu_{s1} = \mu_{s2} = \mu$  for the two-site model, and  $\mu_{lm} = \mu_{lim} = \mu_{sm} = \mu_{sim} = \mu$  for the two-region model. Given the above simplifications, the two-site and two-re-

Given the above simplifications, the two-site and two-region models can be expressed in the same dimensionless form with five independent parameters. For the two-site model, these parameters are

$$P = vL/D$$
  $R = 1 + \rho k/\theta$  [5a,b]

$$\beta = \frac{\theta + f\rho k}{\theta + \rho k}$$
  $\omega = \alpha (1 - \beta)RL/\nu$  [5c,d]

$$\psi = \mu L/\nu \qquad [5e]$$

where L is the length of transport, and for the two-region model

$$P = v_{\rm m} L/D_{\rm m}$$
  $R = 1 + \rho k/\theta$  [6a,b]

$$\beta = \frac{\theta_{\rm m} + f\rho k}{\theta + \rho k} \qquad \omega = \alpha L/q \qquad [6c,d]$$

$$\psi = \frac{\mu L}{\nu} = \frac{\mu L}{\theta_{\rm m} \nu_m}.$$
 [6e]

*P* is commonly called the Peclet number and  $\psi$  is a dimensionless degradation parameter. The parameter  $\beta$  is a dimensionless partitioning coefficient, and  $\omega$  is a dimensionless rate coefficient for either kinetic sorption or mobile-immobile exchange. The above parameters are discussed in detail by van Genuchten and Wagenet (1989).

## **RESULTS AND DISCUSSION**

# Sorption Isotherms

The equilibrium sorption isotherm for atrazine on Harford soil was described with both the linear (s = kc) and nonlinear ( $s = k_c r^n$ ) forms of the Freundlich equation (Fig. 1). Application of the linear form predicted, for the linear range of the curve (first seven data points), k = 1.98 with  $r^2 = 0.99$ , while the nonlinear form predicted  $k_f = 2.46$  and n = 0.87 with  $r^2$ = 0.99 for the entire isotherm. Although the isotherm appears linear over the range of concentrations used in displacement experiments (1-10 µg/mL), sorption nonlinearity affected analysis of miscible-displacement data and was, therefore, considered during the subsequent analysis of the breakthrough curves (BTCs) discussed below. Isotherms for sterilized and unsterilized soil were indistinguishable.

### **Column Displacement Experiments**

A representative column effluent curve for the simultaneous application of Cl and <sup>3</sup>H<sub>2</sub>O on Harford soil is shown in Fig. 2 for the relatively fast flow experiment (v = approximately 6 cm/h). Clearly, the two tracers are eluted symmetrically (without tailing), indicating that, at this v, there were not significant effects of immobile water on transport. Since other Cl and  ${}^{3}\text{H}_{2}\text{O}$  curves measured at other velocities exhibited identical behavior, we decided to use only the two-site formulation in subsequent analysis of the atrazine displacement in Harford soil. Note that the Cl tracer always eluted first, thus providing evidence for anion exclusion, as expected. We assume that tritium is not subject to any sorption, ion-exchange, or anion-exclusion processes. The distribution coefficient k is then zero and R (Eq. [5b]) becomes unity. The assumption of having R = 1 for tritiated water enabled us to estimate v directly from the effluent curve (Parker and van Genuchten, 1984), which was in agreement with direct measurements of v.



Fig. 1. Adsorption isotherms for atrazine on Valois silty loam soil.

Given that R = 1, the program CXT4 was used to estimate the parameters v and D (Table 3) for the two tritiated-water experiments (Exp. Ia, IIa). Using v as estimated from the <sup>3</sup>H<sub>2</sub>O effluent data, we next fitted D and R to the Cl data, while keeping v fixed. Results in Table 3 (Exp. Ib, IIb), show that R generally was ~0.91.

In the experiments conducted with atrazine at two velocities and two concentrations (Exp. III-VI) the BTCs were asymmetrical and tailed, as others have reported (Rao and Davidson, 1979; Goltz and Roberts, 1986). Breakthrough curves measured here for Cl were symmetrical, similar to that reported in Fig. 2. The Cl data were used with R = 0.91 to determine v and D. The atrazine data were then simulated for five cases; the results are summarized in Table 4 and discussed below.

Miscible-displacement experiments were more sensitive to isotherm nonlinearity than was the batchisotherm method, and isotherm nonlinearity was considered in simulations of the BTCs measured in the soil-column experiments. The two-site model formulation assumes a linear isotherm (Eq. [5b]); therefore, linearized values of k were calculated for each initial concentration applied in the miscible-displacement experiments. Rao and Davidson (1980) demonstrated how the ratio of the nonlinear and linear forms (Eq. [7]) of the Freundlich equation can be used to determine a linearized value of k for a particular concentration when the isotherm is, in fact, nonlinear:

$$k = k_f c_o^{n-1}$$
 [7]

For low-concentration experiments ( $c_0 = 0.968$  and 0.985 µg/mL), k = 2.46 mL/g and, for high concentration experiments ( $c_0 = 9.443$  and 9.969 µg/mL), k = 1.82 mL/g. Retardation factors for miscible-displacement experiments were based on these linearized estimates of k and were held constant in all simulations of atrazine BTCs.

Effluent data from atrazine Experiments IIIa ( $v = 0.86, c_o = 0.968 \,\mu\text{g/mL}$ ) and IVa ( $v = 0.93, c_o = 0.985 \,\mu\text{g/mL}$ ) simulated with the two-site model are shown in Fig. 3. In Exp. IIIa (Fig. 3a), a degradation rate ( $\mu = 0.00056 \, \text{h}^{-1}$ ) was estimated from the atrazine mass-balance determination using the effluent data, the



Fig. 2. Representative breakthrough curve for  ${}^{3}H_{2}O$  and Cl in tracer experiments on Valois soil. Pore-water velocity, v = 6.07 cm/h, R is a retardation factor.

amount remaining in the column at the end of the experiment, and the applied mass. This value of  $\mu$  was then used to calculate  $\psi = 0.0266$ . Then, using CXT4 and this value of  $\psi$ , the sorption parameters estimated with the two-site model were  $\alpha = 0.0144$  and f = 0.36(Table 4). It is important to note that the value of  $\alpha$  is consistent with that predicted with the regression equation relating  $\alpha$  and k recently presented by Brusseau and Rao (1989a). For Exp. IVa (Fig. 3b), the parameters  $\alpha$  and f were fixed at the values estimated in the above simulation of Exp. IIIa. A one-parameter optimization was used to estimate  $\psi = 0.0413$ , which approximates the experimentally estimated value of 0.0456. The first simulation (Fig. 3a) demonstrates how nonequilibrium sorption can be estimated when degradation is quantified independently. The second simulation (Fig. 3b) illustrates how a degradation rate can be predicted when the sorption parameters are known. The two processes can be studied simultaneously by way of the two-site model but, given the significant correlation between Rand  $\psi$ , both equilibrium sorption and degradation cannot be determined through curve-fitting the data from a single experiment.

In the low velocity (v = 0.9 cm/h), low concentration ( $c_0 = 1 \ \mu \text{g/mL}$ ) experiments (Exp. IIIa, IVa), 16 to 18% of the applied atrazine was not eluted from the soil column and was recovered by extraction of the soil at the completion of the experiment. Degradation appears as a sink term in the model formulation, and  $\psi$  had to be corrected to include noneluted as well as degraded atrazine in these two cases. The loss of the parent compound to processes other than degradation



Breakthrough curves and model simulations for Exp. Va, IVa, and VIa are shown in Fig. 4a, 4b, and 4c, respectively. Data from Exp. Va (v = 0.88 cm/h,  $c_0 = 9.443 \ \mu g/mL$ ) were simulated with degradation fixed to the mass-balance-determined value of 0.0005 h<sup>-1</sup>, while the sorption parameters  $\alpha$  and f were estimated with the two-site model. The parameters ( $\alpha =$ 0.0132 and f = 0.35) approximated those estimated in Exp. IIIa ( $\alpha = 0.0144$  and f = 0.36). The agreement of the predicted values for these data with different initial concentrations and the ability to simulate the data in both cases demonstrates that linearized values of k can be calculated and used with this model under conditions of isotherm nonlinearity.

The sorption parameters from Exp. Va were then used in simulations of data from Exp. IVa (v = 0.93cm/h,  $c_0 = 0.985 \ \mu g/mL$ ; Fig. 4b) and VIa (v = 6.3cm/h,  $c_0 = 9.969 \ \mu g/mL$ ; Fig. 4c). An accurate prediction of the experimental BTC was obtained when predicting the low-concentration data (IVa) from the parameters estimated with high-concentration data. The predicted value of  $\psi$  also agrees with the measured value. The simulated curve of the high-velocity data (VIa) was shifted to right of the observed values, sug-



Fig. 3. Breakthrough curves in which (3a) sorption parameters were estimated with the two-site model and degradation ( $\psi$ ) was determined independently with mass-balance data, and (3b) the sorption parameters were fixed to the values estimated in (3a) and degradation was estimated with the two-site model. Parameters  $k, f, \alpha$ , and v are defined in Eq. [1] and [2], and  $R, \beta$ , and  $\omega$  are defined in Eq. [5].



Fig. 4. Breakthrough curves in which (4a) sorption parameters were estimated with the two-site model and degradation ( $\psi$ ) was determined independently with mass-balance data, and (4b, 4c) the sorption parameters were fixed to the values estimated in (4a), and degradation was estimated with the two-site model. Parameters k, f,  $\alpha$ , and v are defined in Eq. [1] and [2], and R,  $\beta$ , and  $\omega$  are defined in Eq. [5].



Fig. 5. Measured (van Genuchten et al., 1974) and simulated breakthrough curves for the pesticide 2,4,5-T (pore-water velocity, v =8.73 cm/d) developed with the two-region model for the two cases of no degradation ( $\mu = 0$ ) and degradation ( $\mu > 0$ ). Values of the retardation coefficient (R), Peclet number (P) and sorption rate coefficient ( $\omega$ ) were determined independently with batch and <sup>3</sup>H<sub>2</sub>O data. Parameters  $\psi$ ,  $\beta$ , and  $\mu$  are defined in Eq. [5].

gesting that nonequilibrium may be greater than that which is accounted for with the estimated values of fand  $\alpha$ .

Data from van Genuchten (1974) were used as an additional case to evaluate the application of the tworegion formulation of the model to describe degradation during transport when the nonequilibrium condition results from the presence of immobile water rather than two-site sorption. A BTC for 2,4,5-T herbicide on Glendale silt loam (fine-silty, mixed [calcareous], thermic Typic Torrifluvent) is shown in Fig. 5. The parameters R = 2.14, P = 56, and  $\omega = 0.722$ were determined in batch and  ${}^{3}H_{2}O$  studies and fixed in simulations of the 2,4,5-T BTC. In Case 1 of Fig. 5, the curve was simulated with degradation fixed to zero. The fitted curve overestimates the mass present in the system and, therefore, the concentration in the central region of the curve. In Case 2, the curve was simulated with  $\psi > 0$ , resulting in a better description of the observed data, particularly in the central region of the curve. A value of  $\mu = 0.022 \text{ d}^{-1}$  was predicted and corresponds to a half-life of 32 d. Independent estimates of degradation were not available for these data. However, O'Connor and Wierenga (1973) evaluated the persistence of 2,4,5-T on Glendale silt loam in lysimeter studies and monitored dissipation of the herbicide over a period of several months. They found that the time required for complete degradation of 2,4,5-T varied between 43 and 85 d (O'Connor and Wierenga, 1973), slightly faster than the degradation rate predicted with the two-region model. O'Connor and Wierenga found that degradation was more rapid when the soil had been previously treated with 2,4,5-T; they, in fact, reported data for second and third applications. The lack of soil-column pretreatment with 2,4,5-T may explain the longer half-life predicted here with laboratory miscible-displacement data.

# CONCLUSIONS

Potential applications of the two-site/two-region model for predicting pesticide degradation rates under conditions of chemical and physical nonequilibrium were demonstrated. The inclusion of the degradation parameter in the familiar two-site/two-region model improved the description of effluent data (van Genuchten, 1974) in a case where degradation was considered a confounding process in the original interpretation of experimental results. These techniques are applicable to other nonpesticidal organic-chemical contaminants.

This study demonstrates that proper execution and analysis of organic-chemical displacement experiments is not easy due to the many simultaneous processes and parameters involved. Of course, parsimony of parameters is a serious consideration when these types of models are applied to field conditions. However, we still need to know the relevant processes affecting organic-contaminant transport and transformation. Thus, carefully designed and executed laboratory experiments remain important. Appropriate models of the type used in this study, together with laboratory displacement studies, offer an opportunity to differentiate between various processes and properties. This study only illustrated potential applications of the model. A more comprehensive analysis of organic-chemical transport with degradation also requires a series of batch-type degradation experiments in which, hopefully, some of the degradation parameters can be estimated independently.

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