

COUPLED EFFECTS OF NONLINEAR, RATE-LIMITED SORPTION AND BIODEGRADATION ON TRANSPORT OF 2,4-DICHLOROPHENOXYACETIC ACID IN SOIL

MAX Q. HU† and MARK L. BRUSSEAU*†‡

†Department of Soil, Water and Environmental Science ‡Department of Hydrology and Water Resources,
University of Arizona, Tucson, Arizona 85721, USA

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Abstract—The transport and fate of many contaminants in subsurface systems can be influenced by several coupled processes, such as nonlinear, rate-limited sorption and biodegradation. We investigated the transport in soil of a model organic compound, 2,4-dichlorophenoxyacetic acid (2,4-D), influenced by nonlinear, rate-limited sorption and biodegradation. Miscible displacement and batch sorption experiments were conducted using a wide range of solute concentrations to investigate the impact of concentration-dependent behavior on transport. The sorption isotherm was approximately linear at a low concentration, and nonlinear over the extended range of concentrations. Results from the transport experiments, with the fitted N values approaching 1 at low input concentrations, were consistent with the batch sorption study. Nonlinear sorption significantly influenced the position of the breakthrough curves because of concentration-dependent retardation. However, although both nonlinear and rate-limited sorption influenced the shape of the breakthrough curves, the impact of rate-limited sorption was greater. The effective travel time of 2,4-D transport is influenced by synergistic interactions between sorption and biodegradation. For example, the sequential rightward shift of the breakthrough curves with decreasing input concentration, due to nonlinear sorption of 2,4-D, is enhanced by biodegradation.

Keywords—Coupled effects Sorption Biodegradation Transport

INTRODUCTION

Most solute transport models, especially for field-scale applications, include the assumption that the distribution of solute between liquid and solid phases is a linear process. However, nonlinear isotherms are the norm rather than the exception for many polar organic, as well as inorganic, chemicals. Nonlinear sorption can cause nonideal transport, such as asymmetrical breakthrough curves. In addition, estimates of retardation can be in error if nonlinear sorption is ignored. Rate-limited sorption is another process that influences many solutes and that can cause nonideal transport. Although these processes and their impact on transport are usually examined separately, both processes are likely to be operative in some systems. However, very few experiment-based analyses have been conducted on the influence of coupled nonlinear and rate-limited sorption on solute transport [1–7]. None of these investigations examined transport behavior using several input concentrations spanning a wide range in magnitude.

The coupled effects of nonideal (nonlinear, rate-limited) sorption and biodegradation on the transport of organic solutes have rarely been examined. The influence of combined rate-limited sorption and transformation on transport has been discussed by a few authors [8–12]. The effect of coupled nonlinear sorption and transformation on transport of solutes has been discussed to an even lesser extent [13].

The objective of this paper is to investigate the coupled effects of biodegradation and nonideal sorption on the transport of a model organic compound, 2,4-dichlorophenoxyacetic

acid (2,4-D), in soil. The results from batch and miscible-displacement experiments, conducted using a wide range of concentrations, will be used to investigate concentration-dependent behavior in this system, which is influenced by nonlinear, rate-limited sorption and linear, rate-limited biodegradation. The relative importance of nonlinear and rate-limited sorption, and the synergistic interactions between sorption and biodegradation will be evaluated.

MATERIALS AND METHODS

Materials

The sandy loam soil (sand: 77.7%, silt: 18.1%, clay: 4.2%, organic carbon: 1.4%) used for the experiments was collected from the top 10 cm of an agricultural field that had a history of applications of 2,4-D. Previous experiments demonstrated the existence of a microbial population (*Pseudomonas* species) capable of degrading 2,4-D [11]. Prior to use, the soil was sieved to remove the >2 mm size fraction. For selected experiments, the soil was sterilized by autoclaving at 15 psi and 121°C for 20 min; this step was repeated 2 d later.

Analytical grade 2,4-D was purchased from Aldrich Chemical (Milwaukee, WI, USA). Tritiated water ($^3\text{H}_2\text{O}$) and uniform ring-labeled [^{14}C]2,4-D ($\geq 98\%$ radiochemical purity) were purchased from New England Nuclear (Du Pont, Boston, MA, USA) and Sigma Chemical (St. Louis, MO, USA), respectively. The reported aqueous solubility of 2,4-D is 620 mg/L [14] and 890 mg/L [15] at 25°C.

Batch sorption experiment

A sorption isotherm for 2,4-D was measured using the standard batch procedure. The stock 2,4-D solution was filter-

* To whom correspondence may be addressed
(brusseau@ag.arizona.edu).

sterilized (0.2 μm) and diluted with autoclaved 5 mM CaCl_2 solution. Initial concentrations of 2,4-D in the solutions were 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100, 200, and 500 mg/L. The 2,4-D solutions were then spiked with ^{14}C -labeled 2,4-D, with a specific activity of approximately 3 nCi/ml.

Aliquots of ^{14}C -spiked 2,4-D solutions (10 ml) were added to screw-cap glass tubes containing 10 g of sterile soil (done in triplicate). The glass tubes were placed horizontally in an environmental shaker, which was operated at 320 rpm for 72 h at a constant temperature ($24 \pm 1^\circ\text{C}$). A previous study using this soil showed that no measurable change in 2,4-D concentration occurred beyond this time [11]. Following equilibration, the glass tubes were centrifuged at 2,250 rpm (850 g) for 10 min and the supernatant was filtered with an ultrafine glass microfiber filter (0.7 μm). The ^{14}C -activity in a 0.45-ml aliquot of the supernatant solution was assayed by liquid scintillation counting (Tri-Carb Liquid Scintillation Analyzer, Model 1600TR, Packard, Meriden, CT, USA). The difference between initial and final 2,4-D mass in solution was assumed to be sorbed. Controls showed that the glass tubes and the filtering did not affect the aqueous 2,4-D concentration.

Miscible displacement experiments

Preparative chromatography columns made of precision-bore stainless steel (2.1-cm inner diameter [i.d.], 7.0-cm long; Alltech, Deerfield, NJ, USA) were used in the column experiments. The columns were incrementally packed with dry soil to obtain uniform bulk densities. The packed columns were slowly wetted from the bottom to establish saturation and approximately 100 pore volumes of electrolyte solution (5 mM CaCl_2 , autoclaved) were pumped through the column prior to the transport study. The value of solution pH was about 6.5. For the column packed with the unsterilized soil, a 50-mg/L 2,4-D solution was pumped through the column intermittently to stimulate the activity of microorganisms capable of degrading 2,4-D. Approximately 100 pore volumes of 2,4-D solution were pumped through the column during this 10-d period, after which the column was flushed with the electrolyte solution to remove remaining 2,4-D.

The apparatus and methods employed for the miscible displacement studies were similar to those used previously [16]. A high-performance liquid chromatography (HPLC) pump (SSI Acuflo series II, Fisher Scientific, Tustin, CA, USA) was connected to the column, with a three-way switching valve placed in-line to facilitate switching between solutions with and without the solute of interest. Column effluent fractions were collected with an automated fraction collector (Pharmacia RediFrac, Pharmacia Biotech AB, Uppsala, Sweden), and the activities for ^{14}C 2,4-D and $^3\text{H}_2\text{O}$ in the effluent samples were analyzed by radioassay using liquid scintillation counting. For the experiments conducted with the nonsterile soil, samples of the column effluent were analyzed before and after acidification to a pH < 2. The acidification was done to decrease the solubility of $^{14}\text{CO}_2$, which allowed us to test for the generation of $^{14}\text{CO}_2$. Analysis of effluent samples by HPLC produced no detectable levels of 2,4-dichlorophenol. In addition, the results obtained by liquid scintillation analysis compared well to those obtained by HPLC analysis.

The initial concentrations of 2,4-D used in the transport experiments (0.1, 1, 10, and 100 mg/L) covered a range of three orders of magnitude. Specific activities of tritium and ^{14}C -labeled 2,4-D in the solution were 2 nCi/ml and 1 nCi/ml, respectively. A flow rate of 1.4 ml/min was used for the ex-

periments, corresponding to a pore-water velocity of approximately 60 cm/h. This velocity is representative of forced-gradient systems.

Total viable heterotrophs and 2,4-D degraders were enumerated in the soil samples collected from the column, and these procedures confirmed the occurrence of 2,4-D biodegradation in the system. Enumeration of 2,4-D degraders and total viable heterotrophs was performed as follows. The first half of the soil contained in the column (i.e., column inlet side) was aseptically removed and thoroughly mixed. Five replicate 1-g soil samples were added to 9.0 ml of sterile water. The samples were vortexed vigorously for 2 min and serially diluted. Diluted samples were plated on 2,4-D indicator media to enumerate the 2,4-D degraders. The 2,4-D indicator medium consisted of a mineral salts broth containing per liter: 0.112 g MgSO_4 , 0.005 g ZnSO_4 , 0.0025 g NaMoO_4 , 0.0218 g K_2HPO_4 , 0.014 g CaCl_2 , 0.22 mg FeCl_3 , 0.5 g NH_4Cl , and 20 g noble agar, adjusted to pH 7. The medium was autoclaved and cooled to 60°C , then supplemented with 50 mg/L filter sterilized yeast extract and 500 mg/L filter sterilized 2,4-D. The heterotrophic viable bacterial population was determined by plating the diluted samples on the nonselective solid media, R_2A (Becton Dickinson, Cockeysville, MD, USA).

Mathematical model

A transport model based on nonlinear, rate-limited sorption was used to analyze the results of the experiments. For this model, sorption was conceptualized to occur in two domains (see references in [16])



where

$$S_1 = FK_f C^N \quad (2)$$

$$dS_2/dt = k_1 S_1 - k_2 S_2 \quad (3)$$

and C is the solution-phase solute concentration (mass/length³ [M/L^3]); S_1 is the sorbed-phase concentration (M/M) in the "instantaneous" domain; S_2 is the sorbed-phase concentration (M/M) in the rate-limited domain; K_f is the Freundlich sorption coefficient (L^{3N}/M^N) related to the sorption capacity; N is the Freundlich exponent, which characterizes the degree of nonlinearity; F is the fraction of sorbent for which sorption is instantaneous; and k_1 and k_2 are forward and reverse first-order rate coefficients (T^{-1}), respectively. Note that the Freundlich isotherm is used because it is the mostly widely used isotherm function for many contaminants of interest [17,18].

The following nondimensional equations describe solute transport governed by steady state, one-dimensional water flow, nonlinear, rate-limited sorption, and first-order transformation [13]:

$$\begin{aligned} \frac{\partial C^*}{\partial T} + (\beta R - 1)NC^{*N-1}\frac{\partial C^*}{\partial T} + \omega(C^{*N} - S^*) \\ = \frac{1}{P}\frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} - \epsilon_c C^* - \epsilon_{st} C^{*N} \end{aligned} \quad (4)$$

$$(1 - \beta)R\frac{\partial S^*}{\partial T} = \omega(C^{*N} - S^*) - \epsilon_{s2}S^* \quad (5)$$

with the following definitions for the nondimensional parameters:

$$C^* = C/C_0 \quad (6a)$$

$$T = vt/L \quad (6b)$$

$$S^* = S_2/[(1 - F)K_f C_0^N] \quad (6c)$$

$$X = x/L \quad (6d)$$

$$P = \nu L/D \quad (6e)$$

$$R = 1 + (\rho/\theta)K_f C_0^{N-1} \quad (6f)$$

$$\beta = [1 + F(\rho/\theta)K_f C_0^{N-1}]/R \quad (6g)$$

$$\omega = k_2(1 - \beta)RL/\nu \quad (6h)$$

$$\epsilon_\ell = \mu_\ell L/\nu \quad (6i)$$

$$\epsilon_{s1} = (\beta R - 1)\mu_{s1}L/\nu \quad (6j)$$

$$\epsilon_{s2} = (1 - \beta)R\mu_{s2}L/\nu \quad (6k)$$

where C_0 is the solute input concentration (M/L³), ν is the average pore-water velocity (L/T) (with $\nu = q/\theta$); q is Darcy flux (L/T); x is distance; L is column length; D is the dispersion coefficient (L²/T); ρ is soil bulk density (M/L³); θ is volumetric soil-water content; and μ_i is the first-order rate coefficient (T⁻¹) for transformation in solution (ℓ), equilibrium-sorbed (s_1), and rate-limited-sorbed (s_2) phases, respectively. The parameter P is the Peclet number, R is the retardation factor, β is the fraction of instantaneous retardation, ω is the Damkohler number, and ϵ_i is the nondimensional degradation parameter for each of the three domains (ℓ , s_1 , s_2). The retardation factor, R , is calculated by moment analysis of the breakthrough curves. The size of the input pulse, T_0 , is obtained from the experiment. The typical assumption that 2,4-D is degraded only from the solution phase [19] is employed herein. Recent publications indicate that sorbed fractions of compounds can be utilized by microorganisms through a number of mechanisms [20,21]. However, such observations have not been reported for 2,4-D. For this case, ϵ_{s1} and ϵ_{s2} become 0, leaving ϵ_ℓ as the only transformation parameter of concern. Values for this parameter are obtained by an analysis of the breakthrough curve concentration plateau at steady state [9]. The parameters N , β , ω , and P are obtained by using a nonlinear least-squares program (FITNLE) that includes nonlinear sorption [22]. The modeling analyses are used as a tool to help examine the impact of the coupled processes on transport, and to help elucidate the relative contribution of individual processes to the systems where synergistic effects exist. Caution should be exercised concerning the constraints associated with model calibration. However, if used judiciously, model calibration, which is a widely used approach, can be useful.

RESULTS AND DISCUSSION

Rate-limited sorption and transport

Breakthrough curves for transport of ³H₂O and 2,4-D in the sterile soil are shown in Figure 1. The nonreactive tracer (³H₂O) exhibits a symmetrical, relatively sharp breakthrough curve, indicating that the column has ideal hydrodynamic properties. Conversely, transport of 2,4-D is nonideal, exhibiting asymmetrical breakthrough curves that have extended tailing. The occurrence of tailing at both high ($C/C_0 = 1$) and low ($C/C_0 = 0$) concentrations indicates that rate-limited sorption is contributing to the nonideal transport.

Sorption kinetics parameters for 2,4-D transport with different input concentration are listed in Table 1. The desorption

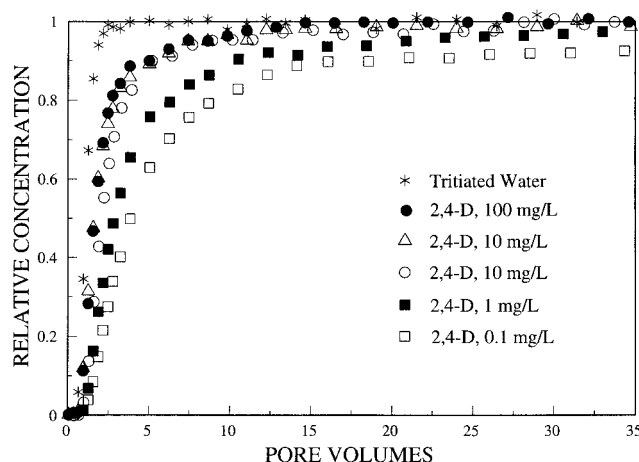


Fig. 1. Measured breakthrough curves for transport of tritiated water and 2,4-dichlorophenoxyacetic acid (2,4-D) with a range of input concentrations through the sterile soil column.

rate coefficient (k_2) decreases as C_0 decreases. Conversely, the F value, the fraction of sorbent for which sorption is instantaneous, appears to remain constant within the range of 0.31 to 0.46 for the C_0 difference of three orders of magnitude. Gamberding et al. [8] reported smaller k_2 values for a higher concentration ($C_0 = 10$ mg/L) than for a lower concentration ($C_0 = 1$ mg/L) for atrazine and cyanazine sorption. However, Rao et al. [2] reported smaller k_2 values for a lower concentration than for a higher concentration for sorption of 2,4-D amine and atrazine. Both of these data sets included only two concentrations.

For a true first-order rate process, the magnitude of the rate coefficient should be independent of concentration. However, the rate-limited sorption of many organic compounds is thought to be caused by intrasorbent diffusion [16,23–25]. Given that the rate of diffusional mass transfer is a function of the concentration gradient, the first-order approximation of the diffusional process possibly could result in concentration-dependent rate coefficients. The apparent correlation between k_2 and C_0 possibly could also be related to the concentration dependency of R (i.e., K_d), which increases as C_0 decreases. For example, inverse correlations between k_2 and K_d have been reported [17].

Nonlinear sorption and transport

A sorption isotherm was measured for 2,4-D using a wide range of initial concentrations (0.1–500 mg/L). The Freundlich equation was used successfully to fit the isotherm data. Regressions were made for various concentration ranges, with the results presented in Table 2 and Figure 2.

For lower concentrations (up to 1 mg/L initial concentration), 2,4-D sorption was essentially linear, with N equal to 0.99. With a molecular weight of 221 mg/L for 2,4-D, this corresponds to an equilibrium aqueous-phase solute concentration of 1.05×10^{-4} M, which is consistent with the reported rule-of-thumb value of 10^{-3} M for linear sorption [26]. Conversely, sorption was nonlinear for the wider concentration range ($N = 0.85$). Similar results have been reported by Young and Ball [27].

The transport of 2,4-D for the experiments with lower input concentration was more retarded than that for the higher input-concentration experiments (see Fig. 1). This change in retardation is associated with the nonlinear sorption of 2,4-D, and

Table 1. Sorption parameters for 2,4-dichlorophenoxyacetic acid obtained from miscible displacement experiments^a

C_0 (mg/L)	ν (cm/h)	R	N	β	ω	k_2 (1/h)	F^b
Nonlinear sorption							
100	63.1	2.51	0.38 (0.35–0.42)	0.63 (0.61–0.64)	0.26 (0.22–0.29)	2.46 (2.03–2.89)	0.38 (0.35–0.40)
10	63.1	3.10	0.49 (0.47–0.52)	0.53 (0.52–0.56)	0.20 (0.18–0.21)	1.23 (1.09–1.39)	0.31 (0.29–0.33)
1	63.7	5.58	0.93 (0.91–0.94)	0.56 (0.55–0.56)	0.17 (0.16–0.18)	0.63 (0.58–0.67)	0.46 (0.45–0.46)
0.1	63.5	9.63	0.96 (0.94–0.99)	0.41 (0.40–0.41)	0.19 (0.18–0.20)	0.30 (0.28–0.32)	0.34 (0.33–0.34)
Linear sorption							
100	63.1	2.51	1	0.67 (0.64–0.69)	0.15 (0.12–0.19)	1.64 (1.20–2.09)	0.44 (0.40–0.48)
10	63.1	3.10	1	0.52 (0.50–0.54)	0.16 (0.13–0.19)	0.97 (0.76–1.20)	0.29 (0.26–0.32)
1	63.7	5.58	1	0.56 (0.55–0.56)	0.16 (0.15–0.17)	0.60 (0.57–0.63)	0.46 (0.45–0.46)
0.1	63.5	9.63	1	0.41 (0.40–0.41)	0.19 (0.17–0.20)	0.30 (0.27–0.32)	0.34 (0.33–0.34)

^a Parameters are defined in the text. Values in parentheses represent 95% confidence intervals.^b $F = (BR - 1)/(R - 1)$. $\rho = 1.62$, $\theta = 0.413$.

is consistent with the results of the batch experiment. The retardation factor will be concentration dependent when sorption is nonlinear (see Eqn. 6f). For example, values of R calculated by moment analysis were 2.51, 3.10, 5.58, and 9.63 for 100, 10, 1, and 0.1 mg/L input concentrations, respectively. Predicting R values for one input concentration using data obtained at another concentration can lead to errors if nonlinear sorption is ignored.

For the column experiments, the fitted N values decreased as the input concentrations increased (see Table 1). Sorption appeared to be almost linear (Freundlich exponent $N > 0.93$) for 2,4-D transport at input concentrations of 0.1 and 1 mg/L. For this low concentration range, the fitted N values are comparable to the N value obtained from the batch study for the equilibrium concentration in the aqueous phase (C_e) < 1 mg/L. Conversely, the N values obtained from the column experiments are smaller than the batch values for high C_0 (10 and 100 mg/L). However, simulated breakthrough curves based on the fitted N values are not significantly different from the simulations obtained by using the batch value (0.85), as shown in Figure 3. This indicates that the usual assumption of a concentration-independent N may not lead to significant error in simulating transport.

Table 2. Regression data for the 2,4-dichlorophenoxyacetic acid (2,4-D) sorption isotherm^a

C_0 range (mg/L)	N	B	R^2	K_f ($\mu\text{g}^{1-N}\text{L}^N/\text{kg}^N$)
0.1–1	0.99	0.54	0.992	3.50
0.1–10	0.85	0.37	0.993	2.32
0.1–100	0.85	0.37	0.998	2.34
0.1–500	0.86	0.37	0.998	2.34

^a C_0 = 2,4-D input concentration. The regression is $\log S_e = N \log C_e + B$; where S_e and C_e are equilibrium concentrations in the sorbed and aqueous phases, respectively. N = Freundlich exponent; B = $\log K_f$; R^2 = correlation coefficient; K_f = Freundlich sorption coefficient.

Relative importance of nonlinear sorption and rate-limited sorption

As the pore-water velocity decreases (increasing residence time), the degree of nonequilibrium due to sorption kinetics tends to decrease. Conversely, the impact of nonlinear sorption on transport is not affected by changes in velocity. Thus, it is expected that the relative contribution of nonlinear sorption to nonideal transport will be more pronounced at slower pore-water velocities compared to that of rate-limited sorption. This is shown in Figure 4, wherein accounting for nonlinearity appears to produce a slightly better description of the experimental data obtained at a lower velocity, whereas accounting for nonlinear sorption has negligible effect for the higher pore-water velocity.

To evaluate the relative impact of nonlinear and rate-limited sorption on breakthrough curve asymmetry, the elution curves for transport of 2,4-D with different C_0 were normalized by

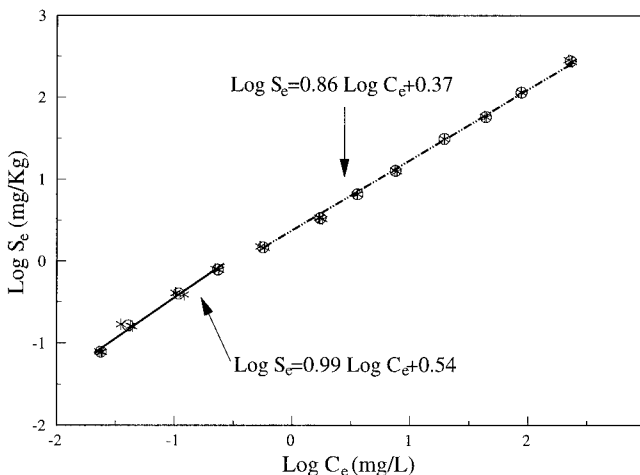


Fig. 2. Isotherm for equilibrium sorption of 2,4-dichlorophenoxyacetic acid. *: triplicate data points, O: mean values of the triplicates; lines are the Freundlich model fitted to the mean data.

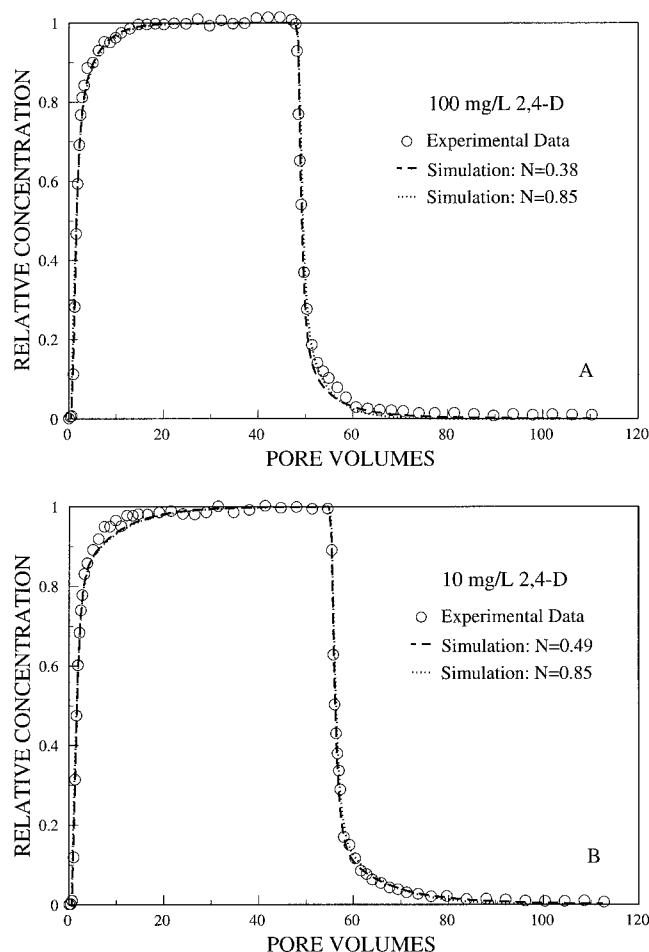


Fig. 3. Illustration of the effect of the Freundlich exponent (N) value on transport of 2,4-dichlorophenoxyacetic acid (2,4-D): (A) solute input concentration (C_0) = 100 mg/L; (B) C_0 = 10 mg/L. For each C_0 , rate-limited sorption parameters (β and ω) are the same for both simulations.

their individual retardation factors. By doing this, the effect of the changing position of the breakthrough curves (concentration-dependent R) is excluded from the analysis. The elution waves for 2,4-D transport, plotted based on the relative pore volumes, are shown in Figure 5A.

To help evaluate the measured data, the results of two sets of simulations are presented in Figures 5B and 5C. The first set illustrates the impact of nonlinear sorption alone on solute elution for the specific case where N changes with C_0 (Fig. 5B). On a relative basis, the elution curves for the higher concentrations begin dropping first and exhibit greater tailing. This is caused by the decrease of N with increasing concentration, which causes greater spreading. The impact of rate-limited sorption on solute elution is shown in Figure 5C for the case where N remains fixed at 0.85 for all concentrations. In this case, the elution curves for the lower concentrations begin dropping first and exhibit greater tailing. This is caused by the decrease in β with decreasing concentration (see Table 1), which leads to a greater degree of nonequilibrium during transport.

The measured data appear to exhibit combined effects of both processes. The lower concentration curves elute first, indicating the influence of rate-limited sorption. However, the higher concentration curves appear to exhibit more extensive tailing, indicating the influence of nonlinear sorption with con-

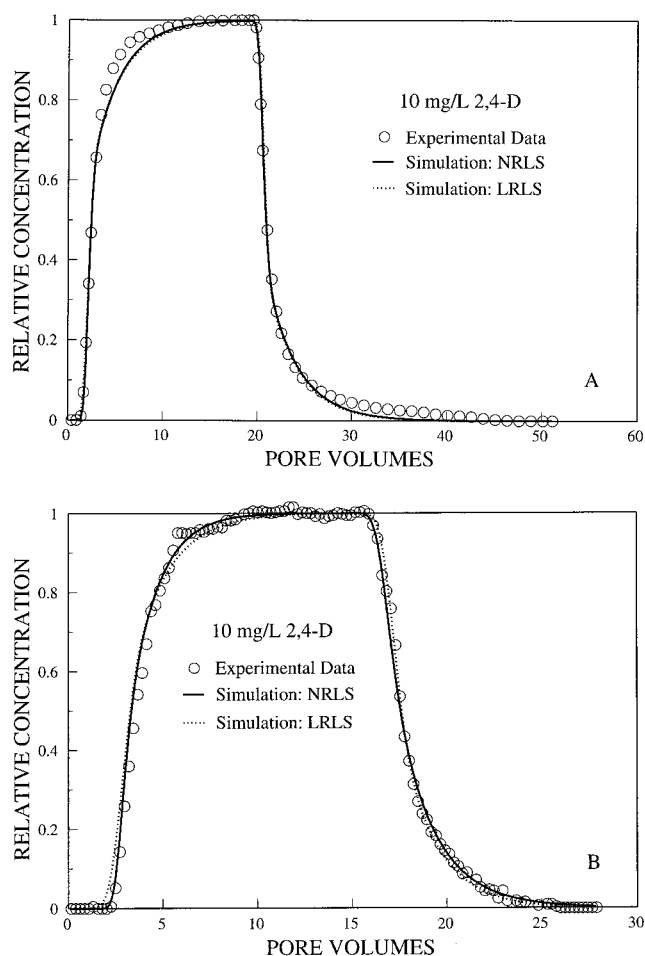


Fig. 4. Experimental data and optimized simulations for 2,4-dichlorophenoxyacetic acid (2,4-D) transport at two velocities: (A) fast (17.6 cm/h); (B) slow (1.40 cm/h). NRLS = nonlinear, rate-limited sorption; LRLS = linear, rate-limited sorption [reproduced from 16].

centration-dependent N values. This behavior illustrates the impact of coupled nonlinear, rate-limited sorption on transport.

To further examine the relative importance of nonlinear and rate-limited sorption on breakthrough curve shape, measured and simulated curves for 2,4-D transport at different input concentrations were compared for a similar pore-water velocity, as illustrated in Figure 6 for C_0 = 1 mg/L. The nonlinear, local equilibrium assumption (NLEA) is the case where N is optimized and sorption is assumed to be instantaneous. The linear, rate-limited sorption (LRLS) case is obtained by fixing N = 1 and accounting for rate-limited sorption. The third case (NRLS) accounts for both nonlinear and rate-limited sorption. Note that in all three cases the R values are from the moment analysis, which means the impact of nonlinear sorption on concentration-dependent retardation has been accounted for in the comparisons.

The simulations produced for the LRLS and NRLS cases are similar for 2,4-D transport at all input concentrations, indicating little impact of nonlinear sorption on breakthrough curve shape. Similar results have been observed by others [1,5,28]. Conversely, the impact of nonlinear sorption on the position of breakthrough curves is very significant. The NRLS simulation cannot reproduce the experimental data if the concentration-dependent R effect is not taken into account. As the input concentration decreases, the impact of rate-limited sorp-

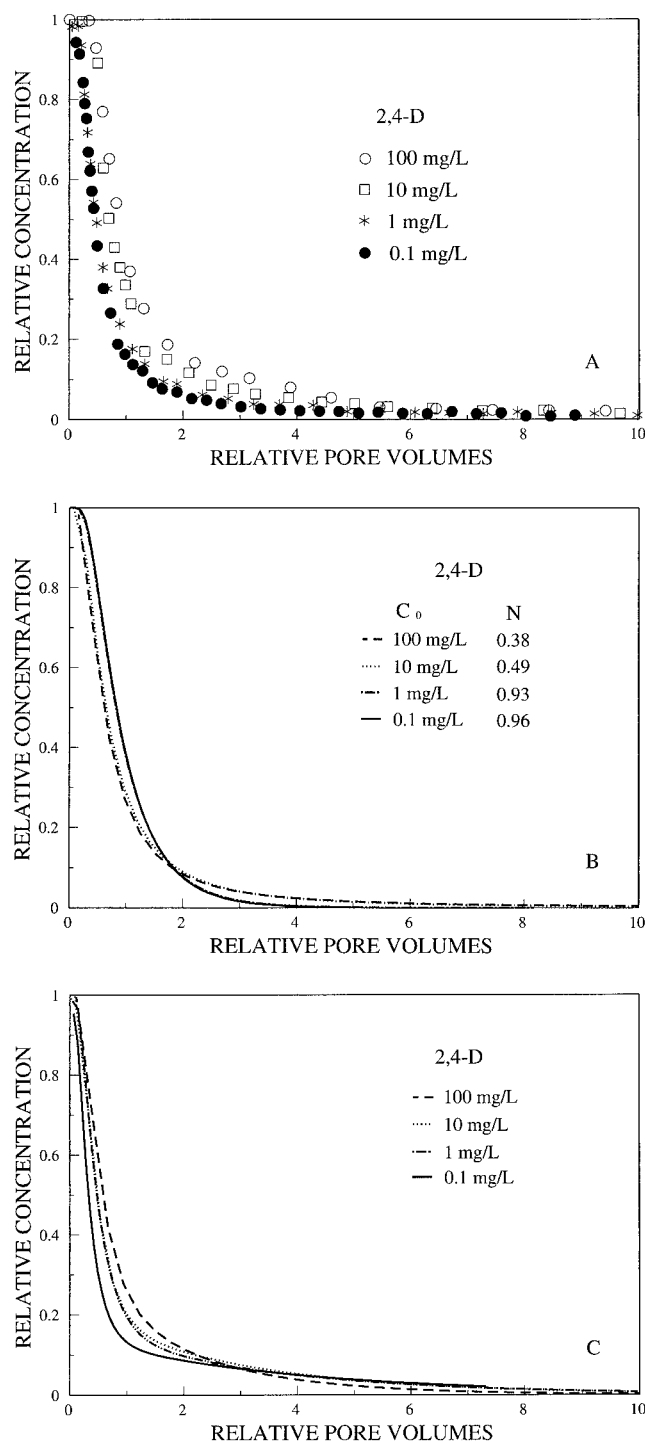


Fig. 5. Comparisons of elution curves for 2,4-dichlorophenoxyacetic acid (2,4-D) transport plotted with normalized pore volumes: (A) measured data; (B) simulation for nonlinear, instantaneous sorption, with the Freundlich exponent (N) a function of concentration; (C) simulation for nonlinear, rate-limited sorption with N fixed at 0.85.

tion on breakthrough curve position becomes more pronounced as a result of the relationship between k_2 and C_0 as well as the reduction in β . In summary, although the position of the breakthrough curves is controlled primarily by nonlinear sorption, the shape of the breakthrough curves is controlled primarily by rate-limited sorption.

To examine the influence of nonlinear sorption on the magnitudes of the sorption kinetics parameters, a set of opti-

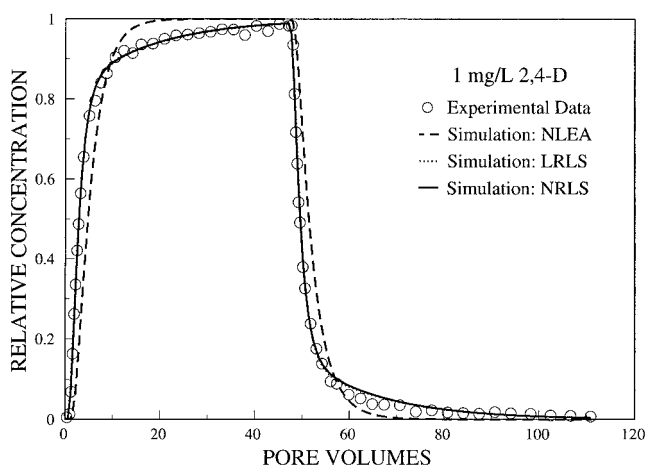


Fig. 6. Experimental data and optimized simulations for 1 mg/L 2,4-dichlorophenoxyacetic acid (2,4-D) transport. NLEA-nonlinear, local equilibrium assumption.

zations was done by fixing $N = 1$. The magnitudes of k_2 and F obtained with the linear-sorption optimizations are similar to those obtained by accounting for nonlinear sorption (see Table 1). This indicates that nonlinear sorption has negligible impact on the values of the sorption-kinetic parameters obtained by fitting, as reported earlier by Nkedi-Kizza et al. [5].

Coupled effects of sorption and biodegradation

The breakthrough curves for transport of 2,4-D in the non-sterile soil plateau at $C/C_0 = 0.8$ (Fig. 7). This behavior indicates that mass loss is occurring during transport. This mass loss is attributed to biodegradation, based on the measurement of $^{14}\text{CO}_2$ in the column effluent, as well as the measured increase of 2,4-D degraders in the soil compared to those obtained for the untreated soil. The number of 2,4-D degraders was in the range of 10^5 to 10^6 colony-forming units (CFUs)/g dry soil; the number of heterotrophs was in the range of 10^8 to 10^9 CFUs/g dry soil. The number of 2,4-D degraders in the column effluent was also monitored, and was found to be about 10^4 to 10^5 CFUs/ml (about 10% of the numbers in the soil). Furthermore, it was found that the soil could maintain a certain level of biodegradation potential, as long as the soil was at least intermittently in contact with substrate.

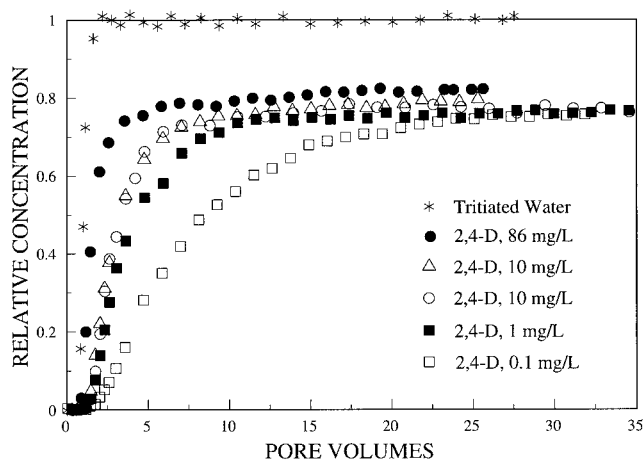


Fig. 7. Measured breakthrough curves for transport of tritiated water and 2,4-dichlorophenoxyacetic acid (2,4-D) with a range of input concentrations through the nonsterile soil column.

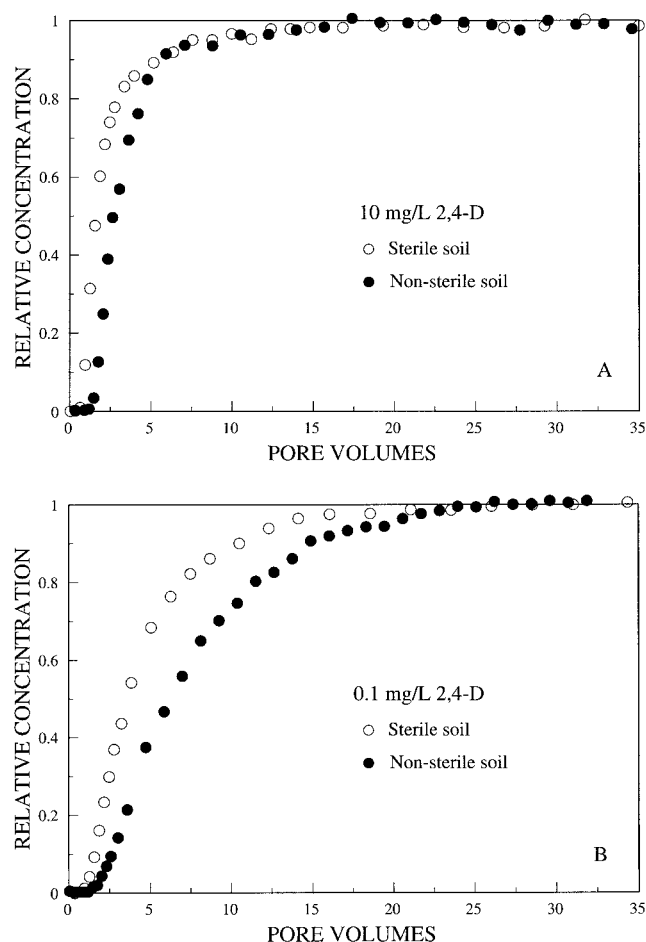


Fig. 8. Comparison of measured breakthrough curves for transport of 2,4-dichlorophenoxyacetic acid (2,4-D) through the column of sterile and nonsterile soil: (A) solute input concentration (C_0) = 10 mg/L; (B). C_0 = 0.1 mg/L. Note that the relative concentrations are normalized by the maximum observed concentration, not by C_0 , to facilitate comparison.

Breakthrough curves for input concentrations of 10, 1, and 0.1 mg/L 2,4-D appear to approach a similar plateau, which would yield similar degradation rate coefficients for these concentrations. The constant-concentration plateau indicates a steady state condition with respect to biodegradation and transport. This indicates that negligible net growth of bacteria occurs during transport. In this case, biodegradation kinetics can be approximated as first order. As confirmed using a mathematical model, which describes transport of contaminants affected by rate-limited sorption, nonlinear sorption, and biodegradation represented by the Monod growth model (i.e., nonlinear biodegradation with biomass growth), identical plateaus are obtained for any C_0 when biodegradation is first order.

The concentration-dependent retardation observed for the sterile systems (Fig. 1), wherein retardation increases with decreasing C_0 as a result of nonlinear sorption, was also observed for the nonsterile system (Fig. 7). However, the separation between breakthrough curves for each input concentration is greater for the cases with biodegradation than for those without biodegradation. This is clearly seen by comparing breakthrough curves for transport of 2,4-D in the sterile and nonsterile soil columns, as illustrated in Figure 8 for the input concentrations of 10 mg/L and 0.1 mg/L. The breakthrough curves for 2,4-D transport with biodegradation are shifted to

Table 3. Comparison of travel time for 2,4-dichlorophenoxyacetic acid transport in sterile and nonsterile soil columns

C_0 (mg/L) ^a	Sterile soil		Non-sterile soil		Difference between travel times (%) ^b
	Mass recovery (%)	Travel time (min)	Mass recovery (%)	Travel time (min)	
100/86 ^c	101.8	16.7	82.1	32.4	95.8
10	100.5	20.6	78.9	45.8	122
1	98.9	37.1	76.2	62.7	68.9
0.1	99.1	63.9	75.6	81.5	27.6

^a C_0 = solute input concentration.

^b Difference is based on the sterile value.

^c C_0 is 100 and 86 mg/L for sterile and nonsterile soil columns, respectively.

the right compared to 2,4-D transport in the sterile soil column. The additional delay is attributed to the influence of biodegradation on transport of a nonlinearly sorbing solute, wherein the reduction in aqueous solute concentration caused by biodegradation results in greater retardation due to the nonlinear sorption [13].

The travel times, calculated from moment analysis, for 2,4-D transport with biodegradation are significantly larger than those without biodegradation (Table 3). The difference in travel time between the cases with and without biodegradation is correlated with the input concentration. At 0.1 mg/L input concentration, the percentage difference is much smaller than at the higher concentrations where the impact of nonlinear sorption is greater. These results illustrate that the position of solute breakthrough curves (i.e., travel times) will be influenced by synergistic interactions between nonlinear sorption and first-order biodegradation. Conversely, the travel time of a solute pulse is not significantly influenced by first-order biodegradation when sorption is linear (for advection-dominated systems).

The relative impact of nonlinear sorption and rate-limited sorption on 2,4-D biodegradation and transport was examined by attempting to predict the data using the model described by Equations 3 and 4. Transport of 2,4-D in the nonsterile soil column was simulated using the program FITNLNED [22], with values for N , R , β , and ω optimized. The simulation based on linear and instantaneous sorption (LLEA), which does not consider the impact of nonlinear sorption on solute retardation, cannot describe the experimental data (Fig. 9). Conversely, the NRLS simulation, which accounts for the impact of nonlinear, and rate-limited sorption, captures the trend of the experimental data well. These results indicate that for the case with biodegradation, the position of the breakthrough curve is controlled primarily by nonlinear sorption, whereas the shape of the breakthrough curve is controlled primarily by rate-limited sorption; this conclusion is consistent with that for transport without biodegradation.

SUMMARY AND CONCLUSIONS

Miscible displacement and batch sorption experiments were conducted using a wide range of solute concentrations to investigate the impact of concentration-dependent behavior on 2,4-D transport in soil. The sorption isotherm was approximately linear at low concentration, and nonlinear over the extended range of concentration. Results from the transport experiments were consistent with the batch sorption study, with the fitted N values approaching 1 at low input concentrations.

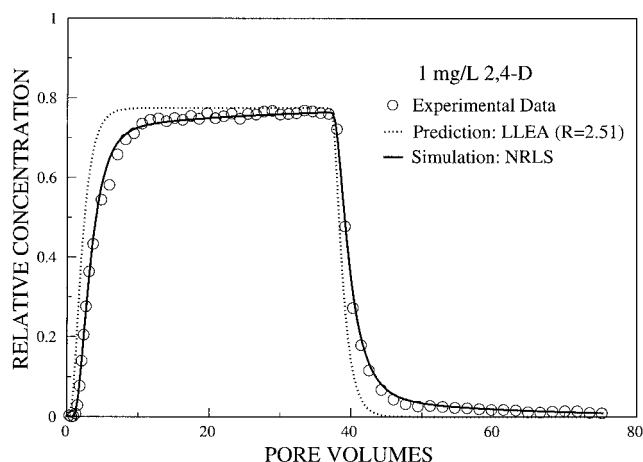


Fig. 9. Experimental data and optimized simulations for 1 mg/L 2,4-dichlorophenoxyacetic acid (2,4-D) transport in the nonsterile soil column. LLEA = linear, local equilibrium assumption.

Nonlinear sorption significantly influenced the position of the breakthrough curves because of concentration-dependent retardation, whereas rate-limited sorption has a greater impact on the shape of the breakthrough curves. The effective travel time of 2,4-D transport is influenced by synergistic interactions between sorption and biodegradation; the sequential rightward shift of the breakthrough curves with decreasing input concentration, due to nonlinear sorption of 2,4-D, is enhanced by biodegradation. Examining the coupled effects of sorption and biodegradation on the transport of organic contaminants is an important research area that has received little attention until recently. Further work is necessary to investigate the coupled effects of sorption and biodegradation, especially for systems wherein biodegradation is nonlinear.

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