Transport of 2,4-D in Soil as Affected by Aggregation and Organic Matter Content

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The transport of 2,4-dichlorophenoxy acetic acid (2,4-D) in the Ap (surface) and Bt (subsurface) horizons of an acid silt loam has been examined using batch and miscible displacement experiments. The batch experiments revealed that the sorption is linear for the Ap horizon and nonlinear for the Bt horizon. The miscible displacement experiments were carried out on soil aggregate whose diameters ranged from 2 to 4.8 mm and on soil without any significant aggregation. Miscible displacement experiments with Cl as a tracer in the well-aggregated soil showed typical nonequilibrium effluent concentration curves. The two-region model was adequate to describe the data. Breakthrough curves in soil without well-defined aggregates were described well by the classical convective-dispersive equation. The 2,4-D breakthrough curves in the aggregated Ap horizon exhibited typical nonequilibrium shape, but the experimental data were not well-described by the two-region model when the batch equilibrium sorption data were applied. However, the two-region model successfully predicted the breakthrough curves in the aggregated Bt horizon. The convective-dispersive equation did not accurately predict the 2,4-D breakthrough curves in the soils without aggregates. It can be concluded that under different flow regimes, different physicochemical processes may control the transport behavior of 2,4-D at high concentrations.

Declining water quality caused by the excessive use of herbicides and insecticides has become an important environmental issue. A potential source of groundwater contamination is the application of herbicides on roadsides to prevent excessive growth of brush and other plants. The soil texture of the roadside environment consists generally of coarse particles, resulting in hydraulic properties that enhance fast flow. Depending on the pesticide application and rainfall events, applied herbicides may move quickly into the soil profile and possibly into the groundwater.

To simulate such conditions on a laboratory scale, soil column experiments were designed to mimic preferential or bypass flow through large pores and flow through the soil matrix. In addition, the effect of high and low contents of soil organic matter on the herbicide sorption and transport was investigated because surface soils contain larger amounts of organic matter than subsoils. Preferential flow and low herbicide adsorption capacity of a subsoil imply low residence time for pesticides and hence greater potential for subsurface contamination.

The objectives of this study were to (a) determine experimentally the transport behavior of 2,4-dichlorophenoxy acetic acid (2,4-D) in soils with and without bypass flow, (b) determine the effect of organic matter content on the transport of 2,4-D, and (c) describe the observed phenomena with the two-site/two-region model.

THEORETICAL

The fate and transport of herbicides in the subsurface environment should be identified in terms of chemical, physical, and biological processes. The fate of pesticides in particular can be characterized by the simultaneous occurrence of transport, sorption, and both chemical and biological degradation. More precisely, when a pesticide molecule enters the soil matrix, it first is translocated primarily by convection through the large pores. Then the solute diffuses through a thin film (film diffusion) into the small pores (particle diffusion) and is finally adsorbed onto the surface of the solid phase. If the solid is made of organic matter, the solute may undergo intraorganic matter diffusion (1). Alternatively, the organic compound may be adsorbed first and then diffuses along the surfaces to other adsorption sites (surface diffusion). If diffusion is rate limiting, then the time-dependent sorption process is generally described as being in a physical nonequilibrium state.

In contrast to these physical processes, chemical reaction mechanisms range from low-energy London-van der Waals bonding, hydrogen bonds, and cation and water bridging to high-energy covalent bonding and ligand exchange, among others (2). Considering the chemical heterogeneity of soils, it is most likely that several of the aforementioned mechanisms may control the sorption of pesticides. Besides the purely chemical processes, organic molecules may be trapped so that the desorption may be incomplete and the reaction may be viewed as irreversible for the time frame of interest. This trapping may be attributed to herbicide sorption onto the interlayer of montmorillonite (3) or to molecular sieves formed by humic acids (4). Besides the chemical and physical processes of dislocation and accumulation, abiotic and biological degradation is one of the most important aspects of pesticide fate in the environment. In the case of soil decontamination, degradation is a process that should be enhanced. In general, heterogeneous physical, chemical, and biological properties of soil often prevent the identification of all processes involved. Hence, model development may be restricted to the use of lumped parameters. In this context the two-site/two-region model is applied in this paper.

The two-site/two-region model is based on a one-dimensional solute differential mass balance with either two reaction sites or a mobile and an immobile fluid phase. The first approach may be interpreted as chemical equilibrium and nonequilib-

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rium, whereas the second may describe physical nonequilibrium. Detailed derivations of these models have been presented by van Genuchten and Wagenet (5). Since the two-region model is more applicable to aggregated soils, only this model is presented:

$$(\theta_m + f\rho k) \frac{\partial c_m}{\partial t} = \theta_m D_m \frac{\partial^2 c_m}{\partial x^2} - \theta_m v \frac{\partial c_m}{\partial x}$$

$$- \alpha(c_m - c_{im}) - (\theta_m \mu_{lm} + f\rho k \mu_{sm})c_m \qquad (1)$$

$$[\theta_{im} + (1 - f)\rho k] \frac{\partial c_{im}}{\partial t}$$

$$= \alpha(c_m - c_{im}) - [\theta_{im}\mu_{lim} + (1 - f)\rho k \mu_{sim}]c_{im} \qquad (2)$$

where

ρ = bulk density ($M\ L^{-3}$),
θ_m = water content of mobile phase ($L^3\ L^{-3}$),
θ_{im} = water content of immobile phase ($L^3\ L^{-3}$),
D = dispersion coefficient ($L^2\ T^{-1}$),
α = mass transfer coefficient (T^{-1}),
v = average pore water velocity ($L\ T^{-1}$),
k = distribution coefficient describing adsorption of pesticide to the solid phase,
f = fraction of sorption sites directly in contact with mobile phase,
μ_{lm} = degradation rate coefficient of mobile liquid phase (T^{-1}),
μ_{lim} = degradation rate coefficient of immobile liquid phase (T^{-1}),
μ_{sm} = degradation rate coefficient for mobile sorbed phase (T^{-1}),
μ_{sim} = degradation rate coefficient for immobile sorbed phase (T^{-1}),
x = distance (L), and
t = time (T).

The following dimensionless groups have been derived for the two-region model:

$$P = v_m L / D_m \qquad (3a)$$

$$R = 1 + \rho k / \theta \qquad (3b)$$

$$\beta = \frac{\theta_m + f\rho k}{\theta + \rho k} \qquad (3c)$$

$$\omega = \frac{\alpha L}{\theta_m v} \qquad (3d)$$

$$\psi = \frac{\mu L}{v} = \frac{\mu L}{\theta_m v_m} \qquad (3e)$$

where

P = Peclet number,
R = retardation factor,
L = column length,
ω = dimensionless rate coefficient,
ψ = dimensionless degradation rate constant, and
β = dimensionless parameter.

Furthermore, it should be noted that the two-region model without degradation is obtained when the degradation constants (μ) are 0. The convective-dispersive equation is also a special case of Equation 1 when the mass transfer to the immobile liquid phase is negligibly small. The solutions of the two-region models as well as the convective-dispersive equation with the appropriate boundary and initial conditions can be found elsewhere (5,6).

Furthermore, the degradation within the different phases cannot be distinguished, and therefore the degradation should be lumped into one degradation rate constant as demonstrated by Gamerdinger et al. (7). More precisely, the degradation is

$$\mu = \mu_{lm} = \mu_{sm} = \mu_{lim} = \mu_{sim}$$

It should be noted that the sorption of a solute is often described by a nonlinear isotherm; hence the model requires modification. Generally, the Freundlich isotherm is assumed to describe a nonlinear isotherm appropriately. Van Genuchten (6) described a procedure by which the Freundlich equation is linearized so that the model introduced is applicable. The Freundlich isotherm can be given as

$$s = Kc^n \qquad (4)$$

where K and n are empirical coefficients. To use this linear model, the distribution coefficient can be approximated by (6)

$$k = Kc_0^{n-1} \qquad (5)$$

where c_0 denotes the pulse concentration.

MATERIALS AND METHODS

The Ap (surface) and the Bt (subsurface) horizons of the Loring silt loam were sampled on the Baton Rouge campus of Louisiana State University. The soil was air-dried and sieved through 4.8- and 2-mm mesh so that aggregates with diameters from 2 to 4.8 mm were separated. The soil was then analyzed for exchangeable cations, organic matter, and pH. The Ap horizon had an organic matter content of 3.04 percent, a pH of 5.65, a sum of exchangeable cations of 5.25 cmol(+) kg^{-1}, whereas the Bt had an organic matter content of 0.67 percent, a pH of 5.15, and a sum of exchangeable cations of 3.40 cmol(+) kg^{-1}.

Batch experiments were performed to obtain sorption isotherms for the Ap and Bt horizons. Portions of 5 g of soil were added to 15-mL glass test tubes with screw caps. Then 5 mL of solutions containing 10, 20, 50, 75, 100, or 150 mg L^{-1} of 2,4-D with 0.005 M Ca(NO$_3$)$_2$ background solute were added to the tubes so that a solution:soil ratio of approximately 1:1 was maintained. The test tubes were vortex-mixed, agitated in a shaker for 24 hr, and placed in a centrifuge to separate the solid and liquid phases. The supernatant aqueous phase was removed and analyzed for 2,4-D by high-pressure liquid chromatography. The experiments for each concentration were triplicated. The amount of sorbed 2,4-D was calculated by the difference of the initial and final solution con-

centration. The isotherm data were used to determine the distribution coefficient and the Freundlich parameter using a nonlinear least-squares procedure similar to that presented by van Genuchten (*6*).

Solute transport experiments were carried out using glass columns with a length of 15 cm and an inner diameter of 4.8 cm (Kontes chromaflex chromatographic columns). Soil aggregates of size ranging from 2 to 4.8 mm as well as soil with aggregates smaller than 2 mm were packed into the columns. The soil was saturated with 0.005 M $Ca(NO_3)_2$ solution. Then a pulse of approximately 48 mg L^{-1} of 2,4-D in 0.005 M $Ca(NO_3)_2$ was passed through the column. Thereafter, the 2,4-D solution was leached out with the $Ca(NO_3)_2$ solution. The effluent was collected with a fraction collector and analyzed for 2,4-D. The parameters describing the experimental conditions for all miscible displacement experiments are presented in Table 1.

The use of the two-region model requires at least three parameters that are difficult to measure independently: the dispersion coefficient D, the dimensionless rate coefficient ω, and the dimensionless parameter β that combines the mobile and total water content (θ_m, θ) with the mass fraction of the solid phase in direct contact with the mobile liquid (f) (see Equation 3). To get an estimate for the immobile water content, aggregates of the Ap and Bt horizons were placed on a stainless steel screen. The screen was then placed on water-saturated filter paper. The aggregates were wetted for approximately 24 hr and then dried at 105°C for 24 hr.

To estimate the hydrodynamic dispersion, tracer breakthrough experiments were performed using 0.1 M $CaCl_2$ solutions. The Cl was analyzed with an ion-selective microelectrode, and the program CXTFIT was then applied to obtain numerical values for the hydrodynamic dispersion coefficient (D) (*8*).

RESULTS AND DISCUSSION OF RESULTS

The isotherm for the Ap horizon is best described by the linear isotherm. The value of the distribution coefficient k is 0.572 ± 0.0100 with a correlation coefficient of $r^2 = .999$. In contrast, the Bt horizon follows the Freundlich isotherm best, which is clearly demonstrated in Figure 1. The value for Freundlich parameters were $K = 1.142 \pm 0.2545$ and $n = 0.75 \pm 0.069$ with a correlation coefficient of .985. Applying Equation 5 and the Freundlich parameters with a c_0 value equal to 50 mg L^{-1} yields a value of 0.429 for the distribution coefficient k. In addition to the average experimental values of the sorption isotherms, the sample standard deviations were denoted with the error bars. At high concentrations some data scatter was noted; however, for the lower concentrations, data from triplicate runs of batch experiments clearly demonstrate good reproducibility. The difference in sorption behavior between the two soil horizons can be attributed to the considerably higher organic matter content of the Ap horizon relative to the Bt horizon.

The Cl breakthrough curves show considerable difference between the aggregates and the nonaggregated soil (Figure 2). The results of the column experiment for the aggregated soil exhibit an asymmetrical shape, indicating an early breakthrough. Since the breakthrough curves of the nonaggregated soil are symmetrical, bypass flow appears to dominate the aggregated soil. On the basis of the shape of the breakthrough curves of the aggregated soil, the parameters for the non-reactive two-region model $(R = 1)$ were determined using CXTFIT and are presented in Table 2 along with the standard error of estimates and the correlation coefficients. To avoid meaningless parameter values, the dimensionless rate coefficient was approximated by the method outlined by Rao et al. (*9,10*). The authors assumed an average aggregate radius of 0.17 cm and a tortuosity factor of 0.4 so that the mass transfer coefficient ranged from 0.9 to 1.2 h^{-1}. The values of the corresponding dimensionless variable are given in Table 2. The results of the immobile water content measurement yielded a value of 0.3 for β, assuming that the retardation factor (R) equals 1 (Equation 3).

Since at least three parameters are needed to determine the transport behavior of solutes using the two-region model, the parameter estimation was performed by optimizing the dispersion coefficient with the approximations of the dimensionless rate coefficient ω and the dimensionless parameter β constant. The correlation coefficients of all parameter optimizations of the same column run are very similar, but some of the parameters change drastically when incorporated into the optimization (Table 2). This was especially true for the slow-velocity experiment of the Ap horizon, where the dispersion increases from 0.001 to 12.47 cm^2 h^{-1} associated with an increase of β from 0.3 to 0.91. Even though the model is physically meaningful, the parameters do not appear to behave independently during the parameter optimization. Also, when all three parameters are optimized, the ratio of mobile to total water content appears to be overestimated. Nevertheless, the parameters may be viewed as empirical coefficients that describe the mixing behavior of nonreactive solutes in soil columns.

TABLE 1 Experimental Conditions for Miscible Displacement Experiments of Cl^- Tracer and 2,4-D in Loring Silt Loam, With and Without Aggregates

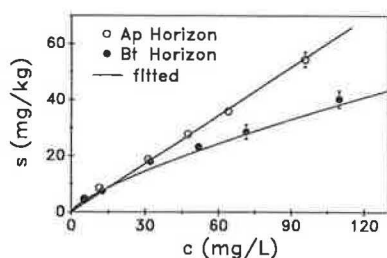| Experimental parameters	Experiments			
	Ap - soil	Ap - aggr.	Bt - soil	Bt - aggr.
ρ (g cm^{-3})	1.16	0.95	1.32	1.04
θ (cm^3 cm^{-3})	0.567	0.589	0.502	0.608
% saturation	89.2	98.9	91.4	92.5
v (cm h^{-1})	2.98	3.04	3.88	3.11
Tracer pulse (V V_0^{-1})	2.00	1.81	2.09	1.61
2,4-D pulse (V V_0^{-1})	8.86	8.09	11.2	8.62

FIGURE 1 Isotherms of 2,4-D in Ap and Bt horizons of Loring silt loam measured using batch experimental techniques.

Using the parameters obtained from the Cl breakthrough curves and assuming that the sorption is well-described by the retardation factor (R), the breakthrough curves of 2,4-D were predicted. Even though the shape of the breakthrough curve of the aggregated Ap horizon closely resembles the experimental data, the curve is more retarded (Figure 3). Hence, the retardation coefficient of the Ap horizon determined from the batch experiment appears to overestimate the retardation. However, the prediction for the aggregated Bt horizon shows excellent fit with the experimental data (Figure 4). Since the organic matter content of the Ap horizon is considerably higher than that of the Bt, the authors assume that the aforementioned breakthrough phenomenon may be attributed to this difference.

The 2,4-D breakthrough curves in the soils with particles and aggregates below 2 mm in diameter show tailing phenomena. In addition, this effect is observed to a lesser extent for the breakthrough curves in the aggregated soils of the Ap horizon. To eliminate sorption nonlinearity as a cause for this phenomenon, the convective-dispersive equation with the Freundlich isotherm was solved numerically for the Bt horizon. The result is plotted as the dashed-dotted line in the upper graph of Figure 4. The tailing is more pronounced for the prediction when the linear sorption breakthrough simulation is used but deviates substantially from the experimental data. Also, the breakthrough front is steeper and the deviation
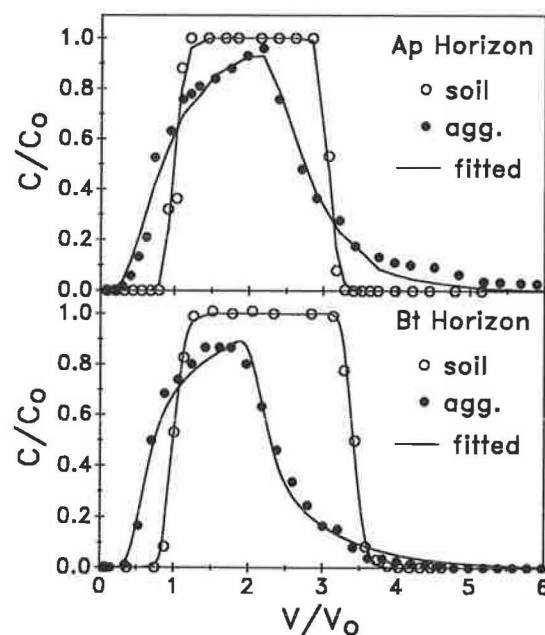

FIGURE 2 Cl breakthrough curves in soil columns with samples from Ap and Bt horizons of Loring silt loam, with and without distinct aggregates.

from the data points increased in comparison with the analytical solution of the linear convective-dispersive equation.

To ensure that the linear equilibrium sorption cannot describe the data adequately, the authors used the transport parameter from the two-region model and the convective-dispersive equation to optimize the retardation factors R for all pesticide breakthrough curves. The results are shown in Figures 3 and 4 as the dashed lines. The curves are shifted toward the origin, especially for the Ap horizon. As indicated in Table 3, the retardation coefficients determined from the transport data are approximately 14 to 36 percent lower than those estimated from the batch experiment. The only exception is the retardation factor of the aggregate's Bt horizon, which is higher than the batch-determined value. However,

TABLE 2 Parameter Estimates of D, β, and ω With Standard Error of Estimate from Cl⁻ Breakthrough Experiments for Ap and Bt Horizons, With and Without Aggregates

Exper.	r^2	D	SE	$\beta^\dagger$	SE*	$\omega^\dagger$	SE*
		---- cm² h⁻¹ ----					
Ap soil	0.983	0.237	0.0627	-	-	-	-
Ap aggr.	0.961	0.001	2.167	0.3	-	1.8	-
Ap aggr.	0.979	12.47	3.034	0.915	0.0848	1.8	-
Ap aggr.	0.968	8.629	1.456	0.766	0.0337	1135.	183.5
Bt soil	0.995	0.471	0.0580	-	-	-	-
Bt aggr.	0.969	0.250	1.867	0.3	-	1.8	-
Bt aggr.	0.986	0.540	0.8325	0.457	0.0348	1.8	-
Bt aggr.	0.991	2.179	0.9108	0.629	0.0444	0.59	0.159

* Blank entries for the standard errors (SE) of either β or ω indicate that the parameter were estimated independently.
† Blank entries for β and ω indicate that the classical convective-dispersive equation was fitted instead of the Two-Region model.
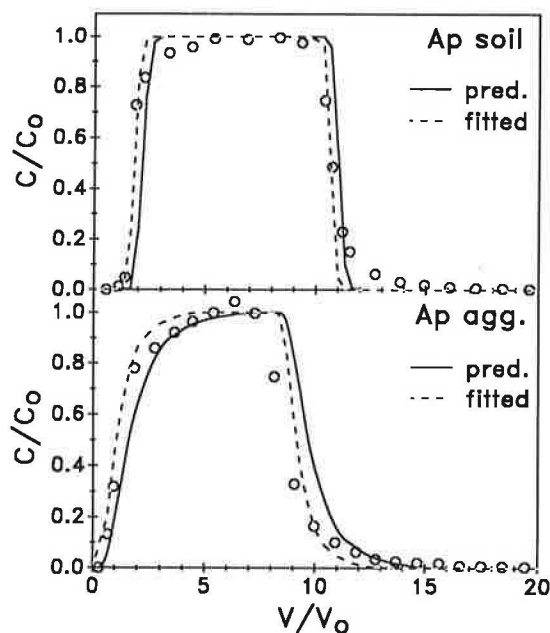
FIGURE 3 2,4-D breakthrough curves in soil columns containing soil and aggregates of Ap horizon of Loring silt loam.
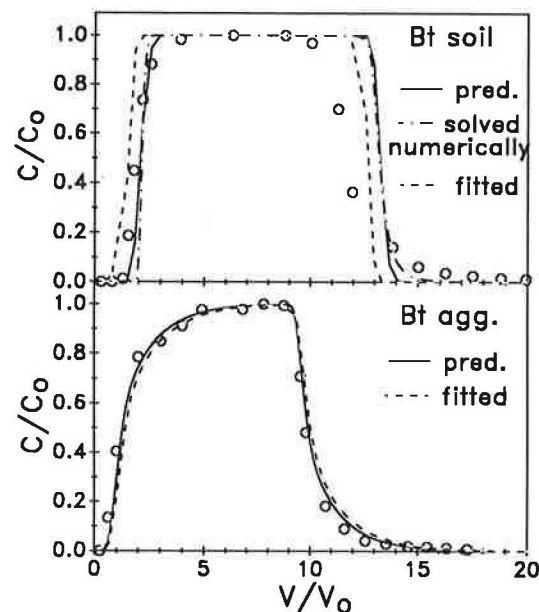

FIGURE 4 2,4-D breakthrough curves in soil columns containing soil and aggregates of Bt horizon of Loring silt loam.

the fitted and the predicted breakthrough curves show great similarities. This indicates that for the aggregated Bt horizon, the physical flow regime dominates the overall effluent concentration so that the breakthrough is relatively insensitive toward the retardation factor (R).

Since the two-region model seems to describe adequately only the nonreactive tracer transport, possible mechanisms explaining the deviation of the predicted and the experimental pesticide data need to be addressed. Nonequilibrium processes are most likely to occur since neither linear nor nonlinear isotherms can explain these findings. Also, the higher organic matter content of the Ap horizon may cause the difference between the breakthrough curves of the aggregated Ap and Bt horizons. Hence, higher organic matter contents seem to pronounce the observed effects that may be attributed to intraorganic matter diffusion as reviewed by Brusseau and Rao (*1*). The underlying concept of intraorganic matter diffusion is that the organic matter consists of polymeric materials so that solutes can diffuse through a mesh-like structure of organic matter. To describe the breakthrough data of the aggregated Ap horizon, an additional kinetic rate equation should be invoked.

The results of this research may be related to practical problems. First, surface soils are usually richer in organic matter than subsoils and hence the distribution coefficient k is expected to be higher in surface soils. Also, high organic matter content is associated with well-structured and highly permeable soils. High distribution coefficients and permeability affect each other adversely—that is, the solute is more retarded whereas the mean pore water velocity is high and therefore the mean residence time is decreased.

Besides the hydraulic properties, well-defined large aggregates as well as macropores caused by biological activity enhance bypass flow. As the depth increases, the organic matter content decreases, as do the aggregation, number, and size of macropores. Hence, the hydraulic properties increase the mean residence time of the solute, but the decreased retardation factor may enhance the transport of pesticides into groundwater. Applying this argument to the Loring silt loam implies that the danger of groundwater contamination is in-

TABLE 3 Parameter Estimates of Retardation Factor from Miscible Displacement Experiments Compared with Retardation Factor from Batch Experiments

Experiment	r^2	R	SE	R^*
Ap soil	0.970	1.806	0.03079	2.171
Ap aggr.	0.972	1.264	0.08014	1.922
Bt soil	0.997	1.531	0.02265	2.118
Bt aggr.	0.969	2.064	0.04157	1.725

* Retardation factor determined from batch experiments

creased when the pesticide concentration is very high since the retardation of 2,4-D decreases in the Bt horizon considerably in comparison with the Ap horizon. Discrepancies between Ap and Bt should be most pronounced especially at concentrations above 75 mg L^{-1}. This also implies that the results are applicable to point source pollution such as accidental spills where the pesticide concentration is very high, rather than to non–point source pollution with low-concentration contamination.

SUMMARY AND CONCLUSIONS

Miscible displacement and batch experiments were performed to determine the effect of sorption and bypass flow on the transport of 2,4-D. The early breakthroughs of Cl in soil made of aggregates 2 to 4.8 mm in diameter showed a typical shape of physical nonequilibrium. These breakthrough curves are well described by the two-region model. In contrast, Cl breakthroughs of the soil that had been passed through a 2-mm sieve were adequately described by the classical convective-dispersive equation. However, the convective-dispersive equation did not provide a good fit for the 2,4-D data for both the Ap and Bt horizons. This deviation could not be attributed to the nonlinearity of the isotherm of the Bt horizon.

In addition, the predicted breakthrough curves for the aggregated Ap horizon were more retarded, which implies that the batch experiments overestimated the retardation. Adjustment of the retardation factors resulted in a shift in breakthrough curves, bringing them closer to the experimental data, but the tailing effect was still underestimated. In contrast, the predicted breakthrough curve of the aggregated Bt horizon agreed well with the experimental data. Increased bypass flow may control the overall effluent concentration in the aggregated Bt horizon, whereas additional chemical processes influence the breakthrough curves of the aggregated Ap horizon. An additional chemical process causing the deviation may be intraorganic matter diffusion, which also may cause the failing of the convective-dispersive model to predict the breakthrough curves in the soil without distinctive aggregates.

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