Field Method for Measuring Mobile/Immobile Water Content and Solute Transfer Rate Coefficient

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ABSTRACT

Numerous field and laboratory studies have documented the occurrence of preferential transport of solutes due to a fraction of the soil water being immobile and not taking part in the transport process. Domain models have been developed that describe these processes, but before we can apply them routinely, we need methods for measuring the required model parameters, particularly the fraction of immobile water to total water θ_{im}/θ and the exchange coefficient between the mobile and immobile domains, α. We developed a field method for measuring both θ_{im}/θ and α. The method uses a sequence of conservative anionic tracers consisting of Br$^-$, pentafluorobenzoate, o-trifluoromethylbenzoate, and 2,6-difluorobenzoate infiltrated with time through a tension infiltrometer. Previous studies have confirmed that these tracers have very similar transport properties in a wide range of soils. The method was applied to an undisturbed loam and a greenhouse soil as an initial test of the approach. Calculated θ_{im}/θ fractions averaged 0.69 and ranged from 0.25 to 0.98, while calculated α values averaged 0.0081 h^{-1} and ranged from 0.0030 to 0.021 h^{-1}. These values compare well with values reported earlier by other investigators. The method is simple and allows routine measurement of transport properties of field soils. The method can also be used to validate the applicability of domain models to specific soils.

STUDIES during the past 20 yr have clearly shown that water and chemicals can move through soil along preferred pathways (Ehlers, 1975; Quisenberry and Phillips, 1976; Kanwar et al., 1985; Rice et al., 1986; Wagenet, 1987). This preferential flow can result in rapid movement of chemicals to the water table or rapid movement of chemicals through the biologically active root zone to depths where degradation and transformation rates are slower and thus the chemicals persist longer. Preferential flow may be a leading cause of water contamination by agrichemicals and may in part explain why screening models that ignore preferential flow do not predict observed spatial patterns of groundwater contamination (U.S. Environmental Protection Agency, 1992).

Widespread observations of preferential flow of solutes have led to the development of numerous conceptual models of solute transport. One approach has been to divide the soil water into zones or domains of mobile and immobile (or much less mobile) water (Coats and Smith, 1964; van Genuchten and Wierenga, 1976). Advection and dispersion are assumed to take place only in the mobile zone, while adsorption–desorption and degradation can take place in either zone, although not necessarily at the same rate. Only diffusion of solutes between the mobile and immobile water zones connects the two domains.

Laboratory studies on columns packed with soil aggregates or sand have shown that the immobile water content varies with soil water flux, water content, and aggregate size (van Genuchten and Wierenga, 1977; Gaudet et al., 1977; Nkedi-Kizza et al., 1983). In field and laboratory studies using undisturbed soil cores, the ratio of immobile water to total soil water content has been found to vary from as little as 0 (i.e., no preferential flow; Cassel, 1971) to 35 to 55% (Smettem, 1984; Gvirtzman and Magaritz, 1986) or even 75% in weakly structured tropical soil (Seyfried and Rao, 1987) and unstructured desert soil (Jaynes et al., 1988). These latter immobile water fractions mean that chemicals could move through the soil profile more than twice as fast as predicted by models not incorporating immobile water concepts.

Following the approach of Coats and Smith (1964), we express transport during steady one-dimensional unsaturated flow of a conservative nonsorbing solute in a soil containing mobile and immobile water as the following:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \quad [1]$$

where θ_m is the mobile water content, θ_{im} is the immobile water content ($\theta_m + \theta_{im} = \theta$, the total water content), C_m and C_{im} are the solute concentration in the mobile and immobile domains, t is time, D_m is the dispersion coefficient, active in the mobile domain only, q is the Darcy flux density, and x is the depth. The exchange rate between the mobile and immobile domains can be expressed by the following:

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha(C_m - C_{im}) \quad [2]$$

where α is the solute exchange coefficient. Chemical distribution with time and space depends on the magnitude of the equation parameters θ_m, θ_{im}, D_m, q, and α.

In applying the two-domain model, the parameters in Eq. [1] and [2] are normally found by adjusting the parameters until the calculated concentrations match the observed (Parker and van Genuchten, 1984; van Genuchten and Wagenet, 1989; Gamerdinger et al., 1990). Although this can result in close agreement between observed and computed data, curve fitting to estimate the parameters does not allow prediction of chemical movement in the absence of breakthrough data. This is particularly true for the parameters θ_m (or θ_{im}) and α where all previous applications have relied on information provided by breakthrough curves of at least one tracer (e.g., Brusseau et al., 1989).

Recently, Clothier et al. (1992) described a method where a tension infiltrometer and a conservative tracer

Abbreviations: PFBA, pentafluorobenzoate; TFMBA, o-trifluoromethylbenzoate; DFBA, 2,6-difluorobenzoate.

could be used to measure the immobile water fraction of field soils. Tension infiltrometers are routinely used to measure soil hydraulic properties at near-saturated conditions (Logsdon and Jaynes, 1993). In the Clothier et al. (1992) method, a conservative tracer (Br^-) is added to the water within the tension infiltrometer after steady-state infiltration has been achieved. After sufficient tracer has infiltrated, soil samples are collected from below the base of the infiltrometer and analyzed for tracer concentration.

If all the soil water is mobile, the tracer concentration in the soil water should equal the input concentration. However, if some soil water is immobile, the concentration of tracer in the soil should be less than the input concentration. Specifically

$$\theta_{im} = \theta\left(1 - \frac{C}{C_o}\right) \qquad [3]$$

where C is the measured tracer concentration in the soil and C_o is the input concentration contained in the infiltrometer. In using Eq. [3], Clothier et al. (1992) assumed that the transfer coefficient α is sufficiently small that very little solute had time to diffuse into the immobile region before they sampled the soil. This method offers a unique way to measure mobile and immobile water fractions without the need for extensive breakthrough studies but gives no information about α.

We developed an extension of the above method that gives estimates of both θ_{im} and α. Rather than using a single tracer, as done by Clothier et al. (1992), we use a sequence of conservative tracers. Each is infiltrated through a tension infiltrometer but for varying periods of time. Assuming that the initial tracer concentration in the soil is 0, the tracer concentration in the mobile water phase is equal to the input concentration, and the measured soil solution concentration is equal to $\theta_m C_m + \theta_{im} C_{im}$, we can separate the variables in Eq. [2] and solve to yield the following:

$$\ln(1 - C/C_o) = \frac{-\alpha}{\theta_{im}}t + \ln\left(\frac{\theta_{im}}{\theta}\right) \qquad [4]$$

Plotting $\ln(1 - C/C_o)$ vs. application time, t, for all of the tracers should result in a straight line with a negative slope. The intercept ($t = 0$) gives us the natural log of the ratio of immobile water to total soil water and multiplying the slope by $-\theta_{im}$ gives us the transfer rate coefficient α.

For the above method to be successful, at least two conservative nonsorbing tracers must be used whose transport properties are nearly identical. Tritiated and deuterated water would be ideal tracers; however, tritium cannot be used in the field for safety reasons. Chloride and Br^- are alternative choices commonly used because they are conservative, do not significantly adsorb to soil, and have been shown to move through soil in a very similar manner. However, most soils have appreciable background concentrations of Cl^-, which would complicate the analysis. In addition, we would prefer to apply

more than two tracers to test the linearity of Eq. [4] and give more reliable estimates of α.

In a series of experiments, Bowman and others (Bowman, 1984; Bowman and Gibbens, 1992; Benson and Bowman, 1994) have identified a series of fluorinated benzoate tracers whose transport properties in soil are very similar to Br^-. Recently, Jaynes (1994) confirmed that three of these organic tracers move very similarly to Br^- through soils of higher organic content typical of the Midwest. These three organic anions, PFBA, TFMBA, and DFBA, along with Br^- should allow us to calculate both θ_{im} and α using Eq. [4].

MATERIAL AND METHODS

Two soils were used to test the proposed procedure. The first soil is a Nicollet loam (fine-loamy, mixed, mesic Aquic Hapludoll) composed of 0.477, 0.268, and 0.255 sand, silt, and clay mass fractions. An undisturbed block of soil 1 by 1 by 1.5 m in size was brought into the laboratory for an unrelated study. Following this study, infiltrometer tests were made at three locations distributed across the block. The second soil is a clay loam (0.298 sand, 0.372 silt, and 0.330 clay mass fractions) contained in a greenhouse plot that had been planted to crops for the past 10 yr. The soil was ≈60 cm deep and underlain by sawdust and undisturbed soil. Between crops, infiltrometer tests were conducted at six locations.

A large-base (230-mm diam.) tension infiltrometer was used to establish a constant infiltration rate at a soil water pressure head of −30 mm. The infiltrometer was filled with a 4 mmol L^{-1} solution of Cl^-. All anions were applied as K salts. This initial solution was used to establish constant molar concentration during the infiltrometer measurements.

On establishment of steady infiltration, the infiltrometer was exchanged with a second infiltrometer set at the same pressure head but filled with a second solution. This solution contained 3 mmol L^{-1} of the initial Cl^- and 1 mmol L^{-1} of either the tracer TFMBA, PFBA, DFBA, or Br^-. The order of tracer addition in the infiltrating solutions was varied between tests to eliminate systematic errors caused by possible nonidentical transport characteristics. The order of application of the tracers during each test is summarized in Table 1. Concentration of the initial Cl^- was reduced so that the total molar concentration (4 mmol L^{-1}) of the infiltrating solution remained the same.

After infiltration of the second solution, a third infiltrometer, filled with a solution containing 2 mmol L^{-1} of Cl^-, 1 mmol L^{-1} of the first, and 1 mmol L^{-1} of a second tracer, was exchanged with the second infiltrometer. The infiltrometer was

Table 1. Final infiltration rate and application time for each tracer used in the tests.

Test	Soil	TFMBA†	Br^-	DFBA†	PFBA†	Infiltration rate
			h			cm h^{-1}
1	loam	3.45	18.10	20.87	24.32	0.20
2	loam	11.82	16.65	20.08	23.55	0.19
3	loam	15.45	20.62	24.15	35.97	0.12
4	clay loam	1.20	2.23	3.57	5.38	1.07
5	clay loam	5.73	4.68	2.77	1.52	1.29
6	clay loam	9.00	6.00	4.00	2.00	0.74
7	clay loam	4.53	3.37	2.37	1.50	1.98
8	clay loam	4.50	3.00	6.00	2.00	1.17
9	clay loam	5.65	4.17	7.43	1.90	0.54
10	clay loam	5.65	3.80	7.87	1.97	0.83

† TFMBA = o-trifluoromethylbenzoate; DFBA = 2,6-difluorobenzoate; PFBA = pentafluorobenzoate.

subsequently exchanged periodically with infiltrometers filled with a progression of tracer solutions until the final infiltrometer contained a 1 mmol L^{-1} solution of the tracers Br^-, TFMBA, DFBA, and PFBA. Thus, at the end of each test, four tracers had been applied to the soil for decreasing lengths of time. Time of application for each tracer varied (Table 1) and depended on infiltration rate and availability of personnel to switch infiltrometers (especially overnight).

After the last tracer had infiltrated, the infiltrometer was removed and small soil cores were collected vertically from directly beneath the infiltrometer base. The final tracer was applied for sufficient time to allow penetration of the soil to a depth estimated to exceed the depth sampled by the cores. Thus, the effect of dispersion around the advancing solute front on measured solute concentrations in the collected soil samples was minimized. Core sizes varied from test to test and ranged from 170 to 275 cm³ in volume and from 2.3 to 3.8 cm long. Soil samples were placed in sealed freezer bags and returned to the laboratory for analysis.

In the laboratory, soil was extruded from each core and thoroughly mixed by hand. For some tests (1–3 and 10), the core samples were split vertically prior to mixing to yield two replicates. Water contents were measured on 20-g subsamples. The remaining soil was extracted with distilled water at a soil to water mass ratio of approximately 1:1. The soil/water mixture was shaken for 5 min on a rotary shaker and allowed to settle for 5 min. The solution was then decanted through an 8.0-μm filter and stored at 2°C until analysis.

Analysis for the tracers was performed on an ion chromatograph (Dionex Series 4500i, West Mont, IL) using the method described by Bowman and Gibbens (1992). For the fluorobenzoates, we used a SAX column (Regis Chemical Co., Morton Grove, IL) with 30 mM KH_2PO_4, adjusted to a pH of 2.65 with H_3PO_4, and 200 mL L^{-1} acetonitrile as the eluting solution. The flow rate was 1 mL min^{-1} and the detection wavelength was set to 205 nm. In several cases, Br^- could not be quantified with the above procedure due to interferences from high NO_3^- concentrations. In these cases, we determined Br^- concentration with a Dionex AG9 guard column followed by an AS9 separator column. The eluting solution was 1 mM Na_2CO_3 and 0.75 mM $NaHCO_3$ at a pH of 10.4 with 12.5 mM H_2SO_4 used for suppression. The flow rate was 1 mL min^{-1}, and electrical conductance was measured with a conductivity detector.

Initial concentrations of the infiltrating tracers were measured by mixing equal masses of oven-dry soil and the last applied tracer solution. The mixtures were shaken and extracted as above. Measured concentrations served as the input concentration C_o in Eq. [4] and corrected for any inefficiencies or biases in the extraction process.

The resulting concentrations were plotted against time of application as per Eq. [4]. A line was fitted to the data by log-linear least sum of squares regression. Values for θ_{im} were determined from the fitted intercept, and measured water content and values of α were determined from the fitted slope multiplied by $-\theta_{im}$.

RESULTS

The measured water contents under the infiltrometers ranged from 0.324 to 0.439 m³ m⁻³ (Table 2). Water contents of split replicate samples also varied, indicating spatial variability in these soils across short distances. If we assume that all of the soil water is mobile, the depth of infiltration by the last tracer applied exceeded the length of the soil core in every test. This is important since we assume that the soil samples are far enough

Table 2. Measured water contents, calculated model parameters (and one standard deviation), and R^2 for log-linear regression to test data.

Test	θ	θ_{im}/θ	α	R^2
	m³ m⁻³		h⁻¹	
1a	0.354	0.67	0.0075	0.95
		0.62–0.73	0.0059–0.0094	
1b	0.358	0.90	0.0122	0.94
		0.81–1.01	0.0090–0.0160	
2a	0.369	0.72	0.0072	0.90
		0.69–0.76	0.0052–0.0093	
2b	0.367	0.98	0.0109	0.89
		0.92–1.05	0.0076–0.0146	
3a	0.329	0.68	0.0030	0.79
		0.63–0.73	0.0018–0.0044	
3b	0.345	0.84	0.0050	0.86
		0.78–0.90	0.0033–0.0070	
4	0.325	0.73	0.0138	0.75
		0.67–0.78	0.0075–0.0210	
5	0.346	0.93	0.0208	0.68
		0.83–1.04	0.0099–0.0340	
6	0.393	0.65	0.0030	0.59
		0.62–0.67	0.0013–0.0048	
7	0.439	0.25	−0.0014	0.05
		0.22–0.29	−0.0053–0.0037	
8	0.345	0.60	0.0102	0.83
		0.57–0.64	0.0061–0.0148	
9	0.324	0.66	0.0096	0.91
		0.63–0.69	0.0072–0.0123	
10a	0.330	0.53	0.0052	0.92
		0.51–0.54	0.0040–0.0065	
10b	0.367	0.50	0.0044	0.88
		0.49–0.52	0.0032–0.0058	

removed from the solute front that hydrodynamic dispersion does not affect the measured tracer concentrations. Sampling within the zone where dispersion affects the concentration would bias the results toward an increased apparent immobile water fraction.

Figure 1 shows the normalized concentrations vs. time for the three tests (two replicates per test) on the Nicollet soil and the fitted regression lines. Results for the six tests conducted on the greenhouse soil are shown in Fig. 2. Computed values for θ_{im}/θ and α from all tests are listed in Table 2.

In some cases, the data suggest a curvilinear behavior, but no consistent pattern can be seen for all tests. Linear
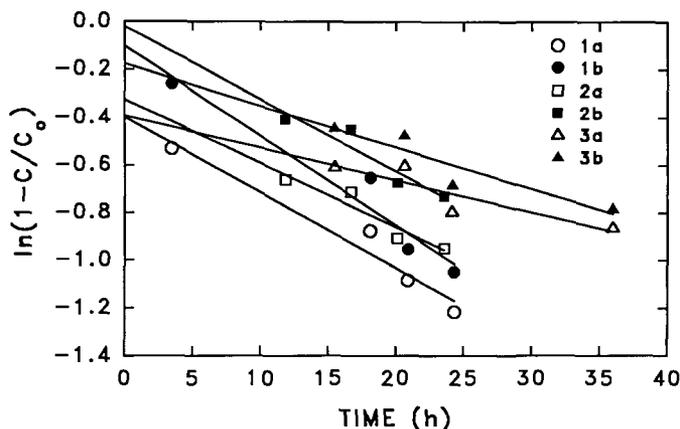

Fig. 1. Normalized concentration of each tracer vs. the time of application for the tests on the Nicollet loam and the best-fit regression line for each test (C = measured tracer concentration in the soil; C_o = input concentration contained in the infiltrometer).
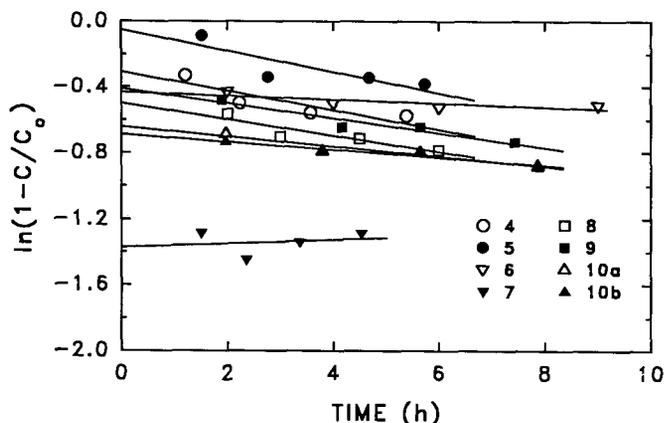
Fig. 2. Normalized concentration of each tracer vs. the time of application for the tests on the greenhouse clay loam and the best-fit regression line for each test (C = measured tracer concentration in the soil; C_o = input concentration contained in the infiltrometer).

behavior is important since it is required if the two-domain model as given in Eq. [2] accurately reflects the physical process within the soil. A systematic testing of this assumption is required and is possible with the multiple tracer technique described here. However, for this initial application of the method, and since no systematic curvature can be seen in Fig. 1 and 2, we assumed the data to reflect the theoretical linear behavior expressed by Eq. [4] and fitted lines to the data with each having the expected negative slopes except for Test 7.

Across all tests, computed θ_{im}/θ fractions were extremely variable, ranging from 0.25 to 0.98 with an average of 0.69 (± 0.19). Computed α values spanned nearly one order of magnitude and ranged from 0.0030 to 0.021 h^{-1} with an average of 0.0081 h^{-1} (± 0.0054).

Test 7 on the greenhouse soil was the only test to yield a negative value for α. While negative values of α are incompatible with mobile/immobile theory, the standard error of this estimate did include 0 or very low transfer rates. Thus, this data might just reflect a very low or negligible transfer rate. Test 7 also yielded a much lower θ_{im}/θ fraction and a greater total water content after infiltration than the other tests. The reason for the different results from this test is unknown.

Computed θ_{im}/θ fractions and α values within the replicates showed as much variation as between the different tests (Table 2). The ratio θ_{im}/θ was much more variable than the measured total water content. Large variations in computed parameters for replicates and individual tests indicate that these parameters vary dramatically across space and that many measurements or measurements on large soil volumes may be necessary to accurately quantify these parameters for a given soil.

While we cannot independently confirm the θ_{im}/θ and α values in these experiments, we can compare them with values reported elsewhere. In field experiments, Clothier et al. (1992) applied Br$^-$ to a fine sandy loam with a tension infiltrometer set at -20 mm pressure head (vs. -30 mm used here). They found an average θ_{im}/θ fraction of 0.49 (± 0.12), which is both lower and less variable than found here but that may be due to differences in soil textures. In other field studies, Gvirtzman and

Magaritz (1986) found immobile water fractions between 0.4 and 0.55 in a natural tracer experiment, while Rice et al. (1986) found fractions as high as 0.8 under surface irrigation. These values encompass the average θ_{im}/θ fraction found here.

Numerous column breakthrough studies have also produced estimates of θ_{im}/θ and α. For instance, Smettem (1984) found θ_{im}/θ fractions between 0.32 and 0.5 and α values between 0.0001 and 0.12 h^{-1} for an undisturbed weakly structured soil. Using packed sandy loam aggregates, Nkedi-Kizza et al. (1983, 1984) found immobile water fractions between 0.04 and 0.56 and generally higher α values of between 0.01 and 2.15 h^{-1}. Using packed clay loam aggregates, van Genuchten and Wierenga (1977) found lower θ_{im}/θ fractions of between 0.060 and 0.275 and lower α values of between 0.002 and 0.01 h^{-1}. Overall, column studies have reported slightly lower immobile water fractions than found here and similar but much more variable α values. Some of the variation in α values may have been due to the differences in final infiltration rate. Kookana et al. (1993) showed that fitted α values reported in numerous studies correlate with pore water velocity. When plotted on their Fig. 6 (not shown), the results found here also follow this log-log linear relationship.

Figures 1 and 2 can also be inspected for any consistent bias in the behavior of the individual tracers. For Tests 1 to 3, Br$^-$ was the third longest tracer applied (Table 1) and appears to show a consistent bias of higher $\ln(1 - C/C_o)$ values (i.e., lower Br$^-$ concentrations) relative to the benzoate tracers (Fig. 1). This implies that Br$^-$ is either excluded from more of the water-filled pores or that the exchange rate is slower for Br$^-$ than for the benzoates. We would not expect slower exchange rates for Br$^-$ than for the benzoates since the diffusion coefficient in water is greater for Br$^-$ than for the benzoates (Brusseau, 1993). However, greater exclusion of Br$^-$ from water-filled pores agrees with earlier work where Br$^-$ had slightly smaller retardation values than the benzoates in column experiments using similar soils (Jaynes, 1994).

No bias is evident in Fig. 2 for the Br$^-$ data or any of the other tracers used. Thus, the apparent bias seen for the tests on the Nicollet soil may have been caused by erroneously high measurements of the initial Br$^-$ concentration. If further tests prove a bias in Br$^-$ transport compared with the benzoates, it may be possible to replace Br$^-$ with one of the tri- or tetrafluorobenzoates recently tested by Benson and Bowman (1994).

CONCLUSIONS

We developed a field method for measuring the immobile water fraction and the solute exchange coefficient between the mobile and immobile zones of an unsaturated soil. The method uses a tension infiltrometer and a sequence of conservative tracers infiltrated with time. Initial tests on two soils demonstrated the feasibility of the method and yielded estimates of the θ_{im}/θ fraction and α that are similar to those found by other investigators. Since tension infiltrometers are routinely used to measure the hydraulic

properties of soils near saturation, incorporation of tracers into the infiltrating water could easily extend these measurements to include chemical transport properties.

Advantages of this method compared with a similar approach used by Clothier et al. (1992) are several. First, θ_{im} can be found with this method even for soils where the infiltration rate is moderately slow in comparison to the mobile/immobile transfer rate. Thus, the assumption made by Clothier et al. (1992) of negligible solute movement into immobile zones before sampling is not required. Second, this new method also measures the exchange coefficient, α, between the immobile and mobile regions, which cannot be found with a single tracer.

A third advantage is that this method can be used to test the underlying assumptions of the two-domain model for field soils. Although domain models have shown promise in laboratory studies, field validation studies are virtually nonexistent. If the tracer concentrations do not prescribe a linear relation with time as indicated in Eq. [4], then the two-domain model is not applicable. If subsequent tests confirm both two-domain theory and identical behavior by the tracers, we anticipate routinely using only two tracers to calculate θ_{im} and α.

Lastly, the method allows simultaneous measurement of both hydraulic conductivity and the solute transport parameters θ_{im} and α. In addition, because of the design of the tension infiltrometer, the method can be used to study the changes in the transport parameters as a function of soil water tension.

For this initial investigation, we have assumed that the tracers used are conservative and nonsorbing. However, leaching studies using these tracers have shown that they exhibit some interaction with the soil matrix, resulting in computed retardation factors <1.0 (Benson and Bowman, 1994; Jaynes, 1994). Incorporation of a retardation factor in Eq. [1] as done by Nkedi-Kizza et al. (1984) would be straightforward but would require further assumptions as to the partitioning of adsorption sites exposed to the mobile and immobile phases.

Finally, while the measurements made on the two soils here fall within the ranges reported in earlier studies, further experiments are needed to verify that the estimates of θ_{im} and α provided by this method are similar to estimates obtained from breakthrough curves in leaching experiments. Direct comparisons are currently underway.

ACKNOWLEDGMENTS

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