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A gas-phase partitioning tracer method for the in situ measurement of soil-water content

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Abstract. The purpose of this paper is to describe a gas-phase partitioning tracer method for the in situ measurement of soil-water content and to illustrate the application and performance of the tracer method in well-defined systems. The method is based on the use of a tracer test with nonpartitioning and partitioning tracers introduced into the system in the gas phase. Partitioning tracers dissolve into the water, which retards their gas-phase transport relative to that of the nonpartitioning tracers. Retardation of the partitioning tracers is a function of the amount of water present. The method provides an integrated field-scale value that complements smaller-scale methods, such as neutron moderation, and regional-scale methods based on remote sensing. Experiments were conducted in the laboratory and in a large weighing lysimeter to test the performance of the gas-phase partitioning tracer method. Soil-water contents estimated from the tracer tests were reasonably close to values obtained using gravimetric and time domain reflectometry measurements, indicating the tracer method has the potential to provide accurate measurements of soil-water content at the field scale.

1. Introduction

Characterizing soil-water content is critical to many activities associated with agriculture, forestry, hydrology, and engineering. For example, knowledge of soil-water content is especially important for management of agricultural resources, for flood control, and for predicting contaminant transport in the vadose zone. Several methods, including neutron moderation, time domain reflectrometry (TDR), and gravimetric analysis of core samples, are commonly used to measure soil-water content. These methods provide a "point" estimate of soil-water content within relatively small sample volumes ($\sim 10^{-3}$ m^3). While this is an advantage for obtaining accurate information at small scales, it is a disadvantage for determining soil-water contents at the larger (field) scales required for many practical applications. Using current methods to determine the three-dimensional distribution of soil-water content at the field scale requires a dense sampling network and application of spatial statistics. Such an approach is constrained by varying levels of uncertainty and is relatively costly and time consuming. A method that could efficiently measure soil-water contents for larger scales would be very useful and would be a valuable tool to complement the smaller-scale methods.

The partitioning tracer method is a new technique for the in situ measurement of soil-water content [*Brusseau et al.*, 1997]. The method is based on the use of a tracer test with nonpartitioning and partitioning tracers introduced into the system in the gas phase. The partitioning tracers dissolve into the water, which retards the gas-phase transport of the partitioning tracers relative to that of the nonpartitioning tracers. Retardation of the partitioning tracers is a function of the amount of water present. The purpose of this paper is to describe this new method and to test its performance in the laboratory and at the intermediate scale in a large weighing lysimeter.

2. Background

2.1. Partitioning Tracers: Previous Work

Partitioning tracers have been used in the petroleum industry since the 1970s to determine residual oil saturation in oil reservoirs [*Cooke*, 1971; *Deans*, 1971; *Tang*, 1995]. More recently, environmental scientists have begun to examine the use of the partitioning tracer method for measuring immiscible organic liquid contamination in water-saturated systems [*Jin et al.*, 1995; *Wilson and Mackay*, 1995; *Nelson and Brusseau*, 1996; *Jin et al.*, 1997; *Annable et al.*, 1998; *Brusseau et al.*, 1999]. A similar concept to that used to measure immiscible organic liquid saturation can also be applied to determine soil-water content in the vadose zone. However, the use of aqueous-phase tracers to determine soil-water content is not practical considering that water movement in the vadose zone is generally much slower than induced-gradient groundwater flow. An alternative approach is to use gas-phase tracers, which provide for a much more rapid measurement.

Brusseau et al. [1997] examined the potential of gas-phase tracers for measuring soil-water content and air-water interfacial area. They demonstrated reasonable success with their initial laboratory-scale experiments using a suite of phase-selective partitioning tracers, including CO_2, to measure the bulk soil-water content of the system. On the basis of the

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retardation of CO_2 as compared to helium (a nonpartitioning tracer), the soil-water content in a column packed with silica sand was estimated to be 0.14 cm^3 cm^{-3}. This value is similar to the gravimetrically measured value of 0.16 cm^3 cm^{-3}. These results indicated that the gas-phase partitioning tracer method has the potential to provide accurate estimates of soil-water content.

2.2. Theory of Partitioning Tracers

The experimental and theoretical basis for the retention of dissolved or gaseous solutes by immobile, immiscible-liquid phases and the resultant impact on solute (tracer) transport has been described previously [*Brusseau*, 1992; *Jin et al.*, 1995; *Brusseau et al.*, 1997]. Essentially, an immobile and immiscible fluid reversibly retains the partitioning tracer, which retards its transport with respect to that of nonpartitioning tracers. For the present application, soil water is considered to be essentially immobile relative to the rate of gas flux associated with induced-gradient gas tracer tests.

The procedure for determining volumetric soil-water content, θ_w, involves measurement of a retardation factor R for the gas-phase partitioning tracer. The retardation factor is defined as the quotient of the mean travel times of the partitioning and nonpartitioning tracers. The mean travel times are obtained by standard moment analysis of the tracer breakthrough curves [e.g., *Skopp*, 1984; *Jin et al.*, 1995].

The retardation factor for gas-phase transport of a tracer retained by the aqueous, sorbed, and gas-water interface phases is given as

$$R = 1 + \frac{\theta_w}{\theta_a K_{\mathrm{H}}} + \frac{\rho_b K_{D\mathrm{sat}}}{\theta_a K_{\mathrm{H}}} + \frac{K_{IA} A_{IA}}{\theta_a}, \qquad (1)$$

where θ_w (cubic centimeters of water per cubic centimeter total) is volumetric water content, θ_a (cubic centimeters of air per cubic centimeter total) is air-filled porosity, K_{H} (cubic centimeters of water per cubic centimeters of air) is Henry's law constant (dimensionless), $K_{D\mathrm{sat}}$ (cm^3 g^{-1}) is the sorption coefficient, ρ_b (g cm^{-3}) is the dry soil bulk density, K_{IA} (centimeters) is the adsorption coefficient between the gas phase and the gas-water interface, and A_{IA} (cm^2 cm^{-3}) is the specific surface area of the gas-water interface. When sorption and interfacial accumulation of the partitioning tracer are negligible, R is given by

$$R = 1 + \frac{\theta_w}{\theta_a K_{\mathrm{H}}} = 1 + \frac{\theta_w}{(\theta_t - \theta_w) K_{\mathrm{H}}} = 1 + \frac{S_w}{(1 - S_w) K_{\mathrm{H}}}, \qquad (2)$$

where θ_t is total porosity and S_w is soil-water saturation.

From (2) it is clear that a gas-phase tracer experiment conducted with nonpartitioning and partitioning tracers can provide a measure of θ_w if either θ_a or θ_t are known. Additionally, soil-water saturation can be determined without knowledge of θ_a or θ_t. In this case the only parameter that must be known is K_{H}. Henry's law constants are often available in the literature and can be measured in the laboratory.

The soil-water content values obtained from partitioning tracer experiments are "global" values, representing an integration of soil-water contents distributed throughout the contacted domain. The magnitude of the observed retardation, and thus of soil-water content, is a function of the areal influence of the tracer test (swept zone) and the volume of water in the swept zone. The scale of measurement corresponds to the size of the swept zone, which is controlled by the placement of the injection and sampling points. Thus the tracer method provides a measure of soil-water content at scales that can be considered as intermediate to the traditional, small-scale methods (e.g., gravimetric analysis of soil cores, neutron probe moderation, and TDR) and regional (e.g., watershed scale) methods based on remote sensing. Additional advantages of the tracer technique include the absence of depth limitations and the ability to tailor the scale of measurement to specific needs.

The partitioning tracer method can be used to determine the areal distribution of soil-water content at the field scale. This can be accomplished, for example, by conducting three tracer tests using a set of three injection wells and one extraction well. The injection wells would be placed in a triangle, with the extraction well at the center. A tracer test would be conducted between each injection well and the extraction well. The use of monitoring wells can provide additional information for determining areal distributions. Furthermore, the use of multilevel sampling in the monitoring wells would allow the vertical distribution of soil-water content to be determined.

The experimental conditions of the tracer test and the characteristics of the physical system can influence the measurement of soil-water content. Thus, it is important to recognize that the tracer test may in some cases measure an "effective" soil-water content, which represents the fraction of the soil-water content contacted by the partitioning tracer. In some cases the effective soil-water content would be expected to be less than the total soil-water content. This may occur, for example, when mass-transfer constraints are significant or when a substantial portion of the air phase (and associated water) is isolated from the tracer pulse.

2.3. Tracer Selection

A tracer selected for use should have the following characteristics: (1) low toxicity, (2) low cost, (3) low background levels, (4) no biodegradation or other transformation reactions, (5) no sorption to porous media or to materials composing the tracer experiment infrastructure such as PVC and stainless steel, (5) low detection levels such that it can be injected at concentrations several orders of magnitude higher than its detection limit, and (6) an appropriate K_{H} value. The Henry's law constant controls the magnitude of retardation for any given soil-water content. A tracer with a suitable K_{H} value would yield a retardation factor large enough to be measurable with some level of certainty but small enough such that the duration of the test remains practical.

The expected transport behavior of three representative tracers with different Henry's law constants in systems with soil-water contents of 0.03 and 0.15 cm^3 cm^{-3} are shown in Figures 1a and 1b, respectively. Figure 1a indicates that tracers with K_{H} values between 0.02 and 0.2 would yield R values that are of an acceptable magnitude for a system with $\theta_w = 0.03$ cm^3 cm^{-3}. However, for a larger θ_w of 0.15 cm^3 cm^{-3}, tracers with K_{H} values between 0.2 and 2 would be more appropriate (Figure 1b). In general, Figure 1 demonstrates that a suitable choice of tracers cannot always be made without an a priori estimate of soil-water content. Therefore it may be desirable to choose several tracers, spanning a range of K_{H} values, to ensure satisfactory results. When two or more partitioning tracers are used, pairs of partitioning tracers may also be used to calculate soil-water contents [e.g., *Jin et al.*, 1995].

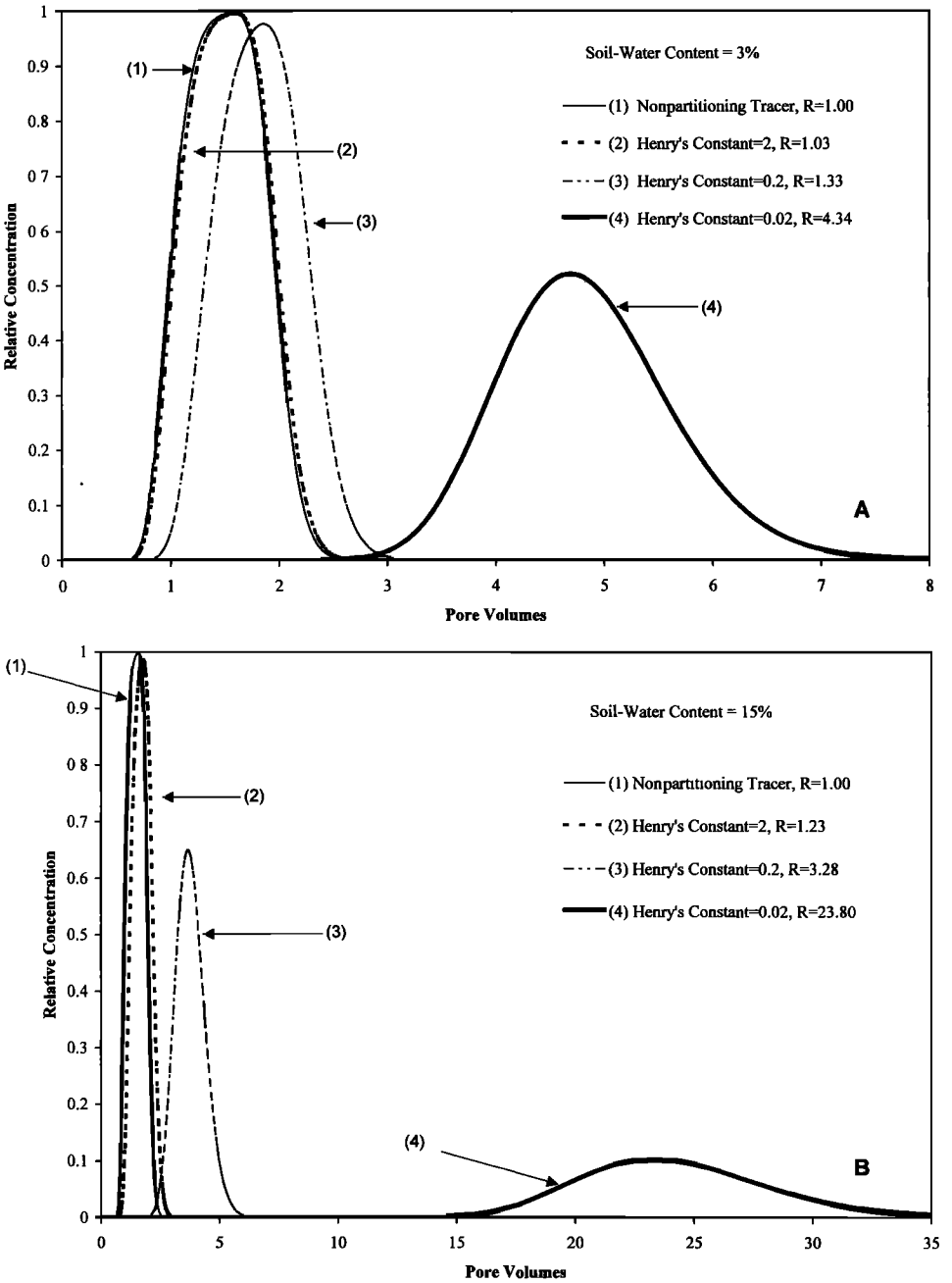

Figure 1. Breakthrough curves for tracers with different K_H values: (a) $\theta_w = 0.03$, and (b) $\theta_w = 0.15$. The curves were produced using a program that plots an analytical solution to the one-dimensional advection-dispersion equation.

3. Materials and Methods

3.1. Laboratory Experiments

The tracer experiments were conducted using uniformly wetted, homogeneous Vinton fine sand (sandy, mixed thermic Typic Torrifluvent). The sand was mixed with a known amount of water and packed wet. Dibromodifluoromethane (BFM) was used as the water-partitioning tracer, and methane served as the nonpartitioning tracer. Both tracers were custom mixed in a balance of nitrogen (Air Products, Long Beach, California, and Spectra Gases, Alpha, New Jersey, respectively). Nitrogen was used as the background gas to establish a steady flow and to obtain a steady flame ionization detector (FID) baseline prior to each tracer experiment. Pertinent properties of the tracers are listed in Table 1. A 10.5-cm-long (5.08-cm ID) stainless steel column (MODcol, St. Louis, Missouri) was used with diffusion plates fitted at both ends to allow an even distribution of vapor across the column cross section. All system components through which the gases flowed were connected with 0.3-cm-ID (1/8 inch) stainless steel tubing and 0.3-cm stainless steel Swagelok fittings (Arizona Valve and Fitting Co., Phoenix, Arizona).

The experimental setup was similar to the gas-phase flow system described by *Brusseau et al.* [1997]. Nitrogen gas, with or without the tracers, was introduced into the system via

high-pressure gas cylinders. Prior to entering the column, the gas passed through a 500-mL gas washing bottle (Pyrex, Ace Glass, Vineland, New Jersey) for humidification to prevent desaturation of the porous medium. Separate humidification bottles were used for gas with and without the tracers to avoid background contamination. The column effluent was passed directly to an on-line FID (Varian 3700, Varian Associates, Inc., Walnut Creek, California) for analysis. The FID signal was routed to a digital voltmeter (Micronta, Fort Worth, Texas) and interfaced to a personal computer using Wedge software (T.A.L. Enterprises, Philadelphia, Pennsylvania). Concentrations (voltage) versus time data were collected in real time at a specified time interval.

Flow rates were regulated by use of stainless steel high-resolution metering valves (Cole-Parmer, Vernon Hills, Illinois). Flow was established at approximately 30.0 mL min^{-1} and monitored using a 25-mL bubble flowmeter (Kimble-Kontes, Vineland, New Jersey) inserted at the detector outlet. This corresponds to an average pore-gas velocity of 3.4 cm min^{-1}.

Soil-water content was measured before and after each experiment. Prior to each experiment, the soil-water content was calculated from the known amount of water added to the known mass of dry sand. After each experiment the column was unpacked and the soil-water content was measured gravimetrically. Small aliquots of soil (<15 g) were taken from the column inlet, midpoint, and outlet to determine spatial distribution. The remaining sand was used to gravimetrically measure an average soil-water content for the column.

The following procedure was used to determine K_H for the partitioning tracers. An aliquot of a gas standard was injected into a 21-mL crimped headspace vial containing 10 mL of distilled, deionized water. Five different-sized aliquots were used to produce five different concentrations within the headspace vial. This was done in triplicate. The vials were placed on a shaker table for 24 hours to equilibrate. A 2.5-mL aliquot of the headspace was then subsampled and placed in a headspace vial. The gas in the headspace vial was then analyzed using gas chromatography (Shimadzu, GC-17) using an electron capture detector and a headspace autosampler (Tekmar). The difference between the initial mass of the sample gas injected into the vial and the final mass of the sample gas in the headspace was assumed to have partitioned to the water phase. The Henry's law constants, calculated as the slope of the concentration in the water plotted against the concentration in the headspace, are presented in Table 1.

3.2. Lysimeter Experiments

The partitioning tracer method was tested with controlled experiments conducted in a large weighing lysimeter located at the University of Arizona's Karsten Turf Center for Research. The lysimeter is 4.0 m deep, 2.5 m in diameter, and contains a homogeneous packing of Vinton fine sand (the same material used in the column experiments). The lysimeter is equipped with 6 tensiometers, 21 TDR probes, a neutron-probe access tube, 3 thermocouples, and 48 porous stainless steel cups for gas injection and sampling. The weighing scales have a capacity of 45 Mg and can detect a 200-g mass change, equivalent to ~0.04 mm of water on the surface. The instrumentation allows the values of soil-water content estimated from the partitioning tracer experiment to be compared to values obtained with established methods. Pressure transducers (model 136PC15G2, Microswitch, Freeport, Illinois) installed in the injection line, extraction line, and at 50-cm increments along the lysimeter allow pressure to be monitored throughout the entire system. All instrumentation (excluding TDR) is connected to a data logger (model CR7, Campbell Scientific, Inc., Logan, Utah) for data collection and storage. Software (PC208W, Campbell Scientific) for a personal computer connected to the data logger allows real-time monitoring of all data during the experiment. Additional information about the lysimeter facility is given by *Young et al.* [1996] and (Z.-Y. Zou et al. (Estimation of unsaturated hydraulic properties from a deep infiltration experiment, submitted to *Water Resources Research*, 1998).

Three tracer experiments were conducted in the lysimeter. For the first experiment a nonpartitioning tracer (SF_6) was used to test the flow system and gas-sampling techniques and to obtain estimates of travel times. For the second experiment, SF_6 was used as the nonpartitioning tracer and bromochlorodifluoromethane (BCF) was used as the water-partitioning tracer. For the third experiment, BFM was used instead of BCF as the water-partitioning tracer.

Steady state flow was established by injecting air into the lysimeter through a length of stainless steel tubing. This stainless steel tubing was connected via a manifold to 18 lengths of 0.64-cm (1/4 inch) Kynar tubing embedded horizontally within a layer of pea gravel at the bottom of the lysimeter. The tubing terminated in porous stainless steel cups (50 mm long, 12.5 mm in diameter, with an air-entry pressure of 20 cm). A 3728.5 W (5 horsepower) air compressor was used to inject air, and a 559.3 W (3/4 horsepower) vacuum pump was used to extract air, at the same rate as it was injected, through four ports drilled into an aluminum lid at the top of the lysimeter (see Table 2 for flow rates). Injection and extraction flow rates were controlled using gate valves and monitored using gas flow rotameters (Dwyer Instruments, Inc., Michigan City, Indiana, or Omega, Stamford, Connecticut).

The gas tracers were contained in a 6.2-m^3 gas cylinder and injected directly into the lysimeter using the method described above for air injection. Two 2-way valves were used to switch between the tracer and tracer-free gas sources. Tracer injection began once steady state gas flow was established. Follow-

Table 1. Tracer Properties

Tracer	Henry's Coefficient	C_0, mg L^{-1}	Detection Limit
SF_6	70*	0.30	0.04 $\mu g\ L^{-1}$
Methane	27.0†	0.07	~1 mg L^{-1}
BCF	2‡	0.30	0.05 $\mu g\ L^{-1}$
BFM	1.55‡	1.33	0.5 $\mu g\ L^{-1}$

BCF, bromochlorodifluoromethane; BFM, dibromodifluoromethane.
Wilson and Mackay [1995].
†*Brusseau et al.* [1997].
‡Measured.

Table 2. Experimental Conditions: Lysimeter

	First Experiment	Second Experiment	Third Experiment
Flow rate, L min^{-1}	15	32	39
Tracer pulse, hours	1.02	2.00	2.00
Tracer pulse (pore volumes)	0.12	0.50	0.60
Total pore volumes	1.72	4.80	6.50

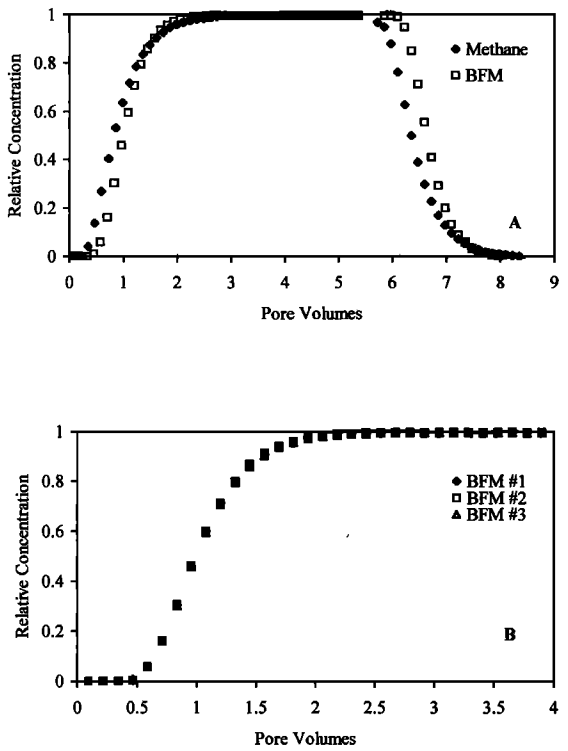

Figure 2. Breakthrough curves measured for the gas-phase transport of tracers in a laboratory column: (a) methane (nonpartitioning) and dibromodifluoromethane (BFM) (partitioning) tracers and (b) triplicate breakthrough curves for BFM.

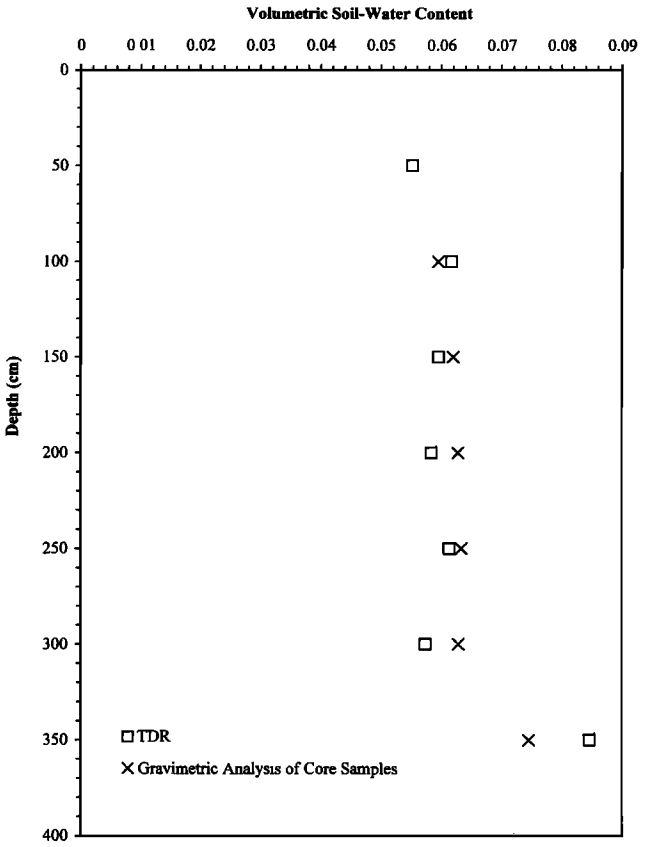

Figure 3. Soil-water content distribution in the lysimeter determined using time domain reflectometry and gravimetric measurements.

ing tracer injection, tracer-free air was injected. The length of the tracer pulse and the total number of pore volumes flushed through the system are presented in Table 2 for each experiment.

The injected air was humidified to greater than 95% by passing it through a water tower prior to injection. The water tower consists of schedule 40 PVC pipe (0.3-m OD and 1.8-m length), in which wire mesh was placed to increase mass transfer. The pipe was filled with 66 L of water. This configuration provided an average residence time of 2 min for the air stream. The tracer pulse bypassed the water tower to prevent retention of the partitioning tracer. The results of calculations assuming equilibrium conditions indicate that no more than 0.063 L of water (0.0032% of the total water) would be removed from the lysimeter because of evaporation during the tracer pulse.

A vacuum test was conducted before the tracer experiment to check for air leaks. The measured leakage rate was approximately 0.29 L min^{-1}, which is about 1% of the flow rates used during the experiments. This test was conducted using a vacuum of 51.6 cm, which is 25 times higher than the vacuum used during the tracer test (2.1 cm) and therefore provides an overestimate of the actual leakage expected during the tracer test. A helium leak test was conducted in addition to the vacuum tests. Helium was pumped into the lysimeter and a helium-leak detector was used to check for leaks at all fittings and connections. Leaks identified by the helium test were corrected before conducting the experiments.

In situ samples were collected from two horizontal planes located at 1.75 m and 3.1 m from the bottom of the lysimeter. The samples were collected from ports located near the center of the lysimeter. For the third experiment a third in situ port, located near the lysimeter wall and 3.1 m from the bottom of the lysimeter, was sampled. The influent- and effluent-gas streams were also sampled. The sampling ports consist of septum injector nuts (Valco Instruments Company, Inc., Houston, Texas), connected to 6.4-mm OD Kynar tubing embedded horizontally within the soil. Inside the lysimeter the Kynar tubing terminates in porous stainless steel cups at various distances from the lysimeter wall. The tubing intersects the lysimeter wall through an airtight fitting. Gas samples were taken by withdrawing samples through the septum into a needle-tipped syringe. The gas samples were then injected from the syringe into evacuated 80-mL aerosol canisters (Tracer Research, Tucson, Arizona). The first volume of gas withdrawn was expelled as a purge volume. The tracers were analyzed by gas chromatography (Shimadzu, GC-17) using an electron capture detector. Pertinent properties of the tracers are listed in Table 1.

Core samples (1.3 cm × 30 cm) were removed from the lysimeter at 50-cm intervals for gravimetric analysis of soil-water content. The samples were placed in airtight containers, weighed, oven dried for 48 hours at 105°C, and weighted again. The gravimetric soil-water content was converted to volumetric soil-water content by using the global average of bulk density of 1.38 Mg m^{-3}. The TDR probes were individually connected to a cable tester (model 1502C, Tektronix Corp., Beaverton, Oregon), and waveforms were read, in duplicate, using software (TACQ, Dynamax, Inc., Houston, Texas) on a personal

Table 3. Independent Measurements of θ_a, θ_w, and S_w

	$\theta_a = \theta_t - \theta_w$ (cores)	θ_w (cores)	S_w (cores)	θ_w (TDR)	S_w (TDR)
Bottom level (1.65 m)	0.40	0.069	0.144	0.074	0.155
Top level, center port (3.00 m)	0.40	0.064	0.134	0.066	0.138
Effluent gas stream (3.85 m)	0.40	0.064	0.134	0.064	0.134

computer. The waveforms were translated to volumetric soil-water content using the Topp equation [*Topp et al.*, 1980].

3.3. Data Analysis

The breakthrough curves for all experiments were analyzed by calculating the zeroth and first temporal moments to quantify mass recovery, travel time, and retardation, as discussed in many references [e.g., *Skopp*, 1984; *Jin et al.*, 1995]. Theoretically, nonequilibrium conditions caused by rate-limited mass transfer do not influence the first temporal moment (travel time). Therefore nonequilibrium conditions should not affect the retardation of the partitioning tracer and the measured soil-water content. However, in practice, the extensive concentration tailing caused by extreme rate-limited mass transfer can influence the calculation of the first moment. For example, the timescale of the tracer test may not be sufficient to capture the mass represented by the extensive tailing. Furthermore, the concentrations associated with extensive tailing can be less than the analytical detection limit for the tracer. Both of these factors can lead to underestimates in the first moment and therefore in the measured soil-water content.

For all breakthrough curves the time axis was converted to pore volumes by dividing by the mean travel time determined for SF_6 at the given location (assumed to be the time for one pore volume). The concentration axis was converted to relative concentration by dividing the measured concentration by the input concentration (C_0). For the column systems, travel time was corrected for the known system dead volume. Additionally, the total observed retardation factor was corrected for BFM retention by the apparatus. Peclet numbers, representing the relative contributions of advection and dispersion to mass transport, were determined using a nonlinear least squares optimization program incorporating the one-dimensional advection-dispersion equation [*van Genuchten*, 1981].

4. Results and Discussion

4.1. Results of Laboratory Experiments

Breakthrough curves for transport of methane and BFM in the packed column are shown in Figure 2a. The curves are symmetric with sharp arrival and elution waves, indicating ideal transport. The transport of BFM is retarded relative to methane, because of retention of BFM by partitioning to water. Good precision was achieved in the replicate runs, with a relative standard deviation of 0.6% for BFM replicates. Reproducibility is demonstrated visually by the overlap of replicate BFM fronts shown in Figure 2b.

Using the known air-filled porosity, 0.38, the soil-water content is estimated to be 0.054 based on the results of the tracer tests. This value, which is somewhat smaller than the gravimetrically measured value of 0.063, was calculated using corrections accounting for the retention associated with the apparatus (e.g., dead volume) characterized in separate experiments.

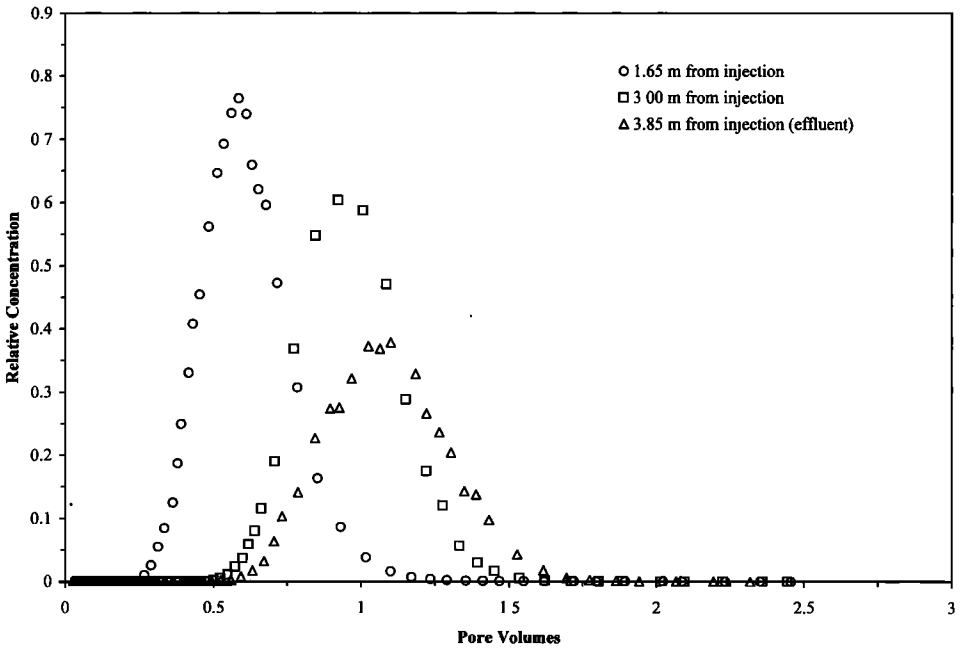

Figure 4. Breakthrough curves measured for gas-phase transport of SF_6 in the lysimeter during the first experiment.

Table 4. SF_6 Results: Lysimeter Experiment 1

Location	Peclet Number	v, cm min^{-1}	θ_a
Bottom level	29.4 (28.0–30.9)	0.87	0.35
Top level	62.3 (59.8–64.9)	0.96	0.32
Effluent gas stream	53.9 (48.7–59.2)	1.08	0.28

A value of 0.071, which is larger than the measured value, was estimated from the tracer-test results using a comparative moment analysis as would typically be done in field applications. For another set of experiments conducted at a higher soil-water content (measured value of 0.090), the value estimated from the tracer-test results using comparative moment analysis was 0.063.

4.2. Results of Lysimeter Experiments

Average measurements of air porosity ($\theta_t - \theta_w$), soil-water content, and soil-water saturation from gravimetric analysis of soil cores and TDR are reported in Table 3. Depthwise profiles of soil-water content in the lysimeter obtained from gravimetric analysis of soil cores and TDR are shown in Figure 3. Both profiles exhibit a uniform soil-water content ranging from 0.060 to 0.065, from 50 cm to 300 cm below ground surface, and a higher soil-water content below 300 cm.

Breakthrough curves for SF_6 at 1.65 m and 3.00 m from the

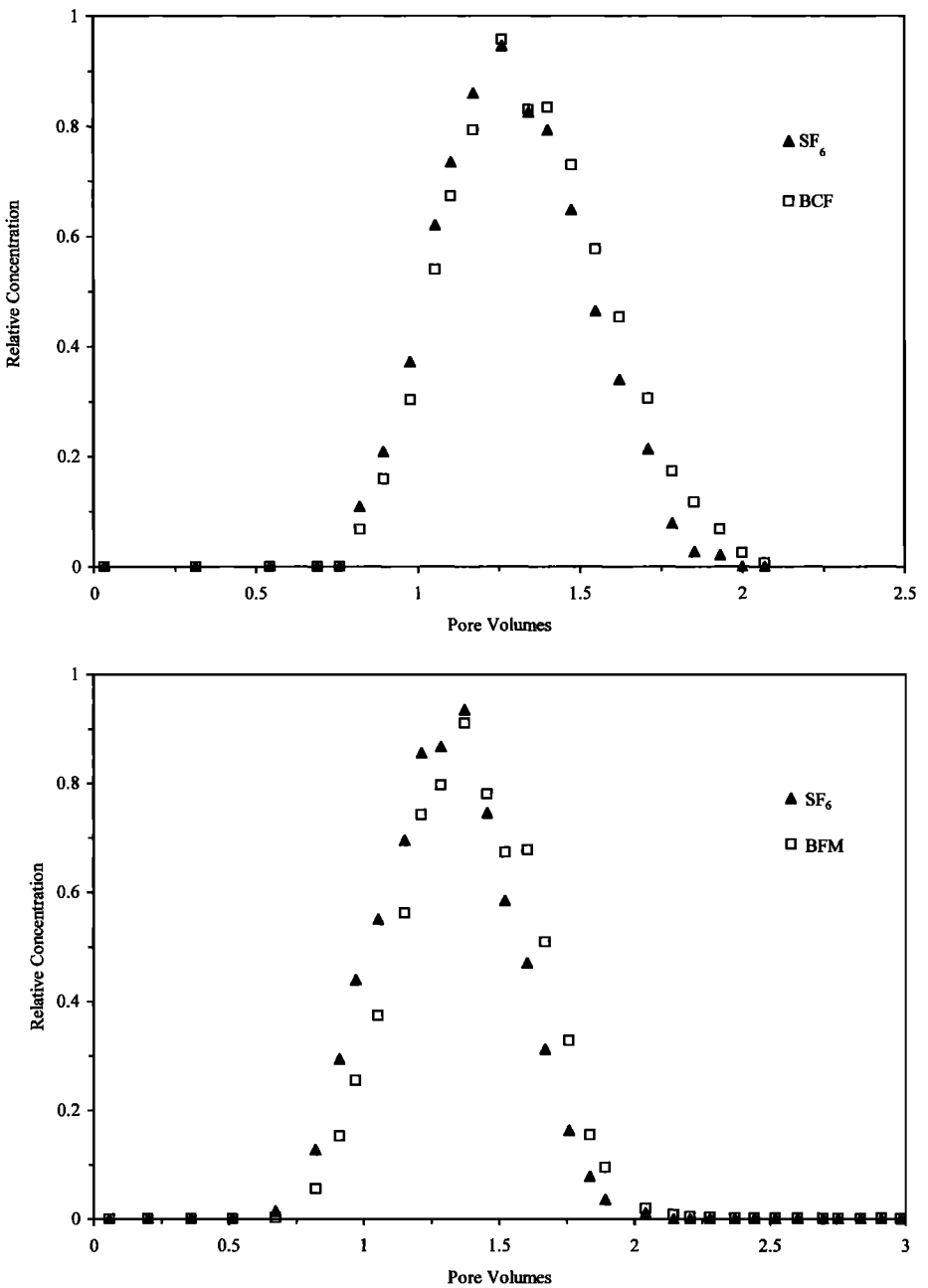

Figure 5. Effluent breakthrough curves for gas-phase transport of nonpartitioning and partitioning tracers in the lysimeter: (a) SF_6 and bromochlorodifluoromethane (BCF) (second experiment) and (b) SF_6 and BFM (third experiment).

Table 5. Results of Lysimeter Experiments

Tracer	v, cm min^{-1}	θ_a	R	S_w	θ_w
	Experiment 2				
Bottom level tracer					
SF_6	1.6	0.41	1*		
BCF	1.5		1.07	0.134	0.057
Top level tracer					
SF_6	1.8	0.36	1*		
BCF	1.7		1.06	0.113	0.043
Effluent gas stream tracer					
SF_6	1.9	0.35	1*		
BCF	1.8		1.05	0.092	0.035
	Experiment 3				
Bottom level tracer					
SF_6	1.98	0.40	1*		
BFM	1.70		1.17	0.207	0.105
Top level, center port tracer					
SF_6	1.75	0.45	1*		
BFM	1.63		1.09	0.123	0.063
Top level, side port tracer					
SF_6	1.85	0.43	1*		
BFM	1.63		1.13	0.169	0.087
Effluent gas stream tracer					
SF_6	1.98	0.40	1*		
BFM	1.82		1.09	0.119	0.058

NA, not applicable.
*Assumed.

injection zone and for the effluent gas stream are shown in Figure 4 for the first experiment. The breakthrough curves are smooth and symmetrical, indicating near-ideal transport. Peclet numbers, pore-gas velocities (travel distance/mean travel time), and estimated air-filled porosities (volumetric flow rate divided by the product of the pore-gas velocity and cross-sectional area) are reported in Table 4.

Effluent breakthrough curves for SF_6 and BCF from experiment two and for SF_6 and BFM from experiment three are shown in Figures 5a and 5b, respectively. The Peclet number obtained for the SF_6 breakthrough curves measured at the effluent sampling location for the second and third experiments are essentially identical to the value obtained during the first experiment. This indicates that the experiments are reproducible. In addition, the Peclet numbers obtained from the effluent breakthrough curves are essentially identical for SF_6 and BCF, indicating that the two tracers exhibited similar near-ideal transport behavior.

Inspection of Figure 5 shows that the partitioning tracer (BCF or BFM) breakthrough curves are slightly delayed and exhibit concentration tailing in comparison to the SF_6 breakthrough curves. Values of pore-gas velocity (v), air porosity (θ_a), retardation factor (R), soil-water content (θ_w), and soil-water saturation (S_w) are reported for all sampling points in Table 5. The measurements of air porosity obtained from the three tracer experiments ranged from 0.350 to 0.450, with a mean of 0.380. The air porosity based on the average gravimetric soil-water content and total porosity ranged from 0.404 to 0.419, with a mean of 0.414. The air porosity based on TDR measurements and total porosity ranged from 0.407 to 0.424, with a mean of 0.414. A comparison of these values indicates that SF_6 contacted approximately 92% of the total air-filled porosity.

The measurements of soil-water content calculated using the SF_6-transport-derived air-filled porosity from experiments two and three ranged from 0.043 to 0.105, with a mean of 0.064. The gravimetric soil-water content measurements ranged from 0.059 to 0.075, with a mean of 0.064. The soil-water contents measured by TDR ranged from 0.054 to 0.071, with a mean of 0.064. The mean of the measurements obtained with the tracer data is the same as the means of the independently determined soil-water contents, indicating that the tracer test provides a good estimate of soil-water content.

The values of soil-water content measured by the two tracer experiments indicate higher soil-water contents at the bottom of the lysimeter. The independently determined gravimetric and TDR measurements also show increasing soil-water content with depth (Figure 3). The soil-water content values obtained from the effluent breakthrough curves are smaller than the values measured at the three point-sampling ports. This may be due, in part, to inherent differences between extraction well samples, which represent transport behavior averaged across the entire swept zone, and point samples, which represent transport behavior along a specific flow line. Although efforts were made to ensure that the lysimeter was homogeneously packed and that soil-water content was spatially uniform, the soil-water content profile (Figure 3) and bulk density profile both exhibit a small degree of heterogeneity. The bulk density ranged from 1.23 to 1.55 Mg M^{-3}, with a mean of 1.38. This heterogeneity may have contributed to spatial variability of soil-water content.

5. Conclusions

The results of the experiments indicate that the tracer tests accurately measured soil-water contents for systems with relatively uniform soil-water contents and homogeneous porous media. This method would complement both the traditional, small-scale methods and the regional-scale (watershed) methods of measuring soil-water content. Although the mean value

of θ_w obtained from the tracer tests in the lysimeter agrees with the values obtained from the gravimetric and TDR measurements, it should be noted that the retardation factors (1.05 to 1.13) are at the lower limit of the acceptable range. For less controlled experiments a retardation factor of 1.1 may not be sufficient to estimate robust values of soil-water content. In addition, it should be stressed that field tests of the partitioning tracer method may not achieve the same level of performance as demonstrated by our experiments. Our well-controlled laboratory and lysimeter experiments minimized factors such as rate-limited mass transfer, nonuniform distribution of soil-water content, and porous media heterogeneity that can constrain the application of the method.

Nonideal transport behavior, caused by factors such as rate-limited mass transfer, variable distribution of water, pneumatic-related factors, and subsurface heterogeneity, can lead to difficulties in interpreting partitioning tracer tests. For example, mass transfer between the gas and water phases may be constrained by rate-limited diffusion of the tracer within the water. Diffusive mass transfer in water is usually considered to be relatively rapid for aqueous-phase systems. However, residence times associated with gas-phase advection are generally much smaller than those for aqueous-phase advection. Thus the timescale of aqueous diffusion coupled with the short residence times of gas-phase transport can cause diffusion within water to be significantly rate limited [e.g., *Popovicová and Brusseau*, 1998]. As a result, mass transfer between the gas and water phases may be rate limited, which may prevent the accurate calculation of moments and therefore cause underestimation of the soil-water content.

The performance of a partitioning tracer test can also be influenced by heterogeneity-related factors. For example, gas may flow primarily around zones of higher soil-water content because of the reduced relative air permeabilities associated with these zones. Such bypass flow may limit the contact of the tracer gas to the periphery of the high-saturation zone, which could result in an underestimation of soil-water content. Porous-media heterogeneity (e.g., spatial variability of intrinsic permeability) may also constrain the effectiveness of partitioning tracer tests. For example, water present in low-permeability zones within or adjacent to high-permeability zones may be undermeasured because of the preferential flow that occurs in such systems.

In general, because of factors such as bypass flow, rate-limited mass transfer, and mass loss, the measured soil-water content values may often be underestimates of the true values. Thus soil-water content measurements obtained with the partitioning tracer method should, at least initially, be considered as underestimates of actual values. Further research on these issues is required prior to complete acceptance of the gas-phase partitioning tracer method as a viable alternative for measuring soil-water content.

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References

Annable, M. D., P. S. C. Rao, K. Hatfield, W. D. Graham, A. L. Wood, K. G. Enfield, Partitioning tracers for measuring residual NAPL: Field-scale test results, *J. Environ. Eng.*, *124*(6), 498–503, 1998.

Brusseau, M. L., Rate-limited mass transfer and transport of organic solutes in porous media that contain immobile immiscible organic liquid, *Water Resour. Res.*, *28*, 33–45, 1992.

Brusseau, M. L., J. Popovicová, and J. Silva, Characterizing gas-water interfacial and bulk-water partitioning for transport of gas-phase contaminants in unsaturated porous media, *Environ. Sci. Technol.*, *31*, 1645–1649, 1997.

Brusseau, M. L., N. T. Nelson, R. B. Cain, The partitioning tracer method for in situ detection and quantification of immiscible liquids in the subsurface, in *Innovative Subsurface Remediation: Field Testing of Innovative Subsurface Remediation and Characterization Technologies*, edited by M. L. Brusseau, D. Sabatini, and J. Gierke, chap. 12, pp. 208–225, Am. Chem. Soc., Washington, D.C., 1999.

Cooke, C. E., U.S. patent number 3,590,923, U.S. Pat. and Trademark Off., Washington, D.C., 1971.

Deans, H. A., U.S. patent number 3,623,82, U.S. Pat. and Trademark Off., Washington, D. C., 1971.

Jin, M., M. Delshad, V. Dwarakanath, D. C. McKinney, G. A. Pope, K. Sepehrnoori, and C. E. Tilburg, Partitioning tracer test for detection, estimation, and remediation performance assessment of subsurface nonaqueous phase liquids, *Water Resour. Res.*, *31*, 1201–1211, 1995.

Jin, M., G. W. Butler, R. E. Jackson, P. E. Mariner, J. F. Pickens, G. A. Pope, C. L. Brown, and D. C. McKinney, Sensitivity models and design protocol for partitioning tracer tests in alluvial aquifers, *Ground Water*, *35*, 964–972, 1997.

Nelson, N. T., and M. L. Brusseau, Field study of the partitioning tracer method for detection of dense nonaqueous phase liquid in a trichloroethene-contaminated aquifer, *Environ. Sci. Technol.*, *30*, 2859–2863, 1996.

Popovicová, J., and M. L. Brusseau, Contaminant mass transfer during gas-phase transport in unsaturated porous media, *Water Resour. Res.*, *34*, 83–92, 1998.

Skopp, J., Analysis of solute movement in structured soils, in *Proceedings of ISSS Symposium on Water and Solute Movement in Heavy Clay Soils*, edited by J. Bouma and P.A.C. Raats, pp. 220–228, Int. Inst. Land Reclam. and Impr., Wageningen, Netherlands, 1984.

Tang, J. S., Partitioning tracers and in-situ fluid-saturation measurements, *SPE Form. Eval.*, 33–39, 1995.

Topp, G. C., J. L. Davis, and A. P. Annan, Electromagnetic determination of soil water content: Measurement in coaxial transmission lines, *Water Resour. Res.*, *16*, 574–582, 1980.

van Genuchten, M. T., Non-equilibrium transport parameters from miscible displacement experiments, *Res. Rep. 119*, U.S. Dep. of Agric., U.S. Salinity Lab., Riverside, Calif., 1981.

Wilson, R. D., and D. M. Mackay, Direct detection of residual nonaqueous phase liquid in the saturated zone using SF_6 as a partitioning tracer, *Environ. Sci. Technol.*, *29*, 1255–1258, 1995.

Young, M. H., P. J. Wierenga, and C. F. Mancino, Large weighing lysimeters for water use and deep percolation studies, *Soil Sci.*, *161*, 491–501, 1996.

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