Measurement of Variation in Soil Solute Tracer Concentration Across a Range of Effective Pore Sizes

Judson W. Harvey

Water Resources Division, U.S. Geological Survey, Menlo Park, California

Solute transport concepts in soil are based on speculation that solutes are distributed nonuniformly within large and small pores. Solute concentrations have not previously been measured across a range of pore sizes and examined in relation to soil hydrological properties. For this study, modified pressure cells were used to measure variation in concentration of a solute tracer across a range of pore sizes. Intact cores were removed from the site of a field tracer experiment, and soil water was eluted from 10 or more discrete classes of pore size. Simultaneous changes in water content and unsaturated hydraulic conductivity were determined on cores using standard pressure cell techniques. Bromide tracer concentration varied by as much as 100% across the range of pore sizes sampled. Immediately following application of the bromide tracer on field plots, bromide was most concentrated in the largest pores; concentrations were lower in pores of progressively smaller sizes. After 27 days, bromide was most dilute in the largest pores and concentrations were higher in the smaller pores. A sharp, threefold decrease in specific water capacity during elution indicated separation of two major pore size classes at a pressure of 47 cm H_2O and a corresponding effective pore diameter of 70 μm. Variation in tracer concentration, on the other hand, was spread across the entire range of pore sizes investigated in this study. A two-porosity characterization of the transport domain, based on water retention criteria, only broadly characterized the pattern of variation in tracer concentration across pore size classes during transport through a macroporous soil.

Introduction

The air- and water-filled domain of soil consists of a complex network of pores of different sizes [*Beven and Germann*, 1982]. Incomplete mixing of soil water between large and small pore networks has been hypothesized to significantly affect solute travel time and chemical transformation as water and solute pass through soil (reviewed by *Neilsen et al.* [1986]; see also *White* [1985]). Early solute transport studies in field soils showed that while the bulk of tracer-labeled water was transported rapidly to depth, a significant proportion of tracer-labeled water lagged behind [*Biggar and Nielsen*, 1976; *Wild and Babiker*, 1976]. The widely accepted interpretation of such data is that solute tracers in soil do not mix uniformly between fast moving water of macropores and stagnant or slow moving water of the small pores of the surrounding soil matrix.

Small-scale variation in concentration of solute in soil has been examined using a variety of techniques. Subcore inventories on dye and solute tracer distribution have been conducted [*Omoti and Wild*, 1979; *Bouma*, 1981; *Germann et al.*, 1984; *Hemond and Chen*, 1990]. Solute concentrations have also been compared in samples from gravity-fed and tension-fed samplers [*Shaffer et al.*, 1979; *Haines et al.*, 1982; *Barbee and Brown*, 1986] or compared from near-identical tension samplers operated at two different tensions [*Jardine et al.*, 1990]. Solute concentrations in soil water collected with tension solution samplers depend on a number of factors, including imposed tensions, flow rate to the sampler, degree of disruption of the local flow pattern, and the relation of the soil volume sampled versus the scale of heterogeneity in solute concentration (reviewed by *Litaor* [1988]). Identification of the source (in terms of location in the pore space) of water collected with tension samplers and

the meaning of the resulting concentrations were questioned by *England* [1974] and *Parker and van Genuchten* [1984]. Current limitations in interpreting field-measured solute concentrations need to be addressed.

Two-porosity transport models are based on the concept that incomplete mixing occurs in soil pore spaces of different size. These models have been critical for the development of a number of physically based and stochastic models that describe the effect of preferred flow paths on solute transport [e.g., *van Genuchten and Wierenga*, 1976; *Jury*, 1982; *Jury et al.*, 1982; *Beven and Young*, 1988]. The approach assumes that microscopic variation in solute concentration within pores of varying size can be characterized by considering two macroscopic pore domains, each with internally equivalent fluxes and concentrations. Two-porosity models have gained increased acceptance because of their parametric efficiency and accuracy in matching observed outflow concentration data in tracer experiments. The physical concepts underlying these models are difficult to test. The macroscopic descriptions of the transport domains that are "backed out" of two-porosity models are not usually compared to independently collected information about pore size distributions or segregation of tracer in large or small pores during transport. Such a comparison would be facilitated by an improved methodology to sample solute concentration in relation to pore size.

Solute tracer concentrations have not previously been measured across a range of pore size classes in soil. Segregation of solute tracer across pore size classes has also not been related directly to physical characteristics of the soil, such as the effective pore size distribution or the water retention characteristics of the soil. The purpose of this paper is to report observations on solute tracer segregation across a range of effective pore sizes made using pressure cells and to relate variations in concentration to water retention and conductance characteristics of the soil. The pressure cell approach to subsampling concentrations within

the wetted pore space is potentially useful to evaluating the physical realism of two-porosity concepts. It also offers a new perspective from which to evaluate the general utility of in situ, tension samplers to studies of solute segregation in soil water.

FIELD SITE DESCRIPTION

The investigation was conducted in a riverine wetland (Eagle Bottom Marsh, 37°18'N, 76°53'W) which borders the Chickahominy River on the coastal plain of Virginia. The site is several miles above where the Chickahominy River flows into the lower James River, which is a subestuary of the Chesapeake Bay. The Chickahominy River experiences semidiurnal tidal fluctuations in this reach, which cause the wetland soil surface to be submersed at high tide. At low tide the wetland soil surface is exposed to the atmosphere for an average of 53% of the time based on local surveying and tidal records [U.S. Department of Commerce, 1989].

Surficial soil in the study wetland is composed of a mixture of clay and silt, soil organic matter ranging from humic to sapric in character, and live roots of the wetland macrophyte, Peltandra virginica. The organic content of the surficial soil (0–30 cm below the surface) is 35%, the bulk density is 0.23 g/cm^3 and the saturated hydraulic conductivity is 10^{-3} cm/s [Harvey, 1990]. Beginning at a depth of 20 cm below the surface the soil grades into a mixture of clay, humified organic matter, and sand which has a hydraulic conductivity that is an order of magnitude lower than the surficial soil. The wetland soil remains near saturation at all times; however, limited desaturation does occur. Water loss from this soil occurs by evapotranspiration and by drainage that occurs between times when the wetland surface is inundated by the river. A typical drawdown in the phreatic surface below the wetland surface at low tide is 7 cm at the site of the present investigation. On the rising tide, river water spreads across the wetland surface and infiltrates the soil, replacing soil water lost by evapotranspiration and drainage. The hydrology of this wetland is described in greater detail by Harvey and Odum [1990].

METHODS

Tracer Application and Core Retrieval

Solute tracer was added to the soil by sprinkling tracer-labeled water (2 M KBr) onto 10 replicated plots that were confined on the soil surface by infiltration rings (707 cm^2). Measured amounts (approximately 200 mL) of tracer-labeled water were sprinkled evenly onto each plot until the soil was saturated. The tracer was applied just prior (<0.5 hours) to arrival of advancing river water on a rising tide, thus simulating as closely as possible a natural infiltration event. Replicate plots were sampled destructively by coring at one of two different sampling times: either just following tracer infiltration (<0.2 days following tracer application) or 27 days later. A single, large-diameter core (10 cm diameter) was removed from each infiltration plot at the appointed time. Cores were taken with minimal compression using a thin-walled, aluminum corer with highly sharpened teeth. The headspace of the corer was sealed with a plumber's test plug to help retain cores within the barrel during removal. The corer and core were removed together from the soil and returned to the laboratory.

Solute Outflow From Pressure Cells

The pressure cell was designed for the purpose of measuring the pressure–water content relation for soil samples [Richards, 1939]. Most pressure cells hold a soil sample of relatively small volume, and significant volumes of water are retained beneath the porous plate which allows mixing during outflow. I constructed larger cells than are typically used (10 cm diameter), and I added a funnel-shaped drain beneath the ceramic plate. The alterations to the typical design increase the volume of water collected per step in pressure and help to minimize mixing and retention of soil water within the apparatus. In other respects these pressure cells were very similar to the design of Reginato and van Bavel [1962].

Soil cores were prepared for cell elution experiments immediately upon arrival at the laboratory by gently extruding them by pushing with a plunger from the core bottom and slicing off the top two 5-cm-long sections with a serrated knife. Care was taken not to seal (by smearing) the visible macropores that were exposed by slicing. Cores (which had a bulk volume of 385 cm^3) were loaded into the pressure cells upside down against presaturated ceramic porous plates (0.5 bar high flow, pore volume of 28 cm^3). The cells were closed and sealed, and then the headspaces were pressurized with nitrogen gas. Low pressures were accurately measured and regulated using a bubble tube manometer filled with water from which the back pressure was fed to the headspace in each cell. The volume of water from cells was measured periodically, and the pressure increased to a new stage when the volume of eluted water ceased to change with time. Sample capture vials beneath the cells were replaced prior to resetting pressures. Elution experiments were carried out for 48 hours, at which point cores were removed and weighed and the length remeasured. Cores were then homogenized into a uniform slurry with 600 mL of deionized water and allowed to stand for 24 hours. Aliquots were then subsampled for bromide analysis. Use of a shaker bath to promote mixing during storage had no effect on results. The remaining homogenized samples were oven-dried at 100°C and reweighed. Oven temperature was not a factor in weight loss, as determined by a test series where samples were first freeze-dried and then ovendried. Bromide concentrations determined on aliquots were adjusted to equivalent soil water concentrations by accounting for the dilution of original soil water by deionized water during homogenization.

All bromide analyses were conducted using an ion specific electrode (Orion 9435BN), a double-junction reference electrode (Orion 900200), and sodium nitrate (5 M) as an ionic strength adjustor. Bromide analyses were conducted by calibration against a standard curve, and measurements were frequently spot-checked by repeating a measurement after 10 new measurements were completed. Recalibration was conducted after 2 hours or when necessary. The rated detection limit for this electrode pair is 3 × 10^{-6} M. Measurement on standards prepared with river water did not differ appreciably except at very low concentrations. The detection limit determined using standards prepared with river water was somewhat higher than the rated limit (2 × 10^{-5} M), due to interference by river water constituents, but this was not prohibitive to conducting the tracer experiment. The coefficient of variation for measurements (0.06)

was estimated from repeated measurements on a standard made over the course of the study.

Relation of Applied Pressure to Pore Size

The effective pore size from which soil water was eluted on any pressure step was calculated from soil pressure potentials by assuming that pores were distributed as a bundle of capillary tubes. "Effective" pore sizes were calculated from critical pressures using the capillary pressure equation [Childs, 1969],

$$\psi = -\frac{(4\sigma \cos \alpha)}{d\rho g}, \qquad (1)$$

where σ is the surface tension of water, α is the contact angle between air and water in relation to the solid surface which is assumed to be zero, d is the effective pore diameter, and ρg is the unit weight of water. Effective pore diameters differ from the actual pore diameters because pores are grouped by their accessibility during air entry and drainage, and not by true diameter [Dullien, 1979]. Pore volumes for specified ranges of effective pore size were calculated as the difference between water content that bounded the extremes of a chosen range of pore size.

Accounting for Dispersion Artifacts During Solute Outflow

During elution from core samples, initial bromide concentrations in soil water might be affected by mixing of core water with antecedent water in the presaturated ceramic plates. The degree to which the pressure cell apparatus influenced the pattern of bromide elution from cores was not quantified directly. However, effects of dispersion through the ceramic plate were quantified in a preliminary experiment, using a ceramic plate containing bromide, and deionized water ponded above the plate as the flushing solution. The normalized bromide concentration in the outflow, C_e, was modeled over time with an analytical solution for the one-dimensional advection-dispersion equation. In the model, distance increases along coordinate x, from 0 at the plate inflow boundary to x_L at the outflow boundary. The initial concentration of pore water in the plate is c_b, and the concentration in the displacing fluid is 0. C_e, X, and T are nondimensional concentration, distance, and time variables computed as c/c_b, x/x_L, and vt/x_L, respectively, where v is the water velocity. A Peclet number (P_e) for the experiment is defined as vx_L/D_L in which D_L is a dispersion coefficient. The appropriate boundary and initial conditions for the experiment are, for X and $T \geq 0$,

$$C_e(0, T) = 0 \qquad C_e(\infty, T) = 1 \qquad C_e(X, 0) = 1. \qquad (2)$$

Assuming that solute tracer distribution and transport inside the plate are unaffected by the presence of the outflow boundary [van Genuchten and Parker, 1984], the solution for the change in outflow concentration subject to boundary and initial conditions is

$$C_e(1, T) = 1 - \{\tfrac{1}{2}\mathrm{erfc}\ [(P_e/4T)^{1/2}(1 - T)]$$

$$+ \tfrac{1}{2}\exp\ (P_e)\ \mathrm{erfc}\ [(P_e/4T)^{1/2}(1 + T)]\}. \qquad (3)$$

The Peclet number in (3) was adjusted to provide a close fit to experimental data. The plate dispersion model was then used to predict effects on soil water elution for the simplified condition of constant concentration at the plate inflow boundary. Here the purpose of the model is as a null model to predict outflow if there were no variation in bromide concentration within soil water. For this case, C_e is normalized in relation to the residual bromide concentration in cores, c_o, and the background bromide concentration in the porous plates, c_b,

$$C_e = \frac{(c - c_b)}{(c_o - c_b)}. \qquad (4)$$

The appropriate boundary and initial conditions for the model are, for X and $T \geq 0$,

$$C_e(0, T) = 1 \qquad C_e(\infty, T) = 0 \qquad C_e(X, 0) = 0. \qquad (5)$$

The solution for the change in outflow concentration subject to the boundary and initial conditions is

$$C_e(1, T) = \tfrac{1}{2}\mathrm{erfc}\ [(P_e/4T)^{1/2}(1 - T)]$$

$$+ \tfrac{1}{2}\exp\ (P_e)\ \mathrm{erfc}\ [(P_e/4T)^{1/2}(1 + T)]. \qquad (6)$$

The Peclet number is known (from the preliminary flushing experiments) so that the result is predicted without fitting.

Water Pressure, Storage Capacity, and Conductance

Specific water capacity, $C(\psi)$, is the change in water content per unit change in pressure potential in a soil sample,

$$C(\psi) \equiv \frac{d\theta}{d\psi} \qquad (7)$$

$$= \frac{\Delta V_w}{(\Delta \psi V_b)},$$

where θ is the water content, ψ is the pressure potential, and $\Delta V_w/V_b$ is the water yield normalized to the volume of the core. I estimated $C(\psi)$ from the slope of the line on plots of normalized water yield versus pressure. Critical pressures that separated distinct classes of the pore space were determined as breakpoints between linear fits to water yield–pressure data.

Changes in saturation are usually assumed to dominate storage processes in soils. Compressive storage is sometimes an important additional contributor to storage in wetland soils. Following Nuttle [1988], specific compressive storativity was estimated for this soil as

$$S_e = \frac{1}{L} \frac{\Delta z}{\Delta \psi}, \qquad (8)$$

where L is the core length at saturation (5 cm), Δz is the total change in core length during pressure cell elution, and $\Delta \psi$ is the total change in pressure during the course of the experiment. Shrinkage of cores in this study was minimal, and the resulting specific compressive storativity was small (4.2 $\times$ 10^{-5} cm^{-1} $\pm$ 0.13 standard error, $n = 20$). S_e was more than an order of magnitude smaller than specific water capacities determined for this soil. The contribution of
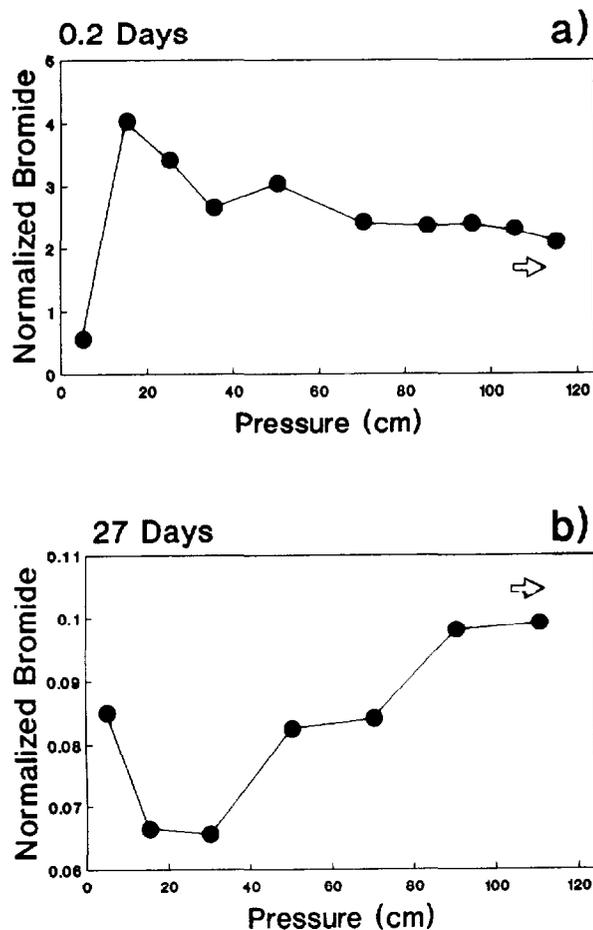
Fig. 1. Normalized bromide concentration (percent of field-applied tracer concentration) versus pressure during elution of soil water from cores. (a) Representative core removed 0.2 days after tracer application. (b) Representative core removed 27 days after tracer application. Eluted samples were collected in steps from low to high pressure. Open arrows indicate the volume-averaged concentrations of residual water determined for cores following elution.

compressibility to storage was small enough (over the total range of applied pressures from 0 to 120 cm compressibility accounted for only 2% of the total water yield) that it could be ignored in subsequent analyses.

Unsaturated hydraulic conductivities were determined at three pressures using a one-step outflow method [*Rijtema*, 1959]. The method provides an estimate of soil water diffusivity, $D(\psi)$, from which unsaturated hydraulic conductivity is calculated for the average pressure on that step as the product of diffusivity and $C(\psi)$. This approximate method can be inaccurate for small values (<1) of a dimensionless parameter, Dt/L^2 [*Towner*, 1982]. Results indicated that the approximate method was satisfactory for this soil at the high water contents associated with this study. Rijtema's method has an advantage over other approximate methods in accounting for and allowing removal of the effects of membrane and contact impedance. Effects of impedance were negligible at 50 and 100 cm pressures, but a correction was required at the 10-cm pressure step.

RESULTS

Variation in Bromide Concentration With Effective Pore Size

Bromide concentration in soil water varied with applied pressure and effective pores size. For cores removed from tracer plots just after tracer addition (0.2 days), maximum concentrations of bromide were measured at low pressures, i.e., in water that was eluted from the pores with largest effective diameters. Bromide concentrations were lower in soil water eluted from smaller pores at higher pressures (Figure 1a). The pattern of bromide segregation in pore size classes changed after 1 month. In cores removed 27 days after tracer application, bromide concentrations were lowest in water eluted from large pores and higher in water eluted from small pores (Figure 1b).

Some variation in the bromide concentration in effluent could potentially be explained by mixing of soil water with antecedent water of the presaturated porous plates. Bromide is plotted versus water yield (normalized to a core volume of
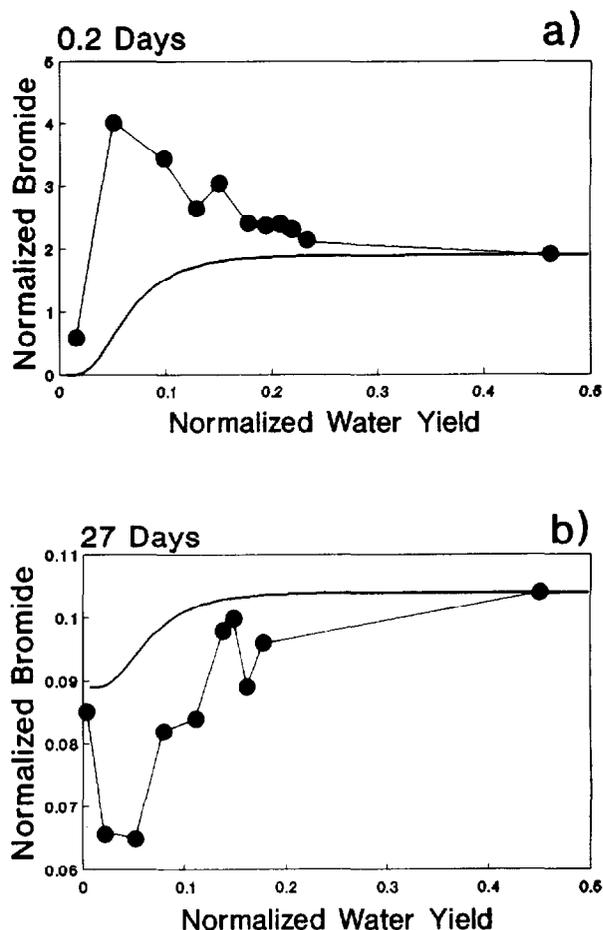

Fig. 2. Normalized bromide concentration (percent of field-applied tracer concentration) versus normalized water yield during elution of soil water from cores (a) 0.2 days after tracer application and (b) 27 days after tracer application. Solid circles are measurements, and lines not connecting the solid circles are model predictions. Final concentration measurements at high water yields are the residual concentrations in cores. The model assumed that outflow was a mix between soil water (with residual concentration) and plate water with a lower initial concentration.

385 cm³) in Figure 2, along with residual concentrations in cores and the predicted results of modeling dispersion of soil water during transport through the porous plate. The model assumed (1) that soil water had a uniform concentration equal to the residual concentration of soil water in cores, and (2) that eluted water was a mix of soil water and plate water which had a lower concentration. Comparison of representative data and model results in Figure 2 illustrates that dispersion in the plate adequately accounts for concentration variation only during the earliest and latest stages of elution. Throughout most stages in elution there were significant departures of measured bromide concentrations from model predictions, supporting the interpretation that those concentrations estimate the actual concentrations of soil water eluted from pores of different size.

It is evident from Figure 2 that mixing between soil water and plate water could potentially reduce or enhance actual bromide concentrations in soil water during early stages of elution, depending upon the bromide concentration of antecedent water in the plate. In the representative runs shown in Figure 2, and in all runs for this study, the effect of dispersion and mixing with plate water was conservative, i.e., the observed differences between eluted concentrations and residual concentrations of soil water are underestimates rather than overestimates of true differences.

Figure 2 also shows that tracer concentrations in large pores were higher or lower than in residual water depending upon time of sampling relative to tracer application. A bromide concentration ratio was computed for all runs by dividing the initial concentration eluted from cores by the residual concentration measured in the same core after pressure cell elution was terminated. Bromide concentration data from all cores are summarized in Figure 3. Maximum

Fig. 4. Normalized water yield and hydraulic conductivity as a function of applied pressure. A typical normalized water yield is shown (diamonds) as well as the average yield for all cores (dashed lines). The slope of the normalized yield versus pressure is $C(\psi)$, which changes from $C(1)$ to $C(2)$ at an average pressure of 47 cm. The solid line connects average values (geometric mean) of the hydraulic conductivity measured at four pressures. The value for K plotted at 0 cm pressure is the saturated hydraulic conductivity determined by field methods [Harvey and Odum, 1990].
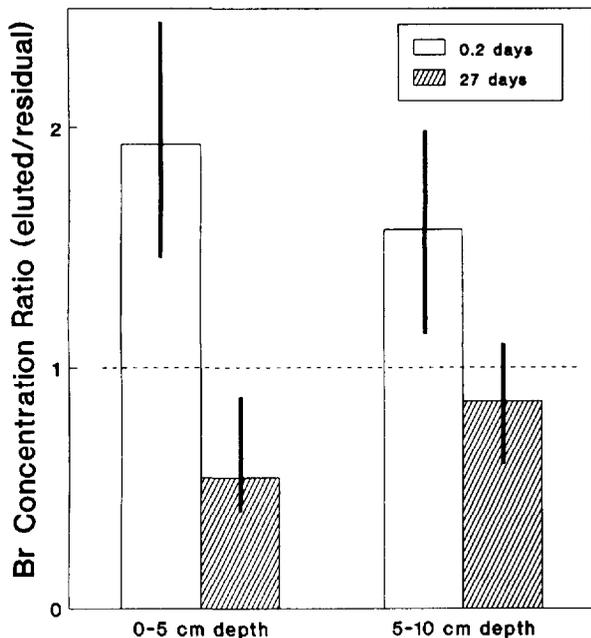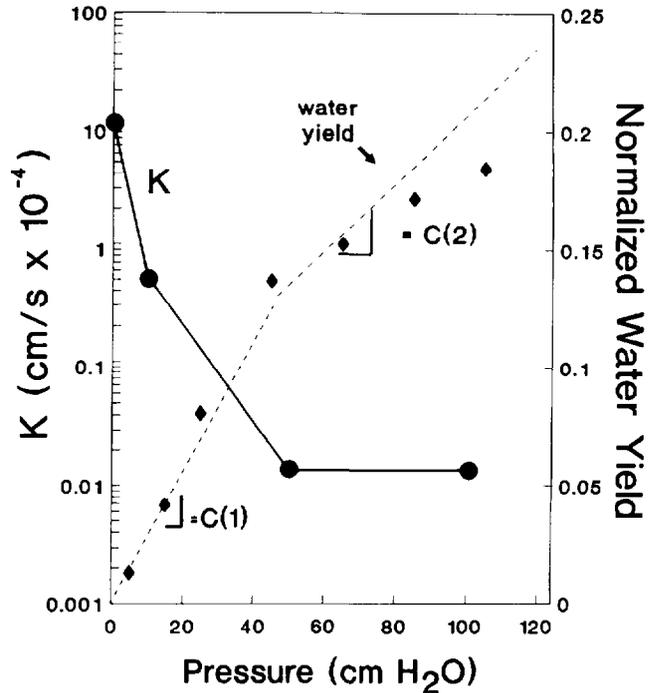

Fig. 3. Bromide concentration ratio in soil water of cores removed after 0.2 and 27 days following tracer application. Ratio computed as maximum (for cores collected at 0.2 days) or minimum (for cores collected at 27 days) concentrations in soil water eluted from cores divided by concentrations of residual water in cores. Bars encompass the range of observations for each category.

variation in concentration detected by the pressure cell method was approximately 100%.

Specific Water Capacity and Hydraulic Conductivity

The pattern of water release as a function of applied pressure indicated that two pore domains with different specific water capacities were present in the soil. The boundary between water storage domains is illustrated in Figure 4 as a single sharp break in the otherwise linear relation between pressure and normalized water yield. For all cores an average normalized volume of 0.11 was eluted from cores before $C(\psi)$ declined sharply (Table 1). The change in $C(\psi)$ took place at an average pressure of 47 cm, which corresponds to an effective pore diameter of approximately 70 μm. Ratios of specific water capacity ($C(1)/C(2)$) indicated that the domain of larger pores had an active water storage capacity that was 3 times larger than the domain of smaller pores (Table 1).

The decline in hydraulic conductivity as a function of pressure was steep at low applied pressures and became more gradual at higher pressures (Figure 4). From its value at saturation (10^{-3} cm/s) K was reduced to approximately 5 × 10^{-5} cm/s at 10 cm pressure, and 10^{-6} cm/s at 50 cm pressure. The rate of change of K as a function of increasing pressure sharply decreased beyond 50 cm pressure, which was roughly coincident with the point where $C(\psi)$ decreased sharply (Figure 4).

TABLE 1. Pore Size Classes Determined From Water Retention Data

Depth Interval, cm	Specific Water Capacity[a] $(\Delta V_W/(\Delta \psi V_B)) \times 10^{-3}$ cm^{-1}		Breakpoint Pressure (ψ_{crit}), cm H$_2$O	Normalized Volume of Macropore Class ($\theta_{sat} - \theta(\psi_{crit})$)
	C(1)	C(2)		
0–5	3.1 (0.4)	1.1 (0.1)	46 (5.1)	0.13 (0.01)
5–10	2.4 (0.6)	0.7 (0.1)	47 (7.5)	0.08 (0.01)

Values in parentheses are standard errors, $n = 20$.
[a]Macropore class, $C(1)$: pressure range of $0 < \psi < \psi_{crit}$; matrix class, $C(2)$: pressure range of $\psi_{crit} < \psi < \psi_{max}$, $\psi_{max} \approx 120$ cm.

DISCUSSION

Effect of Pore Size on Solute Segregation

Two hydrologically distinct pore domains were identified in the soil using water retention criteria. The decrease in $C(\psi)$ in the soil during pressure cell elution resulted from the sudden loss of storage space after a larger class of pores was emptied. There is little agreement about a standard definition for macroporosity in soil [Luxmore, 1981; Beven and Germann, 1982]. One approach is to attempt to define a macropore class on the basis of the volume of pores drained at field capacity, thus distinguishing pores that are significantly effective in drainage. Luxmore [1981] further distinguishes between drainage in macropores and mesopores. A water retention criterion was used in the present study to separate pore size classes, which provided a breakpoint between large and small pores (70 μm) that was near a generally accepted lower limit for macropore (or mesopore) effective diameters [Luxmore et al., 1990]. For the purpose of the present study the larger pore class detected by water retention criteria is referred to as the macropore class (effective diameter >70 μm) and the class of smaller pores is referred to as the micropore class (<70 μm).

Solute tracer concentrations in eluted water provided direct evidence that macropores were the principal conduits for transport of tracer-labeled water at the field site. The response in tracer concentration and recovery toward background levels were greater in macropores than in micropores; tracer responses in micropores were damped. These observations agree with general expectations of solute transport theory, i.e., transmission of water and solute occurred primarily in large pores.

I anticipated that variation in bromide concentration with effective pore size might be concentrated at the sharp breakpoint between pore size classes, in a manner consistent with two-porosity transport theory. Instead, the observed tracer concentrations varied across the entire range of pore sizes investigated. No sharp change in concentration could be detected at the macropore-micropore breakpoint in effective size (equivalent pressure of 47 cm) to suggest a division for concentrations into two corresponding transport domains, in spite of the well-defined division in pore size classes determined by water retention criteria.

Soil Solution Sampling Under Tension

Field-installed tension solution samplers have been widely used in soil hydrology. The validity of assumptions about the source of water to tension solution samplers has been debated [Litaor, 1988]. Sampling soil solute concentrations in outflow from pressure cells has the advantage over tension

sampling that the source of sampled water is more reliably known. Due to the constant applied tension ($P_{atm} - P_{cell}$) and the finite volume of the core, a water sample can be reliably assumed to have been withdrawn from all wetted pores with effective diameters greater than the equivalent diameter of the imposed tension. In contrast, the volume of soil affected by tension samplers is not limited, and the imposed tension decreases with time as soil water enters the sampler. Soil water is mobilized in a progressively smaller subset of pores as the imposed tension decreases. The dominant source of pore water to field-installed samplers could therefore be only from the largest wetted pores, or from pores with effective diameters predicted from (1), or from anywhere in between. Only vague interpretations of the origin of soil water are possible for samples collected at one or more tensions using the traditional tension sampler design. Interpreting the meaning of concentration differences in those samples is consequently problematic. Given the importance of tension samplers to acquiring repeated measurements of solute concentration in field settings, more attention to understanding sampling biases is warranted.

SUMMARY

This study quantified solute concentrations across pore sizes in relation to soil structure and hydraulic properties. The method has two primary advantages over previous tension sampling methods: (1) concentrations can be quantified across a range of effective pore sizes and (2) both solution chemistry and the pressure-storage relation are determined on the same soil sample, using the same equipment, and without interruption between modes of flow or times of sample acquisition. A two-porosity characterization of the soil was supported by water retention criteria and by general observations of segregation of solute tracer between large and small pores. However, solute tracer concentration varied across the entire range of sampled pore sizes, extending from macropores into the micropore range. This work demonstrates that the two-porosity concept may relate only broadly to actual distributions of solute within classes of soil pore sizes. Of equal importance, this work highlights the need to improve understanding of the biases that are inherent to sampling solute concentrations using in situ tension sampler designs.

REFERENCES

Barbee, G. C., and K. W. Brown, Comparison between suction and free-drainage soil solution samplers, Soil Sci., 141, 149–154, 1986.

Beven, K., and P. F. Germann, Macropores and water flow in soils, Water Resour. Res., 18, 1311–1325, 1982.

Beven, K. J., and P. C. Young, An aggregated dead zone model of solute transport through porous media, J. Contam. Hydrol., 3, 129–143, 1988.

Biggar, J. W., and D. R. Nielsen, Spatial variability of the leaching characteristics of a field soil, Water Resour. Res., 12, 78–84, 1976.

Bouma, J., Soil morphology and preferential flow along macropores, Agric. Water Manage., 3, 235–250, 1981.

Childs, E. C., Introduction to the Physical Basis of Soil Water Phenomena, John Wiley, New York, 1969.

Dullien, F. A. L., Porous Media: Fluid Transport and Pore Structure, Academic, San Diego, Calif., 1979.

England, C. B., Comments on "A technique using porous cups for water sampling at any depth in the unsaturated zone" by Warren W. Wood, Water Resour. Res., 10, 1049, 1974.

Germann, P. F., W. M. Edwards, and L. B. Owens, Profiles of bromide and increased soil moisture after infiltration into soils with macropores, Soil. Sci. Soc. Am. J., 48, 237–244, 1984.

Haines, B. L., J. B. Waide, and R. L. Todd, Soil solution nutrient concentrations sampled with tension and zero tension lysimeters: Report of discrepancies, Soil Sci. Soc. Am. J., 46, 658–660, 1982.

Harvey, J. W., Hydrological transport in tidal marsh soils, Ph.D. dissertation, 243 pp., Univ. of Va., Charlottesville, 1990.

Harvey, J. W., and W. E. Odum, The influence of tidal marshes on upland groundwater discharge to estuaries, Biogeochemistry, 10, 217–236, 1990.

Hemond, H. F., and D. G. Chen, Air entry in salt marsh sediments, Soil Sci., 150, 459–468, 1990.

Jardine, P. M., G. V. Wilson, and R. J. Luxmore, Unsaturated solute transport through a forest soil during rain storm events, Geoderma, 46, 103–118, 1990.

Jury, W. A., Simulation of solute transport with a transfer function model, Water Resour. Res., 18, 363–368, 1982.

Jury, W. A., L. H. Stolzy, and P. Shouse, A field test of the transfer function model for predicting solute transport, Water Resour. Res., 18, 369–375, 1982.

Litaor, M. I., Review of soil solution samplers, Water Resour. Res., 24, 727–733, 1988.

Luxmore, R. J., Micro-, meso-, and macroporosity of soil, Soil Sci. Soc. Am. J., 45, 671–672, 1981.

Luxmore, R. J., P. M. Jardine, G. V. Wilson, J. R. Jones, and L. W. Zelany, Physical and chemical controls of preferred flow through a forested hillslope, Geoderma, 46, 139–154, 1990.

Nielsen, D. R., M. T. van Genuchten, and J. W. Biggar, Water flow and solute transport processes in the unsaturated zone, Water Resour. Res., 22, 89S–108S, 1986.

Nuttle, W. K., The interpretation of transient pore pressures in salt marsh sediment, Soil Sci., 146, 391–402, 1988.

Omoti, U., and A. Wild, Use of flourescent dyes to mark the pathways of solute movement through soils under leaching conditions, II, Field experiments, Soil Sci., 128, 98–104, 1979.

Parker, J. C., and M. T. van Genuchten, Flux-averaged and volume-averaged concentrations in continuum approaches to solute transport, Water Resour. Res., 20, 866–872, 1984.

Reginato, R. J., and H. M. van Bavel, Pressure cell for soil cores, Soil Sci. Soc. Am. Proc., 26, 1–3, 1962.

Richards, S. J., Soil moisture content calculations from capillary tension records, Soil Sci. Soc. Am. Proc., 3, 57–64, 1939.

Rijtema, P. E., Calculation of capillary conductivity from pressure plate outflow data with non-negligible membrane impedance, Neth. J. Agric. Sci., 7(3), 209–215, 1959.

Shaffer, K. A., D. D. Fritton, and D. E. Baker, Drainage water sampling in a wet, dual-pore soil system, J. Environ. Qual., 8, 241–246, 1979.

Towner, G. D., Analyzing one-step outflow experiments to calculate soil-water diffusivities, using Gardner's equation, J. Soil Sci., 33, 351–364, 1982.

U.S. Department of Commerce, Tide tables 1989: High and low water predictions for the east coast of North and South America, including Greenland, Natl. Ocean Surv., Natl. Oceanic and Atmos. Admin., Rockville, Md., 1989.

van Genuchten, M. T., and J. C. Parker, Boundary conditions for displacement experiments through short laboratory columns, Soil Sci. Soc. Am. J., 48, 703–708, 1984.

van Genuchten, M. T., and P. J. Wierenga, Mass transfer studies in sorbing porous media, 1, Analytical solutions, Soil Sci. Soc. Am. J., 40, 473–480, 1976.

White, R. E., The influence of macropores on the transport of dissolved and suspended matter through soil, Adv. Soil Sci., 3, 95–120, 1985.

Wild, A., and I. A. Babiker, The asymmetric leaching pattern of NO_3 and Cl in a loamy sand under field conditions, J. Soil Sci., 27, 460–466, 1976.

J. W. Harvey, Water Resources Division, U.S. Geological Survey, Mail Stop 496, 345 Middlefield Road, Menlo Park, CA 94025.