

A Comparison of $^{18}\text{O}\delta$ Composition of Water Extracted from Suction Lysimeters, Centrifugation, and Azeotropic Distillation

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Abstract The representativeness of soil pore water extracted by suction lysimeters in ground-water monitoring studies is a problem that often confounds interpretation of measured data. Current soil water sampling techniques cannot delineate from which soil volume a pore water sample is extracted, neither macroscopic, microscopic, or preferential flowpath. This research was undertaken to compare $\delta^{18}\text{O}$ and Br^- values of extracted suction lysimeters samples from intact soil cores with samples obtained by the direct extraction methods of centrifugation and azeotropic distillation. Also, the study was concerned with determining what portion of soil pore water is sampled by each method and explaining differences in concentrations of the extracted water from each method to allow a determination of the accuracy and viability of the three methods of extraction. Intact soil

cores (30 cm diameter by 40 cm height) were extracted from two different sites. Site 1 was rapid infiltration basin number 50, near Altamonte Springs in Seminole County, Florida. Site 2 was the Missouri Management System Evaluation Area (MSEA) near Centralia in Boone County, Missouri. Isotopically ($^{18}\text{O}\delta$) labeled water and bromide concentrations within water samples taken by suction lysimeters was compared with samples obtained by methods of centrifugation and azeotropic distillation. The $^{18}\text{O}\delta$ water was analyzed by mass spectrometry while bromide concentration, applied in the form of KBr was measured using standard IC procedures. Water collected by centrifugation and azeotropic distillation data were about 0.25‰ more negative than that collected by suction lysimeter values from a sandy soil and about 2–7‰ more negative from a well structured soil. Results indicate that the majority of soil water in well-structured soil is strongly bound to soil grain surfaces and is not easily sampled by suction lysimeters. In cases where a sufficient volume of water has passed through the soil profile and displaced previous pore water, suction lysimeters will collect a representative sample of soil pore water from the sampled depth interval. It is suggested that for stable isotope studies monitoring precipitation and soil water, suction lysimeter be installed at shallow depths (10 cm). Samples should also be coordinated with precipitation events. The data also suggest that each extraction method samples a separate component

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of soil-pore water. Centrifugation can be used with success, particularly for efficient sampling of large areas. Azeotropic distillation is more appropriate when strict qualitative and quantitative data on sorption desorption, and various types of kinetic studies may be needed.

Keywords Soil–water sampling · DeIO18 · Azeotropic distillation · Macropores · Unsaturated zone · Soil–water classes · Capillary water · Gravitational water · Hygroscopic water · Preferential flowpaths

1 Introduction

Bear (1972) suggested that water in the unsaturated zone could be divided into three classes: (1) Gravitational water, the component of soil water that is under the influence of gravity. Relatively high moisture contents, typically greater than 25–30%, are required for gravitational water to exist. This water has a matric potential slightly less than zero; (2) Capillary water, held firmly to the soil at higher soil suction and basically immobile. This water is located in smaller pores. Larger pores usually only fill during periods of high moisture content; and (3) Hygroscopic water or adsorbed water, the component of soil water that is unavailable to plants and can be removed from non-colloidal and colloidal mineral surfaces by heating to 100–110°C. Only by heating to high temperatures (about 450°C for kaolinite) does water that was incorporated during crystallization (structural water) come off (Gardner 1986). The distinction between structural water and adsorbed water is that structural water is part of the mineral lattice itself, whereas adsorbed water is attached to the mineral lattice but is not a structural element of the lattice (Gardner 1986). Separation between this water is sometimes complicated particularly when the temperature at which structural water is released is below 110°C. Of primary interest to this research is the proportion of gravitational and capillary water sampled by suction lysimeters compared to water sampled by azeotropic distillation and centrifugation. At a suction of –60 kPa (as applied to the lysimeters in this study), it would seem probable that more of the less tightly held gravitational water would be collected from the suction lysimeters compared to water extracted from centrifugation or azeotropic distillation.

Because of this, the representativeness of soil-pore water extracted by suction lysimeters in ground-water monitoring studies is a problem that often confounds interpretation of measured data. Current soil water sampling techniques cannot delineate from which soil volume a pore water sample is extracted, neither macroscopic, microscopic, or preferential flowpath. Likewise, differences between the chemical concentration of soil water sampled by suction lysimeters and other sampling methods and chemical concentration in drainage water through the soil is unknown because no comparison has been made between lysimeter extracted samples and direct soil water extraction. Experimental and theoretical experimentation have demonstrated that the chemistry of soil water is heterogeneous throughout its mass (England 1974). Cations differ greatly in degree of dissociation from the surface of negatively charged soil particles. Thus, it is very probable that water drained from large soil pores at low suction will vary considerably in chemical composition from tightly bound soil water obtained from micropores.

Water held in the soil at potentials less than the suction applied to the lysimeter will enter the ceramic cup over time. Litoar (1988) recommended that the suction applied be equivalent to the matric potential of the soil at “field capacity.” Typical sample collection times are 24–48 h, after which the vacuum inside the lysimeter decreases significantly. Recommended monitoring methodology includes (1) use of samplers with similar intake rates, (2) uniform sampler lengths, (3) short sampling period, and (4) same initial vacuum for all samplers (Debyle et al. 1988; Hansen and Harris 1975).

Poulsen et al. (2006) characterized dissolved and suspended matter transport at field scale using bromide tracer breakthrough and natural soil colloid leaching curves for 33 undisturbed soil columns (20-cm diameter by 20-cm height). Columns were collected in a grid of 25×30 m from an agricultural field. A two-region (mobile–immobile water phase, MIM) solute transport model was fitted to the data. The model was used to estimate bromide and colloid transport parameters including mobile and immobile water contents (θ_m , θ_{im}), bromide and colloid advective velocities (v_{Br} , v_{Coll}), and mobile–immobile mass transfer coefficients (α_{br} , α_{coll}). The spatial distributions of soil physical properties, bromide and colloid transport parameters, and leached quantities of par-

ticles were compared. The results suggested that bromide and colloid mass transfer (diffusion) were not controlled by the same soil physical conditions, and that soil structure and macropore flow are more important than the quantity of dispersible colloids in controlling colloid leaching. This also illustrates different water classes within the soil as suggest by Bear (1972).

Swensen (1997) investigated the flow pattern through a sandy, heterogeneous glacial deposit. Soil water was extracted frequently, using suction cups. Infiltrating water (rain and melt water) was traced to a 220-cm depth using Cl⁻, Br⁻ and ¹⁸O as tracers. Different results were obtained according to whether a surface applied solute (e.g., Cl⁻ or Br⁻) or a variation in ¹⁸O/¹⁶O in the water itself was used for flow tracing. High spatial variation in flow velocities and solute concentrations were found. The results are discussed in light of different theories of flow mechanisms. The presence of preferential flow implies that a small soil volume may rapidly conduct a dissolved pollutant down to the groundwater. The subsurface flow is controlled by the presence of preferential flow paths and extreme contrasts in hydraulic conductivity between sedimentary interbeds and fractured basalt flows (Baker et al. 2004).

A suction lysimeter behaves as a suction-point sink that extracts soil water from a spherical area, draining pores of varying sizes depending upon the distance from the source, applied suction, volumetric water content, soil matric potential, and hydraulic conductivity (Wood 1973). Van der Ploeg and Beese (1977) designed a model to calculate soil water concentrations extracted by ceramic cups and plates and found poor correlation between extracted samples and free percolating soil solution, indicating that the solute concentration of free moving soil water may be significantly different than extracted soil water samples. Litoar (1988) determined that when the applied suction creates percolation rates near the cup equal to those in the soil at the same depth, the amount of sample is directly related to the soil percolation rate.

Hansen and Harris (1975) attempted to determine sample variability in lysimeters using nitrate-spiked water applied alternately with tap water. They tested intake rate, sample volume, vacuum levels, and sorption and found that intake rates between lysimeters varied considerably. Additionally, they found that 100 mg l⁻¹ solutions of P and NO₃⁻ moved

through the porous cups much faster than deionized water (likely due to differences in ionic strength) and, that P sorbed onto the ceramic cup while NO₃⁻ did not. Additionally, lysimeters left in the field over long periods of time exhibited a decrease in intake rate that may have been due to clogging.

Tilahun et al. (2003) conducted a field experiment to evaluate the leaching behavior of Br⁻ in comparison with NO₃⁻-N the Bainsvlei soil of South Africa under natural rainfall conditions. The results were analyzed with the one dimensional convective dispersive equation and stream tube models. Two important results were derived from the study: Br⁻ can be used with confidence as a substitute for NO₃⁻-N in studies of the movement of the latter through soils, and that it is more economical and environmentally friendly to distribute the application of nitrate throughout the growing season.

Debyle et al. (1988) found that the first samples collected from new cups had lower sodium and potassium than drainage water, indicating sorption within the cup. Cups that had been in the field for several weeks or longer provide samples that closely resembled drainage water in chemical composition, probably because all exchange sites had been filled. Silkworth and Grigal (1981) compared small (2.2 cm diameter) and large (4.4 cm diameter) lysimeters and found that samples from the small lysimeters had consistently higher levels of Ca⁺⁺, K⁺, Mg⁺⁺, and Na⁺ than the large lysimeters, which was attributed to greater sorption by the larger porous cups. Shaffer et al. (1979) concluded that lysimeters were not applicable for monitoring soil water concentrations during very high soil moisture conditions because lysimeters remove water from smaller pores, while rapidly flowing water through interped cracks moves past the lysimeters, and is not sampled.

Severson and Grigal (1976) tested the effects of extraction time on soil solution concentrations using suction lysimeters in intact soil cores and concluded that for short extraction times, samples represent water moving through preferential pathways and held at matric potentials ≤ -10 kPa. The rationale was that water extracted at this potential closely resembles that moving downward due to gravitational potential.

Previous research addressing interpretation of suction lysimeters data has been extensive (Litoar 1988). Without a comparison to direct extraction, it is difficult to determine how accurate data measurements from

suction lysimeters really are, and to what degree of confidence scientists can rely upon them. The alternative, direct soil water extraction methods are considered detrimental by some researchers due to destructive removal of the soil sample from the research area, making replication over time from a small site untenable. Perhaps because of the destructive nature of direct extraction, none of the previous experiments have attempted to correlate or compare suction lysimeters extractions to direct soil water extraction methods. However, current research is shifting from laboratory and plot scale to field and scales, which makes direct extraction more viable.

Methodologies typically used to test and validate data collection from suction lysimeters include the use of intact soil cores and isotopic and chemical tracers. Intact soil cores have been employed to determine saturated and unsaturated hydraulic conductivity and macropore volume (Germann and Beven 1981; Tindall et al. 1992), identify preferential flow (Priebe and Blackmer 1989; Tyler and Thomas 1981), and test water monitoring equipment (Barbarick et al. 1979; Levin and Jackson 1977). The use of stable isotopes has become an increasingly powerful investigative tool used to trace water movement through the soil and also transport in the vadose and saturated zones (Barnes and Allison 1988; Zimmerman et al. 1967), recharge (Muir and Coplen 1981), and storm flow components (Kennedy et al. 1986; Sklash et al. 1976). In lieu of stable isotopes other researchers have utilized conservative tracers (typically NaCl and KBr) to quantify water movement through soils using breakthrough curves and other representative analysis (Blume et al. 1987; Germann et al. 1984; Tindall et al. 1992; Tyler and Thomas 1981). An excellent review of atmospheric waters and processes affecting their isotopic composition has been presented by Faure (1986). The isotope $H_2^{18}O$ was utilized in this experiment.

A breakthrough curve is a graphical representation of outflow concentration versus time or cumulative water drainage. These curves indicate the relative tracer distribution of the effluent, with respect to the column of the soil matrix under consideration as it relates to either pore volume, time or both. The examination of the breakthrough curve indicates how aggregated the soil is, how wet or dry the soil is, the presence of macropores or preferential flow paths, or presence of adsorption sites. For an ideal medium C/Co , concentration (C) measured on an ion chromatograph divided by initial concentra-

tion applied (Co), would reach 1 or unity. However, this rarely happens in normal conditions due to the effects of mechanical dispersion and molecular diffusion which cause spreading of the curve. Because of this these effects the trace begins to appear in the effluent at the outflow end of the column, before the arrival of traveling water (Tindall et al. 1999).

Hendry et al. (2004) tested a high-resolution 1-D profile for stable isotopes (2H and ^{18}O) in pore water obtained by direct pore water-equilibration of core samples to identify hydrogeologic zones in a thick, complex, till aquitard system in Saskatchewan, Canada. The lack of vertical variability in the stable isotope data in the intermediate zone suggested groundwater flow and solute transport was controlled by a system of interconnected vertical fractures and lateral sand layers. The curved shape of the isotope profile in the lower till zone suggested that solute transport in this zone was controlled mainly by molecular diffusion.

The naturally occurring ^{18}O isotope of water provides an efficient, inexpensive tracer that accurately depicts water movement because the isotopic label is incorporated into the water molecule. The $^{18}O/^{16}O$ ratio is expressed using the delta notation (δ), representing the relative difference in parts per thousand (denoted as per mil, ‰) between the $^{18}O/^{16}O$ ratio of a sample (sp1) and that of a standard (SMOW). Thus $^{18}O\delta$ is defined by:

$$^{18}O\delta = \frac{\left(\frac{^{18}O}{^{16}O}\delta\right)_{sp1} - \left(\frac{^{18}O}{^{16}O}\delta\right)_{SMOW}}{\left(\frac{^{18}O}{^{16}O}\delta\right)_{SMOW}} \quad (1)$$

The $^{18}O/^{16}O$ ratio is analyzed. Stable isotopes are conservative tracers because the isotopic composition of a particular volume of water will not change unless it mixes with water of a different isotopic signature or undergoes phase changes, mainly evaporation. Evaporation leaves water enriched in $H_2^{18}O$, since $H_2^{16}O$ preferentially evaporates due to its higher vapor pressure. Conservative tracers such as potassium bromide (KBr) are often used in conjunction with stable isotopes because of the simplicity of analysis and as a basic comparison.

This research was undertaken to compare $^{18}O\delta$ and Br^- values of extracted suction lysimeters samples from intact soil cores with samples obtained by the

direct extraction methods of centrifugation and azeotropic distillation. Also, the study was concerned with determining what portion of soil pore water is sampled by each method and explaining differences in concentrations of the extracted water from each method to allow a determination of the accuracy and viability of the three methods of extraction.

2 Materials and Methods

2.1 Soils and Field Extraction

Two sets of cores (30 cm diameter by 40 cm height) were extracted from two different sites after the method by Tindall et al. (1992) and modified by Tindall et al. (1995). Three intact soil cores were extracted from site 1 near Altamonte Springs in Seminole County, Florida. These cores were extracted directly from rapid infiltration basin number 50 at the 0–40 cm depth and labeled F1–F3. The rapid infiltration basin is conventionally tilled every other day; thus, the soil is moderately homogeneous, and is classified as a Candler fine sand, hypothermic, uncoated, typical quartzsammments. Five intact soil cores were extracted from site 2 (labeled M1–M5): three from the 0–40 cm depth (M1, M2 and M3) and two from the 40–80 cm depth (M4 and M5) at the Missouri Management System Evaluation Area (MSEA) near Centralia in Boon County, Missouri, are a fine montmorillonitic, mesic Udollic Ochraqualf Mollic albaqualf, and silty loam. Because the soil coring device was only 40-cm in height, the 40–80 cm cores were extracted directly from beneath the locations where the 0–40 cm cores were collected. This would then give a complete profile interpretation and data analysis for the 0–80 cm depth. The purpose of collecting soil cores from each of these sites was to compare soil of weak structure, with one soil having no existing preferential pathways due to frequent tillage (site 1, rapid infiltration basin 50), and the Missouri soil having preferential pathways due to soil cracking and cleavage planes and the presence of root and faunal channels. Also, the soils at site 1 represent one extreme, being about 93% sand, while the soils at site 2 represent another extreme, i.e., the soils at this site are typical claypan subsoils common to the Midwest and are well structured.

2.2 Laboratory Analysis

Two Tracers were used in the experiment: (1) Br^- , a conservative anion added as potassium bromide (KBr) and isotopically labeled water. At initiation of the unsaturated experiments, KBr solution (300 mg l^{-1} ; pulse application) and H_2^{18}O (continuous source) was applied (applied concentrations are listed on figures in results and discussion section) after Tindall et al. (1992). The core was sealed with clear plastic to prevent evaporation (unsaturated experiments only). Matric potential through the core was maintained at -20 kPa during the unsaturated experiments (Tindall et al. 1992, 1995). Extractions with suction lysimeters, centrifugation, and azeotropic distillation were collected from 10, 20, and 30 cm depth within each core.

To determine isotope concentration with depth under conditions of infiltration, the experiment was performed in two parts: (1) determination of pore volume required to replace all existing pore water and (2) comparison of the three methods of extraction. The extraction of soil water by suction lysimeters is considered an indirect method while extraction by centrifugation and azeotropic distillation are considered direct as well as destructive methods, because a soil sample must be replaced within the intact soil cores before sample analysis and extraction could occur. Because the intact soil cores from site 1, Florida, were moderately homogeneous and had larger soil pores, it was assumed that these soils would require less water to obtain an initial $^{18}\text{O}\delta$ concentration with depth. Consequently, intact soil cores M3 and M5 from site 2, Missouri, were used to determine how many pore volumes of water would be necessary to replace all existing pore water throughout the core. Prior to saturation, cores were flushed with CO_2 and then slowly saturated (24–72 h) with tap water (to reduce dispersion effects) from the bottom of the core. A ponded head (5 cm) was used to apply 1, 2, and 5 pore volumes (PV) of isotopically tagged water through each core to determine when a known, uniform isotopic composition of $^{18}\text{O}\delta$ could be achieved prior to commencement of the main experiment. After the allocated amount of water was applied to each core, the core was drained by gravity and permitted to return to unsaturated conditions (about -60 kPa) after which the suction lysimeters were placed under the same suction and sampled after 6 h. This was repeated for each PV

amount (i.e., 1, 2, and 5). Once completed, the cores were cross-sectioned every 10 cm. Each cross section was homogeneously mixed and a soil sample removed; water was extracted from the removed soil sample via azeotropic distillation and centrifugation and analyzed.

Analysis for bromide was performed utilizing the remaining leachate on an ion chromatograph (IC) fitted with an anion/R-Hs 10-cm column. Retention time was approximately 8 min and flow rate was approximately 1.4 ml/min. The effluent was 4 mM PHBA titrated to 8.5 pH. Two blank samples were included at the beginning of the analysis, as well as every twelfth sample. Standards were analyzed at the beginning and at the end of each analysis period. Duplicate samples were included in the analysis at frequent intervals for QA/QC purposes.

2.3 Lysimeter

The laboratory set-up was as described by Tindall et al. (1995) and suction lysimeters were installed vertically, in a triangular array within each core at depths of 10, 20, and 30 cm. Each lysimeters consisted of a 1 bar high flow, tapered neck, round bottom, porous ceramic cup attached to the end of schedule 80-poly vinyl chloride (pvc) pipe (1.5 cm i.d.). Holes of equal diameter (2.2 cm) to the suction lysimeters were bored for placement within the core. Each porous cup was coated with viscous diatomaceous earth slurry to provide good soil contact. A small portion of the slurry was also poured into the bored hole. The area directly surrounding the lysimeter was then lightly tamped with a 0.25 cm diameter wooden dowel and sealed around the top with bentonite to prevent pipe flow along the length of the lysimeter. The porous ceramic cups used on suction lysimeters are constructed from various proportions of alumina, ball clay, kaolin, talc, and other feldspathic materials (Soil Moisture Equipment Corporation 1989). Due to the nature of these materials, a certain amount of cation exchange is evident; this was minimized by soaking the ceramic cup in 1-N HCl and rinsing with excess deionized water prior to suction lysimeter installation.

2.4 Centrifugation

Direct extraction by centrifugation was performed by milling a standard size centrifuge tube so that water

could pass from the soil sample, through a filter paper and porous disk, into a sample chamber below the soil sample. Calculations to determine driving velocity within the soil sample were performed using the model developed by Kinniburgh and Miles (1983). The equation for conversion of rotation speed to angular velocity was:

$$\omega = \frac{2\pi n}{60} \quad (2)$$

Here ω is angular velocity, radians/second, and n is centrifuge speed in rpm. The driving pressure (P_d) was calculated by:

$$P_d(r, \omega) = \left(\frac{\rho\omega^2}{2} (r_2 - r_1)^2 \right) / 1000 \quad (3)$$

Here P_d is the driving pressure (Pa) at midpoint, ρ is the density of water (kg/m^3), ω is angular velocity (radians/second), r is radius to the midpoint of the sample (m), and r_1 and r_2 are the radius to the outer and inner surfaces of the sample (m). The primary assumption was that the soil water is displaced in only those pores for which the driving pressure exceeds the capillary pressure, which holds water within those pores. Thus, at equilibrium capillary pressure (P_c)= P_d and at any point within the sample, P_c varies along the sample length. For release of water from the outer surface at r_1 , it is necessary for matric potential to be near zero at this interface. Thus, a calibration curve was developed to relate rpm to kPa.

2.5 Azeotropic Distillation

This process removes essentially all water from soil particles and is thus, quite useful for comparison of suction lysimeter samples. Water is distilled from the sample, which is immersed in toluene, at a temperature of 84.1°C and separated into a collection funnel at room temperature. The toluene forms an azeotropic mixture at the distillation temperature, but floats on top of water at ambient (room) temperature. The azeotropic mixture was visible as a cloudy compound during the process and water was observed separating from the toluene into the collection funnel. Azeotropic distillation has been shown to be an efficient method for recovering nearly 100% of gravitational and capillary water for isotopic research with an accuracy of $\pm 0.2\%$ (Revesz and Woods 1990). Once the sample

had been distilled, it was homogenized before withdrawing a sub-sample for isotopic analysis.

3 Results and Discussion

The average pore volume for cores from both site 1 and site 2 ranged from about 12–13 l based on an average porosity of about 0.38–0.45. Initial concentrations of soil pore water were determined by extraction of water by azeotropic distillation on soil removed during installation of suction lysimeters. And, because the soil cores at each site were extracted as sets, it was assumed that pore water concentrations within each core were similar. The suction lysimeter data indicate that at least 5 pore volumes of water are required to replace existing soil pore water and approach similar isotopic concentrations throughout the soil. However, for the Missouri soils from site 2, 5 pore volumes brought the sample values from the two methods close, but not as close as for the sand cores

of site 1. 15 PV would be needed to replace existing water in well-structured soils, at least for the Missouri soils used in this study. The suction lysimeters appear to be sampling the added, blank water, since sample values closely approach that added. Additionally, concentrations obtained from azeotropic distillation are more negative at all pore volumes. This may be due to the incomplete displacement for the pre-existing pore water, which should have been isotopically depleted due to soil drainage and other hydrologic processes through time.

Breakthrough curves for KBr and ^{18}O for core M2 (0–40 cm depth) and core M4 (40–80 cm depth) from site 2 and core F1 (0–40 cm depth) from site 1 are given in Figs. 1, 2, and 3. The initial soil pore concentrations of $\delta^{18}\text{O}$ are listed in parenthesis for each depth directly on the figures. These cores are representative of all cores extracted from each of the two sites. Generally, both KBr and ^{18}O exhibit the same trends. Each core shows stratification both chemically and isotopically. Increased KBr and ^{18}O

Fig. 1 Breakthrough curves for KBr (a) and $\delta^{18}\text{O}$ (b) for core M2 (0–40 cm depth) from site 2

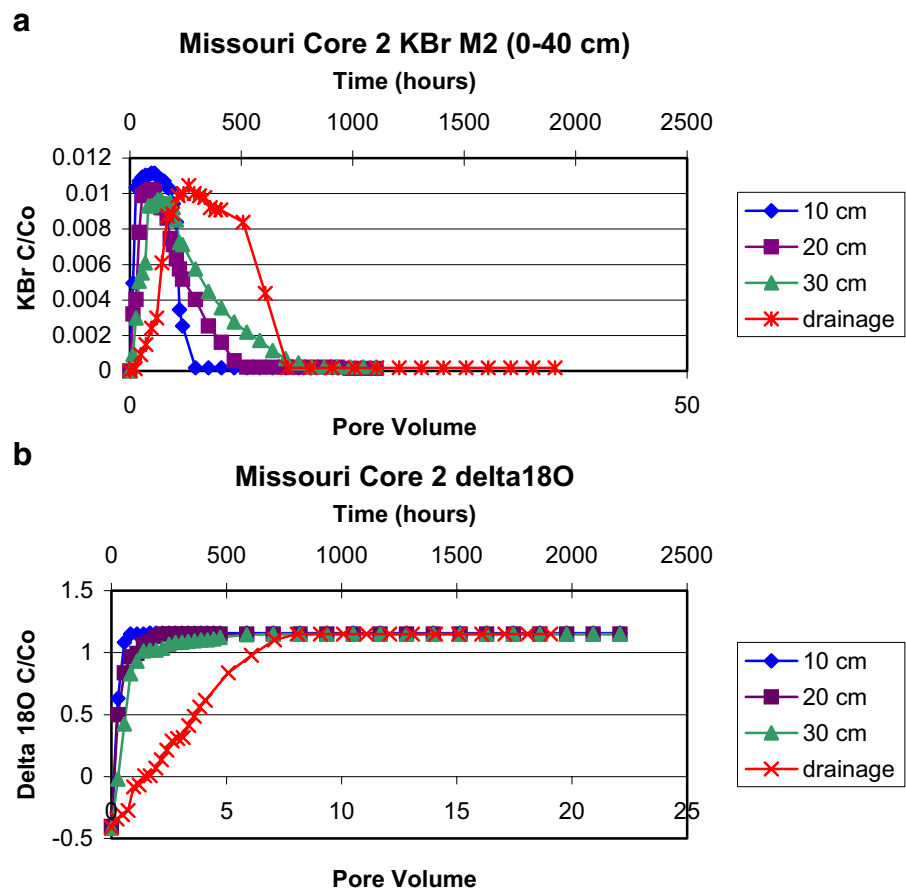
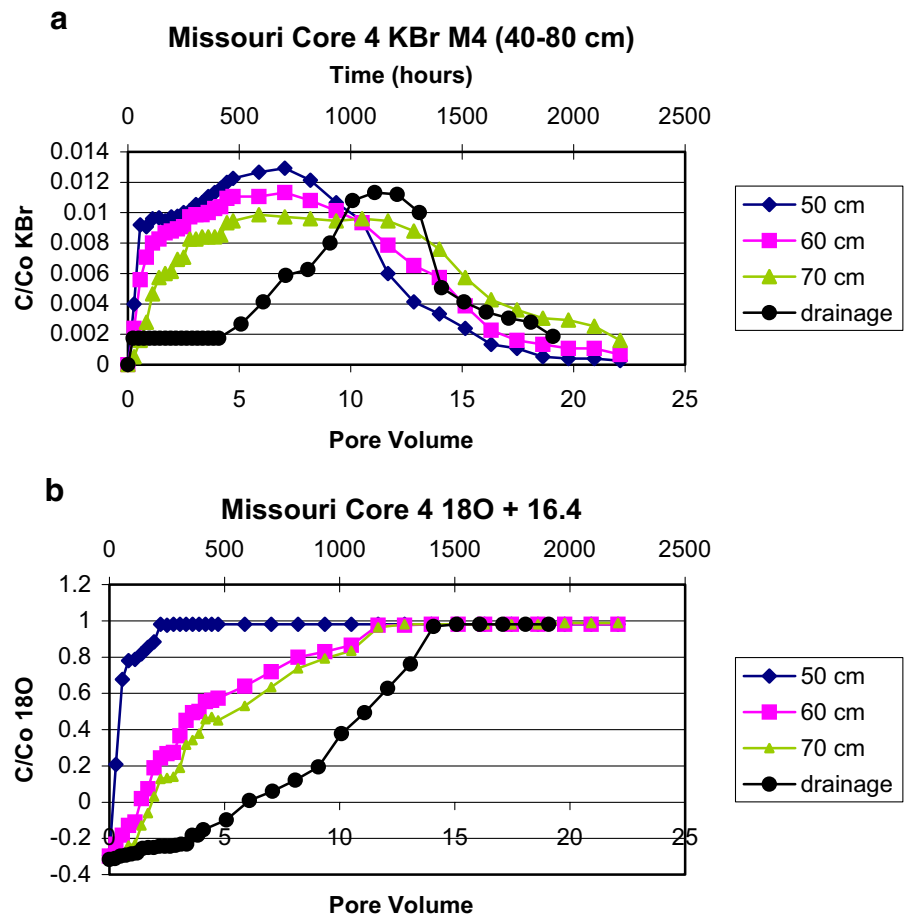


Fig. 2 Breakthrough curves for KBr (a) and $\delta^{18}\text{O}$ (b) for core M4 (40–80 cm depth) from site 2



concentrations are shown as time increased at each depth and in the drainage effluent. The concentrations measured at each depth slowly approached the added concentration.

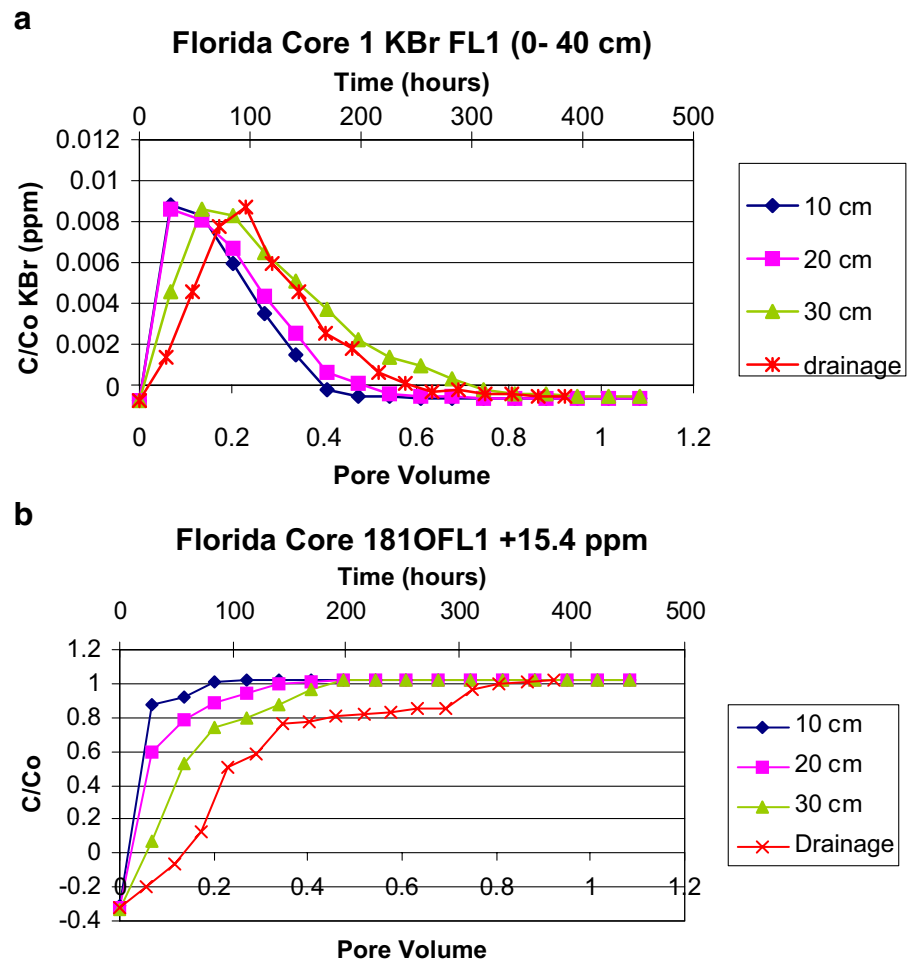
Core M2 from site 2 (Fig. 1a) shows that bromide passed through the soil core at more rapid rate than did $^{18}\text{O}\delta$ except for the 10 cm depth (Fig. 1b). It can be seen in Fig. 1a,b that the peak concentrations of KBr were reached at approximately 550 h compared to 1,000 h for $^{18}\text{O}\delta$. This may have been due to anion exclusion. Thomas and Swobado (1979) reported that in soils with high clay contents, negatively charged clays repel anions, such as Br^- , from the water on clay mineral surfaces. Because water near such surfaces is relatively immobile from a soil physics viewpoint, the net result is that anions can move faster through the soil than would be predicted by complete soil water exchange.

Results from core M4 (40–80 cm depth) show that bromide and $^{18}\text{O}\delta$ moved at relatively the same

velocity (Fig. 2a,b). This would probably be expected since dye studies from soil at this depth indicate large percentages of preferential flowpaths (Tindall and Vencill 1995) due to the presence of a claypan that exhibited large changes in volume with changes in moisture content.

The data for core F1 from site 1 (Fig. 3a,b) shows that the breakthrough of the chemical and isotope are similar. Results for Br^- to about 30 cm generally follow those observed by Pandey and Gupta (1984), who assumed that a dimensionless C/C_0 will be about 0.5 at one pore volume. Nevertheless, this does not hold true for concentration in the drainage effluent, which may be due to the fine sand texture from the site than a more medium textured soil in that study. The higher chemical and isotope concentration extracted by depth from the suction lysimeters, overestimate the actual soil water flux. Van Genuchten and Wierenga (1986) reported that because soil solutions are extracted by suction lysimeters at fixed locations, it is

Fig. 3 Breakthrough curves for KBr (a) and $\delta^{18}\text{O}$ (b) for core F1 (0–40 cm depth) from site 1



unlikely that the observed concentrations are flux concentrations. This suggests that observed concentrations might not exactly match those of resident concentrations.

Comparison of suction lysimeter values to values obtained from azeotropic distillation again reveals a stratified isotopic profile with depth in each of the intact cores. Analysis for core M2, site 2 (Fig. 1a) shows azeotropic distillation values were about 2–5‰ more negative than suction lysimeter values, while analysis of core M4, site 2 (Fig. 2b) had a variance between methods of about 5–7‰. Analysis of core F1, site 1 (Fig. 3) shows only minor variation in isotopic concentrations of suction lysimeter values compared to azeotropic distillation values with depth. However, in all cores, $^{18}\text{O}\delta$ concentrations extracted by suction lysimeters were more positive than those for azeotropic distillation for every depth and were also significantly different ($p < 0.05$) for all depths.

The difference in $^{18}\text{O}\delta$ values between methods of extraction with depth increases (Figs. 1, 2). These differences may be due to the fact that, as the isotope moves through the soil, it mixes with and displaces pre-existing soil water. The isotope also mixes with tightly held water on the surfaces of individual soil grains. This tightly held water might be both capillary and hygroscopic water. Except for the hygroscopic water (all of which cannot be removed, even by heating to 105°C), this tightly bound water is completely replaced by the added input water after a sufficient number of pore volumes have passed through the sample water. The replacement of this water will be both a function of the amount of input water added and contact time. At any point in time, in the upper horizon of each core in this case, more isotopic water will have moved through the system, resulting in greater replacement of the tightly bound water. At deeper depths, less input water will have

moved through the system during the same period and less replacement will occur. By adding larger volumes of input water, complete or near complete replacement of pre-existing water will occur. Here, 5 pore volumes (about 60 l) have passed through the entire system and the values for both the suction lysimeter and those obtained from azeotropic distillation are similar. Also, mixing of soil pore water with tightly held water is likely easier in the sandy soils from site 1 (Fig. 3) because of larger pore sizes than the clay soils of site 2 (Fig. 1a,b).

Analysis of both the suction lysimeter data and azeotropic distillation shows that the suction lysimeters are primarily sampling moderately mobile input water, while samples from azeotropic distillation has removed all soil water and thus, resulted in more negative values with depth (Figs. 1, 2, and 3). Results from a study by Biggar and Nielsen (1962) showed that displacement and equilibrium between isotopically labeled water and pre-existing soil water occurs at about one pore volume. However, the study used disturbed, repacked soils and may, therefore not be indicative of the pore volumes necessary for displacement and equilibrium in well-structured soils.

Several trial runs had been performed prior to analysis of the cores used for this experiment. It was determined that there were only minor differences in the percent water extracted from one pressure versus a slightly higher pressure, or the same pressure for a longer period of time. For example, core F1, site 1 shows 63% of the water present in the sample was extracted at a time of 1 h and a pressure of 300 kPa. Increasing the time by 1 h or the pressure by 200–300 kPa did not significantly change the percent of water extracted from the sample. The same was true for the cores from site 2. Because core F1, site 1 is moderately homogeneous sand, there is little difference in the percent extraction of water by depth. However, for core M2, site 2 there is a large difference between the top 10 cm and the lower depths. This is primarily due to a larger percentage of sand in the upper 12 cm of the soils from site 2, which holds water at a more positive matric potential. This core, along with other cores from this depth (data not shown) produced about the same percentage of water at different extraction times and pressure indicating that, for a particular time of centrifugation at an assigned pressure, water is held at equilibrium against the pressure applied to it. Consequently, longer extrac-

tion times are likely to produce only minor increases in the percent water extracted. At increasing depths, the percent water extracted decreases because of increased clay content.

The more texturally uniform soil with depth (core F1, site 1) had a slightly greater water recovery with increasing centrifugation time. Since all replicates for the cores from site 2 were subjected to the same extraction pressure, the small variation in water extracted is likely due to minor variations in initial moisture content between each sample. While some of the samples may not have reached equilibrium, it is clear that equilibrium is reached relatively quickly and, as implied above, increased pressure will remove only small, additional amounts of water. Replicate samples (about 5–10) were necessary to acquire adequate sample volumes for analysis with this method.

The data for samples taken by azeotropic distillation and suction lysimeters generally follows the trend of Fig. 1a,b. However, the sample values extracted by centrifugation generally falls between the values of the other two methods. The same isotopic stratification occurs with the centrifugation samples as with those of the other two methods. However, near the surface, the $^{18}\text{O}\delta$ samples extracted by centrifugation are relatively close to those of samples by suction lysimeter method. This is probably due to larger soil pore sizes near the surface due to higher sand content and greater textural discontinuity. With increased depth, sample values extracted by centrifugation approach those obtained by azeotropic distillation. Centrifugation and suction lysimeter values were not significantly different from each other at the 10 and 20 cm depth (Fig. 3) however; they were different at 30 cm ($p < 0.005$). At the 30 cm depth, centrifugation and azeotropic distillation values were not significantly different. The difference between $^{18}\text{O}\delta$ values from azeotropic distillation and centrifugation indicate that a concentration gradient exists on soil particle surfaces, with greater concentrations apart from the soil grain surface. An increase in variation with depth is explained by the lower volume of input water that has passed through each soil depth (as mentioned earlier) and, the lysimeters are sampling more mobile or less tightly bound water whereas centrifugation samples less tightly bound water of higher tracer concentrations and some immobile or capillary bound water of lower concentrations. The

trends shown in Fig. 1a are similar to the 40–80 cm depths. As the clay content increases by about 5–10%, the values obtained from centrifugation are within about 2.0‰ of those obtained from azeotropic distillation. For the sandy soils from site 1, values obtained from centrifugation fall between those of the other two methods and are closer to each other as in Fig. 2. This is because most of the water in these soils would be mobile at conditions where the soil drains for a period of less than 24 h.

4 Conclusions

For most monitoring studies, mobile, percolating water is of major interest since it represents the portion of water lost from a system as ground water recharge. The data obtained in this study cannot be completely explained by lysimeter exclusion of immobile or entrapped water because, if this were true, the increase in $^{18}\text{O}\delta$ variation with depth would not exist. It is likely that suction lysimeters do not sample immobile water held more tightly in small entrapped pores and, the amount of such soil sampling exclusion cannot be determined by these data. Also, the difference in the $^{18}\text{O}\delta$ content of the water sampled by each method varies as a function of grain size. In sandy soils the differences between the methods are small but become large in clayey soils.

Results indicate that suction lysimeters will preferentially sample mobile soil water held at lower potentials and excludes strongly bound water on soil grain surfaces. This preferred sampling is partly dependent on the moisture content and soil pressure at the time of sampling. For tracer studies and contaminant monitoring, suction lysimeters will sample water held at lower matric potentials, even though this water may not represent pre-existing soil water. In cases where a sufficient volume of water of a given concentration has passed through the soil profile and displaced all previous pore water, suction lysimeters will collect a representative sample of all the water at that depth interval. This is supported by sample value variation of $^{18}\text{O}\delta$ between the suction lysimeters and azeotropic distillation. Consequently, the question of whether or not suction lysimeters collect a representative sample of soil water is dependent on whether a concentration gradient exists between water held at different potentials in the soil. The centrifugation and

azeotropic distillation data clearly indicate that these methods are removing all soil water. The identification of a chemical and isotopic concentration gradient on the surfaces of soil particles is significant and undoubtedly occurs under many field conditions. This situation could exist when large, rapid fluxes to the soil system occur that do not allow equilibration with all the soil water prior to the sampling of suction lysimeters at relatively shallow depths. This would likely be the situation where there is a significant presence of preferential flowpaths or macropores and also in nature where the isotopic and chemical concentration of rainfall is so variable.

There are advantages for each method of extraction. The major advantages of suction lysimeters are the ability to extract freely mobile water, easy installation, and non-destructive sampling. The disadvantage would be expense when attempting to monitor areas larger than typical experimental plot size e.g., >3–5 ha. It is suggested that for stable isotope studies monitoring precipitation and soil water, suction lysimeters be installed at very shallow depths (10 cm) for increased monitoring capability of precipitation inputs. The timing of sampling should also be coordinated with precipitation events. These sampling procedures are important for the determination of what depth the water has reached or may have reached prior to sampling.

The advantage of the centrifugation method is that it is relatively quick and inexpensive. Because sample values from centrifugation closely match those of suction lysimeters at shallow depths (≤ 10 cm), this method would be ideal for sampling large areas such as basins or watersheds that would be too expensive for suction lysimeters and where destructive sampling is more acceptable. The centrifugation method could also be well utilized on soils without significant clay content ($< 15\%$). However, for this method, the soil must be near “field capacity” so that an adequate volume of water for analysis can be withdrawn from samples. For studies such as sorption, desorption, and kinetic investigations requiring strict qualitative and quantitative data, in which scientists attempt to partition the solid and liquid phases, azeotropic distillation would be the most appropriate methodology. For these types of studies, azeotropic distillation is capable of extracting all the tightly bound water held to the soil particle and thus, the partition phase of chemicals such as herbicides. Consequently, this method is ideally suited to studying the

chemical conversion of pesticides in the soil-water environment.

It is clear from the data that each method is sampling a separate component of soil pore water. Suction lysimeters sample freely moving mobile water; centrifugation samples somewhat mobile water, but also less mobile water and capillary water; azeotropic distillation samples all water, especially tightly bound water to soil particles. This water cannot be sampled by the other two methods. Consequently, stratification exists between each method. However, knowing what portion of soil water is being sampled by each method will allow the researcher to adequately design field and laboratory experiments to properly sample the essential water for analysis for the type of study being done.

Finally, as an experimental note, when using lysimeters of different size (diameter), adsorption may continue for longer periods of time (in large lysimeters compared to small lysimeters). Treating suction lysimeters with a weak HCl solution as described delineates any soil-water ion adsorption problems as soil water passes through the cup. However, failure to saturate the exchange sites on the cup will generally require a 1–3 PV of sample collection before adsorption of ions within soil water ceases to become a problem – with larger cups requiring the greater volume. Experience with this experiment indicated that extracting and discarding 1–2 samples prior to initiation of formal collection was sufficient to delineate any soil–water ion adsorption problems that may be manifest by porous ceramic cups.

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