ELSEVIER

A stable isotope study of soil water: evidence for mixing and preferential flow paths

Carey Gazis[a,*], Xiahong Feng[b,1]

[a] Department of Geological Sciences, Central Washington University, MS 7418, Ellensburg, WA 98926, USA
[b] Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, USA

Abstract

Oxygen isotope compositions of precipitation and soil water from profiles at six sites near Hanover, NH reveal information about rates and mechanisms of soil water movement. The ^{18}O-enrichment of shallow (< 20 cm depth) soil water, observed in most soil profiles, is probably due to evaporation. Isotopic fronts observed shortly after a relatively large, low-^{18}O rainfall event suggest piston-type flow in the shallow soil accompanied by significant mixing with stationary soil water. In contrast, deep (>50 cm depth) soil water is only replaced during snowmelt or by substantial rainfall events and so residence times of this water can be several months or more. There is evidence that some of the water from smaller rainfall events bypasses the deep soil through preferential flow paths. A comparison of profiles from two sites on the same hill with different soil textures and moisture contents suggests that the proportion of immobile soil water and thus the amount of preferential flow can vary on a small scale depending on local soil characteristics. The observed soil water processes may have significant effects on plant water use, which is relevant for interpretations of isotopic tree-ring data as a record of paleoclimate.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Oxygen isotope; Soil water; Preferential flow; Piston flow

1. Introduction

Water in the soil environment plays a crucial role as a nutrient to plants, as a carrier of dissolved and solid species and as a reservoir in the hydrologic cycle. An understanding of water movement in the unsaturated zone is essential for describing movement of contaminants from the surface into the groundwater and surface water reservoirs, for describing transport of chemical weathering products and for describing carbon, nitrogen and other nutrient cycles that are strongly tied to hydrological conditions.

Stable isotope compositions of soil water can be used to reveal information about a number of hydrological processes in soil, including infiltration, evaporation, transpiration and percolation, which is difficult to obtain by other techniques. Because isotopic composition of precipitation may vary seasonally as well as from one event to another, isotopic compositions of precipitation and soil water also provide information about mixing and residence times of water along a soil profile.

* Corresponding author. Tel.: +1-509-963-2820; fax: +1-509-963-2821.
E-mail addresses: cgazis@geology.cwu.edu (C. Gazis), xiahong.feng@Dartmouth.edu (X. Feng).
[1] Tel.: +1-603-646-1712; fax: +1-603-646-3922.

Evaporation of soil water has been relatively well studied over the years. In a seminal study, Zimmerman et al. (1967) characterized the effect of evaporation on hydrogen isotopes in soil water. They showed that evaporation at the surface of a column of saturated soil causes deuterium enrichment near the surface that decreases exponentially with depth. Deuterium and ^{18}O-enrichment in soil water near the surface has been observed in many later studies, including column experiments using sand or soil columns (e.g., Allison, 1982) and field observations of unsaturated soils (e.g., Allison and Hughes, 1983; Allison and Barnes, 1983; Darling and Bath, 1988; Hsieh et al., 1998b). Theory (reviewed in Barnes and Allison, 1988) to explain these profiles has been developed and used to determine evaporation rates (e.g., Allison and Barnes, 1983, 1985; Christmann and Sonntag, 1987). Numerical models have been developed to simulate stable isotope profiles in drying soils (Mathieu and Bariac, 1996a) and movement of different isotopic water species in the unsaturated zone (Shurbaji and Phillips, 1995; Shurbaji et al., 1995; Melayah et al., 1996). In contrast to evaporation, several studies (Zimmerman et al., 1967; Allison et al., 1984; Bariac et al., 1991) have shown that transpiration does not cause isotopic fractionation of soil water.

Infiltration of precipitation and subsequent downward percolation is a complicated process affected by soil texture, structure, wetness and degree of heterogeneity. Two end member scenarios are described to be piston flow, in which water from more recent precipitation events forces the older soil water to flow downward, and preferential flow, in which water is channeled through more permeable pathways. A number of studies documenting tracer movement in the soil column have pointed to the existence of preferential fluid flow through macropores, which can be caused by cracks (in dried soils), decayed plant roots, earthworm burrows, rocks, etc. (e.g., Van Ommen et al., 1989; Komor and Emerson, 1994; Vincent et al., 2001). Additionally, fingered flow, in which wetting front instability gives rise to flow through "fingers" rather than uniformly through a porous medium, is a common phenomenon in coarser soils (e.g., Ritsema et al., 1997; Ritsema and Dekker, 1998). Different flow mechanisms result in different isotopic profiles, particularly when successive rainfall

events are isotopically distinct. Preferential flow allows newer rainwater to pass older water that remains in the soil matrix. Piston flow after an isotopically distinct rainfall event results in an abrupt "isotopic front" within the soil. Therefore, by studying isotopic compositions of both precipitation and soil water, it is possible to identify flow mechanisms dominating a given soil column and mixing of water from different precipitation events.

This study was undertaken in order to examine the variations in oxygen isotopic compositions of soil water in the northeastern US, a region where the isotopic composition of precipitation can change dramatically from one storm to another, in order to understand factors controlling water movement within the unsaturated zone. We present oxygen isotope data for precipitation and soil water profiles from six sites near Hanover, NH, USA sampled over a 2-year time period. The sites vary in soil properties such as texture, moisture content, and drainage characteristics, providing an opportunity for evaluating the effects of these factors on soil water movement.

2. Study sites

Six sites (Table 1) were selected within a fifteen-kilometer radius of Hanover, NH (USA). These sites vary in drainage characteristics, soil pH, soil texture and soil organic content. Precipitation was collected at the Shattuck Observatory of Dartmouth College, about 100 m from one of the soil sampling sites (Bartlett Tower, BT).

The region has a temperate climate characterized by large temperature fluctuations (both daily and seasonal) and year-round precipitation that is evenly distributed (Fig. 1). The average annual precipitation is 93 cm. The precipitation is predominantly snow from November to March. Snowmelt usually occurs in April and May. The summer months (June–August), characterized by high solar input, high potential evapotranspiration (PET) and warm temperatures (18–20 °C), are the main growing season for trees, particularly deciduous trees.

All six sites in this study (Table 1) are forested with mixed hardwood (e.g., oak, maple, birches) and softwood (e.g., white pine, hemlock), and have been

Table 1
Soil sampling sites

Site ID	Site name	Location	Texture	Drainage characteristics	Other site characteristics
BT	Bartlett Tower	Hanover, NH 100 m north of rain collector[a]	sandy loam	well-drained	very rocky soil
BHD	Balch Hill Dry	Hanover, NH 4 km east of rain collector	sandy loam	well-drained	on S facing slope
BHW	Balch Hill Wet	Hanover, NH 4 km east of rain collector	loam	poorly drained	depression on W side of hill, 200 m from BHD
DSF	Downer State Forest	Sharon, VT ≈ 15 km southwest of rain collector	sandy loam	intermediate	soil is organic rich, more carbonate in parent material
NL	Newton Lane	Norwich, VT, 5 km southwest of rain collector	sandy loam → sand at depth	intermediate	contains large roots
SV	Sachem Village	Hanover, NH 2 km south of rain collector	silt loam → sandy loam → sand at depth	intermediate	glacial lake deposits

[a] The rain collector is located in the compound of the Shattuck Observatory on the campus of Dartmouth College.

regrown after post-colonial clearing for agriculture. The soil in the region is developed on 12,000-year-old glacial deposits and crystalline bedrock. In the area surrounding Hanover, glacial Lake Hitchcock was the site of deposition of stratified sands which are the parent material for the soils at the Sachem Village (SV) and Bartlett Tower (BT) sites. The sites in Vermont, particularly Downer State Forest (DSF) tend to have parent material that is richer in carbonates, leading to higher soil pH values. Soils in this area generally belong to the great group of Dystrudept (Soil Survey Staff, 1998). At each site, soil pits were situated on a level to gently sloping location. Soil profiles are generally poorly stratified with thin O horizons (0–4 cm) and poorly developed A (≈ 5–10 cm thick) and B horizons (≈ 60 cm thick), and contain abundant rock chips and tree roots.

3. Analytical techniques

Precipitation was collected every 2 weeks in an All-Weather Rain Gauge, into which a small amount (≈ 3 ml) of mineral oil had been added to prevent evaporation. We have tested this method to ensure that addition of mineral oil does not change the oxygen isotopic composition of water. During the winter months, snow was collected in the same
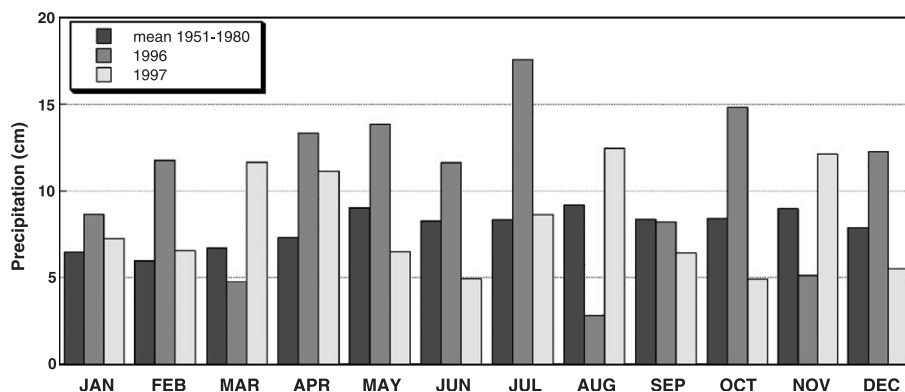

Fig. 1. Monthly precipitation for Hanover, NH. Black bars are mean monthly precipitation for 30-year period from 1951 to 1980. Dark gray and light gray bars are monthly precipitation for 1996 and 1997, respectively. Data source: Climatological Data (1996–1997).

collector and melted to determine the water equivalent. Precipitation was filtered and transferred to sealed glass vials prior to analysis. Oxygen isotope compositions of rainwater were determined using the standard CO_2 equilibration method (Epstein and Mayeda, 1953). We have modified this method slightly by using 8-ml vacutainers with rubber septa as equilibration vessels.

All six sites were sampled between October 5, 1996 and October 17, 1996. During this time interval, one large storm on October 8–10 precipitated 44 mm of rain. Two of the six sites were resampled in August 1997. At each soil sampling site, soil pits were excavated to depths of 67–103 cm. Soil samples were collected every 5–20 cm, the sampling interval depending on stratification within the soil profile and proximity to the soil surface. We sampled in greater detail near the soil surface because this is the area where soil water has the greatest isotopic variability (e.g., Mathieu and Bariac, 1996b; Hsieh et al., 1998b). The temperature was measured at each sampling depth. Samples were placed in screw-top glass vials, sealed with packaging tape to reduce

evaporation. Soil samples were sterilized by radiation as described in Hsieh et al. (1998b) to inhibit microbial respiration and stored in a freezer until analysis.

In the laboratory, moisture content, pH, texture and loss on ignition (LOI) were analyzed with the following methods: Moisture content was determined by drying soils for 24 h at 110 °C. LOI was determined on dried soils by combusting the soils for 10 min at 950 °C. Soil pH was determined on a mixture of 5 g soil and 10 ml of water and soil texture was measured by settling in a LaMotte soil texture kit.

The oxygen isotopic composition of soil water was determined using the CO_2 equilibration technique described in Hsieh et al. (1998a). One modification that we made to the equilibration technique was to transfer a known quantity of CO_2 into the soil equilibration vessel with liquid nitrogen rather than allowing it to expand into the vessel while the soil was frozen with dry ice. For each sample, approximately 10 g of soil was equilibrated with 100–200 μmol of CO_2 for about 24 h at 25 °C. Carbon dioxide gas was extracted from the equilibration

Table 2
Oxygen isotope composition of precipitation

Collection date	Amount (mm)	$\delta^{18}O$ (‰)	Precipitation type	Collection date	Amount (mm)	$\delta^{18}O$ (‰)	Precipitation type
15 December 1995	42.2	−12.9	90% snow	31 October 1996	97.0	−11.3	rain
31 December 1995	12.9	−19.1	snow	15 November 1996	31.6	−4.7	snow + rain
14 January 1996	41.8	−20.6	snow	30 November 1996	29.8	−12.3	mostly snow
31 January 1996	84.1	−6.8	rain + 20% snow	14 December 1996	76.6	−16.1	snow + rain
15 February 1996	10.0	−19.4	snow + rain	31 December 1996	38.8	−13.5	rain + 10% snow
29 February 1996	50.7	−12.0	rain > snow	15 January 1997	21.4	−10.4	snow
15 March 1996	33.0	−20.4	snow + rain	31 January 1997	57.6	−15.8	snow
1 April 1996	13.0	−9.6	rain	15 February 1997	40.8	−14.0	snow
15 April 1996	41.5	−16.5	rain + 20% snow	28 February 1997	21.6	−11.7	snow + some rain
30 April 1996	93.0	−8.0	rain	15 March 1997	58.6	−12.9	snow + rain
15 May 1996	99.8	−9.5	rain	1 April 1997	38.0	−15.5	snowed on March 31
1 June 1996	29.8	−9.8	rain	15 April 1997	10.6	−11.9	rain + some snow
15 June 1996	54.1	−5.0	rain	30 April 1997	79.0	−16.5	snowed on April 17
30 June 1996	48.7	−6.6	rain	15 May 1997	45.4	−8.1	rain
15 July 1996	148.0	−9.2	rain	2 June 1997	15.0	−5.2	rain
31 July 1996	48.0	−6.6	rain	15 June 1997	1.6	−5.2	rain
15 August 1996	16.0	−8.9	rain	30 June 1997	34.0	−5.6	rain
31 August 1996	7.0	−7.3	rain	16 July 1997	74.2	−5.3	rain
15 September 1996	22.2	−8.4	rain	31 July 1997	1.2	+3.3	rain
1 October 1996	39.2	−9.8	rain	15 August 1997	22.6	−5.9	rain
15 October 1996	44.0	−17.2	rain	2 September 1997	97.8	−10.5	rain

vessel by standard techniques and the yield was measured. Yields lower than 90% were considered unacceptable.

Oxygen isotope analyses for CO_2 equilibrated with water and soil water samples were made using a Finnigan MAT 252 isotope ratio mass spectrometer. The results are presented in the standard δ-notation[2] as per mil (‰) difference from Vienna Standard Mean Ocean Water (VSMOW). The uncertainty for water $\delta^{18}O$ is 0.1‰. The uncertainty for soil water $\delta^{18}O$ is considerably greater: seventeen analyses of a natural soil sample had a standard deviation of 0.4‰ and repeat analyses of single samples differ by as much as 0.6‰. However, some of this variability is probably due to sample heterogeneity.

4. Results

Precipitation data and soil data are presented in Tables 2 and 3, respectively. The $\delta^{18}O$ values of precipitation are extremely variable, ranging from $+3.3$‰ to -20.3‰. In general, winter (December to February) precipitation is relatively depleted in ^{18}O compared to summer (June to August) precipitation. The measured $\delta^{18}O$ of soil water ranges from -5.4‰ to -14.0‰ and is usually more enriched in ^{18}O near the soil surface. The water content of soils ranges from 1.9% to 26.7% by weight.

5. Discussion

An examination of the soil water isotope profiles and a comparison of these profiles with the isotopic composition of precipitation prior to sampling can be used to decipher the mechanisms of water movement through the shallow and deep soil and to determine residence times of soil waters at different depths. Comparison of isotope profiles from nearby sites with different soil textures and drainage characteristics allow us to evaluate the importance of these

----

[2]
$$\delta^{18}O = \left(\frac{\frac{^{18}O}{^{16}O_{smp}} - \frac{^{18}O}{^{16}O_{std}}}{\frac{^{18}O}{^{16}O_{std}}} \right) *1000,$$

where smp = sample and std = standard (VSMOW in this study).

local variations on soil water movement. These comparisons and our interpretations are presented in the discussion below. In addition, we compare our results with previous studies of oxygen isotopes in soil water and discuss the implications of our results for tree ring isotope studies.

5.1. Evaporation, mixing and piston flow in shallow soil

The net effect of evaporation is an enrichment of heavy isotopes near the soil surface. Six out of our eight soil profiles (Fig. 2) show increase in the $\delta^{18}O$ of soil water in the upper 20 cm, suggesting the occurrence of evaporation. However, these enrichment trends may occur as a result of several processes, including evaporation, change in isotopic composition of precipitation and mixing of new and old water. While evaporation is widely recognized, we believe that changing isotopic composition in rainfall input and mixing are also important factors controlling the isotopic composition of soil water at these sites.

Mixing of recent precipitation with older soil water in the upper soil profile is suggested by the October 15–17 profiles (Fig. 3). After a significant (44 mm) rainfall event with $\delta^{18}O$ of -17.2‰, the most ^{18}O-depleted soil water (12 and 19 cm depth at the SV site) has a $\delta^{18}O$ of -14.0‰. Given that these profiles were sampled approximately 1 week (5 and 7 days) after the rainfall event (October 8–10) and most of the intervening days were overcast, it is unlikely that the difference between the $\delta^{18}O$ values of soil water and rainwater is due solely to evaporation. Further evidence is given by the NL soil (sampled on October 17), in which the most ^{18}O-depleted water occurs at the surface layer. More likely this is the result of mixing between the rainwater of this event and the soil water that existed prior to the event, which we will call "immobile soil water."

By comparing the oxygen isotopic composition of soil water with that of recent precipitation, we can obtain a crude estimate of the proportion of immobile soil water. We will consider two scenarios: one where evaporation has not significantly altered the isotopic composition of shallow soil water and one in which it has. If evaporation has not altered the $\delta^{18}O$ value of shallow soil water, then the $\delta^{18}O$ of preexisting immobile soil water should lie between -10‰

Table 3
Properties of soil profiles

Site and sample #	Sampling date	Depth (cm)	Temp. (°C)	pH	Sand vol.%	Silt vol.%	Clay vol.%	LOI wt.%	Water wt.%	$\delta^{18}O$ ‰
Balch Hill Dry, 1996										
96-BHD-05	5 October 1996	5	7.1		60	37	3	7.1	9.1	− 6.7
96-BHD-10	5 October 1996	10	7.5	4.8	66	31	3	5.6	7.4	− 6.5
96-BHD-20	5 October 1996	20	8.6	5.1	72	25	3	4.4	6.6	− 6.9
96-BHD-35	5 October 1996	35	10	5.0	73	23	3	3.8	5.0	− 6.8
96-BHD-35	5 October 1996	35	10	5.0	73	23	3	3.8	5.0	− 6.9
96-BHD-50	5 October 1996	50	10.6	5.4	74	23	3	3.0	4.5	− 6.6
96-BHD-65	5 October 1996	65	10.9	5.3	80	16	4	3.1	5.5	− 8.3
96-BHD-80	5 October 1996	80	11	5.4	79	18	3	2.6	4.9	− 8.6
Balch Hill Wet, 1996										
96-BHW-07	5 October 1996	7	7.6	4.6	46	48	6	6.7	22.5	− 8.0
96-BHW-17	5 October 1996	17	8.7	4.6	42	47	11	6.7	15.0	− 8.2
96-BHW-27	5 October 1996	27	9.7	4.7	47	46	7	5.5	22.4	− 9.6
96-BHW-37	5 October 1996	37	10.3	4.8	45	41	15	3.7	18.1	− 9.7
96-BHW-47	5 October 1996	47	10.8	4.8	47	41	12	3.3	16.0	− 9.8
96-BHW-57	5 October 1996	57	11.1	4.9	52	33	15	3.3	16.8	− 9.7
96-BHW-67	5 October 1996	67	11.3	5.3	52	39	9	5.1	15.8	− 10.1
Balch Hill Dry, 1997										
97A-BHD-05	15 August 1997	5	15.7					9.5	12.7	− 5.4
97A-BHD-10	15 August 1997	10	15.1					6.2	12.2	− 8.4
97A-BHD-15	15 August 1997	15	14.6					4.9	10.4	− 6.4
97A-BHD-20	15 August 1997	20	14.5					4.4	6.9	− 6.5
97A-BHD-30	15 August 1997	30	14.5					3.6	4.7	− 8.3
97A-BHD-40	15 August 1997	40	14.4					3.3	4.5	− 11.4
97A-BHD-65	15 August 1997	65	12.7						5.6	− 12.0
Balch Hill Wet, 1997										
97A-BHW-05	15 August 1997	5	14.1					10.7	26.0	− 5.5
97A-BHW-10	15 August 1997	10	14					8.4	26.7	− 6.6
97A-BHW-15	15 August 1997	15	14					6.8	21.1	− 5.6
97A-BHW-20	15 August 1997	20	14.4					4.8	19.3	− 10.6
97A-BHW-30	15 August 1997	30	14.4					4.4	17.3	− 11.7
97A-BHW-40	15 August 1997	40	14					4.0	17.6	− 12.2
97A-BHW-55	15 August 1997	55	13.6					3.5	15.4	− 12.0
97A-BHW-67	15 August 1997	67	13.1					3.4	14.7	− 10.9
Bartlett Tower, 1996										
96-BT-07	5 October 1996	7	7.4	4.5	63	34	3	8.6	17.7	− 6.0
96-BT-14	5 October 1996	14	8.3	4.5	63	34	4	13.0	19.7	− 8.0
96-BT-17	5 October 1996	17	9.4	4.5	58	39	3	7.1	13.9	− 7.9
96-BT-27	5 October 1996	27	10.5	4.4	66	31	3		15.5	− 8.9
96-BT-37	5 October 1996	37	11.2	4.5	56	41	3	4.7	12.6	− 8.6
96-BT-47	5 October 1996	47	11.4	4.5	57	40	3	4.6	10.1	− 7.7
96-BT-57	5 October 1996	57	11.6	4.6	66	31	3	4.1	9.5	− 7.4
96-BT-67	5 October 1996	67		4.5	60	36	3	4.4	9.4	− 7.6
96-BT-67	5 October 1996	67		4.5	60	36	3	4.4	9.0	− 7.1
Downer State Forest, 1996										
96-DSF-10	15 October 1996	10	8.2	5.4	88	9	3	10.9	21.8	− 10.3
96-DSF-20	15 October 1996	20	8.9	5.6	63	34	3	7.0	19.5	− 11.9

Table 3 (*continued*)

Site and sample #	Sampling date	Depth (cm)	Temp. (°C)	pH	Sand vol.%	Silt vol.%	Clay vol.%	LOI wt.%	Water wt.%	$\delta^{18}O$ ‰
Downer State Forest, 1996										
96-DSF-30	15 October 1996	30	9.1	5.5	66	31	3	7.5	20.9	− 10.3
96-DSF-45	15 October 1996	45	9.4	5.6	70	27	3	6.9	18.7	− 8.2
96-DSF-73	15 October 1996	73	9.5	6.0	72	24	3	5.2	10.4	− 7.1
96-DSF-103	15 October 1996	103	10	6.1	69	28	3		9.3	− 7.5
Newton Lane, 1996										
96-NL-09	17 October 1996	9	7.5	4.8	71	27	2	10.2	26.0	− 13.1
96-NL-20	17 October 1996	20	7.8	4.7	73	25	2	6.0	22.7	− 12.0
96-NL-25	17 October 1996	25	7.8	4.6	61	21	18	7.0	19.7	− 10.8
96-NL-32	17 October 1996	32	8.1	4.7	89	7	4	5.0	9.8	− 10.0
96-NL-44	17 October 1996	44	8.6	5.1	95	2	4	2.5	5.1	− 13.0
96-NL-53	17 October 1996	53	8.7	5.0	94	3	3	3.1	7.3	− 8.9
Sachem Village, 1996										
96-SV-06	17 October 1996	6	10	4.6	40	54	6	6.3	17.1	− 12.3
96-SV-12	17 October 1996	12	9.7	5.1	53	45	2	7.8	21.6	− 14.0
96-SV-19	17 October 1996	19	9.5	5.3	60	39	1	6.3	18.1	− 14.0
96-SV-29	17 October 1996	29	9.6	4.7	74	26	1	3.9	14.3	− 9.3
96-SV-41	17 October 1996	41	9.8	4.8	66	33	1	2.8	9.4	− 7.8
96-SV-51	17 October 1996	51	10	4.9	76	20	4	2.8	9.2	− 8.4
96-SV-60	17 October 1996	60	10.2	5.0	79	18	3	2.6	5.2	− 9.7
96-SV-82	17 October 1996	82	10.7		96	2	2	1.9	1.9	− 6.9

Temperature, pH, texture, loss on ignition, water content and oxygen isotopic composition of soil water.

and − 5‰, similar to water at the base of October 15–17 profiles and in the October 5 profiles. Assuming mass balance of two components (precipitation and stationary soil water), soil water with $\delta^{18}O$ of − 13‰ would require a mixture containing 37% (for immobile soil water $\delta^{18}O = − 5$‰) to 61% (for im-
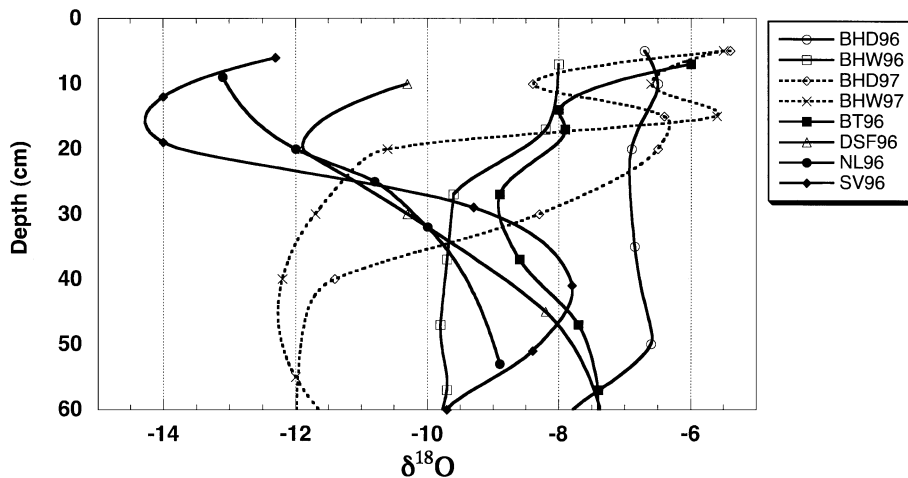

Fig. 2. Eight profiles showing soil–water $\delta^{18}O$ variations with depth at six soil sampling sites. Solid lines are six sites sampled in October 1996. Dashed lines are two sites sampled in August 1997. Sampling site designations (see Table 1 for descriptions): BHD = Balch Hill Dry, BHW = Balch Hill Wet, BT = Bartlett Tower, DSF = Downer State Forest, NL = Newton Lane, SV = Sachem Village.

mobile soil water $\delta^{18}O = -10\permil$) of this immobile soil water. In the second scenario, evaporation, either from immobile soil water prior to the October 8–10 rainfall or after the precipitation event, would reduce the estimated proportion of immobile soil water because it would cause ^{18}O-enrichment in the shallow soil water. Evaporation measured on lakes in southern New Hampshire between October 8 and October 15 was low, totaling only 8 mm (Climatological Data, 1996–1997). Furthermore, observed near-surface ^{18}O-enrichments (e.g., Fig. 2) do not appear to exceed several per mil. Thus immobile soil water probably had $\delta^{18}O \leq 0\permil$, and it is likely that a significant proportion (>20%) of the shallow soil matrix water remained relatively immobile and was not displaced during this 44 mm rainfall event.

Despite this evidence for mixing, abrupt changes in the $\delta^{18}O$ in soil water with depth in the soil profile indicate that partial piston-flow also has occurred. That is, while some soil water remains stationary, the mobile soil water successively displaces pre-existing mobile soil water pushing it downward. For example, the trend with depth in the SV soil column from 12 to 60 cm depth (Fig. 3) is consistent with the isotopic variation of precipitation prior to sampling: the precipitation $\delta^{18}O$ values going back in time are $-17.2\permil$ (44 mm, October 1–15), $-9.1\permil$ (84 mm, August 1 to October 1), $-6.6\permil$ (48 mm, July 15–31) and $-9.2\permil$ (148 mm, July 1–15), while soil water varies from $-14.0\permil$ (12 cm) to $-9.3\permil$ (29 cm) to $-7.8\permil$ (41 cm) to $-9.7\permil$ (60 cm). Mixing is again suggested by the fact that most ^{18}O-enriched ($-14.2\permil$) or -depleted ($-7.8\permil$) soil water is not as enriched or depleted as the rainfall value ($-17.2\permil$ or $-6.6\permil$).

5.2. Deep soil water: residence times and preferential flow

If the soil water at 60 cm depth in the SV profile does in fact correspond to precipitation that fell in early July, this would imply a residence time of at least 3 months for that soil water. Data from the August 1997 sampling of the Balch Hill sites (Fig. 4b), when compared with precedent precipitation (Fig. 5), also suggest residence times of several months or more for deep soil water. In both BHD and BHW profiles, $\delta^{18}O$ values of soil waters at
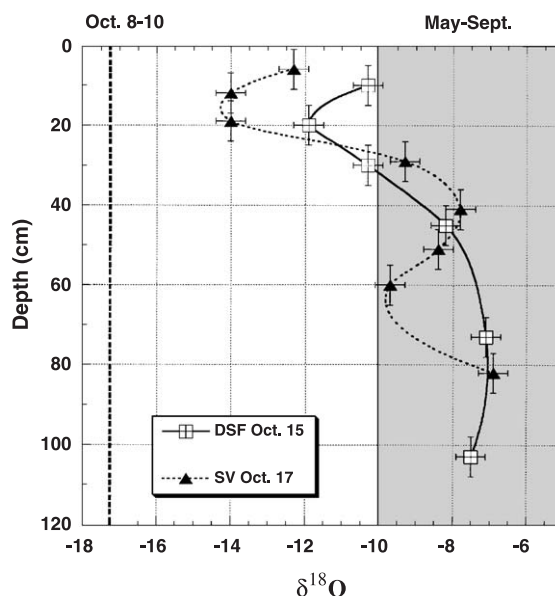

Fig. 3. $\delta^{18}O$-vs.-depth profiles for two sites sampled shortly after 44 mm rainfall event of October 8–10, 1996. Site DSF (crossed boxes) was sampled on October 15, 1996 and site SV (solid triangles) was sampled on October 17, 1996. The vertical dashed line is the isotopic composition of precipitation collected October 1–15, 1996, 95% of which fell during the October 8–10 rainfall event. The solid gray area represents the range of $\delta^{18}O$ values for precipitation falling between May 1 and September 30, 1996.

depths below 40 cm are approximately $-12.0\permil$. The precipitation from April 30 until the sampling date had biweekly $\delta^{18}O$ averages between $-8.4\permil$ and $-6.3\permil$; thus, the $\delta^{18}O$ of precipitation was probably never as low as $-12.0\permil$ during this time interval. Therefore, the deep soil water must contain a substantial proportion of water from the spring rain and snow melt which have $\delta^{18}O$ values ranging from $-10.7\permil$ to $-16.7\permil$. This implies that the residence time in Spring–Summer 1997 for deep soil water was at least 4.5 months. These residence times agree with the conclusion of Tang and Feng (2001), who monitored the oxygen isotopic composition of soil CO_2 near the BT site. Assuming that this CO_2 was in isotopic equilibrium with soil water, Tang and Feng (2001) compared the calculated soil water $\delta^{18}O$ values to precipitation $\delta^{18}O$ values and concluded that soil water at 50 cm depth is only replenished during large storm or melting events.
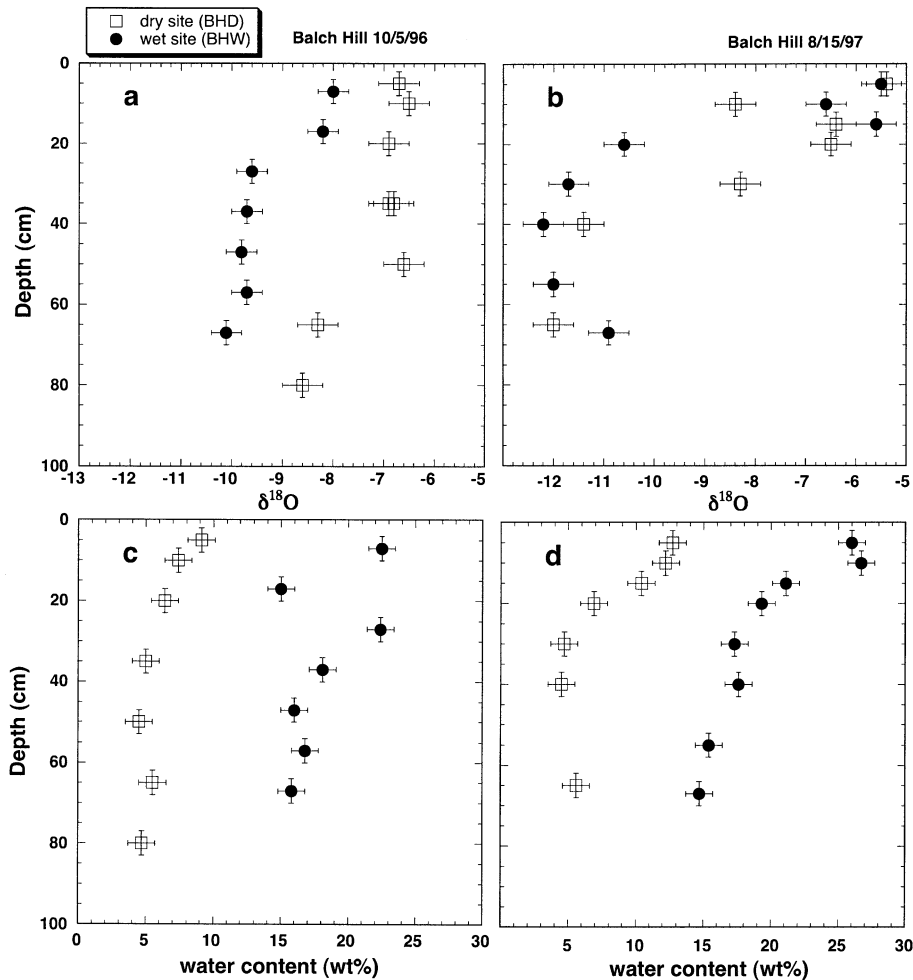
Fig. 4. Soil–water δ^{18}O profiles (a and b) and water content (wt.%) profiles (c and d) for two sites in Hanover, NH. The two sites are located approximately 200 m from each other, but have very different drainage characteristics: one (BHD-crossed squares) is well drained and has relatively dry soil, the other (BHW-solid circles) is poorly drained and has much wetter soil. These sites were sampled twice: on October 5, 1996 (a: δ^{18}O, c: water content) and on August 15, 1997 (b: δ^{18}O, d: water content).

If all of the rain that fell between April 30 and August 15 (19.4 cm) infiltrated into the soil by means of simple piston-type flow, this rainwater would have replenished the deep soil water. We suggest that two explanations account for the several-month-old soil water at depth: (1) evapotranspiration in the upper soil horizons removed infiltrating water before it could reach 40 cm depth. Assuming the average porosity of the soil is 35%, this explanation would require that at least 5.4 cm of the rainwater that fell in May to mid-August was evaporated or transpired by trees before reaching depths of 40 cm or greater. It is likely that the potential evapotranspiration at these sites during this spring/summer period was considerably higher than 5.4 cm and thus evapotranspiration is the major contributor to the fact that there is spring rain and snowmelt at 40 cm depth rather than summer rainfall. (2) Rain which fell during the intervening months passed to depths of 40 cm or greater, but at these depths it was channeled in preferential flow paths and
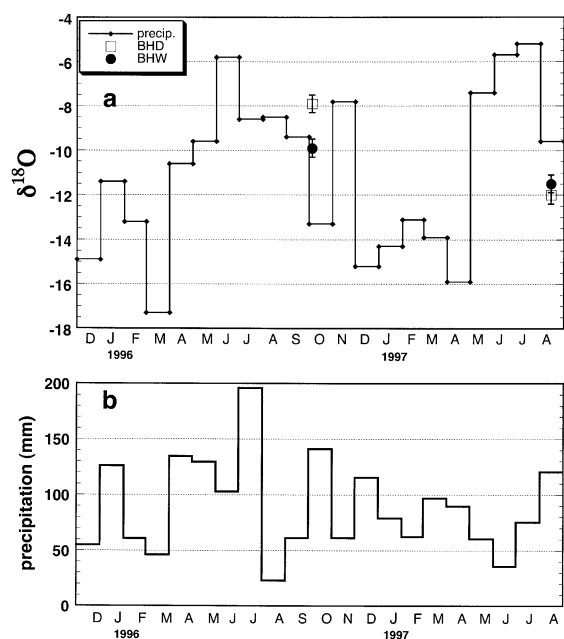
Fig. 5. (a) $\delta^{18}O$ for monthly precipitation (solid line) and soil water at 60-cm depth, collected in October 1996 and August 1997 at two sites in Hanover, NH: the well-drained (BHD-open squares with lines) and the poorly drained (BHW-solid circles) sites on Balch Hill. (b) Corresponding monthly precipitation amount.

did not replace the bulk of the soil water. Hydrograph separation studies by Renshaw et al. (in press) indicate that some amount of preferential flow occurs through the soil profile even during relatively small storms. Renshaw et al. (in press) observed stream discharge in response to 11 storms of various sizes (2–33 mm), in a small headwater catchment near our sampling sites (about 11 km from the Dartmouth Campus). For all storms, stream discharge increased shortly after the onset of the storm, while the infiltration depth observed in soil profiles was only a few centimeters for small storms. By comparing the isotopic compositions of stream water and storm (event) water, they calculated the event water contribution in the stream hydrograph and found that the entire event water contribution was due to direct precipitation onto the channel. Therefore, aside from direct channel precipitation, the increased discharge consisted of old water that existed in the catchment before the storm events. They suggested preferential flow paths as a mechanism for passing the hydraulic pressure from the near surface to the groundwater.

5.3. Local variations due to different drainage characteristics

The two Balch Hill sites (BHW and BHD) are located within 200 m of each other and receive isotopically identical precipitation. The two sites differ markedly in their drainage characteristics, due in part to their different positions and aspects on the hill (BHW is in a shallow depression, BHD is on a gentle south-facing slope) and their differences in soil texture (BHW has higher silt and clay contents). The October 1996 profiles reveal distinctly different isotopic compositions of soil water at the two sites (Fig. 4a). The soil water at the drier site (BHD) is 1.5–3 per mil more enriched in ^{18}O than the soil water at the same depth at the wetter site (BHW). This difference is well beyond the uncertainty of the soil–water $\delta^{18}O$ measurements and occurs systematically at all depths. In contrast, analyses of soil water $\delta^{18}O$ from the same two sites in August 1997 do not show any systematic difference between the two sites (Fig. 4b); the drier site is isotopically lighter at some depths (e.g., 15 and 65 cm) but heavier at others (e.g., 20 and 30 cm).

The 1.5–3 per mil difference in soil water $\delta^{18}O$ between BHW and BHD observed in October 1996 may arise from four general mechanisms: (1) A greater amount of evaporative enrichment at the dry site, if consistently occurring, accompanied by piston flow could cause soil water at all depths at that site to be isotopically heavier. (2) The two sites could have different proportions of immobile vs. mobile soil water, either due to different water retention characteristics or different extents of preferential flow at the two sites. If the mobile soil water is isotopically distinct from the immobile soil water, then different proportions of the two waters could explain the observed profiles. For example, if the immobile water is isotopically lighter than the mobile water, a greater proportion of immobile soil water at the wet site would explain the observed profiles. (3) Overland flow or near-surface horizontal flow could also cause different amounts of rainwater infiltration at the two locations. In this case, as in mechanism 2 above, the observed profiles would be explained by different proportions of mobile soil water (replaced by infiltrating rainwater) and immobile soil water. (4) The two sites have the same proportions of immobile and

mobile soil water, but the immobile soil water at the dry site is isotopically heavier.

The same two sites were sampled in August 1997 and did not display the same differences in soil water $\delta^{18}O$ at that time although the soil water contents were comparable to those in the previous year (Fig. 4c and d). Inasmuch as July and August are the warmest months of the year, this observation suggests that evaporative enrichment alone (explanation 1 above) does not explain the differences in soil water $\delta^{18}O$ at the two sites the previous year. Thus, the differences must be due at least in part to different proportions of mobile and immobile soil water or to differences in the isotopic composition of immobile water (explanations 2–4). Our preferred interpretation is that similar amounts of precipitation infiltrate at the two Balch Hill sites, but that the two sites have different proportions of immobile soil water, which contained a significant amount of spring rain/snowmelt in October 1996. Thus, the observed trends are explained by a larger proportion of immobile soil water at the wet site. This may be due to the finer-grained nature of these wet soils, which leads to larger proportions of micropores and dead-end pores and a greater surface area on which films of immobile water reside. Alternatively, greater infiltration, particularly of snowmelt, may occur at the wetter site because it is in a shallow depression. Focussed snowmelt on a local scale will be affected by factors such as the thickness of the snowpack and the degree of drifting, the timing of melting and the presence or absence of frozen soil. If focused snowmelt was substantial in 1996 but small in 1997, this might also explain the different trends in the 1996 and 1997 profiles.

As discussed above, because it is isotopically lighter than any recent precipitation, the deep soil water in August 1997 appears to consist mostly of precipitation that fell before April 30 (Fig. 5). Because the deep soil water at both the wet and dry site are isotopically identical, it appears that, at both sites, the soil water was thoroughly exchanged during the spring snowmelt and rains. In contrast, for the October 1996 sampling, the $\delta^{18}O$ of deep soil waters at both sites is much heavier than winter and spring precipitation (Fig. 5) and it appears that it has been replaced during high precipitation (148 cm) in early July. However, the wetter site has a slightly lower

$\delta^{18}O$ than the summer precipitation, suggesting that it has retained some of the winter/spring precipitation. Deep soil water at the drier site does not appear to have any of the spring–winter precipitation, although it is possible that evaporative enrichment has obscured the isotopic signature of winter/spring precipitation.

5.4. Comparison with other oxygen isotope studies

A number of previous studies have used oxygen isotopes to characterize soil water movement (e.g., Bengtsson et al., 1987; Hesterberg and Siegenthaler, 1991; Mathieu and Bariac, 1996b; Gehrels et al., 1998; Hsieh et al., 1998b). When comparisons are made between different soil water $\delta^{18}O$ studies, one must keep in mind that different extraction and/or analysis techniques may be measuring different components of soil water. In this study, soil water $\delta^{18}O$ was measured by direct equilibration between wet soil and CO_2. This equilibrating water should include soil matrix water, both mobile and immobile, but not water in a tightly adsorbed monolayer on surfaces or water within clay minerals. Azeotropic distillation (e.g., Revesz and Woods, 1990) also presumably removes only the soil matrix waters. In contrast, vacuum distillation (e.g., Araguás-Araguás et al., 1995), depending on the temperature used, may tend to remove some of these more tightly bound water molecules. Meanwhile wick samplers and some suction lysimeters extract only the mobile component of soil matrix water (e.g., Holder et al., 1991; Landon et al., 1999).

Hsieh et al. (1998b) monitored oxygen isotopes in rainwater and soil water using the direct equilibration method from sites across a climate gradient in Hawaii. In contrast to the results of our study, they observed that, at all of their sites except perhaps the wettest site, deep (>40 cm) soil waters appear to respond immediately to a change in the isotopic composition of rainwater, suggesting a residence time of less than 1 month for deep soil water. However, in their study, the $\delta^{18}O$ of soil water at all depths are consistently heavier than the precipitation, suggesting that some fraction of evaporated water remains in the soil matrix (as immobile soil water) throughout the year. We suggest two factors that explain the different deep soil residence times: (1) The Hawaiian soils have

textures that do not allow for large soil macropores that totally bypass soil matrix water. (2) The precipitation in Hawaii falls almost entirely as rain and the soils do not undergo periods of freezing, followed by thawing and infiltration by snowmelt.

Mathieu and Bariac (1996b) present stable isotope data for precipitation, soil water (extracted by vacuum distillation) and groundwater at a semiarid drainage in West Africa. Based on their isotope data, they conclude that water moves through the soil profile by two means: (1) slow infiltration through the soil matrix and mixing with mobile soil water; (2) fast direct recharge by flow through conducting fissured zones. These two proposed mechanisms are compatible with the observations of this study even though the climate of their study area is quite different from ours.

Some studies in Northwestern Europe (Bengtsson et al., 1987; Gehrels et al., 1998), where the climate is more similar to that in our study area have resulted in different conclusions about soil water movement. Bengtsson et al. (1987) studied oxygen isotope ratios of soil water (extracted by vacuum distillation) at sites in central Sweden, where considerable snow accumulates throughout the winter. They observed evidence for piston-style flow throughout the unsaturated zone, particularly in well-sorted soils. In contrast, Gehrels et al. (1998), in a study of seasonal trends in soil water $\delta^{18}O$ (separated using vacuum distillation and centrifugation), at sites in the Netherlands, observed that groundwater has an isotopic signature similar to the average annual precipitation despite a soil moisture deficit in the summer and a precipitation surplus in the winter. They explain this observation by soil water movement dominated by preferential flow in the root zone. These two studies underline that both careful observation of soil water isotope profiles and mass balance considerations must be used to characterize soil water movement mechanisms and their effect on the soil water budget. Furthermore, movement mechanisms may vary locally depending on factors such as soil texture or depth of root zone.

Hesterberg and Siegenthaler (1991) presented biweekly oxygen isotope data for soil water and precipitation near Bern, Switzerland. In their study, soil water was extracted through semipermeable ceramic tubes connected to evacuated glass flasks, similar in function to a wick sampler. The isotopic composition of soil water was measured at depths of 30 and 80 cm.

Isotopic trends of rainwater are offset by 1–2 months for 30-cm soil water and 5–6 months the 80-cm soil water. In addition, the amplitude of seasonal isotopic variation decreases from precipitation to shallow soil water to deep soil water, but the average $\delta^{18}O$ for all appears to be the same. These observations suggest that the precipitation moves in piston-fashion through the soil, exchanging thoroughly with the mobile soil water. As water percolates downward, it is progressively dispersed and mixed, causing the damping of the seasonal isotopic variations. The results of Hesterberg and Siegenthaler (1991) and not directly comparable with our results because they were probably collecting and analyzing the mobile component of soil water whereas we analyzed the total soil water. A combination of this method and measurement by direct equilibration could provide a means of determining the isotopic composition of both mobile and immobile soil water to better quantify the relative contributions of different rainfall events to soil water at different depths.

5.5. Implications for tree ring isotope studies

The isotopic compositions of tree rings (especially isotopes of hydrogen) are a potentially powerful tool for recent climate reconstructions because they provide annual records spanning back hundreds of years and these records are ubiquitous on the continents. A common assumption in tree ring isotope studies is that the isotopic composition of the rings reflects the isotopic composition of precipitation, which is dependent on temperature and thus climate. Yapp and Epstein (1982) showed that, on a global scale, the hydrogen isotopic composition of tree rings correlates with that of local meteoric water. However, on a local scale where the variations in the isotopic composition of meteoric water are small, other factors such as local hydrology, biological effects and humidity, may cause variations in tree ring hydrogen isotopes comparable to those caused by changes in temperature. Thus, it is important to determine the precise isotopic composition of the source water for wood cellulose and to understand how the isotopic composition of water changes as it travels through the soil, through the roots and stem and is incorporated into the wood.

In the past, it has been assumed that the source water for the wood cellulose is isotopically identical

to the local precipitation. However, soil water is known to become enriched in ^{18}O and D near the soil surface due to evaporation (e.g., Allison and Barnes, 1983). Also, studies in some locations (e.g., Hawaii— Hsieh et al., 1998b) have shown that soil waters have a significantly different $^{18}O/^{16}O$ ratio than rainwater. To address this issue, Tang and Feng (2001) studied the relationship between isotopes in precipitation, soil water and twig water in Hanover, NH (at the same location where precipitation was sampled for this study). They analyzed the isotopic composition of soil CO_2 and, assuming this was in equilibrium with soil water, calculated the isotopic composition of soil water. By comparing the isotopic compositions of soil water and precipitation, these researchers concluded that soil at 50 cm depth only receive water from large storm or melting events. Analysis of twig waters indicated that trees obtain water from shallow soil layers, where evaporation has caused isotopic enrichment of soil water.

The results of our study support the conclusion of Tang and Feng (2001) that deep soil water is only replenished during large storm or melting events and that shallow soil water is isotopically enriched. In addition, our results suggest that soil water at all depths consists of mobile and a stationary components and the ratio of these components is partially dependent on the texture and moisture content of the soil. Because these soil characteristics can vary considerably on a local scale (e.g., Balch Hill), nearby trees may tap isotopically distinct waters. These results also raise the question of which components of soil water are tapped by trees. If trees use only the mobile component of soil water and that soil water reflects the isotopic composition of recent precipitation, then the isotopic composition of tree rings will not be affected by within-site variation in proportions of mobile and stationary soil water. However, if some component of stationary soil water is extracted by trees, then trees in drier localities (e.g., south slopes) would be expected to use water that is enriched in heavy isotopes due to evaporation.

6. Conclusions

Soil water samples from six sites near Hanover, NH (USA) were measured for oxygen isotopic compositions that are compared with the isotopic compo-

sitions of precipitation. The data presented here have allowed us to describe important factors controlling water movement into, out of, and through the soil profile. At all depths, the soil water has stationary and mobile components in terms of how easily they are displaced by with infiltrating rainwater. The presence of stationary soil water indicates some form of preferential fluid flow, either through soil macropores or along more permeable zones within the soil (e.g., fingers). The proportion of soil water that is stationary, and thus the extent of preferential flow, depends on soil texture/drainage characteristics. In addition, the shallow and deep zones in the soil have distinctly different residence times for soil water due to different styles of soil–water flow.

In the upper 20 cm of the soil profile, evaporation is common, causing enrichments in soil water $\delta^{18}O$ that may occur in both the mobile and stationary components of the soil matrix water. A sharp isotopic front at approximately 15 cm depth observed shortly after an isotopically distinct rainfall event suggests that infiltration into the shallow soil occurred as piston flow with newer water pushing older water downward in the soil profile. However, during this process a significant proportion (>20%) of shallow soil water remained stationary.

Based on comparisons between the $\delta^{18}O$ of precipitation and deep soil water, it appears that deeper soil waters are only replaced during snowmelt or substantial rainfall events, giving rise to deep soil water residence times of 4.5 months or more. Although a large amount of rainwater is transpired by plants and never reaches the bottom of the soil profile, it also appears that some water from intermediate-size rain events travels to the saturated zone along preferential flow paths and does not interact with most of the mobile soil water.

A comparison between two nearby sites suggests that the isotopic composition of soil water can vary locally depending on small-scale drainage and soil characteristics. The higher $\delta^{18}O$ of the drier of the two sites is probably due in part to greater amounts of evaporative ^{18}O-enrichment and in part to different proportions of stationary and mobile soil water. The question of the nature and residence of this stationary soil water were not addressed by this study. Future isotopic studies using combinations of different analysis techniques (e.g., direct equilibration along with

collection using wick samplers or soil lysimeters) might help to resolve this question.

The soil processes and their impact on oxygen isotopic distribution of soil moisture may have significant effects on isotopic compositions of the water used by plants. Because soil water near the surface turns over more quickly than that at depth, rooting depth alone may cause within-site variations in water incorporated into tree rings. Our work suggests that the complicated interplay between soil hydrology and plant physiology should be considered in paleoclimate studies using oxygen and hydrogen isotopes of tree rings.

Acknowledgements

References

Allison, G.B., 1982. The relationship between ^{18}O and deuterium in water in sand columns undergoing evaporation. J. Hydrol. 55, 163–169.

Allison, G.B., Barnes, C.J., 1983. Estimation of evaporation from non-vegetated surfaces using natural deuterium. Nature 301, 143–145.

Allison, G.B., Barnes, C.J., 1985. Estimation of evaporation from the normally "dry" Lake Frome in South Australia. J. Hydrol. 78, 229–242.

Allison, G.B., Hughes, M.W., 1983. The use of natural tracers as indicators of soil–water movement in a temperate semi-arid region. J. Hydrol. 60, 157–173.

Allison, G.B., Barnes, C.J., Hughes, M.W., Leaney, F.W.J., 1984. Effect of climate and vegetation on oxygen-18 and deuterium profiles in soils. Proc. IAEA Symp. on Isotopes in Hydrol. 1983, 105–122.

Araguás-Araguás, L., Rozanski, K., Gonfiantini, R., Louvat, D., 1995. Isotope effects accompanying vacuum extraction of soil water for stable isotope analyses. J. Hydrol. 168, 159–171.

Bariac, T., Deleens, E., Gerbaud, A., Andre, M., Mariotti, A., 1991. Isotopic composition (^{18}O, ^{2}H) of water vapor from transpiration; controlling conditions. Geochim. Cosmochim. Acta 55, 3391–3402.

Barnes, C.J., Allison, G.B., 1988. Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen. J. Hydrol. 100, 143–176.

Bengtsson, L., Saxena, R.K., Dressie, Z., 1987. Soil water movement estimated from isotope tracers. Hydrol. Sci. J. 32, 497–520.

Christmann, D., Sonntag, C., 1987. Groundwater evaporation from East-Saharian depressions by means of deuterium and oxygen-18 in soil moisture. Proc. Iso. Tech. Water Resour. Dev. IAEA, 189–204 (Vienna).

Climatological Data, 1996–1997. New England, ISSN 0364-5339, National Climatic Data Center.

Darling, W.G., Bath, A.H., 1988. A stable isotope study of recharge processes in the English Chalk. J. Hydrol. 101, 31–46.

Epstein, S., Mayeda, T., 1953. Variations of ^{18}O content of waters from natural sources. Geochim. Cosmochim. Acta 4, 213–224.

Gehrels, J.C., Peeters, E.M., De Vries, J.J., Dekkers, M., 1998. The mechanism of soil water movement as inferred from ^{18}O stable isotope studies. Hydrol. Sci. J. 43, 579–594.

Hesterberg, R., Siegenthaler, U., 1991. Production and stable isotopic composition of CO_2 in a soil near Bern Switzerland. Tellus 43B, 197–205.

Holder, M., Brown, K.W., Thomas, J.C., Zabcik, D., Murray, H.E., 1991. Capillary wick unsaturated zone soil pore water sampler. Soil Sci. Soc. Am. J. 55, 1195–1202.

Hsieh, J.C.C., Savin, S.M., Kelly, E.F., Chadwick, O.A., 1998a. Measurement of soil–water δ^{18}O values by direct equilibration with CO_2. Geoderma 82, 255–268.

Hsieh, J.C.C., Chadwick, O.A., Kelly, E.F., Savin, S.M., 1998b. Oxygen isotopic composition of soil water: quantifying evaporation and transpiration. Geoderma 82, 269–293.

Komor, S.C., Emerson, D.G., 1994. Movements of water, solutes, and stable isotopes in the unsaturated zones of two sand plains in the upper Midwest. Water Resour. Res. 30, 253–267.

Landon, M.K., Delin, G.N., Komor, S.C., Regan, C.P., 1999. Comparison of the stable-isotopic composition of soil water collected from suction lysimeters, wick samplers, and cores in a sandy unsaturated zone. J. Hydrol. 224, 45–54.

Mathieu, R., Bariac, T., 1996a. A numerical model for the simulation of stable isotope profiles in drying soils. J. Geophys. Res. 101, 12685–12696.

Mathieu, R., Bariac, T., 1996b. An isotopic study (^{2}H and ^{18}O) of water movements in clayey soils under a semiarid climate. Water Resour. Res. 32, 779–789.

Melayah, A., Bruckler, L., Bariac, T., 1996. Modelling the transport of water stable isotopes in unsaturated soils under natural conditions: 1. Theory. Water Resour. Res. 32, 2047–2054.

Revesz, K., Woods, P.H., 1990. A method for oxygen isotope analysis of milligram quantities of water and some of its applications. J. Hydrol. 115, 397–406.

Renshaw, C.E., Feng, X., Sinclair, K.J., Dums, R.H.R., in press. Impact of storm size on isotopically-based hydrograph separations: the role of new water in stormflow generation. J. Hydrol.

Ritsema, C.J., Dekker, L.W., 1998. Three-dimensional patterns of moisture, water repellency, bromide and pH in a sandy soil. J. Contam. Hydrol. 31, 295–313.

Ritsema, C.J., Dekker, L.W., van den Elsen, E.G.M., Oostindie, K., Steenhius, T.S., Nieber, J.L., 1997. Recurring fingered flow pathways in a water repellent sandy field soil. Hydrol. Earth Syst. Sci. 1, 777–786.

Shurbaji, A.-R.M., Phillips, F.M., 1995. A numerical model for the movement of H_2O, $H_2^{18}O$, and ^2HHO in the unsaturated zone. J. Hydrol. 171, 125–142.

Shurbaji, A.M., Phillips, F.M., Campbell, A.R., Knowlton, R.G., 1995. Application of a numerical model for simulating water flow, isotope transport, and heat transfer in the unsaturated zone. J. Hydrol. 171, 143–163.

Soil Survey Staff, 1998. Keys to Soil Taxonomy [Internet], 8th ed. U.S. Department of Agriculture, Natural Resources Conservation Service. 328 pp. [cited 2003 May 10]. Available from: http://soils.usda.gov/classification/main.htm.

Tang, K., Feng, X., 2001. The effect of soil hydrology on the oxygen and hydrogen isotopic compositions of plants' source water. Earth Planet. Sci. Lett. 185, 355–367.

Van Ommen, H.C., Van Genuchten, M.Th., Van der Molen, W.H., Dijksma, R., Hulshof, J., 1989. Experimental and theoretical analysis of solute transport from a diffuse source of pollution. J. Hydrol. 105, 225–251.

Vincent, M., Didon-Lescot, J.-F., Couren, M., 2001. Investigation of the hydrological processes using chemical and isotopic tracers in a small Mediterranean forested catchment during autumn recharge. J. Hydrol. 247, 215–229.

Yapp, C.J., Epstein, S., 1982. A re-examination of cellulose carbon-bound hydrogen δD measurements and some factors affecting plant–water D/H relationships. Geochim. Cosmochim. Acta 46, 955–965.

Zimmerman, U., Ehhalt, D., Münnich, K.O., 1967. Soil–water movement and evapotranspiration: changes in the isotopic composition of the water. Proc. IAEA Symp. Isotopes Hydrol., 567–585.