Stable Isotope Geochemistry: A Tribute to Samuel Epstein
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Stable isotopic composition of waters in a small Piedmont watershed

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Abstract—The oxygen isotopic compositions of rainfall, soil water, groundwater, and streamflow were measured over a one-year period from 1988–1989 at a 23 hectare forested watershed in the Georgia Piedmont. Rainfall was collected at an open area within the watershed and soil water was collected using zero tension and tension lysimeters from four different 5 m^2 plots. Groundwater was collected from two wells; streamflow samples were collected from two flumes on a perennial stream draining the watershed. During this period, the isotopic composition of the rainfall was quite variable; individual rainfall events had $\delta^{18}O$ values varying up to 11 per mil and the volume weighted monthly averages ranged from −1.2 in summer to −7.1 per mil in winter. Significant isotopic dampening of the infiltrating rainfall occurred as shallow as 30 cm in the soil. At greater depths (60 and 120 cm), homogenization was even more complete. This homogenization process occurred as downwardly percolating rainfall exchanged isotopically with a much larger volume of more tightly bound, relatively immobile water in the soil matrix. This process is most apparent with the zero tension lysimeter data, which have $\delta^{18}O$ values intermediate between rain water and the soil matrix water as sampled by the tension lysimeters. During the winter of 1988 when soil moisture was high, these soil waters were similar isotopically to groundwater, which remained isotopically uniform over the year. This suggests that most groundwater recharge occurs only during this (wet) period. The $\delta^{18}O$ of the baseflow in the perennial stream is also uniform, but slightly ^{18}O-enriched compared to groundwater adjacent to the stream channel. This difference is likely due to discharge of evaporated waters from an upstream pond. ^{18}O-enrichment by evaporation was very evident in a downstream pond.

INTRODUCTION

A NUMBER OF investigators have used naturally occurring tracers, such as the stable isotopic composition of rainfall, to evaluate the relationship between rainfall, runoff, and groundwater in small forested watersheds (*e.g.*, FRITZ *et al.*, 1976; SKLASH *et al.*, 1976; KENNEDY *et al.*, 1986; DEWALLE *et al.*, 1988; MCDONNELL *et al.*, 1990). These studies assume that the isotopic signature of the various hydrologic components such as rainfall, soil water in different horizons, and groundwater, all of which can potentially contribute to streamflow, are distinct and remain that way so that their relative contributions can be determined from streamflow using simple mixing models. Most studies, however, have not examined the assumption that the isotopic signatures of these various hydrologic components are distinct and remain identifiable.

The study presented here was designed to monitor the stable isotopic composition of rainfall and waters from upper parts of the unsaturated zone, saturated zone, and the nearby fluvial system over a period of one year. It was undertaken in a small loblolly pine watershed within the N.E. Georgia Piedmont. The specific objectives of this study were to

(1) document the event and seasonal fluctuations in the isotopic compositions of rainfall that reach the ground;

(2) examine how these isotopic signals are propagated into upper parts of the soil zone;

(3) assess whether the isotopic data can be used to constrain the flow mechanisms responsible for downward movement of water through the soil;

(4) ascertain if isotopic data can define what portion of the rainfall recharges the groundwater;

(5) assess what isotopic similarities and differences exist among waters in the upper parts of the soil and the much deeper groundwaters; and

(6) determine how the isotopic composition of the groundwater and base flow of a nearby perennial stream compare.

FIELD SITE DESCRIPTION AND SAMPLING METHODS

Site description

The present study involves collection and ^{18}O-isotopic analysis of water samples within a small 23 hectare forested watershed located in the Georgia Piedmont, approximately 33 km northeast of Athens, near the town of Comer (Fig. 1). Typical slopes for the site range from 6 to 10 percent, but are steeper near the perennial stream.

Individual rainfall event samples were collected from a meteorological area within the watershed, whereas waters from upper parts of the unsaturated zone were obtained from both tension and zero tension lysimeters located within four representative, 5 m^2 instrumented plots. Also within this watershed, samples of the saturated zone were obtained from two wells. Stream samples were obtained from one H-flume located on the perennial stream upstream from a pond and downstream from the instru-

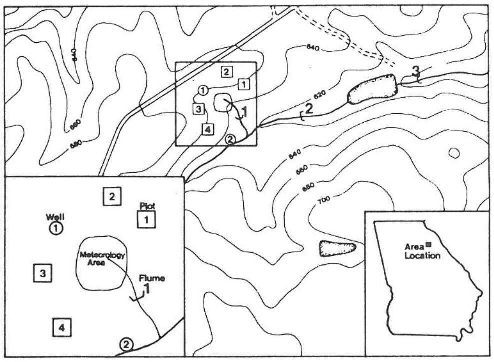

FIG. 1. Site location and experimental design.

mented plots, and one H-flume located at the outflow of the pond.

The site containing the four instrumented plots consists of a three-hectare sub-watershed drained by an ephemeral stream, which in turn drains into a first-order perennial stream that discharges, approximately 0.5 km downstream from the test site, into a 1.2 hectare man-made pond. The sub-watershed is located in a 22-year-old loblolly (*Pinus taeda*) plantation. The trees are from 12 to 15 m tall.

The four instrumented test plots (each 5 m^2 in area) were selected to represent the different geographic and topographic settings and soil types of the area. Three of the four plots (1, 2, and 4; see Fig. 1) occur within a typical, highly weathered Piedmont soil (Cecil series). Such soils form from the gneissic bedrock underlying the area. The A horizon is a reddish brown sandy clay loam, 5 to 20 cm thick, averaging about 13% clay. Below the A horizon is an A/B transition, usually 10 to 20 cm thick. The Bt horizon, a red clay and red clay loam, averages about 47% clay and extends from the base of the A/B transition to depths of 1 m. Below this is saprolite approximately 7 m deep. Plot 3 is located in a small drainage area and is atypical in that a buried sand-rich A-horizon occurs due to slumping. This sandy horizon extends more than 0.5 m deep.

Instrumentation

Each of the 5 m^2 plots shown in Fig. 1 contain the following equipment for collecting water samples:

(1) Four zero-tension lysimeters similar to that described by JORDAN (1968) were placed horizontally within the walls of open pits at depths of 30 and 60 cm below the surface. These lysimeters were designed to sample waters flowing under locally saturated conditions along preferential flow pathways within the unsaturated zone.

(2) Six 1-bar solution-cup (tension) lysimeters, placed vertically at depths of 30, 60, and 120 cm, were used to sample the more tightly bound waters in the soil matrix.

The 23 hectare watershed also contains the following sampling equipment (see Fig. 1):

(1) A meteorological weather station with a non-evaporative rainfall collector.

(2) Three flumes to measure discharge and to collect samples. Flume 1, located on an ephemeral stream close to the instrumented plots, never flowed during the study period and no samples were collected. Flume 2 is an H-flume located on the perennial stream below the site but above a 1.2 hectare pond. Flume 3 is an H-flume located at the overflow of the pond.

(3) Two wells to sample waters from the saturated zone. Well 1 is approximately 10 m deep with the lower 1.5 m screened in gneissic bedrock. The watertable in this well lies approximately 6.5 m below the surface. Well 2 is situated approximately 300 m down-gradient from well 1, six meters from the perennial stream. It is 8.5 m deep and screened in the saprolite. The watertable here is 3.2 m below the surface.

Sampling procedures

Sampling of rainfall and waters from the unsaturated zone, the saturated zone, and the fluvial system began in late January 1988 and was concluded in late January 1989. During this period, northeast Georgia experienced drought conditions that made sampling more variable than anticipated. Rainfall samples were collected as soon as possible after each event. Whenever collection was not possible before another event, samples representing the multiple event were obtained.

When conditions permitted, waters from the unsaturated zone were collected weekly from the 1-bar solution cup (tension) lysimeters located in the test plots. During most of the year, weekly sampling from the lysimeters was not possible because of low soil moisture. Only during February, March, and part of April 1988, and late January 1989, was the soil moisture consistently high enough to permit weekly sampling. During other periods, sampling was only possible after large storm events. To collect samples from the tension lysimeters, a manual pump was used to apply a partial vacuum (approximately 0.6 bar). About 48 hours later, 5 to 40 ml of water was obtained and placed in air-tight glass bottles. Tests conducted on the suction lysimeters demonstrated that no measurable isotopic changes occurred to the water during movement through the porous cup or while it was standing in the partially evacuated lysimeters (FEILD, 1990).

The two observation wells were also sampled weekly. Sampling protocol was to bail three times the well volume, then allow the well to return to its pre-bailed levels. After recovery, the wells were sampled with a bailer. This procedure follows ENVIRONMENTAL PROTECTION AGENCY (1986) guidelines for well sampling. Samples were stored in air-tight bottles.

Stream samples were collected as grab samples from the outlets of flumes 2 and 3 and stored in air-tight bottles.

Sample analysis

Three hundred and fifty five samples were analyzed for $\delta^{18}O$, and these are reported in per mil relative to SMOW. The complete data set is reported by KETCHAM (1989). The CO_2 equilibration technique described by EPSTEIN and MAYEDA (1953) was used in preparation of samples for oxygen isotopic analysis. Isotopic analyses were performed with a Finnigan MAT, model delta E isotope ratio mass spectrometer.

WEATHER PATTERNS, 1983–1989

The isotopic composition of waters in the subsurface reflects the rainfall from the past as well as

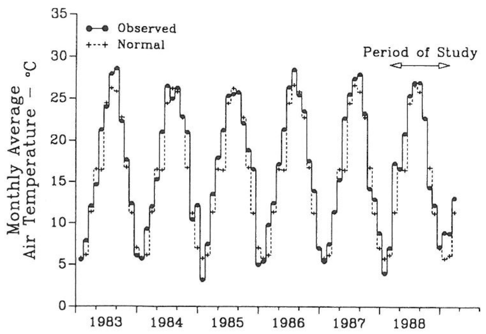

FIG. 2. Monthly average air temperatures (observed) for the period 1983 to 1989 at Athens, Georgia, compared to long-term average (normal) monthly temperatures.

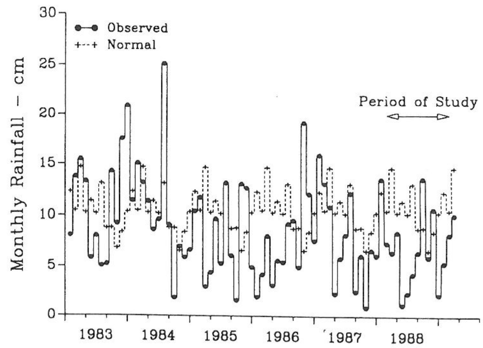

FIG. 3. Monthly average rainfall (observed) for the period 1983 to 1989 at Athens, Georgia, compared to long-term average (normal) monthly rainfall.

the present, and thus it is useful to examine the weather conditions several years prior to and during the time of the study.

Monthly average air temperature data from the closest NOAA weather station in Athens, Georgia (33 km away) is displayed in Fig. 2. For the years prior to this study (1983–1987), monthly average temperatures were from 1 to 6°C above normal. This trend continued through the study period. Of particular importance to this study is the fact that during the last week of December 1988, and extending into February 1989, an unusual shift in the jet stream caused near record high temperatures for most of the southeastern United States. These anomalous temperatures are not evident in Fig. 2 for the month of December 1988, because temperatures for the first part of the month were below normal. The anomalously high average monthly temperatures for January and February 1989 are very apparent in Fig. 2.

Because $\delta^{18}O$ values of rainfall are dependent upon temperature (*e.g.*, YURTSEVER and GAT, 1981), these unusually warm air temperatures almost certainly account for the departure from the normal seasonal isotopic rainfall trends discussed below and shown in Fig. 4.

Rainfall volumes for the period 1983 through 1987 were above average in 1983 and most of 1984 and well below average from late 1984 onward (Fig. 3). In 1983, the yearly rainfall volume was 9.93 cm above normal (50.1 cm). The following four years (1984 through 1987), however, were below normal by 0.8, 12.3, 35.9, and 36.3 cm, respectively. For the study period, monthly rain volumes were 44.9 cm below normal, the lowest within the six-year period. In particular, the months of May, June, and December were extremely dry, having rainfall volumes of 24, 39, and 5%, respectively, below normal. The small amount of rainfall during the whole 1988–89 winter period caused recharge to groundwater to be abnormally low. Normally, recharge below the root zone occurs during winter because of low evapotranspiration rates. This study was conducted during a period of abnormal weather conditions, and thus some of the results observed in this report may be atypical.

DISCUSSION OF ISOTOPIC DATA

Rainfall

Isotopic data and volumes for individual rainfall events are presented in Fig. 4. Also shown are the monthly weighted averages calculated using the formula given by YURTSEVER and GAT (1981):

$$WA = \frac{\Sigma\,(V*\delta)}{\Sigma\,(V)} \qquad (1)$$

where

WA = monthly weighted average
V = volume of rainfall from a single event
δ = isotopic value for a single rainfall event.

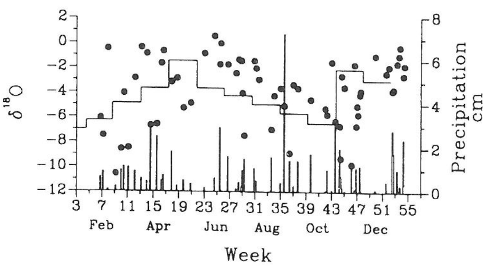

FIG. 4. Oxygen isotopic composition of individual rainfall events (dots), their volumes (spikes), and the volume weighted monthly $\delta^{18}O$ values (line).

As Fig. 4 shows, the $\delta^{18}O$ values of the 64 individual rainfall events are quite erratic, although as a general rule relatively large events are more $\delta^{18}O$ depleted than smaller rainfalls (KETCHAM, 1989).

The monthly weighted average rainfall data shown in Fig. 4 display the typical winter-summer cyclic isotopic variation observed in many continental localities (*e.g.*, GAT and DANSGAARD, 1972), although the later part of the study period (late December 1988 through February 1989) is anomalously ^{18}O-enriched. This ^{18}O-enrichment was almost certainly caused by the abnormally warm air temperatures in the southeastern U.S.A. during this period.

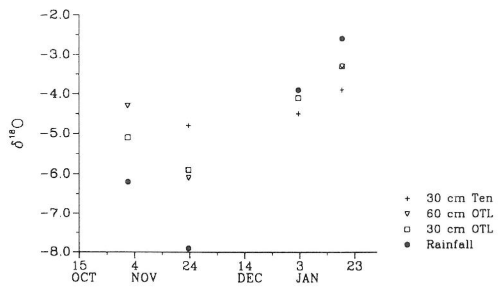

FIG. 5. $\delta^{18}O$ values of waters from zero tension lysimeters (OTL), rainfall events, and tension lysimeters (Ten).

Waters in the forest soil

Zero tension lysimeters. Four zero tension lysimeters were installed in each of the pits (two at 30 cm and two at 60 cm) at each of the plots in July 1988. These lysimeters collect water flowing rapidly through the unsaturated zone along open pathways such as root-soil interfaces, cracks, faunal tunnels, or other zones of extremely high hydraulic conductivity. If these pathways become active, it usually occurs only during large (>2 cm) rainfall events.

Soil moisture during the period after installation was generally low (MILLER, 1989) and sample collection was infrequent. Relatively short period rainfall events of 2.5 cm or more produced samples in some of the zero tension lysimeters within 24 hours of the event. Of the 16 zero tension lysimeters installed, only five produced samples. These five lysimeters were in contact with tree roots. It can probably be assumed that they collected water that flowed along soil/root interfaces.

In all four cases studied, the waters from the zero tension lysimeters differed isotopically from the rainfall event that produced the flow (see Fig. 5). In three instances (November 23, 1988, and January 2 and 18, 1989), the $\delta^{18}O$ values of the waters collected by the zero tension lysimeters were intermediate between the rainfall and waters collected from the tension lysimeters. On November 1, 1988, soil moisture was too low to obtain water from the tension lysimeters. On November 23, 1988, the rainwater $\delta^{18}O$ values were depleted relative to the waters in the zero tension lysimeters. For January 2 and 18, 1989, the $\delta^{18}O$ values of the rainfall were enriched compared to water collected in zero tension lysimeters. The direction of isotopic change in waters collected by the zero tension lysimeters indicates that mixing must occur between rain water flowing along preferential flow paths and the water in the soil matrix. This soil matrix water is probably more tightly bound and probably relatively immobile. Our results indicate that approximately equal proportions of these two "types" of waters underwent mixing.

Because large volumes of water are moving to depth quickly, it might be inferred that macropore flow (BEVAN and GERMANN, 1982) is occurring. However, true macropore flow is a turbulent process with little contact between water in the macropores and water in the soil matrix (SKOPP, 1981). If true closed-system macropore flow existed during infiltration, the $\delta^{18}O$ value of the rain water should not change its isotopic composition upon reaching the zero tension lysimeters at depth. However, our studies clearly indicate that mixing does occur, implying that little if any classic macropore flow occurs in the structured soils of the Piedmont.

Tension lysimeters. Tension lysimeters are designed to sample soil water bound less tightly than about 0.6 bar. Such waters may not be directly associated with any specific rainfall event. It is not well understood what the exact spatial extent is of the waters that tension lysimeters actually sample because the partial vacuum applied to the lysimeter permits all of the less strongly bound water of the soil matrix in the vicinity of the porous cup to flow into the lysimeter. Because mixing can occur between this water and the more tightly bound water during movement to and through the cup, any precise understanding of the water in the soil matrix cannot be made by this method of sampling. Clearly, it is possible that a water sample collected by a tension lysimeter may not be the same as the bulk water in the soil matrix. To overcome this problem, many investigators (*e.g.*, BARNES and ALLISON, 1988) extract all of the water in the soil by vacuum distillation or some other technique. This approach, however, may not provide water samples that are hydrologically important because a substantial portion of moisture in a clay-rich soil is so tightly bound within and between fine-grained clay particles as to be almost completely immobile. For these soils, for example, the water bound more tightly than that which will be driven off by heating the soil to 105°C (H_2O^+) is as much as 4 wt%. The approach used in this study to sample the unsaturated zone with tension lysimeters may actually be the best method for studying the hydrologically and botanically important water. A significant portion of the soil water is more tightly bound than the wilting point and is unavailable to plants in the clay-rich Piedmont soils (PERKINS, 1987).

Data from individual plots

For a given depth, there is considerable inter-plot variability in the isotopic composition of waters obtained from the tension lysimeters (see Fig. 6). The magnitude of this variability diminishes with depth, as is evident by comparison between waters from 30 cm (Fig. 6A) with those at 120 cm (Fig. 6C). It is also clear that the smallest isotopic variation among the different plots at any depth occurs during weeks 4 through 12, and the greatest variation occurs during weeks 48 through 52. Further, at 30 cm depth, plot 4 samples are almost invariably the most ^{18}O-enriched, whereas samples from plot 3 are the most ^{18}O-depleted.

Soil moisture was too low to collect soil water samples with suction lysimeters for much of the study period. After March, samples could not be regularly collected until the following December. In September soil moisture was near the threshold of the ability of the lysimeters to collect water, and some lysimeters yielded samples. Soil texture differences between plots caused marked soil moisture differences. Plot 3, for example, which is sandy to 60 cm, was always drier and yielded less sample. The other three plots had more typical Piedmont soils with significant amounts of clay below 40 cm. These plots were moister than plot 3. The high clay content causes the soil to have a higher porosity and relatively low permeability. This low permeability inhibits water movement and tends to immobilize relatively large water volumes. In contrast, sandy soils are more permeable and contain smaller amounts of more tightly bound water.

The isotopic data obtained from the tension lysimeters at 30 cm are consistent with the differing amounts of soil moisture observed in the soil. In the clay-rich soil underlying plot 4, mixing between a more abundant, largely immobile, ^{18}O-enriched water and an ^{18}O-depleted infiltrating water can account for the tension lysimeter waters from this plot generally being the most ^{18}O enriched (see Fig. 6).

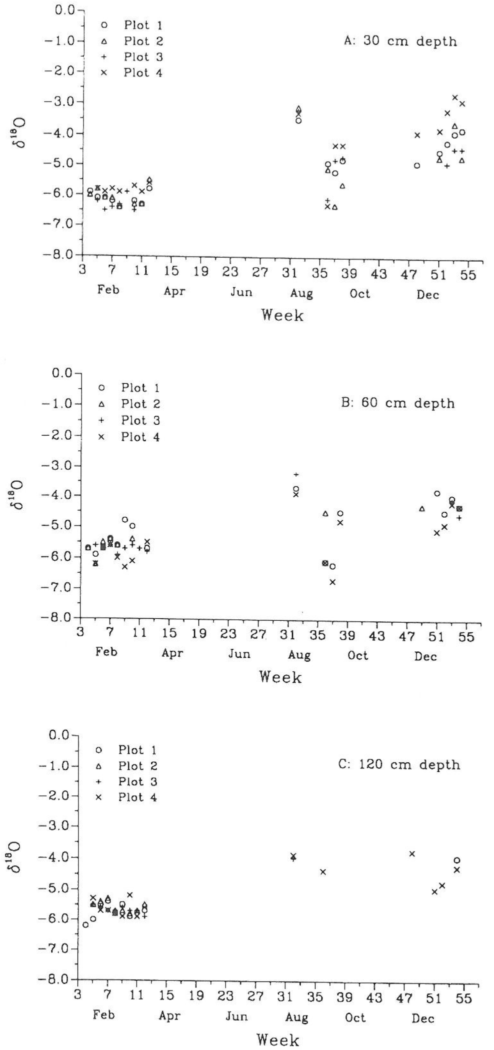

FIG. 6. Comparison of $\delta^{18}O$ values of waters from tension lysimeters from individual plots at 30 cm (A), 60 cm (B), and 120 cm (C) depths.

In the sand-rich soils at plot 3, which contain less tightly bound (largely immobile) water, it might be expected that the $\delta^{18}O$ values of waters collected by the tension lysimeters isotopically would be similar to the infiltrating rain. This is what is observed when comparing the rainfall data for weeks 4–12 (Fig. 4) with lysimeter waters for this same period (Fig. 6).

Data averaged for four plots

Because the four plots are representative of the various soil types within the watershed, it is meaningful to average the data from the individual plots to obtain some insight on the behavior of water movement through the soil in the whole watershed. These data are presented in Fig. 7. Early in the study, from January 16 until March 25, 1988 (weeks 3 through 13), when the soil moisture was at or near field capacity, the average isotopic composition of water from the 30, 60, and 120 cm lysimeters exhibited a narrow range despite the extreme isotopic variability of the rain events (see Fig. 4). The weighted average rainfall $\delta^{18}O$ value during this period was −6.4. However, the four plot average $\delta^{18}O$ values were no more negative than −6.2 and only a few waters at the 30 cm depth were this depleted in ^{18}O. During this period, the $\delta^{18}O$ values at 60 and 120 cm remained relatively uniform at −5.7. Thus, the overall trend was for infiltrating waters to become more ^{18}O enriched with depth. At no time was there an isotopically distinct front from any rainfall event that would indicate a piston flow process such as observed in other studies (ZIMMERMANN *et al.*, 1967; SHARMA and HUGHES, 1985; BARNES and ALLISON, 1988).

These results suggest that some mechanism was buffering the isotopic composition of the water as it percolated through the soil. This process occurs to a large extent before the infiltrating water reached 30 cm. The most obvious explanation for this buffering process is the same one advanced to explain the zero tension data: that infiltrating rainfall mixes with a much larger volume of less mobile water in the soil matrix. This less mobile soil matrix water appears to be relatively ^{18}O enriched during the early winter (weeks 3 to 13) because the tension lysimeters collected waters of about −6.2 per mil, whereas average weighted rainfall during this period was more depleted (−6.7 per mil).

These ^{18}O-enriched, less mobile soil matrix waters might be inherited from the previous summer-fall's rainfall input which was almost certainly more ^{18}O enriched, perhaps augmented by evaporation processes in upper parts of the soil (*e.g.*, BARNES and ALLISON, 1988).

For the latter part of the study period, from late March 1988 and onward, evapotranspiration rates generally exceeded infiltration and few samples were collected from the lysimeters. Of all the samples obtained during this period, only a small percentage of water reached 120 cm deep. Almost certainly little, if any, of this summer rainfall ever reached the saturated zone. During this period, when the monthly weighted rainfall $\delta^{18}O$ values were relatively ^{18}O enriched (most were more positive than −5.7 per mil), the waters collected by the tension lysimeters were in most instances more ^{18}O depleted with depth (*e.g.*, see data for weeks 32, 36, 38, 52, 53, 54 in Fig. 7). This is the opposite of what is observed during weeks 3 to 13 when soil moisture was near field capacity. This pattern of enrichment or depletion is consistent between the tension lysimeters within the various plots as well as in the zero-tension lysimeters discussed previously. It appears that during the latter part of the study period, infiltrating rainfall may have mixed with a more ^{18}O-depleted, less-mobile water in the soil matrix. The apparent pattern of ^{18}O-enriched water occurring in the soil matrix during the early 1988 winter period and a more ^{18}O-depleted water residing in soil matrix in summertime is out of phase with the normal cyclic isotopic rainfall pattern reaching the surface. This implies that some or perhaps much of the water in the soil matrix may remain isolated or largely unexchanged isotopically for long periods time, perhaps many months or more.

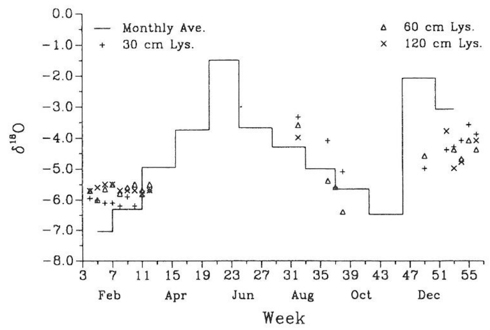

FIG. 7. Comparison of four plot average $\delta^{18}O$ values of waters from tension lysimeters at 30, 60, and 120 cm depths to volume weighted monthly rainfall (line).

In short, it appears that isotopic exchange almost certainly occurs between infiltrating water and less mobile water in the soil matrix. In the clay-rich Bt horizon of the soil, which lies 20 to 40 cm below the surface, this less mobile soil matrix water may be volumetrically quite significant. GVIRTZMAN and MAGARITZ (1986), for example, suggest that up to 55% of the total amount of water in a loess-type soil is "immobile." The clay content of their loess soil is lower than the clay content of a typical Piedmont soil. With clay-rich soils, it is not difficult to see how "new" infiltrating water very quickly takes on the isotopic characteristics of the less mobile "old" water in the soil matrix.

Waters in the saturated zone

Waters from the saturated zone nearest the test plots (well 1) had a nearly constant $\delta^{18}O$ value $= -5.7 \pm 0.1$ throughout the sampling period (Fig. 8). This isotopic composition is virtually the same as that observed in the 60 and 120 cm tension ly-

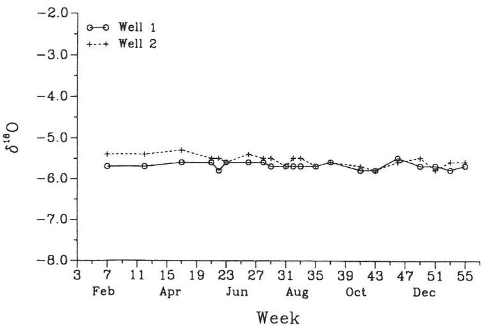

FIG. 8. $\delta^{18}O$ values of groundwaters from two wells.

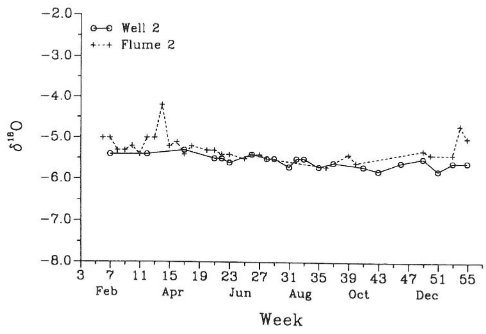

FIG. 9. Comparison of the $\delta^{18}O$ values of the perennial stream sampled at Flume 2 and groundwater at Well 2.

simeters during the first two months of the study period (weeks 4 to 13; see Fig. 7). Waters collected from the tension lysimeters during the remainder of the study period, from April 1988 and onward, however, are not at all similar to waters in the saturated zone. These observations are consistent with the hypothesis that only winter rainfall, and likely only that from "normal" winters when temperatures are seasonal, ever reaches the watertable. This winter recharge occurs because evapotranspiration is high during the rest of the year; very little summer rainfall moves through the soil, even to depths of 120 cm or more. Any significant contribution of summer rainfall to the groundwater should produce more isotopic variation in waters from the saturated zone than we see.

The saturated zone $\delta^{18}O$ values from well 2 near the perennial stream showed slightly more variation than in well 1 (see Fig. 8). This difference may be because this well is shallower and/or closer to the perennial stream, making it more likely to receive waters of differing isotopic compositions from various upslope areas.

Waters from the fluvial system

During base flow, samples from the perennial stream sampled at flume 2 were somewhat ^{18}O-enriched (up to 0.5 per mil) compared to water from well 2 (Fig. 9). This type of enrichment could be explained by evaporation from a lake located approximately 1 km upstream from flume 2 (not shown in Fig. 1). Water discharging from this lake would then have mixed with groundwater emerging in the stream channel to produce the observed isotopic compositions of the base flow in the perennial stream. The ^{18}O-enriched "spikes" in the streamflow pattern shown in Fig. 9 appear to reflect direct channel precipitation of relatively high $^{18}O/^{16}O$ rainfall and/or somewhat larger amounts of discharge of an upstream pond.

The $\delta^{18}O$ values of the water collected from the spillway at flume 3 show a significant ^{18}O enrichment during the period from February to June 1988 (after which flow over the spillway ceased) compared to the $^{18}O/^{16}O$ of waters from the perennial stream feeding it (see Fig. 10). This trend almost certainly reflects evaporation from the lake. Short-term excursions from these patterns at both flumes 2 and 3 reflect input from large rainfall events (>1.0 cm) directly into the stream channel and pond. During weeks 8, 17, and 18, large volume, ^{18}O-depleted rainfall events produced sharp ^{18}O-depletion trends of the lake waters. During weeks 14 and 19, two smaller, ^{18}O-enriched rain events produced a positive ^{18}O peak to the patterns for the perennial stream and the lake.

SUMMARY AND CONCLUSIONS

These studies reveal that despite the large and erratic isotopic variations (up to 11 per mil for oxygen) of individual rainfalls and a seasonal weighted

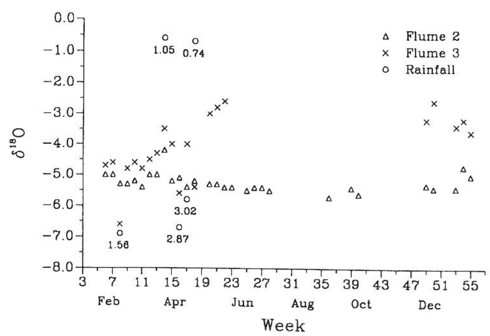

FIG. 10. Comparison of the $\delta^{18}O$ values for the perennial stream sampled at Flume 2 with values sampled at Flume 3, immediately downstream from a 1.2 hectare pond, and selected rainfall events. Rainfall volumes (cm) are printed below each rainfall symbol.

monthly variation ranging from −1.2 per mil in summer to −7.1 in winter, the variable isotopic composition of this rainfall becomes largely homogenized at depths as shallow as 30 cm in the soil. The homogenization process is more complete at depths of 60 cm and at 120 cm. This homogenization or buffering process is especially evident during the first two and one-half months of the study period, from January to March 1988, when soil moisture was greatest.

At times of ground water recharge during "normal" winters when evapotranspiration rates are minimal, these unsaturated zone waters are very similar isotopically to the waters in the saturated zone some ten meters deeper. This suggests that winter rainfall is largely responsible for recharging the watertable in a forested watershed in the southern Piedmont.

The homogenization or buffering process occurring within the upper parts of the soil almost certainly involves extensive mixing between rainfall infiltrating the ground and a much larger volume of water already present in the soil. This mixing process is most clearly demonstrated in instances where water moves rapidly through the soil along preferential pathways and can be collected by zero tension lysimeters. Such infiltrating waters partially exchange with isotopically different waters that are more tightly bound within the soil matrix and can only be collected by tension lysimeters.

The isotopic compositions of these soil matrix waters in four representative 5 m^2 plots in the watershed are themselves quite variable (ranging from 0.5 to 2 per mil) at any given depth. These differences appear to be related to the amount of soil moisture, which is in turn controlled by variations in the size fractions of material in the soil. Clay-rich soils have a greater soil moisture content than more sand-rich soil. We find that the more clay-rich soils, which contain a greater amount of this less mobile water, seem to buffer the isotopic composition of the infiltrating water to the greatest extent. In contrast, infiltrating waters appear to be buffered less in the more sand-rich soils.

The $\delta^{18}O$ values of waters in the saturated zone and the base flow of the perennial stream draining the watershed were observed to be quite uniform during the year-long sampling period. However, the stream samples were on average 0.5 per mil enriched in ^{18}O compared to waters from the saturated zone. This difference indicates that most of the stream water originates from groundwaters flowing into the channel, perhaps mixing with water discharging from an upstream pond undergoing evaporation. Waters from the outflow of a downstream pond in the watershed show significant ^{18}O-enrichment due to summertime evaporation. Both the downstream pond and stream showed short-term isotopic fluctuations due to direct channel precipitation.

The results presented here may in some cases invalidate mixing models that attempt to identify the various components contributing to stormflow. Such models generally assign distinct isotopic compositions to various components of the hydrologic cycle. Two-component models, used for example by FRITZ *et al.* (1976), SKLASH *et al.* (1976), KENNEDY *et al.* (1986), and MCDONNELL *et al.* (1990), distinguish "old" water (the total water in the ground) and "new" water (that added during any rainfall event). Three-component models (*e.g.*, DEWALLE *et al.*, 1988) assign distinct isotopic compositions to groundwater, soil water, and channel precipitation. Our results indicate that most "new" water very quickly loses its isotopic identity when percolating through the upper parts of the soil, and thus the volumetric significance of this "new" water becomes questionable. Three-component models that distinguish soil water from groundwater have little meaning since much of the water in soil appears to be isotopically indistinguishable from groundwater.

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