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Effects of evaporative enrichment on the stable isotope hydrology of a central Florida (USA) river

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Abstract:

The $\delta^{18}O$ characteristics of water masses contributing to flow in the Econlockhatchee River basin, a subtropical low-gradient watershed in central Florida, were monitored to assess the potential for applying hydrograph separation models in the watershed. Daily sampling for a 2-month period in autumn 1992 revealed ranges in precipitation of $-6{\cdot}64$ to $-0{\cdot}17$‰, in surficial groundwater of $-3{\cdot}29$ to $-2{\cdot}90$‰, and in river water of $-2{\cdot}68$ to $-1{\cdot}41$‰. Results indicated that river $\delta^{18}O$ was consistently more enriched than either groundwater or precipitation by about 1‰, prompting the hypothesis that evaporative enrichment significantly altered the $\delta^{18}O$ of river water. Additional monitoring and mass-balance modelling of the entire basin (620 km^2) and a subcatchment (70 km^2) showed that evaporative effects could account for the observed enrichment. Although some enrichment occurred in headwater swamps and wetlands, the field data and modelling results supported the hypothesis that evaporation from the river channel significantly altered the $\delta^{18}O$ of river water. Enrichment elsewhere in the hydrological cycle, such as during throughfall or temporary storage in wetlands or stormwater management ponds, may have contributed to the observed signal of evaporation, but could not be distinguished from headwater or river evaporation. It appears that a sufficient isotopic signal exists in central Florida precipitation to apply hydrograph separation models, but that evaporative isotopic enrichment should be included as a modelling element. Copyright © 2000 John Wiley & Sons, Ltd.

KEY WORDS oxygen stable isotopes; hydrograph separation; evaporative enrichment; recession analysis

INTRODUCTION

The stable isotopes of water, $\delta^{18}O$ and δD, have been used extensively as conservative tracers in hydrological studies to identify sources of flow in rivers over the course of storm event hydrographs (e.g., Kennedy *et al.*, 1986; Sklash, 1990; Buttle, 1994). Most studies have been conducted in temperate climates where the environmental signal, or storm-to-storm variability, in the stable isotopes of precipitation is strong enough to provide statistically reliable data to support mixing models. One example is the widely used two-component hydrograph separation model (Buttle, 1994), which has been implemented in well-known studies of catchments in New Zealand (e.g. Bonnell *et al.*, 1990; Stewart and McDonnell, 1991) and on the Canadian Shield (e.g. Sklash *et al.*, 1976; Wels *et al.*, 1991). Notably absent, however, are data on the isotope hydrology of subtropical, low-gradient watersheds (Buttle, 1994). The only meteoric water-line data for Florida are provided by Swart *et al.* (1989) in an isotopic study of Florida Bay. Meyers *et al.* (1993) investigated Holocene water movement through the surficial and Biscayne aquifers in south Florida and reported that aquifer waters had undergone significant evaporation. Although studies of isotope hydrology have been conducted in the Piedmont of Georgia (Wenner *et al.*, 1991; Rose, 1996), climatic and geological conditions

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in those basins more resembled those of temperate, steep catchments rather than subtropical, low-gradient catchments.

As part of a larger study undertaken to understand the hydrological balance of the Econlockhatchee River in east-central Florida, the $\delta^{18}O$ characteristics of water masses contributing to river flow were evaluated. One goal of the study was to determine whether sufficient variability exists in the $\delta^{18}O$ of central Florida precipitation to apply hydrograph separation models. Daily $\delta^{18}O$ data collected at eight stations in the Econlockhatchee River in the late summer and autumn of 1992 appeared to show that evaporative enrichment was strongly altering river $\delta^{18}O$ during a period of recession. Among the literature on the isotope hydrology of rivers, only Sklash *et al.* (1976) observed evaporative enrichment to be an important component of the isotope mass balance. Presumably evaporation does not alter the $\delta^{18}O$ of river water in other catchment studies because of lower retention times and both lower air temperature and humidity. Because of the lack of precedent in the literature for a recognizable evaporation signal in river water, the primary objective of this study was to evaluate quantitatively the potential for evaporation to alter the isotopic content of river water in the Econlockhatchee basin.

Site description

The Econlockhatchee River basin upstream from station SH (Figure 1) drains approximately 620 km^2 in east-central Florida, and flows northward to the St John's River. The main stem, the Big Econlockhatchee River, has a channel length of approximately 60 km. A major subcatchment, the Little Econlockhatchee River, drains 180 km^2, and has a channel length of approximately 34 km with a total elevation change of about 21 m (Figure 2). The headwaters of the Big Econlockhatchee River are an undisturbed wetland known as the Econlockhatchee Swamp, at an elevation of about 20 m above sea level. The riparian zone of the Big Econlockhatchee River consists of a single meandering channel incised in a floodplain vegetated with a sparse understory; and an overstory dominated by cypress, oak and sabal palm. Almost all of the riparian zone remains undisturbed. Uplands were originally sand pine scrub and longleaf pine flatwoods, punctuated with numerous sinkhole lakes and wetlands. About 5% of the original upland vegetation exists in the Big Econlockhatchee basin, with about 230 km^2 cleared for development, consisting primarily of citrus plantation and range for cattle grazing (Wanielista *et al.*, 1992). The Little Econlockhatchee River begins at an elevation of about 23 m in suburban Orlando, Florida. The original landscape was similar to that of the Big Econlockhatchee River, but has undergone more extensive development. Portions of the riparian zone have been channelized and control structures have been installed to facilitate flood control and drainage (Miller and Miller, 1984).

The surficial aquifer system in the Econlockhatchee River basin is composed of silica sands 15 to 20 m thick, with the water table occurring from about 0·3 to 1·5 m below land surface. The surficial aquifer overlies the Hawthorne semi-confining unit, which overlies the upper Floridan aquifer (Tibbals, 1990). Hydraulic communication between the surficial and Floridan aquifers is believed to be strongly retarded by the Hawthorne layer (Wanielista *et al.*, 1992; Tibbals, 1990).

METHODS

Field sampling in September and October 1992, consisted of daily collection of precipitation at three stations, river water at eight stations, and groundwater from nine wells located at five stations (Figure 1). All water samples collected for isotopic analysis were sealed in 30 mL glass vials with inverted cone (Polyseal™) liners. Precipitation was collected at Stations WHP, CEP and FRP (Figure 1) through Nalgene™ funnels into 4 L Nalgene™ carboys. All precipitation monitoring stations were placed in open areas with no aerial obstruction. Evaporative enrichment of the collected rainfall was prevented by wrapping the carboys in aluminum foil to reflect solar radiation. Additionally rain collectors were checked within 4 h after the end of a storm event, or twice daily during longer storm events. Rain water was measured from each carboy into a graduated cylinder to compute the amounts. Monitoring wells BD1, BR1, FR1, AL1 and HR1 were installed

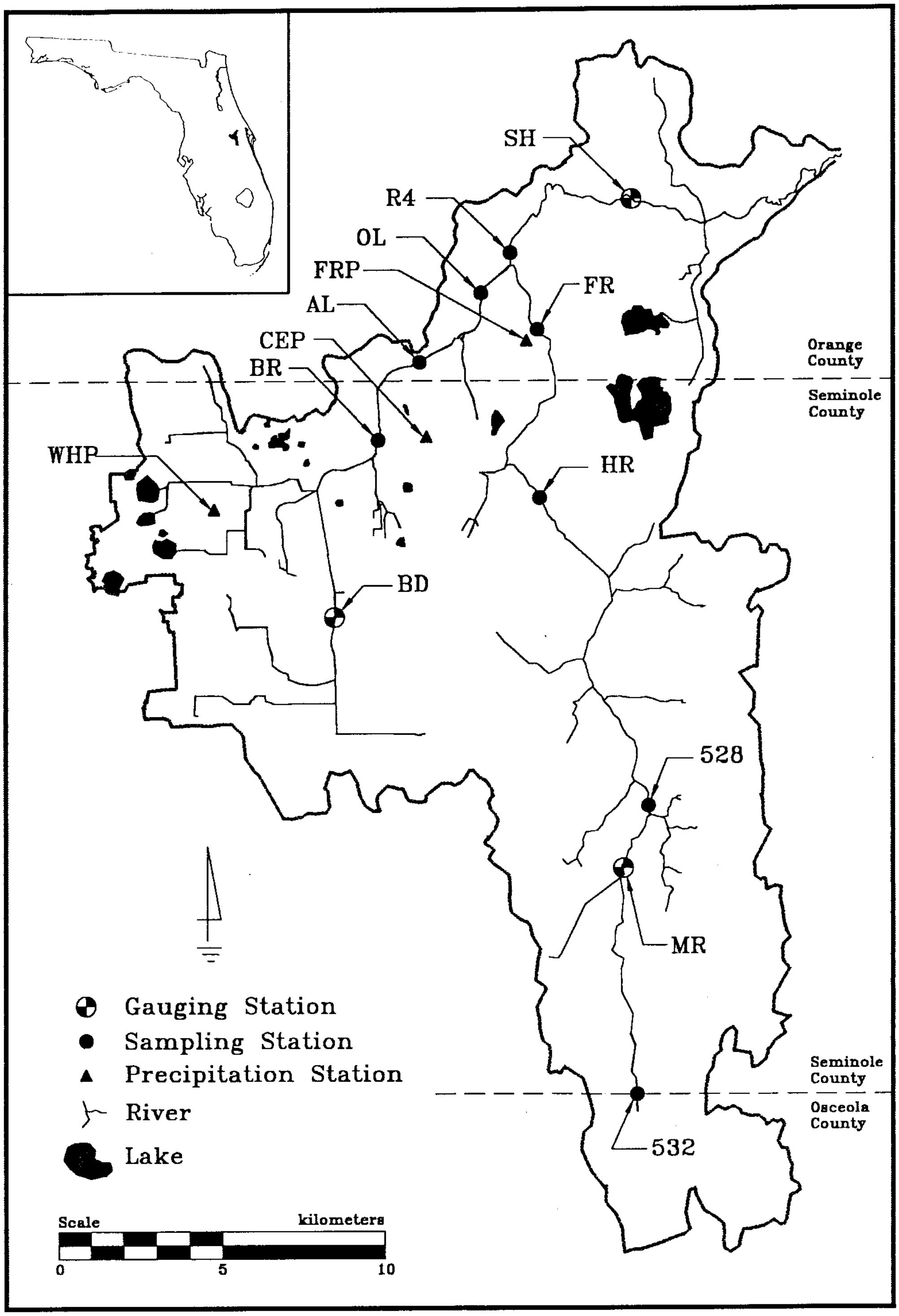

Figure 1. The Econlockhatchee River watershed in east-central Florida

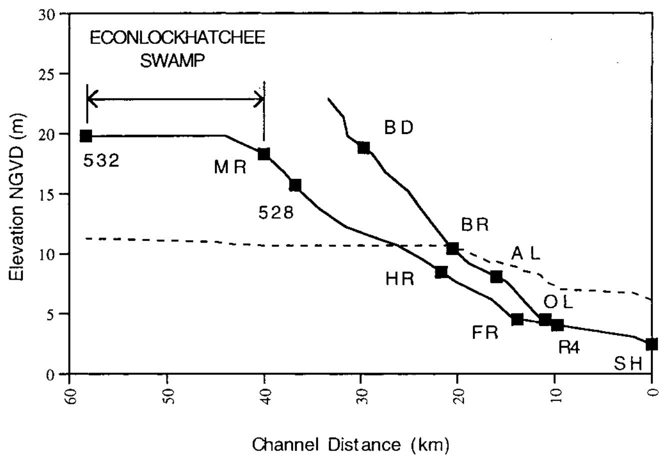

Figure 2. Channel elevations in the Big Econlockhatchee (lower solid line) and Little Econlockhatchee (upper solid line) Rivers. The potentiometric surface of the Floridan aquifer in the vicinity of the river is shown as a segmented line. Elevations are referenced to the national geodetic vertical datum (NGVD) (Sources: Wanielista *et al.*, 1992; Tibbals, 1990)

Table I. Summary of United States Geological Survey permanent gauging stations located in the Econlockhatchee River watershed (Source: USGS National Water Information System: http://water.usgs.gov)

Station name	USGS station number	Latitude	Longitude	Drainage area (km^2)
BD	02233200	28°31′29″	81°14′39″	70
MR	02233001	28°25′27″	81°07′10″	85
SH	02233500	28°40′40″	81°06′51″	620

approximately 15 m from the river shore. Monitoring wells BR2, AL2, FR2 and HR2 were installed approximately 30 m from the river shore. All wells were located near river sampling sites. Wells were installed using a hand auger and cased with 5-cm diameter Polyvinyl chloride pipe, to a depth of 3·0 m below land surface. Wells were screened in the interval 2·0 to 3·0 m below land surface with a 0·04 mm factory slotted screen. Water depth in wells was measured relative to the top of the casing using a Yellow Springs Instruments, Inc., Temperature/Level/Conductivity instrument. Levelling surveys at each site related the top of the casing of each well to staff gauges in the river, providing estimates of aquifer elevations. Wells were sampled using bailers after being purged of five casing volumes to assure that formation water was sampled. River samples were collected either from the shore or bridge deck. The United States Geological Survey (USGS) monitors permanent gauging stations at sites SH and BD (Figure 1 and Table I), and daily average river discharge data were obtained for these sites from the USGS National Water Information System (http://water.usgs.gov).

Water samples were analysed for $\delta^{18}O$ at the University of Florida Geology Department using the method of Socki *et al.* (1992). Precisely 1·5 mL of sample were injected into a 7 mL disposable serum vial containing a fixed amount (approximately 0·5 atm) of purified CO_2. Samples were then equilibrated in a shaker bath for at least 2 h at 30 °C. The CO_2 was then extracted from the vial, purified by cryonic distillation using an off-line vacuum system, and collected cryogenically in a 6 mm Pyrex break-seal tube for admission to a VG-Prism isotope-ratio mass spectrometer (IRMS). Analytical precision was generally better than 0·1‰. The reference gas used in the IRMS was generated from Carerra marble (Hodell *et al.*, 1989) and calibrated against international standards. All data are presented relative to Vienna Standard Mean Ocean Water (VSMOW; NIST, 1992). At least six laboratory working standards were analysed daily and duplicate analyses

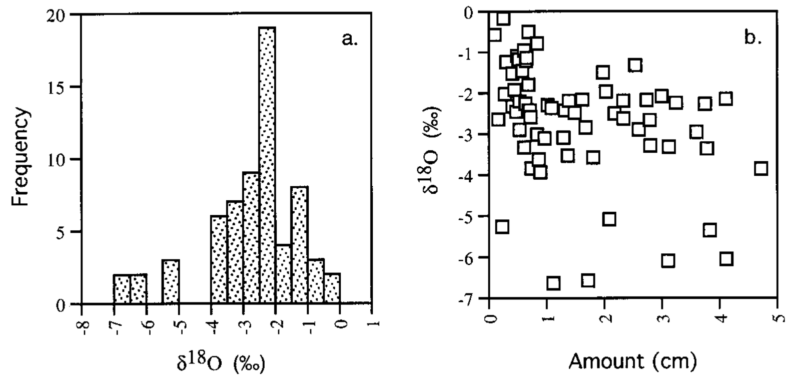

Figure 3. Precipitation data collected at stations WHP, CEP and FRP from August through to October 1992

were performed on approximately 20% of all samples and on suspected outliers. Complete calibration and quality assurance data have been summarized by Gremillion (1994).

RESULTS

Precipitation

Precipitation data collected from 19 August 1992 through to 11 October 1992 are summarized in Figure 3 and daily average precipitation amount and $\delta^{18}O$ are shown in Figure 4c. Amounts in Figure 4c are arithmetic means from three stations and $\delta^{18}O$ values are amount-weighted means. The mean $\delta^{18}O$ of all precipitation observations was $-2{\cdot}68$‰ ($n = 65$) with a standard deviation of 1·41‰. Three storm types were observed during the period of record. From the start of sampling until about 30 September, summer convective storms occurred almost every afternoon. These convective storms were typically small in area and short in duration. As a result, commonly only one or two of the three precipitation stations recorded the same event on a given day. Convective storms in August provided the most isotopically enriched precipitation, with a median $\delta^{18}O$ of $-2{\cdot}5$‰. On 2 October through to 5 October a tropical depression originating in the South Atlantic Ocean brought steady low-intensity rain to the entire watershed, amounting to 5·9 cm with an average $\delta^{18}O$ of $-2{\cdot}65$‰. After the passage of the tropical depression, two convective storms on 7 October and 9 October were followed by a frontal storm on 11 October with a relatively depleted $\delta^{18}O$ of $-6{\cdot}1$‰. A plot of rain $\delta^{18}O$ versus amount (Figure 3b) showed no systematic pattern, except that the most enriched rainfall samples were those associated with low rainfall amounts.

Groundwater

Groundwater was sampled weekly for $\delta^{18}O$. These data are summarized in Table II and Figure 4a. With the exception of the monitoring wells AL1 and AL2, surficial groundwater $\delta^{18}O$ showed little temporal and some spatial variability. Wells AL1 and AL2 (Figure 1) yielded significantly more enriched $\delta^{18}O$ than any other wells in the watershed. These wells were placed approximately 30 m down-gradient from a stormwater detention pond, which likely contained isotopically enriched water owing to evaporation. The apparent effect of the pond on the local surficial aquifer suggests a strong degree of hydraulic connection between the pond and the aquifer.

Among the remaining wells, temporal variation in $\delta^{18}O$ was below detection limits. The standard deviation for individual wells seldom exceeded the analytical precision for the $\delta^{18}O$ test (0·1‰). Distinct spatial variability was observed. The mean and standard deviation of all groundwater samples, excluding wells AL1 and AL2, was $-2{\cdot}92 \pm 0{\cdot}20$‰ ($n = 49$). Sorting the data by subwatershed, the Little Econlockhatchee stations (BD1, BR1 and BR2) showed a combined mean of $-3{\cdot}09 \pm 0{\cdot}13$‰ ($n = 21$). Big Econlockhatchee

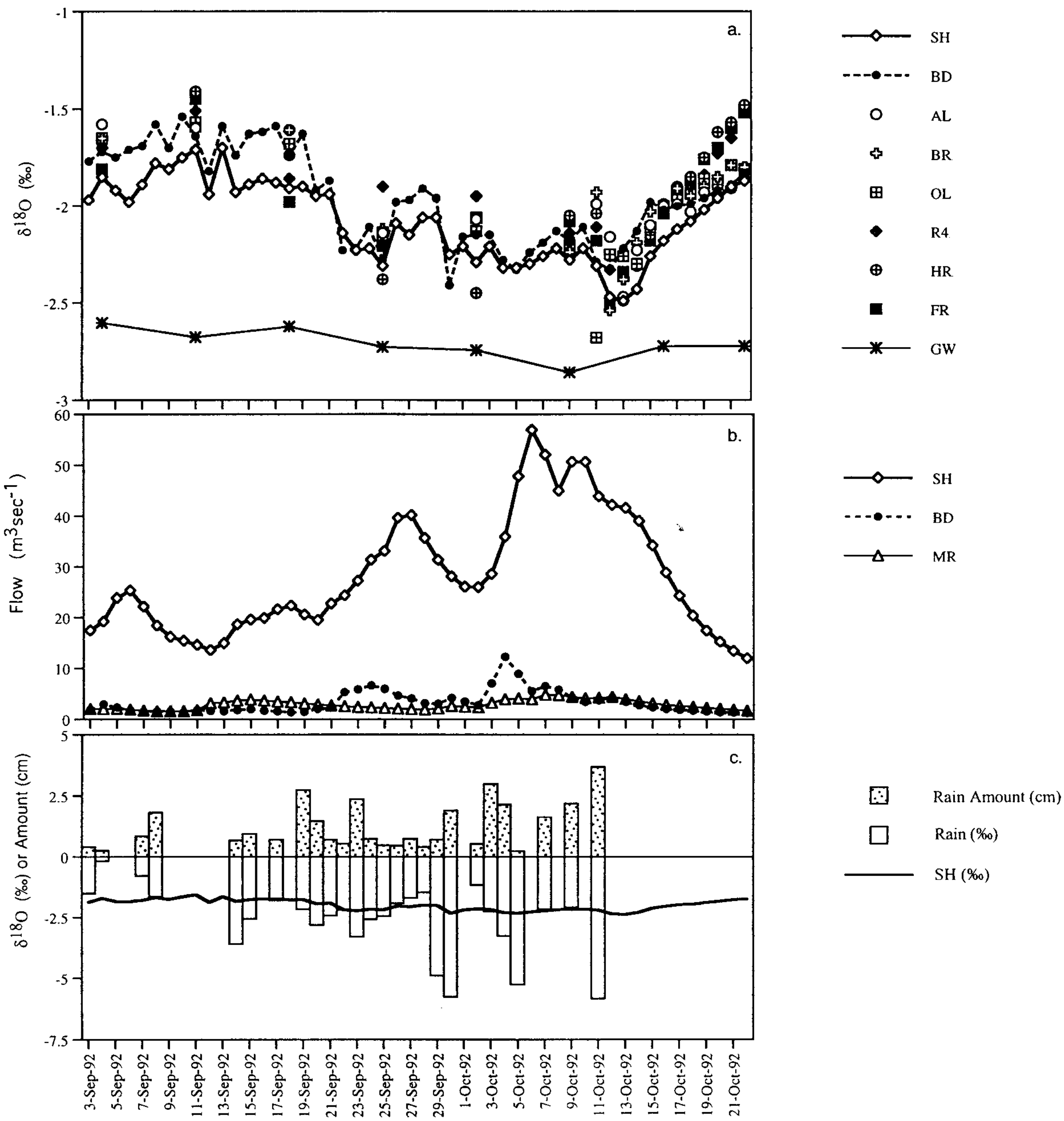

Figure 4. River and groundwater (GW) $\delta^{18}O$ (a), daily flow (b) and daily average rainfall amount and $\delta^{18}O$ (c) observed in the Econlockhatchee watershed. River $\delta^{18}O$ from station SH plotted in (a) were plotted again in (c) to show rainfall $\delta^{18}O$ relative to river conditions. Groundwater $\delta^{18}O$ was the weekly mean from all monitoring well samples

stations (FR1, FR2, HR1 and HR2) averaged $-2{\cdot}79 \pm 0{\cdot}15$‰ ($n = 28$). The Floridan aquifer was sampled from household water supply wells near stations HR and FR and averaged $-1{\cdot}71 \pm 0{\cdot}16$‰ ($n = 5$).

Water elevations were measured daily in all monitoring wells and compared with river elevations to determine hydraulic gradient. In many river systems it is believed that the near-stream surficial aquifer is recharged by the river during periods of high flow, creating bank storage, which is then released back into

Table II. Statistical summaries of $\delta^{18}O$ in the Econlockhatchee River basin from 4 September to 16 October 1992

Location	Sample	n	Mean (‰)	Standard deviation (‰)	Minimum (‰)	Maximum (‰)
Little Econlockhatchee Basin						
River	BD	50	−1·96	0·24	−2·41	−1·54
	BR	18	−1·98	0·25	−2·54	−1·61
	AL	18	−2·00	0·22	−2·47	−1·58
	OL	18	−2·01	0·28	−2·68	−1·57
Groundwater	BD1	7	−3·06	0·06	−3·14	−2·96
	BR1	7	−3·20	0·11	−3·29	−3·04
	BR2	7	−3·01	0·13	−3·27	−2·90
	AL1	7	−2·11	0·32	−2·64	−1·65
	AL2	7	−1·87	0·35	−2·41	−1·60
Big Econlockhatchee Basin						
River	HR	18	−1·94	0·34	−2·49	−1·41
	FR	17	−1·95	0·29	−2·50	−1·45
Groundwater	HR1	7	−2·87	0·09	−2·97	−2·69
	HR2	7	−2·92	0·06	−2·98	−2·80
	FR1	7	−2·78	0·06	−2·85	−2·70
	FR2	7	−2·59	0·08	−2·70	−2·45
Combined Flows						
River	R4	15	−1·94	0·25	−2·43	−1·51
	SH	50	−2·08	0·21	−2·49	−1·70

the channel at low flow (Meyboom, 1961; Todd, 1980). In such systems, the localized mechanisms of exchange between the surficial aquifer and river exert a stronger influence on near-stream hydrology than regional-scale processes, such as regional hydraulic gradients that move water through the surficial aquifer to the river channel. McKenna *et al.* (1992) analysed environmental δD to demonstrate that bank storage comprised a significant amount of recession flow in the Truckee River, Nevada. In the Econlockhatchee River, groundwater elevations observed during the 1992 study were consistently higher than the river elevation, even during storm events, indicating hydraulic gradients toward the river (Gremillion, 1994). Thus the Econlockhatchee River was gaining flow from the surficial aquifer throughout the study period and river water did not recharge the surficial aquifer.

River

River $\delta^{18}O$ was consistently more enriched than contributing water masses throughout the study period. Mean values of precipitation ($-2{\cdot}68 \pm 1{\cdot}41$‰, $n = 65$) and groundwater ($-2{\cdot}71 \pm 0{\cdot}46$‰, $n = 63$) were more enriched than river water ($-1{\cdot}99 \pm 0{\cdot}25$‰, $n = 204$) by an average of 0·7‰ during the study. The periods when river $\delta^{18}O$ approached that of rainfall or groundwater were associated with high or building flow. Plots of river $\delta^{18}O$ versus flow for the BD and SH stations (Figure 5) confirm that higher flows were associated with more depleted river $\delta^{18}O$.

Spatial variability is evident in the river (Figure 4a). Daily river $\delta^{18}O$ measured at station BD, an upstream site, was consistently more enriched than at the farthest downstream station (SH). The pattern of upstream enrichment can be observed in the weekly analyses from the other river stations. During the recession period starting on 12 October, samples from all stations were analysed for $\delta^{18}O$. All stations became more

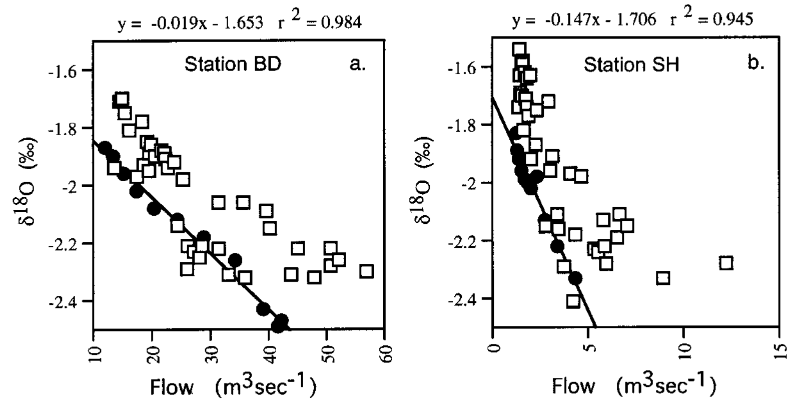

Figure 5. $\delta^{18}O$ versus flow at stations BD (a) and SH (b) from 3 September until 22 October in the Econlockhatchee basin. Recession data are shown as filled circles and pre-recession data are shown as open squares. Least-squares linear regression equations and best-fit lines for recession data are shown for each station

isotopically enriched at about the same rate during recession. Stations HR and FR became distinctly more enriched than other stations. These stations may have carried an imprint of evaporation from the Econlockhatchee Swamp, which was located at the head of that reach.

RECESSION MODELLING

Between 11 October and 23 October 1992 no storm events occurred, allowing a period of recession to be recorded. Classical hydrometric analysis of hydrograph recession has been used to determine baseflow characteristics (Meyboom, 1961; Todd, 1980; Wanielista, 1990; Tallaksen, 1995). Because no other runoff sources exist, river flow during recession represents the release of channel storage and discharge from connected aquifers. Thus it is reasonable to expect that the isotopic content of river water to approach the flow-weighted mean isotopic content of contributing aquifers during an extended period of recession. This has been an important assumption in hydrograph separation studies, because baseflow river conditions have been widely assumed to reflect groundwater tracer concentrations (Gat and Tzur, 1967). Several investigators have verified this assumption by comparing aquifer and river isotopic concentrations (Hooper and Shoemaker, 1986; Kennedy *et al.*, 1986; Hill and Waddington, 1993).

In the Econlockhatchee basin, surficial aquifer $\delta^{18}O$ ranged from about $-3{\cdot}2$ to $-2{\cdot}5$‰. For the 4-week period preceding the onset of recession, most rainfall events were more depleted than $-2{\cdot}5$‰. At peak flow, river $\delta^{18}O$ was about $-2{\cdot}2$‰ at all stations (Figure 5). Paradoxically, during the recession period that followed, river $\delta^{18}O$ became progressively more enriched with decreasing flow, even though the apparent contributing water masses were more depleted. Thus, some factor provided a constant source of isotopic enrichment to the river.

Water masses potentially influencing river flow during recession were the surficial aquifer, the Floridan aquifer, and channel evaporation. Water-elevation measurements from near-stream monitoring wells indicated hydraulic gradients toward the river in the surficial aquifer, even during high-flow periods. Thus the river was always gaining, so bank storage and subsequent release of river water in the surficial aquifer was not a likely explanation for $\delta^{18}O$ enrichment during recession. Monitoring wells were placed in the immediate near-stream zone with the specific intention of sampling formation water contributing to flow. It is possible that the wells were not screened deeply enough to sample surficial aquifer flow originating from distant locations in the watershed, with a longer residence time and potentially distinct isotopic signature. The isotopic rainfall record in central Florida was insufficient to determine whether the seasonal signal was strong enough to support this hypothesis.

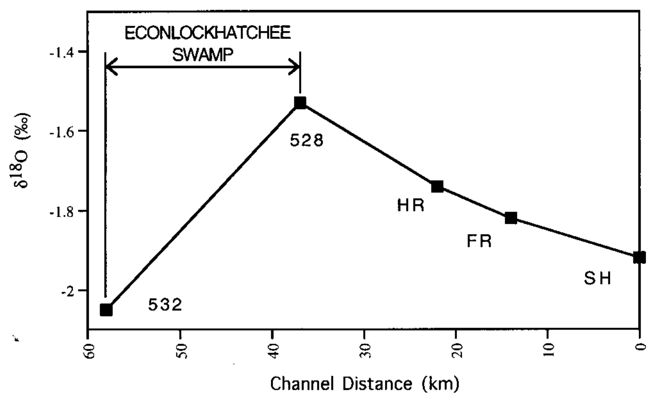

Figure 6. δ^{18}O versus channel distance upstream from station SH in the Big Econlockhatchee River on 19 November 1993

The Floridan aquifer was a potential source of isotopically enriched water in the lower watershed ($-1{\cdot}71 \pm 0{\cdot}16$‰, $n = 5$), but did not appear to contribute significantly to river flow. Two independent hydrological studies of the Econlockhatchee basin (Tibbals, 1990; Wanielista *et al.*, 1992) concluded that the Hawthorne unit prevented significant contribution of flow from the Floridan aquifer. The potentiometric surface of the Floridan aquifer was higher than the river channel in the lower Econlockhatchee basin (Figure 2), but there was no isotopic evidence of Floridan aquifer water in the river. In fact, δ^{18}O at SH, the farthest downstream station, was consistently more depleted than at upstream stations on a given day, and nearly all river observations were more depleted than Floridan aquifer water. Thus the Floridan aquifer was assumed not to affect the isotope hydrology of the river.

The remaining potential source of isotopic enrichment in river water was evaporation. Evaporative enrichment has been identified as a dominant factor in the isotope balance of closed or lentic hydrological systems, such as lakes and wetlands (e.g. Dinçer, 1968; IAEA, 1979; Krabbenhoft *et al.*, 1990; Meyers *et al.*, 1993; Saxena, 1996), but evaporative effects have been considered important in very few isotopic studies of rivers. Sklash *et al.* (1976) observed in a Canadian catchment that baseflow river water was 0·7‰ more enriched than near-stream groundwater and attributed the difference to evaporation.

The extremely low elevation gradient in the Econlockhatchee watershed (Figure 2) and the large surface area of the headwater swamp (Figure 1) created conditions conducive to evaporative enrichment. To determine whether headwater evaporation was a significant factor in the isotope hydrology of the Econlockhatchee basin, water samples were collected upstream and downstream of the Econlockhatchee Swamp on 19 November 1993, which was day 23 of a period of recession and one year after the daily monitoring survey reported in this study. Discharge from the swamp was approximately 0·6 $m^3 s^{-1}$. River δ^{18}O enriched from $-2{\cdot}20$ to $-1{\cdot}69$‰ across the swamp, with steady depletion downstream to a value of $-2{\cdot}07$‰ at station SH (Figure 6). The isotopic enrichment observed in the Econlockhatchee Swamp was consistent with evaporative effects, but flow from the swamp contributed only about 10% of the total flow at station SH (e.g. Figure 2). For evaporative enrichment to have been an important process in the river, significant effects must have been exerted over the entire river system.

Mass-balance modelling

Isotopic enrichment of surface water observed during the recession period that began on 12 October 1992 contradicted expectations that the isotopic composition of surface water would approach that of the surficial aquifer, the apparent source of river flow during recession. Evaporation appeared to be the most likely source of enrichment during recession, although concurrent processes may have either obscured or enhanced evaporative effects. For example, during recession both channel storage and river flow decreased with time, increasing the ratios of surface area to channel volume and surface area to flow, thereby amplifying

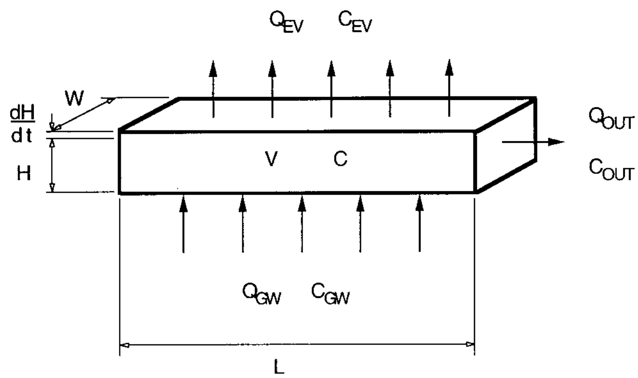

Figure 7. Control surface and boundary parameters for the conservative-tracer mass-balance model, where L is the channel length, W is the average channel width, H is the average water depth, and dH/dt is the change in depth over one time-step. Other terms are defined by Equations (1) and (2)

evaporative effects. However, lower channel storage and flow also may have led to an increased relative contribution of more depleted surficial-aquifer waters, thereby damping evaporative effects.

To determine whether evaporation could account for the phenomenon of isotopic enrichment during recession, a mass-balance model was developed for $\delta^{18}O$ in the watershed. The control surface for the model (Figure 7) was the river channel upstream from a cross-section for which flow and isotopic data were available. Accurate gauging data were available at stations BD and SH, so the model was applied separately for each of those basins.

Equations for flow and $\delta^{18}O$ were derived from the differential form:

$$\frac{dV}{dt} = Q_{GW} - Q_{EV} - Q_{OUT} \tag{1}$$

$$\frac{dCV}{dt} = C_{GW}Q_{GW} - C_{EV}Q_{EV} - C_{OUT}Q_{OUT} \tag{2}$$

where V is channel storage (m^3), Q is flow (m^3 s^{-1}), C is tracer concentration (‰), GW is the surficial aquifer, EV is evaporative loss and OUT is channel outflow.

Equations 1 and 2 were solved assuming non-steady state conditions with respect to channel volume (V) and isotopic content (C) over discrete 1-day time steps Δt

$$\Delta V = V_2 - V_1 = V_{GW} - V_{EV} - V_{OUT} \tag{3}$$

$$\Delta CV + C\Delta V + \Delta C\Delta V = C_2V_2 - C_1V_1 = C_{GW}V_{GW} - C_{EV}V_{EV} - C_{OUT}V_{OUT} \tag{4}$$

where $V_{OUT} = Q_{OUT}\Delta t$ with appropriate unit conversions. Channel storage terms are $V_1 = V_t$ and $V_2 = V_{(t+\Delta t)}$, with similar notation for C. The river channel during a single time-step was considered completely mixed, so that $C_1 = C_{OUT}$ at time t, and $C_2 = C_{OUT}$ at time $(t+\Delta t)$. This assumption was necessary to solve the model by treating the river as a single reach and did not strictly reflect river conditions (Figure 4). A more accurate approach would be to apply a hydrological routing model, or a multiple-reach model. The additional assumptions required to support more complex models, however, may introduce greater error. For example, flow data were available only for three locations on the river. Multiple-reach or routing models would require assumptions regarding the distribution of gained flow along the length of each reach. Instead of solving more complex models, a simple completely mixed reactor model was applied to the river at two locations: a headwater portion of the basin (station BD) and the outflow to the entire basin (station SH). Equations 3 and 4 also carried the assumption that channel flow during recession was generated completely from aquifer discharge as measured by near-stream monitoring wells and the only losses were from discharge at the watershed outlet and channel storage loss ($V_2 - V_1$). Equations (3) and (4) were solved for two unknowns, V_{GW} and $C_2 = C_{OUT(t+\Delta t)}$

$$V_{GW} = V_2 - V_1 + V_{EV} + V_{OUT} \tag{5}$$

$$C_{OUT} = \frac{C_{GW} V_{GW} - C_{EV} V_{EV} + C_1 V_1}{V_{OUT} + V_2} \tag{6}$$

All other terms in the equations could be measured or estimated, so the model predicted the outflow δ^{18}O at the end of each time-step and used that value as the initial river concentration (C_1) at the beginning of the next time-step. The complete modelling run was then compared with measured values of river δ^{18}O. Thus, the input data necessary for each time-step were change in channel storage ($V_2 - V_1$), volume of water evaporated (V_{EV}), volume of outflow (V_{OUT}), and isotopic values for groundwater (C_{GW}) and evaporation (C_{EV}). Spreadsheet software was used to solve the equations, with each time-step occupying one row of the spreadsheet.

Estimates of channel geometry were required for storage terms. Field surveys determined that the river was confined within its incised channel during recession and did not flow over the adjacent floodplain. Thus the channel was modelled as a rectangular prism with an average width of 10 m and an initial depth of 1·2 m for the BD modelling run and 1·5 m for the SH modelling run. Channel length was determined through previous surveys (Miller and Miller, 1984) and measurements from USGS 7·5′ topographic quadrangle sheets. Channel storage was adjusted with each time-step based on daily measurements of river stage. Daily volume of water evaporated was set at 0·003 m day^{-1}, based on long-term average conditions in October for east-central Florida (Wanielista, 1990). Daily outflow volumes for stations BD and SH were taken from USGS gauging records. Daily δ^{18}O groundwater was computed by linear interpolation of weekly mean groundwater isotopic concentrations from monitoring data.

The δ^{18}O of water evaporated from the river was estimated using the Craig and Gordon (1965) model as simplified by Krabbenhoft *et al.* (1990)

$$\delta_{EV} = \frac{\alpha^* \delta_R - h\delta_A - \varepsilon}{1 - h - (\Delta\varepsilon 10^{-3})} \tag{7}$$

where δ_{EV} is the isotopic composition of evaporation (‰), α^* is an equilibrium fractionation factor (*c.* 0·99 at 25 °C), δ_R is the isotopic composition of river water (‰), h is relative humidity (unitless), δ_A is isotopic composition of atmospheric moisture (−11·0‰), ε is a kinetic fractionation factor [1000 $(1 - \alpha^*)$] and $\Delta\varepsilon$ is a total fractionation factor [14·3 $(1 - h)$].

Atmospheric δ^{18}O was not measured directly and was assumed to be in equilibrium with the mean river δ^{18}O, which is an assumption made by Meyers *et al.* (1993) to model evaporation in the Florida Everglades. Sensitivity analyses (Gremillion, 1994) revealed that atmospheric δ^{18}O was a relatively insensitive parameter, so no attempt was made to refine this estimate.

Calibration

Sensitivity analyses (Gremillion, 1994) indicated that predicted values of C_{OUT} were particularly sensitive to two parameters that were not known with great precision: humidity (h) and channel surface area. Humidity strongly influenced the value for atmospheric δ^{18}O and surface area controlled the total mass of δ^{18}O lost through evaporation. As a result, these variables were used to calibrate the model. Calibration consisted of selecting values for humidity and surface area, running the model for the recession period, then computing the error sum of squares (SSE) for the run:

$$\mathrm{SSE} = \sum_{i=1}^{n} (C_{\mathrm{River}_i} - C_{\mathrm{OUT}_i})^2 \tag{8}$$

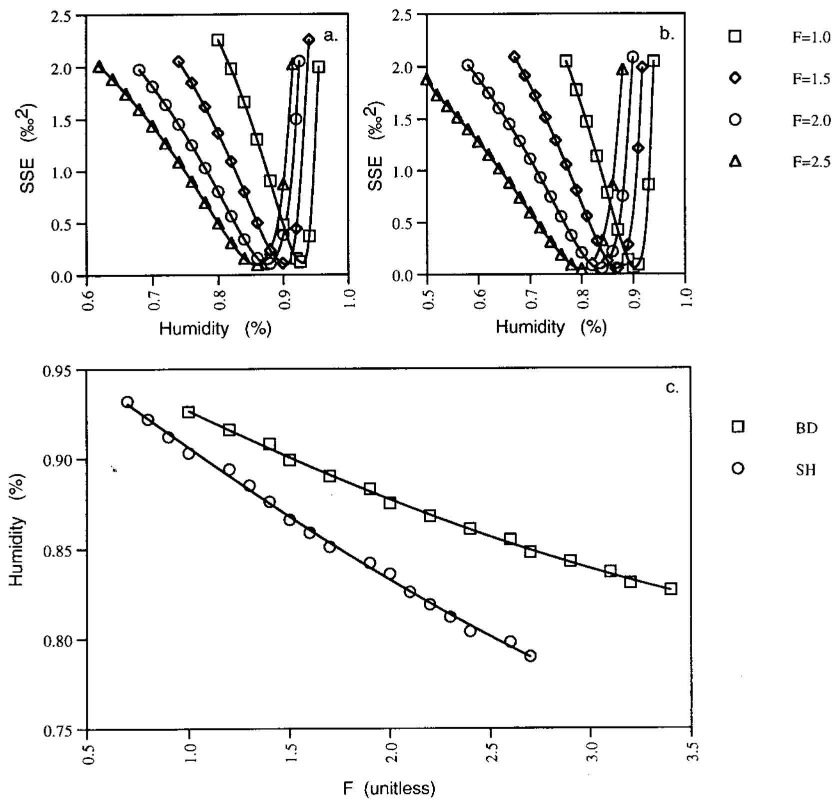

Figure 8. Mass-balance calibration data under recession conditions for stations BD (a) and SH (b), where SSE is the error square of sums (Equation 8) and F is the trial channel surface area divided by the initial estimate of channel surface area. The mass-balance model was solved by selecting trial values of F, varying humidity and computing SSE. Humidity and F combinations that produced SSE minima are plotted as the solution set of the models (c)

where C_{River} is the measured river δ^{18}O at the gauging station (BD or SH) and C_{OUT} is the model prediction for river δ^{18}O on the corresponding day for $n = 10$ days. Minimizing the SSE is the mechanism by which least-squares linear regression analysis is performed (Neter *et al.*, 1990) and can be applied to calibrate analytical models. For this model, SSE was minimized by varying humidity and surface area. Figure 8 (a and b) shows trial observations of humidity for four values of surface area. The trial resulting in the minimum SSE was used to develop the solution set of optimum combinations of humidity and surface area. These combinations are plotted in Figure 8c. Table III presents the calibration data in terms of a variable *F*, the multiplication factor for area, which was computed as the trial channel surface area divided by the original estimate of channel surface area. Model calibration results are plotted in Figure 9, which shows the model solution for each of the multiplication factors included in Table III. These plots demonstrate that the combinations of humidity and channel area that comprise the solution set (Figure 8c) produce nearly identical predictions of C_{OUT}.

The solution sets summarized in Table III show that Equations (6) and (7) accurately modelled the river system under a humidity range of about 85 to 93% for a range of river surface areas up to 2·5 times larger than initial estimates based on field surveys. This humidity range appears to be reasonable, considering the inland, subtropical climate of central Florida and the closed hardwood and cypress canopy of the riparian zone of most of the river system. Consideration of a range of humidity values was necessary because instrumental humidity data for the riparian zone were unavailable and permanent National Weather Service

Table III. Summary of mass-balance model calibration results. The $\delta^{18}O$ of evaporated water was estimated (Equation 7) using parameters computed by the model, so modelling assumptions, particularly humidity, strongly influenced this term

Station	F	Channel area (m^2)	Humidity (%)	Estimated[a] $\delta^{18}O_{EV}$ (‰)	SSE ($\%^2$)
BD	1·0	3·00E+05	92·6	−138·5	0·122
	1·5	4·50E+05	89·9	−99·1	0·110
	2·0	6·00E+05	87·5	−78·4	0·101
	2·5	7·25E+05	85·8	−67·9	0·095
	Regression model				0·012
SH	1·0	4·50E+06	90·3	−103·5	0·059
	1·5	6·50E+06	86·6	−72·5	0·056
	2·0	8·50E+06	83·6	−57·5	0·053
	2·5	1·08E+07	80·1	−45·8	0·050
	Regression model				0·008

[a]Mean value for calibration period.

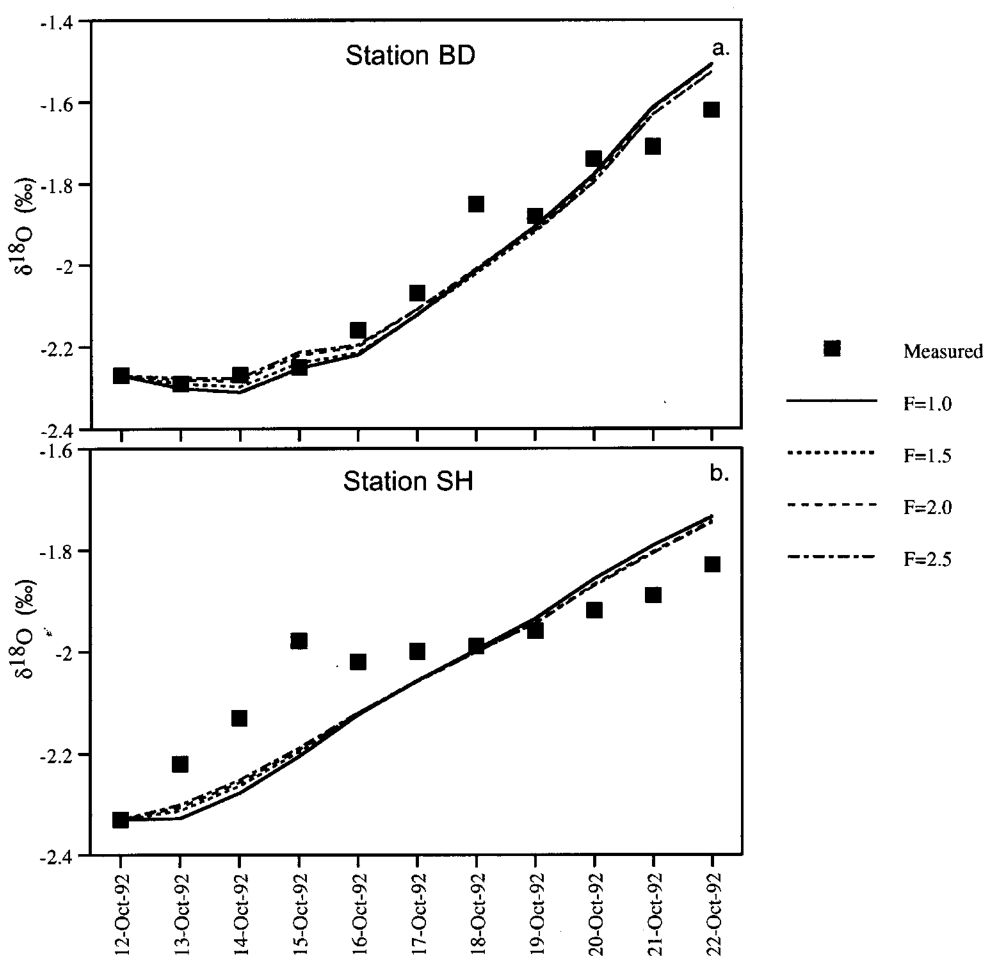

Figure 9. Predicted river $\delta^{18}O$ overlaid with observed river $\delta^{18}O$ for stations BD (a) and SH (b). Mass-balance models were solved for four combinations of F and humidity that resulted in minimum SSE (Figure 8c)

recording stations were believed to underestimate humidity near the air–water interface. With regard to surface area, initial estimates may have been significantly underestimated for several reasons. The source data for channel geometry were intended to support flood-routing models. As a result minor tributaries and headwater lakes and wetlands were not included. In addition, although floodplain in the Econlockhatchee basin was relatively well defined by 7·5′ topographic maps, the incised channel in natural sections of the river meandered, with significant ox-bow formation. The sine-generated path of the ox-bow increases path length in most meandering rivers by a factor of 1·3 to 4·0 (Leopold and Langbein, 1966). Thus the solution set plotted in Figure 8c appears to reflect a reasonable range for humidity and river surface area.

Estimates of humidity strongly affected the calculation for $\delta^{18}O_{EV}$. For the calibration runs summarized in Table III, the computed $\delta^{18}O_{EV}$ varied from $-45{\cdot}8$ to $-138{\cdot}5$‰. These are substantially more depleted than values found elsewhere in the literature. Saxena (1996) estimated a range of $-21{\cdot}6$ to $-40{\cdot}1$‰ for a Swedish lake and Krabbenhoft *et al.* (1990) estimated a range of $-4{\cdot}0$ to $+33{\cdot}2$‰ for water evaporated from a Wisconsin lake. In an earlier study, Zimmerman (1977) computed a $\delta^{18}O_{EV}$ of $-16{\cdot}1$‰ for a German lake. Water evaporated from the Econlockhatchee River may be expected to be more depleted in $\delta^{18}O$ than other published values due to the combination of enriched source water (approximately $-2{\cdot}0$‰), high water temperature, enriched atmospheric $\delta^{18}O$ and high humidity.

Application to pre-recession data

The mass-balance model developed in Equations (1) and (2) assumed that groundwater sources provided the only inflow to the river and that $\delta^{18}O$ measurements of near-stream groundwater accurately represented this inflow. This simplification may be considered appropriate during recession when river hydrology was not complicated by recent runoff events, however, the period of record prior to the 12 October recession featured almost daily storms. It is evident that river flow responded to storm events (Figure 4b), but the mechanism of transport is unclear. In the highly permeable sand aquifer system, rapidly infiltrating rainfall increased the elevation of the surficial aquifer, causing stronger hydraulic gradients toward the river, and consequently higher flow. Bennett (1993) observed this relationship in the Econlockhatchee basin. Through this mechanism it is possible that storm events displaced pre-event water from the surficial aquifer. To test this hypothesis, the mass-balance model, calibrated for a period of recession, was applied to the pre-recession data for stations BD and SH.

To apply the calibrated recession model to the pre-recession data, daily records of flow and river stage, and daily interpolated values of weekly groundwater $\delta^{18}O$ measurements were written into the spreadsheet for the recession mass-balance model. As with the calibration runs, the first value for C_1 (the $\delta^{18}O$ of water in the river at the beginning of the time-step) was set equal to the measured value for that day. Subsequent values of C_1 were set equal to values of C_{OUT} from the previous time-step. For these runs, river surface area factors of $F = 1{\cdot}0$ (Table III) were used for both BD and SH and humidities of 92·6 and 90·3% were used for stations BD and SH, respectively, corresponding to optimum solutions of calibration runs (Table III).

Figure 10(a and b) shows the solution of the mass-balance model overlaid with measured data. The models closely matched observed data at both stations for most of the pre-recession period. Both models predicted more depleted values than observed for river water in the last week of September and the end of the first week in October at both stations. These times were associated with the two distinct hydrograph peaks. Errors at peak flows may be expected, because high flows are likely to contain a greater fraction of recent storm-event water. If this were the case, however, the model should have predicted more enriched values than observed, because most recent storms were more isotopically depleted than river water or groundwater. Alternatively, the observed errors could be due to effects of inaccurate modelling parameters, such as channel geometry, that may be observed only during extreme conditions.

Aside from high-flow episodes, the mass-balance models predicted river $\delta^{18}O$ extremely well, particularly considering the duration of the runs. As each time-step used the river $\delta^{18}O$ value computed from the previous time-step, errors could accumulate during a long run. Evidence of error accumulation was completely absent in both runs. Although the models did not use any daily measurements for river $\delta^{18}O$ after the start of each

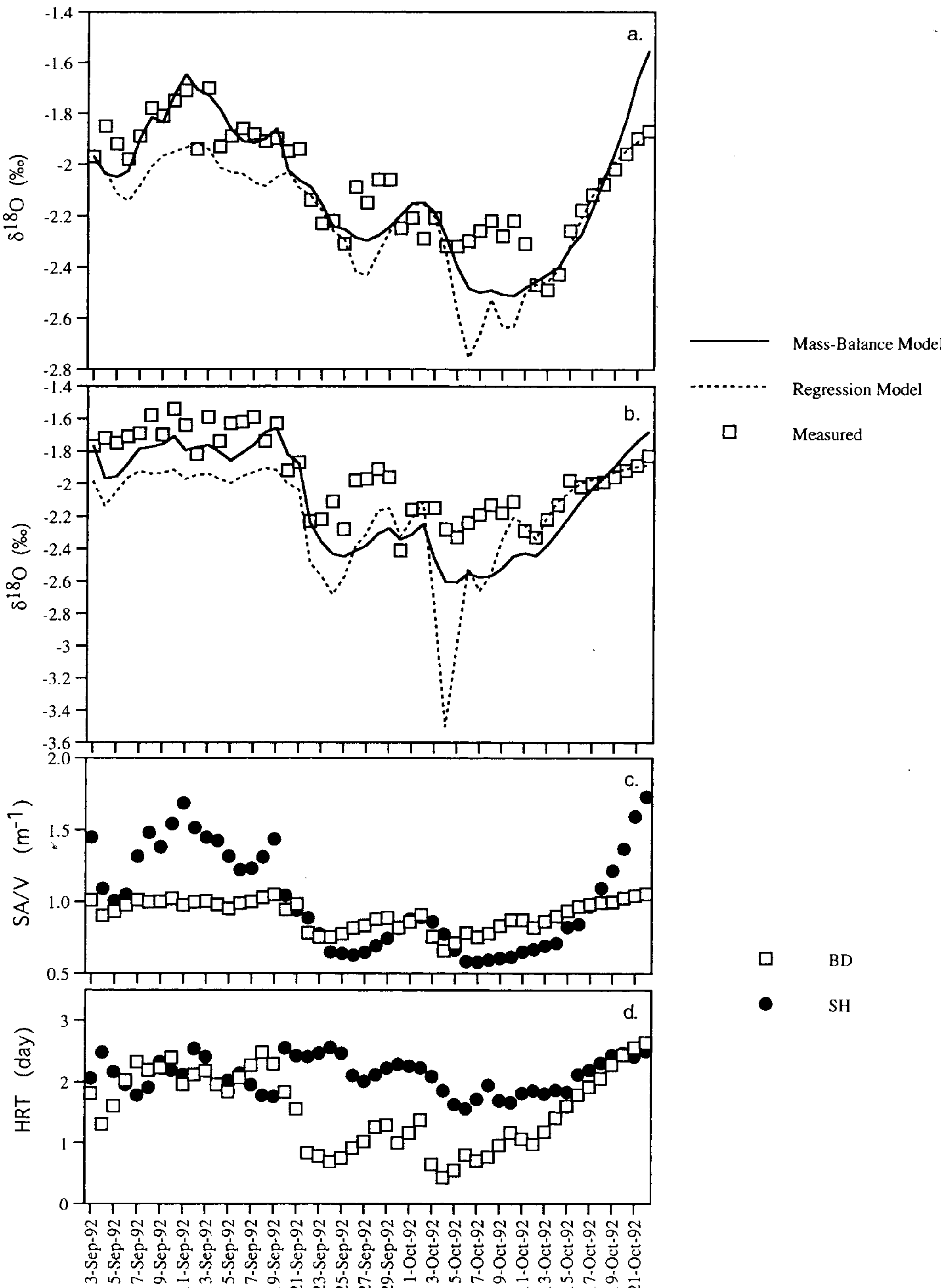

Figure 10. The mass-balance models calibrated under recession conditions were applied to the complete period of record for stations BD (a) and SH (b) assuming $F = 1{\cdot}0$ for both stations and humidities of 92·6 and 90·3% for stations BD and SH, respectively (solid line). Least-squares linear regression equations (Figure 5) were applied to daily flow to predict river $\delta^{18}O$ (segmented line). Ratios of channel surface area to channel volume (SA/V) and hydraulic retention time (channel volume divided by flow, HRT) estimated by the mass-balance model are plotted in (c) and (d)

run, the models did use daily measurements for flow and stage. The remaining parameters were fixed as boundary conditions. It is possible that the mass-balance model was actually reflecting a strong flow-dependence in addition to evaporation dependence in the river.

Flow-based regression modelling

To test the degree of control flow exerted on river $\delta^{18}O$, a simple regression model was developed. Figure 5 shows plots of $\delta^{18}O$ versus flow for the BD and SH stations. A least-squares linear-regression equation was fit to the recession data. The regression equation is shown in Figure 5 and the SSEs for the recession periods are summarized in Table III. The SSEs for the regression models were about one order of magnitude lower than for the mass-balance models, indicating a much better fit to the calibration data. Figure 5 shows that at any given flow, however, the river in recession was more isotopically depleted than during pre-recession periods. This distinct difference in isotopic character between recession and pre-recession is evident in the model run plots of Figure 10(a and b). The regression model consistently predicted more depleted values than observed during the pre-recession period. As with the mass-balance model, the regression model did not accurately predict high flow $\delta^{18}O$ and, in fact, the regression model magnified that error.

DISCUSSION

Monitoring data collected in September and October 1992 to characterize the isotopic content of water masses in the Econlockhatchee basin clearly showed that river water was about 1 per mille more enriched than surficial groundwater and that the $\delta^{18}O$ of precipitation during that time period was variable but generally more depleted than river water. A mass-balance model of the entire catchment and a smaller subcatchment demonstrated that evaporation from the river surface could account for this enrichment. The mass-balance model considered river conditions during hydrological recession, when the only source of flow was groundwater draining from the surficial aquifer. When the model was applied to pre-recession conditions, with almost daily rainfall, the model still predicted river $\delta^{18}O$ accurately, even though groundwater, at a relatively constant $\delta^{18}O$, was the only source the model considered.

Isotopic enrichment during recession

During the recession period that started on 12 October, the river became more isotopically enriched at all stations, whereas basin-wide samples of surficial groundwater remained almost constant and more depleted (Figure 4). Monitoring data and mass-balance modelling results point toward evaporative effects as a significant source of enrichment, probably both from headwaters as well as the main-stem river channel. Samples collected on the same day along a transect starting at the upstream end of the large headwater swamp (Figure 1) and ending at the downstream gauging station (SH) showed isotopic enrichment across the swamp followed by depletion downstream (Figure 6). The controlling processes appear to be evaporative enrichment in the swamp and mixing of more depleted groundwater downstream. Dilution of headwater evaporation can be seen in the 1992 daily monitoring data (Figure 4a), where downstream $\delta^{18}O$ was consistently more depleted than upstream samples on a given day. This is particularly evident toward the end of the recession period, where stations FR and HR were notably more enriched than other river stations. Although evaporative enrichment appears to have been an important process in headwaters, discharge from headwater areas (upstream from stations BD and MR) constituted an average of less than one-quarter of the total flow in the Econlockhatchee basin during the study period (Figure 4b). The mass-balance model showed that evaporative enrichment in the river channel and headwater areas caused progressive enrichment in river $\delta^{18}O$ during recession.

Alternative hypothesis: flow-dependent $\delta^{18}O$

The $\delta^{18}O$ of groundwater entering the river has been assumed to be almost constant regardless of hydrograph characteristics during the study period. This assumption was supported by data collected from shallow monitoring wells located near the river. It is possible that deeper surficial groundwater had a more enriched isotopic content than the shallow groundwater captured by the monitoring wells, resulting in consistently more enriched river water. Because deeper aquifer water originated at more distant locations in the watershed, this water mass may have carried the imprint of evaporated surface waters, such as the numerous sink-hole ponds, storm-water detention ponds, wetlands and depression storage features that exist in the Econlockhatchee basin. The effects of surface water features on the surficial aquifer may have been observed at monitoring wells AL1 and AL2. The $\delta^{18}O$ at these sites was significantly more enriched than other groundwater samples, and these sites were located immediately down-gradient from a stormwater management pond. The theory of heterogeneous $\delta^{18}O$ in the surficial aquifer would explain the strong relationship observed between $\delta^{18}O_{GW}$ and flow (Figure 5) if shallower and more depleted sources contributed proportionally greater flow at low flows. Variable $\delta^{18}O$ with depth may have caused enriched $\delta^{18}O$ in the Econlockhatchee River, but existing data are insufficient to support or refute this theory.

Pre-recession isotope hydrology

The mass-balance model, calibrated under recession conditions (Figure 10), had the unexpected capability to predict river $\delta^{18}O$ during pre-recession conditions, a period of almost daily storm activity resulting in pronounced peaks in the river hydrograph (Figure 4b). After the first day of a model run, the model had no knowledge of measured values of river $\delta^{18}O$. The only isotopic values in the daily input data were the $\delta^{18}O$ of groundwater and evaporated water $\delta^{18}O$. Because the model used computed values of river $\delta^{18}O$ from previous time-steps, error in river $\delta^{18}O$ was expected to accumulate over the course of each model run. The accurate fit of the model to pre-recession data in spite of these limitations suggested that some model parameter governed the prediction of river $\delta^{18}O$. As daily flow data were provided to the model, the observed flow dependence was suspected as the strongest factor in maintaining accurate $\delta^{18}O$ predictions.

The flow regression models did in fact display this dependence, although during recession the relationship between $\delta^{18}O$ and flow was distinctly different than during pre-recession conditions (Figure 5). At any given flow, river $\delta^{18}O$ was more depleted during recession than during pre-recession periods. This is reflected in the application of the regression model to the river data for stations BD and SH (Figure 10), which predicted consistently more depleted values than observed. Two hypotheses to explain this phenomenon are (i) surficial aquifer water became more depleted over time, perhaps as a result of seasonal isotopic changes in water recharging the aquifer or (ii) during pre-recession conditions, the more enriched values reflected the direct and immediate introduction of enriched event-water sources into the river. Neither hypothesis is supported by the groundwater monitoring data and the second hypothesis is inconsistent with precipitation data, unless precipitation was isotopically enriched by intermediate processes, such as those associated with throughfall (Dewalle and Swistock, 1994).

The flow dependence observed both during pre-recession and recession conditions may be explained by evaporation alone. As flow decreased, the ratio of channel surface area to volume increased (Figure 10c) and hydraulic retention time, defined as channel volume divided by daily flow increased (Figure 10d). Greater relative surface area and longer residence time resulted in more pronounced effects of evaporation. In summary, although the data do not rule out changing groundwater characteristics as the cause of flow-dependent variability in river $\delta^{18}O$, the modelling data do support the contention that this variability was controlled by evaporation.

An unresolved aspect of pre-recession modelling remains that of the isotopic effects associated with event waters. In the simplified mass-balance model of Equations (1) and (2), surficial aquifer water was the only inflow. The accuracy of the mass-balance model under pre-recession conditions suggests either that precipitation-event water masses were not an important component of river flow or that their isotopic content was altered, making event water indistinguishable from pre-event surficial aquifer water. The theory of displacement of pre-event water by event water is reasonable for the Econlockhatchee basin considering the high permeability of surficial aquifer sands. If displacement was the controlling mechanism, the isotopic character of individual events may be diminished by the averaging effects of mixing in the aquifer. For example, Wenner *et al.* (1991) examined vertical gradients in soil-column $\delta^{18}O$ and concluded that most water from an individual event quickly loses its isotopic distinctiveness as it mixes downward.

Overlying these processes of displacement and mixing may be changes in the isotopic content of precipitation before it is integrated into the aquifer. Precipitation monitoring for this study did not attempt to assess enrichment resulting from throughfall effects, such as leaf storage, stem-flow and depression storage. Thus the isotopic signature of event waters may have been altered at some intermediate point in the hydrological cycle, further diminishing the signal between event water and groundwater. These averaging processes may have led to event waters that were not separable from surficial groundwater, which could explain the effectiveness of the simplified mass-balance model under pre-recession conditions.

CONCLUSIONS AND RECOMMENDATIONS

It appears that evaporation significantly affected the isotope hydrology of the Econlockhatchee River and that evaporative processes were responsible for a consistent enrichment of 1 or more per mille. Conclusions may be summarized as follows.

1. A mass-balance model for flow and $\delta^{18}O$ in the river during recession indicated that evaporative effects could explain observations of isotopic enrichment.
2. This model, calibrated to recession conditions and executed for pre-recession conditions, further demonstrated that evaporation was influential in controlling the isotopic content of river water throughout the study period. The model had the unexpected result of indicating that additional model terms to account for storm-event water masses were not necessary to predict river $\delta^{18}O$. The mechanisms responsible are unclear, but may be related to displacement and mixing processes in the aquifer and alteration of the event-water isotopic signal by throughfall enrichment.
3. The observed range in $\delta^{18}O$ of central Florida precipitation of $-6{\cdot}64$ to $-0{\cdot}17$‰ provides sufficient variability to use stable isotopes as hydrological tracers, assuming that this signal is not obscured by intermediate enrichment processes.
4. The $\delta^{18}O$ of surficial aquifer groundwater collected in near-stream monitoring wells was homogeneous spatially and temporally during the study period. Shallow subsurface $\delta^{18}O$ probably does change, perhaps seasonally, but recharge areas appear to be large enough that $\delta^{18}O$ of the surficial aquifer changes on the order of months or longer rather than days.
5. Surficial aquifer $\delta^{18}O$ appears to be affected locally by evaporated surface water features. These effects were evident in the data collected from wells AL1 and AL2, which were located down-gradient from a stormwater management pond and recorded more enriched $\delta^{18}O$.

The ultimate objective of this research was to assess the potential of $\delta^{18}O$ as a conservative environmental tracer in hydrograph separation studies. Although the precipitation data were limited to a single autumn season, the observed range in meteoric $\delta^{18}O$ ($-6{\cdot}64$ to $-0{\cdot}17$‰) provides an adequate signal to separate rainfall from river and groundwater sources, assuming enrichment processes are considered.

Although monitoring and modelling data strongly inferred evaporation as an important process in the isotope hydrology of the river, isotopic enrichment resulting from evaporation was not measured directly. Analysis of archived samples for deuterium may enable an evaporation line to be developed (Dansgaard, 1964). These additional data may confirm or disprove the presence of an imprint of evaporation, but would not necessarily reveal which elements in the hydrological cycle of the basin were subjected to evaporative enrichment. Additionally, refinement in the mass-balance models may improve the modelling results. This study relied on the assumption of a single-reach, completely mixed reactor. A multiple-reach model with distributed sources and sinks would more accurately represent river conditions. Finally, meteoric water-line data for central Florida need to be collected to gain a better understanding of seasonal changes in the isotopic content of precipitation.

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