SEPARATION OF STREAMFLOW COMPONENTS IN THE ECONLOCKHATCHEE RIVER SYSTEM USING ENVIRONMENTAL STABLE ISOTOPE TRACERS

by

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ABSTRACT

Naturally occurring, or environmental, stable isotopes may be used to explore a variety of empirical questions in environmental engineering studies. The heavy stable isotope of carbon, ^{13}C, may be used to trace the origin of dissolved inorganic carbon in natural water. The heavy stable isotopes of oxygen, ^{18}O, and hydrogen, ^{2}H, may be used in hydrologic studies to trace the movement of water masses. This dissertation reports a novel procedure for preparing natural-water samples for ^{13}C analysis and describes a research program to define the oxygen isotopic composition of water masses in a central-Florida watershed.

A precise and inexpensive method to extract dissolved inorganic carbon (DIC) from natural water samples for $\delta^{13}C$ analysis was developed. Approximately 5 mL of sample was injected into an evacuated disposable serum vial containing 100 μL anhydrous orthophosphoric acid (H_3PO_4). DIC was quantitatively converted to CO_2 gas. For water samples with total DIC greater than approximately 10 mg C/L, a replicate precision better than $1\sigma=0.1‰$ was attained.

A synoptic survey of the isotope hydrology of the Econlockhatchee River basin in east-central Florida was conducted in the Autumn of 1992 to determine spatial and temporal variability in the $\delta^{18}O$ of water masses in the river system. The objective was to assess the potential for $\delta^{18}O$ as a conservative tracer in hydrograph-separation studies in the basin. Results revealed ranges in precipitation $\delta^{18}O$ of -6.5 to 0.0 ‰, in groundwater from -3.5 to -2.5 ‰, and in river water from -2.5 to -1.5 ‰. Based on the temporal variability of precipitation $\delta^{18}O$ relative to that of groundwater and river water, and the analytical precision of the $\delta^{18}O$ test ($1\sigma=0.1$‰), it was concluded that an adequate isotopic signal existed in the watershed to permit hydrograph separation using environmental $\delta^{18}O$. Monitoring revealed that evaporation of river water resulted in significant isotopic enrichment, particularly during periods of low flow.

A storm event in May 1993 was monitored intensively at two locations on the Econlockhatchee River to conduct hydrograph separation studies using environmental $\delta^{18}O$ as a conservative tracer. The objective was to estimate the amount of *old*, or pre-event, water contributing to the storm hydrograph. The event produced 4.3 inches of precipitation (*new* water) with an amount-weighted mean $\delta^{18}O$ of -4.46 ‰. River $\delta^{18}O$ ranged from -2.26 to -0.02 ‰ during the event. The isotopic composition of old water was estimated using a linear regression equation of $\delta^{18}O$ versus river stage developed from data collected during recession periods prior to and following the event. The isotopic content of old water ranged from -0.72 to +0.10 ‰ during the event. Using a catchment-scale steady-state mass-balance model, it was determined that old water constituted approximately 76 percent of the total storm hydrograph at both river stations. Mass-balance models for unsteady-state conditions and for a discrete river reach were also examined. Recommendations for further research included monitoring additional storms to determine the influences of seasonality and antecedent conditions on old-water contributions to the river and an analysis of archived water samples for δD to refine estimates of evaporative effects in the system.

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DEDICATION

for Nellie and Buddy

FOREWORD

It's everything a river should be.

John Steinbeck, *Cannery Row*, 1945

He was excited by the early morning and the river.

Earnest Hemingway, *Big Two-Hearted River*, 1938

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INTRODUCTION

Background

The origin of streamflow has direct implications for the management of water quality in the Econlockhatchee River basin. Stormwater is responsible for mobilizing *non-point*, or diffuse, sources of pollution. Non-point sources may include deposition of air-borne pollutants, nutrients and sediment mobilized by erosion of agricultural areas, and metals and chemicals washed from urban areas (Wanielista and Yousef 1993).

Until recently, controlling point-sources of pollution has been the principal concern of regulatory agencies. Laws and funding mechanisms put in place decades ago encouraged primary, secondary, and in some cases advanced treatment of sewage and industrial pollution. The growing recognition of the importance of non-point source (NPS) pollution is reflected in the federal legislative emphasis on controlling NPS pollution in the most recent enactment of the Clean Water, Coastal Zone Management, and Safe Drinking Water Acts (Cooper 1991).

Effective control of NPS pollution requires an understanding of the magnitude and origin of streamflow. It is commonly believed that streamflow in most rivers is comprised primarily of *new* water, or runoff water from the storm event that creates a relatively rapid change in the hydrograph. However, as much as 90 percent of the streamflow hydrograph can be composed of *old*, or prestorm, water displaced from the surficial aquifer by rapidly-infiltrated rainfall (Hooper and Shoemaker 1986). In the

Braden River (Manatee County), Florida, up to 90 percent of the yearly streamflow was estimated using convolution integrals to originate from groundwater (Wanielista 1989).

In such watersheds, the surficial aquifer can be the dominant non-point pollutant loading source to the river. This implies that even the most aggressive attempts to control surface-runoff pollution may be ineffective in controlling total pollutant loading to receiving surface waters. The magnitude of hydraulic and pollutant loading from the surficial aquifer to receiving waters can be assessed through *hydrograph-separation* techniques. Recent studies indicate a strong interaction between the surficial aquifer and flow in the Econlockhatchee River (Wanielista, *et al.*, 1992, Bennett 1993, Wanielista, *et al.*, 1993). Investigated in this dissertation are surficial aquifer interactions using environmental (naturally occurring) stable isotope tracers. Understanding these flow mechanisms is a vital step in preserving the ecological integrity and water quality of the Econlockhatchee River system.

Stable Isotopes

The stable isotopes of water (oxygen-18 and deuterium) can be considered truly conservative tracers in natural water systems. They are forms of the water molecule that vary by only their atomic mass. Water masses can develop distinctive ratios of the various isotope forms, that can be used in mass-balance equations. Because these tracers occur naturally in the environment, and are not introduced by the researcher, they are termed *environmental tracers*. The isotopes analyzed for this dissertation are all stable, that is, they do not emit energy through radioactive decay, and thus create no health and safety risk in their handling.

Isotope Characteristics

Isotopes are forms of an element that vary by only the number of neutrons they possess. Additional neutrons add atomic mass, but no charge. The probability that a particular isotope will be involved in a reaction is directly proportional to its abundance. Thus, the common forms of the water molecule are

${}^{1}H^{1}H^{16}O$	Light Water
${}^{1}H^{2}H^{16}O$	Heavy Water
${}^{1}H^{1}H^{18}O$	Heavy Water

Other combinations occur, but are quite rare. All hydrogen and oxygen isotopes, with the exception of tritium (${}^{3}H$), are stable isotopes. Tritium is an unstable, or radioactive, isotope of hydrogen that eventually decays to a stable helium isotope.

Mass Spectrometry

Stable isotopes are analyzed using isotope-ratio mass spectrometers. The original mass spectrometer for stable isotope analysis, developed by Nier (1947), could simultaneously measure the constituents of a pure-gas sample[1] of two or three specified atomic masses. For example, to detect the stable isotopes of hydrogen, the instrument was calibrated to measure the relative quantities of atomic mass 2 (for ${}^{1}H^{1}H$) and atomic mass 3 (to detect ${}^{1}H^{2}H$).

The Nier mass-spectrometer was sufficiently sensitive to provide an accurate mass ratio (*e.g.*, ${}^{2}H/{}^{1}H$), but was unable to maintain adequate calibration to report the absolute quantity of either mass by itself. As a result, the instrument was designed to compare constantly the isotope mass-ratio of a sample against that of a known standard.

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[1] Water samples must be converted to, or equilibrated with, a gas prior to analysis.

Even modern instruments, for every sample analyzed, execute a procedure whereby they analyze a reference gas of known isotope content, then the sample gas, repeating this cycle six to ten times. These instruments solve internally for the deviation of the isotope mass-ratio of the sample relative to a known standard using the following equation:

$$\delta = \frac{R_{sample} - R_{standard}}{R_{standard}} \; x \; 1000 \tag{1}$$

where δ = Isotope content of the sample [‰]
R = Ratio of heavy (rare) to light (abundant) isotopes [unitless]

The Delta Notation

Equation 1 is the general equation for the stable-isotope content of a sample. For hydrogen and oxygen analyses, the conventional reference standard is Standard Mean Ocean Water (SMOW). The equations for hydrogen and oxygen isotope content, relative to SMOW are

$$\delta D = \frac{(D/H)_{sample} - (D/H)_{SMOW}}{(D/H)_{SMOW}} \times 1000 \tag{2}$$

where δD = HDO isotope content[2] [‰]
D = ^2H ion concentration [M/M]
H = ^1H ion concentration [M/M]

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[2] D and ^2H are interchangeable terms for the deuterium ion and δD is the common notation for the ratio D/H relative to a reference standard, commonly SMOW.

$$\delta^{18}O = \frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{SMOW}}{(^{18}O/^{16}O)_{SMOW}} \times 1000 \qquad (3)$$

where $\delta^{18}O$ = Oxygen-18 isotope content [‰]
^{18}O = Oxygen-18 ion concentration [M/M]
^{16}O = Oxygen-16 ion concentration [M/M]

The delta (δ) notation represents the per-mil (‰) deviation of the isotope mass-ratio of a sample to that of SMOW. In the nomenclature of the literature, positive δ values (*e.g.*, δD = +10.0 ‰) are termed *enriched* in the heavy isotope relative to SMOW. Similarly, negative δ values (*e.g.*, δD = -30.0 ‰) are termed *depleted* in the heavy isotope relative to SMOW. These terms are also applied broadly to compare water masses (*e.g.*, "Summer convective precipitation tends to be more *enriched* in deuterium than winter frontal precipitation").

The overwhelming majority of publications reporting stable-isotope data employs the δ notation; and stable-isotope values for this research will be reported in the δ notation. However, absolute concentrations of isotopes are reported occasionally in the literature (*e.g.*, Buttle and Sami 1992) with the units *parts per million* (ppm). The conversion from ‰ to ppm can be derived for each ratio by first considering the relative abundance of the stable isotopes. The National Institute of Standards and Technology (NIST) certifies the oxygen isotopic composition of V-SMOW as (NIST 1992):

99.76206 atom percent ^{16}O
0.03790 atom percent ^{17}O
0.20004 atom percent ^{18}O

The absolute ratio of ^{18}O to ^{16}O is therefore

$$\left[\frac{(^{18}O)}{(^{16}O)}\right]_{SMOW} = \frac{0.20004}{99.76206} = 2.005171(10^{-3}) \tag{4}$$

Expressed in the delta notation, this relationship reduces to

$$\delta^{18}O = \frac{\left[\frac{(^{18}O)}{(^{16}O)}\right]_{SAMPLE} - 2.005171(10^{-3})}{2.005171(10^{-3})} \tag{5}$$

$$2.005171(10^{-6})\delta^{18}O = \left[\frac{(^{18}O)}{(^{16}O)}\right]_{SAMPLE} - 2.115171(10^{-3}) \tag{6}$$

$$\left[\frac{(^{18}O)}{(^{16}O)}\right]_{SAMPLE} = 2.005171(10^{-6})\delta^{18}O + 2.005171(10^{-3}) \tag{7}$$

The ratio of ^{18}O to ^{17}O can be considered constant in all natural waters (Li, *et al.*, 1976):

$$\left[\frac{(^{18}O)}{(^{17}O)}\right]_{SMOW} = \frac{0.20004}{0.03790} = 5.27810 \tag{8}$$

A mass balance for oxygen stable isotopes produces an equation for the atom fraction of oxygen-18 (f^{18}O) as a function of δ^{18}O:

$$1 = f^{18}O + f^{17}O + f^{16}O \tag{9}$$

$$f^{18}O = 1 - f^{17}O + f^{16}O \tag{10}$$

$$f^{18}O = 1 - \frac{f^{18}O}{5.27810} + \frac{f^{18}O}{2.005171(10^{-6})\delta^{18}O + 2.005171(10^{-3})} \tag{11}$$

$$f^{18}O = [1.189462 + (2.005171(10^{-6})\delta^{18}O + 2.001517(10^{-3}))^{-1}]^{-1} \tag{12}$$

Equation 12 can be used to convert oxygen isotope data from the delta notation (‰) to absolute concentration (ppm). Table 1 summarizes $\delta^{18}O$ concentrations for common waters. It is impressive to note that the total range of $\delta^{18}O$ in natural water on Earth is only about 110 ppm (Craig 1961). Identification of meaningful isotopic signatures is still possible because the sensitivity of analytical preparation systems and modern isotope-ratio mass spectrometers is approximately 0.2 ppm.

Fractionation

The relative abundance of light water ($^1H^1H^{16}O$) and heavy water ($^1H^1H^{18}O$ and $^1H^2H^{16}O$) isotopes in natural water varies due to differences in the physical properties of the molecules. Heavier water molecules have lower vapor pressure:

$$p(^1H^1H^{16}O) > p(^1H^1H^{18}O) > p(^1H^2H^{16}O)$$

(Ferronsky and Polyakov 1982). Thus, a water mass subject to evaporation becomes enriched in the heavier isotopes of water. This allows water masses to develop distinct isotope signatures.

Condensation. Two physical processes, condensation and evaporation, determine the isotope composition of water. In the atmosphere, as water vapor condenses into droplets, the isotope content of the liquid phase is determined, under equilibrium conditions (100

Table 1.
OXYGEN-18 OF NATURAL WATERS EXPRESSED IN PER-MIL AND ABSOLUTE CONCENTRATION UNITS.

WATER	$\delta^{18}O$ (‰)	$\delta^{18}O$ (ppm)
Vienna Standard Mean Ocean Water[1] (V-SMOW)	0.0	2000.4
Econlockhatchee River	-2.0	1996.4
Central Florida Surficial Aquifer	-3.0	1994.4
Greenland Ice Sheet Precipitation[1] (GISP)	-24.9	1950.8
Standard Light Antarctic Precipitation[1] (SLAP)	-55.5	1889.6

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[1] NIST (1992)

percent humidity), by the vapor pressures of the isotopes (Ferronsky and Polyakov 1982). As a result, the isotope composition of precipitation is somewhat predictable. In an early empirical study, Craig (1961) plotted δD versus δ^{18}O for more than 400 water samples collected worldwide. In spite of a wide range in δD values (-300 ‰ to +50 ‰) and δ^{18}O values (-46 ‰ to +6 ‰) (Mazor 1991), the data followed a linear relationship with the regression equation of

$$\delta D = 8\delta^{18}O + 10.0 \tag{13}$$

This relationship, known as the World Meteoric Water Line, has been confirmed empirically by numerous investigators and was developed theoretically by Dansgaard (1964).

The Meteoric Water Line can vary regionally due to local climatological and geographic conditions. Dinçer (1968) and Mazor (1991) described factors that affect meteoric isotope composition, some of which are summarized below:

- Isotopic depletion with decreasing temperature of condensation.
- Isotopic depletion with increasing altitude and latitude.
- Isotopic depletion with increasing magnitude of individual rain event or monthly precipitation volume.
- Isotopic depletion with increasing continental distance to the ocean.

For a given location the annual variability in observed δD and $\delta^{18}O$ depends on the variability of the individual factors described above. Regardless of the magnitude of this variability, the ratio of δD to $\delta^{18}O$ for a precipitation sample will remain constant (approximately 8.0 for temperate regions), as described by the Meteoric Water Line of Equation 13.

Evaporation. The Meteoric Water Line can be predictable for a given location because isotope fractionation occurs at equilibrium (100 percent humidity) during condensation. Evaporation, in contrast, typically occurs under non-equilibrium conditions when relative humidity is less than 100 percent. The humidity gradient from an open water surface introduces diffusional (kinetic) isotope fractionation, in addition to equilibrium fractionation, which is stronger for $\delta^{18}O$ than for δD (Siegenthaler 1979). Thus, water that undergoes non-equilibrium evaporation becomes more enriched in $\delta^{18}O$ relative to δD than the Meteoric Water Line (Equation 13) predicts.

To illustrate this phenomenon, consider the hypothetical Meteoric Water Line of Figure 1 (adapted from Fritz, *et al.*, 1976). The axes identify a typical range of δD and $\delta^{18}O$ values. A precipitation sample with $\delta D = -54$ ‰ and $\delta^{18}O = -8$ ‰ is plotted and coincides with the local Meteoric Water Line. If the sample undergoes evaporation under equilibrium conditions, enrichment in both heavy isotopes (δD and $\delta^{18}O$) will be consistent with the Meteoric Water Line, and the sample will move up the line.

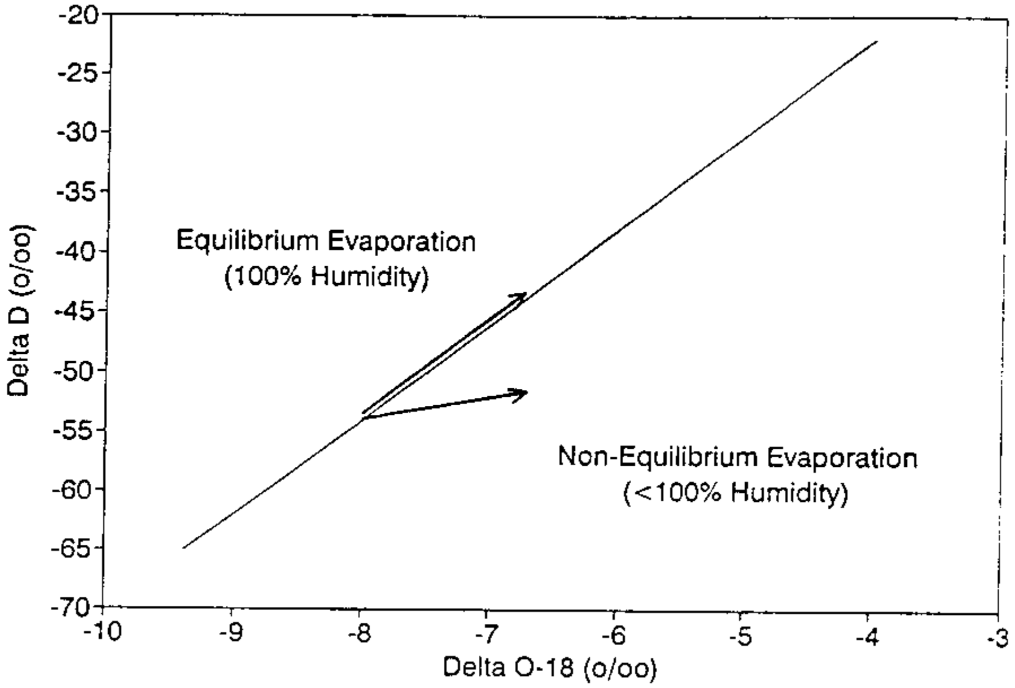

Figure 1. Equilibrium and non-equilibrium evaporation plotted on a hypothetical meteoric water line. (Adapted from Fritz, *et al.*, 1976.)

However, if non-equilibrium evaporation occurs, increased enrichment in $\delta^{18}O$ relative to δD will cause the isotope composition to deviate below the Meteoric Water Line by an amount functionally related to kinetic fractionation. This deviation is consistent enough for some surface waters that a second regression line, known as the *Evaporation Line*, may be fit to surface water data (Dinçer 1970). The magnitude of the deviation is known as *deuterium excess* (Coplen 1993).

Hydrograph Separation

Hydrograph separation involves estimating the source components of river or stream flow. For many hydrology applications, the flow components to be separated are *surface runoff* and *subsurface runoff* (Wanielista 1990, p. 28). Subsurface runoff can be further separated into *base flow* and *interflow*. Base flow is usually defined as streamflow originating from groundwater discharge (Todd 1980). Interflow is defined as quickly-responding flow from groundwater recharge areas nearby the river or stream (Wanielista 1990, p. 155).

Methods of hydrograph separation include analysis of the recession curve (tail of the hydrograph), mathematical modeling of the entire hydrograph, and the use of conservative tracers in mass-balance equations.

Recession Curve Analysis

Hydrograph separation by analysis of recession curves relies on the principle that flow components contributing to the recession limb of the hydrograph can be represented by an exponential decay function of the form

$$Q = Q_i e^{-K_i t_r} \tag{14}$$

where Q = Total streamflow [L^3t^{-1}]
Q_i = Intercept for segment i [L^3t^{-1}]
K_i = Recession coefficient for segment i [t^{-1}]
t_r = Time since peak discharge [t]

An example application of recession curve analysis is shown in Figure 2. The recession curve is composed of three distinct segments, each with a unique slope. The changes in slope indicate transitions in dominance among flow components. For example, using Figure 2 at a time t_r = 4 hours, runoff yields to interflow as the dominant flow component. Thus the exponential decay coefficient (K) for each flow component may be determined (Wanielista 1990, p. 169).

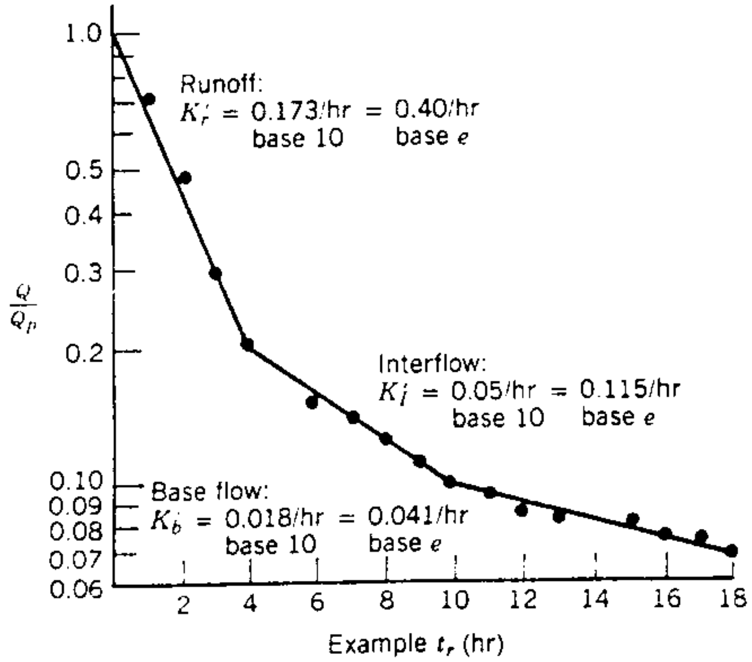

Figure 2. Hydrograph separation by recession curve analysis (Source: Wanielista, *et al.*, 1990).

Convolution Integral

A more sophisticated approach involves modeling the entire hydrograph using *unit-hydrograph* techniques. The unit hydrograph is the discharge generated by one unit of *rainfall excess*[3] (*e.g.*, 1.0 inch) over the watershed resulting from a rainfall of fixed duration (*e.g.*, 0.25 hours). Discharge over time can be computed by multiplying rainfall excess by the unit hydrograph. Individual hydrographs generated by successive rainfall excess increments can be summed to obtain the total storm hydrograph. This procedure can be formalized mathematically, if equations can be developed to represent rainfall excess over time and the shape of the unit hydrograph. The total hydrograph is developed by multiplying these functions and integrating them with respect to time. Two unit-hydrograph methods commonly used are the discrete and continuous models. The continuous model is known as the *continuous convolution integral* (Wanielista and Yousef 1993, p. 77) and has the general form

$$Q_t = \int_0^\infty R(\tau) g(t-\tau) d\tau \tag{15}$$

where Q_t = Discharge as a function of time $[L^3t^{-1}]$
$R(t)$ = Rainfall excess as a function of time $[L^3t^{-1}]$
$g(t-\tau)$ = Routing function offset in real time by τ $[t^{-1}]$

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[3] Rainfall excess is the volume of rainfall which can be translated into runoff.

Conservative Tracer Mass Balance

The concentration of conservative tracers can also be used in simple mass-balance equations to estimate the relative contributions of surface and groundwater. The most widely applied form of the mass-balance equation is

$$Q_R = Q_O + Q_N \tag{16}$$

$$Q_R C_R = Q_O C_O + Q_N C_N \tag{17}$$

$$Q_O = Q_R \frac{C_N - C_R}{C_N - C_O} \tag{18}$$

where Q_R, Q_O, and Q_N are the total river, old, and new discharges, respectively, and C_R, C_O, and C_N are their respective tracer concentrations (after Sklash, *et al.*, 1976). Equation 18 appears in various forms widely in the literature and is referred to as the *two-component model* or *2C model*. Table 2 summarizes the better-known studies that have applied the 2C model. It is interesting to note from Table 2 that new water rarely comprised greater than 50 percent of total storm discharge.

Other research includes a modification of the 2C model which decomposes subsurface flow into two distinct components and is known as the *3C* model (*e.g.*, Hinton, *et al.*, 1994, DeWalle, *et al.*, 1988; with comment by Genereux and Hemond, 1990; and reply by DeWalle, *et al.*, 1990). Several studies have focused on the near-stream zone to examine sources of streamflow (*e.g.*, Pionke, *et al.*, 1988).

A rather remarkable observation is that among the 30 or so refereed journal articles reviewed for this proposal, there were no derivations of the 2C model starting

Table 2.
SELECTED STUDIES THAT HAVE APPLIED THE TWO-COMPONENT HYDROGRAPH SEPARATION MODEL.

CITATION	CATCHMENT NAME	AREA (ha)	ANALYTE δD	δ^{18}O	Si	EC	OTHER	NEW (%)
Hill and Waddington, 1993	Oak Ridges Moraine	n/a		X				10-20
McKenna, *et al.*, 1992	Truckee River	n/a	X	X				n/a
Waddington, *et al.*, 1992	Oak Ridges Moraine	16,000		X			Cl, Li	<10
Buttle and Sami, 1992	Perch Lake SB3	3	X					40
McDonnell, *et al.*, 1991	Maimai M8	4	X			X	Cl	10
Ogunkoya and Jenkins, 1991	Allt a Mharcaidh	998	X					46
			X					12
Tranter and Raiswell, 1991	Gornergletscher	N.A.	X			X		>50
Wells, *et al.*, 1991a	Plastic & Harp	N.A.	X					28
					X		Mg	<10
Wells, *et al.*, 1991b	Plastic 108	3	X		X			35
Bonell, *et al.*, 1990	Otago G1	218	X					22
	Otago G2	310	X					7-12
McDonnell, *et al.*, 1990	Glendhu 2	310	X					22-27
Nolan and Hill, 1990	Permanente	1,060	X	X	X	X	K	43
Caine 1989	Martinelli	8					Cations	>50
Hirata and Murakoya, 1988	Tsukuba	68			X		NO_3	8
Turner, *et al.*, 1987	Salmon	82	X	X			Cl	5-40
Hooper and Shoemaker, 1986	Hubbard Brook W3	42	X		X			25-40
Kennedy, *et al.*, 1986	Mattole River	62,000	X	X	X			20
							^{3}H	50
Kobayashi 1986	Uryu River	12,800				X	Heat	<50
Obradovic and Sklash, 1986	Apex River	6,000		X		X	Mg	40
Pearce, *et al.*, 1986	Maimai	4		X		X	Cl	3
Bottomley, *et al.*, 1984	Harp Lake	300	X	X		X		10-60
Herrmann and Stichler 1980	Lainbach	18,700	X	X				14-47
Pilgrim, *et al.*, 1979	Stanford	<1				X		N.A.
Sklash and Farvolden 1979	Ruisseau 7A	120		X				20-35
	Ruisseau 6	390		X				20
Fritz, *et al.*, 1976	Wilson Creek	2,200		X		X	Na,Ca,Mg	>40
	Kenora (East)	180		X		X	Na,Ca,Mg	55-60
	Big Creek (Kelvin)	13,500		X		X		<50
	Big Otter (Vienna)	70,000		X		X		<50
Martinec 1974	Dischma	4,330					^{3}H	40
Nacamura 1971	Kioto River	10,300				X		<48
Dinçer, *et al.*, 1970	Modry Dul	265					^{3}H	30-40
Pinder and Jones 1969	April Brook	650				X	HCO_3	58
	Fraser Brook	900				X	HCO_3	60
	Sharpe Brook	1,350				X	HCO_3	68

with the differential form of the equation and explicitly stating the specific boundary over which the mass balance was solved. The tacit assumption among the articles has been that the mass balance was solved about the stream channel (stream bed) in headwater catchments. Thus, Equation 18 differs from the rigorous derivation by a channel storage term.

Other researchers (Stewart and McDonnell 1991; Turner and Macpherson 1990; Pearce, *et al.*, 1986) derived the convolution integral (Equation 15) to determine the residence time of groundwater discharging into a river:

$$C_O(t) = \int_0^\infty C_I(\tau) g(t-\tau) d\tau \tag{19}$$

Instead of solving for discharge, Equation 19 was solved for the concentration of a conservative tracer C as a function of time, where C_O was the concentration of the tracer in streamflow and C_I was the input tracer concentration. The calibrated model provided τ, an estimate of the mean residence time of water in the watershed.

In both the derivations of Equation 15 (Wanielista and Yousef 1993) and Equation 19 (Stewart and McDonnell 1991, Turner and Macpherson 1990, Pearce, *et al.*, 1986), the function $g(t-\tau)$ was represented by an exponential decay function.

Two-Component Mass Balance Model

Early applications of the 2C model used inorganic solutes or electrical conductivity (EC) as tracers (*e.g.*, Pinder and Jones 1969 and Nakamura 1971). Dinçer, *et al.* (1970) and Martinec (1974) used tritium (^3H) as a conservative tracer and assumed that radioactive decay of the tritium was small within the time frame of the study. Fritz, *et* *al.* (1976) appears to have innovated the use of oxygen-18 as a conservative tracer and inspired a series of studies that used some combination of oxygen-18 and deuterium with the 2C model.

Using solute tracers, such as EC, silica, and cations, researchers have assumed event water (C_N) to have low or zero concentrations of solute and pre-event water (C_O) to have solute concentrations that reflect geochemical processes in the surficial aquifer (Kennedy 1971). Thus, solute tracers are not truly conservative, since the concentration of the solute in the aquifer may vary with residence time or some local geochemical influence. The stable isotopes of water are truly conservative, in that the only processes that change their concentration are evaporation and mixing.

Old Water

Old water is commonly defined as water resident in the watershed before a storm event. The old-water component is ordinarily assumed to be groundwater draining from the surficial aquifer (Fritz, *et al*, 1976). The isotope content of groundwater is influenced by several factors in the recharge zone, but generally resembles the amount-weighted annual average isotope content of precipitation over the recharge area (Gat and Tzur 1967). Although the integrating effect of the aquifer tends to damp the effects of isotope contribution of individual storms, the isotope composition of groundwater in the surficial aquifer may fluctuate seasonally or in response to large-magnitude storm events.

Several factors may affect the isotopic composition of water infiltrating into the surficial aquifer. Precipitation falling through tree canopies (*throughfall*) may be detained long enough to undergo non-equilibrium evaporation, resulting in isotopic enrichment (DeWalle and Swistock 1994). Evaporative enrichment may also occur while water is stored temporarily in surface depressions (Krabbenhoft, *et al.*, 1990). Evaporation can occur in the phreatic zone (Gat and Tzur 1967), resulting in changes in the isotopic composition along the Meteoric Water Line, for equilibrium evaporation, and below the Meteoric Water Line, for non-equilibrium evaporation.

Wenner, *et al.* (1991), also reported seasonal effects in subsurface isotopic composition, believed to be related to the presence or absence of transpiration in temperate forests. Foliage in the watershed exerts a constant and heavy demand for subsurface water during the spring and summer. As a result, only the larger storm events (which tended to be isotopically depleted) contributed water to the surficial aquifer during warm months, while much wider range of storm events contributed to the aquifer during winter months (Wenner, *et al.*, 1991).

New Water

New water is commonly assumed to have the same isotopic content as precipitation (Kennedy, *et al.*, 1986). Many studies have used the volume-weighted mean isotopic content of the precipitation for C_N (*e.g.*, Pearce, *et al.*, 1984). McDonnell, *et al.* (1990) examined several weighting techniques to determine the mean isotopic content of precipitation and observed a substantial difference in new-water estimates among the methods. Investigators commonly collect sequential samples through the course of storm events to estimate intra-storm variability (*e.g.*, Pionke and DeWalle 1992, McDonnell, *et al.*, 1990). As described above, throughfall and temporary surface storage may result in evaporative enrichment. Thus, the processes that may fractionate rainwater should be recognized before assigning values to C_N.

Relevant Research

Three major research efforts have been responsible for delineating the assumptions under which the 2C model can be applied. The first was that of Fritz, *et al.* (1976) and Sklash, *et al.* (1976) who studied small catchments discharging into *pot-hole* lakes on a geologic formation known as the Precambrian Shield in Manitoba, Canada. Their research was continued by Bottomley, *et al.* (1984), and Wels, *et al.* (1991a and 1991b).

Kennedy, *et al.* (1986), reported a very thorough analysis of hydrograph separation techniques using oxygen-18, deuterium, tritium, chloride, and silica comparing isotope and geochemical analytes as tracers. Their research developed, in part, from studies of silica variation with discharge in the Mattole River basin in northern California (Kennedy 1971). At 62,000 ha, the Mattole River basin was, by far, the largest catchment to which the 2C model has been applied (Table 2).

The third major research effort in isotope or solute hydrograph separation was first reported by Pearce, *et al.* (1984). Their studies of the Maimai, Glendhu, and Otago catchments on the South Island of New Zealand (Table 2) advanced significantly the understanding of subsurface processes in the generation of runoff. Recent research in the Maimai catchment has focused on time-series analysis of long-term data (annual; including multiple storm events) to detect seasonal or other cyclic trends (Stewart and McDonnell 1991, and Turner and Macpherson 1990).

Limitations of the 2C Model

The expression of hydrologic interactions at the watershed scale in the form of a two-component model requires a great many simplifying assumptions. Virtually all of the authors listed in Table 2 recognized at least some of the limitations in applying Equation 18. The major assumptions of the 2C model (after Kennedy, *et al.*, 1986) are described below.

1. The concentration of old water (C_O) remains constant during the storm event.
2. The isotopic content of the old water is significantly different from that of new water.
3. The isotopic content of new water undergoes no changes while being routed through watershed.
4. A steady-state model adequately represents watershed conditions.

Most researchers have estimated C_O as the stream isotopic content of the near-stream groundwater or pre-storm river (DeWalle, *et al.*, 1988, Hooper and Shoemaker 1986) and assumed C_O to remain constant through the storm event (Assumption 1). The requirement for C_N to be significantly different than C_O (Assumption 2) has been considered in many of the studies reviewed. McDonnell, *et al.* (1991) are among the few that provide a quantitative expression of the difference between C_N and C_O relative to the analytical precision of the isotope test (*i.e., signal strength*). Assumption 3 requires that C_N equals the isotopic content of precipitation. Hydrologic processes such as throughfall and temporary surface storage, described above, may result in isotopic enrichment.

The assumption that a steady-state model adequately represents watershed conditions (Assumption 4) is seldom stated in the literature. In fact, of the peer-reviewed journal articles reviewed for this dissertation, none included derivations of the hydrograph separation models from the differential forms of the mass balance equations. This results in the tacit assumption that changes in the volume and isotopic content of channel storage over time are negligible.

Econlockhatchee River

The Econlockhatchee River basin occupies approximately 270 square miles in and east of Orlando, Florida and consists of two major branches, the Big and Little Econlockhatchee Rivers. The Big Econlockhatchee River is about 38 miles long with a watershed of approximately 200 mi^2. Approximately 60 mi^2. are occupied by wetlands, primarily undisturbed forested wetlands. The remaining area, occupied historically by pine flatwoods and sand-pine scrub, has been partially developed for agricultural and range use. The Little Econlockhatchee River has about 15 channel miles and drains approximately 70 mi^2. The watershed is highly urbanized and relatively little of the natural riparian zone is preserved. The Little Econlockhatchee River has 13 major water control structures (Miller & Miller 1984).

Several research projects have investigated the hydrology and water quality of the Econlockhatchee River basin to support the development of state and Federal rules, guidelines, and standards to protect the watershed. This research builds on studies conducted by the Civil & Environmental Engineering Department at University of Central Florida.

Hydrologic Balance

Study activities consisted of statistical analysis of historical records, development of a hydrologic balance of historical and projected watershed development, and recommendation of maintenance of surficial aquifer levels and stormwater management in the basin (Wanielista, *et al.*, 1992). This investigation revealed a measurable lowering in the surficial aquifer, probably related to installation of stormwater management ponds and related urban development. Wanielista, *et al.* (1992) recommended specific measures to protect surficial aquifer levels.

Historical Water Quality

In 1983 several wastewater treatment plants discharging into the Little Econlockhatchee River were upgraded to improve effluent quality. Routine water quality, data collected by Orange County from 1971 to 1991, were analyzed to determine the response of the river system to treatment-plant upgrades. Wanielista and Eaglin (1992) present tabular, graphical, and statistical analyses of water quality parameters. The data indicate an improvement in water quality in the system after 1983.

Pollutant Mixing Analysis

Guidelines to limit pollutant loading from stormwater management facilities are being developed by the Florida Department of Environmental Protection and the United States Environmental Protection Agency (EPA). Standards for water quality are based on the total maximum daily load (TMDL) of pollutants originating from point, non-point, and natural sources. Hydrologic and water quality data collected for previous studies

(Wanielista, *et al.*, 1992, Wanielista and Eaglin 1992) were used to calibrate and verify a pollutant mixing model to evaluate waste load impacts on streams, using empirical statistical distributions of hydrologic and water quality parameters (Eaglin 1993).

Surficial Aquifer Rating Curves

In the development of the hydrologic balance of the Econlockhatchee River Wanielista, *et al.* (1992), observed a strong relationship between the level of the surficial aquifer and river flow during recession periods, not only at monitoring sites near the river, but throughout the watershed. Nonlinear regression analysis quantified this relationship. Basinwide, recession flow was correlated with surficial aquifer elevation at a residual sum of squared errors (SSE) of less than 3 percent of total SSE (Wanielista, *et al.*, 1993).

Prospects for the Econlockhatchee River Watershed

The Econlockhatchee River is located in a region of intense urban development. Measures to preserve undeveloped portions of the watershed resulted in designation of the river system as *Outstanding Florida Waters*, an act that placed stringent controls on water quality in the river (FDER 1992). But the watershed was not protected from further urbanization. In September 1993, Orange County, Florida commissioners voted to approve phase I construction of Avalon Park, a commercial and residential development to be located on the Big Econlockhatchee River. At full build-out, the development would occupy 5,700 acres of currently undeveloped land (Lebowitz and Wellons, 1993).

Developers claimed that extensive environmental protection measures would be exercised, including undisturbed buffer strips on both sides of the river ranging from 550 to 1,100 feet wide (Wellons and Lebowitz 1993). The water quality and hydrologic protection afforded by such buffer strips is uncertain. The research of Wanielista, *et al.* (1993) indicated that river flow is highly responsive to the surficial aquifer throughout the Econlockhatchee River watershed. Thus, changes in the hydrology of the watershed may impact river discharge and water quality patterns. Clearly, the mechanisms of hydrologic transport in the surficial aquifer need to be better understood before meaningful environmental protection can be provided for sensitive ecosystems.

Objectives

The principal objective of this dissertation was to estimate surficial aquifer contribution (new water) to flow in the Econlockhatchee River under varying flow conditions using environmental stable isotope tracers. Intermediate and supporting objectives were to develop and calibrate laboratory methods to analyze water samples for stable isotopes (Chapter 2), evaluate the environmental isotope signal in the Econlockhatchee River watershed to determine the applicability of hydrograph separation using stable isotopes (Chapter 3), and perform hydrograph separations using steady and unsteady-state models (Chapter 4).

Approach

This dissertation documents research conducted in the field and laboratory and has been organized with introductory and concluding chapters (Chapters 1 and 5) and three technical chapters (Chapters 2, 3, and 4), which are each intended to form independent manuscripts. Each manuscript will be edited to conform to format and content requirements for appropriate archival journals.

Although stable isotopes have been used in hydrologic studies (Table 2) relatively few laboratories are equipped to prepare and analyze water samples for these analytes. Prior to this study, only one laboratory in Florida (Rosenstiel School of Marine and Atmospheric Sciences, University of Miami) could perform the required analyses. Thus, a significant component of this research involved design, construction, and calibration of preparation systems at the Geology Department at University of Florida.

The stable isotopes of oxygen, hydrogen, and carbon were investigated for this research. Analytical procedures for $\delta^{18}O$ and δD reproduce published techniques and are described, with calibration and quality assurance data, in Appendix A. A novel procedure was developed by the author for the analysis of $\delta^{13}C$ of dissolved inorganic carbon in natural water. This procedure is described in Chapter 2, and a complete listing of supporting data is provided in Appendix B.

The stable isotope of oxygen was selected for hydrograph-separation analyses; the author analyzed over one thousand water samples for $\delta^{18}O$. In Chapter 3, described are temporal and spatial variability in the $\delta^{18}O$ of precipitation, surface water, and water from the surficial and Floridan aquifers. Appendix C describes field procedures and provides complete field and oxygen isotope data listings. In Chapter 4, two-component hydrograph separations at 2 locations in the watershed are presented with comparative analysis of models for steady-state and unsteady-state conditions. Appendix D provides supporting calculations and listings of modeling data. In Chapter 5, the research is summarized and conclusions and recommendations regarding the surficial aquifer hydrology of the Econlockhatchee River watershed are provided. Appendix E provides a complete list of references.

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CHAPTER 2

ISOTOPIC ANALYSIS OF DISSOLVED INORGANIC CARBON IN NATURAL WATER USING DISPOSABLE PRE-EVACUATED SERUM VIALS

Introduction

Background

The relative abundance of the carbon stable isotopes, ^{12}C and ^{13}C, in organic and inorganic matter can be used as a tracer to investigate geochemical cycles, ecological gradients among trophic levels, and hydrologic flow pathways. The effectiveness of carbon stable isotopes as tracers in most ecological and hydrologic studies relies on the phenomenon that the photosynthetic reaction discriminates against the ^{13}C isotope (Coleman and Fry 1991). This results in an accumulation of ^{12}C in organic matter relative to ^{13}C, expressed quantitatively as *depletion* in $\delta^{13}C$ (Craig 1957):

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{Sample}}{(^{13}C/^{12}C)_{Reference}} - 1 \right] x\ 1000 \qquad (20)$$

with the units of *per mil*, or *parts per thousand* (‰).

Table 3 summarizes data collected in the Econlockhatchee River system in central Florida. Water samples were analyzed for $\delta^{13}C$ of the dissolved inorganic carbon ($\delta^{13}C_{DIC}$). Complete data listings are provided in Appendix B. The Floridan aquifer has

Table 3.
CARBON-13 OF DISSOLVED INORGANIC CARBON IN WATER SAMPLES COLLECTED FROM THE FAWN RUN SAMPLING SITE, ECONLOCKHATCHEE RIVER, SEPTEMBER 16, 1993.

STATION	CODE	N	MEAN (‰)	STANDARD DEVIATION (‰)
River	FRR	1	-18.91	
Surficial Aquifer	FR0	3	-17.21	0.02
	FR1	3	-21.41	0.09
	FR2	3	-21.31	0.09
Floridan Aquifer	FRF	3	-7.98	0.09

a mean $\delta^{13}C_{DIC}$ = -8.0 ‰, an isotopic signature that reflects dissolution of marine carbonates that form the parent material (Fritz, *et al.*, 1978). Coincidentally, -8.0 ‰ is the $\delta^{13}C$ of CO_2 in the present-day atmosphere (Quay, *et al.*, 1992). The $\delta^{13}C_{DIC}$ of river and surficial-aquifer waters (Table 3) are significantly more depleted, with means of -18.9 and -20.0 ‰, respectively, indicating an organic origin for the DIC. If there were significant contribution to river flow from the Floridan aquifer, a more enriched $\delta^{13}C_{DIC}$ would be expected.

Analytical Methods

Two methods are commonly used to analyze $\delta^{13}C_{DIC}$. One method uses strontium chloride ($SrCl_2$) or barium chloride ($BaCl_2$) to precipitate the carbonate from solution (Bishop 1990, Gleason, *et al.*, 1969). The carbonate solid is then filtered, dried, and analyzed for $\delta^{13}C$ using standard methods (McCrea 1950). This method requires a sample size of approximately 150 mL (assuming DIC = 20 mg C/L), and is capable of analytical precision of 0.2 ‰ (1σ, $n=11$, Bishop 1990). The other method uses a weak acid to evolve CO_2 gas from the sample. The gas is stripped away by diffusing nitrogen gas through the sample and collected for analysis (Kroopnick, *et al.*, 1970, Herczeg and Fairbanks 1987). This method requires a sample size of 50 to 100 mL and is capable of analytical precision better than 0.1 ‰.

The method of Kroopnick, *et al.* (1970) was improved by Graber and Aharon (1992), who demonstrated that it was possible to acidify a small (approximately 2 mL) water sample in a sealed reaction vessel, capture and purify that gas by cryogenic pumping through a vacuum system, and measure simultaneously the $\delta^{18}O$, $\delta^{13}C_{DIC}$, and total DIC. This method represented an improvement in previous techniques, as it required a relatively short equilibration time and small sample size and provided simultaneous measurement of three parameters.

Objective

The objective of this study was to determine if the Graber and Aharon (1992) technique could be modified for use with commercially-available disposable serum vials as reaction vessels. Socki, *et al.* (1991) successfully used similar vials as reaction vessels for CO_2 equilibration to analyze water samples for $\delta^{18}O$. As an alternative to the Graber and Aharon (1992) method, the proposed technique would require no specialized glassware and would be procedurally simpler. Because the reaction vessels are disposable, this technique would eliminate the necessity to clean reaction vessels and replace septa. Perhaps most significantly, the proposed procedure is unique in its portability. Serum vials can be brought into the field or shipboard and samples can be injected immediately after collection, obviating the need for field preservation (Socki, 1993, personal communication).

Results reveal that the proposed technique is capable of $\delta^{13}C_{DIC}$ and total DIC analysis at $1\sigma = 0.1$ ‰ and 1.4 mg C/L, respectively. However, extraction for $\delta^{18}O$ was unsuccessful evidently due to interference from a condensible contaminant produced in the vial. This paper describes an accurate and inexpensive alternative for the simultaneous analysis of $\delta^{13}C_{DIC}$ and total DIC and addresses the limitations of disposable pre-evacuated serum vials in stable-isotope research.

Experimental

Preparation

Sample vials were prepared by removing the stoppers, injecting 100 μL orthophosphoric acid in each vial, replacing the stoppers, and drawing a vacuum on each vial. Vials used for this study were Vacutainer™ brand sterile serum tubes, with a nonsiliconized interior and 10 mL draw. Stoppers were removed and orthophosphoric acid was injected into the open vials using a 100 μL micropipette.

Acid was prepared from HPLC-grade 85 percent orthophosphoric acid (H_3PO_4). Water was removed from the acid by boiling at atmospheric pressure in a fume hood until a specific gravity of 1.92 was attained. Acid was immediately sealed in 10 mL ampoules to avoid absorption of atmospheric water.

After acid injection, stoppers were replaced on vials and a vacuum was returned to each vial using the vacuum manifold shown on Figure 3a. This apparatus included

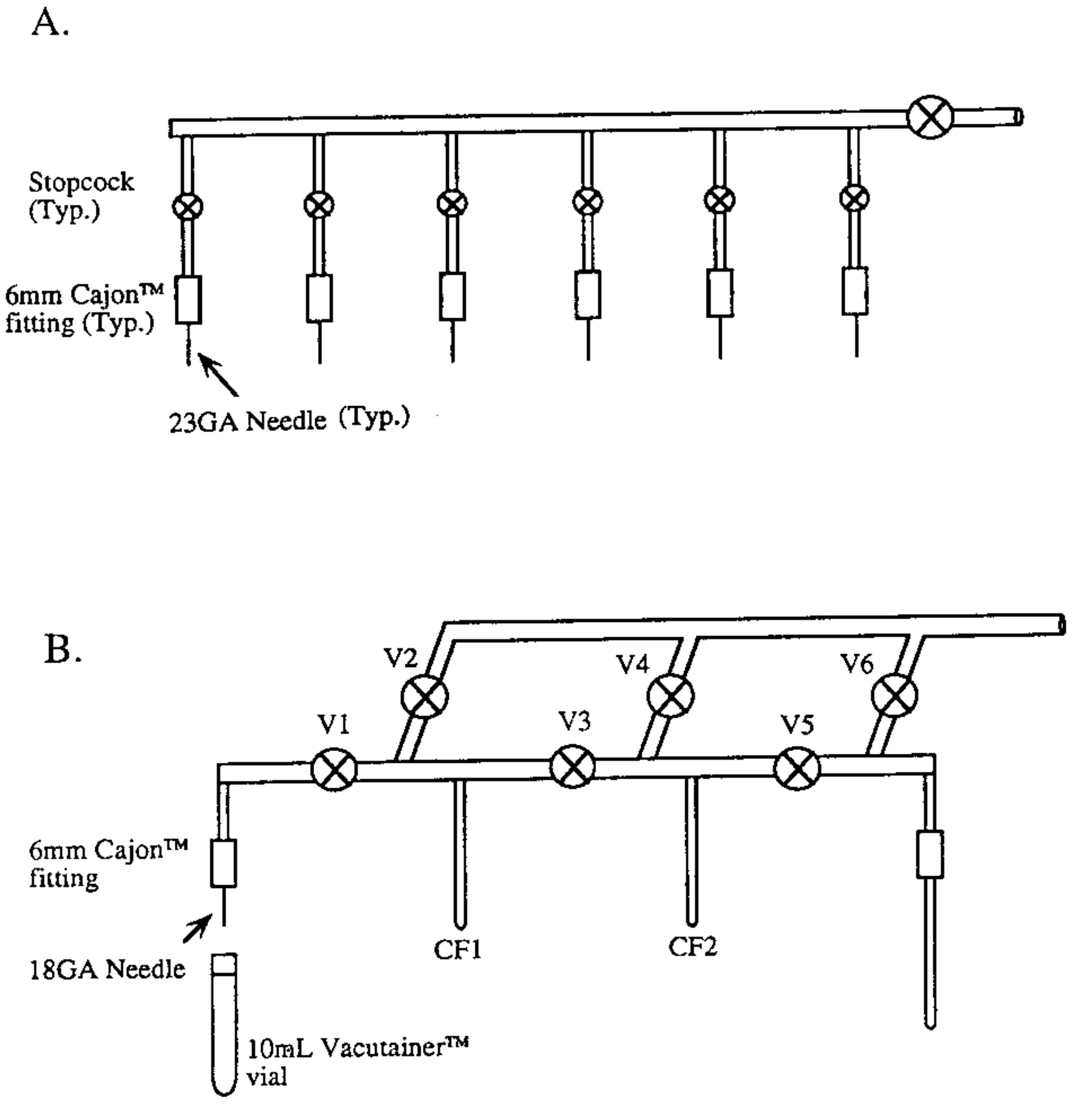

Figure 3. Vacuum Lines for (a) Preparing Serum Vials and (b) Extracting CO_2.

23 gauge Luer-Lok™ hypodermic needles mounted on 6 mm outside-diameter pyrex tubes. Needles were attached to glass tubes using high-vacuum epoxy cement (Epoxi-Patch 1C, Hysol Aerospace & Industrial Products, Pittsburg, California). Socki *et al.* (1992) silver-soldered 20 ga. needles to stainless-steel 10 mm o.d. tubes.

Using the manifold system shown on Figure 3a, six vials were evacuated simultaneously. The vials were placed under active vacuum for 20 minutes to evacuate the vials and draw dissolved gases from the acid. Vials were then removed from the vacuum line and stored for later use. Vials injected with acid may be stored indefinitely prior to use, however if vials were stored longer than approximately one week, the vacuum in vials was improved on the vacuum manifold.

Vial Integrity

Experiments on empty 10 mL serum vials revealed that within 2 hours after an initial vacuum of $3(10^{-5})$ atmospheres was drawn on the vials, they equilibrated to an internal pressure of approximately $2(10^{-2})$ atm. By mass balance, the maximum expected shift in $\delta^{13}C$ due to intrusion of atmospheric CO_2 was computed. Direct measurements indicated the total volume of air entering the vial was less than 0.2 mL at 1.0 atmospheres. Assuming a present-day atmospheric CO_2 content of 350 ppm (Schlesinger, 1991), the volume of atmospheric CO_2 in the vial was

$$\begin{aligned} Volume\ C_{Air} &= 0.2\ mL\ Air\ x\ \frac{350\ mL\ CO_2}{10^6\ mL\ Air}\ x\ \frac{cm^3}{mL} \\ &= 7(10^{-5})\ cm^3\ CO_2 \end{aligned} \tag{21}$$

The mass of elemental carbon in that air was computed using the ideal gas law (Equation 22, CRC 1974)

$$Mass\ C_{AIR} = \frac{1.0\ [atm]\ x\ 7(10^{-5})\ [cm^3]}{82.05\ [atm\ cm^3\ K^{-1}]\ x\ 298\ [K]}\ x\ \frac{mole\ C}{mole\ CO_2} \tag{22}$$

$$= 2.8629(10^{-9})\ moles\ CO_2$$

The mass of elemental carbon in a 5.0 mL water sample with 20 mg C/L DIC is

$$Mass\ C_{SAMPLE} = 5.0\ mL\ x\ 20\ \frac{\mu g}{mL}\ x\ \frac{g}{10^6\ \mu g}\ x\ \frac{mole\ CO_2}{44\ g\ CO_2}\ x\ \frac{mole\ C}{mole\ CO_2} \tag{23}$$

$$= 2.2727(10^{-6})\ moles\ C$$

The mass balance for δ^{13}C shift is

$$\delta^{13}C_{SHIFT} = \frac{(C_{AIR}\ x\ \delta^{13}C_{AIR}) + (C_{SAMPLE}\ x\ \delta^{13}C_{SAMPLE})}{C_{AIR} + C_{SAMPLE}} \tag{24}$$

Assuming present-day air has $\delta^{13}C$ = -8.0 ‰ (Quay, *et al.*, 1992) and the sample has $\delta^{13}C_{DIC}$ = -24.33 ‰ (Table 4), the maximum shift in δ^{13}C due to atmospheric intrusion is

$$\delta^{13}C_{SHIFT} = \frac{(2.8629(10^{-9})\ x\ -8.0) + (2.2727(10^{-6})\ x\ -24.33)}{2.8629(10^{-9}) + 2.2727(10^{-6})} \tag{25}$$

$$= -24.309\ o/oo$$

By Equation 25, the theoretical shift in δ^{13}C due to the air leak was less than +0.020 ‰ for the standard solution. Thus, a consistent and measurable air leak or other loss into the vials existed, but did not contribute significant error to isotopic analysis.

Table 4.
CARBON-13 AND OXYGEN-18 ANALYSIS OF SOLID AND DISSOLVED POTASSIUM CARBONATE STANDARDS.

SAMPLE	N	MEAN $\delta^{13}C$ (‰)	STD $\delta^{13}C$ (‰)	N	MEAN $\delta^{18}O$ (‰)	STD $\delta^{18}O$ (‰)
Solid	11	-24.33	0.22			
Dissolved						
All DIC	28	-24.33	0.11	28	-4.77	2.94
10 mg/L	6	-24.30	0.17	6	-1.76	5.22
20 mg/L	5	-24.38	0.02	5	-5.90	0.22
30 mg/L	6	-24.44	0.03	6	-5.77	0.29
40 mg/L	6	-24.32	0.04	6	-5.02	1.00
50 mg/L	5	-24.22	0.01	5	-5.77	0.16

Note: STD = Standard Deviation

Equilibration

A water sample was injected into each vial using a gas-tight or glass syringe with a 23 ga. or smaller needle and the vials were placed in a shaker bath at 50° C for 30 minutes. A sample volume of 5 mL was used with 10 mL vials. Samples were placed horizontally in a rack and submerged in a temperature-controlled shaker bath. The shaker was set to agitate the samples vigorously in a horizontal motion along the long-axis of the vials. Water temperature was maintained at 50° C. After 30 minutes of agitation, samples were stored in the bath without agitation until extraction. Samples were extracted the same day they were injected and equilibrated.

Extraction

After equilibration, each vial was placed on the vacuum extraction line (Figure 3b) and the CO_2 was extracted and purified. To facilitate gas transfer, a larger diameter needle (18 ga.) was used for extraction than for drawing the initial vacuum. Before extracting CO_2 from the vial, the volume within the needle and up to valve V1 was evacuated by imbedding the needle in the stopper deeply enough to cover the needle opening, but not deeply enough to intrude into the vial. The needle was evacuated by opening valve V1.

Noncondensible gases were withdrawn from the vial by freezing the sample, first in a methanol-dry-ice slush (methanol trap) at -120°C to freeze the water, then in liquid nitrogen (LN trap) at -200°C to condense the CO_2. Socki *et al.* (1992) recommended heating the stopper lightly with a heat gun to evaporate droplets of water adhering to the inside of the stopper. After freezing the sample approximately one minute in liquid nitrogen, the vial was pushed upward allowing the needle to puncture into the vial. The noncondensible gases withdrawn consisted of a combination of dissolved gas from the sample and air leaked into the vial.

When pressure transducer P1 indicated that noncondensible gases were withdrawn, the sample was transferred through cold fingers CF1 and CF2 to remove condensible gases, primarily water vapor, and collected in a 6 mm break-seal tube. To trap CO_2 in CF1, valves V2 and V3 were closed, a methanol trap was placed on the sample vial and a LN trap was placed on cold finger CF1. As CO_2 thawed in the sample vial, it was collected in CF1. Transfer of CO_2 was considered complete when P1 returned to its original reading. Similarly, to trap the sample in CF2 valves V1, V2, V4, and V5 were closed; valve V3 was opened; the LN trap on CF1 was replaced with a methanol trap; and a LN trap was placed on CF2. After the sample was trapped in CF2, it was collected by closing valves V3, V4, and V6; opening valve V5; replacing the LN trap on CF2 with a methanol trap; and placing an LN trap on the break-seal tube. When sample transfer was complete, the tube was detached from the line and sealed using a blowtorch.

Analysis

Unless water samples had DIC concentrations in excess of approximately 40 mg C/L (4.5 μmole C), the small sample volume evolved using this procedure necessitated the use of a cold-finger at the sample inlet of the mass spectrometer. A VG-Prism isotope-ratio mass spectrometer with Faraday collectors focussed to detect masses 44, 45, and 46, was used for this study. To quantify the total volume of DIC generated, the gas sample was frozen into a cold finger at the sample inlet, expanded into a fixed volume of the inlet (sample bellows open and fully compressed), as described by Graber and Aharon (1991), and the major ion beam (mass 44) produced by each sample was recorded. It should be noted that this study used a mass spectrometer that measured ion beam intensity as an amperage, while the Graber and Aharon (1991) study used a mass spectrometer that measured ion beam strength as a voltage. Although the units differ, the procedure is functionally identical.

Once introduced into the mass spectrometer inlet, samples were analyzed for isotopic ratios of mass 45/44 and mass 46/44. Standard calculations were performed to convert the mass 45/44 ratios to per-mil notation relative to PDB (Craig 1957). The reference gas used was generated from Carerra marble and has been calibrated against international standards (Hodell, *et al.*, 1989, Coplen, *et al.*, 1983). The Craig correction (Craig 1957) was employed to account for the mass 45 signal produced by $^{12}C^{17}O^{16}O$. The mass 46/45 ratio was converted to $\delta^{18}O$ relative to V-SMOW (Coplen, *et al.*, 1983).

Standards

A potassium bicarbonate standard was used. Reagent-grade $KHCO_3$ was vacuum-roasted at 100° C for at least one hour to drive off atmospheric moisture and CO_2. Deionized water (DIW) was stripped of dissolved CO_2 by bubbling nitrogen gas through the water for 30 minutes. Standard solutions were prepared by dissolving the reagent into degassed DIW at concentrations of 10, 20, 30, 40, and 50 mg C/L. As Graber and Aharon (1991) noted, the standard solution is highly sensitive to contamination by atmospheric CO_2 and great care must be taken in preparing standard solutions.

Results and Discussion

Carbon-13 and Oxygen-18

Table 4 summarizes the results of isotopic analysis of replicate samples of the standard solutions. Precision is expressed as the standard deviation of the mean of replicate analyses. Accuracy is expressed as a comparison of results against potassium bicarbonate reagent analyzed as a solid using standard methods (McCrea 1950). For 11 replicate solid samples and 28 aqueous samples the arithmetic means are identical at $\delta^{13}C$ = -24.33 ‰, with standard deviations of 0.22 and 0.11 ‰ for solid and aqueous samples, respectively. For DIC greater than 20 mg C/L, there was no systematic response of the mean or standard deviation in $\delta^{13}C$ as a function of sample size. At 10 mg C/L, the precision decreased dramatically, suggesting an interfering agent expressed at low DIC concentrations.

The source of interference for dilute samples was investigated by examining the ratio of ion beam intensity at mass 46 relative to mass 44 over time (ratio trace) during each sample run. The mass spectrometer produced a similar trace for the mass 45/44 ratio. When the mass spectrometer is sufficiently tuned, ratio traces should be flat lines, indicating steady beam intensity over time. For 4 of the 6 replicate analyses of the standard solution at 10 mg C/L (1.14 μmole C) the ratio traces were virtually flat, producing a mean and standard deviation in $\delta^{13}C$ of -24.30 and 0.06 ‰, respectively. The remaining 2 samples produced ratio traces that were tilted in a positive direction with time during sample analysis. The traces were flat during analysis of the reference gas (Figure 4).

Uneven traces during sample analysis may indicate an air leak into the sample side of the mass spectrometer inlet or the presence of a contaminant of approximately mass 45. Calibration tests eliminated the possibility of an air leak into the mass spectrometer. A background scan was performed on the sample gas to determine the composition of the gas. If the sample were significantly contaminated by air, the scan would indicate the presence of ions at masses 28 (N_2) and 40 (Ar). The background scan indicated an ion signal only at mass combinations indicative of CO_2. A possible explanation for the uneven traces is a condensible contaminant of approximately mass 45, produced in the serum vial and extracted with the sample. The presence of the contaminant may have been masked by CO_2 at concentrations greater than 10 mg C/L.

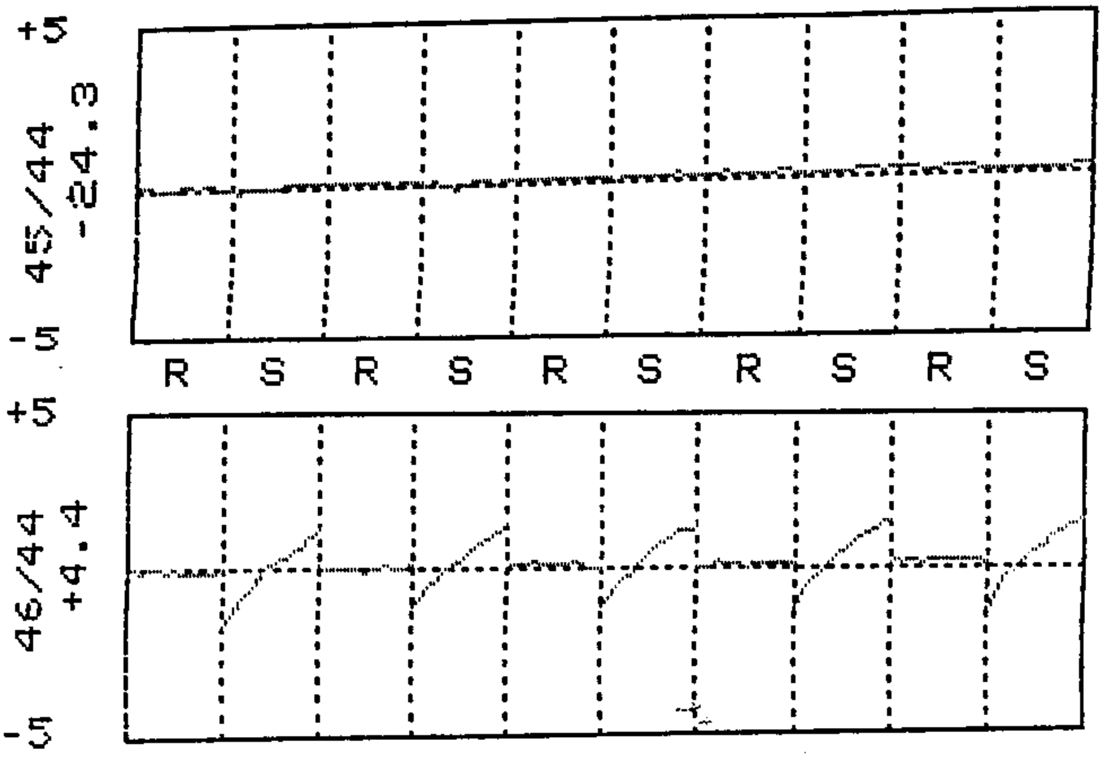

Figure 4. Ratio trace for CO_2 extracted from a 10 mg C/L (1.14 μmole) sample.

The observed analytical interference apparently affects the measurement of $\delta^{13}C$ at low DIC concentrations, but affects $\delta^{18}O$ measurement at a much broader DIC range. Using a similar procedure, but different reaction vessel design, Graber and Aharon (1991) reported simultaneous measurement of $\delta^{13}C$ and $\delta^{18}O$ with standard deviations at or better than 0.1 ‰. Using serum vials, standard deviations of $\delta^{18}O$ measurements were unacceptably large at any DIC concentration evaluated (Table 4).

Serum vials have been used successfully to measure the $\delta^{18}O$ of natural water by equilibrating introduced CO_2 gas at a pressure of approximately 0.5 atm (Socki, *et al.*, 1992) with no observed interference in the mass 45/44 ratio. Because CO_2 was provided externally, the procedure did not require injection of acid to evolve CO_2 from DIC in the sample. It may be inferred that either the interference at mass 45 was present and masked by the large amount of introduced CO_2, or was absent because acid was not injected into the vial. If the latter is the case, it is possible that orthophosphoric acid reacted with the stopper or the interior coating of the vial to produce a condensible contaminant. In any case, the procedure described in this paper produced accurate and reproducible results for analysis of $\delta^{13}C_{DIC}$ at concentrations greater than 10 mg C/L.

Total DIC

The functional relationship between the strength of the major ion beam and total DIC was examined. Table 5 summarizes the major ion beam strength for standard solutions at 5 concentrations. These data are plotted on Figure 5 with a fitted second-order polynomial regression line ($R^2 = 0.9901$) and 95 percent prediction limits.

Table 5.
MAJOR ION BEAM INTENSITY WITH VARYING CONCENTRATION IN A POTASSIUM BICARBONATE STANDARD SOLUTION.

SAMPLE SIZE (mg C/L)	N	MEAN (Amperes)	STD (Amperes)	CV (%)
10	6	$1.66(10^{-9})$	$4.37(10^{-11})$	2.64
20	5	$3.21(10^{-9})$	$5.91(10^{-11})$	1.84
30	6	$4.92(10^{-9})$	$3.08(10^{-10})$	6.27
40	6	$7.13(10^{-9})$	$2.84(10^{-10})$	3.99
50	4	$8.84(10^{-9})$	$2.37(10^{-10})$	2.68

Note: STD = Standard Deviation
CV = Coefficient of Variation

Because the major ion beam (the *independent* variable in Figure 5) was used to predict DIC (the *dependent* variable), a form of regression analysis known as *inverse prediction (Neter, et al.*, 1990) was employed. This analysis indicated that, with 95 percent confidence and based on the experimental data summarized in Table 5, total DIC may be predicted with a standard deviation of 1.40 mg C/L in the range of 20 to 40 mg C/L and with a standard deviation of 1.43 mg C/L above and below that range to the limits of 10 and 50 mg C/L. Because the tuning parameters in the mass spectrometer change over time, it is necessary to verify the regression equation by running daily standards of known DIC. When tuning changes significantly, a new standard curve must be developed (Graber and Aharon 1991).

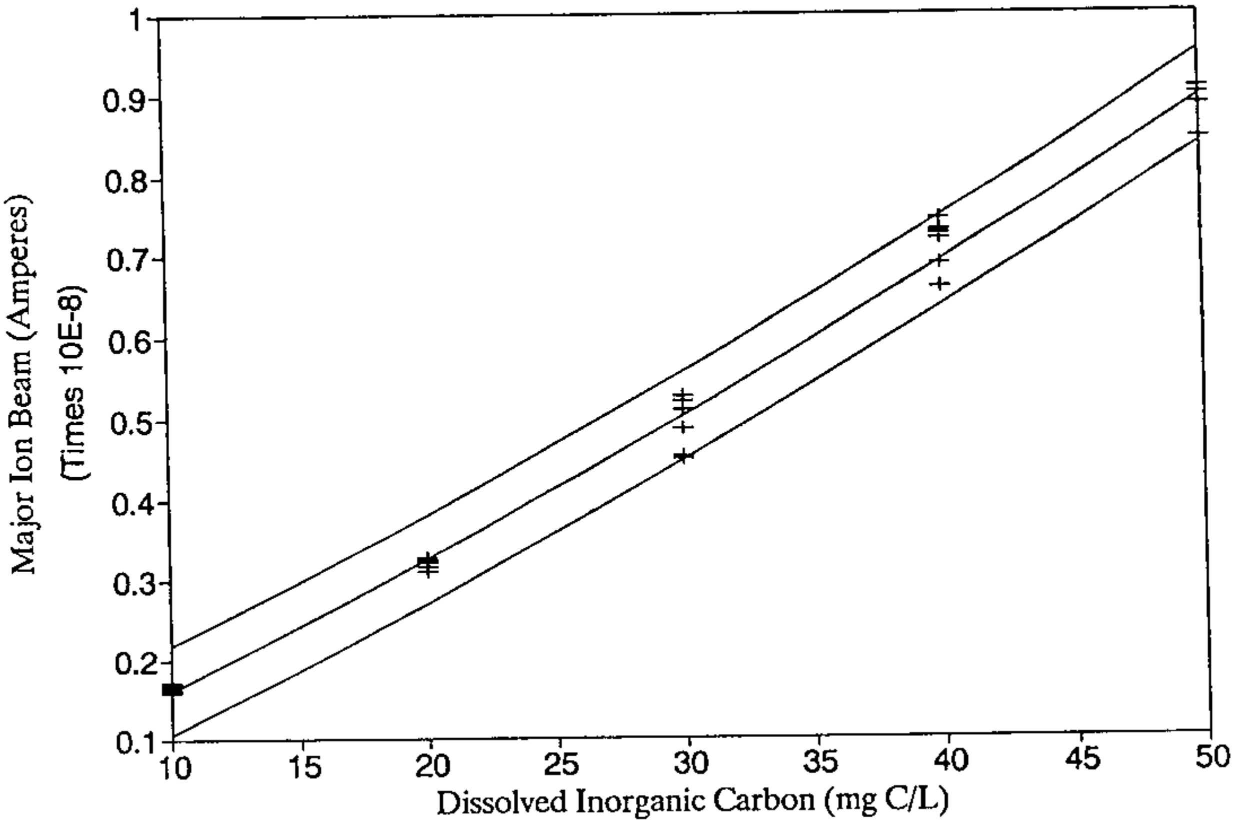

Figure 5. Major Ion Beam as a Function of Dissolved Inorganic Carbon with 95 Percent Prediction Intervals.

Conclusions

A method was evaluated to prepare natural water samples for $\delta^{13}C$ analysis using commercially-available serum vials as reaction vessels. Disposable serum vials have been used successfully for the analysis of $\delta^{18}O$ of natural water (Socki, *et al.*, 1991). The procedure developed for this paper was adapted from that of Graber and Aharon (1991). For water samples with total DIC greater than approximately 10 mg C/L, the authors attained a replicate precision for $\delta^{13}C_{DIC}$ better than $1\sigma = 0.1$ ‰ (n=22). Total DIC can be measured simultaneously using the intensity of the major ion beam at a replicate precision better than $1\sigma = 1.43$ mg C/L.

This research revealed two limitations to the use of pre-evacuated serum vials. The first is the apparent presence of a condensible contaminant that obscures the ion signal at mass 45, preventing $\delta^{18}O$ measurement and apparently introducing error in $\delta^{13}C_{DIC}$ measurement of dilute water samples (10 mg C/L or less). The second limitation is a consistent air leak into the vials. Serum vials used for this study were able to maintain a vacuum of approximately $2(10^{-2})$ atm. Attempts to draw a higher vacuum resulted in equilibration back to $2(10^{-2})$ atm within 2 hours. The observed leak introduced no detectable error in the $\delta^{13}C$ analysis of DIC.

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CHAPTER 3

SYNOPTIC SURVEY OF STABLE ISOTOPES IN A SUBTROPICAL LOW-GRADIENT WATERSHED

Introduction

Under certain conditions, environmental tracers can be used with hydrologic mixing models to estimate the relative contribution of two or more water masses to flow in river systems. This is a form of *hydrograph separation.* A common objective is to determine the fraction of *old*, or prestorm, water present in river flow during a storm hydrograph. The most widely used mixing model is the *two component* model, typically of the form

$$Q_R = Q_O + Q_N \tag{26}$$

$$Q_R C_R = Q_O C_O + Q_N C_N \tag{27}$$

$$Q_O = Q_R \frac{C_N - C_R}{C_N - C_O} \tag{28}$$

where Q_R, Q_O, and Q_N are the total, old, and new discharges, respectively, and C_R, C_O, and C_N are their respective tracer concentrations (after Sklash, *et al.*, 1976). The data requirements for Equation 3 are estimates for Q_T, C_T, C_O, and C_N. Q_T and C_T can be measured directly at one or more stations on the river. C_O and C_N are known as *end* *members*, because they represent the extreme possible concentrations of C_T. They reflect average watershed conditions and may be estimated by sampling representative waters within the watershed.

A variety of tracers has been used in hydrograph separation, including electrical (specific) conductivity, dissolved silica, and various anions and cations (Wels, *et al.*, 1991, Caine 1989, Fritz, *et al.*, 1976, Pinder and Jones 1969). Many recent studies use the stable isotopes of oxygen ($\delta^{18}O$) and hydrogen (δD). Stable isotopes are considered excellent tracers, because they are constituents of the water molecule, rather than a solute transported with the water, and can form distinctive signatures in water masses (McAfee 1989).

The expression of hydrologic interactions at the watershed scale using Equation 28 requires simplifying assumptions, the most important of which are

1. C_O and C_N are constant, or vary predictably with time, over the solution interval of Equation 3.
2. C_O and C_N are significantly different.

Meeting the first assumption requires adequate monitoring within the watershed to characterize temporal and spatial variability in the end members. For isotope studies, the second assumption requires a high degree of annual variability in the isotopic content of rainfall. Because the surficial aquifer is recharged by many storm events, the isotopic content of this reservoir (C_O) is approximately the annual average isotopic content of precipitation recharging the aquifer (Gat and Tzur 1967). C_N is usually taken as the isotopic content of precipitation (Pearce, *et al.*, 1986). A wide annual range in the isotopic content of precipitation increases the chance that, for a particular storm event for which Equation 28 is solved, C_N will be significantly different than C_O. This range may be termed *signal strength.*

The objective of this research was to assess the suitability of $\delta^{18}O$ as an environmental tracer for hydrograph separation in the Econlockhatchee River basin in central Florida by characterizing the isotopic signals of hydrologic components in the watershed. A baseline synoptic survey of the watershed is presented in this paper. The study was designed to monitor temporal and spatial changes in the $\delta^{18}O$ of precipitation, river water, and groundwater in the Econlockhatchee River basin.

Prior to this study, the stable-isotope characteristics of precipitation in central Florida were unknown. Central Florida receives precipitation from maritime tropical systems, continental frontal advances, frontal return systems from the Gulf of Mexico, and convective summer storms (Wanielista 1990, Myers and Ewel, 1990). Each of these storm types may be expected to produce a distinctive range in $\delta^{18}O$, thus it was reasonable to expect that stable isotopes could be used as environmental tracers.

Site Description

The Econlockhatchee River basin drains approximately 270 mi.^{2} in east central Florida, flowing northward to the St. John's River. The main stem, the Big Econlockhatchee River, has a channel length of approximately 33 miles. A major sub-catchment, the Little Econlockhatchee River drains 70 mi.^{2} and has a channel length of approximately 15 miles (Figure 6). Total elevation change in the river bed is approximately 70 ft. (Figure 7).

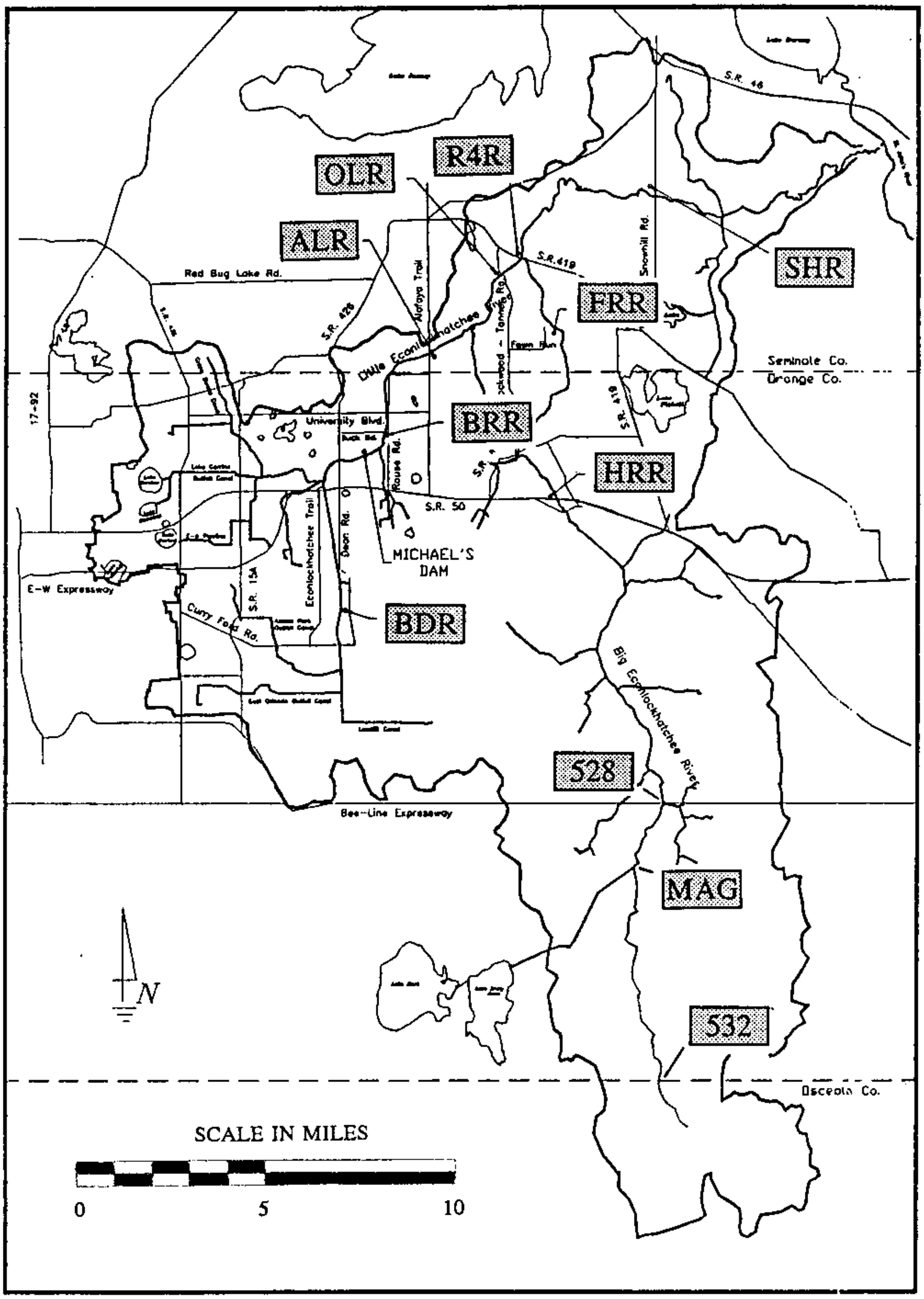

Figure 6. The Econlockhatchee River watershed, with sampling stations identified.

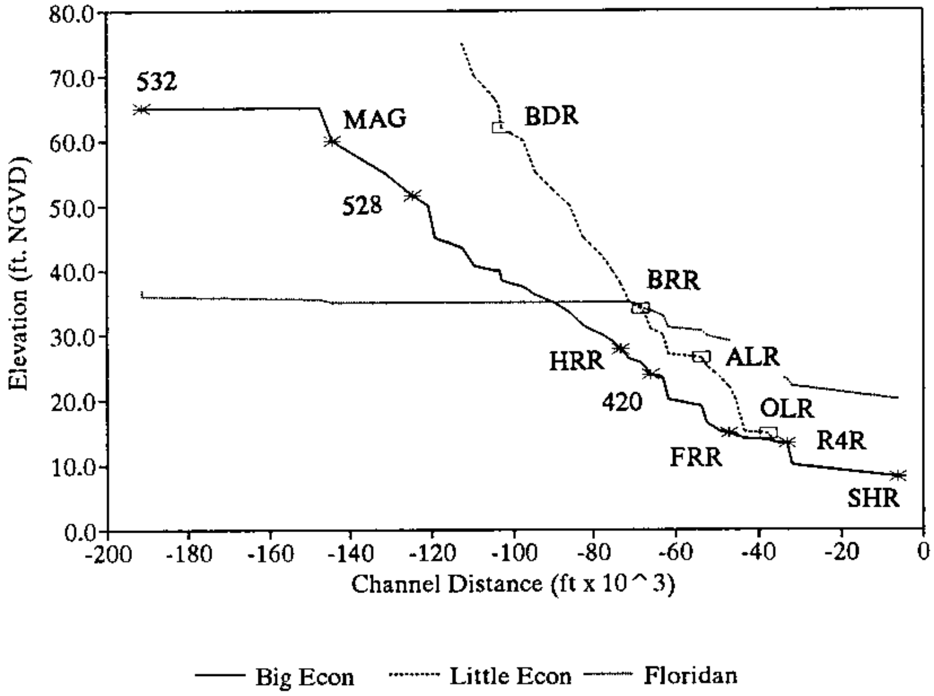

Figure 7. River-bed elevation above mean sea level (National Geodetic Vertical Datum) and Floridan aquifer potentiometric surface versus channel distance from the SHR sampling station.

The headwaters of the Big Econlockhatchee River are an undisturbed forested wetland at an elevation of about 65 ft. above sea level. This area is known as the Econlockhatchee Swamp. The riparian zone of the Big Econlockhatchee River consists of a single channel incised in a floodplain vegetated with overstory dominated by cypress, oak, and sabal palm and sparse understory. 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 percent of the original upland vegetation exists in the Big Econlockhatchee basin, with about 88 mi.^{2} mi.^{2} cleared for development, primarily range for cattle grazing and citrus plantation (Wanielista, *et al.*, 1992).

The Little Econlockhatchee River begins at an elevation of about 75 feet 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 regulate water surface elevations to facilitate flood control and drainage (Miller and Miller, 1984).

The surficial aquifer system in the Econlockhatchee River basin is composed of silica sands 50 to 70 ft. thick, with a potentiometric surface occurring from about 1 to 5 ft. 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, although hydraulic gradients existed for leakage between the aquifers (Figure 2).

Soils are generally well drained. Upland soils are sandy and rich in organic material. At approximately 3 ft. below land surface, a spodic horizon exists, which corresponds approximately to the annual high level of the surficial aquifer. The spodosol is a clay-like layer formed by chemical precipitation of cations in soil water and is very low in permeability. The hydrology of the spodic layer is not well understood, however discontinuities in the spodic layer evidently allow water to infiltrate to the suficial aquifer (Myers and Ewel, 1990).

Sampling Design

A field sampling program was conducted to monitor river water, groundwater, and precipitation in the Econlockhatchee basin. Figure 6 shows the location of all sampling sites. River and groundwater samples were collected daily from September 4, 1992 until October 25, 1992; then weekly until December 15, 1992; and intermittently until June 23, 1993. Precipitation was monitored from August 19, 1992 until May 31, 1993.

Field Methods

River samples were collected either from the shore or bridge deck. Water temperature and specific conductivity were measured in situ using a Yellow Springs Instruments, Inc, Temperature/Level/Conductivity (TLC) meter. Calibration for conductivity and temperature was verified periodically using a National Institute of Standards & Technology calibrated thermometer and conductivity calibration standard solutions. River elevation, specific conductivity, water temperature, station ID, date and time were recorded in a field book. Water samples collected for isotopic analysis were placed in 30 mL glass vials with Poly-Seal™ inverted-cone closures. River samples were identified by the two-letter site name and the suffix R (*e.g.*, SHR, FRR).

Monitoring wells were installed at distances of approximately 50 and 100 ft. perpendicular to the river channel at 5 stations to sample the surficial aquifer. Appendix C provides construction details for the wells. Wells were sampled using Teflon™ or Lucite™ bailers. Wells were purged by pumping at least 20 bailer volumes (approximately 5 well casing volumes) to assure that formation water was sampled. In-situ measurements for temperature and conductivity were made by direct placement of the TLC meter probe in the well after purging and sampling for stable isotopes. Water samples for isotopic analysis were collected in a bailer and poured into 30 mL glass vials. Surficial aquifer samples were identified by the two-letter site name and the well number as a suffix (*e.g.*, FR1, FR2). The Floridan aquifer was sampled at HR and FR stations by collecting water from drinking wells at those sites. Both wells were cased to a depth of at least 100 ft. and penetrated to the upper Floridan aquifer.

Precipitation was collected through Nalgene™ funnels (top diameter, 7.5 or 11.0 cm) into 4 L Nalgene carboys at four stations. All precipitation monitoring stations were placed in open areas with no aerial obstructions. Because of the diversity of overstory vegetation types in the watershed, no attempt was made to analyze throughfall precipitation. Rain collectors were checked within 4 hours after the end of a storm event, or twice daily during protracted events. Rain water was measured from the carboy into a graduated cylinder to compute amount. Samples for isotopic analysis were sealed in 30 mL glass vials. Precipitation samples were identified by the two-letter site name and the suffix P (*e.g.*, WHP, CEP).

Laboratory Methods

Water samples were analyzed for $\delta^{18}O$ at the University of Florida Geology Department using the method of Socki, *et al.* (1992). Approximately 1.5 mL of sample was injected into a 7 mL disposable serum vial containing approximately 0.5 atmospheres of purified (Coleman grade) CO_2. The sample was then equilibrated in a shaker bath for at least 2 hours at 30°C. The CO_2 was then extracted from the vial and purified by cryonic distillation using an off-line vacuum system. Purified CO_2 gas was collected in a 6 mm pyrex break-seal tube for admission to the VG-Prism isotope-ratio mass spectrometer.

Analytical precision was generally better than 0.1 ‰. The reference gas used in the mass spectrometer was generated from Carerra marble (Hodell, *et al.*, 1989) and calibrated against international standards using the method described. At least 6 laboratory working standard samples were analyzed daily (Table 6). Duplicate analyses were performed on approximately 20 percent of all samples and on suspected outliers.

Results and Discussion

Precipitation

Precipitation samples were collected daily at three stations and weekly at one station from August, 19, 1992 until May 30, 1993 to assess temporal and spatial variability in the Econlockhatchee River basin. Figure 8 shows the dates each station was brought into and removed from service. During this time period, three storm types were observed. From the start of sampling until about September 30, summer convective

Table 6.
SUMMARY OF REPLICATE OXYGEN-18 ANALYSES OF INTERNATIONAL AND WORKING LABORATORY STANDARDS

STANDARD	N	MEAN (‰)	STANDARD DEVIATION (‰)
INTERNATIONAL STANDARDS			
SMOW (0.00 ‰)[1]	5	-0.01	0.04
GISP (-24.85 ‰)[1]	4	-24.91	0.13
SLAP (-55.50 ‰)[1]	5	-55.51	0.14
LABORATORY WORKING STANDARDS			
ALPHA	112	-3.15	0.09
CHICHANCANAB	18	3.54	0.12
CONDORERE	17	-14.17	0.12
BLANK	4	-23.80	0.21
ETA	14	-3.54	0.08
OTAP	29	-1.79	0.07
OTAP D	6	-6.54	0.16
OTAP E	4	0.77	0.04
TIWANAKU	4	-13.44	0.02

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[1] Standard isotopic composition (NIST 1992) with an uncertainty of 0.05 ‰.

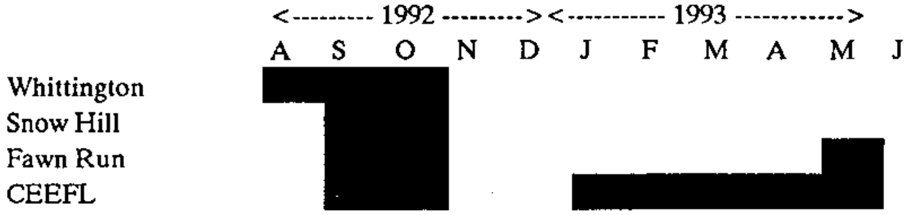
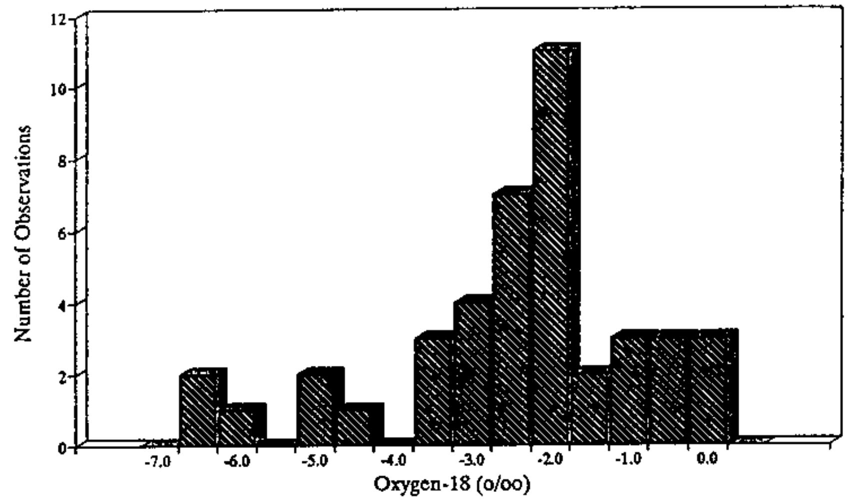


Figure 8. Periods of service for precipitation monitoring stations.

storms occurred almost every afternoon. On October 2 a tropical depression originating in the south Atlantic Ocean brought steady rain to the entire watershed for approximately three days amounting to a total approximately 3.0 in. After the passage of the tropical depression, weather in central Florida became influenced primarily by frontal systems with moisture originating in the Gulf of Mexico, or carried across the continent from Pacific Ocean origins.

Temporal Variability. A histogram of daily rainfall $\delta^{18}O$ from stations CE, FR, and WH (Figure 9a) indicates a range in $\delta^{18}O$ from about -6.5 to 0.0 ‰ with a median value of about -2.0 ‰. This range is substantially broader than the range from -2.5 to -1.5 ‰ observed in river samples collected at the SHR station (Figure 9b). The histograms in Figure 9 count the number of observations within certain $\delta^{18}O$ ranges and are useful in

A.



Snow Hill Road

B.

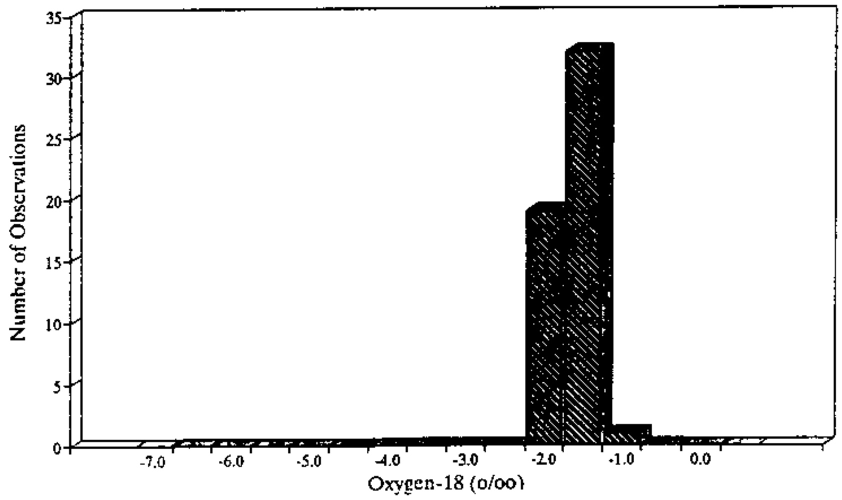


Figure 9. Histograms of daily total precipitation (a.) and daily river $\delta^{18}O$ observations at station SH.

comparing precipitation and river samples, but did not account for the amount of precipitation associated with each observation. The histograms of Figure 10 plot the total amount of precipitation recorded within specified ranges of $\delta^{18}O$ values, thus they reflect the isotopic nature of hydraulic loading within the watershed.

Figure 10 indicates that a significant amount of rainfall during the study period was more isotopically depleted than river water. Figure 11 provides a breakdown of the amount of rain recorded at each station that was more depleted than river water ($\delta^{18}O < -2.5$), within the same isotopic range as river water ($-2.5 <= \delta^{18}O < -1.5$), and more enriched than river water ($\delta^{18}O => -2.5$).

It may be noted that the total amount of rainfall and the isotopic distributions vary considerably from station to station. Spatial variability will be discussed, but the differences observed among stations in Figures 10 and 11 were influenced primarily by the sampling periods for each station (Figure 8). WH recorded 12 summer convective storm events in August prior to the commissioning of any other stations, then was decommissioned in November. As a result, more enriched summer storms, and fewer depleted winter storms were captured at WH. The FR station monitored precipitation from September 1992 until December 1992 and then in May 1993, capturing tropical and spring frontal storms. The CE station, brought into service in September 1992, missed most of the summer convective storms, but captured winter frontal storms. Among the data in Figure 10, the WH distribution (Figure 10c) most closely resembles the distribution for river water (Figure 10b).

Hydrograph separation requires a significant difference between new and old water masses. Considering the analytical precision for $\delta^{18}O$ was approximately $1\sigma=0.1$

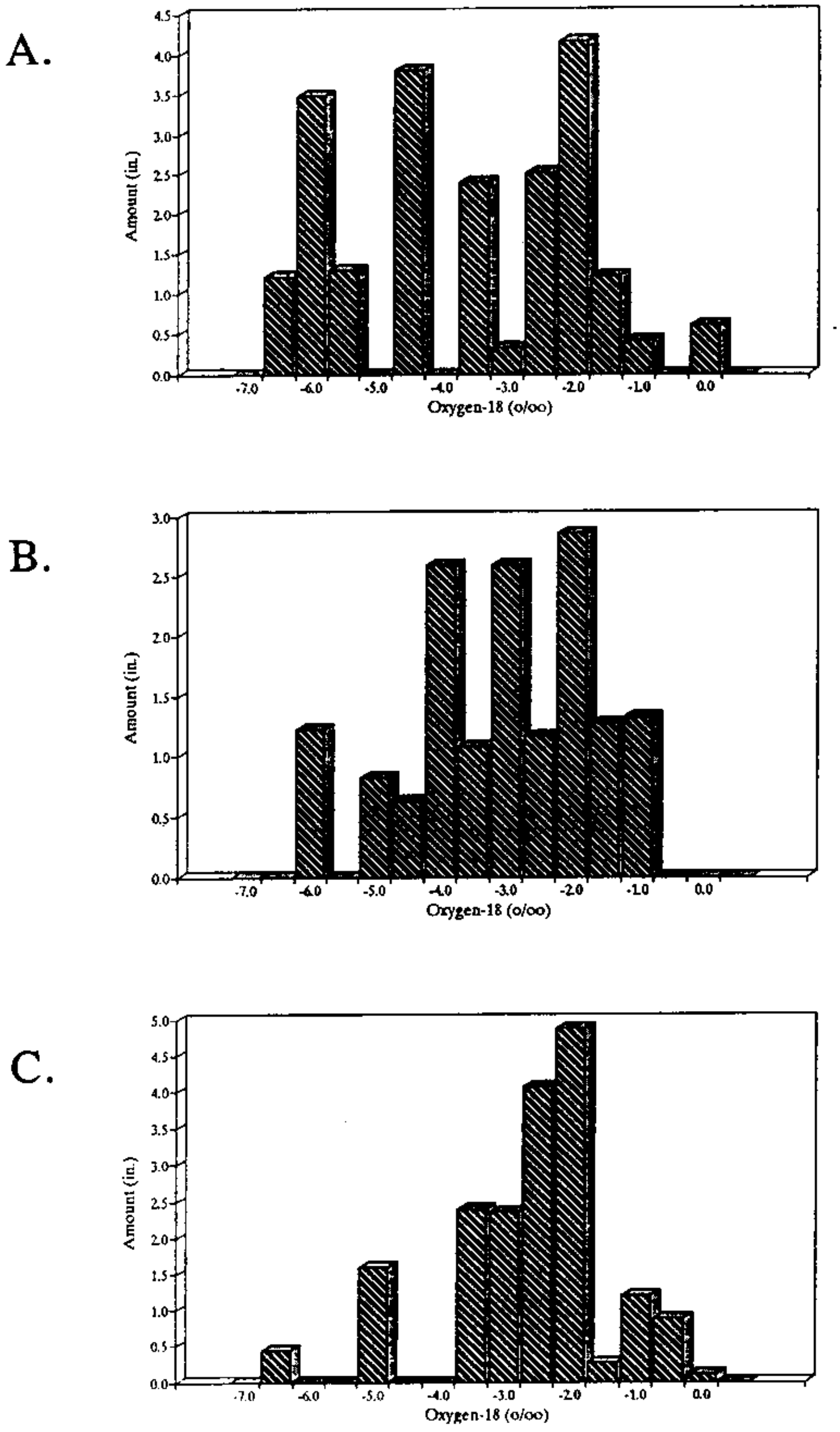


Figure 10. Histograms of daily rainfall amount at stations CE (a.), FR ((b.), and WH (c.).

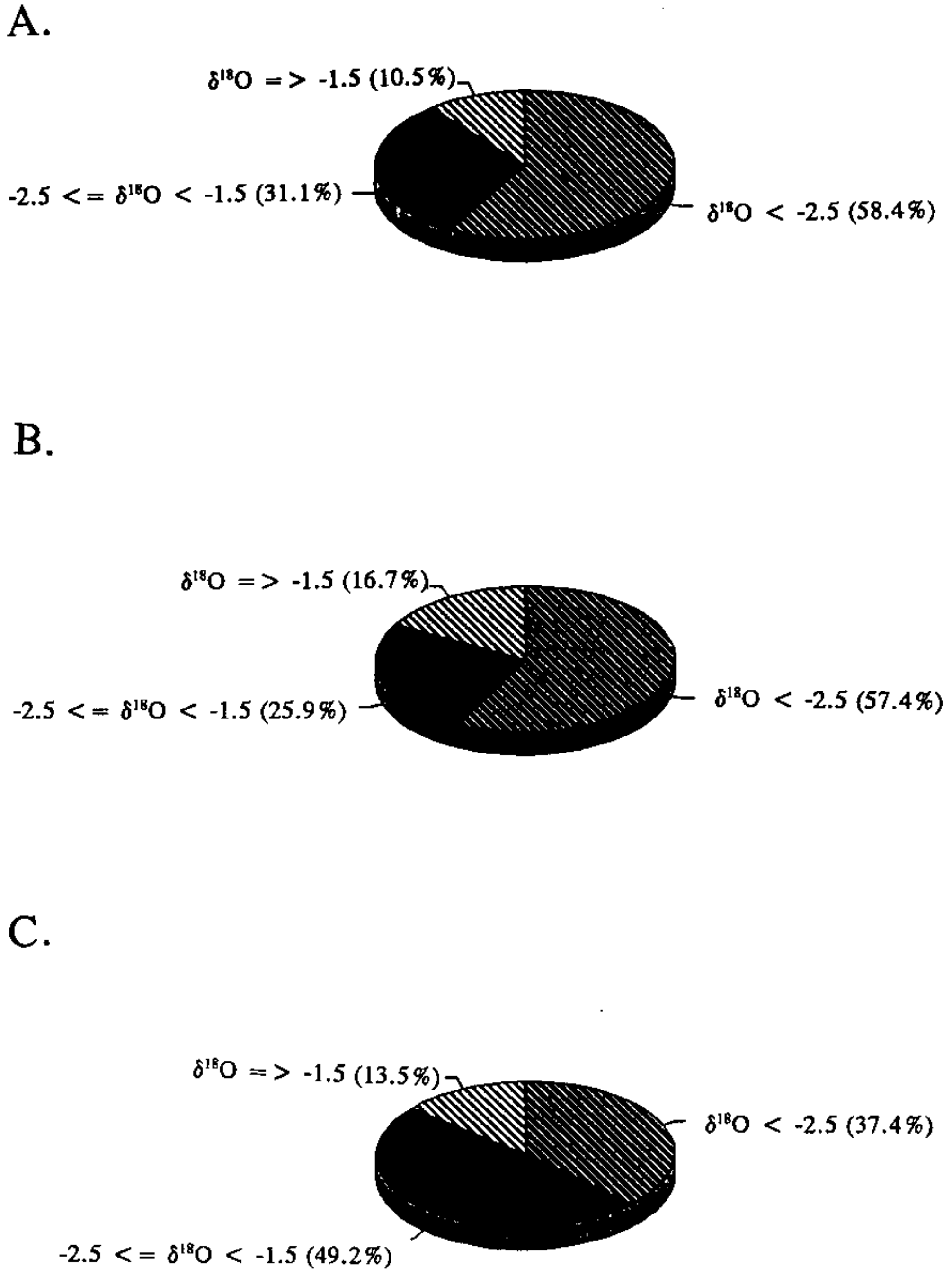


Figure 11. Pie charts of isotopic content of precipitation $\delta^{18}O$ at station CE (a.), FR (b.), and WH (c.). Total amounts for a., b., and c. are 21.44, 15.56, and 18.19 inches, respectively.

‰, an isotopic difference between water masses of about 0.5 ‰ or greater would indicate favorable conditions for hydrograph separation. If the observed isotopic range in river water is assumed to reflect C_O and the range in precipitation to reflect C_N, the potential for hydrograph separation in the Econlockhatchee basin may be assessed. Figure 11 indicates that no greater than 50 percent of all rain collected at a single station fell within the isotopic range of river water. Thus, more than half of all rain collected was either more depleted or enriched than river water.

Based on the observed variability in rainfall $\delta^{18}O$, there appears to be adequate inter-storm variability to allow hydrograph separation. This variability, however, may be damped by a number of interfering processes, such as isotopic change as precipitation passes through the tree canopy (throughfall effects), evaporative enrichment as new water moves through the watershed, and averaging effects due to spatial variability.

Spatial Variability. Rainfall was collected at three stations simultaneously between September 20 and October 11, 1992 to assess spatial variability in the watershed (Table 7). The Econlockhatchee watershed was sufficiently large that summer convective storms seldom covered the watershed evenly. As a result, precipitation may have been recorded at only one or two stations for a particular storm event. The variability in $\delta^{18}O$ for storms recorded at all three stations was analyzed (Table 7). The results indicate that if a storm was large enough to reach all three stations, the standard deviation of the mean tended to be less than 0.8 ‰. This type of quantitative expression of spatial heterogeneity may be used in developing confidence intervals in hydrograph separation analyses.

Table 7.
PRECIPITATION AND δ^{18}O COLLECTED BETWEEN SEPTEMBER 20 AND OCTOBER 11, 1992 AT THREE STATIONS.

DATE	AMOUNT					OXYGEN-18				
	CE (in.)	FR (in.)	WH (in.)	Mean (in.)	Std (in.)	CE (o/oo)	FR (o/oo)	WH (o/oo)	Mean (o/oo)	Std (o/oo)
20-Sep-92	0.34	1.10	1.08	0.84	0.35	-3.62	-2.67	-2.17	-2.82	0.60
21-Sep-92			0.27					-2.43		
22-Sep-92	0.21					-2.20				
23-Sep-92	0.35	1.49	1.89	1.24	0.65	-3.93	-3.36	-3.15	-3.48	0.33
24-Sep-92	0.29					-2.59				
25-Sep-92	0.19					-2.46				
26-Sep-92		0.17					-1.92			
27-Sep-92	0.23		0.64			-1.46		-1.08		
28-Sep-92		0.21	0.11				-1.18	-2.03		
29-Sep-92	0.33	0.06				-3.02	-2.64			
30-Sep-92	0.68	0.82	0.44			-6.57	-5.09	-6.66	-6.11	0.72
01-Oct-92										
02-Oct-92	0.19	0.12	0.25	0.19	0.05	-1.09	-1.23	-1.13	-1.15	0.06
03-Oct-92	1.77	1.48	2.20	1.82	0.30	-2.21	-2.27	-2.40	-2.30	0.08
04-Oct-92	0.71	1.10	0.54	0.78	0.23	-3.58	-3.29	-3.52	-3.46	0.12
05-Oct-92			0.09					-5.26		
06-Oct-92										
07-Oct-92	0.77	0.55	0.64	0.65	0.09	-2.75	-2.19	-2.16	-2.37	0.27
08-Oct-92										
09-Oct-92	0.92	0.80				-2.19	-1.96			
10-Oct-92										
11-Oct-92	1.62	1.22	1.51	1.45	0.17	-6.06	-6.10	-5.36	-5.84	0.34

Larger frontal or tropical storms appear to be the ideal weather systems for watershed-scale hydrograph separation studies, because of the homogeneity of precipitation over the watershed. During the tropical storm of October 2 through 5, 1992, the standard deviation in rainfall $\delta^{18}O$ was 0.15 ‰. This storm had favorable characteristics in terms of even coverage over the watershed and homogeneous isotopic content. Unfortunately, that system fell within the isotopic range of river water, limiting the strength of the isotopic signal it produced.

Meteoric Processes. The resolution of precipitation data collected allowed certain processes to be examined that affect the isotopic composition of storm events, including *rainout*, the isotopic depletion in precipitation over time during a storm (Siegenthaler 1979), and *amount effects*, isotopic change related to storm size (Coplen 1993).

Rainout. During condensation, water droplets preferentially incorporate heavier isotopes of hydrogen and oxygen because of their lower vapor pressure (Ferronsky and Polyakov, 1982). As a result, cloud masses become isotopically depleted over time as water vapor is condensed into rainfall. This is most commonly observed as frontal systems move from the northwest to the southeast United States (Coplen 1993).

The rainout phenomenon can be observed in several storm events captured during the Autumn, 1992 sampling period (Figure 12). At CE, depleting $\delta^{18}O$ can be seen during the October 2 through 5 and October 8 through 12, 1992 events (Figure 12a). At the FR station, isotopic depletion was observed during the events of September 28 through 30 and October 2 through 5, 1992 (Figure 12b). It is interesting to note that,

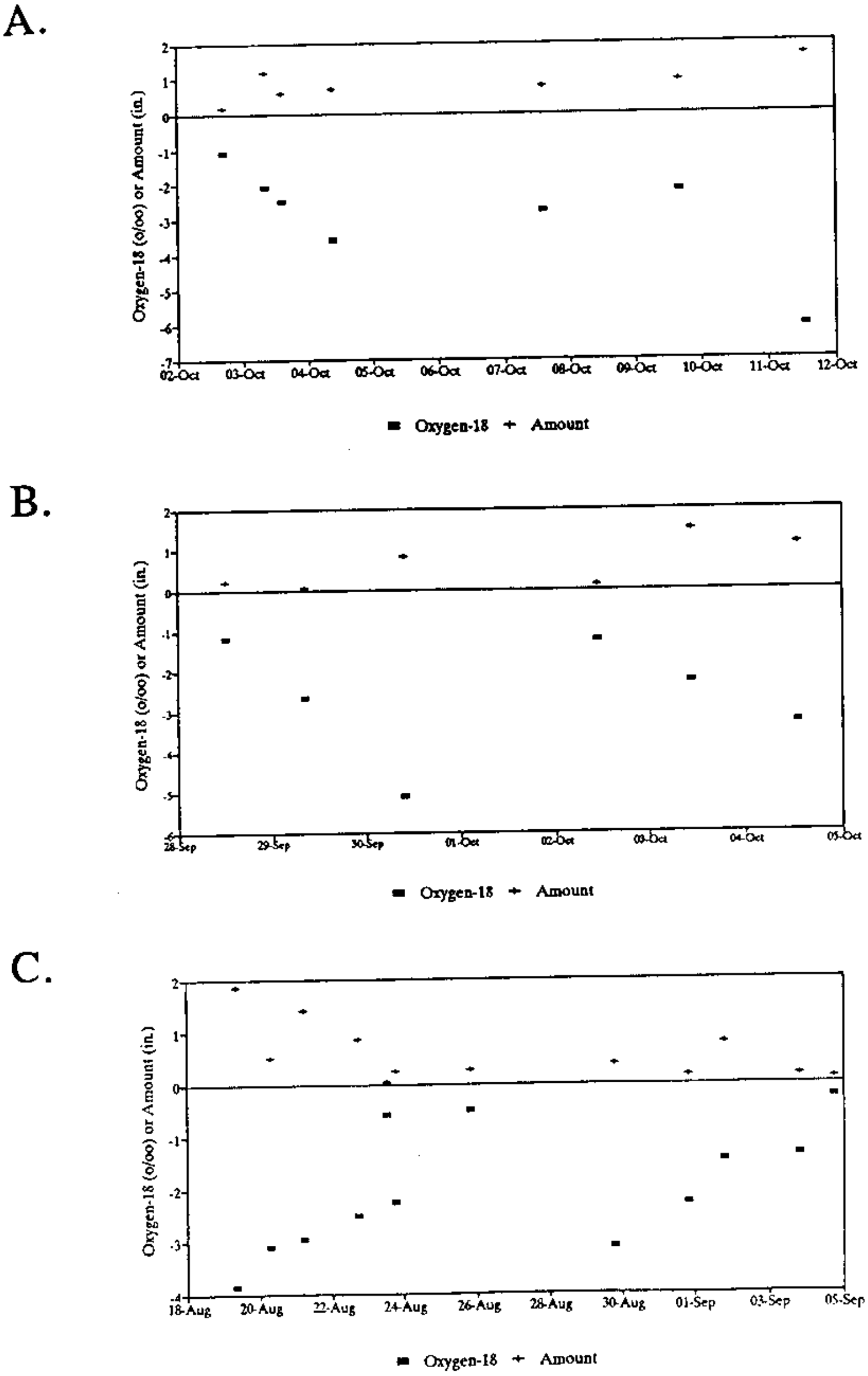


Figure 12. Precipitation amount and $\delta^{18}O$ versus date in 1992 at station CE (a.), FR (b.) and WH (c.).

at the WH station, events over consecutive days from August 18 through September 12, 1992, showed no isotopic depletion over time (Figure 12c). This may indicate that summer convective storms are isotopically independent.

Amount Effects. To determine whether storm event magnitude had any effect on isotopic composition of precipitation, scatter plots were made of $\delta^{18}O$ versus amount (Figure 13) and bar charts were made of $\delta^{18}O$ and amount versus time (Figure 14). Events were categorized as summer convective or non-summer in origin. At the CE station (Figures 13a and 14a), which collected mostly tropical and frontal storms, the data fell into two groupings, an enriched group with a median value of approximately -2.5 ‰ and a depleted group, at about -6.5 ‰. All summer storms fell into the enriched group, but no other trend is evident. Similarly, the FR station (Figures 13b and 14b) recorded no evident trend in $\delta^{18}O$ dependant on amount.

The majority of summer-storm events were recorded at WH (Figures 13c and 14c). It may be seen that the most enriched observations were associated with amounts less than 0.3 ‰. It is possible that non-equilibrium evaporative enrichment occurred as droplets fell through the atmosphere, a phenomenon that has been observed in tropical and sub-tropical systems (Craig 1961).

Groundwater

Groundwater monitoring consisted of daily measurement of elevation and weekly collection of in-situ parameters and samples for isotopic analysis in the Autumn of 1992 in near-stream surficial aquifer wells. Monitoring wells in the Floridan aquifer were

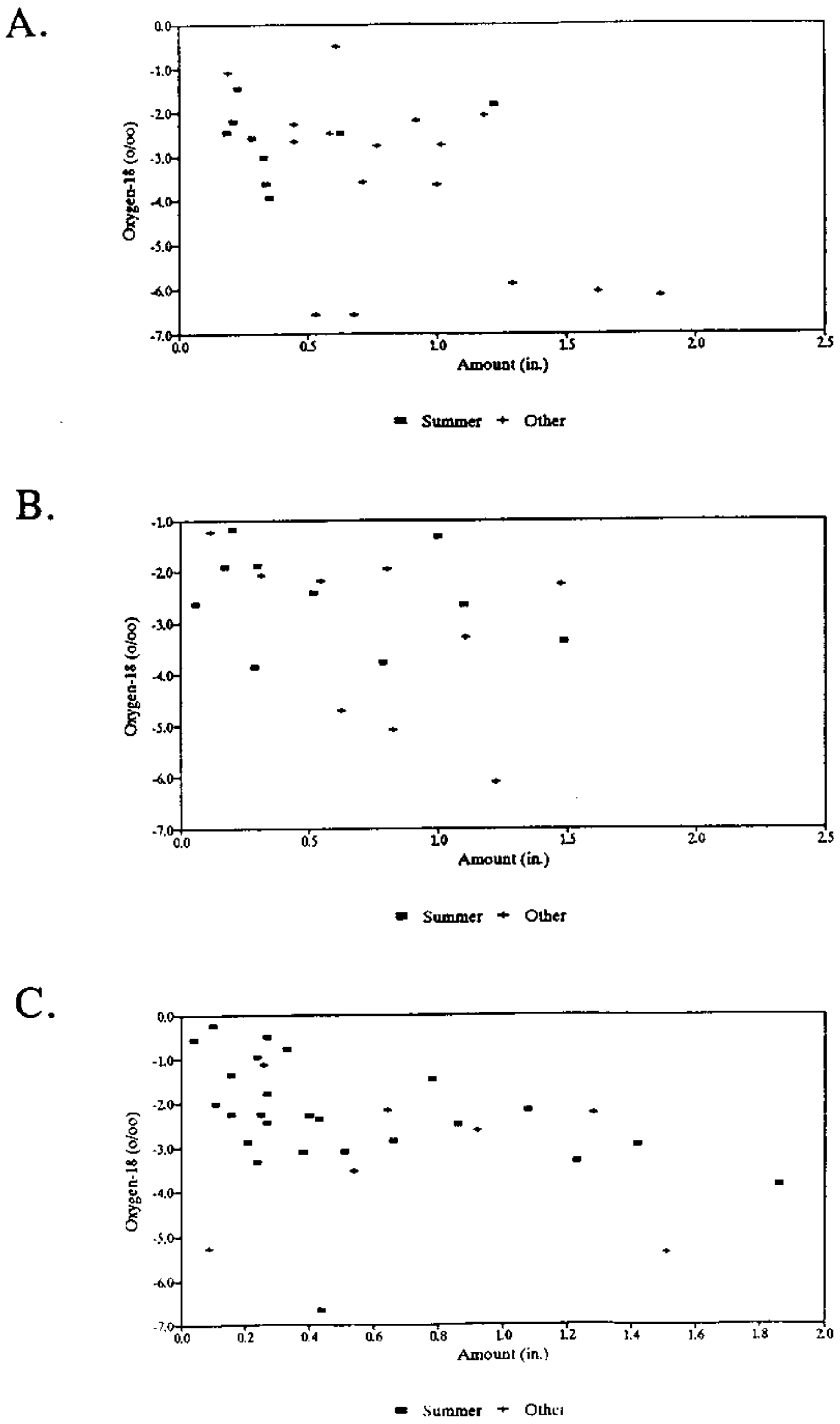


Figure 13. Precipitation $\delta^{18}O$ versus amount for summer-convective and non-summer storms in 1992 and 1993 at station CE (a.), FR (b.), and WH (c.).

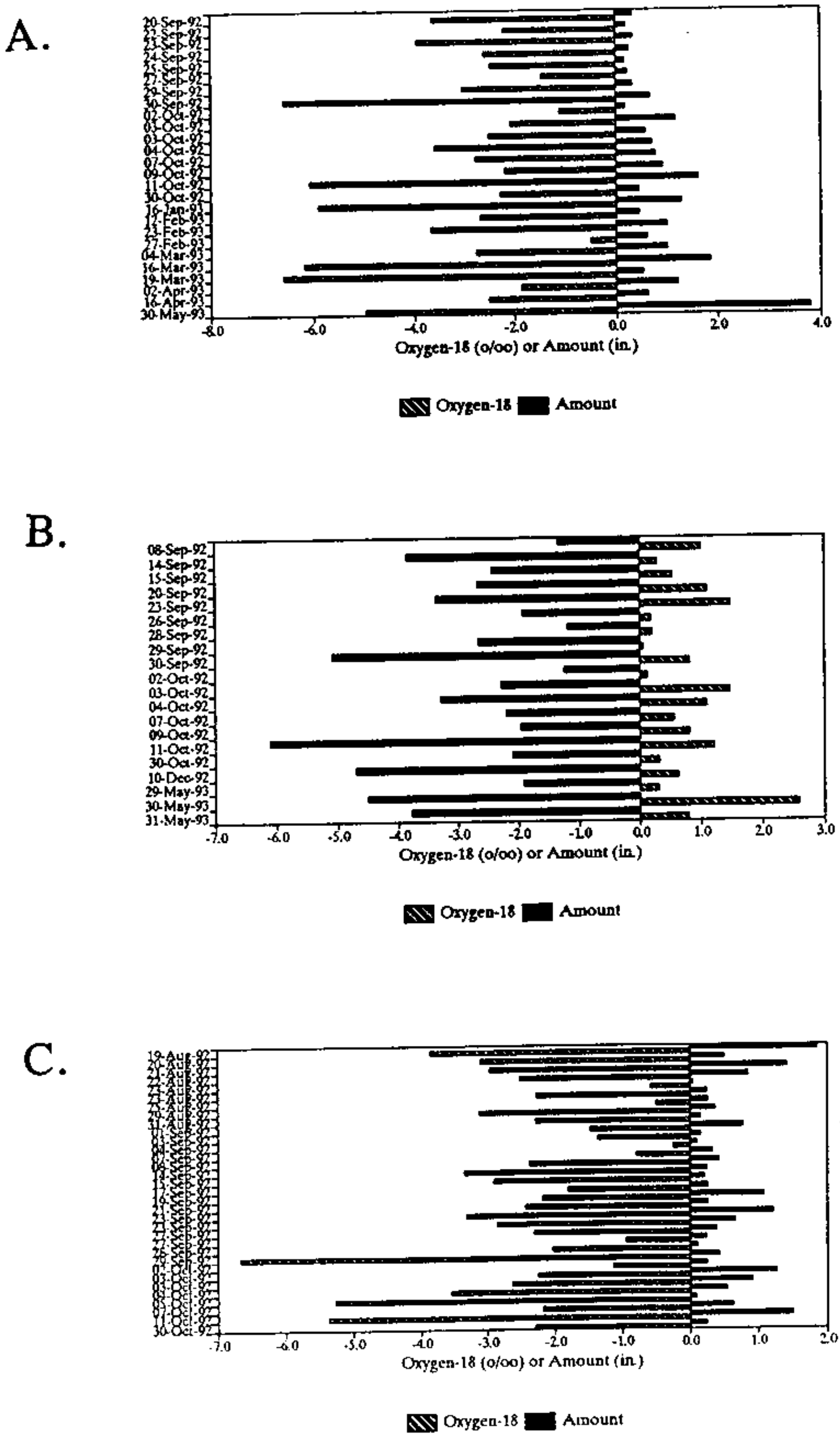


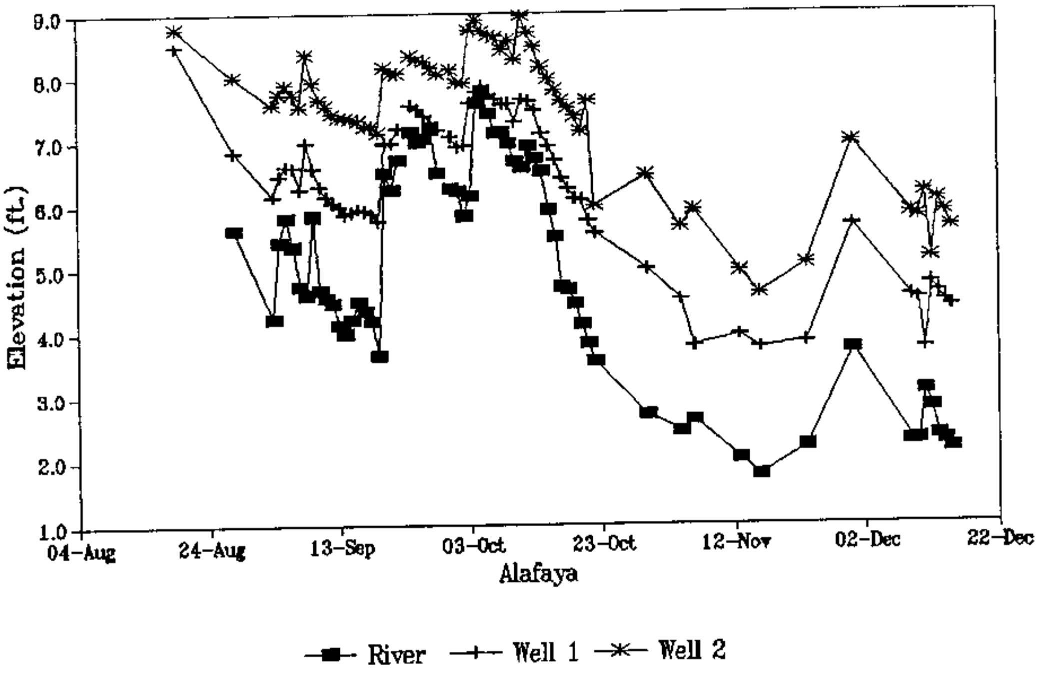
Figure 14. Bar charts of precipitation $\delta^{18}O$ and amount versus date in 1992 and 1993 at station CE (a.), FR (b.), and WH (c.).

sampled intermittently during the sampling period.

Hydraulic Gradients. 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 the channel at low flow (Todd 1980, Meyboom 1961). 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) analyzed environmental deuterium (δD) to demonstrate that bank storage comprised a significant amount of recession flow in the Truckee River, Nevada. From the perspective of hydrograph separation, for there to be a significant contribution of old water to channel flow during a storm hydrograph, hydraulic gradients in the near-stream zone must promote flow toward the river throughout the storm hydrograph.

Near-stream measurements in the Econlockhatchee River basin indicated that surficial aquifer recharge from the river was not an important process. Figures 15 through 19 illustrate river and monitoring-well potentiometric elevations and hydraulic gradients versus time at five stations on the Econlockhatchee River. Under conditions of abrupt rise in river elevation, hydraulic gradients indicated potential for recharge of bank storage, such as stations BR1 and BR2 on September 21 and 22, 1992 (Figure 17) or FR1 and FR2 on September 21, 1992 (Figure 17). These reversals in hydraulic gradient were low in magnitude (<0.03 ft/ft) and existed for durations less than 2 days. Thus minimal and ephemeral bank storage may be associated with these episodes. Some

A.



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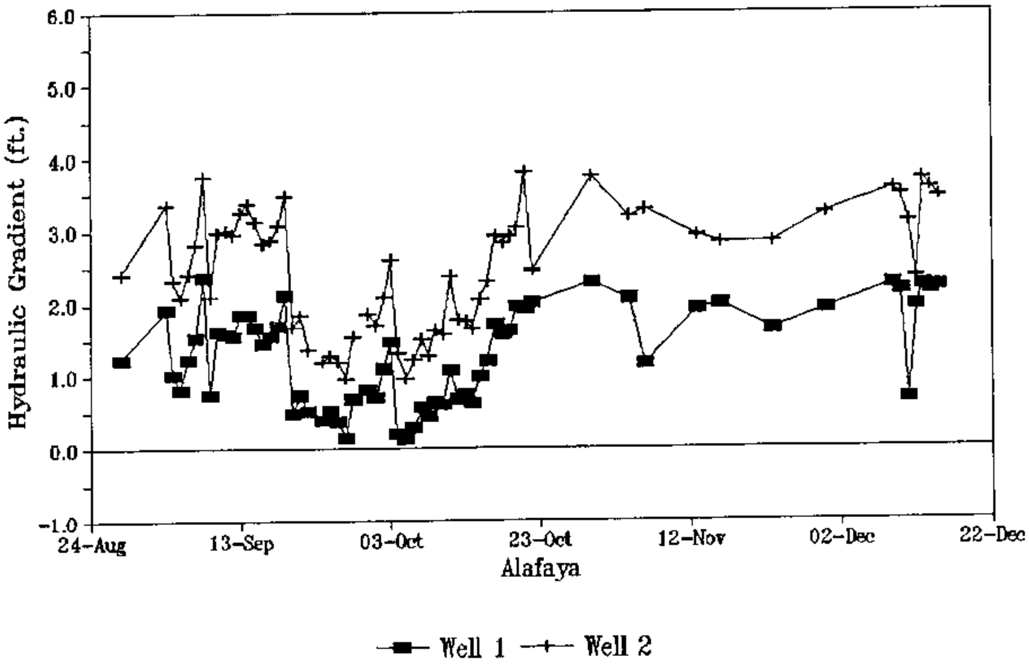


Figure 15. River and monitoring well elevations (a) and hydraulic gradients (b.) at AL in 1992.

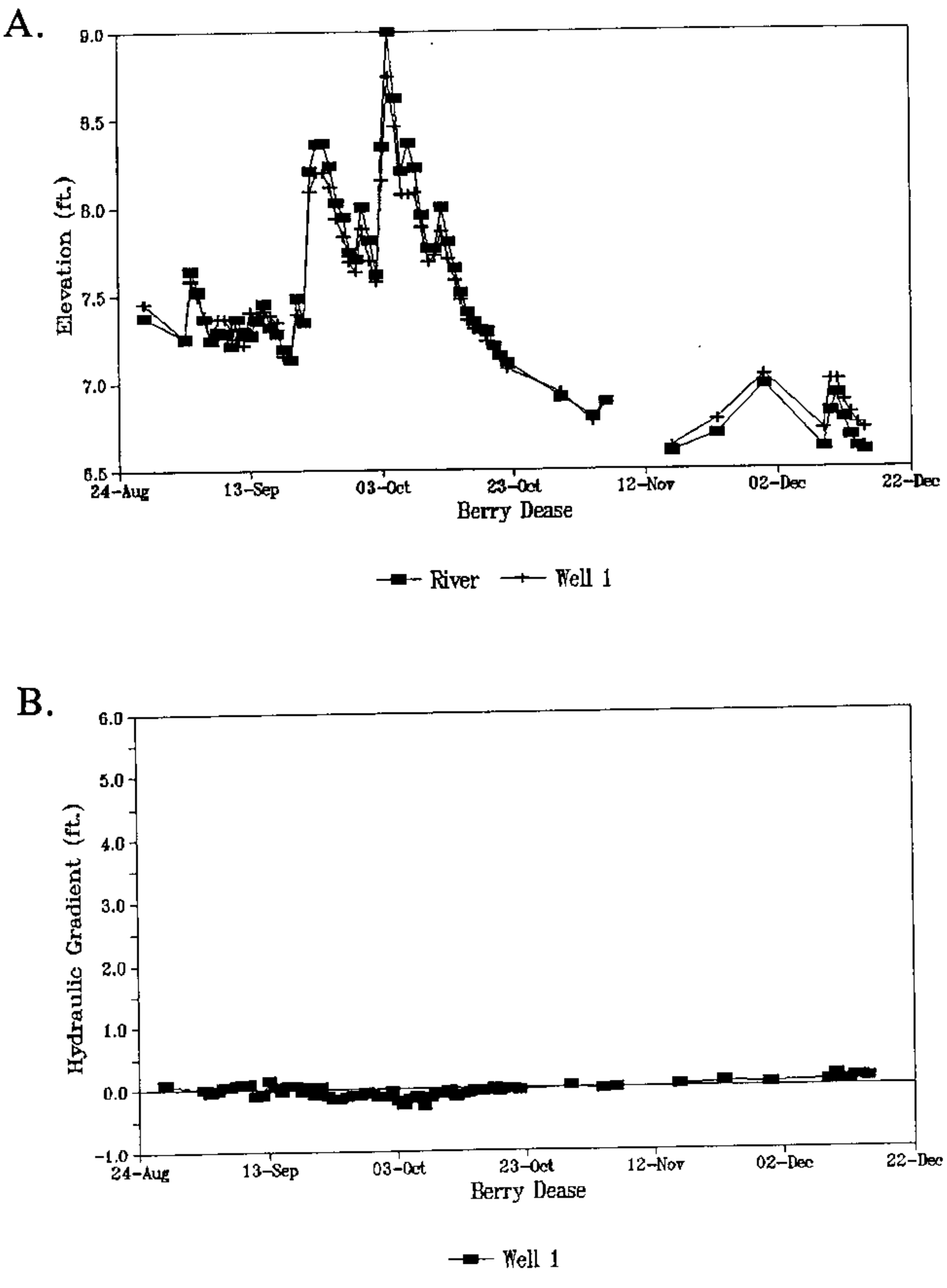


Figure 16. River and monitoring well elevations (a) and hydraulic gradients (b.) at BD in 1992.

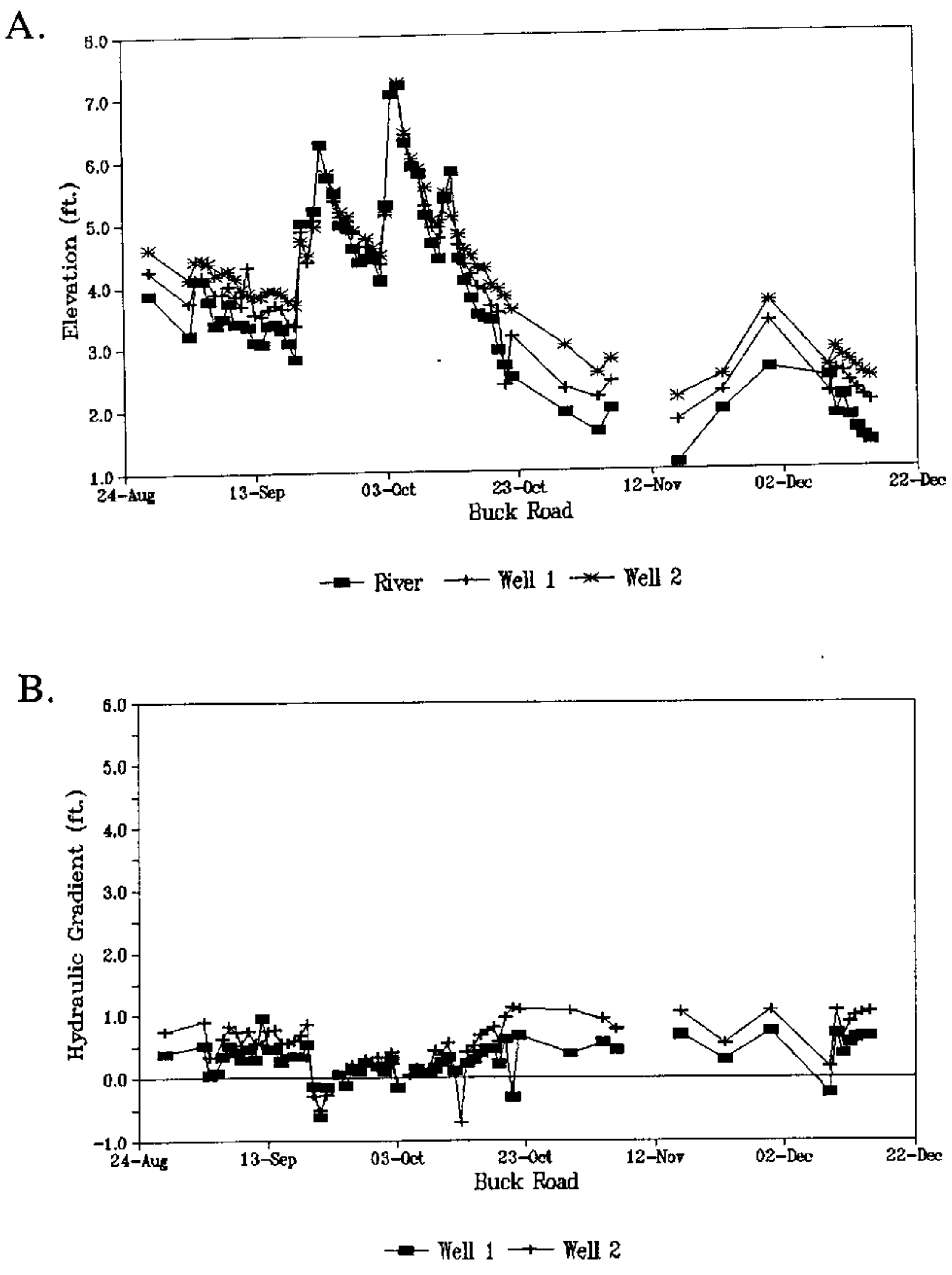
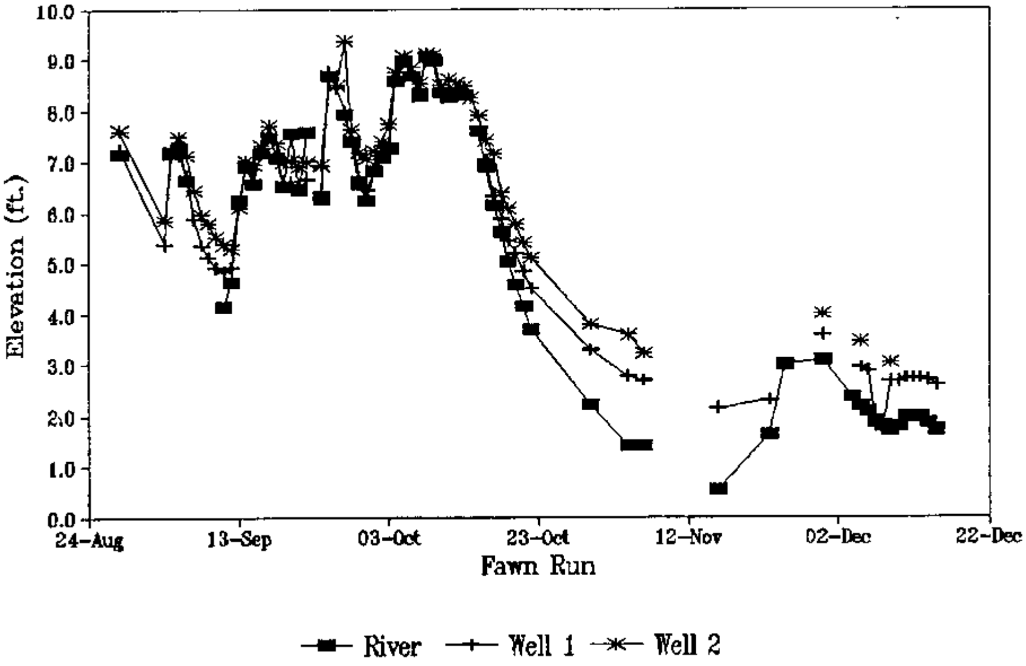


Figure 17. River and monitoring well elevations (a) and hydraulic gradients (b.) at BR in 1992.

A.



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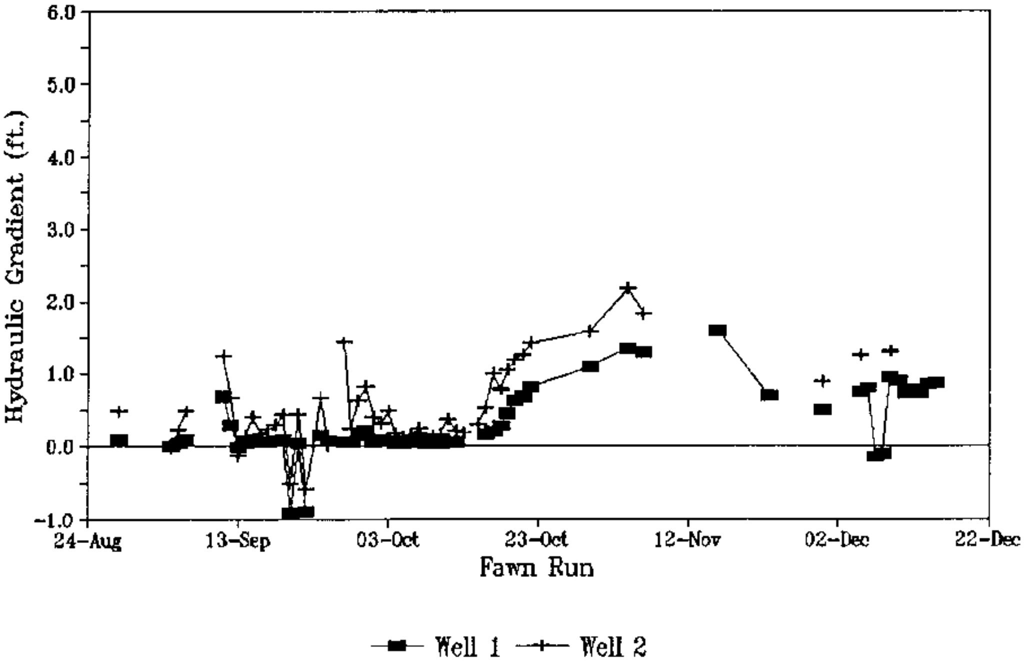


Figure 18. River and monitoring well elevations (a.) and hydraulic gradients (b.) at FR in 1992.

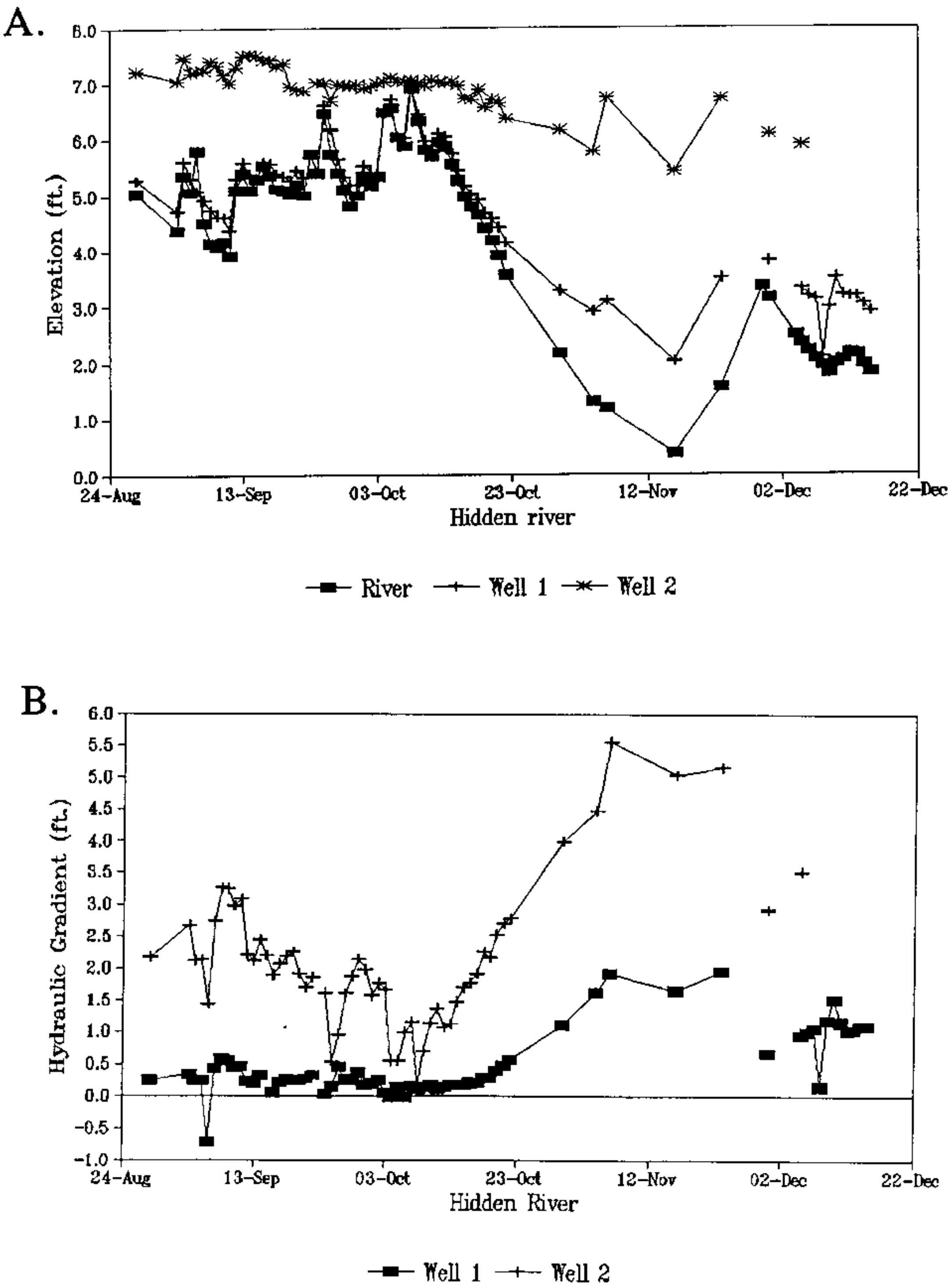


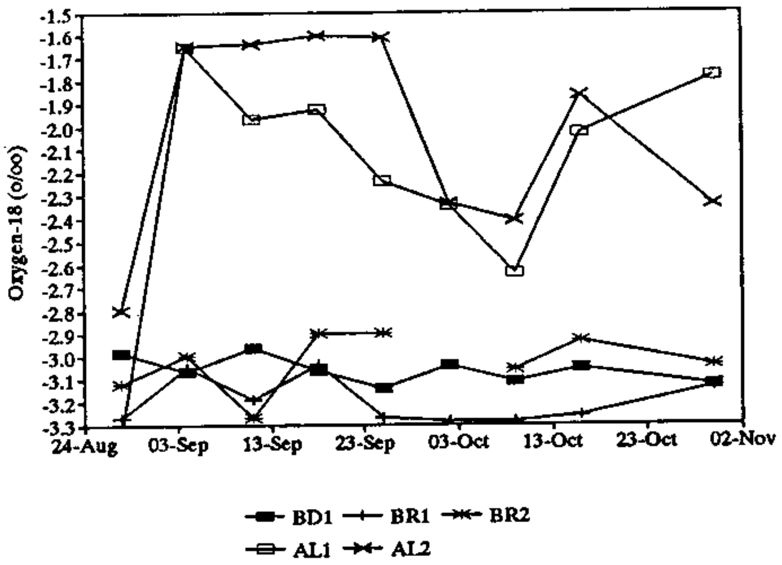
Figure 19. River and monitoring well elevations (a.) and hydraulic gradients (b.) at HR in 1992.

spatial variability was observed in hydraulic gradients in the watershed. AL1 and AL2 demonstrated positive hydraulic gradient under all flow conditions (Figure 15) and BD1 showed very low hydraulic gradient throughout the study period (Figure 16).

An interesting phenomenon was observed at HR2. Figure 19 shows that HR1 elevations closely track river elevation, but HR2 elevations remain consistently higher than the river or HR1. During the extended recession starting on October 5, hydraulic gradients increased for both wells, but HR2 remained at about the same level, developing a very large hydraulic gradient. HR2 was placed near the interface between riparian and upland zones and was screened above the spodic horizon. It appears that the spodic layer created a separate aquifer above what is traditionally regarded as the surficial aquifer. The responsiveness of the surficial aquifer below the spodic layer reported here and in a separate study of the Econlockhatchee River basin by Wanielista, *et al.* (1993), suggests that the spodic horizon must be sufficiently discontinuous to allow free infiltration to the surficial aquifer.

Isotopic Variability. With the exception of the monitoring wells at AL1 and AL2, groundwater in the Econlockhatchee River basin showed little temporal and some spatial isotopic variability. Figure 20 plots $\delta^{18}O$ versus time in monitoring wells along the Little Econlockhatchee (Figure 20a) and Big Econlockhatchee (Figure 20b) Rivers. AL1 and AL2 yielded significantly more enriched $\delta^{18}O$ than any other wells in the watershed. These wells were placed downgradient from a wet-detention pond, which likely contained isotopically enriched water due to evaporation. The effect of the pond on surficial aquifer samples suggests a strong degree of hydraulic communication between the pond

A.



B.

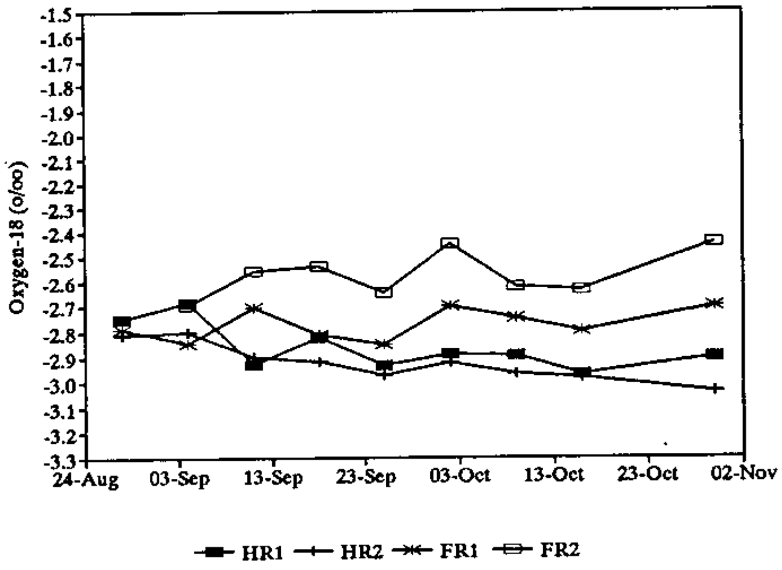


Figure 20. Surficial aquifer $\delta^{18}O$ versus date in 1992 in the Big Econlockhatchee (a.) and Little Econlockhatchee (b.) River basins.

and the aquifer.

Table 8 summarizes $\delta^{18}O$ of surficial aquifer samples collected in 1992. The arithmetic mean $\delta^{18}O$ from individual wells excluding the enriched values from AL1 and AL2 ranged from -3.14 ‰ at BR1 to -2.57 ‰ at FR2. The standard deviation for individual wells seldom exceeded the analytical precision for the $\delta^{18}O$ test (0.1 ‰). It is thus reasonable to assume that there was very low temporal variability in the $\delta^{18}O$ or the near-stream aquifer in 1992.

Distinct spatial variability was observed. The mean and standard deviation of all groundwater samples, excluding AL1 and AL2, was -2.88 ± 0.46 ‰. Breaking out the data by sub-watershed, the Little Econlockhatchee stations (BD1, BR1, and BR2) showed a combined mean of -3.08 ± 0.09 ‰. Big Econlockhatchee (FR1, FR2, HR1, HR2) stations averaged -2.79 ± 0.52 ‰ (Table 8). The Floridan aquifer, sampled at HR and FR, averaged -1.71 ± 0.16 ‰ There were insufficient data to explain the more enriched mean and higher standard deviation in the Big Econlockhatchee basin, but these observations were consistent with differences in recharge characteristics in the surficial aquifer. Widely varying recharge areas or hydraulic transmissivities within the watershed may result in locally distinct residence times for surficial groundwater at particular monitoring wells. Differences in recharge time, combined with seasonal variation in the isotopic composition of the precipitation recharging the aquifer, may result in a locally distinct isotopic content of the surficial aquifer.

For example, the relatively enriched samples collected in Big Econlockhatchee basin wells suggest a low residence time in that region of the surficial aquifer, because the samples were collected at the end of a period of relatively enriched summer storms.

Table 8.
SUMMARY OF RIVER AND GROUNDWATER SAMPLES ANALYZED FOR $\delta^{18}O$ DURING AUTUMN 1992 MONITORING.

RIVER				GROUNDWATER			
Station	n	Mean (o/oo)	Std. (o/oo)	Station	n	Mean (o/oo)	Std. (o/oo)
			LITTLE ECONLOCKHATCHEE BASIN				
BDR	54	-1.93	0.24	BD1	10	-3.07	0.06
BRR	21	-1.95	0.23	BR1	11	-3.17	0.11
				BR2	8	-3.03	0.11
ALR	20	-1.97	0.21	AL1	10	-2.18	0.46
				AL2	9	-2.03	0.41
OLR	20	-1.99	0.26				
			BIG ECONLOCKHATCHEE BASIN				
HRR	25	-1.82	0.40	HR1	10	-2.87	0.08
				HR2	9	-2.92	0.07
				HRF	1	-1.44	
FRR	24	-1.85	0.36	FR1	9	-2.77	0.06
				FR2	8	-2.57	0.08
				FRF	4	-1.78	0.06
R4R	17	-1.91	0.23				
SHR	55	-1.87	0.21				

The slightly more depleted concentration of water in Little Econlockhatchee basin wells suggests that depleted precipitation from the previous winter affected the local isotopic composition of the surficial aquifer. These inferences are highly speculative, however, and are best suited to form working hypotheses in the design of more rigorous isotope hydrology studies.

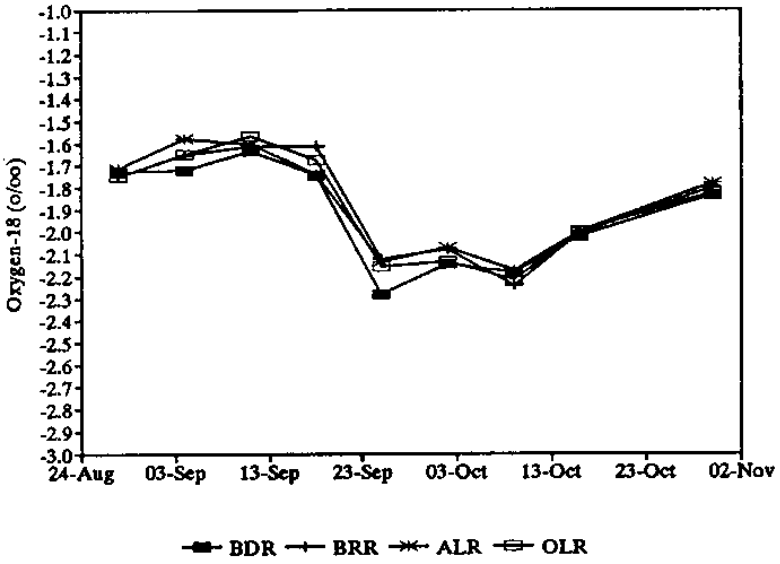
Surface Water

Spatial Variability. Figure 21 shows weekly measurements of $\delta^{18}O$ at river stations in the Little Econlockhatchee (Figure 21a) and Big Econlockhatchee (Figure 21b) River basins. The isotopic record of stations R4R and SHR, located downstream from the confluence of the Big and Little Econlockhatchee Rivers (Figures 6 and 7), reflected mixing from both basins. A statistical summary of river $\delta^{18}O$ appears in Table 8.

Isotopic data indicate that each sub-basin had a distinct isotopic character for at least some of the study period. This is evident in Figure 22, which shows $\delta^{18}O$ versus river position on three sampling dates. Although the isotopic identity of each basin can be distinguished, the basins remained within an isotopic range of approximately 0.3 ‰.

Temporal Variability. Temporal variability in river $\delta^{18}O$ was observed, but was substantially lower than the isotopic variability of precipitation (Figure 23). This isotopic damping in river response to precipitation has been observed in other river systems and led early isotope hydrologists to postulate that old water formed a significant component of storm flow in some rivers (Sklash and Farvolden 1979).

A.



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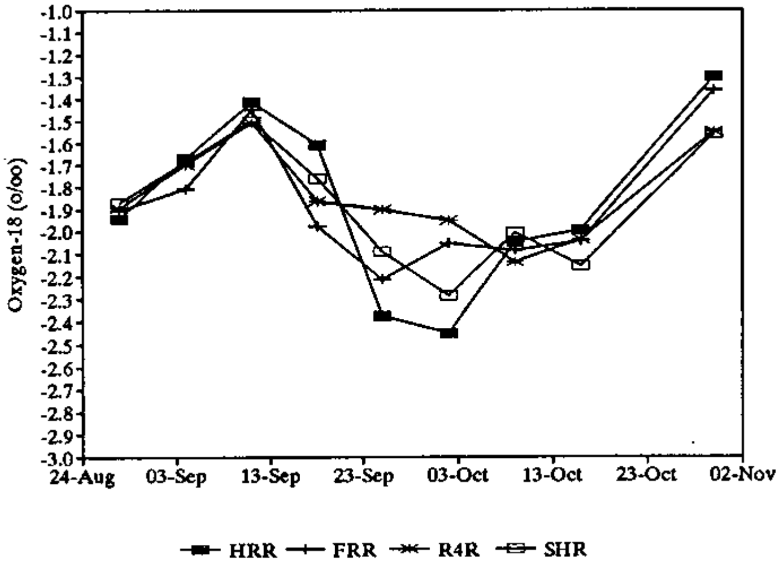

Figure 21. River $\delta^{18}O$ versus date in 1992 in the Big Econlockhatchee (a.) and Little Econlockhatchee (b.) River basins.

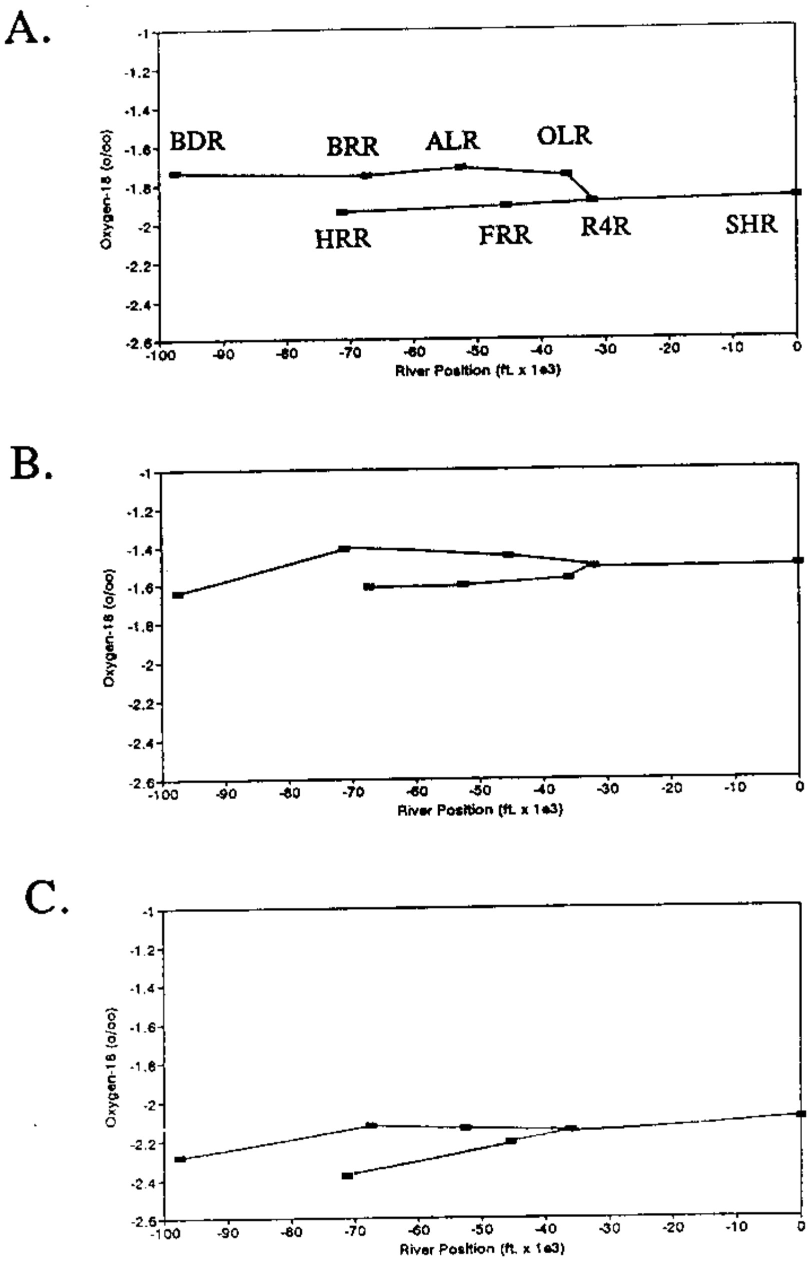

Figure 22. River $\delta^{18}O$ versus channel distance upstream of station SH on August 28, 1992 (a.), September 11, 1992 (b.), and September 25, 1992 (c.).

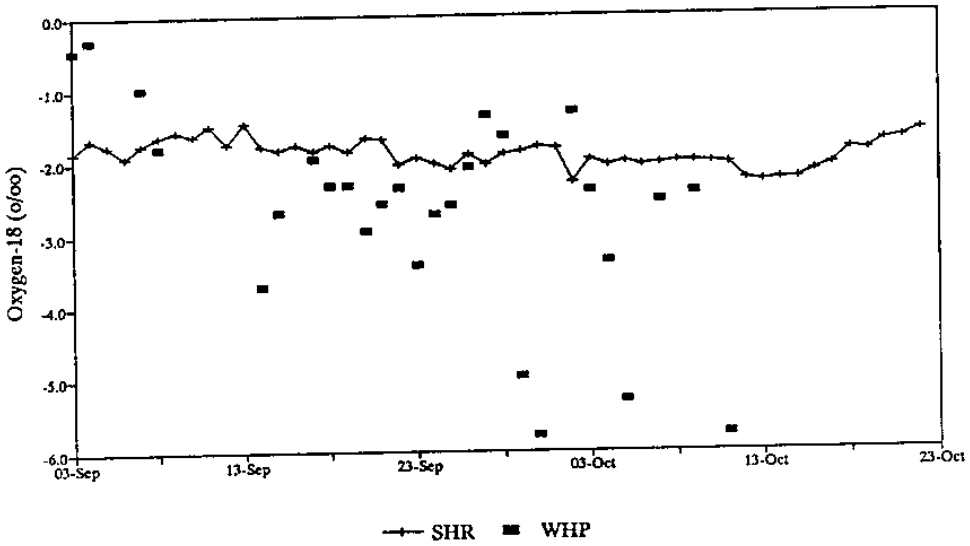

Figure 23. River and precipitation $\delta^{18}O$ versus date in 1992.

It is possible that channel storage accounted for the type of damping in river $\delta^{18}O$ observed in Figure 23, however this was not the case for the Econlockhatchee River system in Autumn 1992. Estimates placed channel storage upstream of SHR at approximately $2(10^8)$ ft.^{3}. Daily hydraulic throughput averaged $8.2(10^7)$ ft.^{3} Thus flushing rates for the river were high enough that isotopic damping from channel storage was not significant.

Plots of $\delta^{18}O$ and flow versus time for the SHR and BDR stations (Figure 24) suggest a relationship between $\delta^{18}O$ and flow. Plots of $\delta^{18}O$ versus flow for SHR and BDR (Figure 25), confirm that higher flows were systematically associated with more depleted $\delta^{18}O$ for the period of record. That relationship is consistent with the rainfall data presented in Figure 24a, which indicate that storms larger in magnitude than 1.0 in./day were more depleted than -3.0 ‰. In fact a stronger apparent relationship existed between river $\delta^{18}O$ versus flow than for the more direct quantity-dependent measure of rainfall $\delta^{18}O$ versus rainfall amount (Figure 13). This phenomenon may have resulted, at least in part, from the sequence of events that produced river flow in Autumn 1992. Storm events occurred almost daily from September 13 until October 5, building flow in the river. Concurrently storms became more depleted in $\delta^{18}O$ over time.

Recession Analysis

After October 12 no storm events occurred in the Econlockhatchee River basin during Autumn 1992 sampling, allowing a period of recession to be recorded. Classical hydrometric analysis of hydrograph recession has been used to determine baseflow characteristics (Wanielista 1990, Todd 1980, Meyboom 1961). Because no other runoff

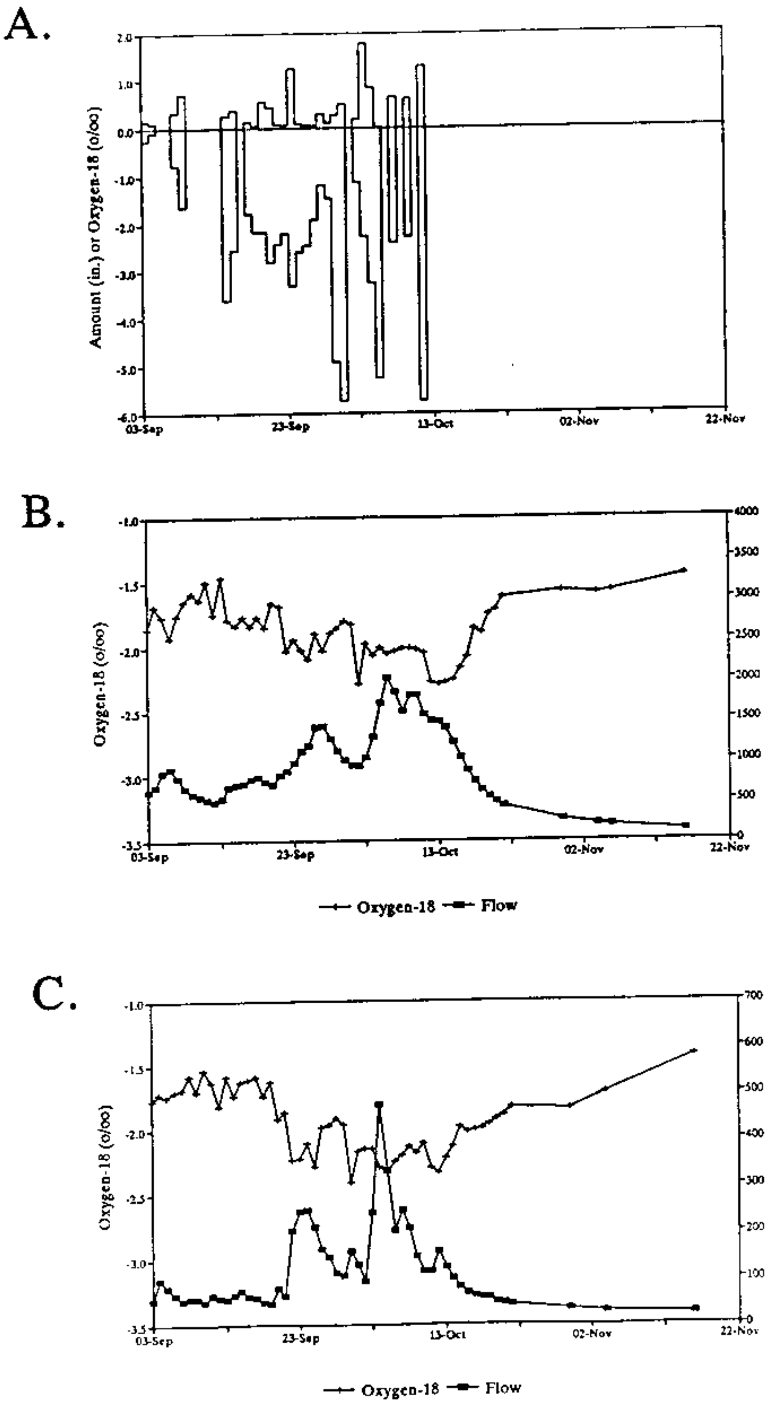

Figure 24. Precipitation amount and $\delta^{18}O$ versus date (a.) and river flow and $\delta^{18}O$ versus date at station BD (b.) and SH (c.) in 1992.

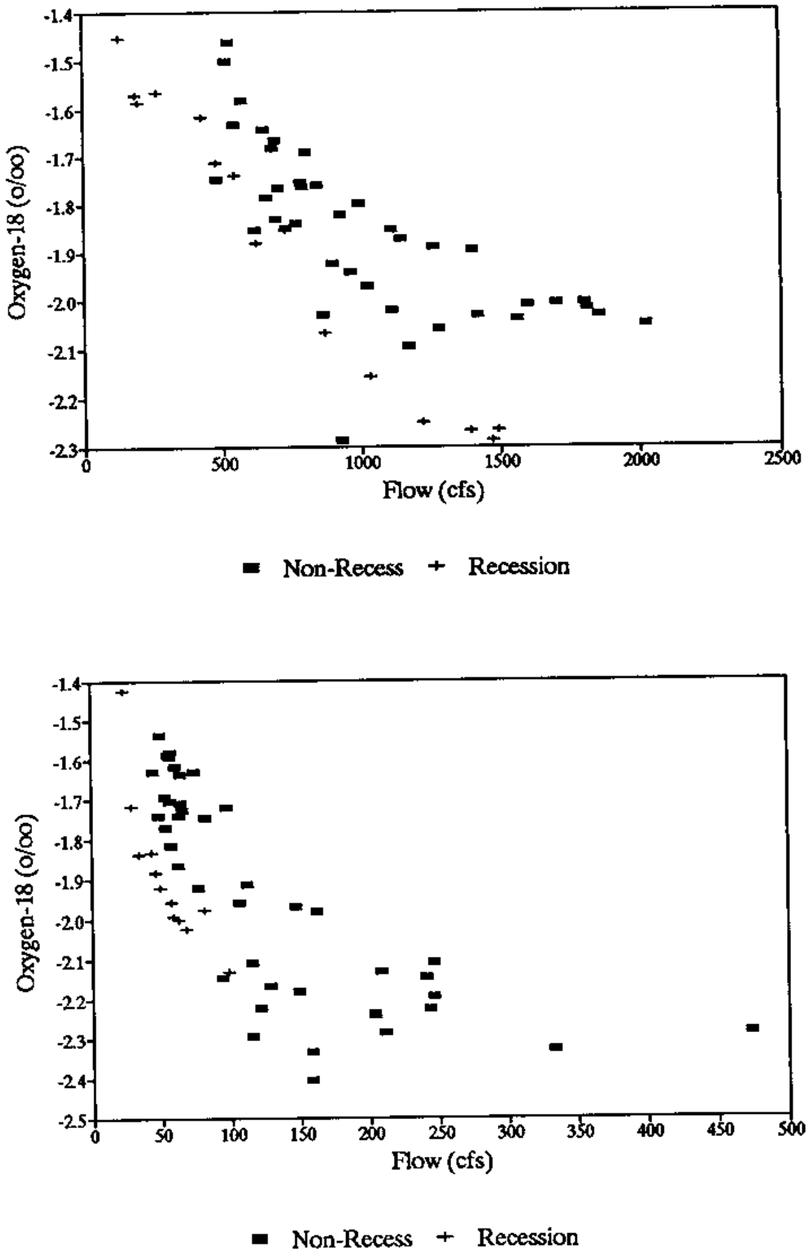

Figure 25. River $\delta^{18}O$ versus flow during Autumn 1992 sampling at station SH (a.) and BD (b.).

sources exist, river flow during recession represents the release of channel storage and discharge from surficial and deeper aquifers. Thus it is reasonable to expect the isotopic content of river water to approach the flow-weighted mean isotopic content of contributing aquifers during an extended period of recession. This is 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 (Hill and Waddington 1993, Hooper and Shoemaker 1986).

In the Econlockhatchee basin, surficial aquifer $\delta^{18}O$ ranged from about -2.3 to -3.2 ‰. For the four-week period preceding the onset of recession, most rainfall events were more depleted than -2.5 ‰. At peak flow, river $\delta^{18}O$ was about -2.2 ‰ at all stations (Figures 21 and 24). Paradoxically, during the recession period that followed, river $\delta^{18}O$ became progressively more *enriched* with decreasing flow (Figures 24b and 24c), even though likely contributing water masses were more *depleted*. Assuming an average channel velocity of 1.0 ft./sec, the travel time for water in the river was less than 2 days. Thus some factor existed in the river system to provide a constant source of isotopic enrichment to channel water.

Evaporative enrichment has been identified as a dominant factor in the isotope balance of closed or lentic hydrologic systems, such as lakes and wetlands (Dinçer 1968), but evaporative effects have been considered important in very few isotopic studies of rivers (Sklash, *et al.*, 1976). Thus alternative explanations to evaporative enrichment were examined, then a quantitative analysis of evaporative effects was undertaken.

Water masses potentially influencing river flow were the surficial aquifer, the Floridan aquifer, and channel evaporation. Hydraulic-gradient measurements from near-stream monitoring wells indicated that, even under high-flow periods, the surficial aquifer had the potential for contribution to river discharge (Figures 15 through 19). Monitoring wells were placed in the immediate near-stream zone with the specific intention of sampling formation water contributing to river flow. It is possible that monitoring wells were not deep enough to sample surficial aquifer flow originating from distant locations in the watershed, with a longer residence time and potentially distinct isotope signature. The isotopic rainfall record in the Econlockhatchee watershed is not long enough to determine whether the seasonal signal is strong enough to support this conjecture.

The Floridan aquifer may have been a source of isotopically enriched water in the lower watershed, but did not appear to contribute significantly to river flow. During recession, isotopic enrichment was observed both at BDR and SHR. River-bed elevations upstream from BDR were significantly higher than the potentiometric surface of the Floridan aquifer (Figure 7), thus any leakage across the Hawthorne semi-confining unit would be *into* the Floridan. In an analysis of historical flow and surficial aquifer levels, Wanielista, *et al.* (1993), noted at low flow a flattening in the slope of aquifer elevation versus river flow and speculated that the change in slope may be due to contribution from the Floridan. Low-flow changes in slope were also observed in plots of $\delta^{18}O$ versus flow at both BDR and SHR (Figure 26). The upper-Floridan aquifer in the Econlockhatchee watershed had an $\delta^{18}O$ value of approximately -1.9 ‰ (Table 8). At SHR, the change in slope is consistent with a contribution of water with the isotopic

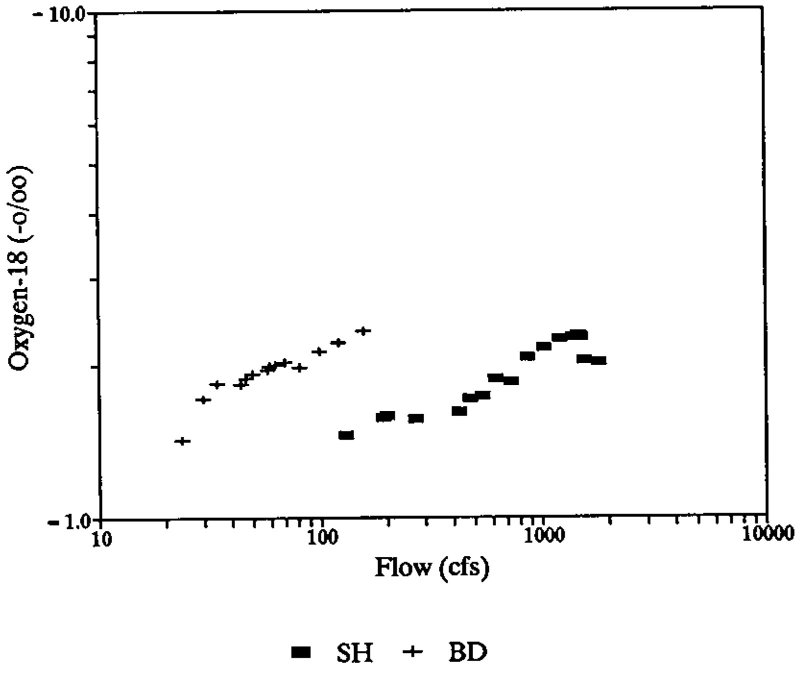

Figure 26. River $\delta^{18}O$ versus flow during recession (after October 12, 1992) at stations SH and BD.

content of the Floridan. However, the change in slope observed at BDR indicates more enriched $\delta^{18}O$ with lower flow, suggesting contribution by a more evaporated water mass than the Floridan. Thus, the influence of the Floridan may have been detected at low-flow, but the contribution of the Floridan aquifer appears to have been quite low.

A third potential source of isotopic enrichment in river water was evaporation. 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 gradient and large surface area of the Econlockhatchee Swamp created conditions conducive to evaporative enrichment. Headwater enrichment was assessed by collecting water samples upstream and downstream of the Econlockhatchee Swamp on November 19, 1993, which was day 23 of a period of recession. Discharge from the swamp was approximately 20 cfs. River $\delta^{18}O$ (Figure 27) enriched from -2.20 to -1.69 ‰ across the swamp, with steady depletion downstream to a value of -2.07 ‰ at SHR. The isotopic enrichment observed in the Econlockhatchee Swamp was consistent with evaporative effects, but the hydraulic loading from the swamp constituted only about 10 percent of the total flow at SHR (Figure 28). For evaporative enrichment to have been an important process in the river system, significant effects must have been exerted over the entire river system.

Recession Modeling

Isotopic enrichment of surface water observed during the recession period that began on October 13, 1992 was contrary to expectations that the isotopic composition of surface water would trend toward that of the surficial aquifer, the apparent source of

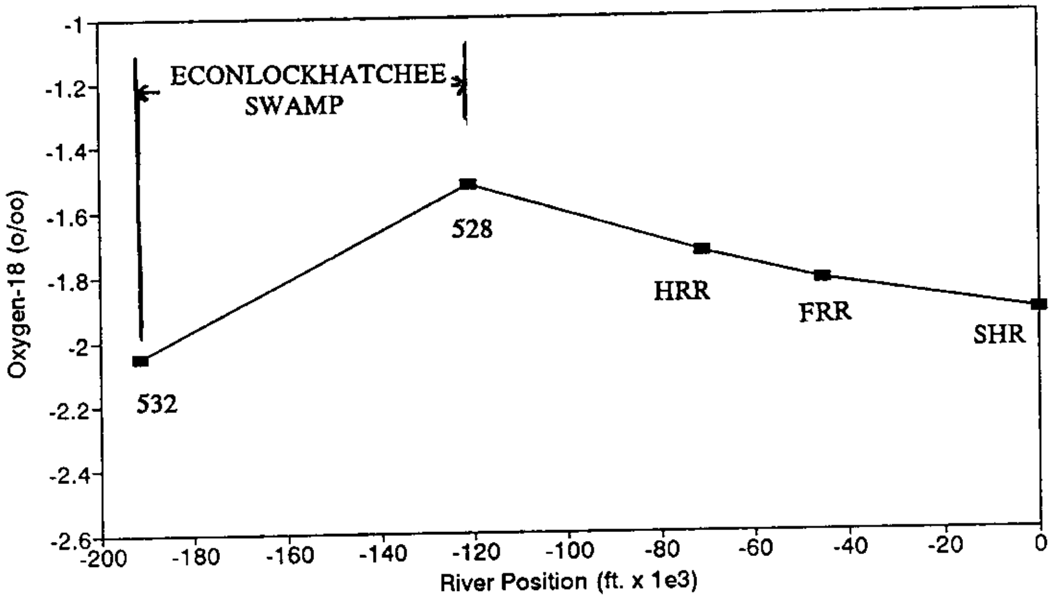

Figure 27. River $\delta^{18}O$ versus channel distance from SH in the Big Econlockhatchee River on November 19, 1993.

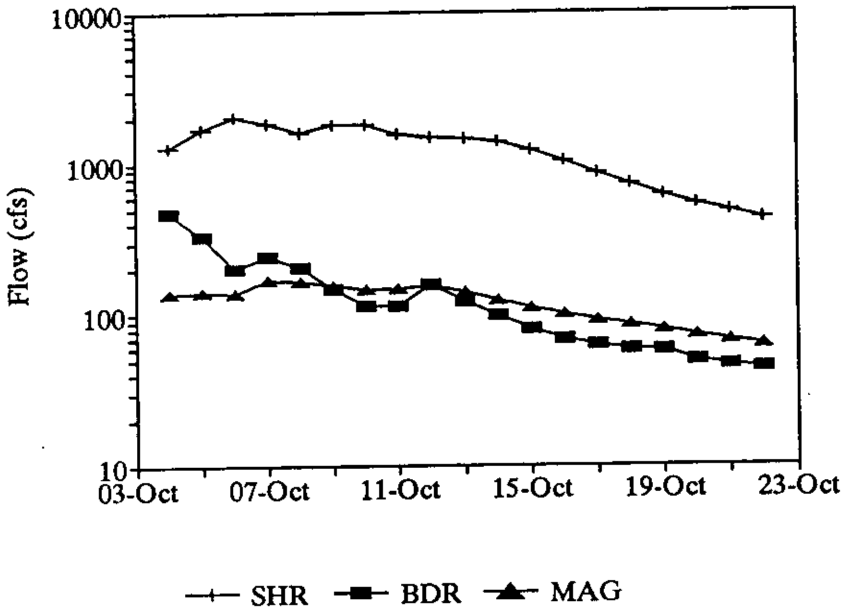

Figure 28. Flow versus date in 1992 at stations BD, MAG, and SH.

river flow during recession. Surface 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 channel throughput, thereby amplifying evaporative effects. However, lower channel storage and flow may have also led to 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 29) was the river channel upstream of a cross-section for which flow and isotopic data were available. Accurate gaging data were available at stations BDR and SHR, so the model was applied separately for each of those basins.

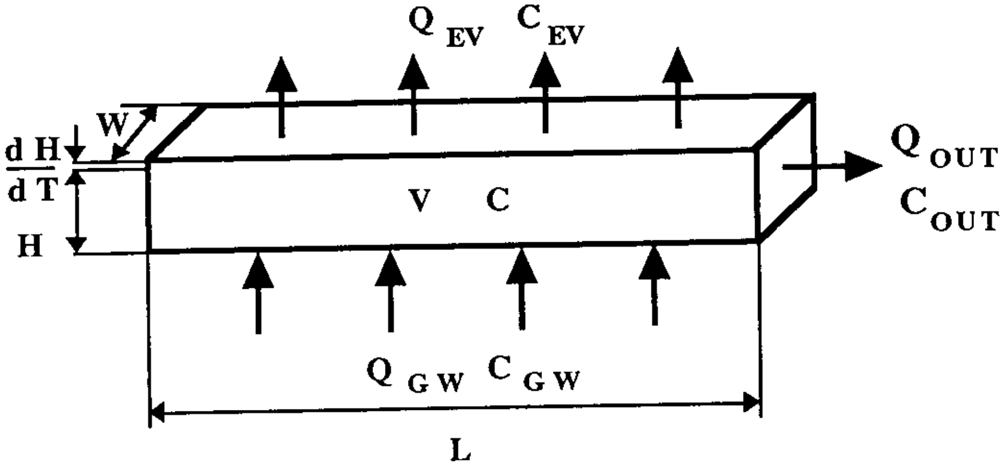

Figure 29. Control surface and boundary parameters for a conservative-tracer mass-balance model.

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

$$\frac{dV}{dt} = Q_{GW} - Q_{EV} - Q_{OUT} \tag{29}$$

$$\frac{dCV}{dt} = C_{GW}Q_{GW} - C_{EV}Q_{EV} - C_{OUT}Q_{OUT} \tag{30}$$

where V = Channel storage [ft^3]
Q = Flow [cfs]
C = Tracer concentration [‰]
GW = Aquifer origin
EV = Evaporative loss
OUT = Channel outflow

Equations 29 and 30 were solved assuming unsteady-state conditions with respect to channel volume (V) and isotopic content (C) over discrete one-day time-steps Δt:

$$\Delta V = V_2 - V_1 = V_{GW} - V_{EV} - V_{OUT} \tag{31}$$

$$\Delta CV + C\Delta V + \Delta C\Delta V = C_2V_2 - C_1V_1 = C_{GW}V_{GW} - C_{EV}V_{EV} - C_{OUT}V_{OUT} \tag{32}$$

where $V_{GW} = Q_{GW}\Delta t$ with appropriate unit conversions and similar computations for V_{EV} and V_{OUT}. Channel storage terms are $V = V_t = V_1$ and $V = V_{t+\Delta t} = V_2$, with similar notation for C. It may be noted that Equation 32, reduced to steady-state conditions, is identical in form to the two-component hydrograph separation model (Equation 27).

The river channel, within 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 supported by monitoring data, which showed each basin of the river to be spatially homogeneous during recession (Figure 30). Station SHR collected water from both the Big and Little Econlockhatchee River basins. During the recession period, the isotopic

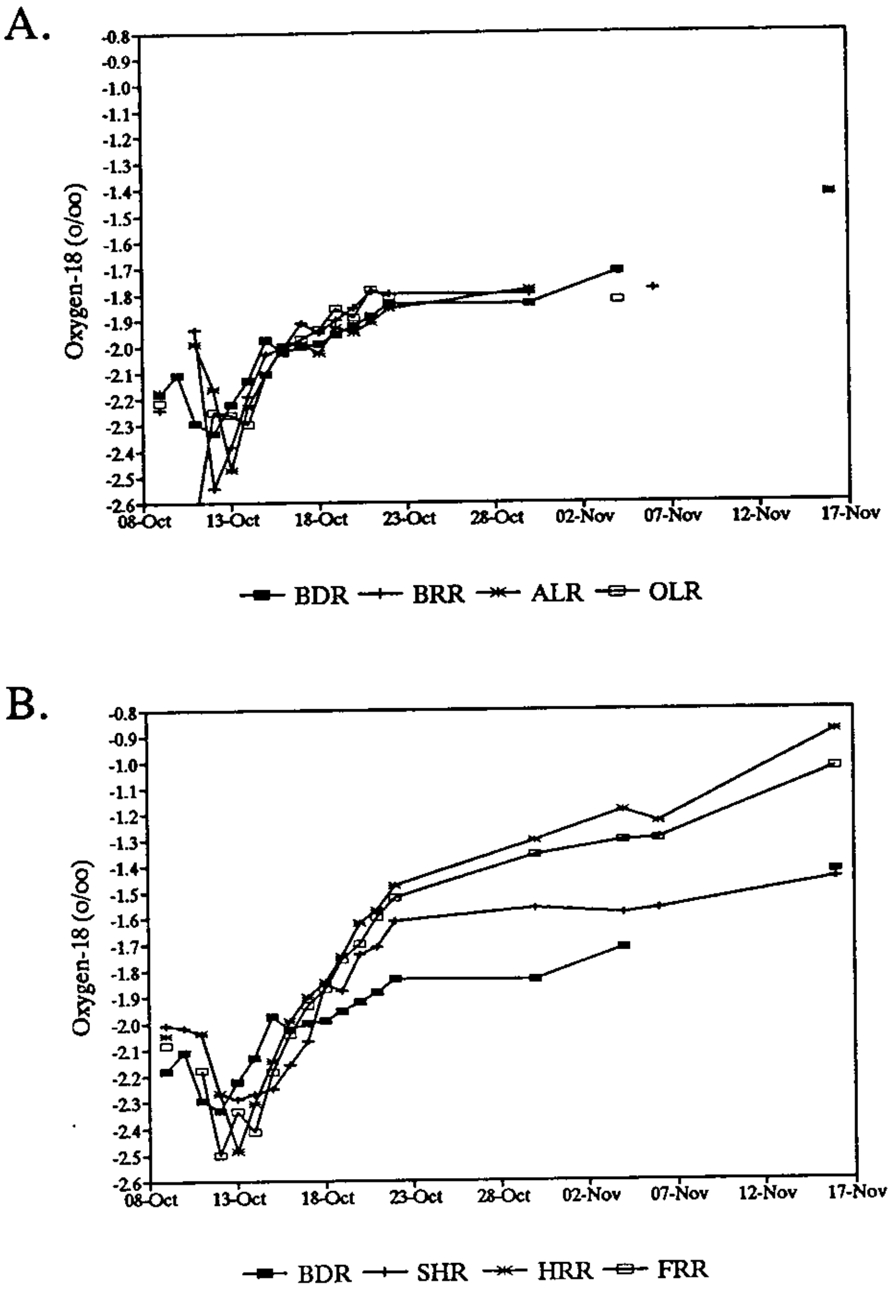

Figure 30. River $\delta^{18}O$ during recession (after October 12, 1992) at all stations in the Big Econlockhatchee (a.) and Little Econlockhatchee (b.) River.

content between these basins differed by less than 0.3 ‰. This difference was not considered sufficiently large to warrant modifying the completely-mixed assumption.

Equations 31 and 32 carry the assumptions that channel flow during recession was generated completely from aquifer discharge and the only losses were from evaporation, discharge at the watershed outlet, and channel storage loss. No distinction was made between surficial and Floridan aquifer contributions. It was assumed that all aquifer discharge originated from the surficial aquifer. This is consistent with earlier hydrogeologic analyses of the region, which concluded that the Hawthorne semi-confining unit significantly retarded hydraulic communication between the upper-Floridan and surficial aquifers (Tibbals 1990) and a recent hydrologic balance of the Econlockhatchee basin, which concluded that net exchange between the Floridan and surficial aquifers comprised less than 1.0 percent of the hydrologic budget of the watershed (Wanielista, *et al.*, 1992, p. 73).

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

$$\begin{aligned} \delta_E &= \frac{\alpha\delta_R - h\delta_A - \epsilon}{1 - h - (\Delta\epsilon\ 10^{-3})} \\ &= \frac{(0.99)(-2.5) - (0.85)(-5.0) - 10.0}{1 - 0.8 - 0.00286} \\ &= -56.0\ o/oo \end{aligned} \tag{33}$$

where
δ_E = Isotopic composition of evaporation [‰]
α = Fractionation factor, approximately 0.99 at 25°C
δ_R = Isotopic composition of river water [-2.5 ‰]
h = Relative humidity [0.85]
δ_A = Isotopic composition of atmospheric moisture [-5.0 ‰]
ϵ = 1000(1-α)

$$\Delta\epsilon = 14.3(1-h)$$

Estimates of the $\delta^{18}O$ of evaporation have been notoriously imprecise, due in part, to the difficulty in attaining accurate values for δ_R and δ_A, which may vary widely as functions of distance from the air/water interface through diffusional processes or turbulent mixing (Craig and Gordon 1965). A high degree of spatial heterogeneity in h and δ_A also may have occurred due to microclimate differences with varying canopy coverage along the river. Estimates for each parameter are provided above in the definition of terms and were intended to produce the most depleted likely value for δ_E, thereby providing an estimate of the greatest potential impact of evaporation on the isotope hydrology of the river. For the input parameters selected, $\delta_E = C_{EV}$ was estimated to be -56 ‰. Daily amounts of evaporation were set at 0.01 ft/day, based on long-term average conditions in October for east-central Florida (Wanielista 1990).

To solve Equations 31 and 32, estimates of channel geometry were required. 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 modeled as a rectangular prism with an average width of 40 ft. and an average depth of 5 ft. for the SHR modeling run and 4 ft. for the BDR modeling run. Channel geometry assumptions were developed from field survey data. Channel length was determined through previous surveys (Miller & Miller 1984) and analysis of USGS 7.5-minute topographic quadrangle sheets[4]. Channel storage was adjusted with each time-step based

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[4] Wanielista, *et al.* (1993), provide a listing of topographic sheets surveying the Econlockhatchee watershed, Figure 2.1, p. 4.

on the daily change in gage height averaged from 8 river stations during the modeling run.

The modeling strategy employed two equations (Equations 31 and 32) to solve for two unknowns (V_{GW} and $C_2 = C_{OUT\,t+\Delta t}$):

$$C_{OUT} = \frac{C_{GW}V_{GW} - C_{EV}V_{EV} + C_1V_1}{V_{OUT} + V_2} \tag{34}$$

Because evaporation was surface-area dependent, the model was calibrated by varying surface area until predicted values for C_{OUT} coincided with observed values. Table 9 summarizes the input and output data for the SHR and BDR modeling runs, respectively, and Figure 31 plots observed and predicted C_{OUT} values.

A sample calculation using data from the SHR station (Table 9a) is provided to clarify the procedure. Time t=12-Oct-92 and time t+Δt=13-Oct-92. Column 1 identifies the sampling date and Columns 2 and 3 are the measured flow (Q_{OUT}) and $\delta^{18}O$ (C_R), respectively, at station SHR. Column 4 is the daily outflow in cubic feet. On 13-Oct-92, V_{OUT} was

$$V_{OUT} = Q \ x \ dt = 1{,}470 \ \frac{ft.^3}{\text{sec}} \ x \ 86{,}400 \ \frac{\text{sec}}{day} = 1.27(10^8) \ ft.^3 \tag{35}$$

Column 5 is the change in gage height in the river averaged over all 8 gaging stations and reflects the loss in channel storage. Column 6 is the river depth computed as the initial channel depth minus the total change in gage height over the sampling period. For 13-Oct-93, h was:

Table 9.
INPUT/OUTPUT SUMMARY FOR MASS-BALANCE MODELING DURING RECESSION.

analys2 \rocky\table4.wq2
05-Mar-94

factor 3

SITE: SHR

h = 5 [ft]
e = 0.01 [ft/day]
Cev = -56.0 [o/oo]
Cgw = -2.8 [o/oo]

w = 40 [ft]
L = 1.16E+06 [ft]
A = 4.64E+07 [ft^2]

	Qout [cfs]	Cout True [o/oo]	Vout [ft^3]	delta h [ft]	h [ft]	V [ft^3]	Vgw	Cout Unlink
12-Oct-92	1490	-2.27			5.00	2.32E+08		-2.27
13-Oct-92	1470	-2.29	1.27E+08	-0.07	4.93	2.29E+08	1.24E+08	-2.39
14-Oct-92	1390	-2.27	1.20E+08	-0.44	4.56	2.12E+08	1.00E+08	-2.41
15-Oct-92	1220	-2.25	1.05E+08	-0.44	4.56	2.11E+08	8.52E+07	-2.28
16-Oct-92	1030	-2.16	8.90E+07	-0.52	4.48	2.08E+08	6.54E+07	-2.15
17-Oct-92	865	-2.07	7.47E+07	-0.52	4.48	2.08E+08	5.09E+07	-2.00
18-Oct-92	726	-1.85	6.27E+07	-0.26	4.74	2.20E+08	5.09E+07	-1.88
19-Oct-92	620	-1.88	5.36E+07	-0.35	4.65	2.16E+08	3.80E+07	-1.83
20-Oct-92	543	-1.74	4.69E+07	-0.40	4.60	2.13E+08	2.86E+07	-1.73
21-Oct-92	479	-1.71	4.14E+07	-0.22	4.78	2.22E+08	3.18E+07	-1.64
22-Oct-92	427	-1.62	3.69E+07	-0.32	4.68	2.17E+08	2.26E+07	-1.58

analys2 \rocky\basin1.wq1
05-Mar-94

SITE: BDR

factor 3

h = 4 [ft]
e = 0.01 [ft/day]
Cev = -56.0 [o/oo]
Cgw = -2.8 [o/oo]

w = 40 [ft]
L = 2.51E+05 [ft]
A = 1.00E+07 [ft^2]

	Qout [cfs]	Cout True [o/oo]	Vout [ft^3]	delta h [ft]	h [ft]	V [ft^3]	Vgw	Cout
12-Oct-92	158.40	-2.33	1.37E+07	0.00	4.00	4.01E+07		-2.33
13-Oct-92	121.70	-2.22	1.05E+07	-0.20	3.80	3.81E+07	8.61E+06	-2.30
14-Oct-92	99.00	-2.13	8.55E+06	-0.15	3.65	3.66E+07	7.15E+06	-2.25
15-Oct-92	80.99	-1.98	7.00E+06	-0.14	3.51	3.52E+07	5.70E+06	-2.19
16-Oct-92	68.77	-2.02	5.94E+06	-0.11	3.40	3.41E+07	4.94E+06	-2.13
17-Oct-92	62.76	-2.00	5.42E+06	-0.06	3.34	3.35E+07	4.93E+06	-2.07
18-Oct-92	59.00	-1.99	5.10E+06	-0.04	3.30	3.31E+07	4.80E+06	-2.01
19-Oct-92	57.99	-1.96	5.01E+06	-0.01	3.29	3.30E+07	5.02E+06	-1.97
20-Oct-92	49.50	-1.92	4.28E+06	-0.09	3.20	3.21E+07	3.48E+06	-1.89
21-Oct-92	46.43	-1.89	4.01E+06	-0.05	3.15	3.16E+07	3.62E+06	-1.82
22-Oct-92	44.07	-1.83	3.81E+06	-0.04	3.11	3.12E+07	3.51E+06	-1.76

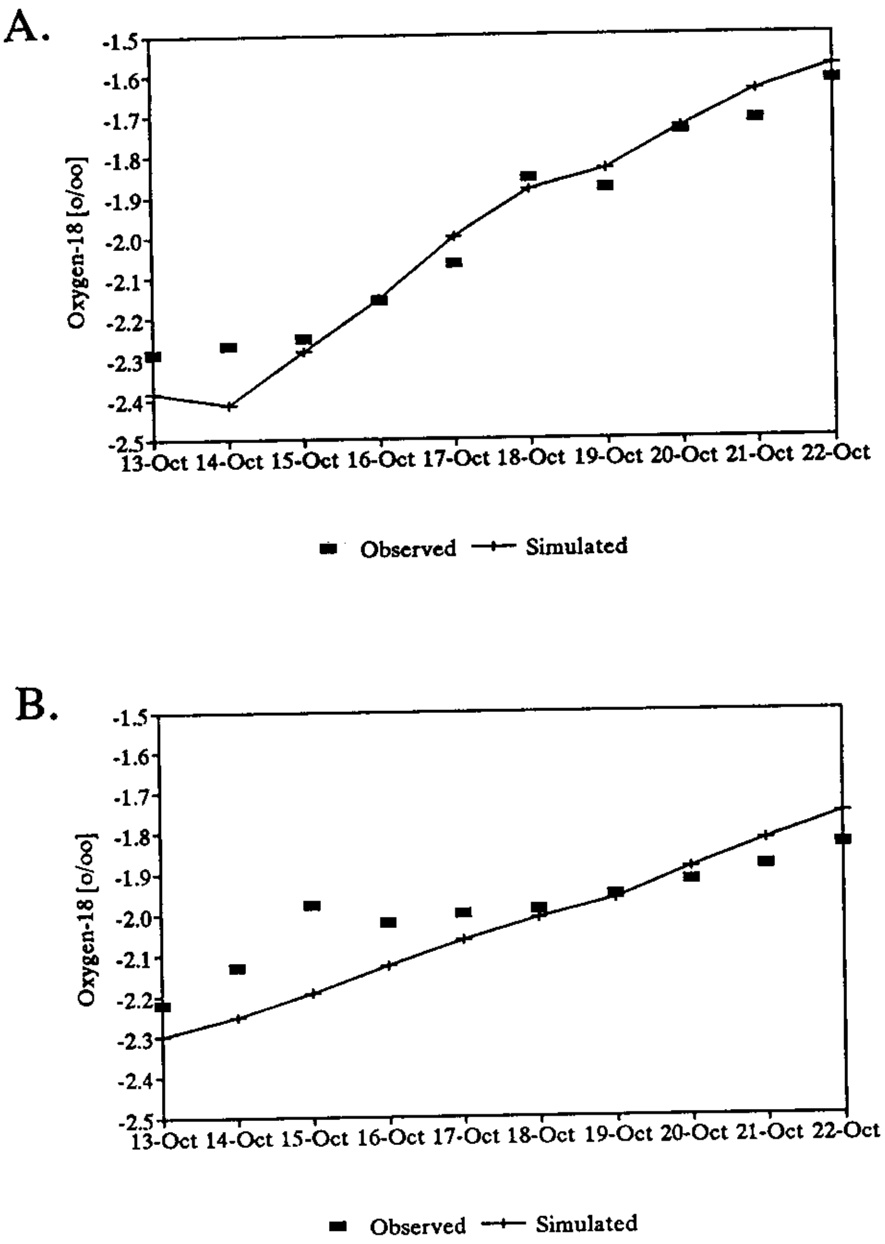

Figure 31. Observed and simulated river $\delta^{18}O$ during recession at station SH (a.) and BD (b.).

$$h = h_0 + \Sigma \Delta h = 5.00 - 0.07 = 4.93 \ ft. \tag{36}$$

The channel volume (Column 7) is the product of channel dimensions. Volumes V_1 and V_2 were:

$$\begin{aligned} V_1 &= W \ x \ L \ x \ h = 40 \ x \ 1.16(10^6) \ x \ 5 = 2.32(10^8) \ ft.^3 \\ V_2 &= 40 \ x \ 1.16(10^6) \ x \ 4.93 = 2.29(10^8) \ ft.^3 \end{aligned} \tag{37}$$

The daily volume contributed by groundwater, V_{GW}, was computed using Equation 31 for 13-Oct-92 where the volume of water evaporated from the river surface V_{EV} is estimated as:

$$V_{EV} = W \ x \ L \ x \ e = 40 \ ft. \ x \ 1.16(10^6) \ ft. \ x \ 0.01 \frac{ft.}{day} = 4.64(10^5) \ ft.^3 \tag{38}$$

$$\begin{aligned} V_{GW} &= V_2 - V_1 + V_{EV} + V_{OUT} \\ &= 2.29(10^8) - 2.32(10^8) + 4.64(10^5) + 1.27(10^8) = 1.24(10^8) \ ft.^3 \end{aligned} \tag{39}$$

The estimated value of $\delta^{18}O$ leaving the reach on 13-Oct-92 was computed using Equation 34:

$$C_{OUT} = \frac{(-2.80 \ x \ 1.24(10^8)) - (-56.0 \ x \ 4.64(10^5)) + (-2.27 \ x \ 2.32(10^8))}{1.27(10^8) + 2.29(10^8)} \tag{40}$$
$$= -2.39 \ o/oo$$

The modeling results indicate that it is possible to attribute isotopic enrichment observed during recession to surface evaporation. Equations 31 and 32 were calibrated to reflect both the magnitude and rate of evaporative enrichment observed at the SHR and BDR stations. To calibrate the model, the initial assumption for channel surface area was increased by a factor of 3. It is plausible that channel length was significantly underestimated in the original modeling assumptions, which were determined based on floodplain length measured from topographic maps and field surveys. While the floodplain in the Econlockhatchee basin was relatively well defined by 7.5-minute 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 & Langbein 1966). Channel surface area may also have been underestimated in the Little Econlockhatchee basin as channels were significantly widened in many reaches and supported with networks of drainage ditches (Miller & Miller 1984).

The sensitivity of the model to changes in input parameters that were not directly measured was examined. Response in C_{OUT} for the SHR modeling run were plotted due to variation in C_{EV} (Figure 32a), C_{GW} (Figure 32b), the surface-area adjustment factor (Figure 33a), and initial channel depth (Figure 33b). This analysis indicated that no input parameter, except perhaps the surface-area adjustment factor, was sensitive enough to result in a significant change in the response variable, within the expected range in magnitude of each parameter.

If Equations 31 and 32 accurately modeled river conditions during recession, then relatively depleted ($\delta^{18}O=-2.8$) water from the surficial aquifer underwent constant and significant isotopic enrichment as channel flow. Implications include (1) that it is reasonable to assume that measurements from near-stream monitoring wells accurately reflected the isotopic composition of aquifer water entering the river channel, (2) river flow during recession originated from the surficial aquifer, (3) estimates for *old* water

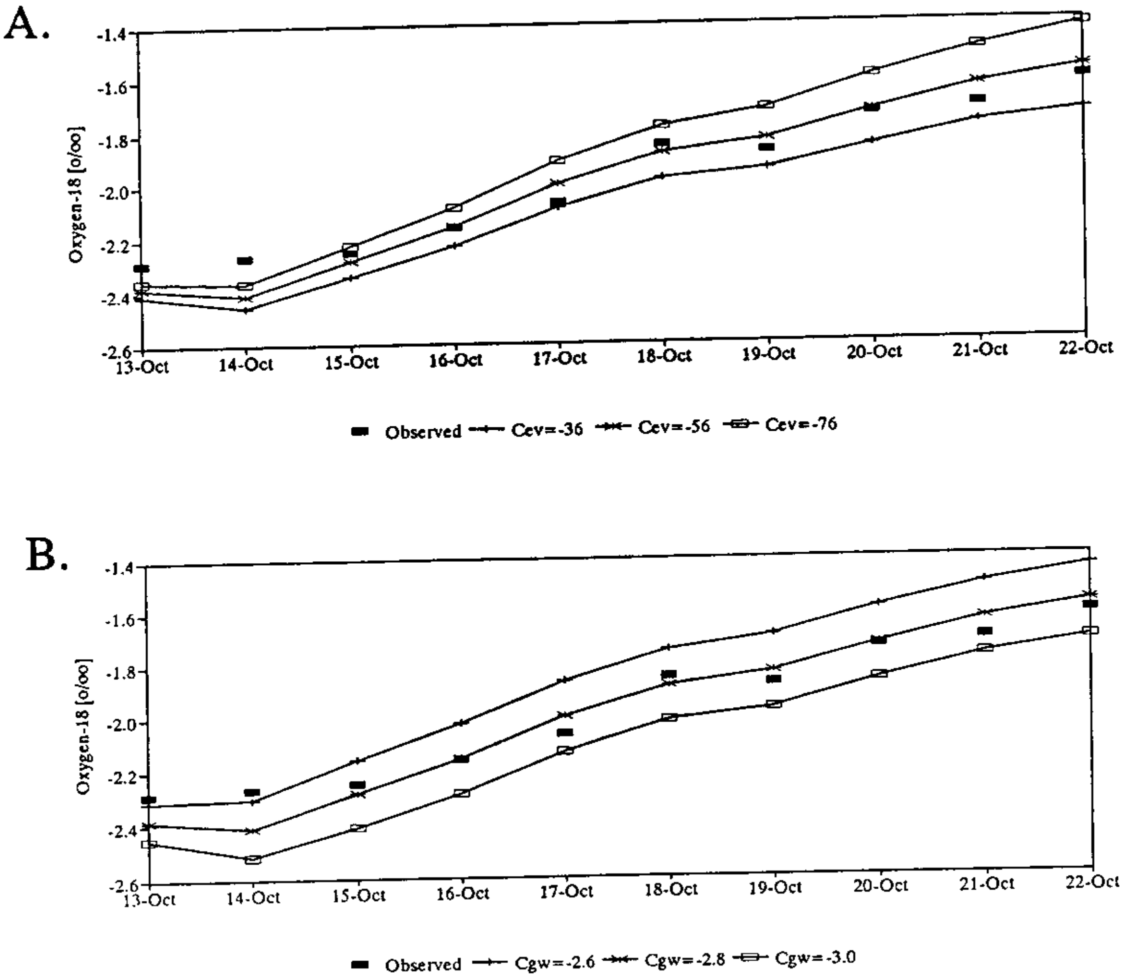

Figure 32. Sensitivity analysis of mass-balance model varying the isotopic compositions of evaporated water (a.) and groundwater (b.).

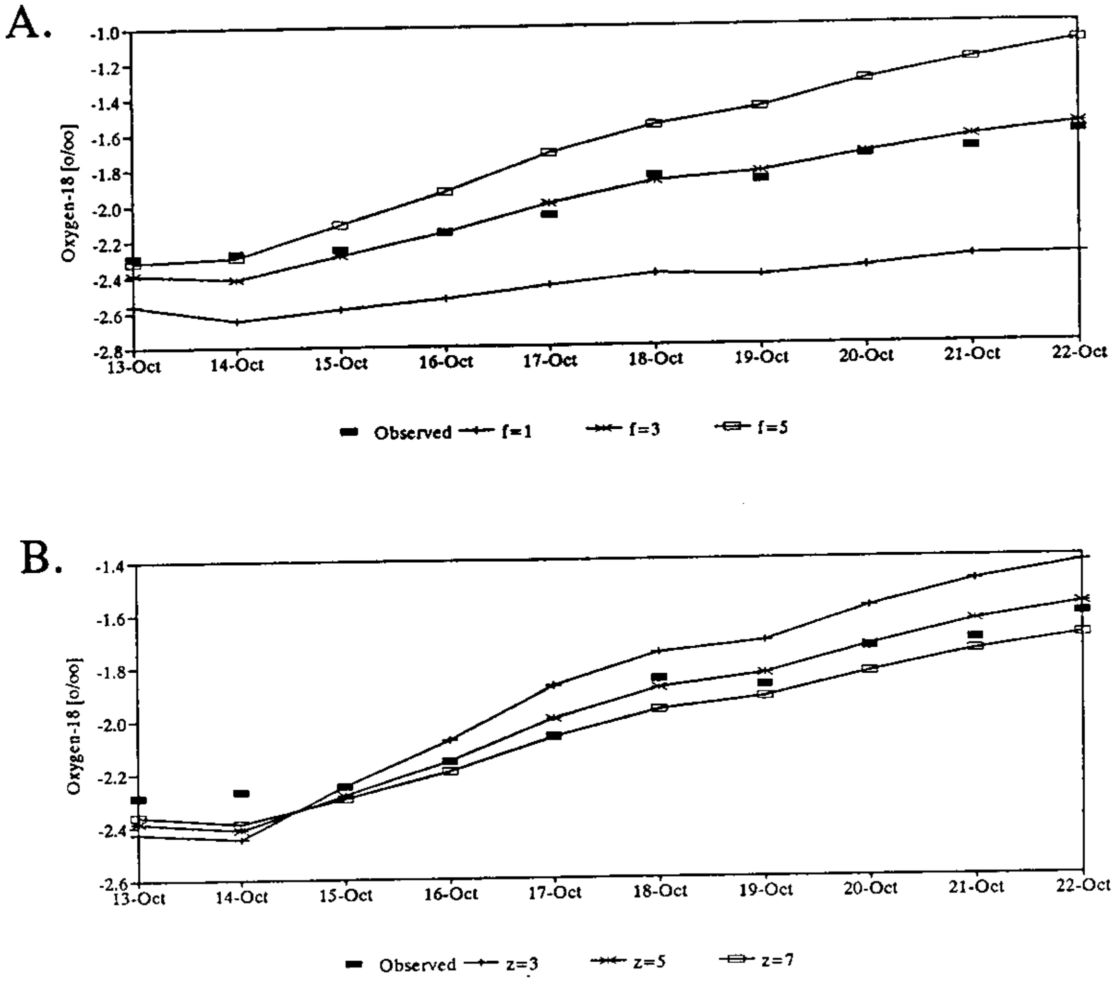

Figure 33. Sensitivity analysis of mass-balance model varying channel surface area (a.) and initial channel depth (b.).

isotopic content should be adjusted for temporal changes due to evaporative enrichment.

Several important *caveats* regarding recession modeling should be recognized. These conclusions are drawn from only one recession period and do not necessarily reflect general hydrologic processes in the basin. Also, input parameters for Equations 6 and 7 were selected specifically to maximize the potential effects of evaporation. The magnitude of evaporation should be verified independently, either through repeated observations of other recession periods or by comparing the rate of enrichment in $\delta^{18}O$ simultaneous with that in δD, a procedure known as *deuterium excess* analysis (Coplen 1993) which may identify the occurrence of *non-equilibrium*[5] evaporation.

Implications for Hydrograph Separation

To apply the environmental tracer mixing model presented in Equation 28, reliable estimates of C_N and C_O are necessary and C_N must be significantly different than C_O. Stable isotope data collected in the Econlockhatchee River basin during Autumn 1992 were examined specifically for their suitability in estimating hydrograph-separation end members.

New Water. Reliable estimation of C_N, commonly assumed to be the isotopic composition of precipitation (Pearce, *et al.*, 1986), requires low spatial variation in $\delta^{18}O$ over the watershed and large inter-storm variation. Spatial variability was observed both in precipitation amount and $\delta^{18}O$, particularly associated with summer convective storms.

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[5] Evaporation which occurs at a relative humidity less than 100 percent.

The data indicated that frontal storms were more regionally homogeneous and better suited for hydrograph separation.

Temporally, precipitation ranged in $\delta^{18}O$ from about -6.5 to 0.0 ‰ during the period of record. Precipitation analyses combining amount and isotopic content of precipitation (Figure 11), compared with the observed range in river $\delta^{18}O$, an indication of expected C_O, revealed that about half of the rain collected during Autumn 1992 was significantly more enriched or depleted than river $\delta^{18}O$. Thus, among the storms sampled, about half were suitable candidates for hydrograph separation on the basis of ability to estimate a C_N significantly different than C_O.

<u>Old Water.</u> The majority of studies employing the two-component hydrograph separation model (Equation 28) assumed that C_O was the pre-storm isotopic composition of the river (*e.g.*, Hooper and Shoemaker 1986). Other studies used direct measurements of near-stream groundwater tracer as C_O or as a separate term in a three-component mixing model (*e.g.*, Hinton, *et al.*, 1994, Dewalle, *et al.*, 1988, Genereux and Hemond 1990).

The disparity between near-stream groundwater $\delta^{18}O$ and river $\delta^{18}O$, apparently due to evaporative enrichment, clearly obviates the use of groundwater tracer alone to derive a C_O term. The pronounced temporal change in river $\delta^{18}O$ observed during recession, again assumed to be due to evaporative effects, suggests that pre-storm river conditions are also inadequate to represent C_O. Two alternatives for estimating C_O during a storm event are (1) a two-component term for C_O which considers C_{GW} and C_{EV} separately and (2) an empirical function for C_O developed from recession data. For the first alternative, a mass-balance model similar in form to Equations 31 and 32 may be used with additional terms for Q_N and C_N. For the second alternative, it may be possible to use a regression equation of river $\delta^{18}O$ versus flow during recession to represent C_O.

Conclusions and Recommendations

A one-season field investigation was conducted on the Econlockhatchee River system in central Florida to determine the suitability of stable isotope tracers in hydrograph separation studies within the system. Spatial and temporal variability was assessed in a synoptic survey of $\delta^{18}O$ in water masses believed to contribute to river flow, including precipitation, surficial and Floridan aquifer water, and river water.

Conclusions

Precipitation monitoring captured three storm types: summer convective, tropical depression, and frontal. Precipitation was observed to vary between -6.5 and 0.0 ‰ during the period of record. Compared with the range in river $\delta^{18}O$ observed during the same time period, 50 percent or more of the precipitation collected was significantly different in $\delta^{18}O$ than river water. It may thus be concluded that the range in isotopic content of precipitation in central Florida was sufficient for hydrograph separation.

The surficial and upper-Floridan aquifers had the potential for contribution to flow in the Econlockhatchee River. The surficial aquifer, measured at 5 locations near the Econlockhatchee River, displayed consistent hydraulic gradients which promoted flow into the river, even during periods of high river flow, indicating that accumulation of bank storage from the river was not an important process. Isotopically, the surficial aquifer exhibited very low temporal variability in $\delta^{18}O$ and some spatial variability between major sub-basins. The $\delta^{18}O$ of the surficial aquifer was -2.88 ± 0.46 ‰. The

Floridan aquifer ($\delta^{18}O = -1.71 \pm 0.16$ ‰) was not an important component in the isotope hydrology of the river system, due primarily to a confining unit separating the Floridan and surficial aquifers, and disadvantageous hydraulic gradients in the upper watershed. In the lower watershed the isotopic influence of the Floridan may have been observed under low-flow conditions.

Surface water displayed low spatial variability in $\delta^{18}O$ and ranged temporally between approximately -2.5 and -1.5 ‰. A consistent disparity in the isotopic composition of near-stream groundwater and river water observed in the Econlockhatchee River led to an analysis of the effects of evaporation during the hydrologically simplified conditions of recession. This analysis revealed that evaporation may account for significant isotopic enrichment inversely related to river flow.

A sufficient isotopic signal existed for hydrograph separation in the Econlockhatchee River system. The storm-specific conditions that must be met for accurate separation of new and old water masses were found to be (1) even coverage of the storm over the watershed or sub-basin of interest, (2) intra-storm heterogeneity or adequate monitoring to account for intra-storm variability, and (3) adequate control on evaporative changes in C_O, either through pre-and post-storm recession monitoring or derivation of a mass-balance model with terms for evaporative enrichment.

Recommendations

To conduct hydrograph-separation studies in the Econlockhatchee basin, or peninsular Florida in general, additional research is necessary in three basic areas: precipitation monitoring, evaporation analysis, and storm capture.

Precipitation Monitoring. The nature of isotopic variability in precipitation in peninsular Florida has not been well documented. Precipitation samples have been collected within the Econlockhatchee River basin over a one-year period, analyzed for $\delta^{18}O$, and archived. It is recommended that precipitation monitoring continue in central Florida and that samples be analyzed for δD and $\delta^{18}O$ to provide a local meteoric water line (Craig 1961) for the region. The archived samples can be held for approximately 5 years, depending on the integrity of the sample container.

Evaporation Analysis. The effects of evaporation have not been considered in most studies of isotope hydrology in rivers. Two promising avenues of research are analysis of spatial and temporal changes in deuterium excess in river water and monitoring to improve estimates of δ_E, the isotopic composition of evaporated water. Deuterium excess analysis may reveal the degree of evaporation a water mass has undergone. The isotopic nature of evaporation has been recognized as a poorly-controlled process. Controlled experiments to improve parameter estimates in the Craig and Gordon (1965) evaporation model would improve estimation of δ_E.

Storm Capture. The synoptic survey conducted in Autumn 1992 produced baseline information on water masses generating flow, although none of the storm events captured were particularly well-suited for hydrograph separation. The high frequency of storm events early in the study period resulted in a hydrograph in which the response of individual events was obscured by other storm events. Additional storms must be monitored that bear the hydrologic and isotopic characteristics necessary to perform the hydrograph separation analysis, as discussed in this paper. It is also necessary for the storms to represent hydrologic conditions of interest for basic study objectives, such as the relative contribution of new water under conditions of high versus low surficial aquifer storage or seasonal effects.

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CHAPTER 4

SEPARATION OF STREAMFLOW COMPONENTS IN A SUBTROPICAL LOW-GRADIENT WATERSHED

Introduction

Hydrograph separation is a classical problem in hydrology for determining the relative influence of various sources of channel flow. Depending on study objectives, flow components may be identified as surface runoff associated with storm events and subsurface components from shallow and deeper aquifers. Because of the rapid response of surface and near-stream subsurface runoff, these components are frequently termed collectively as *new* water, and slower-response subsurface components are known collectively as *old* water.

Early hydrograph separation studies used hydrometric data to analyze the recession limb of hydrographs with the principal objective of understanding the characteristics of baseflow, an important factor in such engineering applications as bridge and reservoir design and flood forecasting (Todd 1980, Singh 1968, Meyboom 1961). More recently, researchers interested in interactions between surface and subsurface components of runoff have applied mass balance models using conservative tracers (*e.g.*, Maulé, *et al.*, 1994, Buttle and Sami 1992, McDonnell, *et al*, 1991, Hooper and Shoemaker 1986, Kennedy, *et al.*, 1986, Sklash and Farvolden 1979, Fritz, *et al.*, 1976).

The common form of the mass balance model is known as the two-component model:

$$Q_R = Q_O + Q_N \tag{41}$$

$$Q_R C_R = Q_O C_O + Q_N C_N \tag{42}$$

$$Q_O = Q_R \frac{C_N - C_R}{C_N - C_O} \tag{43}$$

where Q_R, Q_O, and Q_N are the total, prestorm and storm discharges, respectively and C_R, C_O, and C_N are their respective tracer concentrations (after Sklash, *et al.*, 1976). C_N and C_O are known as *end members*, because they represent the extreme possible concentrations for C_R (Hooper, *et al.*, 1990).

A variety of tracers has been proposed (Table 2). The tracer must be either conservative, *i.e.*, unchanging over time and space, or the behavior of the tracer must be predictable, as in the decay of a radioisotope (Kennedy, *et al.*, 1986, Martinec 1974, Dinçer, *et al.*, 1970). Among the environmental, or naturally occurring, tracers, solute and isotope tracers have been most widely used. Electrical (specific) conductivity (Tranter and Raiswell 1991, Nolan and Hill 1990), dissolved silica (Wells, *et al.*, 1991a and 1991b, Kennedy 1971), and various anions and cations (McDonnell, *et al.*, 1991, Caine 1989, Hirata and Murakoya 1988, Fritz, *et al.*, 1976, Pinder and Jones 1969) have been used in hydrograph separation studies. Solute tracers are seldom truly conservative, as their concentrations in water may vary with residence time or some local geochemical or biological influence (Kennedy, *et al.*, 1986).

The heavy stable isotopes of water, oxygen-18 ($\delta^{18}O$) and deuterium (δD), are considered excellent conservative tracers, because they are constituents of the water molecule itself, rather than a solute transported with water, and can form distinctive signatures in water masses. Bowen (1988) and Coplen (1993) provide introductions to stable isotope properties, measurement, and applications in the environmental sciences.

Equation 43 represents steady-state conditions, applied over an unspecified control surface, presumably the river channel. Spatially, the model is applied at the catchment scale, with Q_R and C_R measured at a single outflow from the catchment. C_O and C_N reflect average tracer concentrations over the watershed. Temporally, Equation 3 is usually solved for average conditions during a single storm hydrograph or is solved over discrete time steps that reflect the availability of field data (McDonnell, *et al.*, 1991).

The expression of hydrologic interactions at the watershed level in form of a two-component model requires a great many simplifying assumptions. Virtually all investigators (Table 2) recognized at least some of the limitations in applying Equation 43. The major assumptions of the 2C model (after Kennedy, *et al.*, 1986) are described below.

1. C_O remains constant during the storm event.
2. C_O is significantly different than C_N.
3. C_N undergoes no changes while being routed through the watershed.
4. A steady-state model adequately represents watershed conditions.

Most researchers have estimated C_O as the isotopic content of the near-stream groundwater or pre-storm river (DeWalle, *et al.*, 1988, Hooper and Shoemaker 1986), and assumed C_O to remain constant through the storm event (Assumption 1). Through analysis of an extended period of hydrologic recession in the Econlockhatchee River (Chapter 3), it was determined that C_O may vary, presumably due to evaporative enrichment. The requirement for C_N to be significantly different than C_O (Assumption 2) has been considered in many of the studies reviewed (Table 2). McDonnell, *et al.* (1991) are among the few that provide a quantitative expression of signal strength. Assumption 3 requires that C_N equal the isotopic content of precipitation. Hydrologic processes such as throughfall and temporary surface storage (DeWalle and Swistock 1994) may result in isotopic enrichment of C_N.

The assumption that a steady-state model adequately represents watershed conditions (Assumption 4) is seldom stated explicitly in the literature. In fact, of the peer-reviewed journal articles reviewed for this dissertation (Table 2), none included derivations of hydrograph separation models from the differential forms of the mass-balance equations. This results in the tacit assumption that changes in the volume and isotopic content of channel storage over time are negligible.

The objectives of this chapter were to (1) derive steady- and unsteady-state forms of the two-component hydrograph-separation model, (2) apply the models to a storm-event to develop an estimate of old-water contribution to channel flow, and (3) assess the validity of the estimate considering limitations imposed by simplifying assumptions.

Study Design

Site Description

The Econlockhatchee River basin occupies approximately 270 mi.^{2} in and east of Orlando, Florida and consists of two major branches, the Big and Little Econlockhatchee Rivers. Data were collected for this chapter within the Big Econlockhatchee basin. The Big Econlockhatchee River is about 38 miles long with a watershed of approximately 200 mi.^{2} Approximately 60 mi.^{2} are occupied by forested wetlands. The remaining area, occupied historically by pine flatwoods and sand-pine scrub, has been partially developed for citrus agricultural and range use. At low flow, the Big Econlockhatchee River is contained within an incised channel which meanders through a relatively undisturbed floodplain. The unconfined aquifer is composed of silica sand with a potentiometric surface occurring at depths ranging from 1 to 5 feet below land surface. The aquifer extends to a depth of approximately 70 ft. where it meets the Hawthorne semi-confining unit, which retards hydraulic communication with the upper Floridan aquifer (Tibbals 1990).

Sampling Design

A field sampling program was conducted to monitor river water, groundwater, and precipitation in the Econlockhatchee basin during the Spring of 1993. The river was in an extended period of recession at the start of sampling. Thus antecedent conditions reflected low storage in both the surfical aquifer and the river channel and high potential for initial abstraction.

Samples were collected from the Big Econlockhatchee River at Stations HR and FR (Figure 6). Station HR is located approximately 5 miles upstream from Station FR and drains approximately 82.3 mi.^{2}. Station FR has a total watershed area of approximately 133.9 mi.^{2} River and groundwater samples were collected daily from May 1 until May 18. A complete set of samples was collected on May 26. In response to a storm event (May 29, 30, and 31), samples were collected twice daily from May 29 until June 7, then daily until June 11, with follow-up sampling events on June 15 and 23.

River samples were collected at the shore. River elevation, specific conductivity, water temperature, station ID, date and time were recorded in a field book. Water samples collected for isotopic analysis were placed in 30 mL glass vials with Poly-Seal™ inverted-cone closures. Monitoring wells were installed at distances of approximately 5, 50, and 100 ft. in a line perpendicular to the river channel at stations HR and FR to sample the surficial aquifer. Appendix C provides construction details for the wells. Wells were sampled using Teflon™ or Lucite™ bailers. Wells were purged by pumping at least 20 bailer volumes (approximately 5 well casing volumes) to assure that formation water was sampled. Water samples for isotopic analysis were collected in a bailer and poured into 30 mL glass vials.

Precipitation was collected through a Nalgene™ funnel (top diameter, 7.5 cm) into a 4 L Nalgene carboy at station FR. The precipitation monitoring station was placed in an open area with no aerial obstructions. Because of the diversity of overstory vegetation types in the watershed, no attempt was made to analyze throughfall precipitation. The rain collector was checked twice daily during the storm event. Rain water was measured from the carboy into a graduated cylinder to compute amount. Samples for isotopic analysis were sealed in 30 mL glass vials.

Hydrologic Gaging

Flow measurements were made at stations HR and FR to develop stage-discharge rating curves. Stream velocity and depth were measured at cross-sections in the vicinity of staff-gages at stations HR and FR using standard United States Geological Survey methods to assure a measurement quality of *good* or *excellent* (Rantz 1983a, 1983b). Appendix C provides a thorough description of field and data-reduction methods. River elevation at staff-gages was recorded before and after each flow measurement and rating curves were developed to relate area and flow as functions of river elevation. Statistical analysis revealed that power transformations of the linear regression equations could be fitted to the gaging data. Least-squares analysis produced the following equations

$$\begin{gathered} Q_{HR} = 13.28\ [z + 1.6]^{1.36} \\ n = 18 \\ R^2 = 0.953 \end{gathered} \tag{44}$$

$$\begin{gathered} Q_{FR} = 16.52\ [z + 1.4]^{1.42} \\ n = 19 \\ R^2 = 0.998 \end{gathered} \tag{45}$$

for the HR (Equation 44) and FR (Equation 45) stations, where Q is river flow [cfs] and z is the river elevation referenced to an arbitrary, site-specific datum [ft.]. Figure 34 presents the rating curves for stations HR and FR. Computational methods for fitting

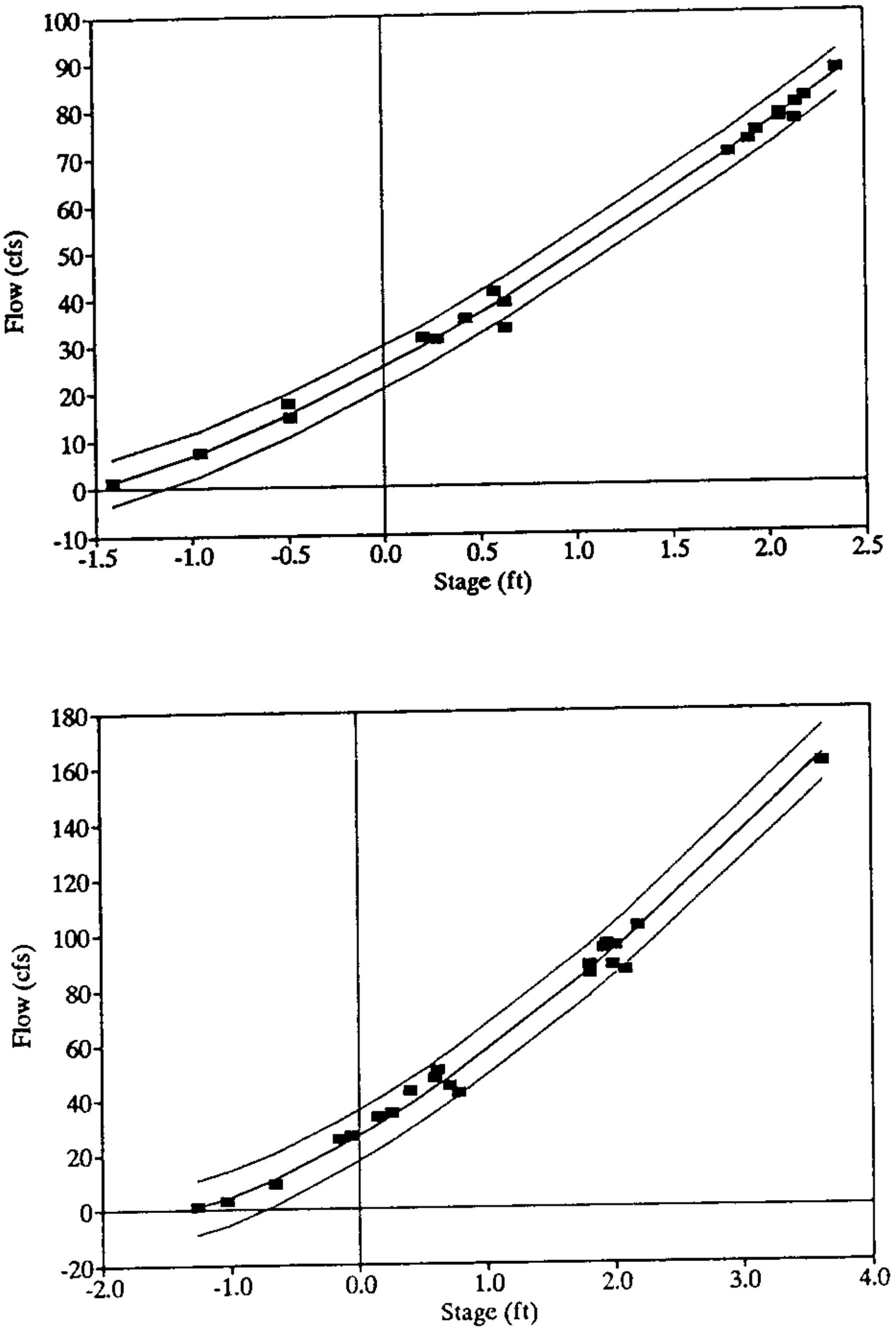

Figure 34. Hydrologic gaging at stations HR (a.) and FR (b.), with fitted regression line and 95 percent prediction intervals. River stages were referenced to arbitrary datums.

the regression equations and determining prediction intervals are provided in Appendix C.

Laboratory Methods

Water samples were analyzed for $\delta^{18}O$ in the University of Florida Department of Geology using the method of Socki, *et al.* (1992). Approximately 1.5 mL of sample was injected into a 7 mL disposable serum vial containing approximately 0.5 atmospheres of purified (Coleman grade) CO_2. The sample was then equilibrated in a shaker bath for at least 2 hours at 30°C. The CO_2 was then extracted from the vial and purified by cryonic distillation using an off-line vacuum system. Purified CO_2 gas was collected in a 6 mm pyrex break-seal tube for admission to the VG-Prism isotope-ratio mass spectrometer.

Analytical precision was generally better than 0.1 ‰. The reference gas used in the mass spectrometer was generated from Carerra marble (Hodell, *et al.*, 1989) and calibrated against international standards using the method described. At least 6 laboratory working standard samples were analyzed daily (Table 6). Duplicate analyses were performed on approximately 20 percent of all samples and on suspected outliers.

Results

Data collected immediately prior to, during, and following a storm event which occurred on May 29 through May 31, 1993 are summarized in Tables 10 and 11 and plotted in Figures 35, 36, and 37. Complete data listings are provided in Appendix C. The river was in an extended period of recession prior to the storm event. Flow at both the HR and FR sampling stations was less than 1.0 cfs at the onset of the event. The

Table 10.
RAINFALL AND RIVER δ^{18}O AND HYDROMETRIC DATA COLLECTED DURING SPRING 1993 MONITORING.

Surface hydrologic and isotope data
08-Apr-94 Revision
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DATE	Rain Amt (in.)	Rain O-18 (o/oo)	Rain Cn (o/oo)	HRR Stage (ft)	HRR Flow (cfs)	HRR O-18 (o/oo)	HRR Co (o/oo)	HRR fo	FRR Stage (ft)	FRR Flow (cfs)	FRR O-18 (o/oo)	FRR Co (o/oo)	FRR fo
n	3	3	23	37	37	37	37	23	37	37	37	37	23
mean	1.43	-3.59	-4.36	-0.53	15.2	-0.84	-0.27	0.77	-0.23	22.4	-1.07	-0.51	0.77
std. dev.	1.27	1.16	0.49	0.70	12.1	0.61	0.22	0.08	0.60	14.6	0.57	0.13	0.08
min	0.30	-4.84	-4.60	-1.72	0.0	-1.95	-0.63	0.64	-1.27	0.9	-2.26	-0.72	0.57
max	3.20	-2.05	-2.05	0.64	38.5	-0.02	0.10	0.92	0.72	48.0	-0.34	-0.28	0.94
01-May-93				-0.42	15.1	-0.13	-0.30		-0.17	22.2	-0.34	-0.52	
02-May-93				-0.53	13.2	-0.09	-0.27		-0.23	20.6	-0.37	-0.51	
03-May-93				-0.58	12.3	-0.24	-0.25		-0.56	12.9	-0.35	-0.44	
04-May-93				-0.59	12.2	-0.20	-0.25		-0.35	17.7	-0.41	-0.48	
05-May-93				-0.65	11.2	-0.23	-0.23		-0.39	16.8	-0.38	-0.47	
06-May-93				-0.75	9.6	-0.19	-0.20		-0.42	16.0	-0.34	-0.47	
07-May-93				-0.74	9.8	-0.24	-0.20		-0.47	14.9	-0.60	-0.46	
08-May-93				-0.79	9.0	-0.29	-0.19		-0.52	13.8	-0.42	-0.45	
09-May-93				-0.86	8.0	-0.32	-0.16		-0.57	12.7	-0.40	-0.43	
10-May-93				-0.86	8.0	-0.15	-0.16		-0.59	12.2	-0.45	-0.43	
11-May-93				-0.96	6.6	-0.14	-0.13		-0.65	11.0	-0.47	-0.42	
18-May-93				-1.41	1.7	-0.02	0.01		-1.03	4.0	-0.39	-0.33	
26-May-93				-1.72	0.0	-0.04	0.10		-1.26	1.0	-0.50	-0.28	
29-May-93				-1.71	0.1	-0.32	0.10		-1.27	0.9	-0.66	-0.28	
29-May-93	0.3	-2.05	-2.05	-1.71	0.1	-0.34	0.10	0.80	-1.27	0.9	-0.69	-0.28	0.77
30-May-93	3.2	-4.84	-4.60	-1.31	2.6	-0.85	-0.03	0.82	-0.25	20.1	-2.26	-0.51	0.57
31-May-93	0.8	-3.87	-4.46	-0.51	13.5	-0.76	-0.27	0.88	0.72	48.0	-1.90	-0.72	0.68
31-May-93			-4.46	-0.46	14.4	-0.68	-0.29	0.91	0.56	42.9	-1.92	-0.69	0.67
01-Jun-93			-4.46	-0.19	19.5	-0.72	-0.37	0.92	0.30	35.1	-1.71	-0.63	0.72
01-Jun-93			-4.46	0.20	27.8	-0.95	-0.49	0.88	0.25	33.6	-1.40	-0.62	0.80
02-Jun-93			-4.46	0.58	36.9	-1.23	-0.61	0.84	0.44	39.2	-1.08	-0.66	0.89
02-Jun-93			-4.46	0.60	37.4	-1.33	-0.62	0.81	0.59	43.8	-0.92	-0.69	0.94
03-Jun-93			-4.46	0.58	36.9	-1.42	-0.61	0.79	0.62	44.8	-1.24	-0.70	0.86
03-Jun-93			-4.46	0.64	38.5	-1.55	-0.63	0.76	0.63	45.1	-1.21	-0.70	0.86
04-Jun-93			-4.46	0.50	34.9	-1.85	-0.59	0.67	0.60	44.1	-1.61	-0.69	0.76
04-Jun-93			-4.46	0.43	33.2	-1.83	-0.57	0.67	0.50	41.1	-1.55	-0.67	0.77
05-Jun-93			-4.46	0.37	31.8	-1.95	-0.55	0.64	0.40	38.0	-1.62	-0.65	0.75
05-Jun-93			-4.46	0.27	29.4	-1.75	-0.52	0.69	0.35	36.5	-1.72	-0.64	0.72
06-Jun-93			-4.46	0.09	25.4·	-1.67	-0.46	0.70	0.15	30.8	-1.65	-0.59	0.73
07-Jun-93			-4.46	-0.31	17.2	-1.53	-0.34	0.71	-0.05	25.3	-1.47	-0.55	0.76
07-Jun-93			-4.46	-0.49	13.9	-1.39	-0.28	0.74	-0.15	22.7	-1.58	-0.53	0.73
08-Jun-93			-4.46	-0.65	11.2	-1.37	-0.23	0.73	-0.33	18.2	-1.61	-0.49	0.72
09-Jun-93			-4.46	-0.92	7.1	-1.25	-0.15	0.74	-0.55	13.1	-1.45	-0.44	0.75
10-Jun-93			-4.46	-1.07	5.2	-1.27	-0.10	0.73	-0.70	10.0	-1.51	-0.40	0.73
11-Jun-93			-4.46	-1.18	3.9	-1.21	-0.07	0.74	-0.81	7.8	-1.37	-0.38	0.76
15-Jun-93			-4.46	-1.25	3.2	-1.01	-0.04	0.78	-0.85	7.1	-1.19	-0.37	0.80
23-Jun-93			-4.46	-1.43	1.6	-0.73	0.01	0.83	-1.15	2.3	-0.76	-0.30	0.89

Notes:		
	C_N	was computed using Equation 55.
	C_O	was computed using Equation 56 for station HR and 57 for station FR.
	f_O	is the fraction of old water estimated to contribute to total flow, computed using Equation 60.

Table 11.
SURFICIAL GROUNDWATER $\delta^{18}O$ AND ELEVATION DATA COLLECTED AT STATIONS HR AND FR DURING SPRING 1993 MONITORING.

DATE	HR0 Stage (ft)	HR0 O-18 (o/oo)	HR1 Stage (ft)	HR1 O-18 (o/oo)	HR2 Stage (ft)	HR2 O-18 (o/oo)	FR0 Stage (ft)	FR0 O-18 (o/oo)
n	19	17	16	9	20	16	21	17
mean	0.29	-3.01	1.77	-3.06	5.51	-3.12	0.70	-3.01
std. dev.	0.66	0.12	0.22	0.15	0.64	0.14	0.50	0.13
min	-1.10	-3.23	1.29	-3.35	3.75	-3.55	-0.25	-3.24
max	0.92	-2.73	2.01	-2.86	6.17	-2.95	1.54	-2.81
01-May-93								
02-May-93								
03-May-93								
04-May-93								
05-May-93				-3.05	5.65	-3.02		
06-May-93		-3.07						-2.89
07-May-93							-0.25	
08-May-93								
09-May-93								
10-May-93								
11-May-93		-2.99						-2.85
18-May-93								
26-May-93	-1.10	-3.08			4.33	-3.06	-0.25	-3.08
29-May-93	-1.04	-3.05			4.19	-3.15	-0.21	-3.01
29-May-93	-1.08	-3.07			3.75	-3.13	-0.23	-3.18
30-May-93		-2.97				-3.07	0.41	-2.96
31-May-93	0.43	-3.12	1.94	-2.91	6.17	-3.07	0.92	-2.81
31-May-93	0.27		1.78		6.07		1.54	
01-Jun-93	0.35	-2.88	1.79	-3.09	6.10	-3.01	0.91	-2.91
01-Jun-93	0.53		1.82		5.95		0.83	
02-Jun-93	0.84	-2.95	1.99	-2.86	5.97	-2.95	0.94	-2.85
02-Jun-93	0.88		1.93		5.85		0.95	
03-Jun-93	0.92	-2.98	2.00	-3.06	5.88	-3.20	1.03	-3.08
03-Jun-93	0.91		2.01		5.77		1.03	
04-Jun-93	0.87	-3.21	1.95	-3.27	5.80	-3.34	1.11	-3.22
04-Jun-93	0.73		1.82		5.67		1.02	
05-Jun-93	0.75	-3.23	1.75	-3.35	5.67	-3.55	1.02	-3.09
05-Jun-93	0.60		1.70		5.57		0.93	
06-Jun-93	0.47	-3.00	1.70	-2.98	5.58	-3.03	0.92	-2.93
07-Jun-93	0.20	-2.92	1.49	-3.01	5.46	-3.06	0.78	-2.99
07-Jun-93	0.03		1.29		5.36		0.65	
08-Jun-93	-0.07		1.29		5.37		0.64	
09-Jun-93		-2.73				-3.07		-2.94
10-Jun-93								
11-Jun-93		-3.05				-3.04		-3.07
15-Jun-93								
23-Jun-93		-2.89				-3.22		-3.24

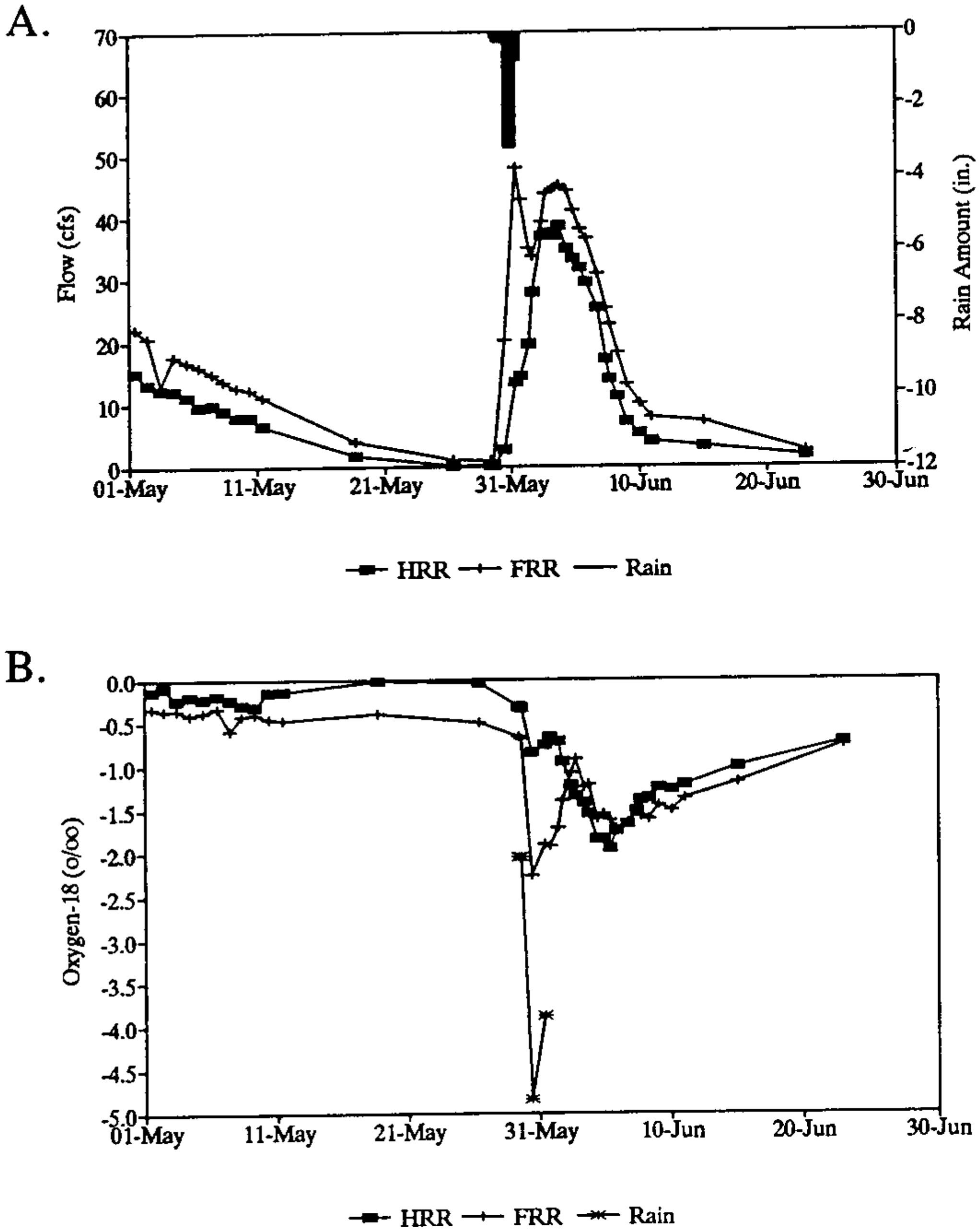

Figure 35. Flow and rainfall amount (a.) and river and rainfall $\delta^{18}O$ during Spring 1993 monitoring.

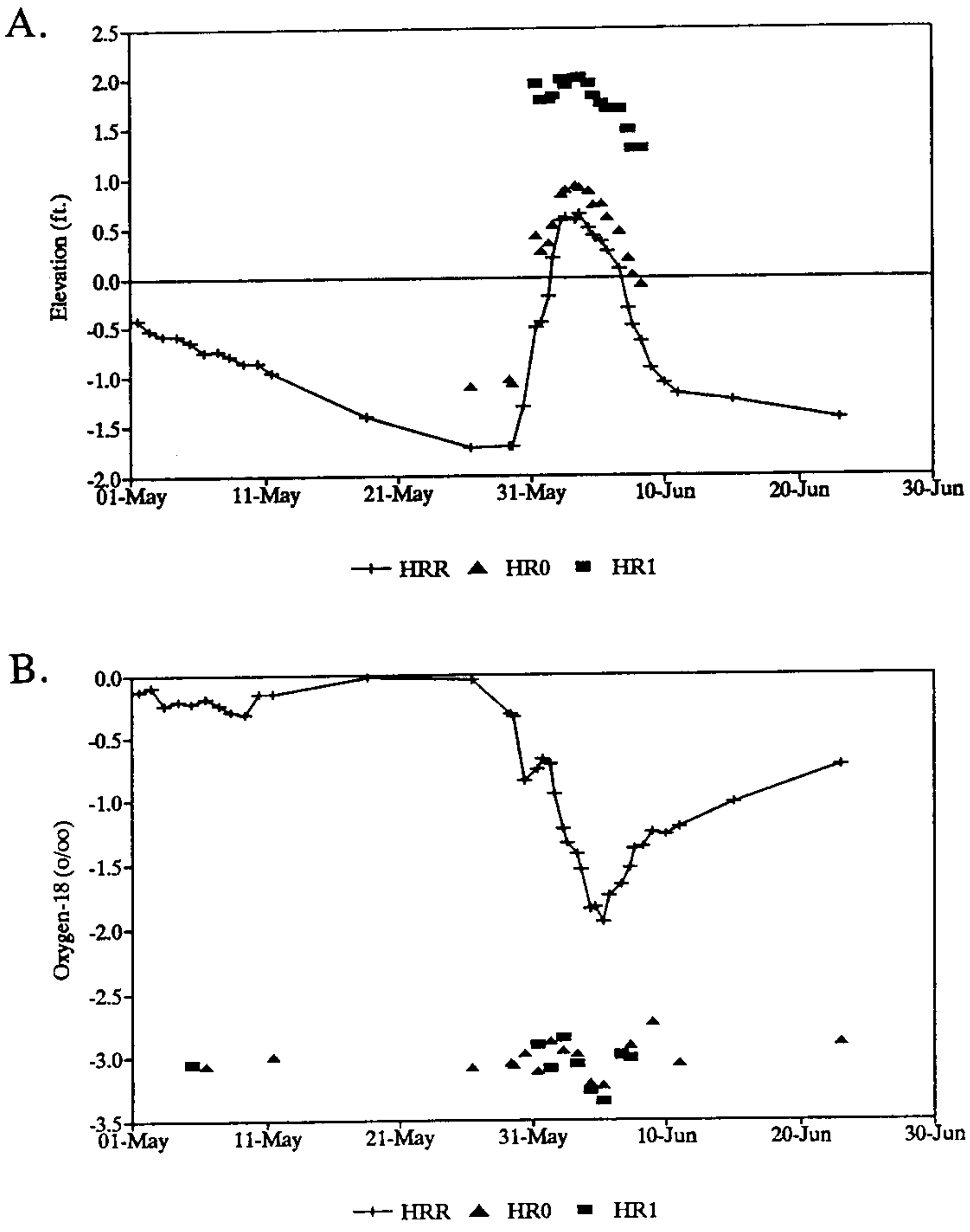

Figure 36. River (HRR) and monitoring well (HR0, HR1) elevations (a.) and $\delta^{18}O$ (b.) at station HR during Spring 1993 monitoring.

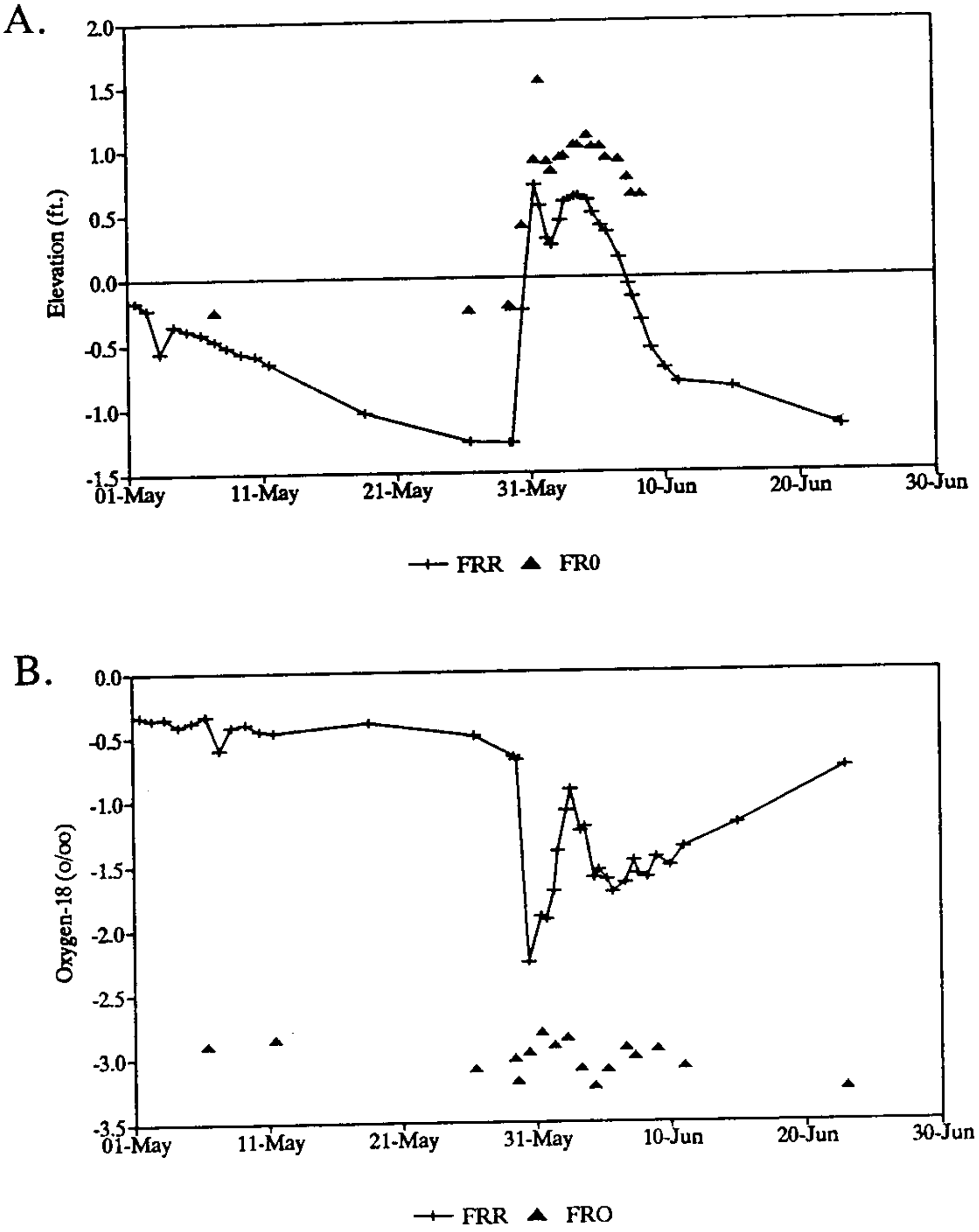

Figure 37. River (FRR) and monitoring well (HR0) elevations (a.) and $\delta^{18}O$ (b.) at station FR during Spring 1993 monitoring.

storm event placed approximately 4.3 in. of rainfall over the watershed with an amount-weighted $\delta^{18}O$ of -4.46 ‰ (Table 10). This event resulted in peak flows of 38.5 and 48.0 cfs at the HR and FR stations, respectively (Figure 35).

Groundwater elevation and $\delta^{18}O$ were monitored during the storm event. The piezometric surface of all monitoring wells remained higher than that of the river throughout the storm event (Figures 36a and 37a) indicating no loss from the river channel to increase bank storage (Meyboom 1961) in the surficial aquifer. Surficial aquifer $\delta^{18}O$ was spatially and temporally homogeneous throughout the Spring 1993 study period, with a mean $\delta^{18}O$ of -3.05 ± 0.14 ‰ (n=59). This was substantially more depleted than river $\delta^{18}O$ (Figures 2c and 3c), which averaged -0.96 ± 0.60 ‰ (n=74) and ranged from -2.26 to +0.02 ‰ during the Spring 1993 study period. The disparity between river and groundwater $\delta^{18}O$ was consistent with Autumn 1992 conditions in the Econlockhatchee River (Chapter 3).

Discussion

Three mass balance models were derived to examine the relative contribution of new water to a storm hydrograph in the Econlockhatchee River using hydrometric and oxygen isotope data. Catchment-scale steady- and unsteady-state models were applied at two sites and a steady-state model was applied for a discrete reach of the river. Estimating the old-water fraction was the primary objective of the modeling exercise, but an essential aspect of the study was to analyze the adequacy of the models in representing the hydrology of the system. Specific areas of concern were the reliability of control over end-members and the assumption of steady-state conditions.

Catchment Model

The differential equations for two-component hydrograph separation at the catchment scale are

$$\frac{dV}{dt} = Q_N + Q_G - Q_E - Q_R \tag{46}$$

$$\frac{dCV}{dt} = C_N Q_N + C_G Q_G - C_E Q_E - C_R Q_R \tag{47}$$

where
V = Channel volume [ft^3]
Q = Flow [$ft^3 sec^{-1}$]
C = Tracer concentration [‰ for $\delta^{18}O$]
N = New water
G = Groundwater
E = Evaporation
R = River water

Lumping groundwater and evaporative terms with an empirical function represented by the subscript *O*, to indicate *old* water and solving for a discrete time interval Δt [sec]

$$V_2 - V_1 = V_N + V_O - V_R \tag{48}$$

$$C_2 V_2 - C_1 V_1 = C_N V_N + C_O V_O - C_R V_R \tag{49}$$

where the subscript 2 indicates values at time t and the subscript 1 indicates values at time t-Δt. V_1 and V_2 are channel volumes and C_1 and C_2 are the tracer concentrations in the channel, assuming completely-mixed conditions. Assuming all values except V_O and V_N can be measured or estimated, Equations 48 and 49 can be reduced to

$$V_O = \frac{V_2(C_N - C_2) - V_1(C_N - C_1) + V_R(C_N - C_O)}{(C_N - C_O)} \tag{50}$$

$$V_N = V_2 + V_R - V_1 - V_O \tag{51}$$

Under steady state conditions

$$\frac{dV}{dt} = \frac{dCV}{dt} = 0 \tag{52}$$

and Equations 50 and 51 reduce to the familiar two-component hydrograph-separation model

$$V_O = V_R \frac{(C_N - C_R)}{(C_N - C_O)} \tag{53}$$

$$V_N = V_R - V_O \tag{54}$$

New Water. The isotopic composition of precipitation C_P was taken to be C_N. This is the common assumption and neglects possible evaporative effects during surface runoff or in translation through tree canopies (throughfall effects, *e.g.*, DeWalle and Swistock, 1994 and Pearce, *et al.*, 1986). Thus new water was assumed to be isotopically identical to precipitation ($C_N = C_{PPT}$). The value C_N at any time t was taken to be the amount-weighted average of all precipitation applied over the catchment up to time t (McDonnell, *et al.*, 1990):

$$C_N = \frac{\Sigma(P\ C_{PPT})}{\Sigma P} \tag{55}$$

where P is rainfall amount. As a result, C_N was updated after every timestep during which rain was recorded, otherwise remained constant. As an example, Figure 38 shows P, C_{PPT}, and C_N computed for a series of precipitation events recorded in the Autumn of 1992 in the Econlockhatchee basin. This method of solving the two-component hydrograph separation model equation appears to be the common convention in the literature of isotope hydrology, although problem-solving mechanics are seldom explained.

Reapplication of C_N over timesteps subsequent to the end of a rainfall event leads to the interesting question of how long *new* water remains new. Alternative approaches in hydrograph separation using time-series analysis and convolution integrals (Stewart and McDonnell 1991, Turner and Macpherson 1990, Pearce, *et al.*, 1986) have applied, in effect, a decay function to diminish the weight of a precipitation event over time. C_N was assumed here to be constant over time following the end of the event because the event was isolated and the resulting hydrograph occurred over a short duration. Analysis of an extended period of record with numerous events, such as presented in Chapter 3, may require a time-variable function for C_N.

Old Water. The isotopic character of old water received significant attention in Chapter 3. Based on the isotopic behavior of the river during recession, it was concluded in Chapter 3 that $\delta^{18}O$ measurements of near-stream groundwater or pre-storm river water were inadequate to describe C_O during a storm hydrograph. Hooper and Shoemaker

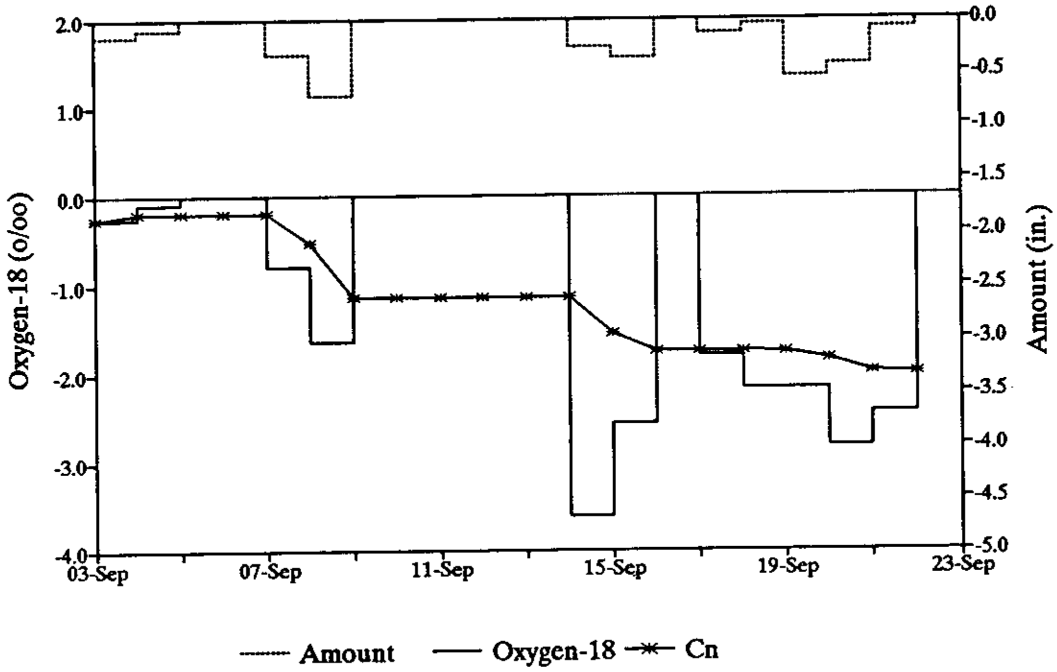

Figure 38. Computation of C_N using Equation 55. Rainfall amount (a.) and $\delta^{18}O$ (b.) were collected in the Fall of 1992.

(1986) observed that C_O appeared to vary over time in the Hubbard Brook Experimental Forest, New Hampshire and attributed a systematic depletion in river isotopic content (δD) to seasonal trends. They accounted for the change by linear interpolation of baseflow river δD before and after storm events.

In the Econlockhatchee basin, however, isotopic enrichment of river water over time appeared to be driven by evaporation and functionally related to flow in the river. This phenomenon was corroborated in river data collected prior to and following the May 1993 storm event. Plots of $\delta^{18}O$ versus stage at the HR and FR stations (Figure 39) indicate that $\delta^{18}O$ can be expressed as a linear function of river elevation during periods of recession for both stations using the regression equations

$$\begin{aligned} C_{O(HR)} &= -0.432 - 0.311z \\ n &= 25 \\ R^2 &= 0.988 \end{aligned} \qquad (56)$$

$$\begin{aligned} C_{O(FR)} &= -0.561 - 0.223z \\ n &= 25 \\ R^2 &= 0.982 \end{aligned} \qquad (57)$$

for the HR (Equation 56) and FR (Equation 57) stations. It was assumed that this linear function accurately represented C_O during the May storm event. River $\delta^{18}O$ during the event hydrograph plotted significantly below the regression line, presumably indicating mixing with the more depleted C_N water mass ($\delta^{18}O$=-4.46‰).

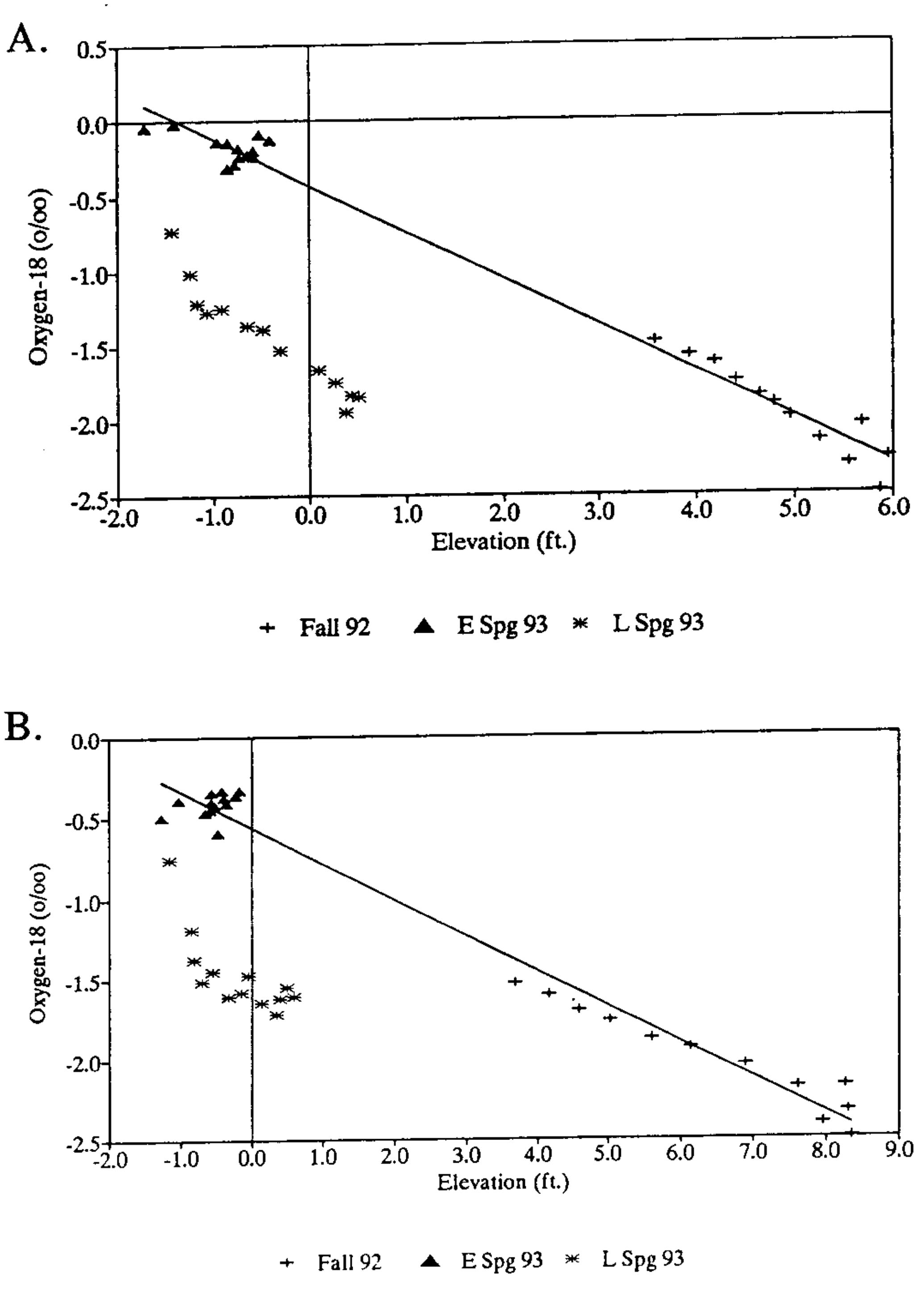

Figure 39. Regression models for C_O at station HR (a.) and FR (b.) using recession data collected in Fall 1992 and Spring 1993.

Hydrograph Separations. Equations 50 and 51 were solved to estimate old water contribution to flow at Stations HR and FR during the May 1993 storm event assuming steady- and unsteady-state conditions.

Steady-State Model. Equations 53 and 54 were solved for each sampling observation after the start of the storm event on May 29, 1993 (Table 10). Timestep duration varied depending on sampling times, but was approximately 12 hours during the storm event and 24 hours otherwise. Appendix D lists all input and output data and provides sample calculations for all steps in the modeling process. Figures 40 and 41 present the steady-state modeling results for Stations HR and FR, respectively. Data are summarized in Table 10 and computations are explained in Appendix D.

Oxygen isotope data indicated that end members were significantly different throughout the storm event at HR and FR. C_O averaged -0.27 ‰ at station HR and -0.51 ‰ at station FR and C_N averaged -4.46 ‰. The 2σ analytical precision for $\delta^{18}O$ was approximately 0.2 ‰, so a significant isotopic signal was evident between the end members. Old water contribution during the storm event was estimated to be 76 and 77 percent of total flow at HR and FR, respectively (Table 10).

The linear regression models for C_O, derived separately for HR and FR (Equations 56 and 57, respectively), indicated that old water became depleted during the storm hydrograph in response to higher flow. At peak flow C_O was 0.73 ‰ more depleted than baseflow C_O at HR and 1.0 ‰ more depleted at FR. The use of a linear function for C_O, rather than a constant baseflow value, reduced the signal strength of the separation (C_N-C_O was a smaller absolute value), but increased the estimate of old water

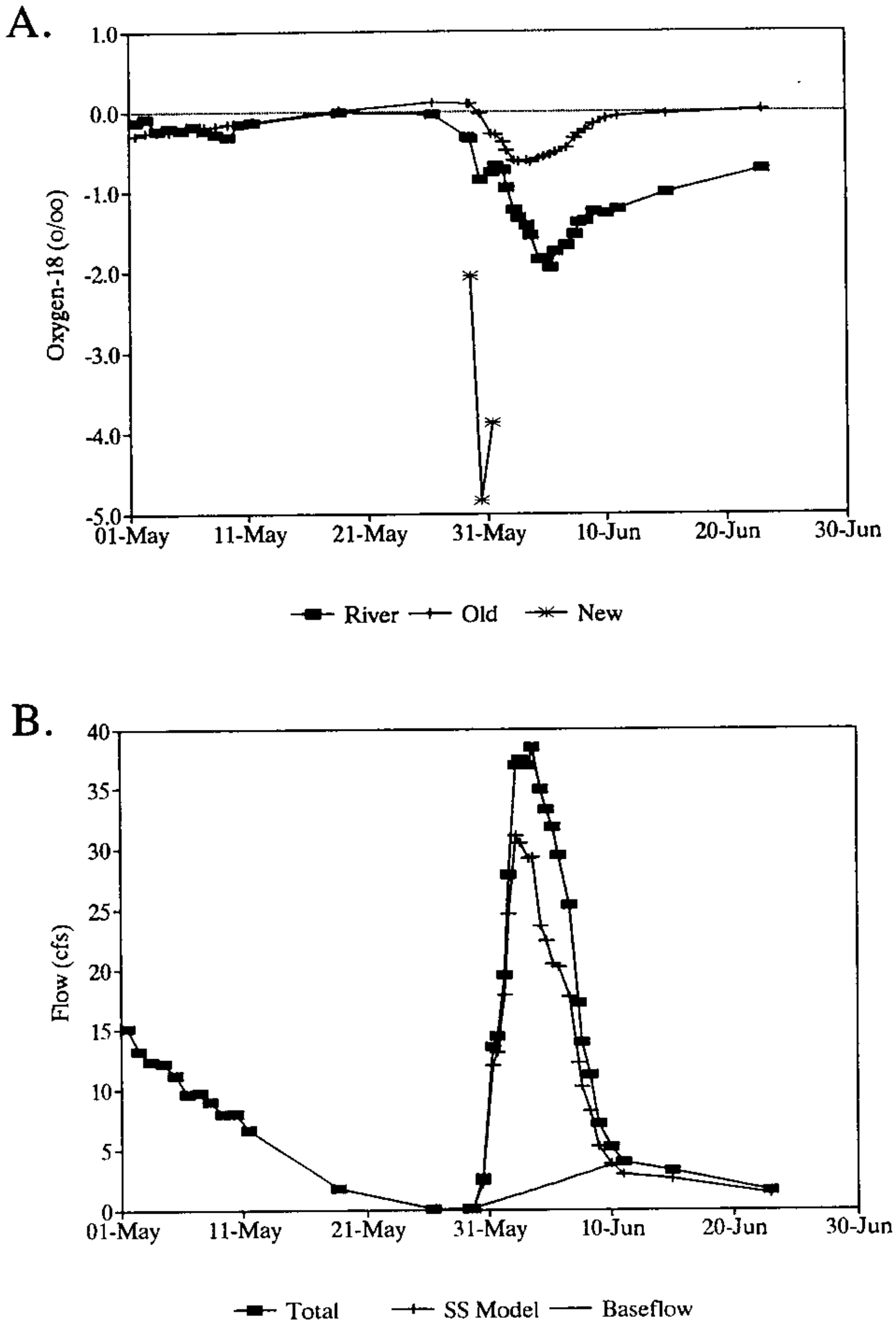

Figure 40. Steady-state two-component hydrograph separation for station HR showing river and end-member $\delta^{18}O$ (a.) and total and old-water river flows (b.).

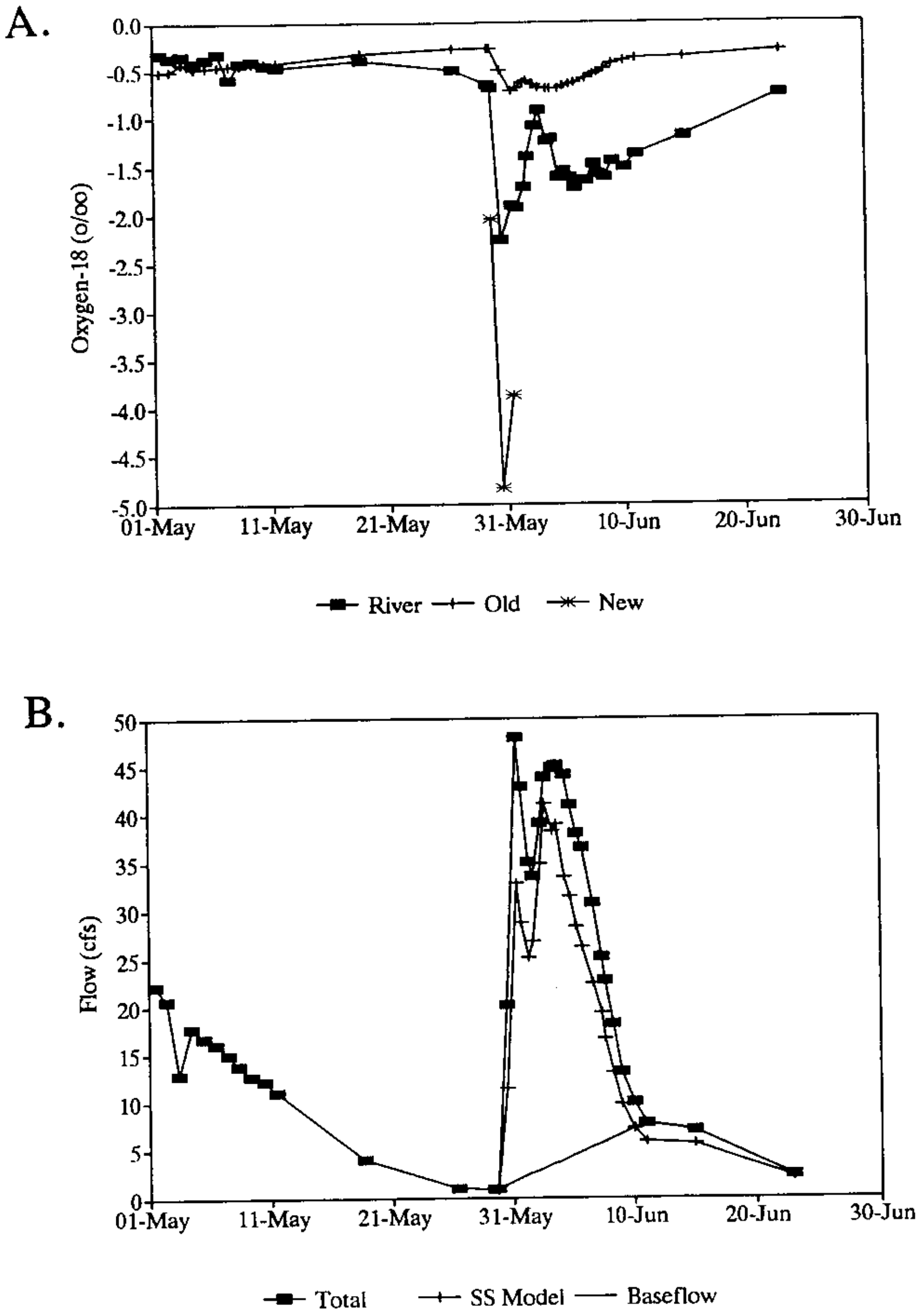

Figure 41. Steady-state two-component hydrograph separation for station FR showing river and end-member $\delta^{18}O$ (a.) and total and old-water river flows (b.).

contribution, since the signal-strength term (C_N-C_O) appeared in the denominator of the hydrograph separation equation (Equation 43 or 54).

Unsteady-State Model. The steady-state model is essentially a linear interpolation between two $\delta^{18}O$ end-members. When the model is derived for unsteady-state conditions (Equations 50 and 51), temporal changes in the quantity and $\delta^{18}O$ of channel storage must be estimated and the model becomes more sensitized to measurement errors. The unsteady-state model was solved for a range of channel volumes, bracketing initial estimates of channel volume by factors of 0.9, 1.0, 1.1, and 1.2.

Flow was contained in the incised channel of the river throughout the storm hydrograph, so morphometric data pertained to the channel rather than the floodplain. Channel dimensions and lengths were derived from site surveys, USGS topographic sheets, and published data (Miller & Miller 1984). These data were used to develop equations for channel volume as a function of river elevation. V_O [ft.^{3}] was computed for each timestep using Equation 50, then converted to Q_O by dividing by the timestep in seconds.

To compare the results of the steady- and unsteady-state models, the old water fraction, or ratio of old water to total volume, was computed for each timestep. In the steady-state model, the fraction of old water may be computed as the quantity of old water divided by river discharge from a control section:

$$f_{O(SS)} = \frac{V_O}{V_R} \tag{58}$$

For the unsteady-state model the fraction of old water at a given timestep is the volume of old water divided by the net flow out of the control section, which consisted of channel discharge out of the control section (V_R) plus the net change in channel storage:

$$f_{O(USS)} = \frac{V_O}{V_2 + V_R - V_1} \tag{59}$$

Figure 42a plots the old water fraction for the steady- and the unsteady-state models at Station HR. Figure 42b plots river channel discharge (V_R), change in storage ($dV=V_2-V_1$), net channel loss (V_R+dV), and old water (V_O). All quantities were expressed as flows (V/dt), since sampling intervals were not uniform. Although the event-mean fraction of old water estimated by the unsteady-state model was approximately equivalent to that estimated by the steady-state model, point estimates of f_O were observed to vary widely (Figure 42a).

Each of the lines in Figure 42a represents modeling conditions that differ only by the estimate of channel volume, to assess the sensitivity of the unsteady-state model to uncertainty in estimates of channel volume. Modeling results indicate that during recession, certain combinations of loss in channel storage and decrease in channel outflow can sensitize the model to the channel volume term. For example, on June 4, 6, and 7, decreases in channel storage resulted in departures from the steady-state assumption that increased with increasing channel volume. The estimate of old water contribution (f_O) averaged over the storm hydrograph was 0.77 for all modeling assumptions (Table 12), suggesting that averaging effects tended to equalize the erratic

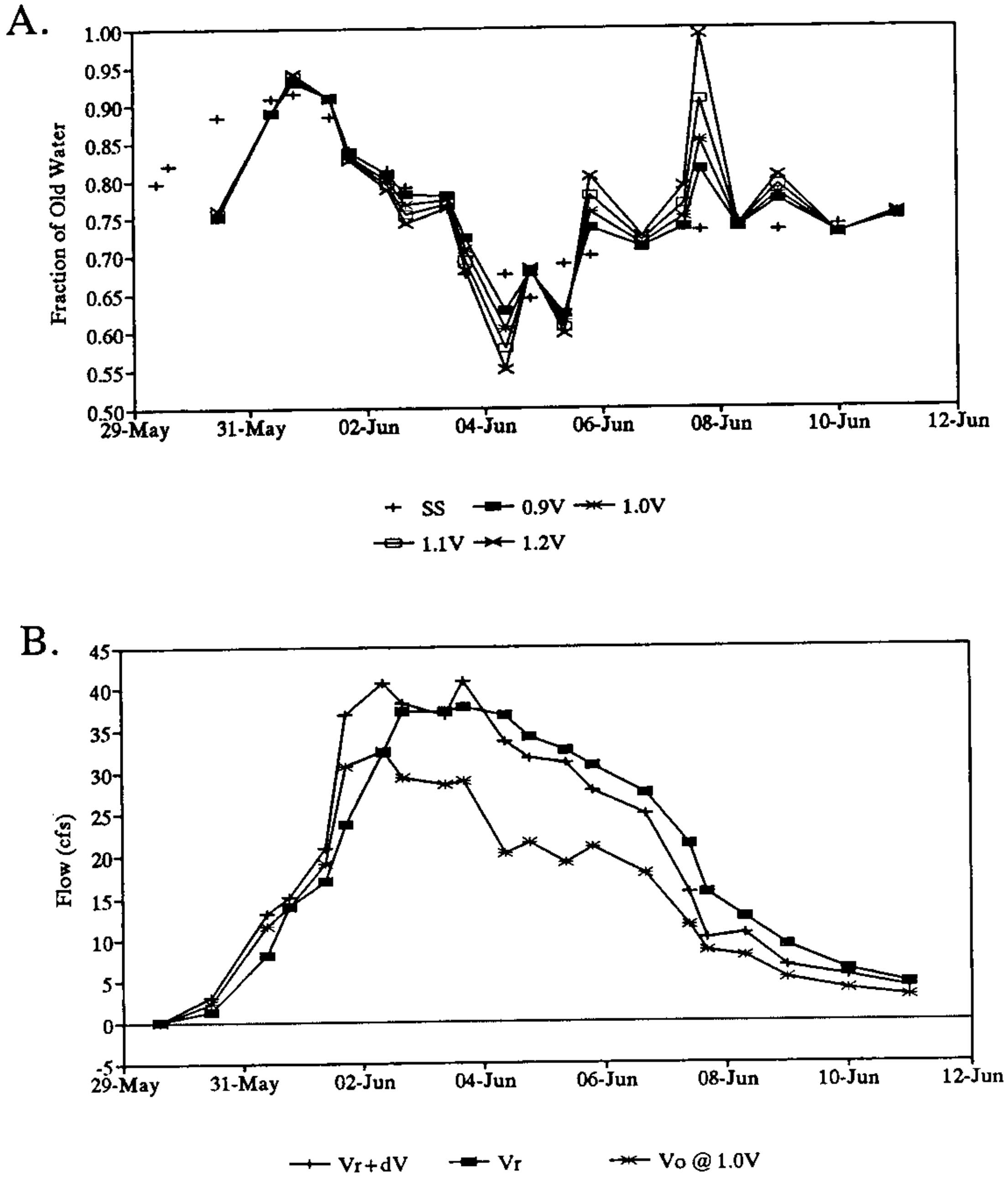

Figure 42. Sensitivity analysis of unsteady-state hydrograph separation.

Table 12.
UNSTEADY-STATE MODELING RESULTS FOR STATION HR.

Channel Properties
L = 50000
D = 2.22 + Stage
W = 0.20 x Q + 5

DATE (1)	dt (sec) (2)	Stage (ft) (3)	Flow (cfs) (4)	Cr (o/oo) (5)	Co (o/oo) (6)	Cn (o/oo) (7)	Depth (ft) (8)	Width (ft) (9)	Volume (ft^3) (10)	SS fo (18)	USS fo (19)	0.9V fo (20)	1.0V fo (21)	1.1V fo (22)	1.2V fo (23)
29-May-93		-1.71	0.1	-0.32	0.10		0.5	5.0	1.28E+05						
29-May-93	1.80E+04	-1.71	0.1	-0.34	0.10	-2.05	0.5	5.0	1.28E+05	0.80					
30-May-93	7.20E+04	-1.31	2.6	-0.85	-0.03	-4.60	0.9	5.5	2.51E+05	0.82	0.75	0.75	0.75	0.76	0.76
31-May-93	8.03E+04	-0.51	13.5	-0.76	-0.27	-4.46	1.7	7.7	6.59E+05	0.88	0.89	0.89	0.89	0.89	0.89
31-May-93	3.24E+04	-0.46	14.4	-0.68	-0.29	-4.46	1.8	7.9	6.94E+05	0.91	0.93	0.93	0.93	0.94	0.94
01-Jun-93	5.33E+04	-0.19	19.5	-0.72	-0.37	-4.46	2.0	8.9	9.03E+05	0.92	0.91	0.91	0.91	0.91	0.91
01-Jun-93	2.84E+04	0.20	27.8	-0.95	-0.49	-4.46	2.4	10.6	1.28E+06	0.88	0.83	0.84	0.83	0.83	0.83
02-Jun-93	5.53E+04	0.58	36.9	-1.23	-0.61	-4.46	2.8	12.4	1.73E+06	0.84	0.80	0.81	0.80	0.79	0.79
02-Jun-93	2.75E+04	0.60	37.4	-1.33	-0.62	-4.46	2.8	12.5	1.76E+06	0.81	0.77	0.78	0.77	0.75	0.74
03-Jun-93	6.12E+04	0.58	36.9	-1.42	-0.61	-4.46	2.8	12.4	1.73E+06	0.79	0.77	0.78	0.77	0.77	0.76
03-Jun-93	2.64E+04	0.64	38.5	-1.55	-0.63	-4.46	2.9	12.7	1.81E+06	0.76	0.71	0.72	0.71	0.69	0.68
04-Jun-93	5.82E+04	0.50	34.9	-1.85	-0.59	-4.46	2.7	12.0	1.63E+06	0.68	0.60	0.63	0.60	0.58	0.55
04-Jun-93	3.60E+04	0.43	33.2	-1.83	-0.57	-4.46	2.7	11.6	1.54E+06	0.67	0.68	0.68	0.68	0.68	0.68
05-Jun-93	5.00E+04	0.37	31.8	-1.95	-0.55	-4.46	2.6	11.4	1.47E+06	0.64	0.61	0.62	0.61	0.61	0.60
05-Jun-93	3.86E+04	0.27	29.4	-1.75	-0.52	-4.46	2.5	10.9	1.36E+06	0.69	0.76	0.73	0.76	0.78	0.80
06-Jun-93	7.52E+04	0.09	25.4	-1.67	-0.46	-4.46	2.3	10.1	1.16E+06	0.70	0.71	0.71	0.71	0.72	0.72
07-Jun-93	6.23E+04	-0.31	17.2	-1.53	-0.34	-4.46	1.9	8.4	8.05E+05	0.71	0.75	0.74	0.75	0.77	0.79
07-Jun-93	2.41E+04	-0.49	13.9	-1.39	-0.28	-4.46	1.7	7.8	6.73E+05	0.74	0.85	0.81	0.85	0.91	0.99
08-Jun-93	5.51E+04	-0.65	11.2	-1.37	-0.23	-4.46	1.6	7.2	5.68E+05	0.73	0.74	0.74	0.74	0.74	0.74
09-Jun-93	6.01E+04	-0.92	7.1	-1.25	-0.15	-4.46	1.3	6.4	4.18E+05	0.74	0.78	0.77	0.78	0.79	0.81
10-Jun-93	8.64E+04	-1.07	5.2	-1.27	-0.10	-4.46	1.2	6.0	3.47E+05	0.73	0.73	0.73	0.73	0.73	0.73
11-Jun-93	8.64E+04	-1.18	3.9	-1.21	-0.07	-4.46	1.0	5.8	3.01E+05	0.74	0.75	0.75	0.75	0.75	0.75
									Mean:	0.77	0.77	0.77	0.77	0.77	0.77

peaks produced by the unsteady-state model.

Analysis of End-Member Assumptions. Water masses directly measured for $\delta^{18}O$ were groundwater, surface water, and precipitation. From these data estimates of C_N and C_O, the old and new $\delta^{18}O$ end-member concentrations, were derived. C_N was assumed to be the $\delta^{18}O$ of precipitation collected within the watershed. No corrections were made in the isotopic data to account for evaporative enrichment of new water as it moved through the hydrologic cycle. Throughfall, the temporary sequestering of water in tree canopies, has been identified as a source of evaporative enrichment in new water. DeWalle and Swistock (1994) observed enrichment averaging 0.17 and 0.32 ‰ for deciduous and pine forests, respectively. The degree of enrichment appeared to vary based on storm intensity, among other factors, but did not appear to exceed approximately 0.5 ‰ (DeWalle and Swistock 1994, Pearce, *et al.*, 1986, Saxena 1986, Gat and Tzur 1967).

Attempts to account for throughfall effects would greatly complicate the task of estimating C_N for waters reaching the river channel for several reasons. The Econlockhatchee watershed had a diversity of vegetative coverage, including range, pine forests, citrus groves, and forested wetlands. Even if throughfall effects specific to vegetative types were established, the relative contribution of new water would vary with the distance to the river channel and other recharge-related characteristics. The potential for error resulting from exclusion of throughfall effects, would be to overestimate the isotopic signal of (C_N-C_O) by approximately 0.5 ‰, since precipitation was more depleted than old water in this study, and result in a lower percentage of old water, since the term (C_N-C_R) would be smaller. Applied to the steady-state hydrograph separation model for station HR (Equations 56 and 57), this level of enrichment in precipitation would reduce the event-average contribution of old water (f_O) from the initial estimate of 0.77 to 0.73. Calculations are shown in Appendix D for the entire event. For a single timestep, the calculation may be demonstrated first by assuming no throughfall enrichment

$$f_O = \frac{(C_N - C_R)}{(C_N - C_O)} = \frac{(-2.05 - -0.34)}{(-2.05 - +0.10)} = 0.80 \tag{60}$$

(Equation 60), then by increasing C_N by 0.5 ‰ (Equation 61)

$$f_O = \frac{(-1.55 - -0.34)}{(-1.55 - +0.10)} = 0.74 \tag{61}$$

Thus, with the isotopic signal present in the May 1993 storm event, throughfall effects within the magnitude reported in the literature would affect the old-water estimate, but would only reduce f_O by approximately 5 percent.

Old water was represented as a flow-dependent linear function of river elevation during recession. Modeling exercises presented in Chapter 3 indicated that evaporation of river water exerted a variable influence toward isotopic enrichment that was predictably stronger at lower flows. This approach relied on the assumption that river $\delta^{18}O$ at a given flow during recession represented C_O throughout a storm hydrograph. This is an important assumption considering the isotopic conditions in the watershed during the Spring of 1993. C_O was consistently more enriched than river water (C_R), which was consistently more enriched than surficial groundwater (C_{GW}) or new water (C_N). As an example, on June 3, during the storm hydrograph:

$$\begin{gathered} C_O > C_R > C_{GW} > C_N \\ -0.6 > -1.3 > -3.0 > -4.5 \end{gathered} \tag{62}$$

A remarkable observation of this series of values is that the isotopic content of the two water masses assumed to contribute to flow in the river, C_{GW} and C_N, were both more depleted than river water (C_R). The empirical functions of Equations 56 and 57 were assumed to represent the interplay between isotopic effects of evaporation (C_E) and surficial groundwater (C_{GW}) (Equations 46 and 47). By estimating C_O using the linear functions of Equations 56 and 57, the contribution of C_{GW} was indirectly fixed for any given river flow. Although this relationship was determined using data on the descending limb of the hydrograph, it was assumed also to be valid for the ascending limb. Considering the monitoring data, this appears to be reasonable. Both the isotopic content (Figures 36b and 37b) and hydraulic gradients (Figures 36a and 37a) in near-stream monitoring wells made no abrupt changes on the ascending limb of the hydrograph. If C_{GW} contributed proportionally more flow than the models predicted, which may not have been evident in the monitoring data, since both C_{GW} and C_N were more depleted than C_R or C_O, there existed the risk that the hydrograph separation model would overestimate the contribution of C_N.

The relationships among C_N, C_O, and C_{GW} and the role of evaporative enrichment may be clarified by sampling storm events for which the isotopic composition of these water masses is distinctly different than the May event. A highly enriched storm, for example, may produce a C_N with a significantly greater value than either C_O or C_{GW}, thus eliminating the ambiguity associated with similar C_{GW} and C_N values.

Comparison With Simple Baseflow Model. A common approach in engineering studies to estimate the old-water hydrograph during a storm event is to interpolate between pre-storm and post-storm flows (Wanielista, 1990, p. 173). This analysis is plotted in Figures 40b and 41b as *Baseflow*. The event-mean fraction of old water using this method was estimated to be 0.11 and 0.15 for stations HR and FR, respectively. The old water hydrographs labeled *SS Model* were developed using the steady-state mixing model and isotopic data, as previously discussed. The steady-state model estimated an event-mean old-water fraction of approximately 0.76 for both HR and FR stations. Thus, assuming the steady-state mixing model accurately represented site conditions, the simple interpolation model underestimated old water contribution by 65 and 61 percent for stations HR and FR respectively.

Discrete Reach Model

The twin peaks of the storm hydrograph at Station FR, superimposed over the single-peak hydrograph of Station HR (Figure 35a) indicate that a component of rapid runoff entered the river between HR and FR. The isotopic response at FR (Figure 35b) suggests that this quickly-translated component was isotopically depleted. To estimate the $\delta^{18}O$ of water entering the river between Stations HR and FR, mass-balance models were derived for a discrete river reach.

$$\frac{dV}{dt} = Q_{HR}+Q_G - Q_{FR} \tag{63}$$

$$\frac{dCV}{dt} = C_{HR}Q_{HR} + C_G Q_G - C_{FR}Q_{FR} \tag{64}$$

which reduces algebraically to

$$C_G = \frac{C_2V_2 + C_{FR}V_{FR} - C_1V_1 - C_{HR}V_{HR}}{V_2 + V_{FR} - V_1 - V_{HR}} \tag{65}$$

Where inflow and outflow subscripts reflect station names: HR for channel inflow and FR for station outflow. Equation 65 reduces to the steady-state form of:

$$C_G = \frac{C_{FR}V_{FR} - C_{HR}V_{HR}}{V_{FR} - V_{HR}} \tag{66}$$

Equation 65 and 66 estimate the concentration of the *gaining* tracer; that which entered the reach by means other than channel inflow. McKenna, *et al.* (1992) examined the release of bank storage in the Truckee River, Nevada using a form of Equation 18 to separate bank storage (old water) and snowmelt (new water) sources.

Figure 43 summarizes the results of steady-state modeling of gain the river between HR and FR. The storm hydrographs (Figure 35a) demonstrate that the twin peaks observed at FR decomposed into two distinct hydrographs. The first hydrograph peaked on May 31 at 48 cfs and was composed of water entering the reach between HR and FR. The second hydrograph peaked on June 1 at 35 cfs and was composed of water entering the reach at HR.

The isotopic mass balance of the reach indicated that the gaining tracer attained a minimum δ^{18}O of -3.52 ‰ on the descending limb of the reach hydrograph, then quickly increased to +1.49 ‰ during the ascending limb of the HR hydrograph before decreasing in a sawtooth pattern on the descending limb of the HR hydrograph. The

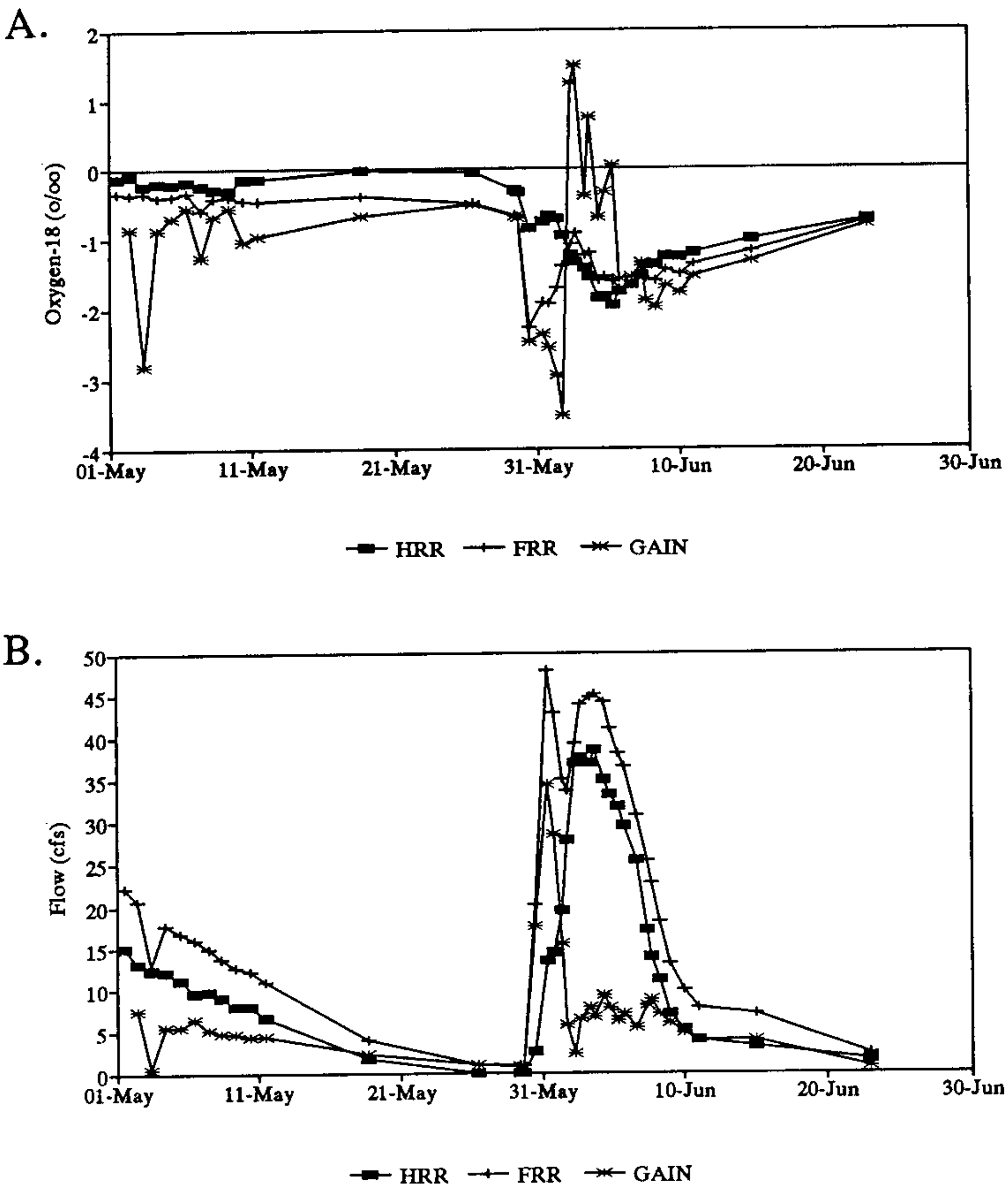

Figure 43. Estimation of the $\delta^{18}O$ (a.) and quantity (b.) of water entering the reach between stations HR and FR (a.).

reach model (Equation 66) produced reasonable estimates of $\delta^{18}O$ of the gaining tracer (C_G) to the point at which C_G minimized at -3.52 ‰. Applying the steady-state hydrograph-separation model (Equation 53), the fraction of old water at the time of minimum C_G was estimated to be:

$$f_{O(SS)} = \frac{V_O}{V_R} = \frac{(C_N - C_R)}{(C_N - C_O)} = \frac{(-4.46 - -3.52)}{(-4.46 - -0.62)} = 0.24 \qquad (67)$$

or by Equation 67, 24 percent of total gain in the reach (V_G) was contributed by old water.

The next 7 estimates of C_G following the C_G minimum were unreasonably enriched in $\delta^{18}O$ and revealed a significant weakness in the reach model. Equations 63 through 66 derive a mixing model in which two inputs, channel inflow (V_{HR}) and gain (V_G), mix to form the outflow (V_{FR}). The two end members, then, are V_{HR} and V_G. V_{FR} is the weighted average of the two end members. Equation 66, in effect, back-calculates C_G, one of the end members. End-member mixing models, such as the simple two-component model (Equation 43 or 53) interpolate between end members, so the result is necessarily bounded by either end member. But when one of the end-members is back-calculated, as in Equation 66, the result could range to infinity.

If all terms in Equation 66 were measured with sufficient accuracy, back-calculation of end members should have produced reasonable results. The sensitivity of Equation 66 to changes in V_{HR} (Figure 44) and V_{FR} was examined using storm hydrograph data. This analysis indicates that small changes in flow measurements into and out of the reach produce dramatic changes in the estimate of C_G. As with the unsteady-state hydrograph-separation model, increased complexity of model structure

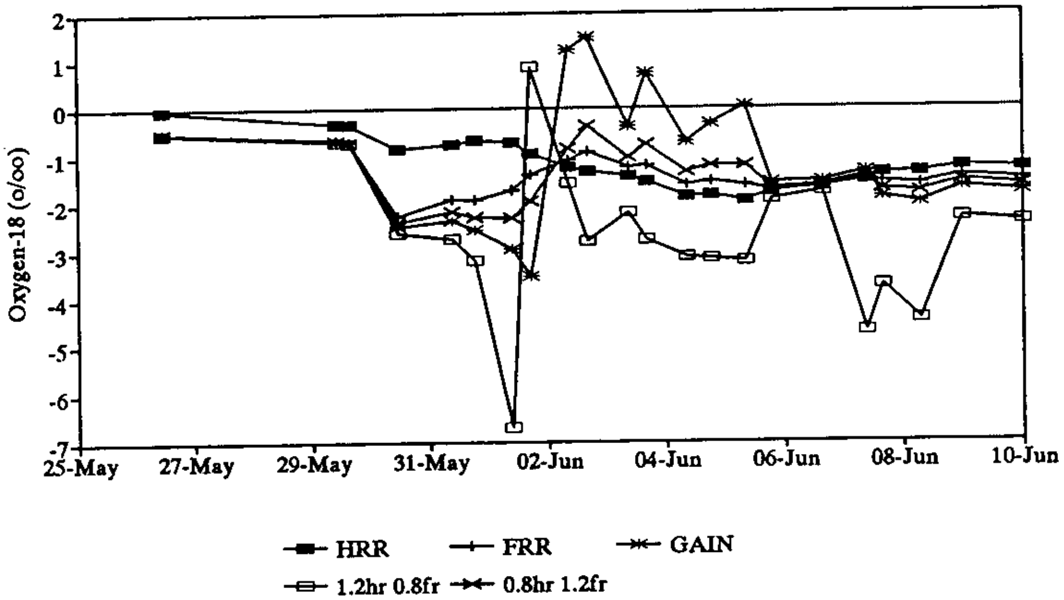

Figure 44. Sensitivity analysis of reach-based model (Equation 26) varying flow into and out of the reach by 20 percent.

appears to demand higher resolution and accuracy in input data.

Conclusions and Recommendations

A study was conducted on the Econlockhatchee River in east central Florida to estimate the contribution of *new* storm-event water relative to total flow during a storm hydrograph. Environmental oxygen-18 was used as a conservative tracer in a series of mass-balance models. Steady- and unsteady-state models were derived at the catchment scale and applied at two sites on the Big Econlockhatchee River. Results of steady-state analyses indicated that approximately 76 percent of the total storm hydrograph was composed of *old*, or prestorm, water. A simple interpolation model for baseflow indicated that linear interpolation between pre-storm and post-storm river flow resulted in an estimate of old water contribution during the event of 11 to 15 percent.

Previous studies have widely applied the two-component hydrograph-separation model, although the assumption of steady-state conditions has not been addressed in the archival literature. Comparison indicates no substantial difference between steady- and unsteady-state modeling results under most conditions, including abrupt increases in flow associated with the rising limb of the hydrograph. Difference between the models did become evident in transient episodes on the descending limb of the hydrograph, presumably associated with loss in channel storage. Both models estimated approximately equal contribution of old water to the total storm hydrograph, indicating that the assumption of steady-state conditions was reasonable given the site modeling parameters employed in this study.

A separate model was derived to estimate indirectly the $\delta^{18}O$ of water entering a discrete river reach (C_G) using a mass-balance on $\delta^{18}O$ entering and leaving the reach. The model produced erratic and unreasonable estimates for C_G. Analysis indicated that C_G estimates were highly sensitive to flow measurements at reach boundaries and small variation in flow measurement resulted in a large range in C_G estimates.

The storm event analyzed in this chapter occurred after a protracted period of recession in the river. Thus antecedent conditions in the watershed may have reflected low storage in the surficial aquifer and river system, and high potential for initial abstraction. To develop estimates of long-term, or annualized, contribution of old water to the river system it is recommended that additional storms be monitored for environmental isotope hydrograph separation.

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CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

This dissertation addresses three aspects of stable isotope applications in environmental engineering. The first, discussed in Chapter 2, is a novel procedure to analyze $\delta^{13}C$ of dissolved inorganic carbon in water. The second, discussed in Chapter 3, is an analysis of the isotope hydrology of the Econlockhatchee River basin in east-central Florida. The third, discussed in Chapter 4, applies the findings of Chapter 3 and presents additional data to perform hydrograph separations on a storm event using environmental oxygen isotopes. This chapter summarizes these findings and presents recommendations for further research.

Carbon-13 Analysis

A method was developed to prepare natural water samples for $\delta^{13}C$ analysis using commercially-available serum vials as reaction vessels. Approximately 5 mL of sample was injected into an evacuated vial with 0.1 mL of anhydrous phosphoric acid (H_3PO_4). Dissolved inorganic carbon in the water was quantitatively converted to carbon dioxide gas. The gas was recovered from the vial and analyzed for $\delta^{13}C$ on an isotope-ratio mass spectrometer. For water samples with total dissolved inorganic carbon (DIC) greater than approximately 10 mg C/L, a replicate precision was attained better than $1\sigma=0.1‰$ (n=22). Total DIC can be measured simultaneously using the intensity of the major ion beam of the mass spectrometer at a replicate precision better than $1\sigma=1.43$ mg C/L.

It is recommended that further research include quantitative measurement of CO_2 recovery from the sample vial. Total yield of CO_2 gas recovered from the sample vial can be measured quantitatively during extraction using a calibrated pressure transducer. This approach would verify that near complete recovery of evolved gas was attained. Incomplete yield would affect estimates of total DIC and may result in isotopic fractionation.

Isotope Hydrology

A monitoring program was established in the Autumn of 1992 within the Econlockhatchee River watershed to evaluate the $\delta^{18}O$ of water masses in the hydrologic cycle. The principal objective was to determine the suitability of environmental (naturally occurring) $\delta^{18}O$ as a tracer for hydrograph-separation studies in the basin. Precipitation, surface water, and groundwater were sampled intensively to asses spatial and temporal $\delta^{18}O$ variability. Results revealed a range in precipitation $\delta^{18}O$ of -6.5 to 0.0 ‰, in groundwater from -3.5 to -2.5 ‰, and in surface water from -2.5 to -1.5 ‰. Spatial variability in precipitation varied with storm type. Summer convective storms were associated with the highest spatial variability, while frontal and tropical storms displayed low spatial variability. Based on the temporal variability of precipitation relative to surface water and groundwater it was concluded that an adequate isotopic signal existed in the watershed to permit hydrograph separation using environmental $\delta^{18}O$.

Mass-balance modeling revealed that evaporation was an important process in the isotope hydrology of the Econlockhatchee River. During recession, channel flow in the river was expected to be composed of water draining from the surficial aquifer.

Groundwater $\delta^{18}O$ was temporally and spatially constant at -2.88 ± 0.46 ‰. Yet river $\delta^{18}O$ varied from -2.27 to -1.62 ‰ during recession, becoming more enriched with decreasing flow. A mass-balance model of the river during recession indicated that this enrichment could be attributed to evaporation.

Recommendations for further research include additional study of river $\delta^{18}O$ during periods of recession to better characterize the influence of evaporation under varying river conditions. Additionally, precipitation events should be monitored and analyzed for $\delta^{18}O$ and δD to develop a meteoric water line for central Florida. River and groundwater samples should also be analyzed for both $\delta^{18}O$ and δD to allow deuterium-excess calculations to be incorporated into mass-balance models. Deuterium excess measures the deviation of a sample from the meteoric water line and can be used to evaluate the degree of evaporation a water mass has undergone. Incorporation of deuterium excess into mass-balance models is expected to improve the reliability of old water estimates.

Hydrograph Separation

Flow measurements and isotopic sampling in Spring 1993 provided data to conduct hydrograph separation studies on a storm event at two stations on the Big Econlockhatchee River using conservative-tracer mixing models. The event of record occurred after an extended period of recession. Pre-storm and recession monitoring, combined with recession studies conducted in the Autumn of 1992, provided $\delta^{18}O$ and hydrometric data to characterize the old water signature at both river stations. The $\delta^{18}O$ of old water (C_O) varied with flow, but averaged -0.27 ‰ during the storm hydrograph, while the amount-weighted average $\delta^{18}O$ of precipitation (C_N) was -4.46 ‰. Considering the analytical precision of the $\delta^{18}O$ test was approximately $1\sigma=0.1$ ‰, an adequate isotopic signal (C_N-C_O) existed for hydrograph separation. River $\delta^{18}O$ varied from -1.95 to -0.02 ‰. Steady-state mass-balance models for $\delta^{18}O$ indicated that approximately 76 percent of the storm hydrograph was composed of old water at both stations.

Comparison of the steady-state mixing model with an unsteady-state form of the same model indicated that the assumption of steady-state conditions was reasonable. The steady-state mixing model was also compared with a simple linear interpolation model for baseflow. The interpolation model estimated the old-water contribution during the storm event to be 11 to 15 percent of the total hydrograph, a significantly lower contribution than estimated by the steady-state mixing model.

A separate model was derived to estimate indirectly the $\delta^{18}O$ of water entering a discrete river reach (C_G) using a mass balance for $\delta^{18}O$ entering and leaving the reach. The model produced erratic and unreasonable estimates for C_G. Analysis indicated that C_G estimates were highly sensitive to flow measurements at reach boundaries and small variation in flow measurements resulted in a large range in C_G estimates. This observation underscored the necessity for accurate field measurements.

Oxygen isotopes were successfully employed to estimate the quantity of old water discharged during a single storm event. To provide a meaningful assessment of the annualized discharge of old water from the Econlockhatchee River system, similar hydrograph-separation studies must be conducted under varying hydrologic and isotopic conditions in the watershed (1) to verify methods employed for the separation analysis and (2) to detect differences in watershed hydrology attributable to seasonal or antecedent conditions. Routine monitoring for $\delta^{18}O$ and δD of rainfall, river water, and groundwater is recommended to allow more comprehensive hydrograph separation studies within the Econlockhatchee River basin.

APPENDIX A

EXTRACTION PROCEDURES AND CALIBRATION DATA FOR OXYGEN AND HYDROGEN STABLE ISOTOPES IN NATURAL WATER

Oxygen-18

The traditional method to prepare water samples for $\delta^{18}O$ analysis was documented by Epstein and Mayeda (1953) and involved placing an aliquot of purified CO_2 gas in contact with a water sample. The oxygen isotopic composition of the gas equilibrated with that of the water sample and the gas was extracted for analysis in an isotope-ratio mass spectrometer. The procedure reported by Epstein and Mayeda (1953) required a sample size of approximately 25 mL of water and an equilibration time of 48 hours. Recently, researchers reported a method to equilibrate a much smaller water sample (approximately 1.5 mL) over a much shorter equilibration time (approximately 90 minutes) using inexpensive equilibration and extraction methods (Socki, *et al.*, 1992).

The experimental procedure for $\delta^{18}O$ analysis of water was to fill disposable serum tubes (7 mL volume) with approximately 0.5 atmospheres of purified CO_2 gas, inject approximately 1.5 mL of sample, equilibrate the sample with the gas in a constant-temperature shaker-bath for approximately 2 hours, extract the CO_2 gas, purify the gas by cryonic distillation, and collect the gas in a break-seal tube for analysis.

Apparatus

Two vacuum systems were used for this procedure. A vacuum manifold (Figure 45a) was used to charge sample vials with CO_2 gas and a separate vacuum line was used to extract and purify CO_2 gas after equilibration (Figure 45b). High-purity carbon dioxide gas (Coleman grade, 99.999 percent CO_2) was admitted to the vacuum line directly from the cylinder using a two-stage regulator with a 6-mm Swageloc^{TM} fitting at the outlet port connected to a NuPro^{TM} plug valve (V3, Figure 45a). The pressure on the second stage of the regulator was set at 10 psig.

Access to the sample vials was afforded through Luer-Loc^{TM} syringe needles mounted on 6-mm outside diameter (O.D.) Pyrex^{TM} tubes. Needles were affixed to the tubes using high-vacuum epoxy cement (Epoxi-Patch 1C, Hysol Aerospace & Industrial Products, Pittsburg, California). Alternatively, Socki, *et al.* (1992) silver-soldered needles to stainless-steel 6-mm O.D. tubes. High-vacuum wax (Apiezon wax) can also be used to affix needles to tubes. For the manifold system (Figure 45a) 23 gauge needles were used and for the extraction line (Figure 45b) 18 gauge needles were used.

Preparation

Disposable pre-evacuated serum vials (Vacutainer^{TM}, 7 mL draw, nonsiliconized interior) were prepared by placing 6 vials on the vacuum manifold (Figure 45a) and opening stopcocks (Ports P1 through P6 and Valves V1 and V2) to place the vials under high vacuum for approximately 2 minutes. An aliquot of CO_2 gas was prepared by closing V2 and opening V3 to equilibrate 10 psig of gas in the line between valve V2 and the cylinder for 2 minutes. The manifold was then taken off of active vacuum by closing

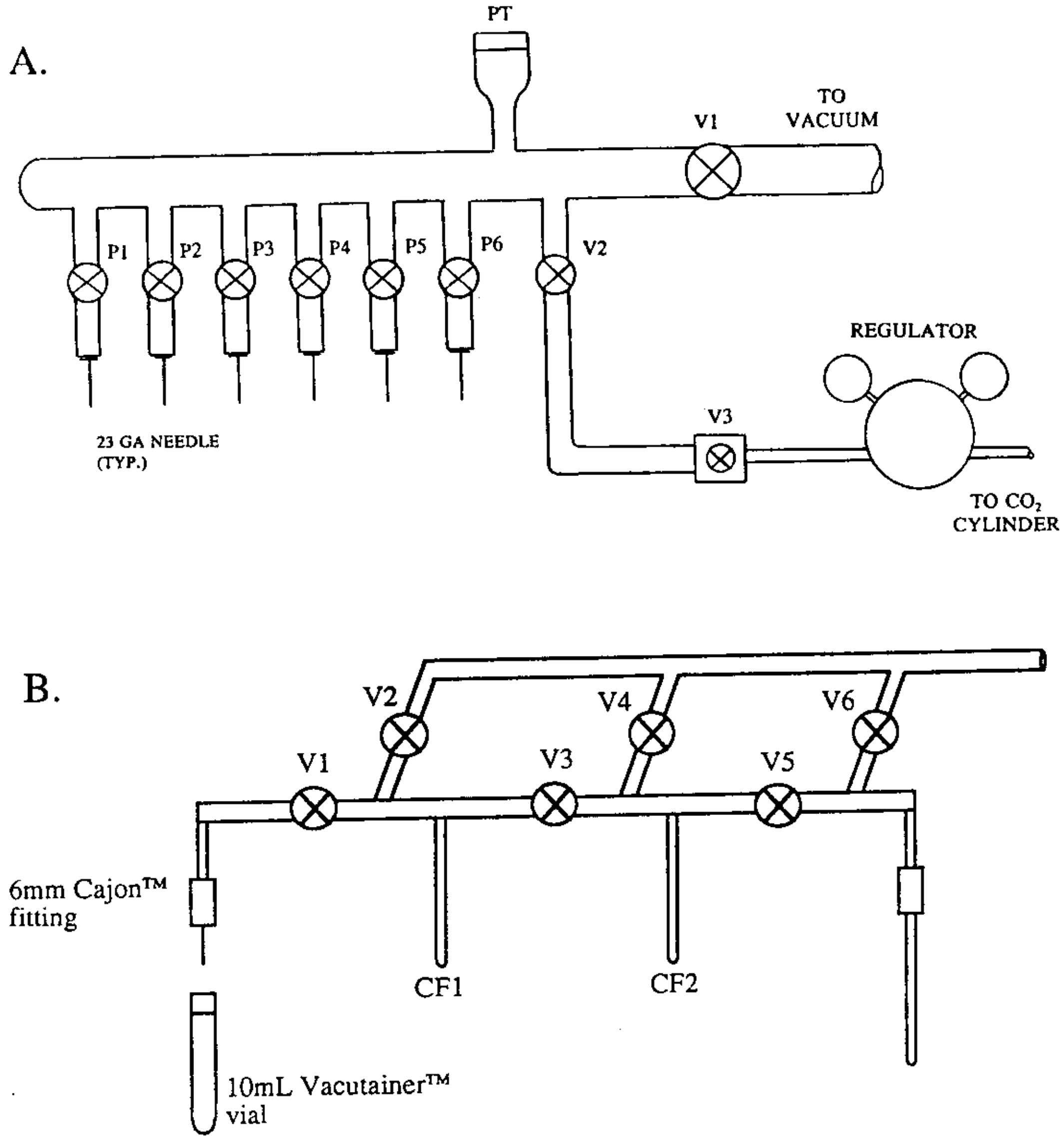

Figure 45. Vacuum lines for (a) preparing serum vials and (b) extracting $CO_2$for oxygen-18 analysis.

valve V1, with ports P1 through P6 remaining open. Valve V3 was closed to isolate the aliquot then valve V2 was opened to expand the aliquot into the manifold and 6 serum vials. The volume of gas trapped between valves V2 and V3 was adjusted experimentally to arrive at an equilibrium gas pressure of approximately 0.5 atmospheres in the manifold. The gas was allowed to equilibrate for 5 minutes. After equilibration, ports P1 through P6 were closed and the vials were removed from the manifold. Vials charged with CO_2 were stored for as long as approximately 2 weeks prior to sample injection without deterioration in data quality.

Sample Equilibration and Extraction

Vials were injected with approximately 1.5 mL of sample using clean, dry 5-mL glass syringes. Vials were secured horizontally in racks and placed in a shaker-bath set at 30° C. Samples were equilibrated under moderate agitation (approximately 1 cycle per second) for at least two hours. Vials were kept in the bath until extracted to prevent re-equilibration at laboratory room temperature (approximately 27° C).

After equilibration, each vial was placed on the vacuum extraction line (Figure 45b) and the CO_2 was extracted and purified. To facilitate gas transfer, a larger diameter needle (18 ga.) was used for extraction than for charging the vial. Before extracting CO_2 from the vial, the volume within the needle and up to valve V1 was evacuated by imbedding the needle in the stopper deeply enough to cover the needle opening, but not deeply enough to intrude into the vial. The needle was evacuated by opening valve V1.

Noncondensible gases were withdrawn from the vial by freezing the sample, first in a methanol-dry-ice slush (methanol trap) at -120°C to freeze the water, then in liquid nitrogen (LN trap) at -200°C to condense the CO_2. Socki *et al.* (1992) recommended heating the stopper lightly with a heat gun to evaporate droplets of water adhering to the inside of the stopper. After freezing the sample approximately one minute in liquid nitrogen, the vial was pushed upward allowing the needle to puncture into the vial. The noncondensible gases withdrawn consisted of a combination of dissolved gas from the sample and air leaked into the vial.

When pressure transducer PT indicated that noncondensible gases were withdrawn, the sample was transferred through cold fingers CF1 and CF2 to remove condensible gases, primarily water vapor, and collected in a 6 mm break-seal tube. To trap CO_2 in CF1, valves V2 and V3 were closed, a methanol trap was placed on the sample vial and a LN trap was placed on cold finger CF1. As CO_2 thawed in the sample vial, it was collected in CF1. Transfer of CO_2 was considered complete when P1 returned to its original reading. Similarly, to trap the sample in CF2 valves V1, V2, V4, and V5 were closed; valve V3 was opened; the LN trap on CF1 was replaced with a methanol trap; and a LN trap was placed on CF2. After the sample was trapped in CF2, it was collected by closing valves V3, V4, and V6; opening valve V5; replacing the LN trap on CF2 with a methanol trap; and placing an LN trap on the break-seal tube. When sample transfer was complete, the tube was detached from the line and sealed using a blowtorch.

Analysis

Samples were analyzed at the University of Florida, Department of Geology using a VG-Prism isotope-ratio mass spectrometer, which detected isotopic ratios of mass 45/44 and mass 46/44. Standard calculations (Craig 1957) were performed to convert the mass 46/44 ($^{12}C^{16}O^{18}O/^{12}C^{16}O^{16}O$) ratio to per-mil notation relative to Standard Mean Ocean Water (SMOW, NIST 1992).

Machine Calibration

The reference gas used was generated from Carerra marble (Hodell, *et al.*, 1989) and has been calibrated against international standards. The mass spectrometer used to analyze samples for this dissertation research used the same reference gas for all analyses and the machine computed a $\delta^{18}O$ value relative to that reference gas ($\delta^{18}O_{UF}$). A calibration curve to convert to $\delta^{18}O$ relative to SMOW ($\delta^{18}O_{SMOW}$) was developed by analyzing standards of known isotopic content. The three commonly recognized standards for isotopic analysis of water (NIST 1992) are Standard Mean Ocean Water (SMOW), Greenland Ice Sheet Precipitation (GISP), and Standard Light Antarctic Precipitation (SLAP). Replicate analyses of these standards were performed using the procedures described above and a machine calibration curve was developed through linear regression analysis (Table 13 and Figure 46). The calibration equation used to convert to $\delta^{18}O_{SMOW}$ was

$$\delta^{18}O_{SMOW} = 0.2322 + 1.0364\delta^{18}O_{UF} \tag{68}$$

International standards are available only in very small quantities. Laboratories are typically permitted to purchase only 30 mL of each standard every two years. Thus an important aspect of laboratory quality assurance is the analysis of internal working standard samples. Ordinarily three standards were analyzed at the beginning of each

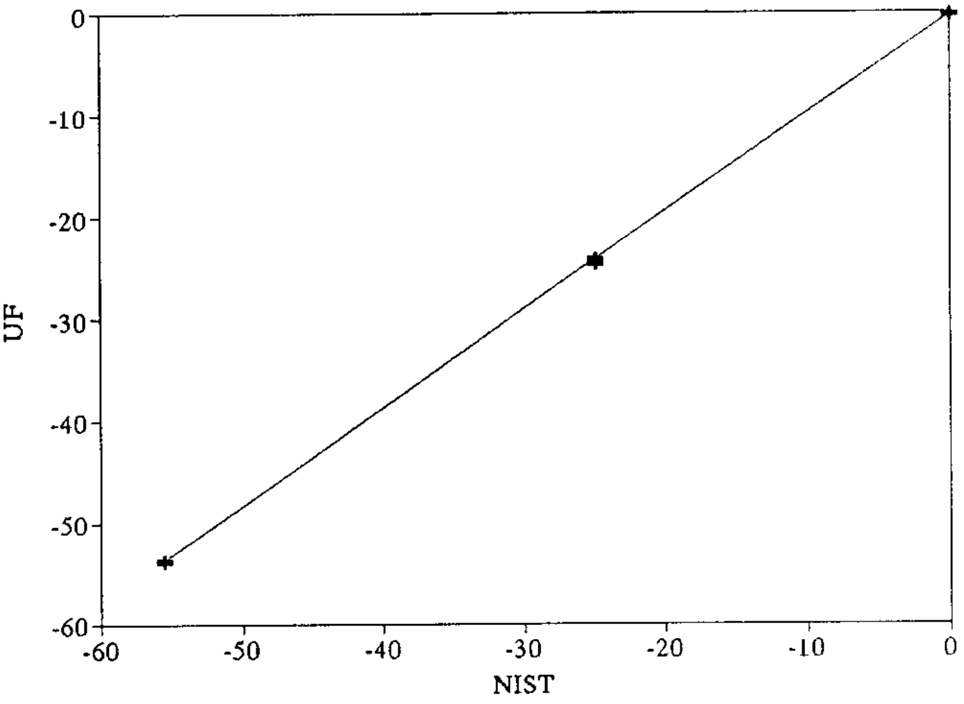

Figure 46. Machine calibration curve for oxygen-18.

Table 13.
COMPLETE LISTING OF OXYGEN-18 ANALYSES OF INTERNATIONAL STANDARDS FOR MACHINE CALIBRATION.

REGRESSION ANALYSIS

$$Y = b_0 + Xb_1$$

Variables
Y = Standard Relative to SMOW ($\delta^{18}O_{SMOW}$)
X = Standard Relative to UFRef ($\delta^{18}O_{UFRef}$)
Number of Observations = 14
Degrees of Freedom = 12
R^2 = 0.999986
Regression Parameters
b0 = 0.2322
b1 = 1.0364
Standard Error of Regression Parameters
b0 = 0.0962
b1 = 0.0011

SOURCE DATA

STANDARD	$\delta^{18}O_{SMOW}$ (‰)	$\delta^{18}O_{UFRef}$ (‰)	$E(\delta^{18}O_{SMOW})$ (‰)
SMOW	0.00	-0.29	-0.07
SMOW	0.00	-0.19	0.04
SMOW	0.00	-0.22	0.00
SMOW	0.00	-0.24	-0.02
SMOW	0.00	-0.25	-0.03
GISP	-24.85	-24.19	-24.84
GISP	-24.85	-24.13	-24.78
GISP	-24.85	-24.24	-24.89
GISP	-24.85	-24.13	-24.78
SLAP	-55.50	-53.62	-55.34
SLAP	-55.50	-53.64	-55.36
SLAP	-55.50	-53.89	-55.62
SLAP	-55.50	-53.94	-55.67
SLAP	-55.50	-53.83	-55.56

day's sample run and three standards were analyzed at the end of the run. The three standards most commonly analyzed were a central-Florida rainwater standard (Alpha) with a mean $\delta^{18}O$ of -3.15±0.09‰ (n=112); an enriched sample from Lake Chichancanab in the Yucatan, Mexico with a mean $\delta^{18}O$ of +3.54±0.12‰ (n=18); and a depleted sample from Lake Condorere, a high-altitude Bolivian lake, with a mean of −14.17±0.12‰ (n=17). A statistical summary of the international and working standards is provided in Table 14 and a complete data listing is presented in Table 15.

Equilibration Time

To determine the minimum acceptable equilibration time for samples in the constant-temperature shaker bath, an equilibration study was undertaken. The Alpha sample was analyzed for $\delta^{18}O$ at equilibration times ranging from 0 to 600 minutes (0 to 10 hours). Additionally, aliquots of the cylinder CO_2 gas was analyzed prior to contact with a water sample. The results are summarized in Table 16 and plotted in Figure 47. Results indicate that the CO_2 equilibrated with the sample by approximately 45 minutes after placement in the shaker bath. The minimum equilibration time used for analyses reported in this dissertation was 120 minutes (2 hours).

Deuterium

Two commonly used procedures for analyzing water samples for deuterium involve dissociating the water molecule to produce hydrogen gas. The earlier of the two procedures, known as *uranium reduction* (Bigeleisen, *et al.*, 1952 and Friedman, *et al.*, 1958; cited in Coleman, *et al.*, 1982) uses a vacuum furnace containing uranium, in

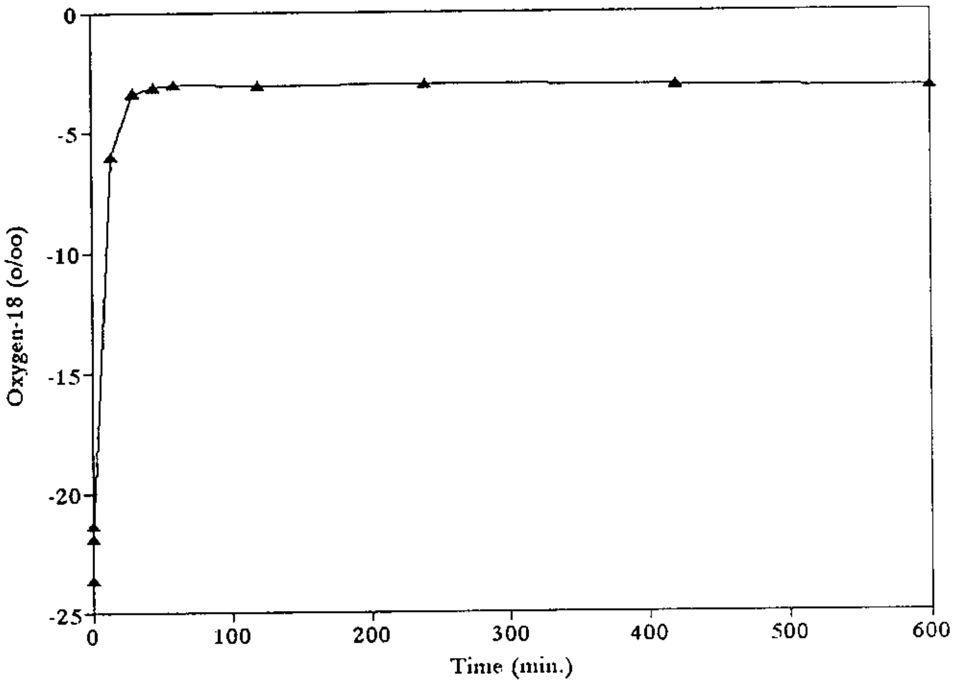

Figure 47. Equilibration time study for oxygen-18.

Table 14.
SUMMARY OF REPLICATE OXYGEN-18 ANALYSES OF INTERNATIONAL AND WORKING LABORATORY STANDARDS

STANDARD	N	MEAN (‰)	STANDARD DEVIATION (‰)
INTERNATIONAL STANDARDS			
SMOW (0.00 ‰)[1]	5	-0.01	0.04
GISP (-24.85 ‰)[1]	4	-24.91	0.13
SLAP (-55.50 ‰)[1]	5	-55.51	0.14
LABORATORY WORKING STANDARDS			
ALPHA	112	-3.15	0.09
CHICHANCANAB	18	3.54	0.12
CONDORERE	17	-14.17	0.12
BLANK	4	-23.80	0.21
ETA	14	-3.54	0.08
OTAP	29	-1.79	0.07
OTAP D	6	-6.54	0.16
OTAP E	4	0.77	0.04
TIWANAKU	4	-13.44	0.02

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[1] Standard isotopic composition (NIST 1992) with an uncertainty of 0.05 ‰.

which uranium is oxidized with water. The resulting hydrogen gas is collected using a mercury (Toepler) pump and introduced to the mass spectrometer for analysis. The procedure can be reliable, with analytical precision of 1.0 ‰ or better, but is time consuming; and the health and safety issues associated with handling mercury and uranium are self-evident.

Table 15.
COMPLETE LISTING OF OXYGEN-18 ANALYSES OF LABORATORY WORKING STANDARDS.

SAMPLE	DATE	46/44	45/44	O-18	PRES
Alpha	10-Jun-93	-28.904	-3.228	-3.11	12.0
Alpha	10-Jun-93	-26.088	-3.271	-3.16	12.8
Alpha	10-Jun-93	-28.873	-3.292	-3.18	12.8
Alpha	12-Jun-93	-28.985	-3.274	-3.16	11.2
Alpha	12-Jun-93	-28.975	-3.295	-3.18	14.1
Alpha	12-Jun-93	-28.923	-3.253	-3.14	11.2
Alpha	17-Jun-93	-28.640	-3.269	-3.16	10.7
Alpha	17-Jun-93	-28.670	-3.221	-3.11	11.7
Alpha	18-Jun-93	-28.935	-3.319	-3.21	11.2
Alpha	19-Jun-93	-28.927	-3.160	-3.04	11.5
Alpha	19-Jun-93	-28.921	-3.154	-3.04	
Alpha	19-Jun-93	-28.873	-3.228	-3.11	12.0
Alpha	20-Jun-93	-28.971	-3.380	-3.27	11.7
Alpha	20-Jun-93	-28.887	-3.194	-3.08	10.7
Alpha	21-Jun-93	-28.935	-3.207	-3.09	10.9
Alpha	24-Jun-93	-29.042	-3.213	-3.10	
Alpha	24-Jun-93	-28.915	-3.257	-3.14	13.8
Alpha	24-Jun-93	-28.885	-3.363	-3.25	13.3
Alpha	24-Jun-93	-28.912	-3.217	-3.10	15.6
Alpha	24-Jun-93	-28.624	-3.175	-3.06	15.6
Alpha	26-Jun-93	-29.063	-3.392	-3.28	12.8
Alpha	26-Jun-93	-29.009	-3.254	-3.14	12.2
Alpha	26-Jun-93	-28.975	-3.265	-3.15	12.2
Alpha	26-Jun-93	-28.948	-3.273	-3.16	12.8
Alpha	27-Jun-93	-28.813	-3.236	-3.12	12.0
Alpha	27-Jun-93	-28.875	-3.264	-3.15	12.0
Alpha	27-Jun-93	-28.865	-3.236	-3.12	12.0
Alpha	27-Jun-93	-28.861	-3.288	-3.18	12.8
Alpha	28-Jun-93	-28.953	-3.296	-3.18	13.0
Alpha	28-Jun-93	-28.932	-3.278	-3.17	12.0
Alpha	28-Jun-93	-28.971	-3.243	-3.13	12.8
Alpha	28-Jun-93	-28.978	-3.262	-3.15	12.5
Alpha	01-Jul-93	-28.565	-3.215	-3.10	12.8
Alpha	01-Jul-93	-28.540	-3.227	-3.11	11.7
Alpha	01-Jul-93	-28.583	-3.172	-3.06	12.0
Alpha	01-Jul-93	-28.594	-3.210	-3.09	11.7
Alpha	03-Jul-93	-28.672	-3.094	-2.97	12.8
Alpha	03-Jul-93	-28.564	-3.216	-3.10	13.0
Alpha	03-Jul-93	-28.635	-3.133	-3.01	11.5
Alpha	03-Jul-93	-28.562	-3.206	-3.09	11.5

Table 15.
COMPLETE LISTING OF OXYGEN-18 ANALYSES OF LABORATORY WORKING STANDARDS (Continued).

SAMPLE	DATE	46/44	45/44	O-18	PRES
Alpha	04-Jul-93	-28.935	-3.250	-3.14	12.8
Alpha	04-Jul-93	-28.769	-3.334	-3.22	12.8
Alpha	04-Jul-93	-28.827	-3.364	-3.25	11.7
Alpha	04-Jul-93	-28.738	-3.158	-3.04	12.5
Alpha	04-Jul-93	-28.773	-3.392	-3.28	12.0
Alpha	04-Jul-93	-28.699	-3.196	-3.08	11.7
Alpha	07-Jul-93	-28.795	-3.419	-3.31	12.2
Alpha	07-Jul-93	-28.794	-3.199	-3.08	12.5
Alpha	07-Jul-93	-28.764	-3.383	-3.27	12.0
Alpha	07-Jul-93	-28.789	-3.441	-3.33	11.5
Alpha	07-Jul-93	-28.779	-3.192	-3.08	12.0
Alpha	07-Jul-93	-28.889	-3.540	-3.44	11.7
Alpha	10-Jul-93	-28.781	-3.434	-3.33	11.2
Alpha	10-Jul-93	-28.801	-3.456	-3.35	11.5
Alpha	12-Aug-93	-28.717	-3.123	-3.00	9.9
Alpha	12-Aug-93	-25.802	-3.252	-3.14	10.2
Alpha	12-Aug-93	-25.853	-3.205	-3.09	10.9
Alpha	12-Aug-93	-25.719	-3.239	-3.12	10.9
Alpha	12-Aug-93	-25.991	-3.229	-3.11	10.7
Alpha	12-Aug-93	-29.028	-3.258	-3.14	11.2
Alpha	12-Aug-93	-19.001	-3.249	-3.14	11.2
Alpha	13-Aug-93	-28.781	-3.152	-3.03	10.4
Alpha	13-Aug-93	-28.601	-3.188	-3.07	12.2
Alpha	13-Aug-93	-25.968	-3.149	-3.03	10.7
Alpha	13-Aug-93	-28.576	-3.212	-3.10	10.9
Alpha	13-Aug-93	-28.934	-3.108	-2.99	10.4
Alpha	13-Aug-93	-28.597	-3.189	-3.07	12.0
Alpha	14-Aug-93	-28.589	-3.222	-3.11	11.7
Alpha	14-Aug-93	-28.841	-3.275	-3.16	12.5
Alpha	14-Aug-93	-28.787	-3.262	-3.15	11.5
Alpha	14-Aug-93	-28.591	-3.209	-3.09	11.2
Alpha	14-Aug-93	-28.559	-3.195	-3.08	12.0
Alpha	14-Aug-93	-28.740	-3.218	-3.10	11.2
Alpha	15-Aug-93	-28.874	-3.229	-3.11	12.5
Alpha	15-Aug-93	-28.885	-3.266	-3.15	11.5
Alpha	15-Aug-93	-28.896	-3.293	-3.18	12.0
Alpha	15-Aug-93	-28.896	-3.301	-3.19	10.9
Alpha	15-Aug-93	-28.869	-3.262	-3.15	10.9
Alpha	31-Aug-93	-29.030	-3.412	-3.30	11.2
Alpha	08-Sep-93	-28.906	-3.236	-3.12	10.9

Table 15.
COMPLETE LISTING OF OXYGEN-18 ANALYSES OF LABORATORY WORKING STANDARDS (Continued).

SAMPLE	DATE	46/44	45/44	O-18	PRES
Alpha	08-Sep-93	-28.922	-3.248	-3.13	10.9
Alpha	08-Sep-93	-28.980	-3.232	-3.12	11.7
Alpha	08-Sep-93	-28.980	-3.168	-3.05	10.7
Alpha	11-Sep-93	-29.015	-3.443	-3.34	10.9
Alpha	11-Sep-93	-29.086	-3.521	-3.42	11.2
Alpha	11-Sep-93	-28.774	-3.551	-3.45	10.7
Alpha	11-Sep-93	-28.967	-3.327	-3.22	10.2
Alpha	17-Sep-93	-28.321	-3.283	-3.17	10.7
Alpha	17-Sep-93	-28.357	-3.242	-3.13	9.9
Alpha	19-Sep-93	-27.620	-3.187	-3.07	
Alpha	19-Sep-93	-27.583	-3.170	-3.05	
Alpha	19-Sep-93	-27.768	-3.374	-3.26	
Alpha	25-Sep-93	-27.790	-3.239	-3.12	
Alpha	25-Sep-93	-27.756	-3.326	-3.21	
Alpha	26-Sep-93	-28.900	-3.417	-3.31	9.4
Alpha	26-Sep-93	-28.677	-3.366	-3.26	10.2
Alpha	02-Oct-93	-28.820	-3.315	-3.20	
Alpha	02-Oct-93	-28.838	-3.491	-3.39	
Alpha	29-Nov-93		-3.301	-3.19	
Alpha	29-Nov-93		-3.337	-3.23	
Alpha	29-Nov-93		-3.259	-3.15	
Alpha	29-Nov-93		-3.278	-3.17	
Chichancanab	15-Aug-93	-27.853	3.290	3.64	12.0
Chichancanab	15-Aug-93	-28.081	3.279	3.63	12.2
Chichancanab	08-Sep-93	-26.002	3.362	3.72	10.9
Chichancanab	11-Sep-93	-27.891	2.958	3.30	10.7
Chichancanab	11-Sep-93	-27.683	3.222	3.57	10.4
Chichancanab	11-Sep-93	-27.881	3.252	3.60	11.5
Chichancanab	11-Sep-93	-27.807	3.056	3.40	11.2
Chichancanab	11-Sep-93	-27.766	3.112	3.46	11.5
Chichancanab	19-Sep-93	-26.453	3.189	3.54	9.9
Chichancanab	25-Sep-93	-26.494	3.196	3.54	10.4
Chichancanab	26-Sep-93	-27.000	3.194	3.54	11.5
Chichancanab	26-Sep-93	-26.466	3.184	3.53	10.2
Chichancanab	02-Oct-93	-27.039	3.147	3.49	
Chichancanab	02-Oct-93	-27.402	2.926	3.26	
Chichancanab	29-Nov-93		3.268	3.62	
Chichancanab	29-Nov-93		3.242	3.59	
Chichancanab	29-Nov-93		3.291	3.64	
Chichancanab	29-Nov-93		3.267	3.62	

Table 15.
COMPLETE LISTING OF OXYGEN-18 ANALYSES OF LABORATORY WORKING STANDARDS (Continued).

SAMPLE	DATE	46/44	45/44	O-18	PRES
Condorere	08-Sep-93	-27.163	-13.761	-14.03	10.7
Condorere	11-Sep-93	-29.245	-13.994	-14.27	10.9
Condorere	11-Sep-93	-29.109	-14.060	-14.34	11.2
Condorere	17-Sep-93	-28.700	-13.884	-14.16	10.9
Condorere	17-Sep-93	-28.744	-13.938	-14.21	
Condorere	19-Sep-93	-27.982	-13.718	-13.99	
Condorere	19-Sep-93	-27.991	-13.676	-13.94	
Condorere	19-Sep-93	-28.142	-13.963	-14.24	9.4
Condorere	25-Sep-93	-28.075	-13.803	-14.07	8.9
Condorere	26-Sep-93	-28.262	-14.009	-14.29	10.9
Condorere	26-Sep-93	-28.205	-13.978	-14.25	
Condorere	02-Oct-93	-29.091	-13.732	-14.00	
Condorere	02-Oct-93	-28.580	-14.079	-14.36	
Condorere	29-Nov-93		-13.965	-14.24	
Condorere	29-Nov-93		-13.868	-14.14	
Condorere	29-Nov-93		-13.838	-14.11	
Condorere	29-Nov-93		-13.902	-14.18	
Blank	10-Jun-93	-29.668	-23.513	-24.14	15.1
Blank	21-Jun-93	-29.755	-23.199	-23.81	14.3
Eta	20-Jun-93	-28.946	-3.525	-3.42	11.5
Eta	24-Jun-93	-28.925	-3.561	-3.46	12.8
Eta	24-Jun-93	-28.999	-3.548	-3.44	14.3
Eta	26-Jun-93	-29.083	-3.793	-3.70	12.0
Eta	26-Jun-93	-29.133	-3.743	-3.65	12.0
Eta	27-Jun-93	-28.999	-3.651	-3.55	11.7
Eta	28-Jun-93	-29.076	-3.658	-3.56	12.5
Eta	28-Jun-93	-29.036	-3.678	-3.58	11.7
Eta	28-Jun-93	-29.051	-3.690	-3.59	11.7
Eta	01-Jul-93	-28.749	-3.551	-3.45	12.0
Eta	01-Jul-93	-28.824	-3.643	-3.54	12.0
Eta	01-Jul-93	-28.717	-3.597	-3.50	11.2
Eta	01-Jul-93	-28.938	-3.649	-3.55	12.0
Eta	03-Jul-93	-28.769	-3.714	-3.62	11.7
OTAP	30-May-93	-27.748	-1.930	-1.77	12.2
OTAP	30-May-93	-27.744	-1.945	-1.78	12.0
OTAP	30-May-93	-27.786	-1.916	-1.75	9.1
OTAP	10-Jun-93	-27.754	-2.065	-1.91	12.0
OTAP	10-Jun-93	-27.778	-2.069	-1.91	12.2
OTAP	10-Jun-93	-27.763	-2.029	-1.87	13.3
OTAP	12-Jun-93	-27.859	-1.938	-1.78	12.2

Table 15.
COMPLETE LISTING OF OXYGEN-18 ANALYSES OF LABORATORY WORKING STANDARDS (Concluded).

SAMPLE	DATE	46/44	45/44	O-18	PRES
OTAP	12-Jun-93	-27.803	-1.984	-1.82	11.7
OTAP	12-Jun-93	-27.796	-1.993	-1.83	11.7
OTAP	12-Jun-93	-27.798	-1.882	-1.72	11.7
OTAP	12-Jun-93	-27.654	-1.802	-1.64	9.4
OTAP	17-Jun-93	-27.545	-1.870	-1.71	10.4
OTAP	17-Jun-93	-27.711	-1.914	-1.75	12.5
OTAP	17-Jun-93	-27.125	-2.077	-1.92	12.2
OTAP	17-Jun-93	-27.461	-1.969	-1.81	11.2
OTAP	17-Jun-93	-27.486	-1.955	-1.79	11.7
OTAP	17-Jun-93	-27.858	-1.855	-1.69	
OTAP	18-Jun-93	-27.681	-1.970	-1.81	11.5
OTAP	18-Jun-93	-27.834	-2.058	-1.90	12.0
OTAP	18-Jun-93	-27.543	-1.968	-1.81	
OTAP	18-Jun-93	-27.854	-1.984	-1.82	11.5
OTAP	19-Jun-93	-27.725	-1.940	-1.78	10.7
OTAP	19-Jun-93	-27.281	-1.892	-1.73	11.2
OTAP	20-Jun-93	-27.350	-1.946	-1.78	
OTAP	20-Jun-93	-27.781	-1.993	-1.83	
OTAP	21-Jun-93	-27.600	-1.907	-1.74	12.0
OTAP	21-Jun-93	-28.092	-1.817	-1.65	
OTAP	21-Jun-93	-27.560	-1.876	-1.71	11.2
OTAP	17-Sep-93	-28.151	-1.990	-1.83	
OTAP D	30-May-93	-28.482	-6.389	-6.39	13.0
OTAP D	30-May-93	-28.508	-6.341	-6.34	12.0
OTAP D	01-Jul-93	-28.640	-6.462	-6.47	13.0
OTAP D	31-Aug-93	-28.687	-6.583	-6.59	11.7
OTAP D	31-Aug-93	-28.728	-6.818	-6.83	11.7
OTAP D	31-Aug-93	-28.727	-6.596	-6.60	12.0
OTAP E	30-May-93	-28.344	0.485	0.73	13.0
OTAP E	30-May-93	-28.300	0.488	0.74	
OTAP E	30-May-93	-28.304	0.586	0.84	
OTAP E	30-May-93	-28.302	0.507	0.76	12.2
Tiwanaku	08-Sep-93	-26.327	-13.169	-13.42	9.9
Tiwanaku	08-Sep-93	-26.313	-13.183	-13.43	10.7
Tiwanaku	08-Sep-93	-27.987	-13.181	-13.43	
Tiwanaku	08-Sep-93	-28.079	-13.231	-13.48	
Tahoe	17-Sep-93	-26.837	-5.620	-5.59	
OTAP	17-Sep-93	-28.151	-1.990	-1.83	

Table 16.
EQUILIBRATION TIME STUDY FOR OXYGEN-18 ANALYSIS.

EQUILIBRATION TIME (HOURS:MINUTES)	N	MEAN (‰)	STANDARD DEVIATION (‰)
>0:45	10	-3.10	0.04
Blank[1]	2	-23.62	0.04
0:00	3	-21.70	0.30
0:15	1	-6.00	
0:30	2	-3.36	0.04
0:45	2	-3.13	<0.01
1:00	1	-3.05	
2:00	2	-3.09	0.02
4:00	2	-3.06	<0.01
7:00	2	-3.12	0.02
10:00	1	-3.17	

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[1] CO_2 gas from source cylinder.

An alternative method, *zinc reduction*, was presented by Coleman, *et al.* (1982). A small water sample (< 10 μL) is sealed in an evacuated glass tube with approximately 100 mg of zinc metal. The tube is placed in a furnace at 500° C for 20 minutes. The water is converted quantitatively to zinc oxide and hydrogen gas. The hydrogen gas can then be analyzed by the mass spectrometer. This method has the advantages of allowing large numbers of samples to be prepared in batches, requiring a modest preparation system, and avoiding the use of uranium and mercury.

Coleman, *et al.* (1982), reported replicate precision of 0.2 to 0.4 ‰ for the zinc-reduction procedure. There is wide agreement in the literature that this level of precision is virtually unattainable. For reasons not completely known, this method is only capable of an analytical precision of 1.0 to 2.0 ‰. Kendall and Coplen (1985) speculated that the source of variability was interaction between hydrogen and the molecular structure of the glassware containing the hydrogen gas. Tanweer (1990) attributed variability to contaminants resident on the surface of the zinc-metal reagent. In a rigorous comparison of methods, Schimmelmann and DeNiro (1993) concluded that for water samples, Pyrex™ did not react with hydrogen gas, but that the zinc-metal reagent contains a "deuterium-depleted hydrogen blank," a systematic offset in analytical results that can be corrected with an appropriate standard curve.

Experimental

A 3 μL water sample was collected in a 6-mm O.D. Pyrex™ tube containing 100 mg of zinc-metal reagent using the apparatus shown in Figure 48. The zinc was supplied by the Biogeochemical Laboratories at University of Indiana. To prevent contact with atmospheric oxygen and moisture, bulk zinc reagent was stored *in vacuo* in 6-mm pyrex tubes until use. For each sample, 100 mg zinc was weighed into a 12-inch long 6-mm pyrex tube, affixed to the apparatus shown in Figure 48, and placed under vacuum for 30 minutes. The zinc was heated for 10 seconds using the flame from a blowtorch at 10 minute intervals to drive off moisture. After 30 minutes of evacuation, the stopcock was closed to remove the apparatus from active vacuum. The water sample was introduced by injection using a 5 μL micro-syringe (Hamilton Gastight™ Series 1700) through a 9-mm single-wall septum. The water was collected in the bottom of the sample tube, with the zinc reagent, by immersing the bottom of the tube in liquid nitrogen. The remainder

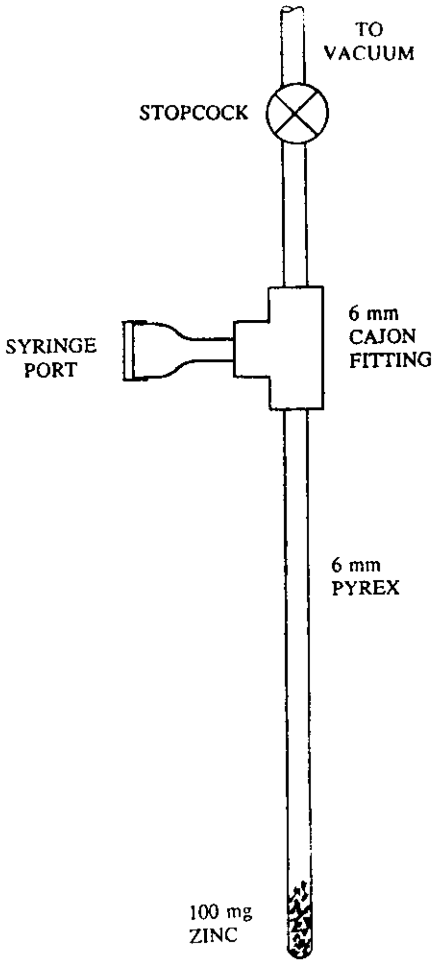

Figure 48. Vacuum preparation system for deuterium by zinc reduction.

of the apparatus was heated gently with a flameless heat gun for two minutes to assure that the sample had completely distilled into the sample tube. While the sample tube was still immersed in liquid nitrogen, the tube was sealed and removed from the apparatus using a blowtorch.

Hydrogen gas was produced in the sample tube by placing the tube in a furnace pre-heated to 500° C for 20 minutes. Tubes were identified by wrapping each tube in an aluminum foil sheet embossed using a dull pencil with appropriate ID numbers. Samples were introduced to the mass spectrometer using a tube-cracker system mounted on an inlet-side manifold. To prevent zinc dust and glass fragments from entering the mass spectrometer vacuum system, sintered-metal frits (0.5 μm, Part # *-696-526, Jax Valve and Fitting, Co., Jacksonville, Florida) were placed in the cracker system.

Machine Calibration

Samples were analyzed on a VG-Prism isotope-ratio mass spectrometer, outfitted with a hydrogen/deuterium spur and collector. The reference gas was provided by OzTech Trading Corporation (Dallas, Texas) in a 1.0 L cylinder at approximately 2.0 atmospheres internal pressure. Delta values were computed by the mass spectrometer relative to this gas. As with oxygen-18 measurements, a calibration curve was developed to convert δD relative to the reference gas (δD_{UF}) to δD relative to SMOW (δD_{SMOW}). The calibration curve was derived from replicate analyses of the three commonly recognized international standards. The results are summarized in Table 17 and Figure 49. The regression equation for δD calibration was

$$\delta D_{SMOW} = 27.311 + 1.041 \delta D_{UF} \tag{69}$$

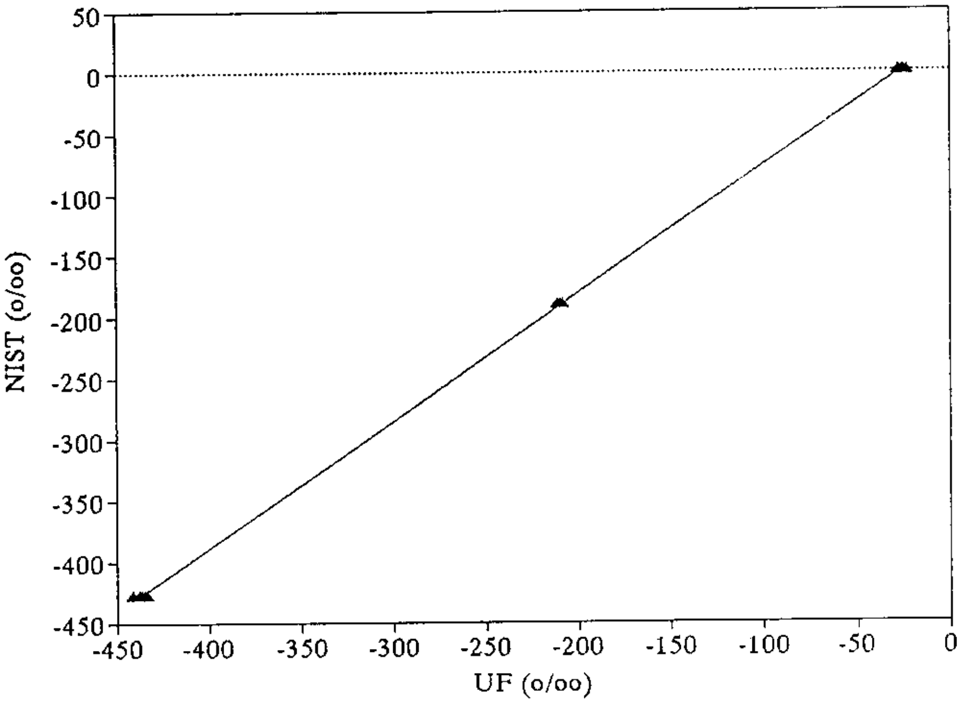

Figure 49. Machine calibration curve for deuterium.

Table 17.
COMPLETE LISTING OF DEUTERIUM ANALYSES OF INTERNATIONAL STANDARDS FOR MACHINE CALIBRATION.

REGRESSION ANALYSIS

$$Y = b_0 + Xb_1$$

Variables
Y = Standard Relative to SMOW ($\delta^{18}O_{SMOW}$)
X = Standard Relative to UFRef ($\delta^{18}O_{UFRef}$)
Number of Observations = 16
Degrees of Freedom = 14
R^2 = 0.999987
Regression Parameters
b0 = 27.311
b1 = 1.041
Standard Error of Regression Parameters
b0 = 2.229
b1 = 0.003

SOURCE DATA

STANDARD	$\delta^{18}O_{SMOW}$ (‰)	$\delta^{18}O_{UFRef}$ (‰)	$E(\delta^{18}O_{SMOW})$ (‰)
SMOW	0.0	-23.36	-3.0
SMOW	0.0	-25.88	0.4
SMOW	0.0	-27.50	-1.3
SMOW	0.0	-24.85	1.4
SMOW	0.0	-27.62	-1.5
SMOW	0.0	-24.30	2.0
SMOW	0.0	-28.31	-2.2
GISP	-189.8	-208.60	-189.9
GISP	-189.8	-208.16	-189.5
GISP	-189.8	-209.58	-191.0
GISP	-189.8	-210.93	-192.4
SLAP	-428.0	-433.76	-424.4
SLAP	-428.0	-435.11	-425.8
SLAP	-428.0	-438.09	-428.9
SLAP	-428.0	-441.28	-432.3
SLAP	-428.0	-436.02	-426.8

Replicate precision for the analysis of each of the international standards is summarized in Table 18. Within the isotopic range of natural waters in temperate to subtropical regions, such as Florida, the analytical precision attained was better than 2.0 ‰.

Table 18.
SUMMARY OF REPLICATE DEUTERIUM ANALYSES OF INTERNATIONAL STANDARDS

STANDARD	N	MEAN (‰)	STANDARD DEVIATION (‰)
SMOW (0.0 ‰)[1]	7	0.3	1.8
GISP (-189.8 ‰)[1]	4	-190.7	1.1
SLAP (-428.0 ‰)[1]	5	-427.7	2.7

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[1] Standard isotopic composition (NIST 1992) with an uncertainty of 0.5 ‰.

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APPENDIX B

CARBON-13 COMPLETE SOURCE DATA LISTINGS

Carbon-13 data are listed in Tables 19 and 20. Table 19 presents a complete listing of analyses of standard solutions and Table 20 presents a complete listing of $\delta^{13}C_{DIC}$ of water samples collected in the Econlockhatchee River system. Natural water samples were collected in 100 mL sample containers and field-preserved using 1.0 g mercuric chloride.

References

Craig, H., 1957. Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochimica et Cosmochimica Acta*, 12:133-149.

Table 19.
COMPLETE LISTING OF CARBON-13 CALIBRATION
DATA USING A POTASSIUM BICARBONATE STANDARD SOLUTION.

CONC.	BEAM 1	45/44	46/44
50	$7.22(10^{-9})$	-24.210	-5.911
50	$9.07(10^{-9})$	-24.223	-5.794
50	$8.98(10^{-9})$	-24.189	-5.471
50	$8.45(10^{-9})$	-24.231	-5.742
50	$8.86(10^{-9})$	-24.224	-5.919
40	$6.90(10^{-9})$	-24.339	-6.063
40	$7.21(10^{-9})$	-24.380	-5.676
40	$7.27(10^{-9})$	-24.286	-5.410
40	$6.61(10^{-9})$	-24.308	-5.278
40	$7.45(10^{-9})$	-24.349	-4.721
40	$7.31(10^{-9})$	-24.278	-2.981
30	$5.11(10^{-9})$	-24.423	-5.974
30	$5.27(10^{-9})$	-24.455	-5.865
30	$4.53(10^{-9})$	-24.398	-5.824
30	$4.51(10^{-9})$	-24.480	-6.141
30	$5.22(10^{-9})$	-24.437	-5.235
30	$4.88(10^{-9})$	-24.421	-5.584
20	$3.28(10^{-9})$	-24.356	-6.107
20	$3.18(10^{-9})$	-24.379	-6.045
20	$3.22(10^{-9})$	-24.364	-6.042
20	$3.25(10^{-9})$	-24.399	-5.775
20	$3.11(10^{-9})$	-24.389	-5.516
10	$1.64(10^{-9})$	-24.400	-6.300
10	$1.67(10^{-9})$	-24.323	-5.993
10	$1.72(10^{-9})$	-24.500	-4.437
10	$1.70(10^{-9})$	-24.393	-4.854
10		-23.983	-4.547
10		-24.178	-6.495

Note: CONC. = $KHCO_3$ Concentration [mg/L]
BEAM 1 = Major Ion Beam (Mass 44) [Amperes]
45/44 = $\delta^{13}C$ Relative to PDB, Craig (1957) Corrected
46/44 = $\delta^{18}O$ Relative to UF Ref. Gas

Table 20.
COMPLETE LISTING OF CARBON-13 ANALYSES
OF NATURAL WATER IN THE ECONLOCKHATCHEE RIVER BASIN.

SITE	DATE	$\delta^{13}C$	MEAN	S.D.
FR0	9-16-93	-17.186	-17.21	0.02
		-17.197		
		-17.234		
FR1	9-16-93	-21.502	-21.41	0.09
		-21.444		
		-21.289		
FR2	9-16-93	-21.434	-21.31	0.09
		-21.252		
		-21.249		
FRF	9-16-93	-8.079	-7.98	0.09
		-7.852		
		-8.009		
HRR	9-16-93	-18.508	-18.68	0.17
		-18.855		
HR0	9-16-93	-16.055	-16.07	0.02
		-16.060		
		-16.095		
HR1	9-16-93	-23.591	-23.66	0.05
		-23.696		
		-23.696		
HR2	9-16-93	-18.562	-18.58	0.02
		-18.568		
		-18.604		
BDR	9-16-93	-14.535	-14.46	0.17
		-14.619		
		-14.234		
BD1	9-16-93	-11.311	-11.30	0.05
		-11.353		
		-11.239		
BR1	9-16-93	-19.330	-19.19	0.10
		-19.119		
		-19.125		
BR2	9-16-93	-19.020	-19.04	0.01
		-19.044		
		-19.043		

Note: S.D. = Standard Deviation
All units are ‰

APPENDIX C

SAMPLING METHODS AND COMPLETE LISTINGS FOR FIELD PARAMETERS AND OXYGEN ISOTOPE DATA

This section provides descriptions of sampling locations and protocols for in-situ physical and chemical determinations and sample collection. Descriptions of field sampling excursions and complete listings of in-situ field data and oxygen isotope analyses are also included. Table 21 provides descriptions of analytical parameters and abbreviations for column headings in subsequent tables.

Site Descriptions

Sampling locations are summarized in Table 22 and are described below. Consistent with USGS terminology (Rantz 1983a and 1983b), descriptions of the *left* and *right* shores of the river assume the observer is facing upstream. Table 23 summarizes location and depths of monitoring wells.

Alafaya

Samples were collected where Alafaya Trail crosses the Little Econlockhatchee River. A staff gage was installed near the right shore of the river approximately 200 ft. upstream of the Alafaya Trail bridge with an arbitrary datum. Monitoring wells were

Table 21.
DESCRIPTION OF COLUMN HEADINGS.

HEADING	UNITS	DESCRIPTION
AMT	[inch]	Depth of precipitation collected.
DATE	[dd-mmm-yy]	Day (numeric), month (alpha), and year (numeric) of sample collection.
DEPL	[ ]	Duration of deployment of precipitation collector: DY = Daily collection. WK = Weekly collection.
EC	[μScm^{-1}]	Electrical (specific) conductivity in micro-Siemens (micro-Mhos) per centimeter.
E(FLOW)	[ft^{3}sec^{-1}]	Point estimate of flow.
ELE	[ft]	River or groundwater elevation relative to a site-specific datum.
FLOW	[ft^{3}sec^{-1}]	River discharge, point measurement.
L95	[ ]	Lower 95 percent prediction limit.
MEAN	[‰]	Arithmetic mean of replicate O-18 analyses.
N	[ ]	Number of replicate O-18 analyses.
O-18	[‰]	Oxygen-18, δ^{18}O relative to SMOW.
S^2	[ ]	Point estimate of variance.
SITE	[ ]	Sampling location, identified by name or site code.
STD	[‰]	Standard deviation of the mean of replicate O-18 analyses.
TEMP	[°C]	Water temperature.
TIME	[hh:mm]	Hour and minute of sample collection.
U95	[ ]	Upper 95 percent prediction limit.

installed at distances of 36 (AL1) and 78 ft. (AL2) from the staff gage, aligned perpendicular to the shore.

Berry Dease

Samples were collected at the existing USGS gaging station (Station ID: 02233200) located where Berry Dease Road meets the Little Econlockhatchee River. A staff gage and continuous level recorder were located immediately downstream of an abandoned bridge embankment on the left shore. Elevations were referenced to the

Table 22.
SAMPLING SITES WITHIN THE ECONLOCKHATCHEE RIVER BASIN.

NAME	TYPE	CODE	ENABLED	DISABLED
Alafaya	River	ALR	19-Aug-92	19-Nov-93
	Surficial Aquifer	AL1		19-Nov-93
		AL2		19-Nov-93
Berry Dease	River	BDR		19-Nov-93
	Surficial Aquifer	BD1		19-Nov-93
		BD2		19-Nov-93
Buck Road	River	BRR		19-Nov-93
	Surficial Aquifer	BR1		19-Nov-93
		BR2		19-Nov-93
CEEFL	Precipitation	CE	17-Sep-92	30-May-93
Fawn Run	River	FRR		19-Nov-93
	Surficial Aquifer	FR0		19-Nov-93
		FR1		19-Nov-93
		FR2		19-Nov-93
	Floridan Aquifer	FRF		19-Nov-93
	Precipitation	FR	06-Sep-92	02-Jul-93
Hidden River	River	HRR		19-Nov-93
	Surficial Aquifer	HR0		19-Nov-93
		HR1		19-Nov-93
		HR2		19-Nov-93
	Floridan Aquifer	HRF		19-Nov-93
Old Lockwood Road	River	OLR		19-Nov-93
Route 419	River	R4R		19-Nov-93
Snow Hill Road	River	SHR		19-Nov-93
	Precipitation	SH	03-Sep-92	25-Nov-92
Whittington Road	Precipitation	WH	18-Aug-92	30-Oct-92

Table 23.
MONITORING WELL DETAILS.

WELL	LS	TOC	BOC	SHORE
AL1	8.13	9.69	2.54	36
AL2	9.43	10.88	3.32	78
BD0	3.72	7.29	-0.78	2
BD1	7.76	9.54	2.45	43
BR1	4.98	6.95	-0.74	20
BR2	6.48	7.72	0.14	70
FR0	3.20	6.80	-1.80	4
FR1	4.96	8.23	-0.38	19
FR2	6.72	9.22	0.46	37
HR0	1.24	4.12	-3.56	5
HR1	2.95	6.49	-2.51	35
HR2	7.72	9.14	5.02	64

Notes: Elevations are referenced to site-specific arbitrary datum

WELL = Site ID
LS = Land surface elevation [ft.]
TOC = Top-of-casing elevation [ft.]
BOC = Bottom-of-casing elevation (TOC-BOC=well depth) [ft]
SHORE = Distance from incised river channel shore [ft.]

USGS datum and flow measurements were provided by the USGS, based on their ongoing gaging program. Monitoring wells were installed at distances of 2 (BD0) and 43 ft. (BD1) from the shore, aligned perpendicular to the river.

Buck Road

A staff gage was placed on a downstream pier of the Buck Road bridge over the Little Econlockhatchee River with an arbitrary datum. Monitoring wells were referenced to this datum and were installed approximately 50 ft. downstream from Buck Road distances of 20 (BR1) and 70 ft. (BR2) perpendicular to the river shore.

CEEFL

Precipitation samples were collected at the Civil and Environmental Engineering Field Laboratory (CEEFL) located on the University of Central Florida campus.

Fawn Run

River, surficial aquifer, Floridan aquifer, and precipitation samples were collected where the Big Econlockhatchee River crosses the property of Steven Hastings, near the intersection of Fawn Run and Scrub Oak roads. A staff gage with arbitrary datum was placed near the right shore of the river. Monitoring wells were placed distances of 4 (FR0), 19 (FR1), and 37 ft. (FR2) from the river to sample the surficial aquifer. The Floridan aquifer was sampled from a water supply well (FRF) located approximately 2,000 ft. from the river at a depth of approximately 75 ft. below land surface.

Hidden River

River, surficial aquifer, and Floridan aquifer samples were collected near the intersection of the Big Econlockhatchee River and State Route 50 at the Hidden River Trailer Park. A staff gage was installed with arbitrary datum at a boat dock approximately 1,500 ft. downstream of Route 50 on the right shore. Monitoring wells were installed approximately 200 ft. upstream of the gage at distances of 5 (HR0), 35 (HR1), and 64 (HR2) ft. perpendicular to the shore. The Floridan aquifer was sampled from a water supply well (HRF) located approximately 1,000 ft. downstream from Route

50 and 750 ft. perpendicular to the right shore at a depth of approximately 100 ft. below land surface.

Michael's Dam

River samples were collected at Michael's Dam, located on the Little Econlockhatchee River in Blanchard Park, an Orange County, Florida facility. River elevations were recorded from an existing staff gage referenced to the National Geodetic Vertical Datum (NGVD). Water samples collected at this site were archived, but not analyzed for oxygen isotopes.

Old Lockwood Road

River samples were collected at the intersection of Old Lockwood Road and the Little Econlockhatchee River. River elevations were measured from the bridge deck and referenced to an arbitrary datum.

Seminole County Route 419

River samples were collected at the intersection of Route 419 and the Econlockhatchee River, approximately 1,000 ft. downstream of the confluence of the Little Econlockhatchee and Big Econlockhatchee Rivers. River elevations were measured from the bridge deck and referenced to an arbitrary datum. All measurements were made prior to construction of a new bridge to that site. On or about September 1993 the old bridge was taken out of service and replaced by the new bridge.

Snow Hill Road

River and precipitation samples were collected at the intersection of Snow Hill Road and the Econlockhatchee River. This is the farthest downstream that the river was monitored. River elevations were recorded from an existing USGS continuous gaging station (Station ID: 02233500). Flow measurements were provided by the USGS. Precipitation samples were collected in an open field approximately 1,000 ft. upstream from Snow Hill Road at a perpendicular distance of approximately 2,000 ft. from the right shore.

Whittington Drive

Precipitation samples were collected from an elevated platform located near the intersection of University Drive and Dean Road in the Little Econlockhatchee River Watershed.

Sampling Methods

River Monitoring

River samples were collected either from the shore at the staff gage or from the bridge deck. Water temperature and specific conductivity were measured in situ using a Yellow Springs Instruments Temperature/Level/Conductivity (TLC) meter. Calibration for conductivity and temperature were verified periodically using a National Institute of Standards & Technology calibrated thermometer and conductivity calibration standard solutions. River elevation, specific conductivity, water temperature, station ID, date, and time were recorded in a field book. Water samples collected for isotopic analysis were placed in 30 mL glass vials with Poly-Seal™ inverted-cone closures. Samples were labeled with the date and site identification code (*e.g.*, FRR 12-11-92).

Groundwater Monitoring

Monitoring wells were installed at five locations (Tables 22 and 23). Wells were constructed of 2 inch outside diameter, schedule 40, Polyvinyl Chloride™. The lower 2.5 ft. of the wells consisted of 0.01 inch factory slotted screen. Borings were cut using a hand auger. The well was placed in the auger hole and backfilled with 20/30 silica sand to a depth of approximately 0.5 ft. above the top of the screen. Bentonite pellets were packed approximately 1 ft. deep above the sand to seal the annulus of the auger hole. Native soil was packed into the annulus to land surface, as necessary. Wells FR0 and HR0 were completed to land surface with concrete grout. All wells were developed by pumping with a bailer volumes of approximately 20 gallons. Well elevations were referenced to staff gages using optical leveling techniques. Table 23 summarizes ground surface, top of casing (TOC), and total depth data for all wells.

For every site visit, water level in each well was measured using a fiberglass tape or the YSI TLC meter. The distance from TOC to water surface was subtracted from the previously-measured datum for TOC to arrive at the well water elevation relative to the site datum. For site visits requiring groundwater sampling, wells were pumped for at least 20 bailer volumes (approximately 5 casing volumes) to assure that formation water was being sampled. In-situ measurements for temperature and conductivity were made by direct placement of the TLC meter probe in the well. Water samples for isotopic analysis were collected in a bailer and poured into 30 mL glass vials. Sampling of the Floridan aquifer (HRF and FRF) consisted of collecting water from taps at wellheads.

Precipitation Monitoring

Precipitation was collected in 4 L Nalgene™ carboys covered with aluminum foil to minimize insolation. A Nalgene funnel (top diameter = 7.5 or 11.0 cm) was fixed to the mouth of each carboy. At Sites CEEFL, SHP, and FRP the carboys were mounted to vertical PVC pipes at elevations of approximately 3 ft. above ground surface. No aerial obstructions prevented free fall of precipitation into the funnels. At Site WHP carboys and a tipping-bucket rain gage were placed on a platform at an elevation of approximately 6 ft. above ground surface.

Rain collectors were checked either daily or weekly. Daily collectors were checked within 4 hours after the end of a storm event or twice daily during protracted storm events. Rain water was poured from carboys into graduated cylinders to measure total volume. Amount of rain was computed using the following conversion:

$$Amt = \left(\frac{4\ V\ [mL]}{\pi(D\ [cm])^2}\right) x\ \frac{cm^3}{mL}\ x\ \frac{inch}{2.54\ cm} \tag{70}$$

where Amt = Amount of precipitation [inch]
V = Precipitation volume collected [mL]
D = Diameter of funnel [cm]

Measurements made at Site WHP using both the tipping-bucket gage and direct measurement of rain volume were identical within 0.01 inches. Thus direct measurement of rain volume was considered an accurate method to measure rain amount at all sampling sites.

The possibility existed for isotopic fractionation to occur in the carboy prior to sample collection. Approximately 2 mL of vegetable oil was placed in carboys at every station to form a sheen over the sample and inhibit evaporation. To test for the effects of oil and evaporation, Sites CEEFL and WHP were equipped with rain collectors without oil. Table 24 summarizes the results of $\delta^{18}O$ analyses of side-by-side samples. Results indicated that the average difference in $\delta^{18}O$ between samples preserved and unpreserved with oil was $-0.04 \pm 0.14‰$ ($n=10$), which was well below the precision of the $\delta^{18}O$ test ($1\sigma=0.1‰$). Thus it was concluded that evaporation was insignificant for the period of time samples were held in the carboys and that the presence of the oil had no effect on the isotopic composition of the sample.

After measurement of rain volume, precipitation was filtered through wads of Kimwipes™ in a Nalgene funnel to remove excess oil. The filtrate was collected in 30 mL glass vials. At least two field aliquots (*splits*) were collected from each rain sample. Field notes were made of date, time, site name, rain volume in mL, funnel size, and whether or not the sample was preserved with oil. Each Nalgene carboy and funnel was replaced with a clean, dry set.

Stream Gaging

This dissertation uses flow data collected at Sites BDR, SHR, HRR, and FRR. Sites BDR and SHR were permanent USGS gauging stations and flow data were provided by the USGS for the time periods required. Rating curves relating flow and stage (river elevation) were developed for Sites HRR and FRR to support this dissertation research. Methods conformed to standard USGS protocols (Rantz 1983a and 1983b).

Table 24.
COMPARISON OF RAINFALL SAMPLES COLLECTED WITH AND WITHOUT OIL EVAPORATION INHIBITOR.

SITE	DATE	O	X	X-O
WH	02-OCT-92	-1.21	-1.13	0.08
WH	30-OCT-92	-1.89	-2.29	-0.40
CE	12-FEB-93	-2.66	-2.70	-0.04
CE	23-FEB-93	-3.65	-3.60	0.05
CE	27-FEB-93	-0.48	-0.50	-0.02
CE	04-MAR-93	-2.74	-2.88	-0.14
CE	16-MAR-93	-6.16	-6.16	0.00
CE	19-MAR-93	-6.65	-6.57	0.08
CE	02-APR-93	-1.85	-1.85	0.00
CE	16-APR-93	-2.34	-2.48	-0.14
CE	30-MAY-93	-5.00	-4.96	0.04
			n =	10
			Mean =	-0.04
			S.D. =	0.14

Note: O = δ^{18}O of sample preserved with oil [‰]
X = δ^{18}O of unpreserved sample [‰]

Velocity (v), depth (z), and distance from shore (x) were measured at n positions along a fixed transect at each site, dividing the transect into n imaginary partitions (Figure 50). Velocity was measured using a Price Pygmy meter attached to a steel rod. If the depth was less than 2.0 ft. a single velocity measurement was made at a depth of 0.6 times the total depth, measured from the river bed. If the depth was greater than 2.0 ft. velocity measurements were made at depths of 0.2 and 0.8 times the total depth and averaged. The area of each partition i was computed to be

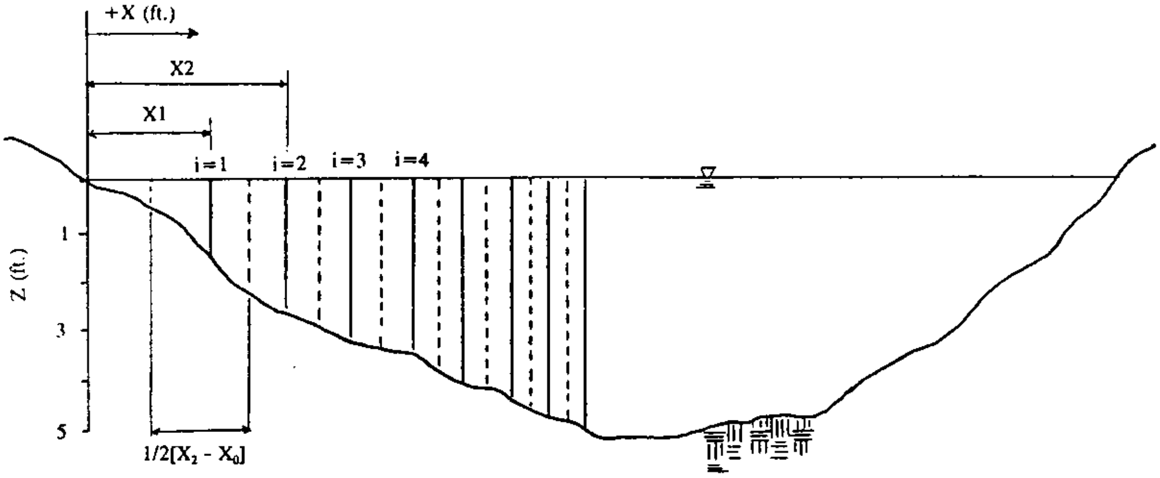

Figure 50. Stream cross section for flow computation.

$$A_i = \left[\frac{X_i - X_{i-1}}{2} + \frac{X_{i+1} - X_i}{2}\right] Z_i = \frac{1}{2}[X_{i+1} - X_{i-1}] Z_i \tag{71}$$

The flow in each partition equals the velocity multiplied by partition area ($Q_i = V_i A_i$) and the cross-sectional area and discharge for the complete cross section were computed using the following equations:

$$\begin{aligned} A &= \sum_{i=1}^{n} A_i \\ Q &= \sum_{i=1}^{n} V_i A_i \end{aligned} \tag{72}$$

A sufficient number of velocity measurements was made for each flow measurement to assure that each single flow computation, Q_i, constituted *no* greater than 5 percent of total flow. This required velocity measurements at an average of 35 points along the transect for each flow measurement. River elevation at staff gages was recorded before and after flow measurements were made.

Rating curves were developed to relate area and flow as functions of river elevation. Statistical analysis revealed that power transformations of linear regression equations could be fitted to the rating curve data. Table 25 provides complete listings of gaging data with supporting regression analysis data. Plots of the gaging data with 95% prediction limits are provided in Chapter 4 of the main text of this document (Figure 34).

Complete calculations for the Hidden River flow rating curve are presented in Table 26. Column 1 lists the date of the particular gaging event. Columns 2 and 3 list the corresponding river elevation, z, and measured flow, Q. Because river elevation

Table 25.
COMPLETE LISTING OF GAGING RECORDS FOR
HIDDEN RIVER AND FAWN RUN.

Site: HRR

DATE	ELE	FLOW	E(FLOW)	S^2	U95	L95
18-May-93	-1.41	1.3	1.4	5.36	6.27	-3.50
11-May-93	-0.96	7.4	7.2	5.05	11.97	2.49
31-May-93	-0.49	17.8	15.2	4.80	19.84	10.59
07-Jun-93	-0.49	14.7	15.4	4.79	20.02	10.78
01-Jun-93	0.20	31.5	29.6	4.56	34.08	25.08
05-Jun-93	0.28	31.3	31.3	4.54	35.77	26.78
04-Jun-93	0.43	35.3	34.7	4.51	39.21	30.25
02-Jun-93	0.58	41.2	38.3	4.49	42.75	33.81
13-Nov-92	0.63	33.3	39.6	4.48	44.07	35.14
03-Jun-93	0.63	38.9	39.6	4.48	44.07	35.14
09-Dec-92	1.80	70.1	70.4	4.58	74.87	65.84
10-Dec-92	1.91	72.8	73.3	4.61	77.87	68.80
08-Dec-92	1.95	74.7	74.5	4.63	79.02	69.94
11-Dec-92	2.06	77.4	77.8	4.66	82.35	73.23
07-Dec-92	2.07	78.4	77.9	4.67	82.49	73.38
12-Dec-92	2.15	77.0	80.3	4.70	84.83	75.69
13-Dec-92	2.15	80.4	80.4	4.70	84.98	75.83
06-Dec-92	2.20	81.8	81.7	4.72	86.31	77.14
05-Dec-92	2.36	87.7	86.6	4.79	91.22	81.99

Table 25.
COMPLETE LISTING OF GAGING RECORDS FOR
HIDDEN RIVER AND FAWN RUN (Continued).

Site: HRR

DATE	ELE	AREA	E(AREA)	S^2	U95	L95
11-May-93	-0.96	4.0	3.5	141.60	28.75	-21.71
31-May-93	-0.49	7.1	9.8	128.26	33.86	-14.16
07-Jun-93	-0.49	14.9	10.0	128.01	34.01	-13.96
01-Jun-93	0.20	16.9	26.2	114.73	48.92	3.51
05-Jun-93	0.28	30.7	28.5	113.72	51.12	5.90
04-Jun-93	0.43	32.6	33.4	111.99	55.85	10.98
02-Jun-93	0.58	24.5	38.8	110.61	61.05	16.45
03-Jun-93	0.63	39.6	40.8	110.19	63.07	18.56
13-Nov-92	0.63	65.4	40.8	110.19	63.07	18.56
09-Dec-92	1.80	86.3	99.2	112.72	121.75	76.73
10-Dec-92	1.91	117.8	105.9	114.01	128.52	83.25
08-Dec-92	1.95	123.9	108.5	114.55	131.16	85.78
11-Dec-92	2.06	121.4	116.1	116.24	138.97	93.26
07-Dec-92	2.07	124.5	116.5	116.31	139.32	93.59
12-Dec-92	2.15	129.4	122.0	117.62	144.95	98.96
13-Dec-92	2.15	127.6	122.3	117.70	145.30	99.30
06-Dec-92	2.20	126.1	125.5	118.48	148.54	102.38
05-Dec-92	2.36	123.4	137.4	121.63	160.80	114.04

Table 25.
COMPLETE LISTING OF GAGING RECORDS FOR HIDDEN RIVER AND FAWN RUN (Continued).

Site: FRR

DATE	ELE	FLOW	E(FLOW)	S^2	U95	L95
26-May-93	-1.26	1.1	1.0	22.04	10.84	-8.81
18-May-93	-1.03	3.3	4.0	21.47	13.73	-5.67
11-May-93	-0.65	9.3	11.0	20.67	20.50	1.47
07-Jun-93	-0.15	25.4	22.7	19.88	32.00	13.33
07-Jun-93	-0.06	26.7	25.1	19.76	34.45	15.84
06-Jun-93	0.15	33.3	30.8	19.54	40.01	21.50
01-Jun-93	0.26	34.8	33.9	19.45	43.12	24.66
05-Jun-93	0.40	42.7	38.0	19.35	47.23	28.81
04-Jun-93	0.60	47.4	44.0	19.24	53.17	34.81
03-Jun-93	0.62	50.2	44.8	19.23	53.96	35.60
31-May-93	0.71	44.3	47.6	19.20	56.80	38.46
13-Nov-92	0.78	42.0	49.9	19.19	59.06	40.72
10-Dec-92	1.80	88.1	86.0	19.61	95.26	76.72
08-Dec-92	1.81	85.2	86.4	19.62	95.64	77.10
07-Dec-92	1.92	94.1	90.6	19.74	99.90	81.30
12-Dec-92	1.95	95.5	91.6	19.77	100.88	82.27
13-Dec-92	1.99	88.0	93.3	19.83	102.64	84.00
11-Dec-92	2.01	94.9	94.1	19.85	103.43	84.78
06-Dec-92	2.09	86.1	97.1	19.95	106.40	87.71
05-Dec-92	2.19	102.1	101.2	20.10	110.61	91.85
25-Jul-93	3.63	160.3	163.1	23.44	173.24	152.97

Table 25.
COMPLETE LISTING OF GAGING RECORDS FOR HIDDEN RIVER AND FAWN RUN (Concluded).

Site: FRR

DATE	ELE	AREA	E(AREA)	S^2	U95	L95
26-May-93	-1.26	1.6	1.4	2.17	4.51	-1.71
18-May-93	-1.03	4.3	4.8	2.10	7.89	1.77
11-May-93	-0.65	10.9	11.9	2.01	14.88	8.91
07-Jun-93	-0.15	24.4	22.8	1.92	25.74	19.90
07-Jun-93	-0.06	24.1	25.1	1.90	27.97	22.15
06-Jun-93	0.15	30.7	30.0	1.88	32.92	27.14
01-Jun-93	0.26	32.1	32.8	1.87	35.66	29.89
05-Jun-93	0.40	38.0	36.3	1.86	39.22	33.46
04-Jun-93	0.60	42.2	41.4	1.85	44.31	38.56
03-Jun-93	0.62	43.6	42.1	1.85	44.97	39.22
31-May-93	0.71	43.8	44.5	1.85	47.37	41.63
13-Nov-92	0.78	44.3	46.4	1.85	49.27	43.52
08-Dec-92	1.81	76.3	76.0	1.94	78.94	73.07
07-Dec-92	1.92	81.3	79.3	1.96	82.30	76.39
12-Dec-92	1.95	82.5	80.1	1.96	83.06	77.15
13-Dec-92	1.99	80.5	81.5	1.97	84.45	78.52
11-Dec-92	2.01	83.4	82.1	1.98	85.06	79.13
06-Dec-92	2.09	83.1	84.4	1.99	87.38	81.43
05-Dec-92	2.19	87.4	87.7	2.01	90.66	84.67

Table 26.
CALCULATIONS FOR RATING CURVE DEVELOPMENT AT STATION HR.

HRR Date (1)	Z Ele. (ft) (2)	Q Flow (cfs) (3)	ln Ele.+1.6 (4)	ln Flow (5)	Qhat E(Flow) (cfs) (6)	(Z-Zbar)^2 (7)	(Q-Qhat)^2 (8)	s^2{(Qh(new)} (9)	Upper 95 (10)	Lower 95 (11)
18-May-93	-1.41	1.3	-1.66	0.27	1.4	5.6	0.0	5.36	6.27	-3.50
11-May-93	-0.96	7.4	-0.45	2.00	7.2	3.6	0.0	5.05	11.97	2.49
31-May-93	-0.49	17.8	0.10	2.88	15.2	2.1	6.7	4.80	19.84	10.59
07-Jun-93	-0.49	14.7	0.11	2.68	15.4	2.1	0.6	4.79	20.02	10.78
01-Jun-93	0.20	31.5	0.59	3.45	29.6	0.8	3.6	4.56	34.08	25.08
05-Jun-93	0.28	31.3	0.63	3.44	31.3	0.5	0.0	4.54	35.77	26.78
04-Jun-93	0.43	35.3	0.71	3.57	34.7	0.3	0.4	4.51	39.21	30.25
02-Jun-93	0.58	41.2	0.78	3.72	38.3	0.1	8.2	4.49	42.75	33.81
13-Nov-92	0.63	33.3	0.80	3.51	39.6	0.1	39.5	4 48	44.07	35 14
03-Jun-93	0.63	38.9	0.80	3.66	39.6	0.1	0.6	4.48	44.07	35 14
09-Dec-92	1.80	70.1	1.22	4.25	70.4	0.7	0.1	4.58	74.87	65.84
10-Dec-92	1.91	72.8	1.25	4.29	73.3	0.9	0.3	4.61	77.87	68.80
08-Dec-92	1.95	74.7	1.27	4.31	74.5	1.0	0.1	4.63	79.02	69.94
11-Dec-92	2.06	77.4	1.30	4.35	77.8	1.2	0.1	4.66	82.35	73.23
07-Dec-92	2.07	78.4	1.30	4.36	77.9	1.2	0.2	4.67	82.49	73.38
12-Dec-92	2.15	77.0	1.32	4.34	80.3	1.4	10 6	4.70	84.83	75 69
13-Dec-92	2.15	80.4	1.32	4.39	80.4	1.4	0.0	4 70	84.98	75 83
06-Dec-92	2.20	81.8	1.33	4.40	81.7	1.6	0.0	4.72	86.31	77 14
05-Dec-92	2.36	87.7	1.38	4.47	86.6	2.0	1.2	4 79	91.22	81 99
					Sum =	26.5098	72.1311			

Indep =	ln(Q) = Column 5			
Dep =	ln(Ele.+1 6) = Column 4		MSE =	4.2430
	Regression Output		t(0.975,17)	2.11
Constant		2 5862	Ybar =	0.9479
Std Err of Q Est		0.0652		
R Squared		0.9964		
No of Observations		19		
Degrees of Freedom		17		

(Column 2) was log transformed, an arbitrary offset was added to the elevation to assure that all elevation values were greater than zero. This offset was adjusted to minimize the residual sum of squares (SSE). Column 4 adds an offset of 1.6 to river elevation and takes the natural log (ln) of that value. Column 5 is the natural log of flow (Column 3).

Linear regression analysis using the method of least squares was performed with log-transformed river elevation (Column 4) as the independent variable and log-flow (Column 5) as the dependent variable, producing the equation:

$$\ln(Q) = 2.5862 + 1.3625\ln(z+1.6) \tag{73}$$

which can be simplified to

$$\hat{Q} = 13.2792[z + 1.6]^{1.3625} \tag{74}$$

Column 6 solves Equation 74 to provide E(Q), or $\hat{Q}$, a point estimate of flow at a given stage.

Columns 7 through 11 were used to compute prediction intervals using the following equations (Neter, *et al.*, 1990):

$$PI = \hat{Q} \pm t(1 - \alpha/2;\, n-2)\, s\{\hat{Q}\} \tag{75}$$

$$s^2\{Q_{h(new)}\} = MSE\left[1 + \frac{1}{n} + \frac{(z_{h(new)} - \bar{z})^2}{\sum (z_i - \bar{z})^2}\right] \tag{76}$$

$$MSE = \frac{\sum (Q_i - \hat{Q}_i)^2}{n-2} \tag{77}$$

The *h(new)* subscript is added in Equations 76 and 77 to distinguish those values of z and Q as being outside the set of values of source data, which was designated i = 1,...,n. In this case, the same data are used to produce the regression model and to compute prediction limits, but the utility of the model lies in the capability to predict a large number of new values of Q from a relatively small set of z and Q pairs.

Columns 7 and 8 list supporting calculations for Equations 76 and 77. Column 9 lists point estimates of variance for each gaging observation. Columns 10 and 11 list the solutions of Equation 75 for the upper and lower 95% prediction limits. For Hidden River, the general equation for 95% prediction limits was

$$PI = \hat{Q}_h(new) \pm 2.11\sqrt{4.4663 + \frac{(z-0.9479)^2}{6.2479}} \tag{78}$$

where $\hat{Q}_{h(new)}$ was computed using Equation 74.

Sampling Excursions and Data Listings

Most field data were collected during three sampling excursions, identified in this dissertation as Fall 1992, Winter 1992, and Spring 1993. Additional sampling was conducted to provide specific data, such as a basin-wide sampling event on November 19, 1993. Table 27 provides complete listings for precipitation data, Table 28 provides complete listings for Fall and Winter 1992 data, and Table 29 provides complete listings of Spring 1993 data.

Fall 1992 monitoring started on September 3, 1992 and ended on October 22, 1992 and consisted of daily and weekly sampling at all extant stations. Daily measurements were made of precipitation; monitoring well elevations; and river

Table 27.
COMPLETE LISTING OF PRECIPITATION AMOUNT
AND OXYGEN-18 DATA.

DATE	TIME	SITE	AMT	DEPL	N	MEAN	STD
19-Aug-92	08:50	WH1	1.86	DY	1	-3.86	
19-Aug-92	08:50	WH2	1.86	DY			
20-Aug-92	07:17	WH1	0.51	DY	2	-3.10	0.04
20-Aug-92	07:17	WH2	0.51	DY			
21-Aug-92	05:00	WH1	1.42	DY	1	-2.95	
21-Aug-92	05:00	WH2	1.42	DY			
22-Aug-92	17:30	WH1	0.86	DY			
22-Aug-92	17:30	WH2	0.86	DY	3	-2.50	0.02
23-Aug-92	12:30	WH2	0.04	DY	1	-0.57	
23-Aug-92	19:00	WH3	0.25	DY	2	-2.26	0.03
25-Aug-92	19:30	WH1	0.27	DY	1	-0.50	
25-Aug-92	19:30	WH2	0.27	DY			
29-Aug-92	18:50	WH1	0.38	DY	2	-3.11	0.03
29-Aug-92	18:50	WH2	0.38	DY			
31-Aug-92	20:00	WH1	0.16	DY	1	-2.27	
31-Aug-92	20:00	WH2	0.16	DY			
01-Sep-92	19:25	WH1	0.78	DY			
01-Sep-92	19:25	WH2	0.78	DY	1	-1.47	
03-Sep-92	19:40	WH1	0.16	DY	1	-1.36	
04-Sep-92	18:00	WH1	0.10	DY	1	-0.25	
07-Sep-92	08:40	WH1	0.33	DY	2	-0.78	0.06
08-Sep-92	16:03	FRP	1.00	DY	2	-1.32	0.03
08-Sep-92	19:00	WH1	0.43	DY	1	-2.36	
11-Sep-92	08:46	SHP	0.71	WK	1	-2.56	
14-Sep-92	09:19	FRP	0.29	DY	2	-3.84	0.09
14-Sep-92	11:44	WH1	0.24	DY	1	-3.33	
15-Sep-92		WH1	0.21	DY	2	-2.90	0.16
15-Sep-92	10:20	FRP	0.52	DY	1	-2.43	
17-Sep-92		WH1	0.27	DY	1	-1.79	
18-Sep-92	09:05	SHP	0.49	WK	1	-2.43	
18-Sep-92	12:08	WH1	0.11	DY			
19-Sep-92	22:00	WH1	1.08	DY	1	-2.17	
20-Sep-92	07:30	CEP	0.34	DY	1	-3.62	
20-Sep-92	08:49	FRP	1.10	DY	1	-2.67	
20-Sep-92	10:00	SHP	0.28	DY	1	-2.42	
21-Sep-92	19:30	WH1	0.27	DY	2	-2.43	0.07
21-Sep-92	19:30	WH2	0.27	DY			
22-Sep-92	07:30	CEP	0.21	DY	1	-2.20	
23-Sep-92	07:23	CEP	0.35	DY	1	-3.93	
23-Sep-92	08:15	WH1	1.23	DY	1	-3.32	

Table 27.
COMPLETE LISTING OF PRECIPITATION AMOUNT AND OXYGEN-18 DATA (Continued).

DATE	TIME	SITE	AMT	DEPL	N	MEAN	STD
23-Sep-92	10:15	FRP	1.49	DY	1	-3.36	
23-Sep-92	22:50	WH2	0.66	DY	2	-2.84	0.08
24-Sep-92	07:21	CEP	0.29	DY	1	-2.59	
25-Sep-92	09:00	SHP	0.48	WK	1	-2.92	
25-Sep-92	15:00	CEP	0.19	DY	1	-2.46	
26-Sep-92	14:45	FRP	0.17	DY	1	-1.92	
27-Sep-92	07:00	WH1	0.40	DY	1	-2.30	
27-Sep-92	08:00	CEP	0.23	DY	2	-1.46	0.05
27-Sep-92	12:12	WH2	0.24	DY	1	-0.95	
28-Sep-92	12:12	FRP	0.21	DY	1	-1.18	
28-Sep-92	17:00	WH1	0.11	DY	1	-2.03	
29-Sep-92	06:45	CEP	0.33	DY	1	-3.02	
29-Sep-92	08:20	FRP	0.06	DY	1	-2.64	
29-Sep-92	18:00	WH1	0.44	DY	3	-6.66	0.14
30-Sep-92	07:00	CEP	0.68	DY	1	-6.57	
30-Sep-92	09:50	FRP	0.82	DY	1	-5.09	
02-Oct-92	09:08	SHP	0.86	WK	1	-3.27	
02-Oct-92	10:50	FRP	0.12	DY	1	-1.23	
02-Oct-92	16:40	CEP	0.19	DY	1	-1.09	
02-Oct-92	17:30	WHO	0.25	DY	1	-1.21	
02-Oct-92	17:30	WHX	0.26	DY	1	-1.13	
03-Oct-92	07:00	W1O	1.28	DY			
03-Oct-92	07:00	W1X	1.28	DY	2	-2.24	0.04
03-Oct-92	08:05	CE1	1.18	DY	1	-2.08	
03-Oct-92	09:26	SHP	1.62	DY	1	-2.15	
03-Oct-92	10:30	FRP	1.48	DY	1	-2.27	
03-Oct-92	14:00	CE2	0.59	DY	1	-2.48	
03-Oct-92	14:20	W2O	0.92	DY			
03-Oct-92	14:20	W2X	0.92	DY	1	-2.62	
04-Oct-92	07:50	W1X	0.54	DY	1	-3.52	
04-Oct-92	07:50	W1O	0.54	DY			
04-Oct-92	09:00	CE1	0.71	DY	1	-3.58	
04-Oct-92	11:31	SHP	1.03	DY	1	-2.89	
04-Oct-92	12:53	FRP	1.10	DY	1	-3.29	0.09
05-Oct-92	14:00	W1X	0.09		1	-5.26	
05-Oct-92	14:00	W10	0.09				
07-Oct-92	08:23	FRP	0.55	DY	1	-2.19	
07-Oct-92	11:25	W1X	0.64	DY	2	-2.16	0.00
07-Oct-92	11:25	W1O	0.64	DY			
07-Oct-92	14:00	CE1	0.77	DY	1	-2.75	

Table 27.
COMPLETE LISTING OF PRECIPITATION AMOUNT AND OXYGEN-18 DATA (Continued).

DATE	TIME	SITE	AMT	DEPL	N	MEAN	STD
09-Oct-92	11:00	SHP	0.71		1	-2.79	
09-Oct-92	11:50	FRP	0.80		1	-1.96	
09-Oct-92	16:10	CEP	0.92		1	-2.19	
11-Oct-92	11:05	SHP	0.85		1	-5.30	
11-Oct-92	12:02	FRP	1.22		1	-6.10	
11-Oct-92	13:00	CEP	1.62		1	-6.06	
11-Oct-92	14:00	W1X	1.51		2	-5.36	0.02
11-Oct-92	14:00	W1O	1.51				
30-Oct-92	08:30	W1X	0.25	WK	1	-2.29	
30-Oct-92	08:30	W1O	0.29	WK	1	-1.89	
30-Oct-92	10:45	FRP	0.32	WK	2	-2.08	0.04
30-Oct-92	12:27	SHP	0.61	WK	1	-2.37	
30-Oct-92	15:52	CEP	0.45	WK	1	-2.27	
06-Nov-92	07:00	CEP	0.31	WK			
06-Nov-92	09:07	FRP	0.37	WK			
23-Nov-92	10:10	FRP	1.27	WK			
25-Nov-92	14:39	SHP	2.93	WK			
25-Nov-92	15:00	FRP	0.81	WK			
30-Nov-92	11:45	FRP	0.14	WK			
10-Dec-92	14:00	FRP	0.63	DY	2	-4.70	0.04
16-Jan-93		CEP			2	-5.88	0.04
27-Jan-93		CEO					
27-Jan-93		CEX					
07-Feb-93		CEO					
07-Feb-93		CEX					
10-Feb-93		CEO					
10-Feb-93		CEX					
12-Feb-93		CEO	0.44		2	-2.70	0.08
12-Feb-93		CEX	0.45		1	-2.66	
16-Feb-93		FRP	0.17				
23-Feb-93		CEO	1.01		1	-3.60	
23-Feb-93		CEX	1.00		1	-3.65	
27-Feb-93		CEO	0.62		2	-0.50	0.04
27-Feb-93		CEX	0.61		1	-0.48	
04-Mar-93		CEO	1.05		1	-2.88	
04-Mar-93		CEX	1.01		1	-2.74	
16-Mar-93		CEO	1.43		1	-6.16	
16-Mar-93		CEX	1.86		1	-6.16	
19-Mar-93		CEO	0.53		1	-6.65	
19-Mar-93		CEX	0.53		1	-6.57	

Table 27.
COMPLETE LISTING OF PRECIPITATION AMOUNT
AND OXYGEN-18 DATA (Concluded).

DATE	TIME	SITE	AMT	DEPL	N	MEAN	STD
22-Mar-93		CEO	0.65				
22-Mar-93		CEX	0.64				
25-Mar-93		CEO	0.26				
25-Mar-93		CEX	0.26				
30-Mar-93		FRP	1.36				
02-Apr-93		CEO	1.24		2	-1.85	0.00
02-Apr-93		CEX	1.22		1	-1.85	
05-Apr-93		CEO	0.40				
05-Apr-93		CEX	0.40				
13-Apr-93		FRP	1.13				
16-Apr-93		CEO	0.62		2	-2.34	0.02
16-Apr-93		CEX	0.63		2	-2.48	0.01
30-Apr-93		FRP	0.49				
05-May-93		FRP	0.08				
29-May-93	10:00	CEO	0.11		1	-5.00	MISLABLD
29-May-93	10:00	CEX	0.11		1	-4.96	30MAY
29-May-93	10:00	FRP	0.30		2	-1.90	0.04
30-May-93	10:00	CEO	3.77				
30-May-93	10:00	CEX	3.80				
30-May-93	11:00	FRP	2.59		3	-4.49	0.09
31-May-93	09:30	FRP	0.79		2	-3.78	0.04

Table 28.

COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA.

DATE	ELE	O-18	EC	TEMP
Site: ALR				
28-Aug-92	5.60	-1.71	139	27.7
03-Sep-92	4.22		156	26.3
04-Sep-92	5.42	-1.58	181	26.6
05-Sep-92	5.79		176	27.1
06-Sep-92	5.34		171	26.7
07-Sep-92	4.72		166	26.7
08-Sep-92	4.60		200	27.4
09-Sep-92	5.83		161	26.5
10-Sep-92	4.67		161	26.6
11-Sep-92	4.55	-1.60	212	26.7
12-Sep-92	4.47		197	27.0
13-Sep-92	4.11		182	26.4
14-Sep-92	3.99		184	26.0
15-Sep-92	4.21		154	26.3
16-Sep-92	4.49		180	26.4
17-Sep-92	4.35		181	26.3
18-Sep-92	4.17	-1.74	182	26.7
19-Sep-92	3.65		169	26.4
20-Sep-92	6.49		152	26.2
21-Sep-92	6.23		145	26.3
22-Sep-92	6.69		130	26.8
24-Sep-92	7.15		122	26.5
25-Sep-92	6.99	-2.14	130	26.6
26-Sep-92	7.04		129	26.4
27-Sep-92	7.17		126	25.9
28-Sep-92	6.49		136	26.1
30-Sep-92	6.26		153	25.4
01-Oct-92	6.21		155	24.9
02-Oct-92	5.83	-2.07	127	23.9
03-Oct-92	6.13		134	
04-Oct-92	7.58		143	24.3
05-Oct-92	7.74		124	24.3
06-Oct-92	7.43		110	23.3
07-Oct-92	7.11		123	22.9
08-Oct-92	7.14		134	24.0
09-Oct-92	6.95	-2.18	120	24.0
10-Oct-92	6.68		146	25.0
11-Oct-92	6.57	-1.99	145	24.9
12-Oct-92	6.93	-2.16	153	23.6
13-Oct-92	6.72	-2.47	142	22.0
14-Oct-92	6.51	-2.23	129	21.8
15-Oct-92	5.92	-2.10	146	22.0
16-Oct-92	5.50	-2.00	164	22.9
17-Oct-92	4.71	-1.99	161	22.2
18-Oct-92	4.68	-2.03	177	22.4
19-Oct-92	4.46	-1.93	165	22.2
20-Oct-92	4.12	-1.95	159	21.2
21-Oct-92	3.82	-1.91	196	
22-Oct-92	3.54	-1.86	217	21.9
30-Oct-92	2.70	-1.78	215	23.3
04-Nov-92	2.44		235	24.9
06-Nov-92	2.61		208	24.5
13-Nov-92	2.02			23.0
16-Nov-92	1.76		233	20.4
23-Nov-92	2.21		226	23.1
30-Nov-92	3.73		158	17.5
09-Dec-92	2.28		230	18.3
10-Dec-92	2.30		227	18.5
11-Dec-92	3.06		207	18.1
12-Dec-92	2.79		197	16.0
13-Dec-92	2.36		171	15.5
14-Dec-92	2.28		201	16.3
15-Dec-92	2.16		196	16.8
Site: AL1				
19-Aug-92	8.50			
28-Aug-92	6.83	-3.34	153	25.8
03-Sep-92	6.13			
04-Sep-92	6.44	-1.65	142	25.5
05-Sep-92	6.60			
06-Sep-92	6.58			
07-Sep-92	6.25			
08-Sep-92	6.97			
09-Sep-92	6.57			
10-Sep-92	6.29			
11-Sep-92	6.13	-1.97	161	25.6
12-Sep-92	6.02			
13-Sep-92	5.96			
14-Sep-92	5.84			
15-Sep-92	5.88			

Table 28.
COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE	ELE	O-18	EC	TEMP
16-Sep-92	5.93			
17-Sep-92	5.90			
18-Sep-92	5.86	-1.92	161	26.4
19-Sep-92	5.75			
20-Sep-92	6.96			
21-Sep-92	6.96			
22-Sep-92	7.19			
24-Sep-92	7.54			
25-Sep-92	7.49	-2.24	178	26.2
26-Sep-92	7.40			
27-Sep-92	7.30			
28-Sep-92	7.17			
30-Sep-92	7.07			
01-Oct-92	6.91			
02-Oct-92	6.93	-2.35	147	25.5
03-Oct-92	7.60			
04-Oct-92	7.77			
05-Oct-92	7.86		139	25.1
06-Oct-92	7.72			
07-Oct-92	7.66			
08-Oct-92	7.57			
09-Oct-92	7.58	-2.64	161	25.4
10-Oct-92	7.28			
11-Oct-92	7.64			
12-Oct-92	7.61			
13-Oct-92	7.47			
14-Oct-92	7.12			
15-Oct-92	6.91			
16-Oct-92	6.69	-2.03	137	24.8
17-Oct-92	6.42			
18-Oct-92	6.24			
19-Oct-92	6.08		96	24.0
20-Oct-92	6.07			
21-Oct-92	5.74			
22-Oct-92	5.55		109	23.5
30-Oct-92	4.99	-1.79	141	24.0
04-Nov-92	4.50		142	24.4
06-Nov-92	3.78		169	23.8
13-Nov-92	3.94			
16-Nov-92	3.74		159	23.7
23-Nov-92	3.84		160	26.0
30-Nov-92	5.65		111	22.1
09-Dec-92	4.54		154	21.1
10-Dec-92	4.48		157	21.2
11-Dec-92	3.73		134	20.2
12-Dec-92	4.74	-1.87	138	19.7
13-Dec-92	4.60		127	20.4
14-Dec-92	4.45		143	21.1
15-Dec-92	4.38		140	21.2
	Site:	**AL2**		
19-Aug-92	8.77			
28-Aug-92	8.01	-2.80	145	29.0
03-Sep-92	7.57			
04-Sep-92	7.74	-1.65	169	28.2
05-Sep-92	7.87			
06-Sep-92	7.74			
07-Sep-92	7.53			
08-Sep-92	8.35			
09-Sep-92	7.92			
10-Sep-92	7.64			
11-Sep-92	7.55	-1.64	183	29.2
12-Sep-92	7.42			
13-Sep-92	7.36			
14-Sep-92	7.36			
15-Sep-92	7.34			
16-Sep-92	7.32			
17-Sep-92	7.22			
18-Sep-92	7.24	-1.60	174	29.0
19-Sep-92	7.13			
20-Sep-92	8.16			
21-Sep-92	8.06			
22-Sep-92	8.06			
24-Sep-92	8.34			
25-Sep-92	8.26	-1.61	178	28.1
26-Sep-92	8.24			
27-Sep-92	8.14			
28-Sep-92	8.04			
30-Sep-92	8.12			
01-Oct-92	7.91			
02-Oct-92	7.91	-2.33	163	27.4

Table 28.
COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE	ELE	O-18	EC	TEMP
03-Oct-92	8.73			
04-Oct-92	8.90			
05-Oct-92	8.71		171	27.9
06-Oct-92	8.65			
07-Oct-92	8.62			
08-Oct-92	8.42			
09-Oct-92	8.58	-2.41	176	27.6
10-Oct-92	8.26			
11-Oct-92	8.94			
12-Oct-92	8.70			
13-Oct-92	8.47			
14-Oct-92	8.15			
15-Oct-92	7.97			
16-Oct-92	7.80	-1.87	162	26.5
17-Oct-92	7.63			
18-Oct-92	7.50			
19-Oct-92	7.38		168	24.9
20-Oct-92	7.15			
21-Oct-92	7.63			
22-Oct-92	5.98		163	24.5
30-Oct-92	6.44	-2.34	209	24.5
04-Nov-92	5.64		209	23.5
06-Nov-92	5.90		223	22.7
13-Nov-92	4.94		217	22.7
16-Nov-92	4.59		221	23.4
23-Nov-92	5.05		234	22.9
30-Nov-92	6.96		246	22.7
09-Dec-92	5.84		167	21.3
10-Dec-92	5.78		164	21.7
11-Dec-92	6.17		153	21.3
12-Dec-92	5.14		160	20.8
13-Dec-92	6.05		147	20.3
14-Dec-92	5.85		172	21.0
15-Dec-92	5.61		174	20.1
Site: BDR				
28-Aug-92	7.37	-1.73	117	26.5
03-Sep-92	7.25	-1.77	132	26.2
04-Sep-92	7.64	-1.72	113	26.0
05-Sep-92	7.52	-1.75	123	26.2
06-Sep-92	7.36	-1.71	131	26.5
07-Sep-92	7.24	-1.69	135	27.0
08-Sep-92	7.29	-1.58	136	26.8
09-Sep-92	7.28	-1.70	135	25.7
10-Sep-92	7.21	-1.54	138	25.9
11-Sep-92	7.36	-1.64	126	26.0
12-Sep-92	7.29	-1.82	124	25.9
13-Sep-92	7.27	-1.59	130	26.1
14-Sep-92	7.35	-1.74	121	24.7
15-Sep-92	7.45	-1.63	122	25.0
16-Sep-92	7.32	-1.62	123	25.9
17-Sep-92	7.28	-1.59	121	25.7
18-Sep-92	7.19	-1.74	124	26.0
19-Sep-92	7.13	-1.63	125	25.8
20-Sep-92	7.48	-1.92	129	25.7
21-Sep-92	7.34	-1.87	122	26.0
22-Sep-92	8.20	-2.23	95	25.5
23-Sep-92	8.35	-2.22	105	26.1
24-Sep-92	8.36	-2.11	94	25.6
25-Sep-92	8.23	-2.28	81	25.4
26-Sep-92	8.02	-1.98	90	26.1
27-Sep-92	7.94	-1.97	98	25.4
28-Sep-92	7.74	-1.91	102	25.2
29-Sep-92	7.70	-1.96	107	25.0
30-Sep-92	8.00	-2.41	105	24.1
01-Oct-92	7.81	-2.16	102	23.7
02-Oct-92	7.61	-2.15	107	23.3
03-Oct-92	8.34	-2.15	113	23.2
04-Oct-92	9.00	-2.28	70	23.8
05-Oct-92	8.62	-2.33	88	23.3
06-Oct-92	8.20	-2.24	93	22.0
07-Oct-92	8.36	-2.19	105	22.6
08-Oct-92	8.22	-2.13	96	23.8
09-Oct-92	7.95	-2.18	102	24.6
10-Oct-92	7.76	-2.11	107	25.2
11-Oct-92	7.76	-2.29	107	23.6
12-Oct-92	8.00	-2.33	113	22.3
13-Oct-92	7.80	-2.22	109	20.5
14-Oct-92	7.65	-2.13	112	20.7
15-Oct-92	7.51	-1.98	114	21.8
16-Oct-92	7.40	-2.02	121	19.8

Table 28.
COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE	ELE	O-18	EC	TEMP
17-Oct-92	7.34	-2.00	121	21.9
18-Oct-92	7.30	-1.99	126	21.2
19-Oct-92	7.29	-1.96		21.2
20-Oct-92	7.20	-1.92	126	19.7
21-Oct-92	7.15	-1.89	128	19.0
22-Oct-92	7.11	-1.83	130	18.7
30-Oct-92	6.91	-1.84	136	21.6
04-Nov-92	6.80		140	24.1
06-Nov-92	6.88		143	23.0
16-Nov-92	6.60		137	17.3
23-Nov-92	6.70		141	23.3
30-Nov-92	6.98		139	15.9
09-Dec-92	6.62		146	16.6
10-Dec-92	6.82		144	17.2
11-Dec-92	6.92		125	15.8
12-Dec-92	6.78		123	13.2
13-Dec-92	6.68		126	13.3
14-Dec-92	6.62		129	14.6
15-Dec-92	6.60		126	18.7
	Site:	**BD1**		
28-Aug-92	7.45	-2.98	475	23.4
03-Sep-92	7.25			
04-Sep-92	7.58	-3.07	476	23.5
05-Sep-92	7.49			
06-Sep-92	7.38			
07-Sep-92	7.26			
08-Sep-92	7.36			
09-Sep-92	7.36			
10-Sep-92	7.31			
11-Sep-92	7.25	-2.96	476	24.0
12-Sep-92	7.21			
13-Sep-92	7.40			
14-Sep-92	7.38			
15-Sep-92	7.41			
16-Sep-92	7.38			
17-Sep-92	7.34			
18-Sep-92	7.15	-3.06	471	24.1
19-Sep-92	7.15			
20-Sep-92	7.39			
21-Sep-92	7.36			
22-Sep-92	8.09			
23-Sep-92	8.19			
24-Sep-92	8.19			
25-Sep-92	8.11	-3.14	470	23.6
26-Sep-92	7.93			
27-Sep-92	7.83			
28-Sep-92	7.68			
29-Sep-92	7.63			
30-Sep-92	7.87			
01-Oct-92	7.69			
02-Oct-92	7.57	-3.04	475	23.2
03-Oct-92	8.15			
04-Oct-92	8.74			
05-Oct-92	8.46		470	23.1
06-Oct-92	8.07			
07-Oct-92	8.07			
08-Oct-92	8.08			
09-Oct-92	7.88	-3.11	475	23.9
10-Oct-92	7.68			
11-Oct-92	7.72			
12-Oct-92	7.86			
13-Oct-92	7.70			
14-Oct-92	7.58			
15-Oct-92	7.47			
16-Oct-92	7.35	-3.05	479	20.0
17-Oct-92	7.30			
18-Oct-92	7.30			
19-Oct-92	7.23		468	22.1
20-Oct-92	7.19			
21-Oct-92	7.14			
22-Oct-92	7.07		450	20.7
30-Oct-92	6.94	-3.13	445	22.3
04-Nov-92	6.77		443	22.5
06-Nov-92	6.88		451	22.0
16-Nov-92	6.63		442	21.6
23-Nov-92	6.78		449	22.1
30-Nov-92	7.03		453	20.9
09-Dec-92	6.72		442	19.2
10-Dec-92	7.00		455	19.3
11-Dec-92	7.00		391	19.3

Table 28.
COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE	ELE	O-18	EC	TEMP
12-Dec-92	6.88	-3.12	397	19.0
13-Dec-92	6.81		404	19.3
14-Dec-92	6.75		401	19.5
15-Dec-92	6.72		394	19.5
	Site:	**BRR**		
19-Aug-92			86	26.3
28-Aug-92	3.86	-1.75	123	27.3
03-Sep-92	3.22		152	26.8
04-Sep-92	4.09	-1.65	145	27.1
05-Sep-92	4.09		136	27.0
06-Sep-92	3.75		136	26.9
07-Sep-92	3.37		138	27.7
08-Sep-92	3.48		140	27.2
09-Sep-92	3.73		145	27.1
10-Sep-92	3.39		149	26.7
11-Sep-92	3.39	-1.61	144	27.1
12-Sep-92	3.35		138	27.0
13-Sep-92	3.08		142	26.8
14-Sep-92	3.06		141	26.4
15-Sep-92	3.36		136	26.2
16-Sep-92	3.37		140	26.4
17-Sep-92	3.29		133	27.0
18-Sep-92	3.07	-1.61	132	26.9
19-Sep-92	2.82		136	26.6
20-Sep-92	4.99		135	26.2
21-Sep-92	4.99		107	25.9
22-Sep-92	5.20		114	25.9
23-Sep-92	6.26		117	26.3
24-Sep-92	5.72		119	26.1
25-Sep-92	5.46	-2.12	102	26.3
26-Sep-92	4.96		100	26.5
27-Sep-92	4.90		104	26.1
28-Sep-92	4.59		113	25.9
29-Sep-92	4.36		115	25.5
30-Sep-92	4.43		116	24.8
01-Oct-92	4.40		116	24.5
02-Oct-92	4.06	-2.08	121	23.5
03-Oct-92	5.28		125	23.3
04-Oct-92	7.05		120	23.7
05-Oct-92	7.20		105	23.9

DATE	ELE	O-18	EC	TEMP
06-Oct-92	6.28		103	22.7
07-Oct-92	5.88		109	22.6
08-Oct-92	5.76		111	23.9
09-Oct-92	5.13	-2.24	111	25.4
10-Oct-92	4.66		112	25.5
11-Oct-92	4.42	-1.93	120	24.7
12-Oct-92	5.35	-2.54	127	22.9
13-Oct-92	5.80	-2.38	119	22.0
14-Oct-92	4.40	-2.19	123	21.4
15-Oct-92	4.05	-2.03	123	22.5
16-Oct-92	3.78	-2.01	129	21.6
17-Oct-92	3.51	-1.91	132	22.0
18-Oct-92	3.46	-1.95	135	22.8
19-Oct-92	3.42	-1.90	135	22.7
20-Oct-92	2.94	-1.85	139	21.7
21-Oct-92	2.69	-1.79	140	20.1
22-Oct-92	2.49	-1.80	144	20.4
30-Oct-92	1.93	-1.80	156	
04-Nov-92	1.60		164	24.2
06-Nov-92	1.99	-1.79	163	24.0
16-Nov-92	1.10		171	19.3
23-Nov-92	1.95		173	23.7
30-Nov-92	2.60		151	17.5
09-Dec-92	2.45		170	17.4
10-Dec-92	1.85		169	17.7
11-Dec-92	2.15		146	17.2
12-Dec-92	1.82		150	16.0
13-Dec-92	1.62		151	15.5
14-Dec-92	1.48		151	13.0
15-Dec-92	1.41		146	15.1
	Site:	**BR1**		
28-Aug-92	4.24	-3.27	319	24.4
03-Sep-92	3.73			
04-Sep-92	4.13	-3.05	305	24.5
05-Sep-92	4.16			
06-Sep-92	4.09			
07-Sep-92	3.87			
08-Sep-92	3.88			
09-Sep-92	4.00			
10-Sep-92	3.84			

Table 28.
COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE	ELE	O-18	EC	TEMP
11-Sep-92	3.67	-3.19	329	24.4
12-Sep-92	4.30			
13-Sep-92	3.53			
14-Sep-92	3.51			
15-Sep-92	3.62			
16-Sep-92	3.69			
17-Sep-92	3.63			
18-Sep-92	3.39	-3.04	335	24.7
19-Sep-92	3.35			
20-Sep-92	4.85			
21-Sep-92	4.36			
22-Sep-92	5.03			
24-Sep-92	5.78			
25-Sep-92	5.34	-3.27	324	24.6
26-Sep-92	5.09			
27-Sep-92	5.01			
28-Sep-92	4.83			
30-Sep-92	4.61			
01-Oct-92	4.51			
02-Oct-92	4.34	-3.29	323	24.3
03-Oct-92	5.12			
06-Oct-92	6.42			
07-Oct-92	5.96		328	24.2
08-Oct-92	5.84			
09-Oct-92	5.28	-3.29	321	24.8
10-Oct-92	4.91			
11-Oct-92	4.73			
12-Oct-92	5.46			
14-Oct-92	4.63			
15-Oct-92	4.33			
16-Oct-92	4.16	-3.26	346	21.5
17-Oct-92	3.96			
18-Oct-92	3.91			
19-Oct-92	3.64		342	23.3
20-Oct-92	3.55			
21-Oct-92	2.38			
22-Oct-92	3.15		346	20.1
30-Oct-92	2.31	-3.14	355	22.4
04-Nov-92	2.16		323	23.0
06-Nov-92	2.42	-3.12	342	22.7

DATE	ELE	O-18	EC	TEMP
16-Nov-92	1.78		324	22.4
23-Nov-92	2.24		332	23.1
30-Nov-92	3.35		323	21.9
09-Dec-92	2.20		327	20.8
10-Dec-92	2.55		327	20.5
11-Dec-92	2.52	-2.95	277	20.1
12-Dec-92	2.36		289	20.3
13-Dec-92	2.25		291	21.1
14-Dec-92	2.13		286	20.4
15-Dec-92	2.06		280	20.2
	Site:	**BR2**		
28-Aug-92	4.60	-3.12	344	25.0
03-Sep-92	4.12			
04-Sep-92	4.41	-3.00	440	25.5
05-Sep-92	4.42			
06-Sep-92	4.37			
07-Sep-92	4.18			
08-Sep-92	4.21			
09-Sep-92	4.24			
10-Sep-92	4.13			
11-Sep-92	3.94	-3.27	300	25.4
12-Sep-92	3.88			
13-Sep-92	3.83			
14-Sep-92	3.82			
15-Sep-92	3.91			
16-Sep-92	3.92			
17-Sep-92	3.88			
18-Sep-92	3.75	-2.90	227	25.9
19-Sep-92	3.68			
20-Sep-92	4.70			
21-Sep-92	4.46			
22-Sep-92	4.93			
24-Sep-92	5.78			
25-Sep-92	5.51	-2.90	267	25.6
26-Sep-92	5.17			
27-Sep-92	5.10			
28-Sep-92	4.87			
30-Sep-92	4.75			
01-Oct-92	4.60			
02-Oct-92	4.47		174	25.2

Table 28.
COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE	ELE	O-18	EC	TEMP
03-Oct-92	5.17			
05-Oct-92	7.24		406	24.4
06-Oct-92	6.43			
07-Oct-92	6.02			
08-Oct-92	5.86			
09-Oct-92	5.56	-3.06	222	25.7
10-Oct-92	5.03			
11-Oct-92	4.98			
12-Oct-92	5.46			
13-Oct-92	5.08			
14-Oct-92	4.80			
15-Oct-92	4.55			
16-Oct-92	4.46	-2.93	132	23.4
17-Oct-92	4.26			
18-Oct-92	4.26			
19-Oct-92	3.99		130	24.4
20-Oct-92	3.91			
21-Oct-92	3.80			
22-Oct-92	3.57		157	21.7
30-Oct-92	3.00	-3.04	170	23.7
04-Nov-92	2.54		146	24.3
06-Nov-92	2.76		149	24.2
16-Nov-92	2.15		131	24.1
23-Nov-92	2.49		154	24.3
30-Nov-92	3.67			23.5
09-Dec-92	2.61		243	22.0
10-Dec-92	2.91			22.3
11-Dec-92	2.77		156	21.5
12-Dec-92	2.70		156	21.7
13-Dec-92	2.60		159	21.6
14-Dec-92	2.50		155	21.7
15-Dec-92	2.45		150	21.5
	Site:	**FRR**		
28-Aug-92	7.13	-1.91	67	26.0
03-Sep-92			78	25.0
04-Sep-92	7.18	-1.81	68	24.9
05-Sep-92	7.27		74	26.1
06-Sep-92	6.63		77	25.7
07-Sep-92			81	25.3
08-Sep-92			83	25.6
09-Sep-92			84	24.7
10-Sep-92			84	25.2
11-Sep-92	4.14	-1.45		24.7
12-Sep-92	4.61		86	24.8
13-Sep-92	6.22		89	24.7
14-Sep-92	6.89		75	24.4
15-Sep-92	6.56		78	24.7
16-Sep-92	7.16		81	25.1
17-Sep-92	7.46		79	25.4
18-Sep-92	7.05	-1.98	80	25.3
19-Sep-92	6.52		81	24.7
20-Sep-92	7.54		76	24.6
21-Sep-92	6.44		77	25.2
22-Sep-92	7.56		83	25.4
24-Sep-92	6.26		80	25.3
25-Sep-92	8.69	-2.21	65	25.4
27-Sep-92	7.94		72	25.3
28-Sep-92	7.38		78	25.2
29-Sep-92	6.56		81	24.8
30-Sep-92	6.23		83	24.3
01-Oct-92	6.82		91	23.7
02-Oct-92	7.08	-2.06	93	23.0
03-Oct-92	7.26		89	23.0
04-Oct-92	8.57		91	24.5
05-Oct-92	8.96		81	23.6
06-Oct-92	8.69		81	22.3
07-Oct-92	8.29		82	22.1
08-Oct-92	9.06		81	23.2
09-Oct-92	8.96	-2.08	73	23.6
10-Oct-92	8.35		80	24.4
11-Oct-92	8.26	-2.18	79	23.7
12-Oct-92	8.35	-2.50	83	22.1
13-Oct-92	8.30	-2.34	82	20.8
15-Oct-92	7.61	-2.18	80	21.3
16-Oct-92	6.88	-2.04	80	20.3
17-Oct-92	6.14	-1.93	81	21.0
18-Oct-92	5.60	-1.87	83	21.4
19-Oct-92	5.02	-1.76	85	21.2
20-Oct-92	4.58	-1.70	85	19.1
21-Oct-92	4.15	-1.60	86	19.2

Table 28.
COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE	ELE	O-18	EC	TEMP
22-Oct-92	3.68	-1.52	87	19.8
30-Oct-92	2.21	-1.36	107	21.8
04-Nov-92	1.41		129	22.7
06-Nov-92	1.40		124	23.2
16-Nov-92	0.56		157	17.4
23-Nov-92	1.62		153	22.7
25-Nov-92	3.00		158	
30-Nov-92	3.10		125	14.5
05-Dec-92	2.19	-1.23	117	15.0
06-Dec-92	2.09	-1.24	114	14.6
07-Dec-92	1.92	-1.36	117	16.0
08-Dec-92	1.81	-1.19	117	17.9
09-Dec-92	1.72	-1.18	118	16.1
10-Dec-92	1.78	-1.26	119	16.6
11-Dec-92	2.00	-1.49	101	16.0
12-Dec-92	1.96	-1.41	108	13.9
13-Dec-92	2.00	-1.55	106	11.9
14-Dec-92	1.86	-1.39	122	12.4
15-Dec-92	1.72	-1.44	117	14.1
	Site:	**FR1**		
28-Aug-92	7.23	-2.79	43	24.5
03-Sep-92	5.37			
04-Sep-92	7.18	-2.84	51	24.5
05-Sep-92	7.31			
06-Sep-92	6.73			
07-Sep-92	5.88			
08-Sep-92	5.35			
09-Sep-92	5.11			
10-Sep-92	4.91			
11-Sep-92	4.82	-2.70	53	24.2
12-Sep-92	4.90		51	24.5
13-Sep-92	6.21			
14-Sep-92	6.91			
15-Sep-92	6.66			
16-Sep-92	7.22			
17-Sep-92	7.52			
18-Sep-92	7.12	-2.81	48	24.3
19-Sep-92	6.62			
20-Sep-92	6.62			
21-Sep-92	6.47			

DATE	ELE	O-18	EC	TEMP
22-Sep-92	6.66			
24-Sep-92	6.40			
25-Sep-92	8.76	-2.85	42	24.1
26-Sep-92	8.44			
27-Sep-92	7.99			
28-Sep-92	7.43			
29-Sep-92	6.70			
30-Sep-92	6.44			
01-Oct-92	6.87			
02-Oct-92	7.17	-2.70	44	23.9
03-Oct-92	7.33			
04-Oct-92	8.59			
05-Oct-92	9.00		41	23.8
06-Oct-92	8.74			
07-Oct-92	8.40			
08-Oct-92	9.10			
09-Oct-92	9.05	-2.75	42	24.0
10-Oct-92	8.39			
11-Oct-92	8.32			
12-Oct-92	8.40			
16-Oct-92	7.04	-2.80	38	21.9
17-Oct-92	6.33			
18-Oct-92	5.87			
19-Oct-92	5.45		42	22.8
20-Oct-92	5.19			
21-Oct-92	4.83			
22-Oct-92	4.50		32	22.7
30-Oct-92	3.30	-2.70	27	22.9
04-Nov-92	2.76		23	22.5
06-Nov-92	2.68		24	22.5
16-Nov-92	2.14		25	22.5
23-Nov-92	2.31		28	23.2
30-Nov-92	3.59		27	22.1
05-Dec-92	2.94	-2.60	28	21.3
06-Dec-92	2.89	-2.98	30	20.4
07-Dec-92	1.77	-2.91	30	23.7
08-Dec-92	1.70	-2.90	30	20.6
09-Dec-92	2.67	-2.98	36	20.7
10-Dec-92	2.67	-3.01	36	21.2
11-Dec-92	2.73	-3.00	26	20.1

Table 28.
COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE	ELE	O-18	EC	TEMP
12-Dec-92	2.73	-3.00	27	20.1
13-Dec-92	2.73	-3.08	26	20.1
14-Dec-92	2.70		31	20.6
15-Dec-92	2.59	-2.63	28	20.4
	Site:	**FR2**		
28-Aug-92	7.60		42	24.7
03-Sep-92	5.84			
04-Sep-92	7.15	-2.70	34	25.4
05-Sep-92	7.49			
06-Sep-92	7.11			
07-Sep-92	6.44			
08-Sep-92	5.96			
09-Sep-92	5.77			
10-Sep-92	5.50			
11-Sep-92	5.37	-2.56	30	25.1
12-Sep-92	5.27			
13-Sep-92	6.08			
14-Sep-92	7.02			
15-Sep-92	6.95			
16-Sep-92	7.32			
17-Sep-92	7.69			
18-Sep-92	7.34	-2.54	34	25.1
19-Sep-92	6.96			
20-Sep-92	7.02			
21-Sep-92	6.88			
22-Sep-92	6.98			
24-Sep-92	6.93			
25-Sep-92	8.69	-2.65	34	25.2
26-Sep-92	8.50			
27-Sep-92	9.37			
28-Sep-92	7.62			
29-Sep-92	7.18			
30-Sep-92	7.04			
01-Oct-92	7.22			
02-Oct-92	7.39	-2.45	36	24.8
03-Oct-92	7.73			
04-Oct-92	8.75			
05-Oct-92	9.08		33	24.8
06-Oct-92	8.84			
07-Oct-92	8.53			
08-Oct-92	9.12			
09-Oct-92	9.10	-2.62	37	24.9
10-Oct-92	8.50			
11-Oct-92	8.62			
12-Oct-92	8.55			
13-Oct-92	8.47			
14-Oct-92	8.24			
15-Oct-92	7.89			
16-Oct-92	7.40	-2.64	31	22.7
17-Oct-92	7.13			
18-Oct-92	6.37			
19-Oct-92	6.06		30	23.7
20-Oct-92	5.76			
21-Oct-92	5.40			
22-Oct-92	5.09		20	23.2
30-Oct-92	3.79	-2.45	20	23.2
04-Nov-92	3.59			22.7
06-Nov-92	3.22			
30-Nov-92	4.00		26	22.1
05-Dec-92	3.44			
09-Dec-92	3.03			
	Site:	**HRR**		
28-Aug-92	5.03	-1.94	67	25.9
03-Sep-92	4.38		78	25.2
04-Sep-92	5.35	-1.67	73	25.1
05-Sep-92	5.06		77	25.9
06-Sep-92	5.79		80	25.8
07-Sep-92	4.50		82	25.9
08-Sep-92	4.14		84	25.5
09-Sep-92	4.08		86	24.8
10-Sep-92	4.17		90	24.7
11-Sep-92	3.92	-1.41	94	25.0
12-Sep-92	5.08		90	25.5
13-Sep-92	5.38		74	25.0
14-Sep-92	5.08		79	24.7
15-Sep-92	5.29		83	24.4
16-Sep-92	5.52		82	25.1
17-Sep-92	5.35		83	25.1
18-Sep-92	5.12	-1.61	81	25.3
19-Sep-92	5.09		79	25.0

Table 28.
COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE	ELE	O-18	EC	TEMP
20-Sep-92	5.02		77	24.9
21-Sep-92	5.18		78	25.2
22-Sep-92	5.00		83	25.2
23-Sep-92	5.72		80	25.8
24-Sep-92	5.39		80	25.3
25-Sep-92	6.46	-2.38	61	25.4
26-Sep-92	5.72		70	25.8
27-Sep-92	5.39		75	25.4
28-Sep-92	5.08		81	25.0
29-Sep-92	4.81		84	24.7
30-Sep-92	5.00		88	24.1
01-Oct-92	5.32	-2.19	94	23.6
02-Oct-92	5.16	-2.45	94	23.1
03-Oct-92	5.34		94	22.9
04-Oct-92	6.48		96	23.6
05-Oct-92	6.56		85	23.4
06-Oct-92	6.04		83	22.4
07-Oct-92	5.88		85	22.0
08-Oct-92	6.90		72	23.4
09-Oct-92	6.31	-2.05	77	24.2
10-Oct-92	5.81		79	24.7
11-Oct-92	5.69	-2.04	83	23.9
12-Oct-92	5.95	-2.26	86	22.6
13-Oct-92	5.87	-2.49	84	20.7
14-Oct-92	5.56	-2.31	82	20.6
15-Oct-92	5.26	-2.15	81	23.2
16-Oct-92	4.96	-1.99	81	20.8
17-Oct-92	4.79	-1.90	82	20.8
18-Oct-92	4.64	-1.85	86	20.5
19-Oct-92	4.40	-1.75	86	20.7
20-Oct-92	4.18	-1.62	86	18.7
21-Oct-92	3.93	-1.57		18.7
22-Oct-92	3.57	-1.48	88	18.8
30-Oct-92	2.16	-1.30	128	21.6
04-Nov-92	1.30		138	23.8
06-Nov-92	1.18		132	23.4
16-Nov-92	0.38		163	17.5
23-Nov-92	1.56		115	23.3
29-Nov-92	3.37		130	
30-Nov-92	3.16		125	13.5

DATE	ELE	O-18	EC	TEMP
05-Dec-92	2.36	-1.24	117	15.2
06-Dec-92	2.20	-0.93	119	15.1
07-Dec-92	2.07	-1.20	117	15.8
08-Dec-92	1.95	-1.36	117	13.0
09-Dec-92	1.81	-1.20	122	15.4
10-Dec-92	2.00	-1.40	122	17.2
11-Dec-92	2.06	-1.38	104	15.1
12-Dec-92	2.16	-1.36	110	12.3
13-Dec-92	2.15	-1.24	114	11.2
14-Dec-92	1.96	-1.34	122	13.1
15-Dec-92	1.82	-1.77	115	15.3
	Site:	**HR1**		
28-Aug-92	5.28	-2.75	184	25.9
03-Sep-92	4.72			
04-Sep-92	5.60	-2.69	179	23.9
05-Sep-92	5.31			
06-Sep-92	5.07			
07-Sep-92	4.92			
08-Sep-92	4.73			
09-Sep-92	4.62		171	
10-Sep-92	4.60		169	
11-Sep-92	4.37	-2.93	166	23.8
12-Sep-92	5.31		170	23.9
13-Sep-92	5.58		175	23.8
14-Sep-92	5.39			
16-Sep-92	5.58		178	23.7
17-Sep-92	5.57		180	23.7
18-Sep-92	5.38	-2.82	179	23.8
19-Sep-92	5.34		182	23.9
20-Sep-92	5.26		179	23.9
21-Sep-92	5.45			
22-Sep-92	5.32		179	23.7
23-Sep-92			176	23.7
24-Sep-92	5.41		179	23.7
25-Sep-92	6.61	-2.93	184	24.0
26-Sep-92	6.17		183	23.9
27-Sep-92	5.65		181	24.1
28-Sep-92	5.32		174	23.6
29-Sep-92	5.18		179	23.6
30-Sep-92	5.18		176	23.4

Table 28.
COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE	ELE	O-18	EC	TEMP
01-Oct-92	5.52		177	23.5
02-Oct-92	5.40	-2.89	178	23.5
03-Oct-92	5.40	-2.90	176	23.5
04-Oct-92	6.47		174	23.6
05-Oct-92	6.70		185	23.2
06-Oct-92	6.01		173	22.9
07-Oct-92	6.04		172	23.3
08-Oct-92	7.01		167	23.7
09-Oct-92	6.44	-2.89	171	23.5
10-Oct-92	5.98		169	23.5
11-Oct-92	5.80		167	23.0
12-Oct-92	6.09		166	22.7
13-Oct-92	6.05		163	22.5
14-Oct-92	5.74		162	22.7
15-Oct-92	5.44		163	23.1
16-Oct-92	5.16	-2.97	186	21.0
17-Oct-92	5.01		167	20.9
18-Oct-92	4.92		171	21.6
19-Oct-92	4.69			22.2
20-Oct-92	4.57		177	21.7
21-Oct-92	4.41		178	21.3
22-Oct-92	4.14		178	21.4
30-Oct-92	3.28	-2.90	134	21.9
04-Nov-92	2.91		105	22.6
06-Nov-92	3.10		112	21.7
16-Nov-92	2.03		107	21.5
23-Nov-92	3.51		172	21.8
30-Nov-92	3.82		117	20.8
05-Dec-92	3.31	-2.66	111	19.8
06-Dec-92	3.20	-2.99	110	19.6
07-Dec-92	3.13	-2.94	107	19.2
08-Dec-92	2.10	-2.86	106	23.6
09-Dec-92	2.99	-2.92	108	19.1
10-Dec-92	3.51	-2.96	108	19.0
11-Dec-92	3.21	-2.95	86	18.7
12-Dec-92	3.18	-3.06	89	18.4
13-Dec-92	3.18	-3.05	87	18.7
14-Dec-92	3.04	-2.94	94	18.7
15-Dec-92	2.91	-2.38	90	19.5

Site: HR2

DATE	ELE	O-18	EC	TEMP
28-Aug-92	7.21	-2.81	159	23.7
03-Sep-92	7.05			
04-Sep-92	7.47	-2.80	162	23.8
05-Sep-92	7.19			
06-Sep-92	7.23			
07-Sep-92	7.23			
08-Sep-92	7.40			
09-Sep-92	7.33			
10-Sep-92	7.15			
11-Sep-92	7.00	-2.90	159	23.9
12-Sep-92	7.30			
13-Sep-92	7.50			
14-Sep-92	7.53			
15-Sep-92	7.49			
16-Sep-92	7.41			
17-Sep-92	7.41			
18-Sep-92	7.31	-2.92	164	23.9
19-Sep-92	7.35			
20-Sep-92	6.93			
21-Sep-92	6.88			
22-Sep-92	6.86			
24-Sep-92	7.01			
25-Sep-92	7.00	-2.97	159	24.0
26-Sep-92	6.68			
27-Sep-92	6.99			
28-Sep-92	6.96			
29-Sep-92	6.95			
30-Sep-92	6.99			
01-Oct-92	6.90			
02-Oct-92	6.93	-2.92	169	23.5
03-Oct-92	7.00			
04-Oct-92	7.03			
05-Oct-92	7.11		172	23.3
06-Oct-92	7.03			
07-Oct-92	7.03			
08-Oct-92	7.06			
09-Oct-92	7.01	-2.96	165	23.6
10-Oct-92	6.95			
11-Oct-92	7.06			
12-Oct-92	7.02			

Table 28.
COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE	ELE	O-18	EC	TEMP
13-Oct-92	7.00			
14-Oct-92	7.03			
15-Oct-92	6.96			
16-Oct-92	6.72	-2.98	169	20.2
17-Oct-92	6.70			
18-Oct-92	6.89			
19-Oct-92	6.57		167	22.1
20-Oct-92	6.71			
21-Oct-92	6.64			
22-Oct-92	6.36		156	21.2
30-Oct-92	6.16	-3.04	159	22.0
04-Nov-92	5.77		147	22.4
06-Nov-92	6.74		161	22.0
16-Nov-92	5.42		158	21.4
23-Nov-92	6.72		157	22.2
30-Nov-92	6.08		156	20.9
05-Dec-92	5.88	-2.93	151	20.3
06-Dec-92		-3.14	154	20.0
07-Dec-92		-3.17	152	19.8
08-Dec-92		-3.11	157	21.9
09-Dec-92		-3.19	154	19.2
10-Dec-92		-3.14	160	19.9
11-Dec-92		-3.12	121	19.3
12-Dec-92		-3.15	128	18.7
13-Dec-92		-3.19	126	19.4
14-Dec-92		-3.04	137	19.6
15-Dec-92		-3.10	131	19.6
	Site:	**MDR**		
28-Aug-92	44.50		124	27.6
03-Sep-92	44.60		137	26.6
04-Sep-92	44.65		144	26.0
05-Sep-92	44.60		135	26.1
06-Sep-92	44.50		128	26.4
07-Sep-92	44.50		132	27.3
08-Sep-92	44.50		136	26.8
09-Sep-92	44.50		141	26.8
10-Sep-92	44.45		142	26.3
11-Sep-92	44.51		143	28.6
12-Sep-92	44.50		134	26.1
13-Sep-92	44.40		133	26.6
14-Sep-92	44.40		140	26.3
15-Sep-92	44.50		133	26.0
16-Sep-92			126	25.9
17-Sep-92	44.45		127	26.3
18-Sep-92			125	25.4
19-Sep-92			125	25.8
20-Sep-92	44.80		107	25.5
21-Sep-92	44.70		108	25.9
22-Sep-92	45.00		106	25.8
23-Sep-92	45.20		118	26.3
24-Sep-92	44.90		114	26.2
25-Sep-92	44.90		98	26.1
26-Sep-92	44.80		94	26.2
27-Sep-92	44.80		104	25.8
28-Sep-92	44.70		111	25.8
29-Sep-92	48.65		113	25.7
30-Sep-92	44.70		119	25.1
01-Oct-92	44.65		115	24.3
02-Oct-92	44.70		118	23.7
03-Oct-92	45.00		129	23.4
04-Oct-92			78	23.8
05-Oct-92	45.30		104	24.2
06-Oct-92	44.95		102	22.6
07-Oct-92	44.95		108	22.5
08-Oct-92	44.95		111	23.9
09-Oct-92	44.80		107	25.0
10-Oct-92	44.80		110	24.8
11-Oct-92	44.75		118	25.1
12-Oct-92	44.85		120	23.1
13-Oct-92	44.75		120	21.8
14-Oct-92	44.70		124	21.5
15-Oct-92	44.60		118	22.5
16-Oct-92	44.60		128	20.5
17-Oct-92	44.45		125	21.8
18-Oct-92	44.50		145	21.6
19-Oct-92	44.50			22.3
20-Oct-92	44.40		137	21.6
21-Oct-92	44.50		139	19.8
22-Oct-92	44.35		143	19.7
30-Oct-92	44.40		155	22.0

Table 28.
COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE	ELE	O-18	EC	TEMP
04-Nov-92	44.40		161	22.7
06-Nov-92	44.40		160	23.8
16-Nov-92	44.40		166	19.4
23-Nov-92	44.40		164	23.0
30-Nov-92	44.40		148	16.6
09-Dec-92	44.40		161	17.1
10-Dec-92	44.40		165	17.9
11-Dec-92	44.40		141	17.1
12-Dec-92	44.40		148	15.7
13-Dec-92	44.40		147	14.6
14-Dec-92	44.40		146	14.1
15-Dec-92	44.40		141	17.1
	Site:	**OLR**		
19-Aug-92			102	26.6
28-Aug-92	33.39	-1.75	157	26.8
03-Sep-92	31.15		188	26.4
04-Sep-92	32.15	-1.65	184	26.4
05-Sep-92	32.90		165	26.6
06-Sep-92	32.80		170	26.5
07-Sep-92	31.95		171	26.7
08-Sep-92	31.36		164	26.9
09-Sep-92	31.38		191	26.6
10-Sep-92	31.44		192	26.7
11-Sep-92	30.93	-1.57	209	26.3
12-Sep-92	30.89		179	27.0
13-Sep-92	31.06		197	26.5
14-Sep-92	31.43			24.4
15-Sep-92	31.40		179	26.3
16-Sep-92	31.70		187	26.4
17-Sep-92	31.92		175	26.3
18-Sep-92	31.79	-1.68	173	26.5
19-Sep-92	31.39		189	26.3
20-Sep-92	31.65		189	26.0
21-Sep-92	33.48		152	26.0
22-Sep-92	32.96			
24-Sep-92	35.11		128	26.1
25-Sep-92	34.91	-2.15	139	26.1
26-Sep-92	35.08		120	26.2
27-Sep-92	34.68		131	25.8
28-Sep-92			135	25.6
29-Sep-92	33.69		147	25.5
30-Sep-92	33.60		149	25.0
01-Oct-92	33.27		144	24.4
02-Oct-92	33.20	-2.13	161	23.9
03-Oct-92	33.62		157	23.6
04-Oct-92	35.76		148	24.2
05-Oct-92	36.19		120	23.8
06-Oct-92	36.15		121	23.0
07-Oct-92	35.62		127	22.6
08-Oct-92	35.48		131	23.4
09-Oct-92	35.78	-2.22	138	23.9
10-Oct-92	35.00		139	24.9
11-Oct-92	34.86	-2.68	139	24.0
12-Oct-92	35.30	-2.25	142	23.2
13-Oct-92	35.11	-2.26	148	21.6
14-Oct-92	34.50	-2.30	138	21.7
15-Oct-92	33.85	-2.11	150	21.9
16-Oct-92	33.04	-2.00	156	19.7
17-Oct-92	32.20	-1.97	163	21.9
18-Oct-92	31.87	-1.94	173	22.4
19-Oct-92	31.29	-1.86	177	22.3
20-Oct-92	30.34	-1.89	181	20.7
21-Oct-92	30.64	-1.79	193	21.0
22-Oct-92	30.23	-1.81	197	21.8
29-Oct-92	29.63			21.4
30-Oct-92	29.36	-1.82	219	22.9
04-Nov-92	28.92		226	24.6
06-Nov-92	29.00		237	23.9
16-Nov-92	28.40		231	19.5
23-Nov-92	28.90		233	22.9
29-Nov-92			175	
30-Nov-92	29.87			18.1
09-Dec-92	28.95		220	17.8
10-Dec-92	29.04		226	17.9
11-Dec-92	28.45		191	17.7
12-Dec-92	29.39		194	16.0
13-Dec-92	29.13		194	15.2
14-Dec-92	28.96		197	16.2
15-Dec-92	28.88		216	17.0
	Site:	**R4R**		

Table 28.
COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE	ELE	O-18	EC	TEMP
28-Aug-92	36.34	-1.89	94	26.2
03-Sep-92	33.91		130	25.7
04-Sep-92	34.75	-1.70	109	25.1
05-Sep-92	35.80		93	25.7
06-Sep-92	35.56		105	25.9
07-Sep-92	34.75		100	25.9
08-Sep-92	34.02		115	26.3
09-Sep-92	33.87		143	25.9
10-Sep-92	33.79		141	26.0
11-Sep-92	33.58	-1.51	155	25.4
12-Sep-92	33.36		132	26.2
13-Sep-92	34.00		122	25.2
14-Sep-92	34.83		97	25.0
15-Sep-92	34.51		104	25.0
16-Sep-92	34.87		98	25.2
17-Sep-92	35.28		91	25.2
18-Sep-92	35.14	-1.86	90	25.4
19-Sep-92	34.69		97	25.1
20-Sep-92			93	25.0
21-Sep-92	35.76		79	25.4
22-Sep-92	35.53		87	25.6
24-Sep-92	36.97		84	25.7
25-Sep-92	37.32	-1.90	75	25.3
26-Sep-92	38.14		63	25.5
27-Sep-92	37.60		68	25.1
28-Sep-92	36.90		76	25.3
29-Sep-92	36.28		80	25.1
30-Sep-92	35.89		84	24.4
01-Oct-92	35.20		86	23.9
02-Oct-92	35.89	-1.95	92	23.1
03-Oct-92	36.19		92	22.8
04-Oct-92	38.03		69	23.8
05-Oct-92	39.27		83	23.4
06-Oct-92	39.11		81	22.4
07-Oct-92	37.84		95	22.2
08-Oct-92	38.32		83	23.6
09-Oct-92	39.04	-2.14	76	23.0
10-Oct-92	38.15		78	24.2
11-Oct-92	37.74	-2.11	80	23.8
12-Oct-92	37.91	-2.33	78	22.7
14-Oct-92	37.43	-2.43	76	21.2
16-Oct-92	36.00	-2.04	81	20.3
17-Oct-92	35.22	-1.96	98	20.9
18-Oct-92	34.71	-1.91	105	21.7
19-Oct-92	34.10	-1.84		21.4
20-Oct-92	33.66	-1.73	122	20.2
21-Oct-92	33.23	-1.65		
22-Oct-92	32.77		142	21.1
30-Oct-92	31.42	-1.55	171	21.9
04-Nov-92	30.78		173	23.8
06-Nov-92	30.72		212	23.8
16-Nov-92	29.86		190	18.7
23-Nov-92	30.72		185	22.8
29-Nov-92	32.90		163	
30-Nov-92	32.57		164	16.6
09-Dec-92	29.68		157	16.9
10-Dec-92	29.81		161	17.6
11-Dec-92	31.03		154	16.6
12-Dec-92	28.77		147	14.3
13-Dec-92	28.55		151	13.7
14-Dec-92	28.26		155	14.3
15-Dec-92	28.22		159	15.3
	Site:	**SHR**		
19-Aug-92	10.75			
28-Aug-92	8.83	-1.87	104	26.3
03-Sep-92	6.56	-1.85	138	25.7
04-Sep-92	6.75	-1.68	127	25.7
05-Sep-92	7.50	-1.76	120	26.6
06-Sep-92	7.65	-1.92	119	26.4
07-Sep-92	7.29	-1.76	127	26.1
08-Sep-92	6.57	-1.64	147	26.5
09-Sep-92	6.30	-1.58	142	25.8
10-Sep-92	6.15	-1.63	146	26.0
11-Sep-92	6.05	-1.50	153	25.5
12-Sep-92	5.80	-1.75	171	26.9
13-Sep-92	5.90	-1.46	149	25.5
14-Sep-92	6.58	-1.79	121	24.7
15-Sep-92	6.75	-1.83	125	25.2
16-Sep-92	6.75	-1.77	120	25.4
17-Sep-92	7.03	-1.84	119	25.6

Table 28.

COMPLETE LISTINGS OF 1992 FIELD AND OXYGEN ISOTOPIC DATA (Concluded).

DATE	ELE	O-18	EC	TEMP
18-Sep-92	7.16	-1.76	118	25.6
19-Sep-92	6.98	-1.85	121	25.3
20-Sep-92	6.70	-1.67	131	25.1
21-Sep-92	7.20	-1.69	126	25.9
22-Sep-92	7.45	-2.03	117	25.7
23-Sep-92	7.75	-1.94	121	26.0
24-Sep-92	8.52	-2.02	120	25.9
25-Sep-92	8.70	-2.09	114	26.0
26-Sep-92	9.90	-1.90	95	26.3
27-Sep-92	9.94	-2.03	95	25.4
28-Sep-92	9.29	-1.89	103	25.5
29-Sep-92	8.68	-1.85	114	25.2
30-Sep-92	8.10	-1.80	128	24.9
01-Oct-92	7.79	-1.82	129	24.4
02-Oct-92	7.80	-2.29	124	23.7
03-Oct-92	8.05	-1.97	134	23.3
04-Oct-92	9.20	-2.06	144	23.6
05-Oct-92	10.32	-2.01	121	23.8
06-Oct-92	11.28	-2.05	107	22.7
07-Oct-92	11.08	-2.03	108	22.5
08-Oct-92	10.38	-2.01	109	23.6
09-Oct-92	10.89	-2.01	104	23.2
10-Oct-92	10.80	-2.02	103	24.4
11-Oct-92	10.32	-2.04	111	23.9
12-Oct-92	10.10	-2.27	115	23.3
13-Oct-92	10.08	-2.29	115	21.8
14-Oct-92	9.85	-2.27	111	21.7
15-Oct-92	9.38	-2.25	113	21.4
16-Oct-92	8.59	-2.16	125	21.0
17-Oct-92	8.05	-2.07	134	21.1
18-Oct-92	7.59	-1.85	139	21.7
19-Oct-92	7.10	-1.88		21.8
20-Oct-92	6.82	-1.74	153	20.8
21-Oct-92	6.50	-1.71	158	20.8
22-Oct-92	6.18	-1.62	178	21.4
30-Oct-92	5.05	-1.56	221	21.7
04-Nov-92			271	23.9
06-Nov-92	4.20		274	23.8
16-Nov-92	3.20		308	19.6
23-Nov-92	3.35		298	22.9
30-Nov-92	4.90		177	17.6
09-Dec-92	3.50		255	17.1
10-Dec-92	3.25		259	18.0
11-Dec-92	3.60		203	16.6
12-Dec-92	3.70		195	15.3
13-Dec-92	3.62		200	14.6
14-Dec-92	3.40		204	14.5
15-Dec-92	3.35		214	15.2

Table 29.
COMPLETE LISTING OF SPRING 1993 FIELD AND OXYGEN ISOTOPIC DATA.

DATE		ELE	FLOW	O-18	EC
Site: HRR					
01-May-93	pm	-0.42	15.1	-0.13	103
02-May-93	am	-0.53	13.2	-0.09	105
03-May-93	am	-0.58	12.3	-0.24	106
04-May-93	am	-0.59	12.2	-0.20	108
05-May-93	am	-0.65	11.2	-0.23	111
06-May-93	am	-0.75	9.6	-0.19	117
07-May-93	am	-0.74	9.8	-0.24	120
08-May-93	am	-0.79	9.0	-0.29	133
09-May-93	am	-0.86	8.0	-0.32	151
10-May-93	am	-0.86	8.0	-0.15	167
11-May-93	am	-0.96	6.6	-0.14	182
18-May-93	pm	-1.41	1.7	-0.02	210
26-May-93	am	-1.72	0.0	-0.04	233
29-May-93	am	-1.71	0.1	-0.32	251
29-May-93	pm	-1.71	0.1	-0.34	236
30-May-93	am	-1.31	2.6	-0.85	230
31-May-93	am	-0.51	13.5	-0.76	232
31-May-93	pm	-0.46	14.4	-0.68	241
01-Jun-93	am	-0.19	19.5	-0.72	263
01-Jun-93	pm	0.20	27.8	-0.95	283
02-Jun-93	am	0.58	36.9	-1.23	274
02-Jun-93	pm	0.60	37.4	-1.33	236
03-Jun-93	am	0.58	36.9	-1.42	226
03-Jun-93	pm	0.64	38.5	-1.55	210
04-Jun-93	am	0.50	34.9	-1.85	210
04-Jun-93	pm	0.43	33.2	-1.83	200
05-Jun-93	am	0.37	31.8	-1.95	198
05-Jun-93	pm	0.27	29.4	-1.75	196
06-Jun-93	pm	0.09	25.4	-1.67	196
07-Jun-93	am	-0.31	17.2	-1.53	196
07-Jun-93	pm	-0.49	13.9	-1.39	196
08-Jun-93	am	-0.65	11.2	-1.37	195
09-Jun-93	am	-0.92	7.1	-1.25	192
10-Jun-93	am	-1.07	5.2	-1.27	188
11-Jun-93	am	-1.18	3.9	-1.21	186
15-Jun-93	am	-1.25	3.2	-1.01	185
23-Jun-93	am	-1.43	1.6	-0.73	
03-Jul-93	am			-1.43	
Site: HR0					
06-May-93	am			-3.07	179
11-May-93	am			-2.99	191
26-May-93	am	-1.10		-3.08	197
29-May-93	am	-1.04		-3.05	210
29-May-93	pm	-1.08		-3.07	208
30-May-93	am			-2.97	208
31-May-93	am	0.43		-3.12	209
31-May-93	pm	0.27			
01-Jun-93	am	0.35		-2.88	117
01-Jun-93	pm	0.53			
02-Jun-93	am	0.84		-2.95	199
02-Jun-93	pm	0.88			
03-Jun-93	am	0.92		-2.98	180
03-Jun-93	pm	0.91			
04-Jun-93	am	0.87		-3.21	181
04-Jun-93	pm	0.73			
05-Jun-93	am	0.75		-3.23	186
05-Jun-93	pm	0.60			
06-Jun-93	pm	0.47		-3.00	186
07-Jun-93	am	0.20		-2.92	194
07-Jun-93	pm	0.03			
08-Jun-93	am	-0.07			
09-Jun-93	am			-2.73	199
11-Jun-93	am			-3.05	197
23-Jun-93	am			-2.89	
03-Jul-93	am			-2.95	
Site: HR1					
05-May-93	am			-3.05	98
31-May-93	am	1.94		-2.91	116
31-May-93	pm	1.78			
01-Jun-93	am	1.79		-3.09	205
01-Jun-93	pm	1.82			
02-Jun-93	am	1.99		-2.86	114
02-Jun-93	pm	1.93			
03-Jun-93	am	2.00		-3.06	101
03-Jun-93	pm	2.01			
04-Jun-93	am	1.95		-3.27	100
04-Jun-93	pm	1.82			
05-Jun-93	am	1.75		-3.35	103
05-Jun-93	pm	1.70			

Table 29.
COMPLETE LISTING OF SPRING 1993 FIELD AND OXYGEN ISOTOPIC DATA (Continued).

DATE		ELE	FLOW	O-18	EC
06-Jun-93	pm	1.70		-2.98	106
07-Jun-93	am	1.49		-3.01	108
07-Jun-93	pm	1.29			
08-Jun-93	am	1.29			
03-Jul-93	am			-2.97	
Site: HR2					
05-May-93	am	5.65		-3.02	179
26-May-93	am	4.33		-3.06	
29-May-93	am	4.19		-3.15	
29-May-93	pm	3.75		-3.13	196
30-May-93	am			-3.07	200
31-May-93	am	6.17		-3.07	219
31-May-93	pm	6.07			
01-Jun-93	am	6.10		-3.01	212
01-Jun-93	pm	5.95			
02-Jun-93	am	5.97		-2.95	196
02-Jun-93	pm	5.85			
03-Jun-93	am	5.88		-3.20	172
03-Jun-93	pm	5.77			
04-Jun-93	am	5.80		-3.34	170
04-Jun-93	pm	5.67			
05-Jun-93	am	5.67		-3.55	169
05-Jun-93	pm	5.57			
06-Jun-93	pm	5.58		-3.03	168
07-Jun-93	am	5.46		-3.06	170
07-Jun-93	pm	5.36			
08-Jun-93	am	5.37			
09-Jun-93	am			-3.07	168
11-Jun-93	am			-3.04	168
23-Jun-93	am			-3.22	
03-Jul-93	am			-3.02	
Site: Route 420					
01-May-93	pm	4.59	17.7	-0.24	110
02-May-93	am	4.34	12.5	-0.14	110
03-May-93	am	4.26	10.9	-0.23	112
04-May-93	am	4.49	15.7	-0.36	117
05-May-93	am	4.48	15.5	-0.42	124
06-May-93	am	4.42	14.2	-0.45	123
07-May-93	am			-0.30	123
08-May-93	am	4.28	11.3	-0.44	127
09-May-93	am	4.20	9.6	-0.27	145
10-May-93	am	4.22	10.1	-0.15	164
11-May-93	am	4.10	7.6	-0.25	171
18-May-93	pm	3.60	0.2	-0.24	221
26-May-93	am			-0.35	249
30-May-93	am				157
31-May-93	am	5.45	35.6	-1.58	195
31-May-93	pm	5.28	32.0	-1.26	202
01-Jun-93	am	5.20	30.4	-0.96	228
01-Jun-93	pm	5.33	33.1	-0.86	255
02-Jun-93	am	5.71	41.0	-1.21	280
02-Jun-93	pm	5.80	42.8	-1.24	243
03-Jun-93	am	5.74	41.6	-1.37	224
03-Jun-93	pm	5.82	43.2	-1.41	211
04-Jun-93	am	5.68	40.3	-1.78	209
04-Jun-93	pm	5.58	38.3	-1.80	203
05-Jun-93	am	5.50	36.6	-1.84	198
05-Jun-93	pm	5.42	34.9	-1.74	198
06-Jun-93	pm	5.09	28.1	-1.66	197
07-Jun-93	am	4.83	22.7	-1.47	196
07-Jun-93	pm	4.70	20.0	-1.48	195
08-Jun-93	am	4.48	15.5	-1.46	197
09-Jun-93	am	4.20	9.6	-1.46	198
10-Jun-93	am	4.02	5.9	-1.32	195
11-Jun-93	am	3.88	3.0	-1.30	192
15-Jun-93	am	3.96	4.7	-0.97	183
23-Jun-93	am			-0.64	
Site: FRR					
01-May-93	pm	-0.17	22.2	-0.34	115
02-May-93	am	-0.23	20.6	-0.37	116
03-May-93	am	-0.56	12.9	-0.35	118
04-May-93	am	-0.35	17.7	-0.41	119
05-May-93	am	-0.39	16.8	-0.38	118
06-May-93	am	-0.42	16.0	-0.34	120
07-May-93	am	-0.47	14.9	-0.60	127
08-May-93	am	-0.52	13.8	-0.42	130
09-May-93	am	-0.57	12.7	-0.40	135
10-May-93	am	-0.59	12.2	-0.45	135
11-May-93	am	-0.65	11.0	-0.47	139
18-May-93	pm	-1.03	4.0	-0.39	197

Table 29.
COMPLETE LISTING OF SPRING 1993 FIELD AND OXYGEN ISOTOPIC DATA (Concluded).

DATE	ELE	FLOW	O-18	EC
26-May-93 am	-1.26	1.0	-0.50	224
29-May-93 am	-1.27	0.9	-0.66	119
29-May-93 pm	-1.27	0.9	-0.69	224
30-May-93 am	-0.25	20.1	-2.26	
31-May-93 am	0.72	48.0	-1.90	196
31-May-93 pm	0.56	42.9	-1.92	186
01-Jun-93 am	0.30	35.1	-1.71	166
01-Jun-93 pm	0.25	33.6	-1.40	190
02-Jun-93 am	0.44	39.2	-1.08	221
02-Jun-93 pm	0.59	43.8	-0.92	217
03-Jun-93 am	0.62	44.8	-1.24	234
03-Jun-93 pm	0.63	45.1	-1.21	227
04-Jun-93 am	0.60	44.1	-1.61	220
04-Jun-93 pm	0.50	41.1	-1.55	206
05-Jun-93 am	0.40	38.0	-1.62	202
05-Jun-93 pm	0.35	36.5	-1.72	198
06-Jun-93 pm	0.15	30.8	-1.65	196
07-Jun-93 am	-0.05	25.3	-1.47	194
07-Jun-93 pm	-0.15	22.7	-1.58	195
08-Jun-93 am	-0.33	18.2	-1.61	194
09-Jun-93 am	-0.55	13.1	-1.45	194
10-Jun-93 am	-0.70	10.0	-1.51	196
11-Jun-93 am	-0.81	7.8	-1.37	192
15-Jun-93 am	-0.85	7.1	-1.19	189
23-Jun-93 am	-1.15	2.3	-0.76	
03-Jul-93 am			-1.07	
Site: FR0				
06-May-93 am			-2.89	122
07-May-93 am	-0.25			
11-May-93 am			-2.85	120
26-May-93 am	-0.25		-3.08	112
29-May-93 am	-0.21		-3.01	229
29-May-93 pm	-0.23		-3.18	120
30-May-93 am	0.41		-2.96	126
31-May-93 am	0.92		-2.81	116
31-May-93 pm	1.54			
01-Jun-93 am	0.91		-2.91	110
01-Jun-93 pm	0.83			
02-Jun-93 am	0.94		-2.85	118
02-Jun-93 pm	0.95			
03-Jun-93 am	1.03		-3.08	95
03-Jun-93 pm	1.03			
04-Jun-93 am	1.11		-3.22	104
04-Jun-93 pm	1.02			
05-Jun-93 am	1.02		-3.09	98
05-Jun-93 pm	0.93			
06-Jun-93 pm	0.92		-2.93	105
07-Jun-93 am	0.78		-2.99	105
07-Jun-93 pm	0.65			
08-Jun-93 am	0.64			
09-Jun-93 am			-2.94	101

elevation, temperature, and conductivity. Monitoring wells were monitored weekly for temperature and conductivity (Table 28). Water samples were collected for isotope analysis daily at river stations, weekly from monitoring wells, and at precipitation stations after storm events. Winter 1992 sampling was conducted from December 9, 1992 through December 15, 1992 and consisted of daily monitoring at the Hidden River and Fawn Run sites for river and monitoring well elevation, conductivity, and temperature (Table 28). Water samples were collected from the river and monitoring wells and the river was gaged daily at FRR and HRR to develop rating curves. Spring 1993 sampling was conducted from May 1, 1993 through June 23, 1993 and consisted of river and monitoring well sampling at Hidden River and Fawn Run stations. Sampling design was similar to that of Winter 1992. Field data for Spring 1993 are presented in Table 28 and gaging data are provided in Table 25.

References

Neter, J., W. Wasserman, and M.H. Kutner, 1990. *Applied Linear Statistical Models*. Richard D. Irwin, Inc., pp. 173-176.

Rantz, S.E., 1983a. *Measurement and Computation of Streamflow, Volume 1: Measurement of Stage and Discharge*. Geological Survey Water-Supply Paper 2175, United States Govenment Printing Office, Washington, DC, 284pp.

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APPENDIX D

DATA LISTINGS AND SAMPLE CALCULATIONS FOR HYDROGRAPH SEPARATIONS

Chapter 4 of the main text applies several mass-balance models using hydrometric and isotopic data for hydrograph separations. This appendix provides complete listings of the modeling data and sample calculations for each model applied.

Steady-State Catchment Model

The steady-state catchment model was solved using Equation 53, which is reproduced below.

$$V_O = V_R \frac{(C_N - C_R)}{(C_N - C_O)} \tag{53}$$

The solution of the model for the Spring 1993 storm event at station HR is presented in Table 30 and for station FR in Table 31. A sample calculation is provided for 30-May-93 at the HR station.

In Table 30, field data are presented in Columns 1 through 5. Column 6 is the *old* water $\delta^{18}O$, estimated as a linear function of stage using Equation 56. Using the river stage data for 30-May-93, C_O was computed in Column 6 to be

$$\begin{aligned} C_{O(HR)} &= -0.432 - 0.311z \\ &= -0.432 - 0.311(-1.31) = 0.03 \; o/oo \end{aligned} \tag{79}$$

Table 30.
DATA LISTING AND COMPUTATIONS FOR STEADY-STATE HYDROGRAPH SEPARATION AT STATION HR.

DATE (1)	dt (sec) (2)	Stage (ft) (3)	Flow (cfs) (4)	O-18 (o/oo) (5)	Co (o/oo) (6)	Cp (o/oo) (7)	P (in) (8)	SigmaP (in) (9)	CpP (in.o/oo) (10)	SigmaCp (in.o/oo) (11)	Cn (o/oo) (12)	fo (13)	Qo (cfs) (14)	Vr (ft^3) (15)	Vo (ft^3) (16)
01-May-93		-0.42	15.1	-0.13	-0.30										
02-May-93	7.96E+04	-0.53	13.2	-0.09	-0.27										
03-May-93	8.33E+04	-0.58	12.3	-0.24	-0.25										
04-May-93	8.92E+04	-0.59	12.2	-0.20	-0.25										
05-May-93	8.64E+04	-0.65	11.2	-0.23	-0.23										
06-May-93	8.64E+04	-0.75	9.6	-0.19	-0.20										
07-May-93	8.64E+04	-0.74	9.8	-0.24	-0.20										
08-May-93	7.61E+04	-0.79	9.0	-0.29	-0.19										
09-May-93	9.05E+04	-0.86	8.0	-0.32	-0.16										
10-May-93	9.00E+04	-0.86	8.0	-0.15	-0.16										
11-May-93	8.89E+04	-0.96	6.6	-0.14	-0.13										
18-May-93	6.24E+05	-1.41	1.7	-0.02	0.01										
26-May-93	6.72E+05	-1.72	0.0	-0.04	0.10										
29-May-93	2.56E+05	-1.71	0.1	-0.32	0.10										
29-May-93	1.80E+04	-1.71	0.1	-0.34	0.10	-2.05	0.3	0.3	-0.61	-0.61	-2.05	0.80	0.0	1.03E+03	8.21E+02
30-May-93	7.20E+04	-1.31	2.6	-0.85	-0.03	-4.84	3.2	3.5	-15.49	-16.10	-4.60	0.82	2.1	1.87E+05	1.54E+05
31-May-93	8.03E+04	-0.51	13.5	-0.76	-0.27	-3.87	0.8	4.3	-3.10	-19.20	-4.46	0.88	12.0	1.09E+06	9.61E+05
31-May-93	3.24E+04	-0.46	14.4	-0.68	-0.29			4.3		-19.20	-4.46	0.91	13.1	4.67E+05	4.24E+05
01-Jun-93	5.33E+04	-0.19	19.5	-0.72	-0.37			4.3		-19.20	-4.46	0.92	17.9	1.04E+06	9.51E+05
01-Jun-93	2.84E+04	0.20	27.8	-0.95	-0.49			4.3		-19.20	-4.46	0.88	24.6	7.91E+05	6.99E+05
02-Jun-93	5.53E+04	0.58	36.9	-1.23	-0.61			4.3		-19.20	-4.46	0.84	31.0	2.04E+06	1.72E+06
02-Jun-93	2.75E+04	0.60	37.4	-1.33	-0.62			4.3		-19.20	-4.46	0.81	30.5	1.03E+06	8.38E+05
03-Jun-93	6.12E+04	0.58	36.9	-1.42	-0.61			4.3		-19.20	-4.46	0.79	29.2	2.26E+06	1.79E+06
03-Jun-93	2.64E+04	0.64	38.5	-1.55	-0.63			4.3		-19.20	-4.46	0.76	29.3	1.01E+06	7.72E+05
04-Jun-93	5.82E+04	0.50	34.9	-1.85	-0.59			4.3		-19.20	-4.46	0.68	23.6	2.03E+06	1.37E+06
04-Jun-93	3.60E+04	0.43	33.2	-1.83	-0.57			4.3		-19.20	-4.46	0.67	22.4	1.20E+06	8.07E+05
05-Jun-93	5.00E+04	0.37	31.8	-1.95	-0.55			4.3		-19.20	-4.46	0.64	20.4	1.59E+06	1.02E+06
05-Jun-93	3.86E+04	0.27	29.4	-1.75	-0.52			4.3		-19.20	-4.46	0.69	20.2	1.13E+06	7.80E+05
06-Jun-93	7.52E+04	0.09	25.4	-1.67	-0.46			4.3		-19.20	-4.46	0.70	17.7	1.91E+06	1.33E+06
07-Jun-93	6.23E+04	-0.31	17.2	-1.53	-0.34			4.3		-19.20	-4.46	0.71	12.2	1.07E+06	7.60E+05
07-Jun-93	2.41E+04	-0.49	13.9	-1.39	-0.28			4.3		-19.20	-4.46	0.74	10.2	3.35E+05	2.46E+05
08-Jun-93	5.51E+04	-0.65	11.2	-1.37	-0.23			4.3		-19.20	-4.46	0.73	8.2	6.16E+05	4.51E+05
09-Jun-93	6.01E+04	-0.92	7.1	-1.25	-0.15			4.3		-19.20	-4.46	0.74	5.3	4.29E+05	3.19E+05
10-Jun-93	8.64E+04	-1.07	5.2	-1.27	-0.10			4.3		-19.20	-4.46	0.73	3.8	4.49E+05	3.29E+05
11-Jun-93	8.64E+04	-1.18	3.9	-1.21	-0.07			4.3		-19.20	-4.46	0.74	2.9	3.39E+05	2.51E+05
15-Jun-93	3.46E+05	-1.25	3.2	-1.01	-0.04			4.3		-19.20	-4.46	0.78	2.5	1.10E+06	8.60E+05
23-Jun-93	6.91E+05	-1.43	1.6	-0.73	0.01			4.3		-19.20	-4.46	0.83	1.3	1.08E+06	9.04E+05
													SUMS	2.32E+07	1.77E+07
													f	0.76	

Table 31.
DATA LISTING AND COMPUTATIONS FOR STEADY-STATE HYDROGRAPH SEPARATION AT STATION FR.

DATE (1)	dt (sec) (2)	Stage (ft) (3)	Flow (cfs) (4)	O-18 (o/oo) (5)	Co (o/oo) (6)	Cp (o/oo) (7)	P (in.) (8)	SigmaP (in.) (9)	CpP (in.o/oo) (10)	SigmaCp (in.o/oo) (11)	Cn (o/oo) (12)	fo (13)	Qo (cfs) (14)	Vr (ft^3) (15)	Vo (ft^3) (16)
01-May-93		-0.17	22.2	-0.34	-0.52										
02-May-93	7.96E+04	-0.23	20.6	-0.37	-0.51										
03-May-93	8.33E+04	-0.56	12.9	-0.35	-0.44										
04-May-93	8.92E+04	-0.35	17.7	-0.41	-0.48										
05-May-93	8.64E+04	-0.39	16.8	-0.38	-0.47										
06-May-93	8.64E+04	-0.42	16.0	-0.34	-0.47										
07-May-93	8.64E+04	-0.47	14.9	-0.60	-0.46										
08-May-93	7.61E+04	-0.52	13.8	-0.42	-0.45										
09-May-93	9.05E+04	-0.57	12.7	-0.40	-0.43										
10-May-93	9.00E+04	-0.59	12.2	-0.45	-0.43										
11-May-93	8.89E+04	-0.65	11.0	-0.47	-0.42										
18-May-93	6.24E+05	-1.03	4.0	-0.39	-0.33										
26-May-93	6.72E+05	-1.26	1.0	-0.50	-0.28										
29-May-93	2.56E+05	-1.27	0.9	-0.66	-0.28										
29-May-93	1.80E+04	-1.27	0.9	-0.69	-0.28	-2.05	0.3	0.3	-0.61	-0.61	-2.05	0.77	0.7	1.65E+04	1.26E+04
30-May-93	7.20E+04	-0.25	20.1	-2.26	-0.51	-4.84	3.2	3.5	-15.49	-16.10	-4.60	0.57	11.5	7.58E+05	4.33E+05
31-May-93	8.03E+04	0.72	48.0	-1.90	-0.72	-3.87	0.8	4.3	-3.10	-19.20	-4.46	0.68	32.8	2.73E+06	1.87E+06
31-May-93	3.24E+04	0.56	42.9	-1.92	-0.69			4.3		-19.20	-4.46	0.67	28.8	1.47E+06	9.89E+05
01-Jun-93	5.33E+04	0.30	35.1	-1.71	-0.63			4.3		-19.20	-4.46	0.72	25.2	2.08E+06	1.49E+06
01-Jun-93	2.84E+04	0.25	33.6	-1.40	-0.62			4.3		-19.20	-4.46	0.80	26.8	9.76E+05	7.79E+05
02-Jun-93	5.53E+04	0.44	39.2	-1.08	-0.66			4.3		-19.20	-4.46	0.89	34.9	2.01E+06	1.79E+06
02-Jun-93	2.75E+04	0.59	43.8	-0.92	-0.69			4.3		-19.20	-4.46	0.94	41.2	1.14E+06	1.07E+06
03-Jun-93	6.12E+04	0.62	44.8	-1.24	-0.70			4.3		-19.20	-4.46	0.86	38.3	2.71E+06	2.32E+06
03-Jun-93	2.64E+04	0.63	45.1	-1.21	-0.70			4.3		-19.20	-4.46	0.87	39.0	1.19E+06	1.03E+06
04-Jun-93	5.82E+04	0.60	44.1	-1.61	-0.69			4.3		-19.20	-4.46	0.76	33.5	2.60E+06	1.97E+06
04-Jun-93	3.60E+04	0.50	41.1	-1.55	-0.67			4.3		-19.20	-4.46	0.77	31.6	1.53E+06	1.18E+06
05-Jun-93	5.00E+04	0.40	38.0	-1.62	-0.65			4.3		-19.20	-4.46	0.75	28.4	1.98E+06	1.48E+06
05-Jun-93	3.86E+04	0.35	36.5	-1.72	-0.64			4.3		-19.20	-4.46	0.72	26.2	1.44E+06	1.03E+06
06-Jun-93	7.52E+04	0.15	30.8	-1.65	-0.59			4.3		-19.20	-4.46	0.73	22.4	2.53E+06	1.84E+06
07-Jun-93	6.23E+04	-0.05	25.3	-1.47	-0.55			4.3		-19.20	-4.46	0.76	19.3	1.74E+06	1.33E+06
07-Jun-93	2.41E+04	-0.15	22.7	-1.58	-0.53			4.3		-19.20	-4.46	0.73	16.6	5.78E+05	4.24E+05
08-Jun-93	5.51E+04	-0.33	18.2	-1.61	-0.49			4.3		-19.20	-4.46	0.72	13.1	1.12E+06	8.08E+05
09-Jun-93	6.01E+04	-0.55	13.1	-1.45	-0.44			4.3		-19.20	-4.46	0.75	9.8	9.41E+05	7.05E+05
10-Jun-93	8.64E+04	-0.70	10.0	-1.51	-0.40			4.3		-19.20	-4.46	0.73	7.2	9.97E+05	7.24E+05
11-Jun-93	8.64E+04	-0.81	7.8	-1.37	-0.38			4.3		-19.20	-4.46	0.76	5.9	7.68E+05	5.82E+05
15-Jun-93	3.46E+05	-0.85	7.1	-1.19	-0.37			4.3		-19.20	-4.46	0.80	5.7	2.57E+06	2.06E+06
23-Jun-93	6.91E+05	-1.15	2.3	-0.76	-0.30			4.3		-19.20	-4.46	0.89	2.1	3.24E+06	2.89E+06
													SUMS	3.05E+07	2.33E+07
													f	0.76	

New water, C_N, was computed as the amount-weighted average $\delta^{18}O$ of all precipitation observed up to and including the timestep of interest using Equation 55:

$$C_N = \frac{\Sigma(P\ C_{PPT})}{\Sigma P} \tag{55}$$

Columns 7 and 8 provide isotopic and amount data for precipitation. Column 9 is the total amount of precipitation observed for the storm event, ΣP:

$$\Sigma P = 0.3 + 3.2 = 3.5\ \textit{inches} \tag{80}$$

Column 10 is the product of precipitation amount and $\delta^{18}O$:

$$C_{PPT}P = -4.84\ x\ 3.2 = -15.49\ \textit{in.o/oo} \tag{81}$$

and Column 11 is the sum of Column 10 up to and including the timestep of interest:

$$\Sigma(C_{PPT}P) = -0.61 + -15.49 = -16.10\ \textit{in.o/oo} \tag{82}$$

and finally, C_N is computed in Column 12 as Column 11 divided by Column 9:

$$C_N = \frac{-16.10\ \textit{in.o/oo}}{3.5\ \textit{in.}} = -4.60\ \textit{o/oo} \tag{83}$$

The fraction of old water, or V_O/V_R, was computed in Column 12 as

$$f_O = \frac{V_R}{V_O} = \frac{C_N - C_R}{C_N - C_O} = \frac{-4.60\ -\ -0.85}{-4.60\ -\ -0.03} = 0.82 \tag{84}$$

The old water flow during the timestep of interest was computed as:

$$Q_O = Q_R \; x \; f_O = 2.6 \; x \; 0.82 = 2.1 \; cfs \tag{85}$$

The total and old water volumes of flow, V_R and V_O respectively, were computed in Columns 15 and 16 so that their sums could be used to determine an event-mean fraction of old water. Volumes were computed as follows:

$$V = Q\Delta t$$

$$V_R = 2.6 \; \frac{ft.^3}{\text{sec}} \; x \; 7.20(10^4) \text{ sec} = 1.87(10^5) \; ft.^3 \tag{86}$$

$$V_O = 2.1 \; \frac{ft.^3}{\text{sec}} \; x \; 7.20(10^4) \text{ sec} = 1.54(10^5) \; ft.^3$$

Unsteady-State Sensitivity Analysis

The unsteady-state model includes terms for the volume and isotopic content of channel storage at the beginning and end of each timestep. Equation 50 is the derived hydrograph separation equation for the unsteady-state case:

$$V_O = \frac{V_2(C_N - C_2) - V_1(C_N - C_1) + V_r(C_N - C_O)}{(C_N - C_O)} \tag{50}$$

Setting all channel-storage terms equal to zero reduced Equation 50 to the steady-state form of the model (Equation 53).

Table 32 presents solutions for the unsteady-state model for the Spring 1993 storm event at station HR under varying assumptions of channel storage volume. Other relevant assumptions are discussed in the main text (Chapter 4). In Table 32, Columns 1 through 7 are reproduced from Table 30. Column 8 is the channel depth, which was estimated using measurements of river stage (Column 1). The arbitrary vertical datum

Table 32.
DATA LISTING AND COMPUTATIONS FOR SENSITIVITY ANALYSIS OF UNSTEADY-STATE HYDROGRAPH SEPARATION AT STATION HR.

SENSITIVITY ANALYSIS OF UNSTEADY-STATE MODEL
HIDDEN RIVER DATA

Revised 07-Apr-94
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Channel Properties
L = 50000
D = 2.22 + Stage
W = 0.20 x Q + 5

DATE (1)	dt (sec) (2)	Stage (ft) (3)	Flow (cfs) (4)	Cr (o/oo) (5)	Co (o/oo) (6)	Cn (o/oo) (7)	Depth (ft) (8)	Width (ft) (9)	Volume (ft^3) (10)	V2-V1 (ft^3) (11)	Vr (ft^3) (12)	Vo (ft^3) (13)	V2-V1/ (cfs) (14)	Qr+dV (cfs) (15)	Vr/dt (cfs) (16)	Vo/dt (cfs) (17)	SS fo (18)	USS fo (19)	0.9V fo (20)	1.0V fo (21)	1.1V fo (22)	1.2V fo (23)
29-May-93		-1.71	0.1	-0.32	0.10		0.5	5.0	1.28E+05													
29-May-93	1.80E+04	-1.71	0.1	-0.34	0.10	-2.05	0.5	5.0	1.28E+05	0.00E+00	1.03E+03	-3.19E+02	0.0	0.1	0.1	-0.0	0.80					
30-May-93	7.20E+04	-1.31	2.6	-0.85	-0.03	-4.60	0.9	5.5	2.51E+05	1.23E+05	9.57E+04	1.65E+05	1.7	3.0	1.3	2.3	0.82	0.75	0.75	0.75	0.76	0.76
31-May-93	8.03E+04	-0.51	13.5	-0.76	-0.27	-4.46	1.7	7.7	6.59E+05	4.08E+05	6.48E+05	9.39E+05	5.1	13.1	8.1	11.7	0.88	0.89	0.89	0.89	0.89	0.89
31-May-93	3.24E+04	-0.46	14.4	-0.68	-0.29	-4.46	1.8	7.9	6.94E+05	3.47E+04	4.53E+05	4.55E+05	1.1	15.0	14.0	14.0	0.91	0.93	0.93	0.93	0.94	0.94
01-Jun-93	5.33E+04	-0.19	19.5	-0.72	-0.37	-4.46	2.0	8.9	9.03E+05	2.10E+05	9.03E+05	1.01E+06	3.9	20.9	17.0	19.0	0.92	0.91	0.91	0.91	0.91	0.91
01-Jun-93	2.84E+04	0.20	27.8	-0.95	-0.49	-4.46	2.4	10.6	1.28E+06	3.75E+05	6.73E+05	8.73E+05	13.2	36.8	23.7	30.7	0.88	0.83	0.84	0.83	0.83	0.83
02-Jun-93	5.53E+04	0.58	36.9	-1.23	-0.61	-4.46	2.8	12.4	1.73E+06	4.56E+05	1.79E+06	1.80E+06	8.2	40.6	32.4	32.5	0.84	0.80	0.81	0.80	0.79	0.79
02-Jun-93	2.75E+04	0.60	37.4	-1.33	-0.62	-4.46	2.8	12.5	1.76E+06	2.66E+04	1.02E+06	8.05E+05	1.0	38.2	37.2	29.3	0.81	0.77	0.78	0.77	0.75	0.74
03-Jun-93	6.12E+04	0.58	36.9	-1.42	-0.61	-4.46	2.8	12.4	1.73E+06	-2.66E+04	2.28E+06	1.74E+06	-0.4	36.7	37.2	28.4	0.79	0.77	0.78	0.77	0.77	0.76
03-Jun-93	2.64E+04	0.64	38.5	-1.55	-0.63	-4.46	2.9	12.7	1.81E+06	8.08E+04	9.95E+05	7.61E+05	3.1	40.8	37.7	28.8	0.76	0.71	0.72	0.71	0.69	0.68
04-Jun-93	5.82E+04	0.50	34.9	-1.85	-0.59	-4.46	2.7	12.0	1.63E+06	-1.85E+05	2.14E+06	1.18E+06	-3.2	33.5	36.7	20.2	0.68	0.60	0.63	0.60	0.58	0.55
04-Jun-93	3.60E+04	0.43	33.2	-1.83	-0.57	-4.46	2.7	11.6	1.54E+06	-8.74E+04	1.23E+06	7.74E+05	-2.4	31.6	34.1	21.5	0.67	0.68	0.68	0.68	0.68	0.68
05-Jun-93	5.00E+04	0.37	31.8	-1.95	-0.55	-4.46	2.6	11.4	1.47E+06	-7.23E+04	1.63E+06	9.55E+05	-1.4	31.1	32.5	19.1	0.64	0.61	0.62	0.61	0.61	0.60
05-Jun-93	3.86E+04	0.27	29.4	-1.75	-0.52	-4.46	2.5	10.9	1.36E+06	-1.15E+05	1.18E+06	8.05E+05	-3.0	27.6	30.6	20.9	0.69	0.76	0.73	0.76	0.78	0.80
06-Jun-93	7.52E+04	0.09	25.4	-1.67	-0.46	-4.46	2.3	10.1	1.16E+06	-1.92E+05	2.06E+06	1.33E+06	-2.6	24.8	27.4	17.7	0.70	0.71	0.71	0.71	0.72	0.72
07-Jun-93	6.23E+04	-0.31	17.2	-1.53	-0.34	-4.46	1.9	8.4	8.05E+05	-3.58E+05	1.32E+06	7.24E+05	-5.7	15.5	21.3	11.6	0.71	0.75	0.74	0.75	0.77	0.79
07-Jun-93	2.41E+04	-0.49	13.9	-1.39	-0.28	-4.46	1.7	7.8	6.73E+05	-1.33E+05	3.74E+05	2.06E+05	-5.5	10.0	15.5	8.5	0.74	0.85	0.81	0.85	0.91	0.99
08-Jun-93	5.51E+04	-0.65	11.2	-1.37	-0.23	-4.46	1.6	7.2	5.68E+05	-1.05E+05	6.90E+05	4.32E+05	-1.9	10.6	12.5	7.8	0.73	0.74	0.74	0.74	0.74	0.74
09-Jun-93	6.01E+04	-0.92	7.1	-1.25	-0.15	-4.46	1.3	6.4	4.18E+05	-1.50E+05	5.51E+05	3.13E+05	-2.5	6.7	9.2	5.2	0.74	0.78	0.77	0.78	0.79	0.81
10-Jun-93	8.64E+04	-1.07	5.2	-1.27	-0.10	-4.46	1.2	6.0	3.47E+05	-7.05E+04	5.33E+05	3.37E+05	-0.8	5.4	6.2	3.9	0.73	0.73	0.73	0.73	0.73	0.73
11-Jun-93	8.64E+04	-1.18	3.9	-1.21	-0.07	-4.46	1.0	5.8	3.01E+05	-4.65E+04	3.94E+05	2.62E+05	-0.5	4.0	4.6	3.0	0.74	0.75	0.75	0.75	0.75	0.75
																Mean:	0.77	0.77	0.77	0.77	0.77	0.77

for site HR corresponded to a channel depth of approximately 2.22 ft. Again, using 30-May-93 as for sample calculations,

$$D = 2.22 + z = 2.22 + -1.31 = 0.91\ ft. \tag{87}$$

Channel width was estimated in Column 9, based on site survey data, using an empirical function of flow:

$$W = 0.2Q + 5.0 = (0.2\ x\ 2.6) + 5.0 = 5.5\ ft. \tag{88}$$

Channel volume at the end of each timestep (V_2) was computed in Column 10 as the product of length, width, and depth. Channel length was estimated using USGS topographic maps and site survey data to be approximately 50,000 ft. upstream of station HR. For 30-May-93, V_2 was computed as

$$V_2 = L\ x\ W\ x\ D = 50{,}000\ x\ 5.5\ x\ 0.9 = 2.51(10^5)\ ft.^3 \tag{89}$$

Column 11 is the change in storage volume over the timestep of interest:

$$V_2 - V_1 = V_t - V_{t-\Delta t} = 2.51(10^5) - 1.28(10^5) = 1.23(10^5)\ ft.^3 \tag{90}$$

Column 12 is the average inflow volume during the timestep of interest:

$$\begin{aligned} V_R &= \frac{1}{2}(Q_t + Q_{t-\Delta t})\Delta t \\ &= \frac{1}{2}(2.6 + 0.1)\ x\ 7.20(10^4) = 9.57(10^4)\ ft.^3 \end{aligned} \tag{91}$$

The volume of old water is computed in Column 13 using Equation 50:

$$V_O = \frac{2.51(10^5)(-4.60+0.85)\ -\ 1.28(10^5)(-4.60+0.34)\ +\ 9.57(10^4)(-4.60+0.03)}{(-4.60+0.34)}$$

$$= 1.65(10^5)\ ft.^3 \qquad (92)$$

Columns 14 through 17 normalize various components of the flow mass balance into flows by multiplying volumes (ft.^{3}sec^{-1}) by the duration of the timestep (sec). Column 19 is the unsteady-state fraction of old water ($f_{o(USS)}$) computed using Equation 59:

$$f_{O(USS)} = \frac{V_O}{V_2 + V_R - V_1} \qquad (59)$$

$$f_{O(USS)} = \frac{1.65(10^5)}{2.512(10^5)\ +\ 9.57(10^4)\ -\ 1.28(10^5)} = 0.75 \qquad (93)$$

Columns 20 through 23 examine the effect of changes in channel volume on the estimate of old water fraction under unsteady-state conditions. In Column 20, the estimates of all channel volumes tabulated in Column 10 are reduced uniformly by 10 percent and $f_{O(USS)}$ is calculated as described above. In Columns 22 and 23, the initial assumption of channel volume is increased by 10 and 20 percent, respectively.

Throughfall Enrichment Effects Analysis

Table 33 solves the steady-state hydrograph-separation model at station HR assuming throughfall effects result in an enrichment of 0.5 ‰ in new water. The data in Table 33 are identical to those presented in Table 30, except that all terms in Column 7 were increased by +0.5. A sample calculation is provided in the main text (Chapter

Table 33.
DATA LISTING AND COMPUTATIONS FOR THROUGHFALL EFFECTS ANALYSIS USING THE STEADY-STATE HYDROGRAPH SEPARATION MODEL AT STATION HR.

DATE (1)	dt (sec) (2)	Stage (ft) (3)	Flow (cfs) (4)	O-18 (o/oo) (5)	Co (o/oo) (6)	Cp (o/oo) (7)	P (in) (8)	SigmaP (in) (9)	CpP (in.o/oo) (10)	SigmaCp (in.o/oo) (11)	Cn (o/oo) (12)	fo (13)	Qo (cfs) (14)	Vr (ft^3) (15)	Vo (ft^3) (16)
01-May-93		-0.42	15.1	-0.13	-0.30										
02-May-93	7.96E+04	-0.53	13.2	-0.09	-0.27										
03-May-93	8.33E+04	-0.58	12.3	-0.24	-0.25										
04-May-93	8.92E+04	-0.59	12.2	-0.20	-0.25										
05-May-93	8.64E+04	-0.65	11.2	-0.23	-0.23										
06-May-93	8.64E+04	-0.75	9.6	-0.19	-0.20										
07-May-93	8.64E+04	-0.74	9.8	-0.24	-0.20										
08-May-93	7.61E+04	-0.79	9.0	-0.29	-0.19										
09-May-93	9.05E+04	-0.86	8.0	-0.32	-0.16										
10-May-93	9.00E+04	-0.86	8.0	-0.15	-0.16										
11-May-93	8.89E+04	-0.96	6.6	-0.14	-0.13										
18-May-93	6.24E+05	-1.41	1.7	-0.02	0.01										
26-May-93	6.72E+05	-1.72	0.0	-0.04	0.10										
29-May-93	2.56E+05	-1.71	0.1	-0.32	0.10										
29-May-93	1.80E+04	-1.71	0.1	-0.34	0.10	-1.55	0.3	0.3	-0.46	-0.46	-1.55	0.74	0.0	1.03E+03	7.58E+02
30-May-93	7.20E+04	-1.31	2.6	-0.85	-0.03	-4.34	3.2	3.5	-13.89	-14.35	-4.10	0.80	2.1	1.87E+05	1.49E+05
31-May-93	8.03E+04	-0.51	13.5	-0.76	-0.27	-3.37	0.8	4.3	-2.70	-17.05	-3.96	0.87	11.8	1.09E+06	9.44E+05
31-May-93	3.24E+04	-0.46	14.4	-0.68	-0.29			4.3		-17.05	-3.96	0.89	12.9	4.67E+05	4.18E+05
01-Jun-93	5.33E+04	-0.19	19.5	-0.72	-0.37			4.3		-17.05	-3.96	0.90	17.6	1.04E+06	9.39E+05
01-Jun-93	2.84E+04	0.20	27.8	-0.95	-0.49			4.3		-17.05	-3.96	0.87	24.1	7.91E+05	6.86E+05
02-Jun-93	5.53E+04	0.58	36.9	-1.23	-0.61			4.3		-17.05	-3.96	0.82	30.2	2.04E+06	1.67E+06
02-Jun-93	2.75E+04	0.60	37.4	-1.33	-0.62			4.3		-17.05	-3.96	0.79	29.4	1.03E+06	8.09E+05
03-Jun-93	6.12E+04	0.58	36.9	-1.42	-0.61			4.3		-17.05	-3.96	0.76	28.0	2.26E+06	1.72E+06
03-Jun-93	2.64E+04	0.64	38.5	-1.55	-0.63			4.3		-17.05	-3.96	0.73	27.9	1.01E+06	7.36E+05
04-Jun-93	5.82E+04	0.50	34.9	-1.85	-0.59			4.3		-17.05	-3.96	0.63	21.9	2.03E+06	1.28E+06
04-Jun-93	3.60E+04	0.43	33.2	-1.83	-0.57			4.3		-17.05	-3.96	0.63	20.8	1.20E+06	7.49E+05
05-Jun-93	5.00E+04	0.37	31.8	-1.95	-0.55			4.3		-17.05	-3.96	0.59	18.8	1.59E+06	9.39E+05
05-Jun-93	3.86E+04	0.27	29.4	-1.75	-0.52			4.3		-17.05	-3.96	0.64	18.9	1.13E+06	7.28E+05
06-Jun-93	7.52E+04	0.09	25.4	-1.67	-0.46			4.3		-17.05	-3.96	0.66	16.6	1.91E+06	1.25E+06
07-Jun-93	6.23E+04	-0.31	17.2	-1.53	-0.34			4.3		-17.05	-3.96	0.67	11.5	1.07E+06	7.17E+05
07-Jun-93	2.41E+04	-0.49	13.9	-1.39	-0.28			4.3		-17.05	-3.96	0.70	9.7	3.35E+05	2.34E+05
08-Jun-93	5.51E+04	-0.65	11.2	-1.37	-0.23			4.3		-17.05	-3.96	0.70	7.8	6.16E+05	4.28E+05
09-Jun-93	6.01E+04	-0.92	7.1	-1.25	-0.15			4.3		-17.05	-3.96	0.71	5.1	4.29E+05	3.05E+05
10-Jun-93	8.64E+04	-1.07	5.2	-1.27	-0.10			4.3		-17.05	-3.96	0.70	3.6	4.49E+05	3.13E+05
11-Jun-93	8.64E+04	-1.18	3.9	-1.21	-0.07			4.3		-17.05	-3.96	0.71	2.8	3.39E+05	2.39E+05
15-Jun-93	3.46E+05	-1.25	3.2	-1.01	-0.04			4.3		-17.05	-3.96	0.75	2.4	1.10E+06	8.29E+05
23-Jun-93	6.91E+05	-1.43	1.6	-0.73	0.01			4.3		-17.05	-3.96	0.81	1.3	1.08E+06	8.81E+05
													SUMS	2.32E+07	1.70E+07
													f	0.73	

4, Equations 60 and 61).

Discrete Reach Model

The isotopic content of a conservative tracer associated with the gain observed in a discrete reach of the river was estimated using a steady-state mass-balance model (Equation 66). To determine the level of sensitivity of the model to precision in flow measurements, flow terms in the model were varied by a range of 40 percent. The modeling data are summarized in Table 34 and a sample calculation for 30-May-93 is provided below.

Columns 1 through 6 present field and isotopic data for stations HR and FR, the upstream and downstream boundaries of the study reach. Column 7 is the amount of gain in flow over the reach:

$$\frac{dV}{dt} = 0 = Q_{HR} + Q_G - Q_{FR} \qquad (94)$$

$$Q_G = Q_{FR} - Q_{HR} = 16.1 - 2.1 = 14.0 \ cfs$$

Column 8 is the steady-state solution for the gaining tracer (C_G):

$$C_G = \frac{C_{FR}V_{FR} - C_{HR}V_{HR}}{V_{FR} - V_{HR}} \qquad (66)$$

$$C_G = \frac{(-2.26 \ x \ 16.1) - (-0.85 \ x \ 2.1)}{16.1 - 2.1} = -2.47 \ o/oo \qquad (95)$$

Since the model was solved under steady-state conditions, the volume terms (*e.g.*, V_{FR}) were substituted for flow terms (*e.g.*., Q_{FR}) in Equation 95.

Table 34.
DATA LISTING AND COMPUTATIONS FOR DISCRETE-REACH HYDROGRAPH SEPARATION MODEL.

DATE (1)	dt (sec) (2)	HRR Flow (cfs) (3)	HRR O-18 (o/oo) (4)	FRR Flow (cfs) (5)	FRR O-18 (o/oo) (6)	Qt (cfs) (7)	SS Cg (o/oo) (8)	hr 1.2 fr 1.2 Cg (o/oo) (9)	hr 1.2 fr 0.8 Cg (o/oo) (10)	hr 0.8 fr 1.2 Cg (o/oo) (11)	hr 0.8 fr 0.8 Cg (o/oo) (12)
26-May-93	2.95E+09	0.0	-0.04	0.8	-0.50	0.8	-0.52	-0.52	-0.53	-0.51	-0.52
29-May-93	2.56E+05	0.0	-0.32	0.7	-0.66	0.7	-0.69	-0.69	-0.70	-0.68	-0.69
29-May-93	1.80E+04	0.0	-0.34	0.7	-0.69	0.7	-0.71	-0.71	-0.73	-0.70	-0.71
30-May-93	7.20E+04	2.1	-0.85	16.1	-2.26	14.0	-2.47	-2.47	-2.60	-2.40	-2.47
31-May-93	8.03E+04	10.8	-0.76	38.4	-1.90	27.5	-2.35	-2.35	-2.74	-2.17	-2.35
31-May-93	3.24E+04	11.5	-0.68	34.3	-1.92	22.8	-2.56	-2.56	-3.19	-2.28	-2.56
01-Jun-93	5.33E+04	15.6	-0.72	28.0	-1.71	12.4	-2.95	-2.95	-6.70	-2.29	-2.95
01-Jun-93	2.84E+04	22.3	-0.95	26.9	-1.40	4.6	-3.52	-3.52	0.87	-1.94	-3.52
02-Jun-93	5.53E+04	29.5	-1.23	31.4	-1.08	1.8	1.24	1.24	-1.58	-0.84	1.24
02-Jun-93	2.75E+04	29.9	-1.33	35.1	-0.92	5.1	1.49	1.49	-2.80	-0.38	1.49
03-Jun-93	6.12E+04	29.5	-1.42	35.8	-1.24	6.3	-0.40	-0.40	-2.18	-1.02	-0.40
03-Jun-93	2.64E+04	30.8	-1.55	36.1	-1.21	5.3	0.75	0.75	-2.76	-0.76	0.75
04-Jun-93	5.82E+04	27.9	-1.85	35.3	-1.61	7.4	-0.70	-0.70	-3.12	-1.34	-0.70
04-Jun-93	3.60E+04	26.6	-1.83	32.8	-1.55	6.3	-0.34	-0.34	-3.17	-1.22	-0.34
05-Jun-93	5.00E+04	25.4	-1.95	30.4	-1.62	5.0	0.04	0.04	-3.23	-1.21	0.04
05-Jun-93	3.86E+04	23.5	-1.75	29.2	-1.72	5.7	-1.58	-1.58	-1.91	-1.68	-1.58
06-Jun-93	7.52E+04	20.3	-1.67	24.6	-1.65	4.3	-1.55	-1.55	-1.75	-1.62	-1.55
07-Jun-93	6.23E+04	13.7	-1.53	20.2	-1.47	6.5	-1.35	-1.35	-4.69	-1.42	-1.35
07-Jun-93	2.41E+04	11.1	-1.39	18.1	-1.58	7.0	-1.88	-1.88	-3.73	-1.71	-1.88
08-Jun-93	5.51E+04	8.9	-1.37	14.5	-1.61	5.6	-1.99	-1.99	-4.47	-1.77	-1.99
09-Jun-93	6.01E+04	5.7	-1.25	10.5	-1.45	4.8	-1.68	-1.68	-2.31	-1.56	-1.68
10-Jun-93	8.64E+04	4.2	-1.27	8.0	-1.51	3.8	-1.78	-1.78	-2.39	-1.64	-1.78

Columns 9 through 12 vary the flow terms Q_{HR} and Q_{FR} by plus and minus 20 percent. As an example, Column 10 increases flow at HR by 20 percent and decreases flow at FR by 20 percent:

$$C_G = \frac{(-2.26\ x\ 16.1\ x\ 1.2) - (-0.85\ x\ 2.1\ x\ 0.8)}{(16.1\ x\ 1.2) - (2.1\ x\ 0.8)} = -2.60\ o/oo \qquad (96)$$

APPENDIX E

COMPLETE REFERENCES

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