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Stable Isotopic Investigation of the Hydrological Cycle of West-Central Florida

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STABLE ISOTOPIC INVESTIGATION
OF THE HYDROLOGICAL CYCLE
OF WEST-CENTRAL FLORIDA

by

TOEDSIT NETRATANAWONG

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Marine Science
University of South Florida

August 1995

Major Professor: William M. Sackett, Ph.D.

Graduate School
University of South Florida
Tampa, Florida

CERTIFICATE OF APPROVAL

Ph.D. Dissertation

This is to certify that the Ph.D. Dissertation of

TOEDSIT NETRATANAWONG

with a major in Marine Science has been approved by
the Examining Committee on March 29, 1995
as satisfactory for the Dissertation requirement
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An Abstract

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Stable isotopic compositions of oxygen, carbon, and hydrogen were used to identify the sources of water and of organic matter, pathway reactions, evaporation processes, and transfer mechanisms among various water types as well as the extent of water-rock reactions. An attempt to understand the isotopic compositions of the hydrological cycle of west-central Florida, their variations, baseline levels and controlling mechanisms constitutes parts of this dissertation.

A comparison of $\delta^{18}O$ in rainwater (weighted mean = -4.4 o/oo) and surficial ground water (mean = -4.1 o/oo) indicates that rainwater recharges the surficial aquifer with only a minor isotopic change. $\delta^{18}O$ vs δD plots of rainwater and ground waters suggest that recently recharged water in the upper Floridan aquifer is similar to today's rainwater. As shown by calculations, carbonate aquifers react extensively with the ground waters in the upper Floridan aquifer through time to cause a shift of $\delta^{18}O$ from -4.4 to -2.8 o/oo. Changes in $\delta^{18}O$ and $\delta^{13}C_{DIC}$ in ground waters of the upper Floridan aquifer in two flow paths suggest that the confined nature of the aquifer causes the difference. Parts of the upper Floridan aquifer supply freshwater to rivers discharging into Tampa Bay as evidenced by similarities in $\delta^{18}O$ and $\delta^{13}C_{DIC}$ of both freshwater types. Evaporation may play a role in shifting the $\delta^{18}O$ of rivers from ground-water source of -2.8 o/oo to -2.3 o/oo.

Precipitation compositions obey the global Rayleigh distillation model. Atmospheric water vapor is kinetically separated, isotopically, from water bodies with a mixed signature from transpired and evaporative waters. Trees act as conduits for ground-water transfer into the atmosphere without changes in isotopic compositions. Transpiration seems to contribute more to the total evaporation than free-water evaporation based on O-18 compositions of surficial aquifer water and of rainfall. Pan evaporation experiments provide support for the theoretical and observed isotopic behavior of atmospheric water vapor.

$\delta^{18}O$ and $\delta^{13}C$ in Tampa-Bay water correlate linearly with salinity. Based on isotopic mass balance calculations, the replacement time of Tampa-Bay water is about 67 days. Mirror Lake has invariant $\delta^{18}O$ during a one-year study, and has a calculated replacement time for its water of 43 days.

Abstract Approved: ___ ____

Major Professor: William M. Sackett, Ph.D.
Distinguished Professor, Department of Marine Science

Date Approved: ___ ______________

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CHAPTER 1

GENERAL INTRODUCTION

The hydrological cycle covers movement of water from the oceans into the atmosphere, precipitation onto the land, and further runoff of surface and ground waters into the oceans. The cycle is perpetuated by the heat received from the sun. The latitudinal heat gradients further drive various atmospheric-circulation cells which result in different weather patterns, both seasonally and perennially. Physico-chemical processes govern the amount of water, types of clouds, and humidity in concordance with the reservoirs' geological parameters and evapo-transpiration processes. An attempt to better understand the hydrological cycle of west-central Florida (Figure 1) based on stable oxygen and carbon isotopes is the goal of this dissertation.

Direct measurements of different types of water and their contributions to different reservoirs are difficult and often rely on meteorological data. For example, the amount of water vapor in the atmosphere is calculated from relative humidity, air temperature, and saturation water pressure (McIlveen, 1992; Appendix 1); evaporation is estimated from calculation of the heat or energy mass balance (Knapp, 1985). An insight into identification of source, sink and recycled waters obtained using the above methods is limited. However, with the introduction of chemical and isotopic tracers, detailed mechanisms of water transfer in the hydrological cycle began to be understood (Epstein and Mayeda, 1953; Dansgaard, 1953).

Natural chemical tracers, such as oxygen-18 or hydrogen-2 (deuterium), are intrinsic in nature because they constitute parts of the water molecules themselves. Oxygen-18 comprises about 0.20 % of the total abundance of all stable oxygen atoms (oxygen-16 = 99.76 %; oxygen-17 = 0.04%) in the Earth's crust (summarized in

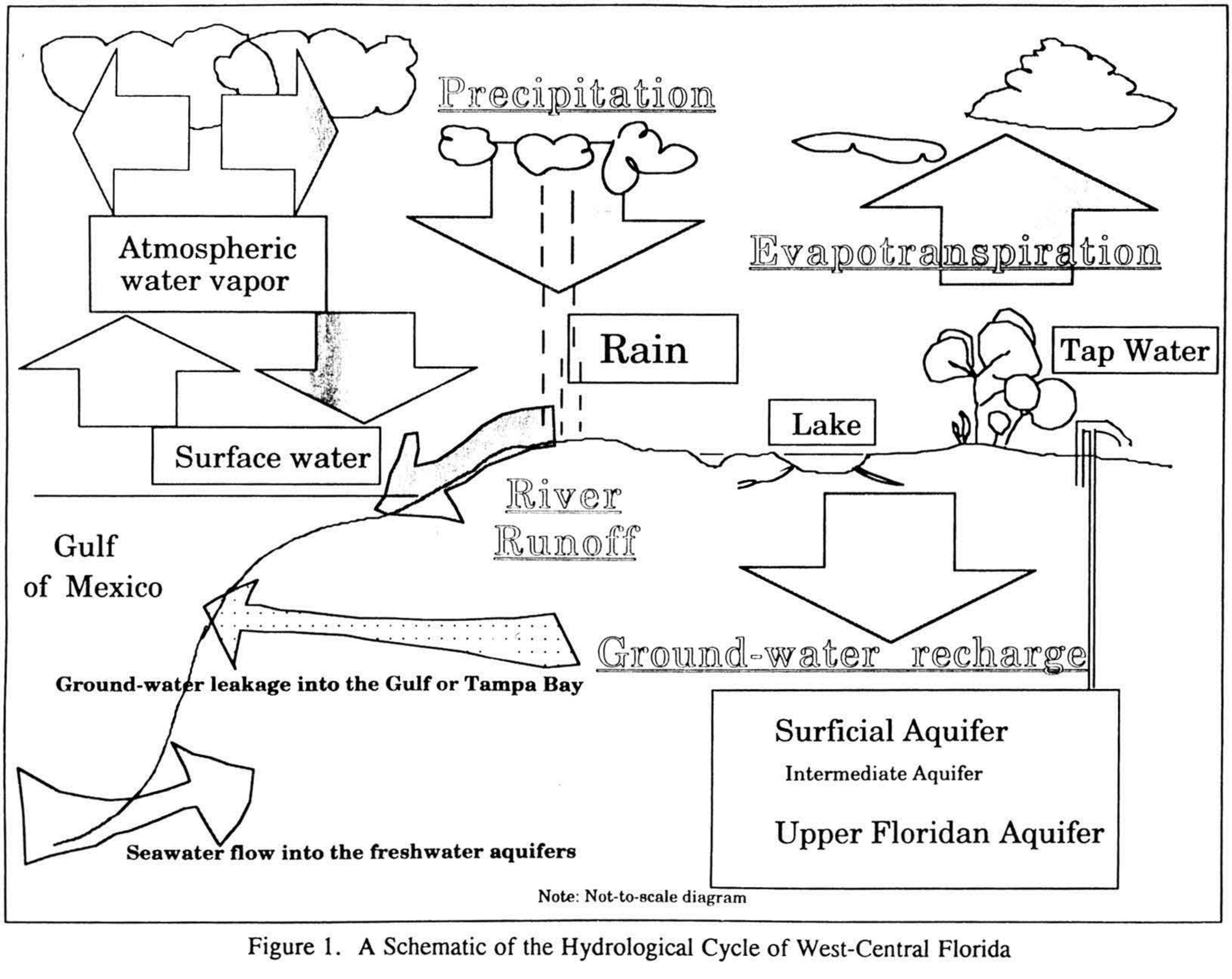


Figure 1. A Schematic of the Hydrological Cycle of West-Central Florida

Hoefs, 1987). It is difficult to analyze the amount of oxygen-18 directly, as the bulk of water is in the oxygen-16 form. Fortunately, with the invention of the isotope-ratio mass spectrometer, IRMS (McKinney et al., 1950), and an understanding of the factors which regulate the isotopic fractionation (discussed later), as well as the evolution of measurement techniques for oxygen-18 in samples, precise determinations of oxygen isotopic ratios in samples were made possible (Urey, 1947; Epstein and Mayeda, 1953).

The oxygen-18 determination is performed by means of a gaseous carbon-dioxide (CO_{2g}) surrogate. The dried CO_{2g} is processed from samples using one of several methodologies (see last section in Standards section of Methods of Study). The $CO_{2(g)}$ carries the stable isotopic signature of oxygen (oxygen -16, -17, and -18) obtained from the water sample. The ^{18}O (oxygen-18) of the sample gas is ratioed to the ^{16}O (oxygen-16) of the sample gas compared to those of the standard gas, with minor correction for oxygen-17 (Craig, 1957). The comparison is made with a great precision on the IRMS. This $CO_{2(g)}$ also carries the $^{13}C^{17}O^{16}O$, which is corrected for during the calculation of oxygen isotopic ratios on the IRMS. The small deviation of these ratios from unity is the delta oxygen-18 ($\delta^{18}O$) value in parts per thousand (o/oo) of the sample. A representative equation is

$$(^{18}O/^{16}O)_{sample} / (^{18}O/^{16}O)_{standard} = 1 + \delta^{18}O/1000 \qquad \text{(1a) or}$$

$$\delta^{18}O = [\{(^{18}O/^{16}O)_{sample} / (^{18}O/^{16}O)_{standard}\} - 1]1000 \qquad \text{(1b).}$$

The $\delta^{18}O$ of the standard is usually set to zero by definition. The standards for O-18 determination, whether they are carbonate standards or seawater standards, have well-defined absolute concentrations of both oxygen -16, -17, and -18 (McCrea, 1950; Epstein and Mayeda, 1953; Craig, 1957; Baertschi, 1976; Gonfiantini, 1978).

The isotopic fractionation factor (α) is defined similarly to a chemical equilibrium, e.g.

$$2H_2{}^{18}O_{(liquid)} + C^{16}O^{16}O_{(gaseous)} \longleftrightarrow 2H_2{}^{16}O_{(liquid)} + C^{18}O^{18}O_{(gaseous)} \quad (2)\ \text{and}$$

$$K = \frac{[H_2{}^{16}O]^2[C^{18}O^{18}O]}{[H_2{}^{18}O]^2[C^{16}O^{16}O]} = \text{equilibrium constant}$$

$$= \frac{[C^{18}O^{18}O]/[C^{16}O^{16}O]}{[H_2{}^{18}O]^2/[H_2{}^{16}O]^2}$$

If α (fractionation factor) = $({}^{18}O/{}^{16}O)_{gaseous\ CO_2}/\ ({}^{18}O/{}^{16}O)_{liquid\ water}$, where

$\alpha = K^{1/n}$; where n = 2 = the maximum number of exchangeable oxygens in any one of the molecules for the above reaction, then

$$\alpha = \frac{[2C^{18}O_2 + C^{16}O^{18}O]/[C^{16}O^{18}O + 2C^{16}O]}{[H_2{}^{18}O/H_2{}^{16}O]} \quad (3)$$

$$= \frac{[C^{18}O_2/C^{16}O_2]^{1/2}}{[H_2{}^{18}O/H_2{}^{16}O]} \quad (4)$$

(Urey, 1947; Epstein, 1959).

The rate of the above reaction is controlled by temperature (Urey, 1947). The basic isotope-ratio measurement for O-18 composition in water is the comparison of ${}^{18}O/{}^{16}O$ compositions in the isotopically equilibrated CO_2 gas with the water samples to those of the standard water. The $\delta^{18}O$ of sample is usually reported in parts per thousand (o/oo) deviation from the standard.

For stable carbon (carbon-13) isotopic studies on total dissolved inorganic carbonate in ground water and estuarine water as well as on aquifer carbonate minerals, the isotopic fractionation factors govern the isotopic behavior and resulting $CO_{2(g)}$ composition (e.g. Urey, 1947; Craig, 1953; McCrea, 1950; Sackett and Moore, 1966). Carbon-13 comprises about 1.10 % of the total abundance of stable carbon isotopes, while carbon-12 comprises 98.9 % of the total abundance (Hoefs, 1987). Biological metabolism and biochemical pathways affect, to a great extent, the $^{13}C/^{12}C$ distribution in natural organic tissues (Craig, 1953; O'Leary, 1981; Sackett, 1989).

Since the $CO_{2(g)}$ is used also in the determination of stable carbon isotopes (on an IRMS), the carbon and oxygen stable isotopes are interrelated instrumentally (e.g. Craig, 1957). The $^{18}O/^{16}O$ of sample can affect the $^{13}C/^{12}C$ signal, and vice versa - because of the mass overlapping of $^{12}C^{18}O^{16}O$ and $^{13}C^{16}O^{17}O$ (mass 46), and $^{13}C^{16}O^{16}O$ and $^{12}C^{16}O^{17}O$ (mass 45). Under the isotope-ratio mass spectrometer, the corrected $\delta^{18}O$ and $\delta^{13}C$ are

$$\delta^{18}O_{corr} = A\delta^{18}O_{meas} + c\delta^{13}C \tag{5}$$

$$\delta^{13}C_{corr} = B\delta^{13}C_{meas} + d\delta^{18}O \tag{6}$$

where

$_{corr}$ = corrected value

$_{meas}$ = measured value

A, B - factors involving $^{13}C^{16}O^{17}O$ and $^{12}C^{16}O^{17}O$, respectively,

c, d - factors involving ^{17}O species.

The final delta values on modern IRMS instruments (1980 onwards) have been corrected and adjusted for oxygen-17.

In order to improve coherence and continuity of the dissertation because of the wealth of information in the hydrological cycle, the main text is arranged as follows:

Chapter 3: Water cycle, rainwater, atmospheric water vapor, and evaporation,

Chapter 4: River, and estuarine waters in Tampa Bay,

Chapter 5: Ground water, and Mirror-Lake water.

Each chapter (3 through 5) contains previous and current studies, as well as data generated by the author, and chapter discussion and brief summary. Each is almost complete and independent of other chapters. General discussion based on the author's works on both oxygen and carbon isotopes follow as Chapter 6. Conclusions appear in Chapter 7.

Objectives of This Dissertation

Since there are no background data on rainwater $\delta^{18}O$ in west-central Florida (IAEA, 1981; Rozanski et al., 1993) nor is there basic oxygen isotopic data on the evaporation and estuarine processes, the acquisition of these baseline data is important. In addition, temporal distribution of $\delta^{18}O$ in ground water is not known (Swancar and Hutchinson, 1992). The goals of this dissertation can be categorized as follows:

1. To monitor $\delta^{18}O$ of rainwater in St. Petersburg, Florida for two years.
2. To determine the causal factors (temperature, amount, etc.) which regulate the O-18 composition of rainwater.
3. To establish the relationship between the $\delta^{18}O$ of rainwater, atmospheric water vapor and ground water in west-central Florida.
4. To characterize Floridan ground water from recharge in the Green Swamp area to the discharge area in southwest Hillsborough County of west-central Florida in terms of its O-18 and C-13 (inorganic) compositions, and the effects of confined aquifers upon its O-18 and C-13 (inorganic).
5. To examine the temporal and seasonal changes in $\delta^{18}O$ and $\delta^{13}C$ (inorganic) in 2 ground-water sites (Roy Haynes, Tampa and Baum-Wimauma, Wimauma) for surficial, intermediate, and Floridan aquifer waters.
6. To estimate the degree of exchange of oxygen-18 between aquifer carbonate minerals and upper Floridan aquifer water.
7. To determine the $\delta^{18}O$ of water in Mirror Lake, a small enclosed-basin lake in St. Petersburg, Florida, for possible connections between rainwater, surficial ground water, and evaporation process during weekly sampling for one year.

8. To estimate the evaporation parameters from bodies of water in nature, and from pan experiments, and their relations with relative humidity and δ^{18}O in water and atmospheric water vapor.
9. To establish the relationship between the δ^{18}O of transpired water from tree leaves and soil water (ground water).
10. To establish the relationships among salinity, δ^{13}C and δ^{18}O of estuarine water in Tampa Bay.
11. To estimate the degree of exchange of surface waters with ground waters and to model the distribution of water types in different reservoirs of the hydrological cycle in west-central Florida.

CHAPTER 2

METHODS OF STUDY

Sampling, Storage, Treatment, Handling Techniques, and Study Areas

General Sampling Storage

$\delta^{18}O$

All water samples for $\delta^{18}O$ analyses were stored and sealed in glass jars or small glass vials at room temperature (23-26 °C). The glass containers help reduce loss of $H_2{}^{16}O$ through evaporation or "breathing" of water through the surface of the containers. As long as there was no loss of water through evaporation, the water samples could be stored for months without significant changes in $\delta^{18}O$ (Stewart, 1981). Preservative chemicals were not added to any of the water samples. For ground water and Mirror Lake samples the glass jars were completely filled, and capped tightly. This storage applied to the δD analyses.

$\delta^{13}C$

For water samples analyzed for $\delta^{13}C$ of total dissolved inorganic carbon, the storage of samples at 5-8 °C was necessary. The cool temperature was thought to reduce bacterial oxidation of dissolved organic matter, which could alter the $\delta^{13}C$ (inorganic) of samples. However, there has been no laboratory study to determine the range of temperature of optimal storage for $\delta^{13}C$ analysis. Mercuric chloride or other preservatives was not added to samples for $\delta^{13}C$ analyses. Samples were analyzed as soon as possible (usually within one week of samplings).

Rainwater

Samples of rainwater were collected in a 25-cm plastic funnel (with small end closed, Figure 2a). The collecting funnel was placed on top of the roof of Department of Marine Science's Laboratory building (MSL), University of South Florida (St. Petersburg, Florida; latitude: 27.76 °N; longitude: 82.63 °W). The rainwater samples were analyzed for $\delta^{18}O$ within one week. Most samples, which were collected over the weekends, were discarded because there were water droplets condensed inside the rain gauge. The condensation suggested that evaporation of water took place. All samples were analyzed for $\delta^{18}O$ in duplicate. The $\delta^{18}O$ study of rainwater was performed over a two-year period (1991-1992). The amount of rainwater was measured using a standard meteorological rain gauge (see Figure 2b). Average air temperatures were measured at nearby Albert Whitted Airport (Federal Aviation Administration's Control Tower; approximately 1 km northeast of the MSL building). The daily temperature data for the rainy days were obtained from the National Weather Service (Ruskin, Florida). These temperature readings were used to represent the temperatures at the MSL building.

Lake Water

Mirror Lake in downtown St. Petersburg was monitored weekly for O-18 composition during a one-year period (1991). Surface samples were taken from the southern side of the Lake by scooping lake water into glass jars. The jars were completely filled with water. All samples were analyzed for $\delta^{18}O$ in duplicate. The Lake water was assumed to be well mixed during 1991. Unfortunately, the average water temperature reading was not taken at the time of sampling, but it was expected to be within a few degrees of air temperature.

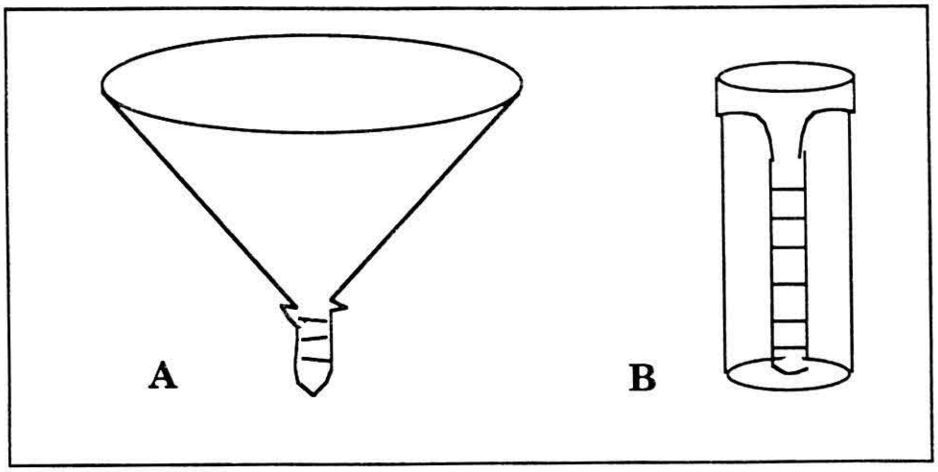


Figure 2. Diagrams of the Funnel (A) and Rain Gauge (B) Used in the Study

Estuarine Water

Estuarine-water samples from Tampa Bay were collected at 2 different periods: March, 1990 (mainly by Beth Holmes), and January, 1993 (by the author). One sample collected from each station was left at room temperature for $\delta^{18}O$ analysis, while another was kept cold in a cold box ($\approx$ 5 °C) for $\delta^{13}C$ analysis. Locations of the sampling sites are depicted in Figure 3. Salinity was also determined for these samples using a micro-chlorinity titration (to be described in the Analytical Techniques section).

Atmospheric-Water Vapor, and Transpired Water from Plants' Leaves

Either open moist air or moisture from the enclosure bag on a branch of leaves was pumped at a rate of 1 to 1½ liter/minute through a single-step glass trap which was maintained at -85 °C using a slush of isopropanol-liquid nitrogen (Figure 4a). The slush was prepared by adding enough liquid nitrogen to isopropanol until the alcohol became a cold slush. Schoch-Fischer et al. (1984) showed that both temperature and

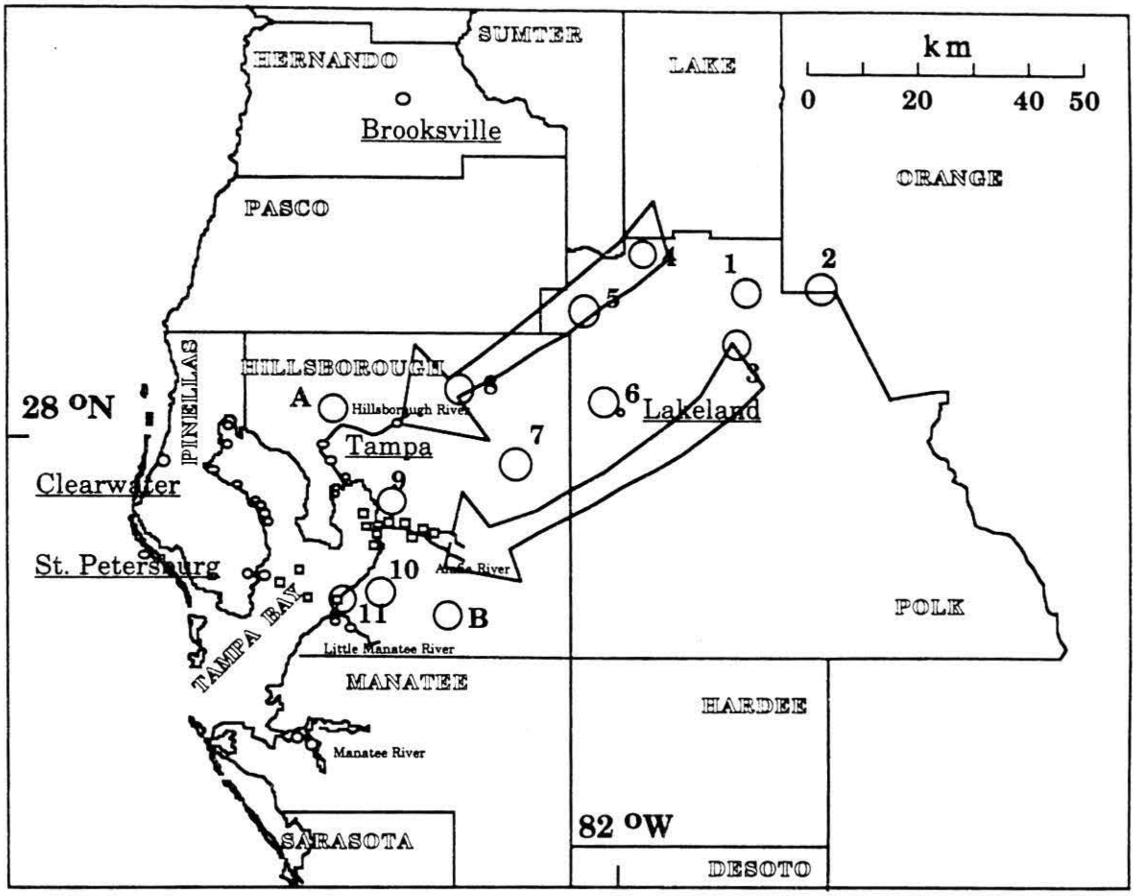


Figure 3. Sampling Locations for Estuarine Waters, Ground Waters, and Rainwater. The Big Circles are Ground-Water Sites (See Chapter 5 for Details). The Small Circles and Squares in the Tampa Bay and Adjacent Rivers are Estuarine-Water Sites during March, 1990 and January, 1993, Respectively. Ground-Water Flow Paths from the Green Swamp to Coastal West-Central Florida are Represented as 2 Arrows.

flow rate of this moisture-trapping method affected the total amount of water vapor collected, and the subsequent degree of O-18 fractionation. At an air temperature of 10 °C, relative humidity of 70 %, flow rate of 0.5 liters/minute, and a trapping temperature of -80 °C, the fractionation of $\delta^{18}O$ caused by incomplete condensation is negligible (< 0.05 o/oo vs SMOW). The time required to trap atmospheric water vapor was dependent on humidity and air temperature levels on the sampling days and sites. Typically, the pump was run at a rate of 1½- 2 L/minute for about 5 hours to condense enough water vapor (≥ 3 mL) for the analysis (see Appendix 1 for example).

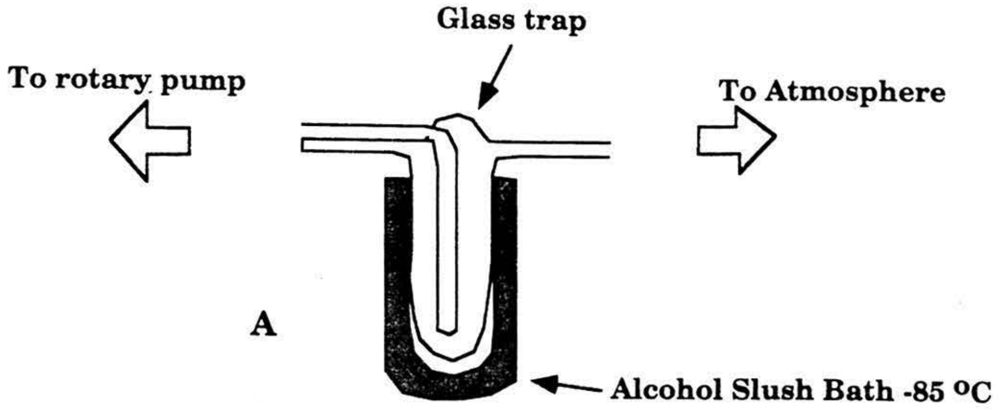


Figure 4a. Single Trap Used to Collect Atmospheric Water Vapor

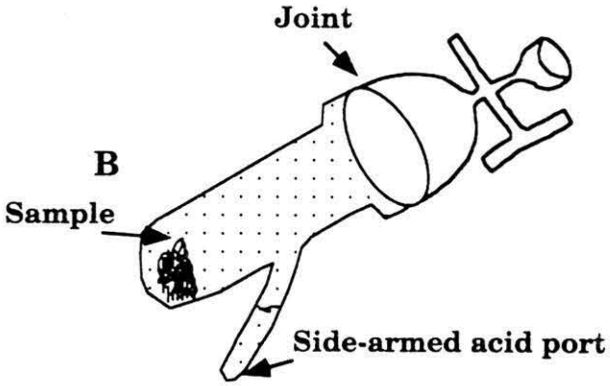


Figure 4b. Reaction Vessel for Release of CO_2 from Ground Carbonate Samples

Relative humidity and temperature were measured using an electrical hygrometer (thermo-resistor cell).

Atmospheric-water vapor from outside of the MSL building was collected in late 1991, and during summer, 1993. Transpired water was collected from oak trees at the Boyd Hill Nature Trail (St. Petersburg, Florida) during late 1993. Because of the small amount of sample that could be obtained in a reasonable working time (see total amount of water vapor in Appendix 1), only one $\delta^{18}O$ determination per sample was performed. The samples were not analyzed for δD nor $\delta^{13}C_{DIC}$.

Ground Water

Ground water wells were purged for 3-well volumes (of the entire well length) before collecting samples. This step was necessary to replace stagnant ground water lying in the well casing. A few tests on the number of purges required for ground water were conducted using O-18 composition of selected wells. This test would provide a minimum purge which was necessary to yield representative samples for the stable oxygen analyses. Test results showed that for $\delta^{18}O$ only 1½ well volume purges were sufficient for replacing the stagnant ground water (Table 1). However, in order to be compatible with other published chemical data, all ground water samples were purged for 3 well volumes before collecting samples for $\delta^{18}O$ and $\delta^{13}C_{DIC}$ analyses. Two sites, Roy Haynes in north Tampa and Baum-Wimauma near Sun City Center (Florida), were monitored for both $\delta^{18}O$ and $\delta^{13}C_{DIC}$ in surficial and the upper Floridan aquifer waters on a bimonthly basis from February, 1992 through October, 1993. Another transect study of ground waters from the recharge area in the Green Swamp to a discharge area in southwest Hillsborough County (Figures 3 and 5) was performed over 3 periods: March, 1992; August, 1992; February, 1993. All ground water samples were analyzed for $\delta^{18}O$ in duplicate. However, only one $\delta^{13}C_{DIC}$ analysis per sample was performed.

Table 1. Effects of Numbers of Well Volume Purges on the $\delta^{18}O$ of Ground Waters (Uncorrected Raw Data), and Stratigraphic Depths of Wells and Depths at Which Rock Samples were Taken

	3 well volume purges	1½ well volume purges
Green Swamp (Floridan) aquifer	-4.04	-3.95
Roy Haynes (Floridan) aquifer	-2.69	-2.62

Wells	Stratigraphic Unit and Total Depth (depths in feet)	Stratigraphic Unit and Casing Depth (depths in feet)	Stratigraphic Unit and Carbonate Rock Sample Depth (depths in feet)
Green Swamp	Avon Park (285)	Ocala (80)	Ocala (110)
88	Avon Park (385)	Avon Park (195)	Avon Park (220)
Romp 87	Avon Park (380)	Avon Park (300)	Avon Park (330)
Romp 68-2	Ocala (221)	Tampa (120)	Ocala (150)
Roy Haynes	Tampa (80)	Tampa (70)	Unknown (?)
Romp TR 10-2	Tampa (125)	Tampa (115)	No Sample
Loughman	Avon Park (247)	Ocala (85)	Ocala (110)
Lake Alfred 1	Avon Park (425)	Ocala (102)	Ocala (120)
Lake Alfred 2	Avon Park (?)	Ocala (102)	Peace River (90)
Lakeland	Tampa (127)	Tampa? (98)	No Sample
Romp DV-2	Suwannee (130)	Suwannee (108)	Suwannee (115)
Baum-Wimauma	Hawthorn (100)	Hawthorn (80)	Hawthorn (80)
Romp TR 9-2	Hawthorn (148)	Hawthorn (118)	Hawthorn (130)
Romp TR 9-1	Tampa (288)	Hawthorn (124)	Hawthorn (150)

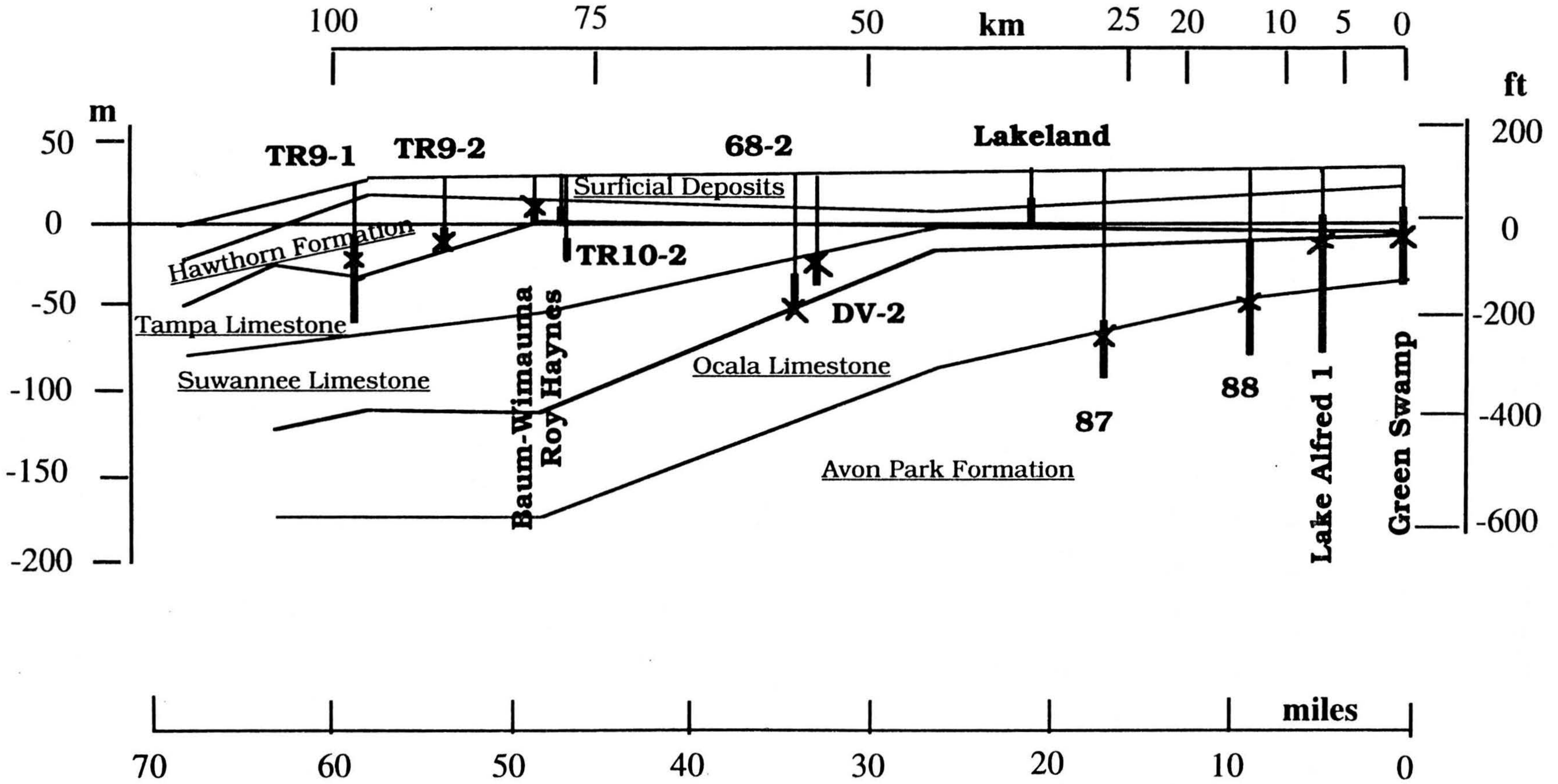


Figure 5. Cross Section of Aquifers from the Recharge Area in Green Swamp to Coastal Discharge Area of West-Central Florida. The Thin Vertical Bar Represents the Casing Depths; the Thick Vertical Bar is the Depth from the Open Casing to the Bottom of Well. The Total Well Depths are the Addition of the Thin and Thick Vertical Bars. Carbonate Aquifer Samples were Taken from the X Marks.

Carbonate Aquifer Samples

Carbonate rock samples from aquifers in the above transect (Figure 5 and Table 1; mostly from the upper Floridan aquifers) were obtained from a depository of the Florida Geological Survey (Tallahassee, Florida). The whole samples were ground into fine powder before roasting at 400 °C (McCrea, 1950) for 2 hours under vacuum to drive off volatile organic matter. This volatile organic matter could interfere with the liberated CO_2 from the sample during processing. The roasting temperature was below the decomposition temperature of the carbonate structure, so there was no loss of carbon or oxygen isotopes. There was no attempt to separate the size fractions of the ground samples. The samples were allowed to cool under vacuum, and were packed in aluminum foil. All carbonate samples were analyzed in duplicate for $\delta^{18}O$ and $\delta^{13}C_{DIC}$ by reacting with 100 % phosphoric acid, H_3PO_4. All ground carbonate rock samples were determined for their mineralogy (see Appendix 2).

Pan Experiments

Free evaporation of water in 2 eleven-liter pans was conducted on the roof of the MSL building. The water in these two pans was evaporated to dryness. Evaporated water vapor and pan water were collected periodically during the course of evaporation (before complete dryness), and analyzed for $\delta^{18}O$. A "constant-feeding pan" (where the water level was maintained at a constant level by adding water with a known isotopic ratio) was set up in parallel with the free evaporation pans, and monitored for changes in $\delta^{18}O$. Relative humidity and air temperature were recorded for a set of data generated from all these pans. Ten milliliter sub-sample was taken periodically from the pan water for $\delta^{18}O$ analysis. This subsample was assumed not to affect the bulk oxygen isotopes of remaining water in the pan. However, because of the small sample size of water sample (for both pan water and evaporated water), only one analysis of $\delta^{18}O$ per sample was conducted. The δD analyses were not performed on water samples from this pan experiment.

Analytical Techniques

Standards

O-18 Standard

$\delta^{18}O$ of water samples was analyzed by equilibrating a known amount of CO_2 with a known amount of water in a closed container (Epstein and Mayeda, 1953; Craig, 1961; Dansgaard, 1964). The isotopically equilibrated gaseous CO_2 from the sample was then dried, and run against the gaseous CO_2 from the standard, generated in a similar fashion, on the same isotope ratio mass spectrometer (IRMS). The gaseous CO_2 carried the O-18 composition of water through the partition (fractionation) chemistry of the isotope during the equilibration. Epstein and Mayeda (1953) used the gaseous CO_2 produced by reacting a reference carbonate material with 100 % phosphoric acid, H_3PO_4, at 25 °C (McCrea, 1950) as a standard. Dansgaard (1964) used local tap water in Denmark as a standard water in his laboratory during earlier works. However, Craig (1961) preferred using equilibrated CO_2 prepared from Standard Mean Ocean Water (SMOW) as a reference gas for the O-18 determination. At 25 °C, Craig's standard (gaseous CO_2) is 0.20 o/oo lighter than the gaseous CO_2 prepared from PDB standard (Belemnite from the Pee Dee Formation, South Carolina, USA). These surprisingly close values (0.20 o/oo difference) of the two standards may, at first, lead to an erroneous idea that both standards are interchangeable within analytical error. In fact, the reaction of carbonate with H_3PO_4 at 25 °C causes a fractionation of O-18 (by ≈ +10.3 o/oo) in the evolved gaseous CO_2 with respect to carbonate in the system $CaCO_3(s)$-$CO_2(g)$ (Sharma and Clayton, 1965). But the water-CO_2 equilibration at 25 °C causes a fractionation of O-18 (by ≈ +41.2 o/oo) in the final residual gaseous CO_2 with respect to water in the system $H_2O(l)$-$CO_2(g)$ (O'Neil et al., 1975). Friedman and O'Neil (1977) clarified this misunderstanding in some detail and gave a conversion equation for the PDB and SMOW standards for $\delta^{18}O$ at 25 °C. Since the measurements of isotopic ratios on the IRMS involve comparison between CO_2 of the sample and the standard, the resultant isotopic data are always reported in relative abundance (in o/oo) with respect to a standard at a given temperature. Temperature adjustment on the $\delta^{18}O$ is needed if the experiments for the samples are conducted at different temperatures than the standard's.

The working SMOW standard was obtained from deep water of the Gulf of Mexico (depth ≈ 1,000 m; salinity ≈ 34.3 o/oo) during the Septembers of 1990 and 1991, and treated as 0 o/oo vs international SMOW standard. The $\delta^{18}O$ of these 2 standards were identical within analytical error. The USF working SMOW standard was within ± 0.3 o/oo to the working SMOW standard used in the USGS's Menlo Park laboratory (Carol Kendall's Lab.; see further discussion in Chapter 6).

C-13 Standard

$\delta^{13}C$ of both carbonate samples and total dissolved inorganic carbon (in water samples) were measured against a Solenhofen standard (Bundesanstalt fur Geowissenschaften und Rohstoffe, Germany). This standard has $\delta^{13}C$ of -0.15 o/oo and $\delta^{18}O$ of -4.99 o/oo vs PDB at 25 °C.

δ^{18}O of Water Samples (Rainwater, Atmospheric Water Vapor, Ground Water, Lake Water, and Transpired Water)

A modification of the Epstein and Mayeda (1953)'s technique was adopted for determination of the O-18 composition of water. In practice, a 20 mL water sample was introduced first into a plastic syringe, followed by 20 mL of high-grade CO_2 (Figure 6). The plastic syringe was equipped with a two-way stopcock. The syringe was agitated vigorously at 2.5 Hz for 1½ hours on a paint shaker at room temperature. The ratio of atomic oxygen in water compared to that in gaseous CO_2, initially, was approximately 600:1, that is

$$\frac{[20\text{ mL of water sample}][1\text{ g/mL}]}{[18\text{ g/mole}]} : \frac{[20\text{ mL of }CO_2][2\text{ mole/1 mole }CO_2]}{[22.4\text{ x}1000\text{ mL/mole}]}.$$

However, the actual ratio was slightly lower than 600:1, but not significantly low for the O-18 composition of gaseous CO_2 to control the O-18 composition of the final equilibrated residual gaseous CO_2 (see Craig [1957] for further discussion). In other words, the δ^{18}O of the water primarily controlled the δ^{18}O of the final residual gaseous CO_2. The equilibrated CO_2 should be processed as soon as possible (preferably within 5 hours) to avoid loss of $^{12}C^{16}O^{16}O$ through the wall of the syringe (Figure 7; see also Yoshida and Mizutani, 1986). The syringe was put on an adapter coupling with a plastic threaded joint and an O-ring (Figure 6). A septum technique was not recommended because a serious leak could occur. The residual gas was then withdrawn and cryogenically trapped at liquid-nitrogen temperature (-185 °C), while water vapor was separately trapped at -85 °C (using a cold slush of isopropanol). The dried CO_2 was later run on an isotope-ratio mass spectrometer, Finnigan MAT 250 with triple collectors, using a working SMOW standard as a reference gas (0 o/oo).

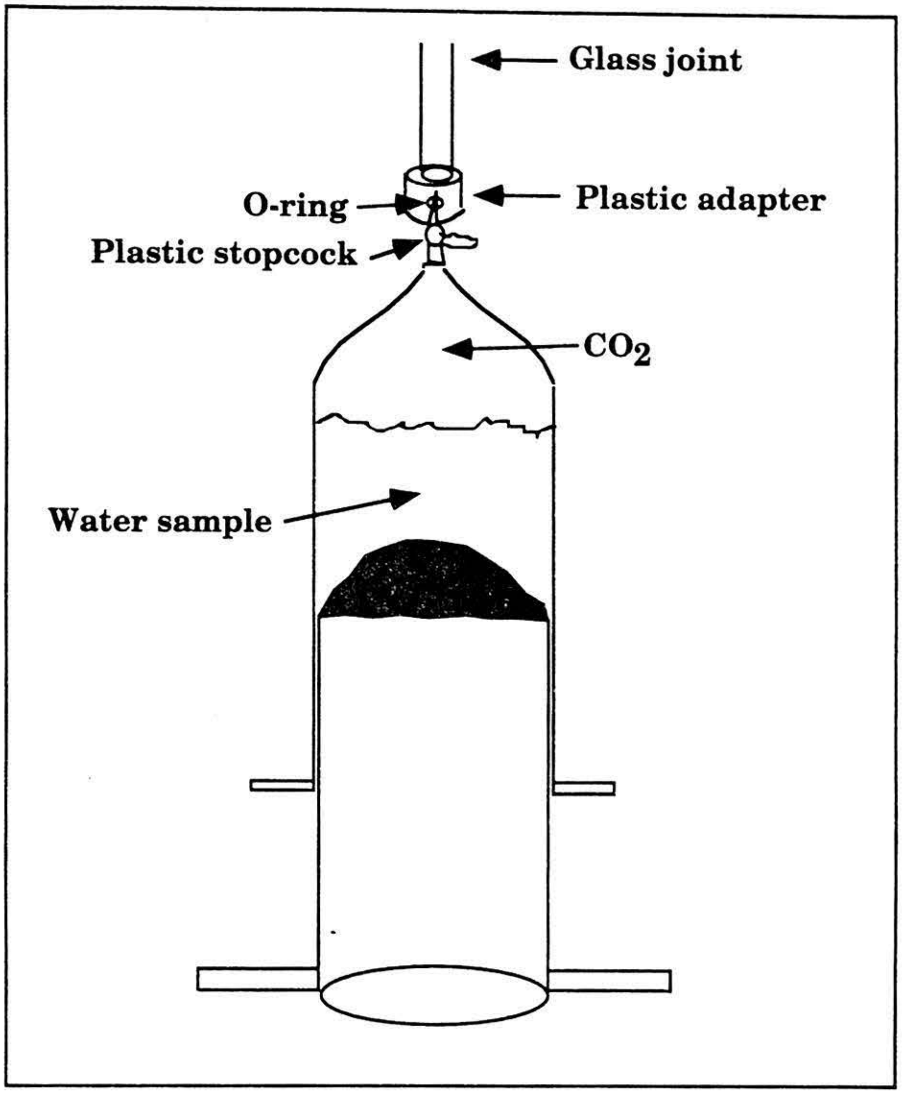


Figure 6. Diagram of the Plastic Syringe with Plastic Stopcock and a Special O-ring Seal Used to Equilibrate $CO_{2(g)}$ with Water Samples

The agitation time (90 minutes) used in this study (Figure 8) was determined experimentally, and was close to the 100 minute equilibration time of Roether (1970; 18 °C and 2.4 Hz agitation).

Since the agitations were conducted at a room temperature other than at exactly 25 °C, the temperature correction of -0.2 o/oo per degree Celsius (Vogel et al., 1970) was adopted. By giving

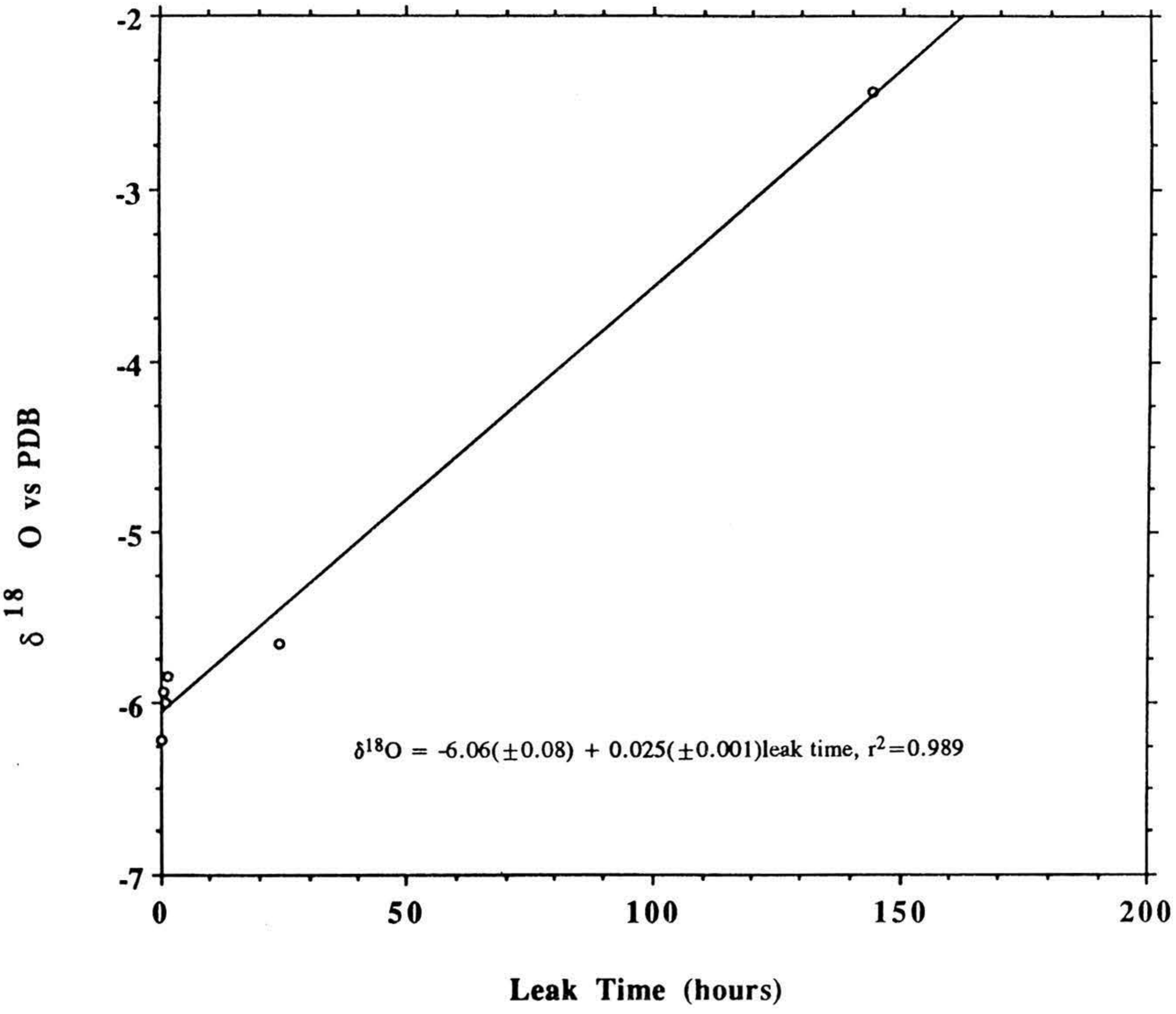
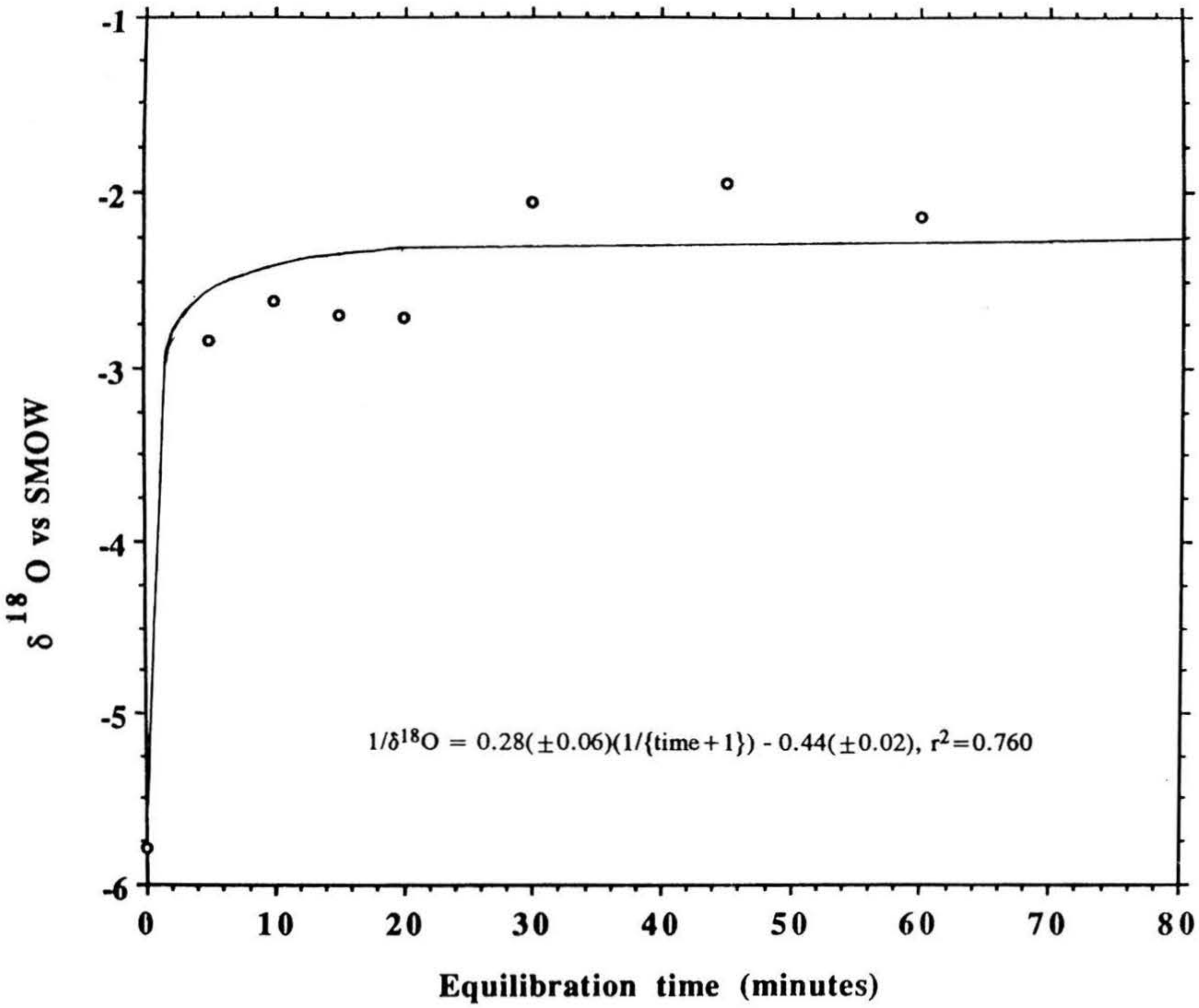


Figure 7. A Linear Plot of the Change of the $\delta^{18}O$ of Residual $CO_{2(g)}$ with Time



igure 8. Equilibration Time Needed to Reach Isotopic equilibrium between Water Sample and Added $CO_{2(g)}$. The $\delta^{18}O$ of Equilibrated CO_2 is Shown on the Ordinate.

A = the adjusted (corrected) $\delta^{18}O$ of sample (in o/oo),

M = the measured $\delta^{18}O$ of sample (in o/oo),

$t_{(std)}$ = the temperature (°C) at which the standard was processed,

$t_{(samp)}$ = the temperature (°C) at which the sample was processed,

$$A = M - [(t_{(samp)} - t_{(std)})(-0.20)] \qquad (7)$$

The precision of the analysis was estimated from one degree Celsius error in temperature difference plus the error in the repeated analyses of the same CO_2 gas on both inlets of the mass spectrometer. The one degree difference translated into 0.20 o/oo (Vogel et al., 1970), while the instrument error was 0.10 o/oo (-0.034 ± 0.067, n=147). Therefore, the applicable uncertainty for $\delta^{18}O$ analysis was ± 0.30 o/oo (0.20 + 0.10). This uncertainty was calculated by assuming that there was a relationship between the instrument variables and the temperature of the experiment in which they were not independent from another. The total error was, then, a summation of each error.

δD of Water Samples

Five rainwater samples were sent to analyzed for δD at USGS laboratory in Menlo Park, California (which is managed by Carol Kendall). Water samples were converted to hydrogen gas using $Zn_{(s)}$ reduction technique at 450 °C (Coleman et al., 1982). The purified $H_{2(g)}$ was run for δD on a mass spectrometer against a SMOW standard with a correction of H_3^+. Analytical error was ± 1.5 o/oo.

$\delta^{13}C$ of Total Dissolved Inorganic Carbon of Water Samples

Following techniques that were suggested by Sackett and Moore (1966), each 60 mL water sample was reacted with 85 % H_3PO_4 at room temperature (23-26 °C) in a special, side-armed glass flask. Mook et al. (1974) showed that temperature effect on

$\delta^{13}C$ exchange in the system $CO_2(g)$ - $HCO_3(aq)$ was 0.30 o/oo in the 23-26 °C temperature range ($\approx$ - 0.10 o/oo per degree Celsius). The gaseous CO_2 evolved from the reaction was cryogenically separated from water vapor similarly to that for the $\delta^{18}O$ described previously. A Solenhofen limestone sample was used to generate a standard gas for $\delta^{13}C$. For comparable precision, each reaction vessel was left for at least 15 minutes at 25 °C in a water bath. Analytical uncertainty was estimated to be $\pm$ 0.15 o/oo ($\pm$ 0.10 o/oo instrument error plus $\pm$ 0.05 o/oo for the technique; assuming the variables are not independent).

$\delta^{18}O$ and $\delta^{13}C$ of Carbonate Rock Samples

Using the McCrea (1950) technique, powdered carbonate rock sample was reacted with 100 % H_3PO_4 under partial vacuum at 25 °C in a special side-armed flask for 12 hours or longer (see Figure 4b). The 100 % H_3PO_4 was prepared by reacting enough solid phosphorus pentoxide (P_2O_5) with 85 % H_3PO_4, stoichiometrically (see Appendix 3 for detailed calculation). Since the reaction, which generated CO_2, involved only two-third of the total oxygen atoms from carbonate (McCrea, 1950), temperature control of the reaction was critical. McCrea (1950) suggested using a prolonged reaction time at 25 °C for 24 hours. Based on temperature effect on $\delta^{18}O$ of evolved gaseous CO_2, I would suggest that the reaction processes should be done at room temperature (see the discussion in the section of analysis of $\delta^{18}O$ in water). If the experiment were performed at 50, or 70, or 90 °C, there is a possibility that the evolved gaseous CO_2 might re-equilibrate with the equal molar amount of water at a different temperature during cryogenic separation steps. A Solenhofen limestone sample was used as a standard for both $\delta^{13}C$ and $\delta^{18}O$ in this carbonate study. Analytical uncertainty was estimated to be $\pm$ 0.10 o/oo for $\delta^{13}C$ and $\pm$ 0.30 o/oo for $\delta^{18}O$ (assuming the variables are not independent). The amount of evolved CO_2 from the reaction was measured manometrically. Percentage of carbonate in the sample was calculated from the measured CO_2 amount, and the sample's dried weight.

Salinity Analysis

A micro-chlorinity titration of water samples with silver nitrate, $AgNO_3$, was adopted for salinity determination (Grasshoff, 1983). The chloride ions in water samples were titrated with silver ions in a flask which was periodically swirled manually. The white silver chloride precipitated and sank to the bottom of flask. The end point was determined by observing the change of color of white precipitate (AgCl) to light pink using a sodium-fluoresceinate indicator. Analytical uncertainty of the technique was within ± 0.3 o/oo.

Statistical Analyses

All linear regression lines performed in this study were at 95 % confidence level. Computer programmes, based on Excel and StatGraphics, were used to assist the calculation.

Chapter 3

WATER CYCLE, RAINWATER, ATMOSPHERIC WATER VAPOR, AND EVAPORATION

As mentioned in the Introduction, the hydrological cycle is driven mainly by the heat received from the sun, and a variety of physical processes acting upon water molecules. During evaporation, a kinetic control of exchange of water molecules between liquid and vapor phases occurs (Penman, 1948; Craig and Gordon, 1965; Knapp, 1985; Steinhorn, 1991). This process is mainly dependent on the vapor-pressure gradient, mass-transfer coefficient, and wind speed. The evaporation also affects the $^{18}O/^{16}O$ distribution between liquid water and water vapor (Craig and Gordon, 1965; Dansgaard, 1953, 1964). Under isotopic equilibrium, any evaporation from surface water can be explained simply by a Rayleigh distillation process[1] (Dansgaard, 1953). This distillation mechanism depends on the partitioning of isotopes between liquid water and water vapor at a given temperature, $\alpha(H_2O_l)$-$\alpha(H_2O_v)$ (Majoube, 1971). For example, at 25 °C, liquid water with $\delta^{18}O$ of 0.0 o/oo evaporating into the atmosphere yields a theoretical water vapor with $\delta^{18}O$ of -9.3 o/oo. In fact, early studies (e.g. Craig and Gordon, 1965) have suggested that the kinetic factor involved during evaporation plays a great role in shifting the observed $\delta^{18}O$ of atmospheric water vapor to -13.0 o/oo at 75 % relative humidity instead of the predicted value of -9 o/oo. Under wet atmospheric conditions (100 % relative

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[1] Rayleigh process is a fractionation process which depends on the initial fraction of liquid phase and the remaining vapor phase during the evaporation or condensation of water molecules. The representative equation is $R/R_o = f^{(\alpha-1)}$, where $R = {}^{18}O/{}^{16}O$ of remaining vapor, $R_o = {}^{18}O/{}^{16}O$ of original vapor, f=fraction of remaining water vapor, α=isotopic fractionation factor.

humidity) the observed $\delta^{18}O$ of water vapor will then be equal to the theoretical value at a given temperature (Craig et al., 1963; Craig and Gordon, 1965).

During evaporation, $H_2{}^{16}O$ is preferentially released into the atmosphere (Dansgaard, 1964; Merlivat, 1978). The condensation process reverses the trend - the $H_2{}^{18}O$ is preferentially concentrated in the precipitation. However, since not all of $H_2{}^{18}O$ is initially evaporated into the air, the first condensate (as rain) will have $\delta^{18}O$ lighter than the original water (e.g. rainwater's $\delta^{18}O$ = -4 o/oo from the source water of $\delta^{18}O$ water = 0 o/oo). This condensation process is described by a similar Rayleigh process (Dansgaard, 1953, 1964).

As evaporation of surface ocean water occurs mostly in the equatorial zone (the warmest part of the oceans), the precipitation will separate $H_2{}^{16}O$ from the $H_2{}^{18}O$ through atmospheric circulation cells from the tropics to the subtropics, and, finally, reaching the polar regions. Globally, the $\delta^{18}O$ in precipitation has distribution patterns parallel to the latitudes, and becomes more negative (lighter) polewards (Yurtsever and Gat, 1981). In addition, seasonal effects on the $\delta^{18}O$ of precipitation have been documented (Lawrence and White, 1991).

In general, the heavier the precipitation, the lighter is its $\delta^{18}O$. This process was coined "the amount effect" by Dansgaard (1964). The amount effect may be used to estimate $\delta^{18}O$ of precipitation from the average amount of observed precipitation in a geographical area. The calculation, depends on a relationship equation, such as

$$\delta^{18}O = \text{constant}_1 + \text{slope(amount of rainfall)}.$$

The $\delta^{18}O$ of precipitation seems to vary linearly with surface air temperature which is less than 15 °C (confer Dansgaard, 1964; Jacob and Sonntag, 1991; Joussaume and Jouzel, 1993; Rozanski et al., 1993). This relationship caused enthusiasm within scientific communities as a possible means of estimating the surface air temperature in the past based on palaeo-water studies and information from precipitation (e.g. snow). However, the air temperature-$\delta^{18}O$ (precipitation) relation breaks down at temperature greater than 15 °C (e.g. Jacob and Sonntag, 1991; St. Petersburg data below). In addition, the history of rain-cloud formation and the travel paths of precipitation may complicate the usefulness of this type of relationship (Jouzel, 1986).

In water molecules, hydrogen comprises twice the molar ratio to oxygen atoms. Natural abundances of stable hydrogen isotopes are: $^{1}H = 99.985$ %, ^{2}H (or D) = 0.015 % (Hoefs, 1987). In natural precipitation the observed $\delta^{18}O$ varies linearly with the δD as exemplified by the equation: $\delta D = 8\delta^{18}O + 10$, the equation for Global Meteoric Water Line (Craig, 1961). The intercept (= 10) here is called the deuterium excess. The excess is obtained from linear regression of δD vs $\delta^{18}O$ data. This deuterium excess value is dependent upon the relative humidity and temperature of the evaporating body of water (Merlivat and Jouzel, 1979; Petit et al., 1991). Petit and co-workers (1991) have shown, based on the deuterium excess of surface snow in Antarctica and on modelling, that the source of water vapor for snow in Antarctica is water vapor from the ocean around 30-40 °S. This idea may have major implications for palaeo-climatic studies in the near future.

The slope of 8 in the Meteoric Water Line is valid for precipitation throughout the world (Dansgaard, 1964; Rozanski et al., 1993). During evaporation, the slope value is lowered to around 3-5 depending on the humidity, air temperature and degree of rainout (Gat and Bowser, 1991). The degree of rainout depends upon the Rayleigh process and the remaining water vapor compared with the fraction of original water vapor. By examining the slope of the δD and $\delta^{18}O$ alone in a water type for evidence of evaporation may not be correct as processes such as interaction of meteoric water with carbonates on ground and exchange of precipitation with atmospheric water vapor could alter the slope as if evaporation takes place. Evaporative parameters, e.g. δ_s and m (equations 9-11), are better for prediction the degree of evaporation (the fraction of water which evaporates into the atmosphere from a body of water), the changing δ values, and extent of fractionation factor of water in a system.

During evaporation the equilibrium fractionation factor can be denoted as α^* (e.g. for H_2O_l ---» H_2O_g, $\alpha^* = 0.99071$ at 25 °C; Majoube, 1971). Craig and Gordon (1965) introduced another term called ϵ^*, which under evaporation, is equal to $(1-\alpha^*)1000$. The ϵ^* for the previous α^* is equal to 9.2866. The ϵ^* term is often taken from $(\alpha^+ - 1)1000$ for convenience, which equals 9.3736 at 25 °C. (The α^+ is the fractionation factor for the reaction H_2O_g ---» H_2O_l, and is 1.0093736 at 25 °C; $\alpha^* = 1/\alpha^+$) Within analytical error, the ϵ^* and $(\alpha^+ - 1)1000$ terms are very close, and often are used interchangeably by Craig and other workers.

The evaporation process at the air-water interface seems to be complicated by an inclusion of kinetic effects on equilibrium fractionation. The contribution from this kinetic factor is called $\Delta\epsilon$. This kinetic factor depends upon the relative humidity of the overlying atmosphere ($\Delta\epsilon = 16(1-h)/1000$; h=relative humidity; Gat, 1970). The total enrichment factor during evaporation of liquid water into atmosphere is ϵ; $\epsilon = \epsilon^* + \Delta\epsilon$. Based on studies by Craig and Gordon (1965) and Merlivat and Coantic (1975) there is a laminar layer of air overlying the water interface during the evaporation from water to the bulk, more turbulent atmosphere. The laminar layer resists the evaporation occurring at the water-air interface. The isotopic $\Delta\epsilon$ and ρ (isotopic transport resistance in the water/air interface) are the responsible resistance terms in the isotopic evaporation equations.

Craig and Gordon (1965) derived an equation for the isotopic content of oxygen or hydrogen in evaporative water vapor, δ_E, as

$$\delta_E = \frac{(\alpha^*)\delta\mathrm{water}(1 + E\rho^*_L) - h\delta_a - \epsilon}{1 - h + \Delta\epsilon + (\alpha^*)E\rho^*_L} \tag{8}$$

where E = evaporation rate

ρ^*_L = isotopic transport resistance in the liquid

h = (air) relative humidity normalized to surface water temperature

δ_a = isotopic content of atmospheric water vapor.

Welhan and Fritz (1977) further expanded the above equation to a steady-state condition (of δ_s), in which the fraction of water that remained is close to zero, as

$$\delta_s = (h\delta_a + \epsilon)/(h - \epsilon) \qquad (9),$$

$$(\delta-\delta_s)/(\delta_0-\delta_s) = f^m \qquad (10),$$

$$\text{and} \quad m = (\delta_E-\delta)/(\delta-\delta_s) \qquad (11).$$

where δ_s = steady-state isotopic content ($=\text{limit}_{f\to 0}\,\delta$)

δ_0 = initial isotopic content of liquid at $f = 1.0$

δ = isotopic content of liquid at $f < 1.0$

f = fraction of remaining liquid = V/V_0 (volume at time t/volume at time 0)

$$m = (h-\epsilon)/(1-h+\Delta\epsilon+(\alpha^*)E\rho^*_U) \qquad (12).$$

δ_s and m are unique for evaporation under various pan experimental conditions. The parameters obtained from the evaporative pan experiments can be used to estimate δ_E of lakes or other land-locked bodies of water. The estimated δ_E is comparable with the evaporation data obtained from energy budget and mass-transfer methods (Welhan and Fritz, 1977).

Rainfall in West-Central Florida

Florida receives rainwater throughout the year. Rainfall is common during the summertime, and generally appears as thunderstorms, showers, and heavy rainfall. Convective rain cloud formation is responsible for the Florida's summer rainfall (Winsberg, 1990). During the wintertime, frontal precipitation is predominant, but the amount of rainwater is smaller compared to the summer rainfall. The rainfall in west-central Florida occurs more frequently during the afternoon (Schwartz and Bosart, 1979). Fifty-year averages of rainfall amount and surface air temperature for the Tampa and St. Petersburg areas are shown in Figures 9a and 9b. The 1991-1992 rainfall amounts ($\approx$ 1,130 mm) were below the 50-year average ($\approx$ 1,300 mm), while

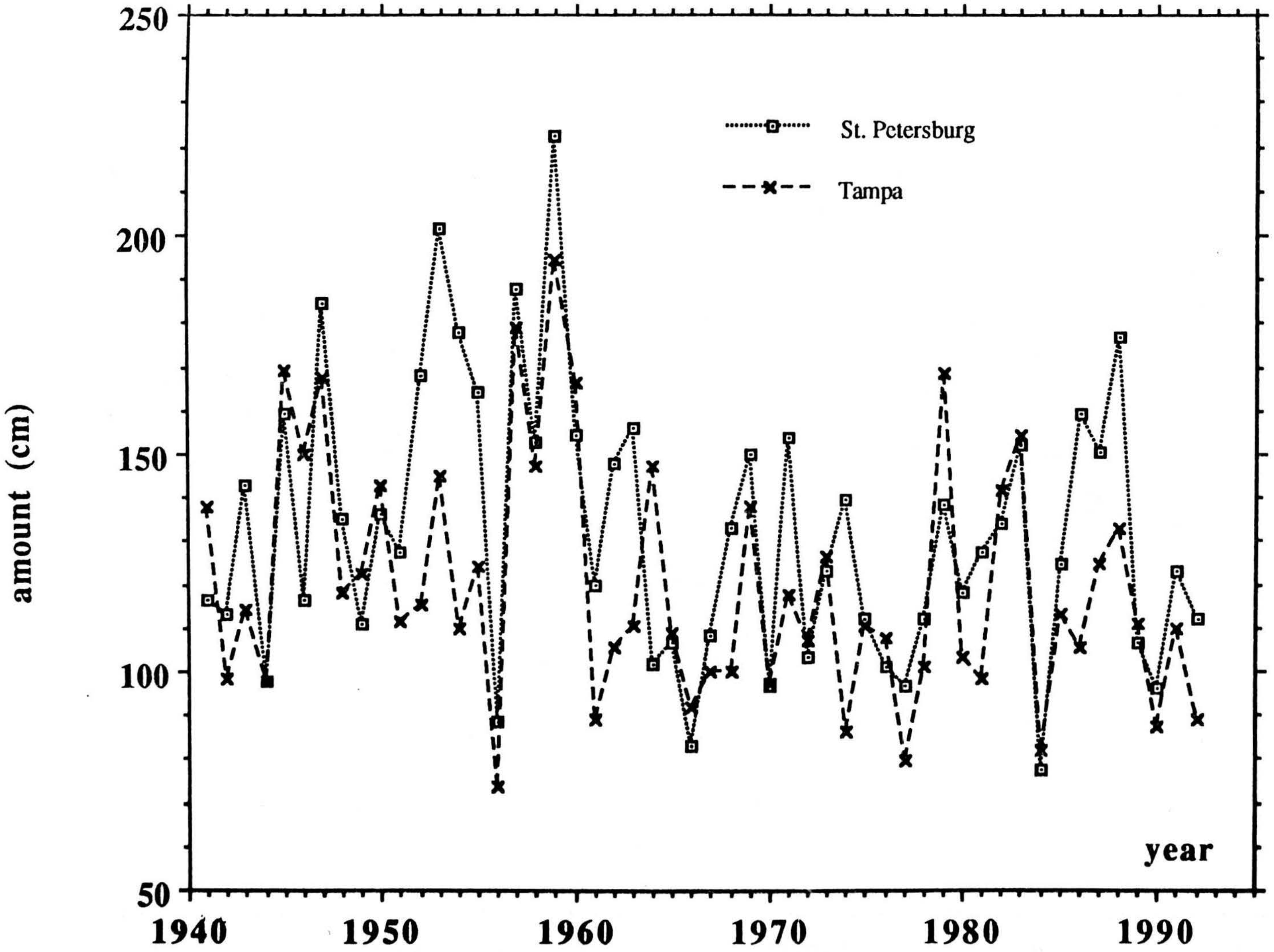

Figure 9a. Fifty-Year Variation of the Average Rainwater's Amounts in West-Central Florida. The Average Amounts for Tampa and St. Petersburg are 119.8 and 132.7 cm, Respectively (47.2 and 52.2 Inches, Respectively; NOAA 1941 -1992).

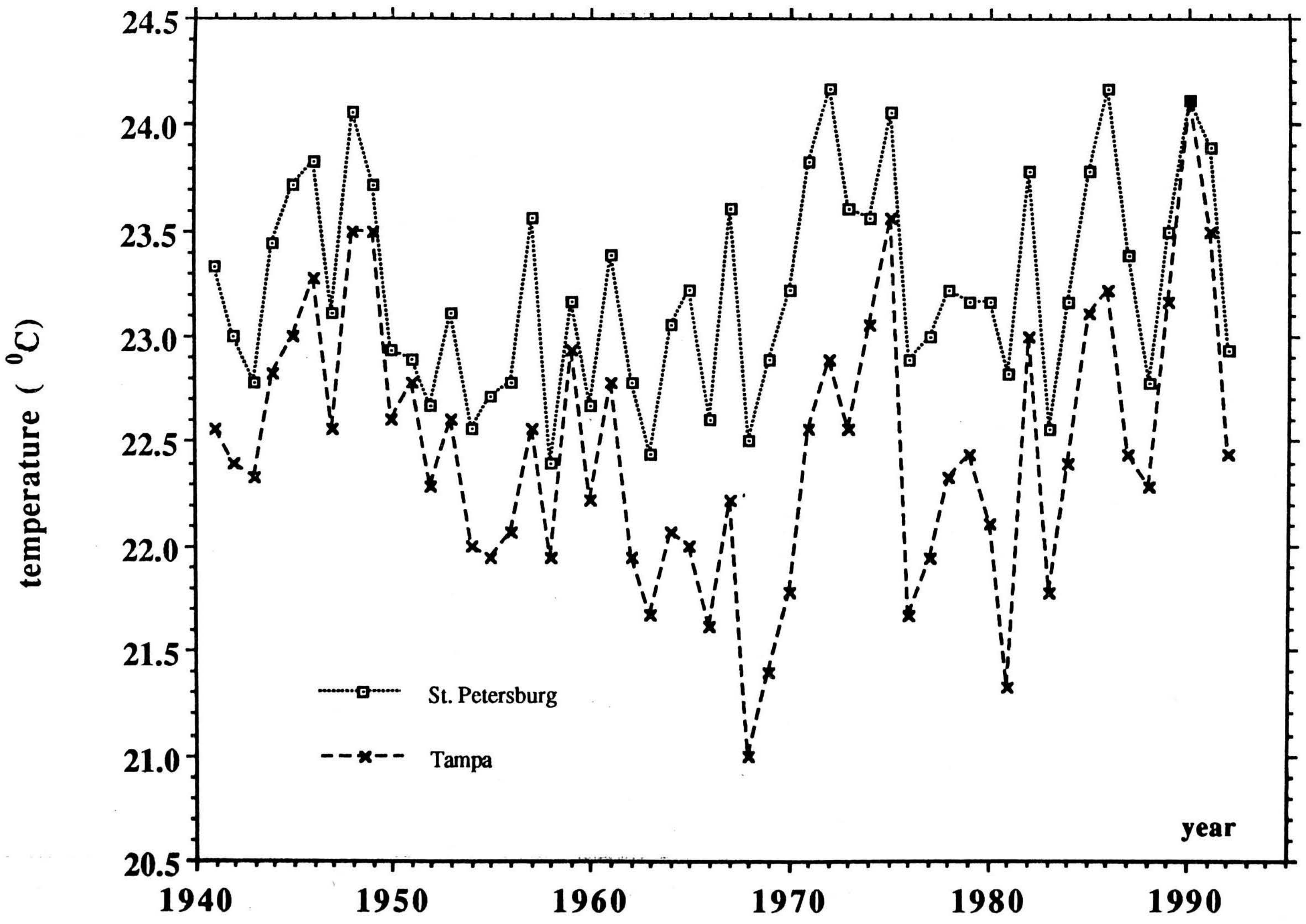

Figure 9b. Fifty-Year Variation of the Average Air Temperature in West-Central Florida. The Average Temperatures of Tampa and St. Petersburg are 22.5 and 23.2 °C, Respectively (72.4 and 73.8 °F, Respectively; NOAA 1941-1992).

the 1991-1992 temperatures were close to the long-term average (≈ 23 °C). Figure 10 illustrates variations of $\delta^{18}O$ of individual rainfall in St. Petersburg collected in the present study. The sample most depleted in ^{18}O ($\delta^{18}O$ = -11.6 o/oo) was obtained during a tornado in 1992 and represented one of the heaviest rainfall events (4.5" or 114 mm). A weighted mean[2] for the $\delta^{18}O$ in rainwater during 1991-1992 is -4.4 o/oo; a normal mean[3] of $\delta^{18}O$ for the same rainwater is -3.3 o/oo.

Table 2 describes regression equations among rainwater $\delta^{18}O$, amount, and surface air temperature. A linear relationship between the amount of rainwater (independent variable) and its $\delta^{18}O$ (dependent variable) was not high (r^2=0.252; equation 14; Figure 11a). Multiple correlation between the amount of rainwater (independent variable) and its $\delta^{18}O$, and air temperature (dependent variables) is weak (r^2=0.251; equation 15). There is relationship between $\delta^{18}O$ in rainwater and surface air temperature (Figure 11b).

Carol Kendall (USGS, Menlo Park) performed analyses of five rainwater samples for δD. These δD data were regressed with the $\delta^{18}O$ data to construct a "St. Petersburg" meteoric water line [$\delta D = 7.65(\pm 0.20)\delta^{18}O + 10.57\ (\pm 1.14)$; r^2 = 0.998, n = 5]. This relationship (Table 2) is close to the one that Craig (1961) has found ($\delta D = 8\delta^{18}O + 10$, a Global Meteoric Water Line; see also Figure 22 in Chapter 5). The similarities in the δD and $\delta^{18}O$ of rainwater in St. Petersburg and Global Meteoric Water Line suggest that similar evaporation-condensation processes control the rainfall pattern.

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[2] weighted mean = $\Sigma_i\{(\text{amount}_i)(\delta_i)\}/\{\Sigma_i(\text{amount})\}$ IAEA(1981) (13a)

[3] normal mean = $\Sigma_i(\delta_i)/\Sigma_i$ (13b)

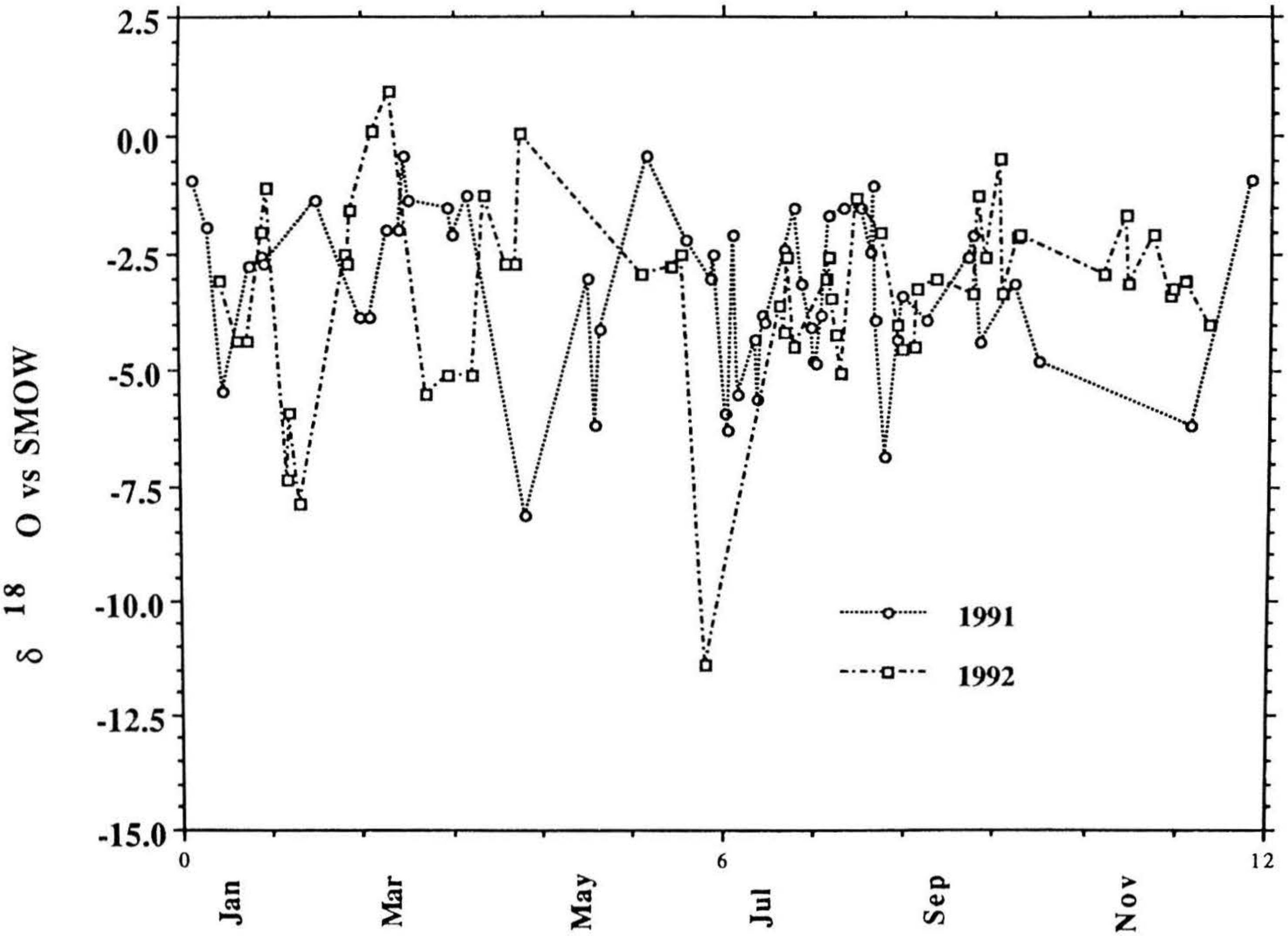

Figure 10. $\delta^{18}O$ Variation of Rainwater during the Year 1991 and 1992 in St. Petersburg, Florida. The Weighted Mean is -4.4 o/oo.

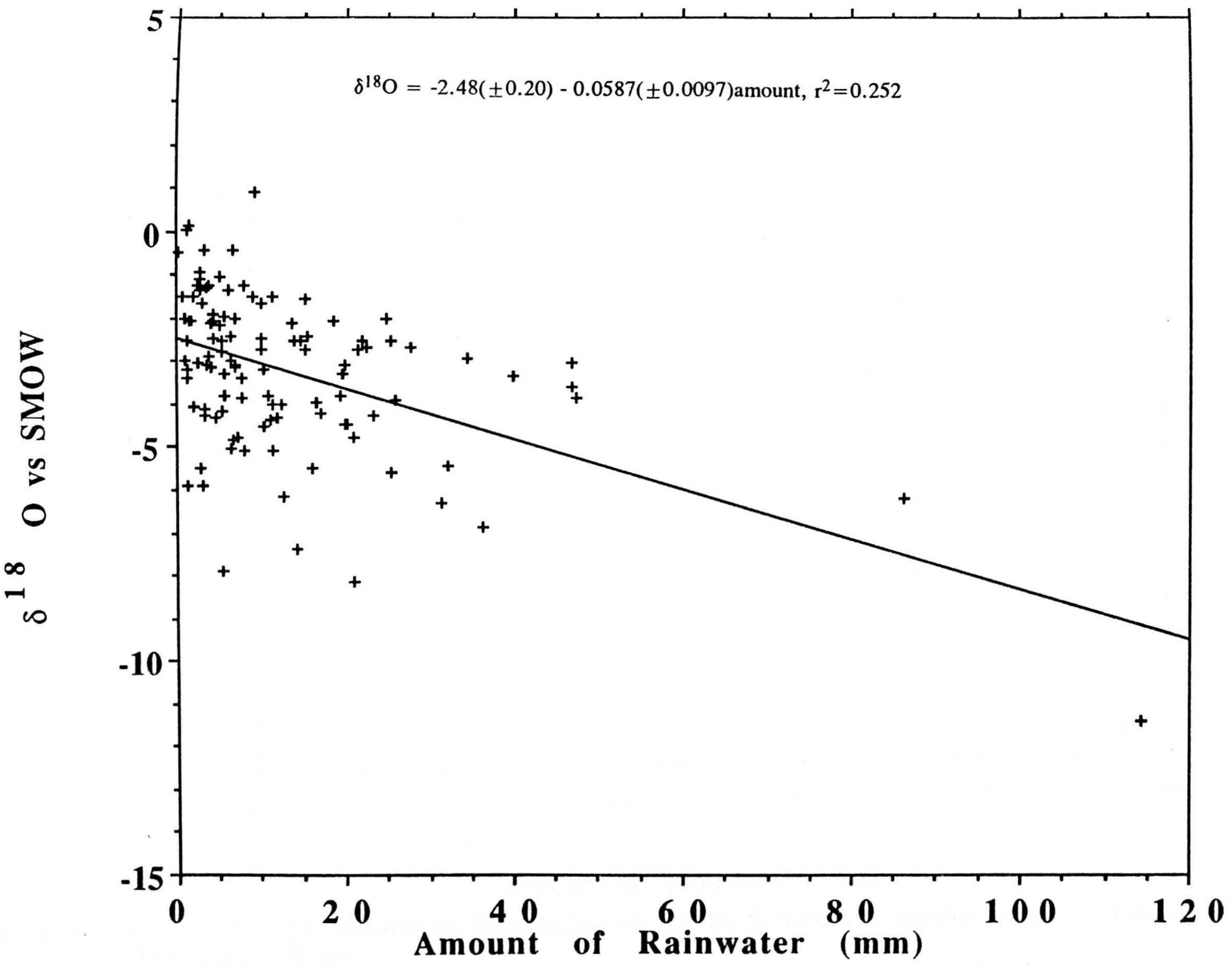

Figure 11a. Linear Relationship between the Amount of Rainwater and Its $\delta^{18}O$ in St. Petersburg, Florida

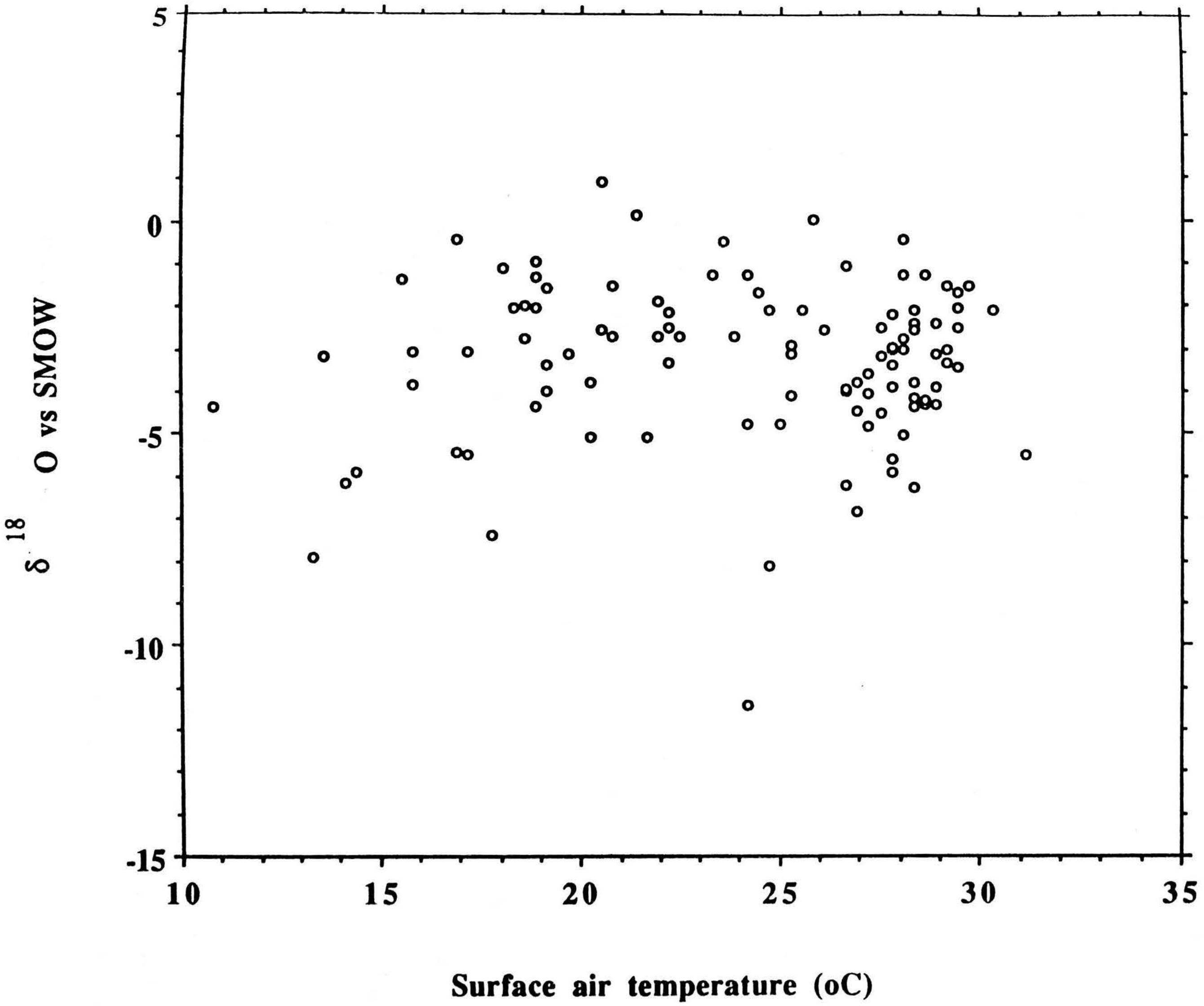

Figure 11b. A Scatter Diagram Showing the Relationship between the Surface Air Temperature and δ^{18}O in Precipitation at St. Petersburg, Florida

Table 2. Regression Equations for Rainfall, Its Amount, Temperature, $\delta^{18}O$ and δD

$$\delta^{18}O = -2.48(\pm0.20) - 0.0587(\pm0.0097)\text{amount (in mm)}, \quad r^2=0.252, \; n=110 \qquad (14)$$

$$\delta^{18}O = 3.54(\pm0.818) - 0.0597(\pm0.009)\text{amount(mm)} + 0.0445(\pm0.033)t(^\circ C)$$

$$r^2=0.251, \; n=110 \qquad (15)$$

$$\delta D = 7.649(\pm0.201)\delta^{18}O + 10.569(\pm1.14), \quad r^2=0.998, \; n=5 \qquad (16)$$

Atmospheric Water Vapor in West-Central Florida

Average $\delta^{18}O$ of atmospheric water vapor, which was collected outside USF's Marine Science Building, is -13.5 (± 1.9) o/oo (n=22, Table 3). This value (-13.5 o/oo) is lighter than the transpired water ($\delta^{18}O$=-11.8 [± 1.4] o/oo, n=5) from leaves in Boyd Hill's Environmental Research Area, ERA. However, the $\delta^{18}O$ of atmospheric water vapor (-13.5 o/oo) is slightly heavier than the evaporative water vapor, obtained from pan experiments, ($\delta^{18}O$=-13.9 [±1.1] o/oo; n=9). Assuming the water vapor in the atmosphere is a mixture of transpired water and evaporative water, contributions from each water vapor compartment can be derived. Calculation[4] suggests that the transpired water accounts for about 20 %, while the evaporative water vapor contributes about 80 % of the total average atmospheric water vapor for coastal west-central Florida during the summer and fall seasons. The predominant contribution of evaporative water vapor was expected since the sampling location is located near the water of Bayboro Harbor. Salt contents in seawater did not affect the δ_E of evaporative

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4. By setting up equation: $(x)\delta_{evap} + (1-x)\delta_{transp} = -13.5$, and letting $\delta_{evap} = -13.9$ o/oo and $\delta_{transp} = -11.8$ o/oo ---> $x \approx 0.80$

Table 3. $\delta^{18}O$ in Average Atmospheric Water Vapor, Transpired Water from Leaves, and Evaporative Water from Pan Experiments

3.1 Atmospheric Water Vapor

11-Sep-91	-13.79	5-Apr-93	-13.16
13-Sep-91	-13.05	13-May-93	-11.95
17-Sep-91	-14.54	18-May-93	-12.92
18-Sep-91	-12.59	25-May-93	-13.04
18-Sep-91	-16.51	15-Jun-93	-13.72
23-Sep-91	-12.84	16-Jun-93	-13.01
2-Oct-91	-13.74	17-Jun-93	-13.39
22-Oct-91	-13.52	12-Jul-93	-12.99
29-Oct-91	-13.28	13-Jul-93	-13.44
31-Oct-91	-13.56	21-Jul-93	-14.57
		24-Aug-93	-15.2
		26-Aug-93	-13.24
	n	22	
	mean	-13.55	
	std. deviation	0.96	

$\ln \alpha+ = 1.137*1000/(T*T) - 0.4156/T - 2.0667/1000$ (Majoube, 1971)

$T = 273.15 + t$ (oC)

3.2 Transpired Water from Leaves

Boyd Hill

% rel hum	oC	sat. wat vapor	$\alpha+$	$\delta^{18}O$ (obs)	atm. press.	q (g/kg)	$\alpha*$	$\varepsilon*$	$\Delta\varepsilon$	eq.8	eq. 20
59.9	28.36	23.13	1.0091	-10.72	1021.8	0.01408	0.99097	0.0090211	0.006416	-0.02525	0.00622
60.54	28.76	23.92	1.00907	-10.12	1018.5	0.01461	0.991	0.0089901	0.0063136	-0.0251	0.00603
61.51	26.98	21.91	1.00921	-12.31	1016.1	0.01341	0.99087	0.009129	0.0061584	-0.02535	0.00591
71.88	25.31	23.2	1.00935	-13.43	1010.6	0.01428	0.99073	0.0092617	0.0044992	-0.02429	0.00327
66.7	24.09	20.02	1.00945	-12.64	1016.1	0.01225	0.99063	0.0093601	0.005328	-0.02539	0.00475

Given 64.1 % relative humidity and 26.7 degree C, and relationship $\delta^{18}O = -18.87 + 0.4818q$
the calculated $\delta^{18}O$ is equal to -12.23 o/oo

3.3 Evaporative Water from Pan Experiments

Constant-feeding pans

rel hum %	oC	$\alpha+$	$\delta^{18}O$ (obs)	$\alpha*$	$\varepsilon*$	$\Delta\varepsilon$	eq. 8	eq. 20
34.3	40.6	1.00819	-15.71	0.99187	0.0081257	0.01051	-0.01543	0.01242
50.6	35.9	1.00853	-14.21	0.9915	0.0084568	0.007904	-0.01159	0.008334
40.5	38.4	1.00835	-12.82	0.9917	0.0082789	0.00952	-0.01426	0.01089
48	36	1.00852	-12.86	0.99155	0.0084496	0.00832	-0.01246	0.009031
38.6	37.4	1.00842	-14.92	0.99165	0.0083495	0.009824	-0.01483	0.01148
35.8	38.7	1.00833	-12.86	0.99174	0.0082578	0.01027	-0.01531	0.01214
46	34	1.00867	-14.81	0.9914	0.0085951	0.00864	-0.01334	0.009718
42.6	35.9	1.00853	-13.88	0.99154	0.0084569	0.009184	-0.01403	0.0105
42.5	36.2	1.00851	-13.07	0.99156	0.0084353	0.0092	-0.01402	0.01051
		average $\delta^{18}O$	-13.9					
average hum	**average deg**							
42	37	1.00845		0.99162	0.008378	0.00928	-0.01405	

water vapor unless the ionic strengths of water samples were higher than 2.0 (Craig and Gordon, 1965; Sofer and Gat, 1972).

During transpiration, the root water was found to travel through xylem and leaves' stems without isotopic fractionation (Zimmermann et al., 1967). Since the soil water and leaf water have been not studied here, root water is assumed not to fractionate the oxygen isotopes. The evaporation should take place at the leaves' stomata and depends primarily on the water temperature inside leaves (α^{+}, fractionation factor) and relative humidity (h, and $\Delta \epsilon$). The relative humidity, air temperature, and atmospheric pressure can be used to calculate a specific amount of water vapor called specific humidity (Appendix 1). A linear correlation between the specific humidity and $\delta^{18}O$ of transpired water (Figure 12) can be used to compute the unknown $\delta^{18}O$ of transpired water if the relative humidity and air temperature are known (see the calculation of specific humidity in Appendix 1).

Using the average relative humidity (64.1%) and temperature (26.7 °C) readings from the bag enclosure around leaves of oak trees in the ERA area, and assuming that the water temperature inside the leaves during the evaporation equals those of air, $\delta^{18}O$ of transpired water vapor of -12.23 o/oo is calculated from an equation (Figure 12; Table 3): $\delta^{18}O = -18.9 + 0.482q$, $r^2=0.581$. This value is close to the average "in-bag" measured $\delta^{18}O$ of transpired water of -11.8 o/oo (Table 3). White and Gedzelman (1984) found that, in air monitoring at Lamont Doherty Geological Observatory, the δD and q correlated linearly ($r^2 \approx 0.80$), and the extrapolation of q value to 100 % humidity results in a δD of local ground water. At 100 % relative humidity and 34.5 °C temperature, the calculated q equals to 0.03330 (33.30 g of water per kg of air) and the computed $\delta^{18}O$ of water vapor is -2.8 o/oo. This value is similar to the ground water's $\delta^{18}O$ (= -2.8 o/oo) in the ERA. The similarity is caused by a stationary state of evaporation of surface water as explained by Craig and Gordon

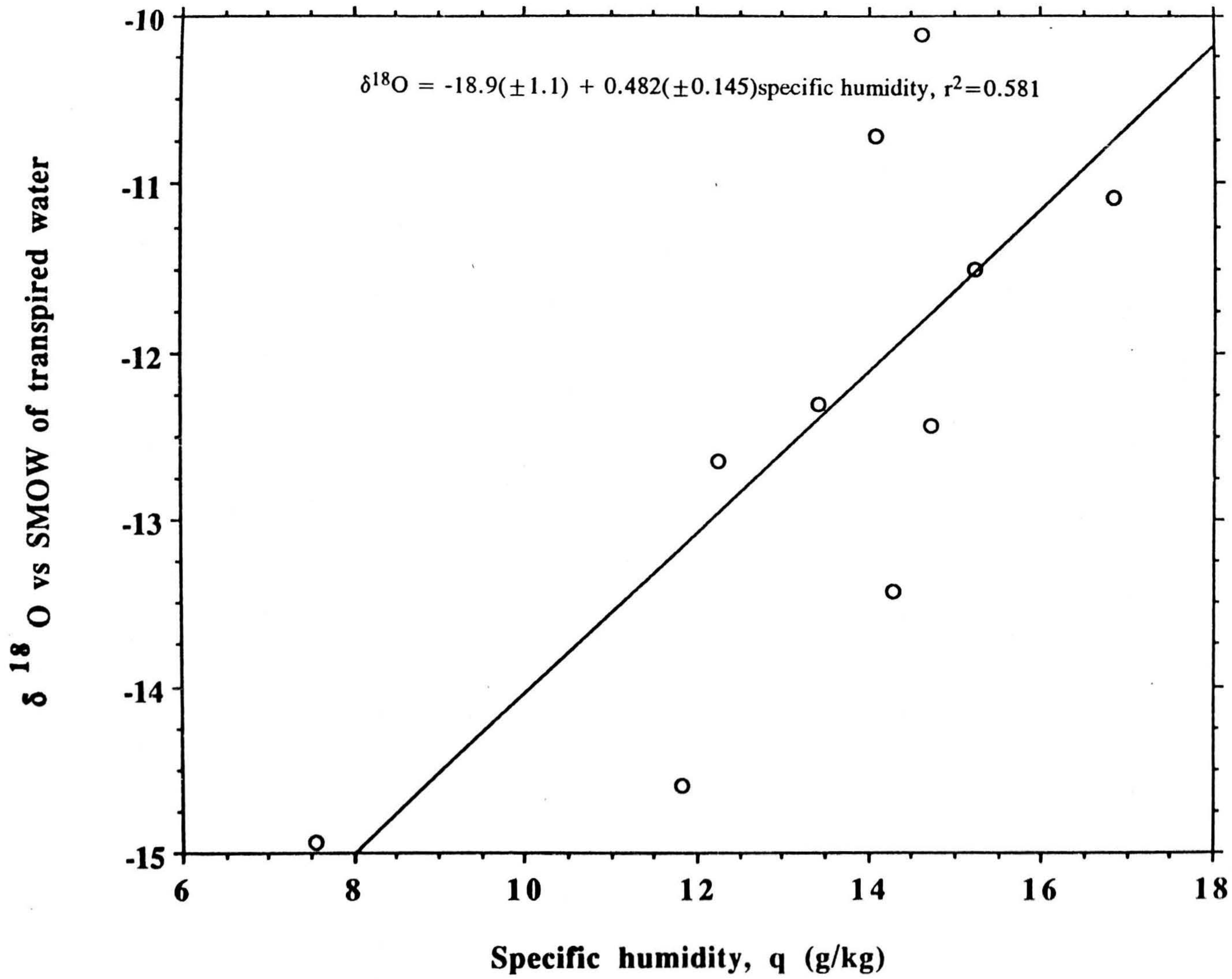

Figure 12. Linear Correlation between the Specific Humidity and the $\delta^{18}O$ of Transpired Water in Boyd Hill's Environmental Research Area

(1965), i.e. $\delta_{sE}=\delta_{sL}$ (steady state δ_E of evaporative water vapor is equal to steady state δ_L of body of water at 100 % humidity after a long, complete isotopic exchange).

During transpiration, the loss of stem water through leaves can cause the water vapor to deplete in oxygen isotopic ratio up to a maximum of 28.5 o/oo relative stem water (under purely diffusion-controlled process). The transpiration process combines the effects of fractionation factor (ϵ^*), kinetic enrichment (ϵ_k), and the relative humidity. A maximum ^{18}O enrichment (δ_{max}) of leaf water, relative to source stem water, δ_i, can be calculated from:

$$\delta_{max} = \epsilon^* + \epsilon_k + (\delta_A - \epsilon_k)h \quad \text{(Dongmann et al., 1974)} \qquad (17)$$

$\delta_A = \delta^{18}O$ of measured atmospheric water vapor

$\delta_i = \delta^{18}O$ of uptake water by plant

Other symbols are as defined earlier.

$\epsilon_k = (28.5)(2/3)$ = kinetic enrichment (Dongmann et al., 1974; Merlivat 1978; Flanagan and Ehleringer, 1991, p. 273; the 2/3 is an average contribution from diffusion and turbulence conditions under normal transpiration)

measured δ_A=-13.5 o/oo vs SMOW; h=64 %; t(°C)=26.5;

δ_i= -2.8 o/oo vs SMOW

calculated δ_{max} = +8.46 o/oo relative to source stem water

= +5.66 o/oo vs SMOW.

This value is close to the range of calculated δ_L (average +6.05 o/oo vs SMOW for the first three data points; equation 21, described later; Table 3). In addition the calculated δ_E ($\approx$ -25.0 o/oo) explains that the diffusion process (Dongmann et al., 1974) is predominant during the evaporation of leaf water in the Boyd Hill area.

West-Central Florida's Evaporation

Isotopically, the evaporation of surface water is governed by a small laminar layer just above the air/water interface, and the Rayleigh distillation process (Craig and Gordon, 1965; Merlivat and Coantic, 1975). It obeys the following equation (Craig et al. 1963):

$$\lambda - \lambda_0 = (\alpha^* - 1)\ln(f) \qquad (18)$$

where $\lambda = \ln(1+\delta)$ (19)

α^*, fractionation factor of $H_2O_l \dashrightarrow H_2O_g$

f = fraction of remaining liquid (surface water)

$\delta = \delta^{18}O$ or δD.

The slope, α^*-1, can be used to calculate the fractionation factor for water during evaporation under physical conditions appropriate for a geographical area. Using the data from 2 pan experiments and δ_0 = -2.42 o/oo the slope (=[α^*-1], Table 4) of the pan 3 (6.392 L) and pan 1 (3.428 L) equal -10.27 and -7.01 o/oo, respectively (r^2 = 0.955 and 0.834, respectively). Since the pan 3 has dimensions closer to a standard Class A evaporative pan (which has been used to estimate evaporation rate by National Weather Service), in terms of surface area to depth ratio, the slope of -10.27 o/oo is preferred. This slope is equal to -ϵ^*, so the experimental α^+ is 1.01037 which is slightly heavier than an average value of 1.00837 in the temperature range of the pan experiments (average air temperature in the exposed sunlight ≈ 38 °C; see Table 3). Although the actual water temperature could be a few degrees cooler, there is still a small difference between the experimental α^+ and theoretical α^+. Craig et al. (1963) suggested that this difference was caused by the inclusion of the kinetic effect acting upon the water body. In addition, they (Craig and co-workers) found that the evaporation rate had no effect on the experimental α^+.

Table 4. Evaporative Pan Experiments, and the Inferred Fractionation Factor, α^+

	diameter/depth	pan3		pan1	
Class A, evaporation pan	4.8	V/V_0	$\delta^{18}O$	V/V_0	$\delta^{18}O$
pan 3 $V_0=6.39$ L	7.67	1	-2.42	1	-2.42
pan 1 $V_0=3.43$ L	15.1	0.929	-1.06	0.900	-0.09
		0.906	-0.49	0.867	-0.36
		0.777	0.804	0.734	1.623
		0.750	0.94	0.634	1.816
		0.594	4.08	0.618	2.88
		0.429	6.14	0.435	6.05
		0.358	7.29	0.102	11.69

By using the equation: $\lambda - \lambda_0 = (\alpha^* - 1)\ln(f)$, the best fitted curves give:

	pan3	pan1
intercept	0	0
r^2	0.9551	0.8338
slope$=(\alpha^*-1)= -\epsilon^*$	-0.01027	-0.007015
α^*	0.98973	0.99299
$\alpha^+=1/\alpha^*$	1.01038	1.007064

Following Welhan and Fritz (1977) and Allison et al. (1979), the parameters m and δ_s (equation 10) were calculated from a linear equation by varying the initial guess of δ_s and obtaining the calculated m, and the correlation coefficient (r). The process was repeated until the best r and smallest residual sum square of errors between the predicted δ_s and observed δ were reached. A QBasic program written for solving the m and r constants is given in Appendix 4. For pan 3, the best-fit δ_s is +12.22 o/oo while the m is 1.041. However, the calculated m (0.6771) from humidity [$m \approx (h-\epsilon)/(1-h+\Delta\epsilon)$; a modification of equation 12] seems to be much lower for the h=0.418 and t=38.3 °C (the first three data); at the same time the calculated δ_s of +29.79 o/oo is much higher than the +12.22 o/oo regression δ_s. The lower m value (=0.67) could be a result of bias of humidity measurements towards the daytime averages rather than the full daily cycle. But the larger δ_s value (=29.8) may be caused by utilizing of air temperature instead of water temperature during the calculation of ϵ.

If the average water temperature of 37 °C in pan and relative humidity of 42 % (n=9; pan 2 - a constant-feeding pan) are used for calculation of δ_E using equation 8, the computed δ_E is -14.05 o/oo. This δ_E is very close to the measured value of -13.9 o/oo. In addition, by applying an equation:

$$\delta_L = \delta_I(1-h) + h\delta_A + \epsilon \qquad (20),$$

the calculated δ_L (the final δ of the liquid) equals +10.58 o/oo which is close to the above regression +12.22 o/oo δ_s. The difference here is attributed to the fact that the +10.58 o/oo δ_L is calculated from a constant-feeding pan, while the +12.22 o/oo δ_L is obtained from evaporative pan experiments.

Chapter Discussion

Rainfall

Rainwater, obtained during a 1991-1992 period ($\approx$ 1130 mm), was below normal rainfall (1,327 mm; 50-year average). The weighted $\delta^{18}O$ (= -4.4 o/oo) of the 1991-1992 rainfall is thus assumed to be a mere average. St. Petersburg rainwater has a stable isotopic composition ($\delta^{18}O$ and δD) similar to the meteoric water line, and the $\delta^{18}O$ is within a -4 o/oo isopleth of $\delta^{18}O$ contour lines depicted globally by Yurtsever and Gat (1981). Strangely, the St. Petersburg winter and summer rainfall's $\delta^{18}O$ does not fall on the another $\delta^{18}O$ contour lines generated from the IAEA database (Lawrence and White, 1991). These differences may be due to:

1. There are no IAEA sampling stations in the vicinity of central Florida, and/or
2. The $\delta^{18}O$ of rainwater does not correlate at all with surface air temperature, but only is correlated with the its amount, and/or
3. Other meteorological conditions predominate (e.g. cloud formation, source of atmospheric water vapor which varies from year to year), and/or
4. Lawrence and White (1991) utilized a biased set of data.

It is likely that variations in the source of water vapor may control the rainwater's isotopic compositions, especially during the wintertime in Florida. As shown by Newell and Zhu (1994), there are filamentary structures within atmospheric water vapor pathways which travel around the globe and shift directions seasonally. During the summer, a local source of water vapor with invariant surface water temperature from the Gulf of Mexico and the adjacent Gulf Stream is likely to contribute more to the rainfall's $\delta^{18}O$ in Florida.

Jacob and Sonntag (1991) conducted an 8-year monitoring of $\delta^{18}O$ and δD in precipitation in Heidelberg, Germany, and found that the correlation between the $\delta^{18}O$

and surface air temperature did not exist for those samples collected where the annual air temperature exceeded 15 °C. Similar findings were reported by Rozanski et al. (1993) for 30-year IAEA database and by the data presented in this dissertation. It is possible that the re-equilibration of precipitation droplets with the water vapor and/or evaporation while still aloft may override the temperature-$\delta^{18}O$ correlation in the vicinity of $t > 15$ °C and 30 °N (e.g. Woodcock and Friedman, 1963; Stewart, 1975; Joussaume and Jouzel, 1993; Gedzelman and Arnold, 1994).

Coincidentally, from the $\delta^{18}O$-amount linear relationship (Table 2) an intercept of -2.5 ($\pm$0.2) o/oo was found for a very small amount of rainfall. (If the limit of rainwater amount is approaching zero, there would be no $\delta^{18}O$ data - a paradox of the relationship.) This value is close to river endmember's $\delta^{18}O$ (-2.2 $\pm$[0.3]) and suggests that the similar water source and alteration processes (e.g. evaporation) operate on the freshwater endmember of Tampa Bay (see Chapter 4) and during light precipitation.

There may be questions regarding the validity of weighted mean of rainwater, especially on the effect of the most depleted rainwater in O-18 composition ($\delta^{18}O$ = -11.7 o/oo in one sample in 1992) on the 1991-1992 weighted mean. Yearly weighted means of rainwater are -4.1 and -4.7 o/oo for 1991 and 1992, respectively. These yearly weighted means indicate that the majority of rainfall events control the $\delta^{18}O_{\text{weighted mean}}$.

Atmospheric Water Vapor

The 20/80 ratio for the plants' transpiration and surface water evaporation could become larger if followed inland since the studied sites are located near the open water of the Tampa Bay. $\delta^{18}O$ contribution of inland transpiration, if analyzed, could become the largest comparing to free-water evaporation in the total evaporation budget as shown in $\delta^{18}O$ data of surficial aquifer water in Roy Haynes site (see Chapter 5 for discussion).

Only the local oak trees were studied for the transpired water. It is possible that minor variations could occur in other plants. At least the $\delta^{18}O$ of transpired water extrapolated to 100 % humidity helps suggest that the source of water used by the oak trees comes from the ground.

Evaporation

It can be seen that the evaporation of surface water fractionates $^{18}O/^{16}O$ more than the equilibrium conditions suggest. The extra enrichment (or kinetics) is implicated within the ϵ factor (as $\Delta\epsilon$), which depends on the humidity and water temperature. Generally, the liquid isotopic resistance, ρ^*_L, is very small compared to the (1-h) factor, and is often ignored during the calculation of δ_E (Craig and Gordon, 1965; Welhan and Fritz, 1977). Merlivat and Coantic (1975) and Merlivat (1978) found that the turbulent surface of the water (up to 7 m/s wind) did not affect the δ_E extensively.

For pan experiments, if the air temperature is assumed for the water temperature, the calculated δ_E could approach its minimum limit while the calculated δ_L should be close to its maximum (Table 3). From observed data, the δ_E (-13.9 o/oo) agreed well with the calculated δ_E (-14.1 o/oo), but the calculated δ_L (+10.6 o/oo) is lighter than the measured ones (+12.2). The difference for the latter is caused by uncertainty in the calculation of δ_E (evaporative pan experiments) from the parameters m and δ_s, which depend indirectly upon the curve-fitting method.

The exact agreement (Table 5) between the two calculated δ_E in the close-system equation (Craig and Gordon, 1965; see the above equation 8) and Allison and Leaney (1982)'s constant-feed pan experiment (the pan no. 2 experiment in this study) suggests

Table 5. Comparison of the Calculated δ_E from Craig and Gordon (1965; See Equation 8 Here) and Allison and Leaney (1982)'s Constant-Feeding Pans

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Allison and Leaney (1982) extended the equations 8 to 11 (in this dissertation) with their constant-feeding pan experiments to give

$$\delta_{E\ \text{lake or pan}} = (m+1)(\delta_{\text{lake or pan}} - K) + \delta_I \qquad (21)$$

$\delta_E = \delta^{18}O$ of evaporative water
m = m factor of Welhan and Fritz (1977) = $(h-\epsilon)/(1-h+\Delta\epsilon)$ [see equation 12 in Chapter 3]
$\delta_I = \delta^{18}O$ of input water = -2.42 o/oo vs SMOW
$K = \delta_I/(m+1) + m(h\delta_a+\epsilon)/\{(m+1)(h-\epsilon)\}$
δ_a = -13.5 o/oo (measured)
δ_{pan} = +3.74 o/oo (observed)
$\Delta\epsilon = 16(1-h)*10^{-3}$

h	^oC	α^+	$\delta^{18}O$	α^*	ϵ^*	$\Delta\epsilon$	eq. 8	eq. 21	eq. 20
34.3	40.6	1.008192	-15.71	0.99187	0.008126	0.01051	-0.01543	-0.01543	0.01242
50.6	35.9	1.008529	-14.21	0.99154	0.008457	0.007904	-0.01160	-0.01160	0.008334
40.5	38.4	1.008348	-12.82	0.99172	0.008279	0.00952	-0.01426	-0.01426	0.01089
48	36	1.008522	-12.86	0.99155	0.008450	0.00832	-0.01246	-0.01246	0.009031
38.6	37.4	1.008420	-14.92	0.99165	0.008350	0.009824	-0.01483	-0.01483	0.01148
35.8	38.7	1.008327	-12.86	0.99174	0.008258	0.01027	-0.01531	-0.01531	0.01214
46	34	1.008670	-14.81	0.99140	0.008595	0.00864	-0.01334	-0.01334	0.009718
42.6	35.9	1.008529	-13.88	0.99154	0.008457	0.009184	-0.01403	-0.01403	0.01050
42.5	36.2	1.008507	-13.07	0.99156	0.008435	0.00920	-0.01402	-0.01402	0.01051

that the observed air temperature does not differ much from the pan's water temperature and the correct m should be close to 0.6771.

Summary

A 1991-1992 monitoring of rainwater's $\delta^{18}O$ in St. Petersburg, Florida provided a weighted mean $\delta^{18}O$ of -4.4 o/oo. The correlation between the surface air temperature and the $\delta^{18}O$ does not exist. The relationship between the amount of rainfall and its $\delta^{18}O$ is not very well correlated.

$\delta^{18}O$ of transpired water (-11.8 o/oo) is heavier than $\delta^{18}O$ of atmospheric water vapor (-13.9 o/oo). Calculations based on a relationship between $\delta^{18}O$ of transpired water and specific humidity suggest that plant uses ground water without major isotopic fractionation within the xylem. The calculated δ_E of the leaves of oak tree suggest that a diffusion process predominates during the evaporation process.

Both constant-feeding pan and free pan evaporation experiments provide a total enrichment factor (ϵ) of 1.01027 (-10.27 o/oo in terms of fractionation for evaporation of water) during the summertime. The linearly-regressed evaporative parameters, m and δ_s, are 1.041 and +12.2 o/oo, respectively. A good agreement was found between the measured δ_E (-13.9 o/oo) and computed δ_E (-14.1 o/oo) in the pan experiments.

Chapter 4

RIVER, AND ESTUARINE WATERS IN TAMPA BAY

Tampa Bay is the largest body of estuarine water along the west-Florida shelf (Figure 3). The bay area is 1,031 km^2, with an average depth of 3.7 m. The drainage area (watershed) is 4,600 km^2 (NOAA, 1993). The estimated freshwater flow rate (runoff into the Bay) varies from 50 to 72 m^3/s (Goetz and Goodwin, 1980; Hutchinson, 1983; Zarbock, 1991; Table 6). The Hillsborough river is the major contributor of freshwater to the Bay ($\approx$ 29 %), and is followed by the Alafia ($\approx$ 21%), Manatee ($\approx$ 16%), and Little Manatee ($\approx$ 11 %) rivers (Table 6). The Tampa Bay Bypass Canal supplies 2.6 % of the freshwater input to the Bay. Salinities in the Tampa Bay range from 20 o/oo in the northern area (Hillsborough Bay) to 30 o/oo in the southern area near the mouth of the Bay during January and June months (Tampa Bay National Estuary Program, 1992; NOAA, 1993). In September months, the salinity range increases by 5 to 7 o/oo. Water temperature varies from 12 °C in the winter to 33 °C in the summer (NOAA, 1993). Strong horizontal salinity gradients develop seasonally in the Bay water. The flushing rate is unknown, but is estimated by the author to be on the order of 53-67 days (see the calculation below). The evaporation rate ranges from 40" (1.016 m) per year to 56" (1.414 m) per year (Cherry et al., 1970; Hastenroth and Lamb, 1978; Fransworth and Thompson, 1982; Bush and Johnston, 1988). Based on 15-year data of pan evaporation study, Fransworth and Thompson (1982) gave a 50" (1.27 m) estimation of annual evaporation rate in west-central Florida.

Table 6. Estimated Freshwater Flow Rate into Tampa Bay (After Zarbock, 1991)

Current conditions *Authors cited by Zarbock*	flow rate (m^3/s)
Dooris	50.7
Goodwin/Hutchinson	63.6
Flannery	56.9
Dames and Moore	71.6
Historical conditions	
Dames and Moore	64.6

Surface water discharges to Tampa Bay (after Hutchinson, 1983)

	flow rate (m^3/s)
Hillsborough River	18.0
Sulphur Spring	1.18
Alafia River	13.0
Little Manatee River	6.79
Manatee River	9.99
Ungauged areas	9.73
Rocky Creek	1.31
Sweetwater Creek	0.613
Lake Tarpon Canal	0.832
Tampa Bypass Canal	1.62
Total	63.08

Surface sediments of Tampa Bay consist mostly of quartz sand with minor amounts of siliceous and calcareous detritus (Doyle, 1985). The underlying sections are

Suwannee and Ocala Limestones ($\approx$ 100 m below mean sea level; Ryder, 1985). Hutchinson (1983) showed that the leakage of fresh ground water from the Floridan aquifer into Tampa Bay could be as large as 4.4 m^3/s. More recently, Brooks et al. (1993) gave estimates ranging from 3.6-3.9 m^3/s in the dry season to 3.9-4.3 m^3/s in the wet season. However, the extent and the direction of this underground water leakage or the reversal process (salt-water intrusion) depends on the ground water flow paths, potentiometric surfaces (heights of water head), water consumption by well pumping, and changes in the rates of recharge and discharge of ground water, as well as climatic modification. Freshwater drainage as well as ground water feed the rivers. In the Green Swamp area, the Floridan ground water contributes up to 11 % by volume of the Hillsborough river (Pride et al., 1966). The underlying geology will be described in detail later in the Ground Water Section.

The geology and geochemistry of drainage basins and river beds control the chemistry and the $\delta^{18}O$ of the water and $\delta^{13}C$ of the total dissolved inorganic carbon (DIC). Sackett and Moore (1966) and Mook (1986) suggested that in riverwater the reaction between a limestone of marine origin ($\delta^{13}C$ = +2 o/oo) and CO_2 derived from organic matter ($\delta^{13}C$ = -27 o/oo) should produce a $\delta^{13}C_{DIC}$ of -12.5 o/oo (={[+2][1]+[-27][1]}/{[1+1]}). This calculation was based on an equal contribution of CO_2 from organic matter and limestone. A representative equation is

$$CaCO_{3(s)} + CO_{2(g)} + H_2O_{(l)} \text{ ----> } 2HCO_3^-{}_{(aq)} + Ca^{2+}{}_{(aq)} \qquad (22).$$

The $\delta^{18}O$ the river endmember depends upon the contributions from rainwater, evaporation and groundwater (e.g. Gat and Dansgaard, 1972).

Previous USGS studies in the 1970s showed that in Tampa Bay the average total dissolved organic carbon was 4.5 x 10^{-4} M, and the pH ranged from 7.7 in Hillsborough Bay to 8.5 in southern part of the Bay (Goetz and Goodwin, 1980).

$\delta^{18}O$ and $\delta^{13}C$ (DIC) in Tampa Bay Waters

Sackett et al. (1991) conducted a pilot isotopic study during March, 1990, for which the results are included here (in Figures 13a and 13b). Figures 13a and 13b illustrate the distribution of $\delta^{18}O$ and $\delta^{13}C$ (DIC) in Tampa Bay estuarine waters. The results of two sampling periods (March, 1990 and January, 1993) give linear correlations between the salinity and $\delta^{18}O$ as well as between salinity and $\delta^{13}C$. For $\delta^{13}C$, the slopes and intercepts of the two equations are similar within errors despite the spreading of the March, 1990 data. The samples in March, 1990 were collected nearshore, while the samples for January, 1993 were taken from a boat. The extrapolated $\delta^{18}O$ for the river endmember, based on averaging of the equations for the two periods, is -2.3 o/oo vs SMOW, while that of surface water (salinity = 32.02 o/oo during January) of the Gulf of Mexico is +1.00 o/oo (both with ± 0.3 o/oo, n=38). The extrapolated river source of $\delta^{13}C_{DIC}$ is -10.5 o/oo vs PDB, and the surface water's $\delta^{13}C_{DIC}$ of the Gulf of Mexico is -2.6 o/oo vs PDB (±0.9 o/oo; n=34). A plot of the concentration of the total dissolved inorganic carbon (ΣCO_2) against its $\delta^{13}C$ shows some scattering for the combined 1990 and 1993 data. Only the 1993 data shows a trend displaying a moderate linearity ($r^2=0.214$; Figure 14a). In addition, a weak correlation between the ΣCO_2 and its salinity is found ($r^2=0.182$; Figure 14b).

Chapter Discussion

The good correlations between the $\delta^{18}O$ and $\delta^{13}C$ (DIC) and salinity suggest that both $\delta^{13}C_{DIC}$ and $\delta^{18}O$ behave conservatively along salinity gradient. The $\delta^{18}O$ of water in Tampa Bay is a result of mixing between the freshwater and saline waters. For $\delta^{18}O$, the lower correlation coefficient for the March, 1990 sampling is attributed

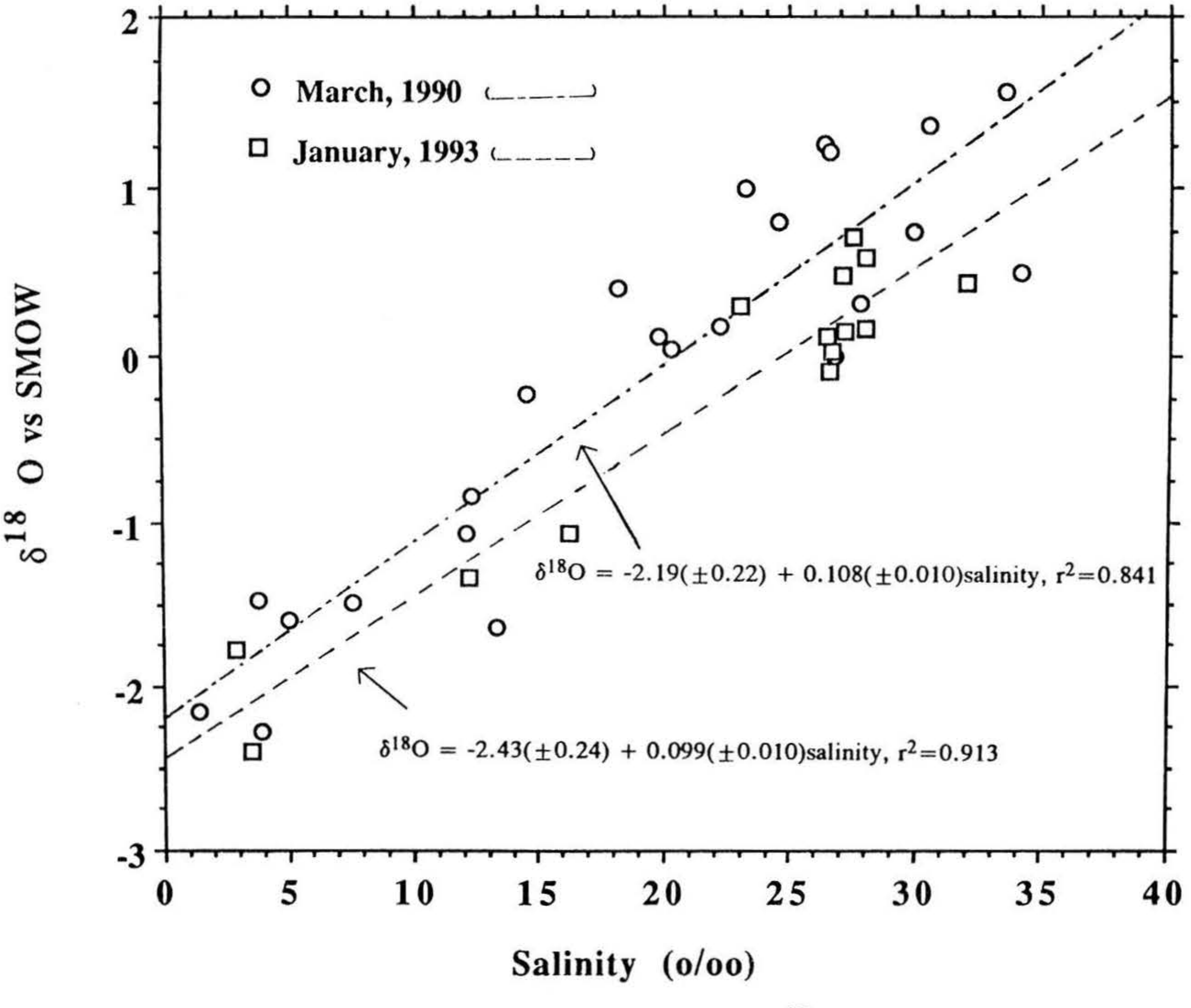

Figure 13a. Linear Correlation between Salinity and $\delta^{18}O$ in Tampa Bay, Florida

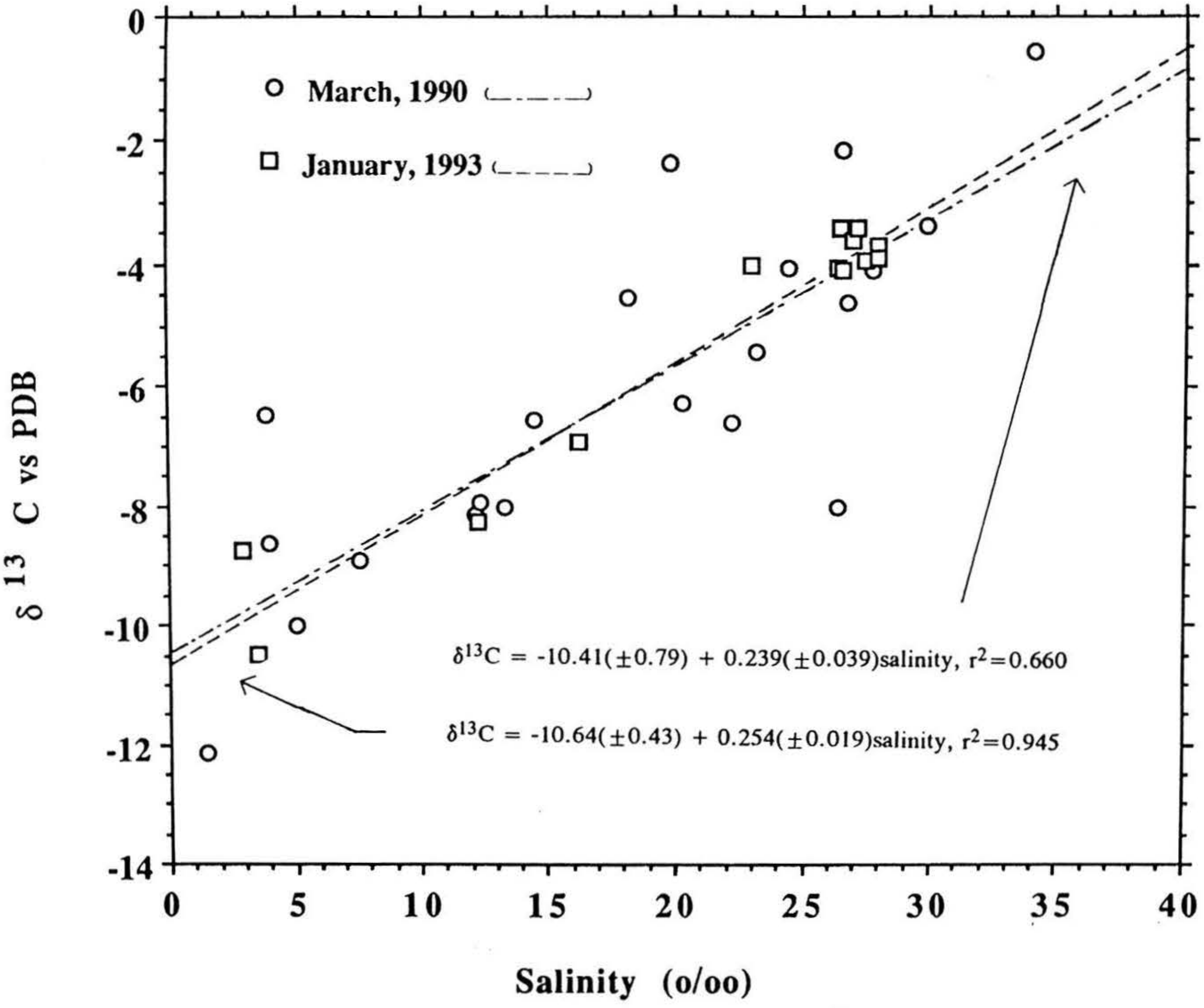

Figure 13b. Linear Correlation between Salinity and $\delta^{13}C$ in Tampa Bay, Florida

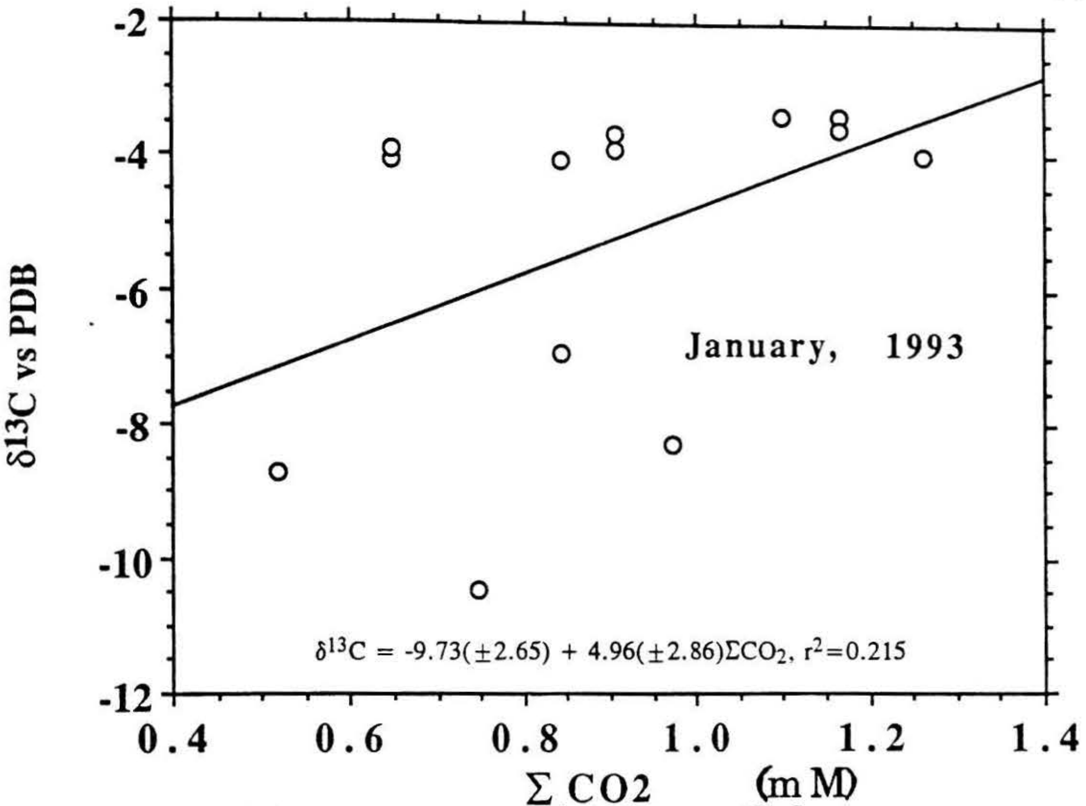

Figure 14a Variation of Total Dissolved CO_2 and Its $\delta^{13}C$ in Tampa-Bay Estuarine Waters

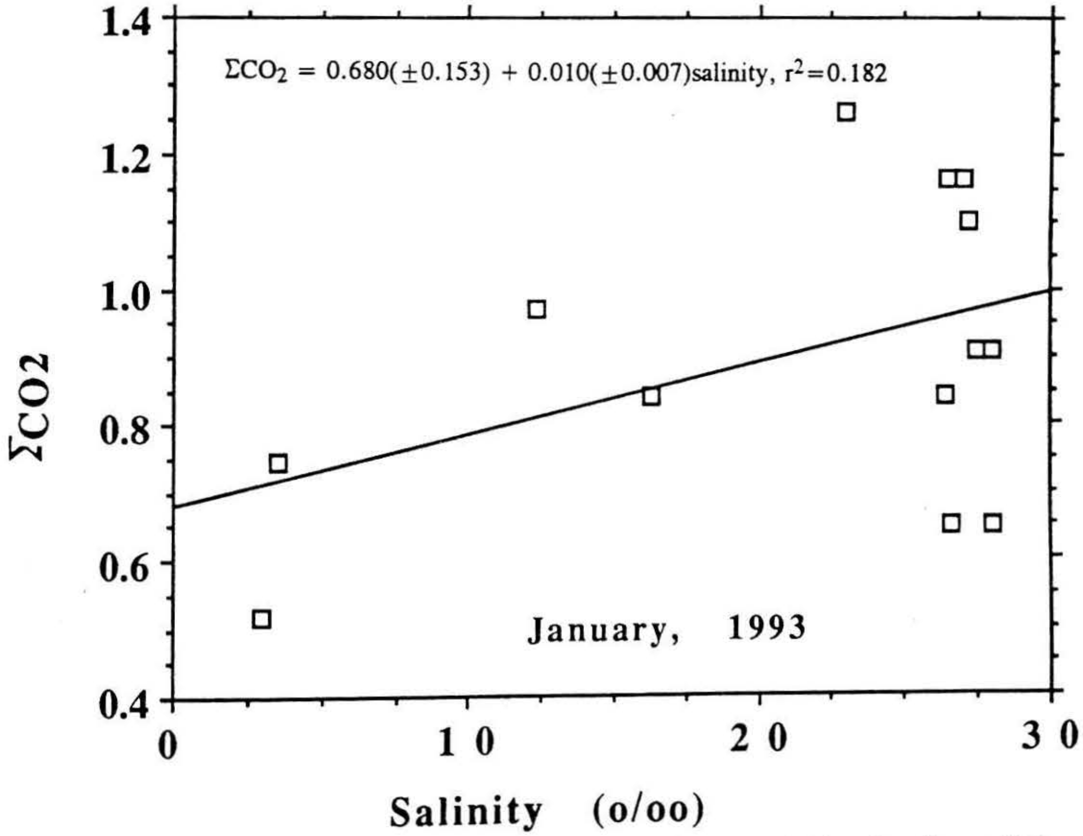

Figure 14b Variation of Total Dissolved CO_2 along a Salinity Gradient of Tampa Bay

to storage which was not designed for $\delta^{18}O$ analyses, and to the difference between shore and ship samplings. The $\delta^{13}C_{DIC}$ of shore samples in March, 1990 can be affected by atmospheric CO_2 exchange and stagnant waters.

The river endmember's $\delta^{18}O$ is a result of combination effects of natural evaporation, ground water seepage, and natural runoff. The ground water seepage is likely to contribute mostly to the river endmember as the $\delta^{18}O$ of the upper Floridan water is around -2.8 o/oo (see Chapter 5). The 0.5 o/oo (= [-2.3] - [-2.8]) positive shift of the river endmember represents a 4.7 % water loss from the ground water. (The calculation is performed using equations 18 and 19, described in Chapter 3, and parameters, δ_0 = -2.8 o/oo, δ = -2.3 o/oo.) Most direct rainwater on the drainage basin is likely to evaporate into the atmosphere (evaporation rate ≈ 1.27 m/year; precipitation rate ≈ 1.33 m/year); only a small fraction of water from the drainage basin contributes directly to the river heads. If the ΣCO_2 of ground water is similar to that of seawater endmember, the correlation between the ΣCO_2 and salinity should not be found or be very weak (Figure 14b). The similarities in ΣCO_2 of the river endmember (≈ 1 mM) and the ground water (≈ 1 mM) support the idea that ground water feeds the river head.

The $\delta^{13}C$ (DIC) in the water is dependent on

1. The CO_2 sources depleted in C-13 which, generally, are predominantly from the oxidation of local organic matter (C-3 land plants),
2. The CO_2 sources enriched in C-13 which are atmospheric CO_2 and products of weathering of carbonate materials (see Mook, 1986; Mook and Tan, 1991 for further discussion).
3. The extent of isotopic exchange of carbon-13 between the atmospheric CO_2 and the water body (see e.g. Mook, 1986; Sackett et al., 1991).

As shown earlier a simple mixing model for two sources produces $\delta^{13}C_{DIC}$ of -12.5 o/oo vs PDB. The heavier $\delta^{13}C$ of river endmember can be caused by

1. Partial contribution of phytoplankton and terrestrial plants on the derived CO_2.
2. A partial kinetic exchange with atmospheric CO_2, which tends to enrich the water body in carbon-13 through time.
3. As shown in Chapter 5, the ground water may be the only major source of river endmember in Tampa Bay. The $\delta^{13}C_{DIC}$ of ground water is -10.4 o/oo vs PDB, which is almost exactly equal to the value of the river endmember (-10.5 o/oo).

Carbonate species in the water, i.e. CO_{2g}, CO_{2aq}, $HCO_3^-{}_{aq}$, $CO_3^{2-}{}_{aq}$, have associated pair of fractionation factor, e.g.
the $HCO_3^-{}_{(aq)}$ «---» $CO_{2(aq)}$ has a fractionation factor of ^{13}C of -8.97 o/oo at 25 °C,
the $CO_{2(aq)}$ «--» $CO_{2(g)}$ has a fractionation factor of ^{13}C of +1.06 o/oo at 25 °C
(Mook et al., 1974).

The $\delta^{13}C$ of the dissolved bicarbonate is not the same as the $\delta^{13}C$ of the total dissolved inorganic carbon since for the $\delta^{13}C_{total}$ the ^{13}C contribution of all carbonate species have to be accounted for. As pH of the estuarine water was not measured for the samples in either 1990 and 1993, the $\delta^{13}C_{bicarbonate}$ cannot be calculated directly (e.g. Mook and Koene, 1975; Mook, 1986). Further discussion on the exchange effect of the atmospheric CO_2 on the marine endmember of Tampa Bay based on $\delta^{13}C$ is not possible.

The slope of the linearly regressed line of the salinity and $\delta^{13}C_{DIC}$ of Tampa Bay water is +0.247 (±0.044) which is similar to the Florida Bay water (slope=+0.286 [±0.03]; Holmes, 1992). The freshwater $\delta^{13}C_{DIC}$ intercepts are -10.5(±0.9) and -11.7(±0.8) o/oo for the waters in Tampa Bay and Florida Bay, respectively. The difference in the $\delta^{13}C_{DIC}$ of river endmembers is attributed to variations in hydrology of the drainage areas and the differences in ground waters. The drainage areas in Tampa Bay consist of sandy soils, and mixtures of quartz sand, and carbonate fragments. The upper Floridan ground water seems to contribute mostly to Tampa Bay compared to the surficial and intermediate waters (Brooks et al., 1993). In south

Florida, the Everglades and networks of canals (Klein et al., 1975) keep the drainage water in longer contact with the organic-rich bogs, therefore the $\delta^{13}C_{DIC}$ is slighter lighter. Surficial ground water is the important source of freshwater flow out onto Florida Bay (Klein and Hall, 1978).

Using a simple one-dimensional box model proposed by Bowden (1967) and inclusions of the leakage of the Floridan water into the Bay, the evaporation, and precipitation directly onto the Bay, the replacement time[5], the surface outflow's volume, and the bottom inflow's volume can be calculated (Figure 15). The two equations, used in the model here, are for the conservation of volume and of water molecules (in terms of $\delta^{18}O$):

$$V_p + V_r + V_g + V_b = V_s + V_e \qquad (23a)$$

$$V_p\delta_p + V_r\delta_r + V_g\delta_g + V_b\delta_b = V_s\delta_s + V_e\delta_e \qquad (23b)$$

Upon manipulation: $V_s =$

$$[V_p\delta_p + V_r\delta_r + V_g\delta_g - V_e\delta_e - \delta_b(V_p + V_r + V_g - V_e)]/(\delta_s - \delta_b) \qquad (24)$$

The replacement time for the Tampa Bay is the volume of the Bay (3.483 km^3; NOAA/EPA, 1989) divided by the rate of surface outflow at the Bay mouth.

The chosen parameters are

V_e, evaporation rate = 50" per year (41.5 m^3/s)

V_p, rainfall = (2/3) of 50-year annual average = (2/3)(132.67 cm/year)

---» 28.93 m^3/s (using Bay area = 1,031 km^2) - for the 1991-1992 condition; and during normal rainfall, V_p = 43.4 m^3/s

V_r, river runoff = 55 m^3/s (low estimate)

V_g, ground water seepage into the Bay from the Floridan aquifer = 4.4 m^3/s

δ_b, $\delta^{18}O$ of bottom inflow volume = +0.6 o/oo

δ_p, $\delta^{18}O$ of rainwater = -4.4 o/oo

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5. Time required to replace the entire volume of a studied body of water. In this case it is equal to the volume of Tampa Bay divided by flux of surface outflow water from Tampa Bay into Gulf of Mexico (V_s).

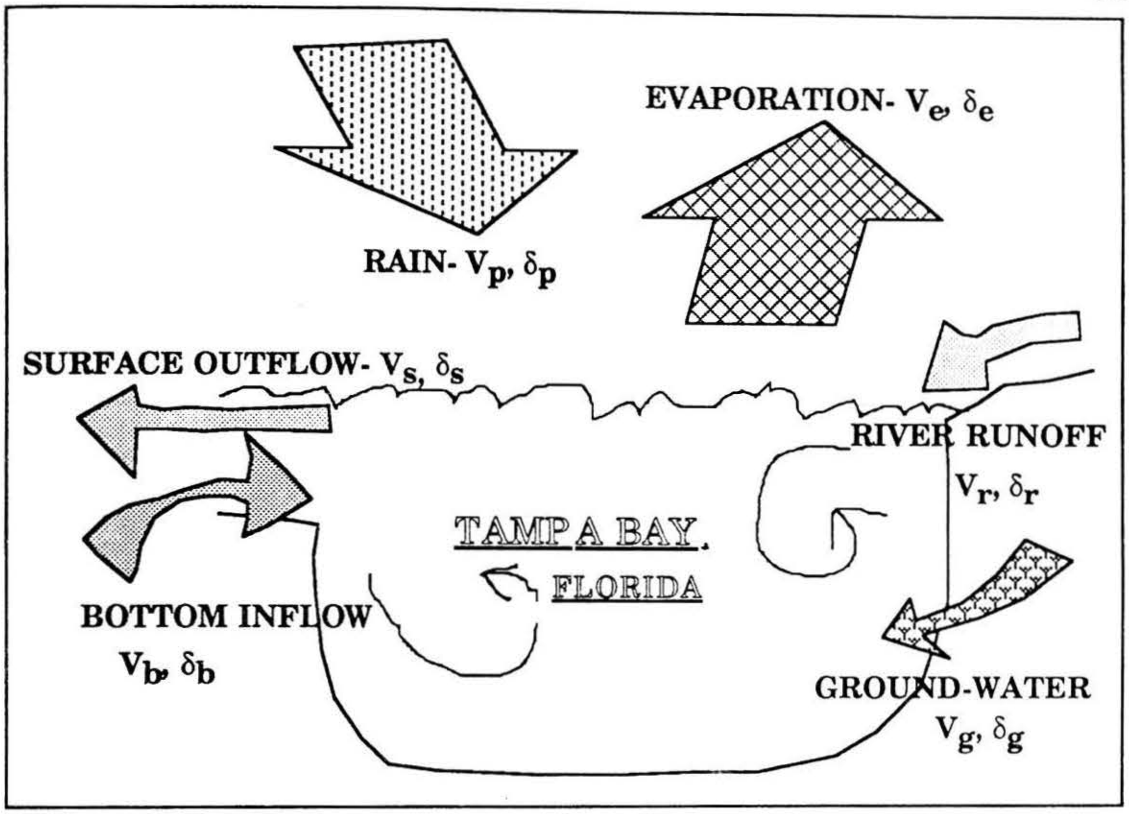

Figure 15. A Box Model of Inputs and Outputs of Waters from Tampa Bay, Florida

δ_r, $\delta^{18}O$ of river = -2.2 o/oo

δ_s, $\delta^{18}O$ of marine surface water = +0.956 o/oo

δ_g, $\delta^{18}O$ of Floridan water = -2.8 o/oo (to be shown in details later in the next Chapter)

δ_e, $\delta^{18}O$ of evaporative water vapor = -13.9 o/oo (see Chapter 3)

The unknown terms are

V_s, rate of surface outflow

V_b, rate of bottom inflow

The calculated flow volume of the V_s, V_b and the replacement time are shown in Table 7 below:

Table 7. Calculated V_s, V_b, ΔV ($=V_s-V_b$), and Replacement Time of Tampa-Bay Water

	V_s (m^3/s)	V_b (m^3/s)	ΔV (m^3/s)	replacement time (days)
2/3 rainfall	762.7	715.9	46.8	52.9
normal rainfall	606.2	544.9	61.3	66.5

The largest controlling factor other than the surface outflow ($V_s\delta_s$) and bottom inflow ($V_b\delta_b$) of water at the mouth of the Bay is the evaporation effect ($V_e\delta_e$). The ground-water leakage (directly into Tampa Bay, not from rivers) does not contribute significantly to the overall oxygen isotopic budget nor the lower-than-normal rainfall.

From this information, the calculated replacement time of water in the Tampa Bay is about 67 days for average rainfall condition. It should be noted that this is a minimum estimate.

Summary

The $\delta^{13}C_{DIC}$ and $\delta^{18}O$ in Tampa-Bay water correlate well with salinity. The extrapolation of $\delta^{13}C_{DIC}$ to zero salinity gives $\delta^{13}C_{DIC}$ of -10.5 o/oo (±0.9) vs PDB, which is assumed to be equal to the freshwater endmember. In a similar fashion, the extrapolated $\delta^{18}O$ yields -2.3 o/oo (± 0.3) vs SMOW. In Tampa Bay, the ΣCO_2 does not correlate with salinity nor $\delta^{13}C_{DIC}$. The similarities of $\delta^{13}C_{DIC}$ and $\delta^{18}O$ values of freshwater endmember and that of ground water (to be shown in Chapter 5) suggest that the source of river endmember is the upper Floridan water.

Calculations based on a simple isotopic mass balance of all water inputs and outputs from the Tampa Bay show that the time required to replace all water in Tampa Bay is on the order of 67 days. Reduced rainfall does not affect the computed replacement time much. Surprisingly, the direct ground water input into the Bay is negligibly small in the calculation.

Chapter 5

GROUND WATER AND MIRROR LAKE WATER

Ground Water in West-Central Florida

In the Southwest Florida Water Management District (SWFWMD), 83 % of the total water use for public sectors is obtained from ground water (Marella, 1992, Table 8). In Pinellas, Hillsborough, Polk, Pasco, Hernando, Manatee and Sarasota the ground water accounts for up to 86 % of the total freshwater consumption. Ninety-one percent of this ground water use comes from the upper Floridan aquifer (Marella, 1992).

The upper Floridan aquifer is a part of a complex aquifer system, which acts as a water reservoir in the State of Florida. In west-central Florida the main hydrological sections are surficial, intermediate, and the Floridan aquifers (Figures 5 and 16). Above the very thick igneous and metamorphic basements, gypsum ($CaSO_4.2H_2O$), and anhydrite ($CaSO_4$), were laid down, and followed by a calcite-dolomite section which was overlain by a calcite section. The Floridan aquifer is located in the calcite-dolomite and calcite sections. The lower Floridan water is saline, while the upper Floridan water is fresh and potable. In most locations a confining layer separates the upper Floridan and the lower Floridan sections.

The overlying and confining strata are mixtures of dolomite, calcite, phosphatic and clay minerals which are called the Hawthorn Group, and act as confining beds, and intermediate aquifers. Closer to the surface, the remaining quartz-rich layers of sands and the mixtures of calcite, dolomite, aragonite, and shells constitute the surficial aquifer (Ryder, 1985; Scott, 1991).

Table 8. Estimated Freshwater Uses for the Year 1990 in West-Central Florida (Units in Million Gallons Per Day, After Marella, 1992)

	total withdrawals	ground water	surface water
SWFWMD	1,572	1,302 (83%)	269 (17%)

break-down categories of ground waters

	ground waters				surface water
	Total	Surficial	Intermediate	Upper Floridan	
Pinellas	48.1	0.2	0	47.9	1.4
Hillsborough	179.7	0.35	2.2	177.2	88.9
Polk	353.7	7.2	10.7	335.9	83.8
Pasco	138.7	0.21	0	138.5	2.4
Hernando	45.5	0.02	0	45.5	0.35
Manatee	96.5	0	6.7	89.8	45.3
Sarasota	59.5	1.2	29.2	29.2	3.2

fresh ground waters/{fresh ground waters + surface freshwaters} = 86 %

Floridan water/{surficial + intermediate + Floridan waters} = 91 %

System	Series	Stratigraphic unit	Hydrogeologic unit			
			System	North of Tampa Bay	East of Tampa Bay	South of Tampa Bay
Quaternary	Holocene and Pleistocene	Terrace deposits	Surficial aquifer system	Absent or surficial aquifer	Surficial aquifer	Surficial aquifer
Tertiary	Pliocene	Caloosahatchee Marl and Tamiami Formation	Intermediate aquifer system or intermediate confining unit[2]	Absent or confining unit[2]	Upper confining unit[2]	Semiconfining unit[4]
	Miocene	Hawthorn Group[1] Peace River Formation			Intermediate aquifer[2]	Tamiami-Upper Hawthorn aquifer[5]
						Semiconfining unit[4]
		Arcadia Formation				Lower Hawthorn-Upper Tampa aquifer[5]
		Tampa Member			Lower confining unit[2]	Lower Tampa semiconfining unit[4]
	Oligocene	Suwannee Limestone	Floridan aquifer system[3]	Upper Floridan aquifer[3]	Upper Floridan aquifer[3]	Suwannee permeable zone[4]
	Eocene	Ocala Limestone				Lower Suwannee-Ocala semiconfining unit[4]
		Avon Park Formation[3]				Ocala-Avon Park moderately permeable zone[4]
						Avon Park highly permeable zone[4]
				Middle confining unit[3]	Middle confining unit[3]	Middle confining unit[3]
		Oldsmar and Cedar Keys Formations		Lower Floridan aquifer[3]	Lower Floridan aquifer[3]	Lower Floridan aquifer[3]
	Paleocene					

[1] Based on nomenclature of Scott (1988)
[2] Based on nomenclature of Southeastern Geological Society (1986).
[3] Based on nomenclature of Miller (1986).
[4] Based on nomenclature of Hutchinson (in press).
[5] Based on nomenclature of Wolansky (1983).

Figure 16. Hydrogeological Sections of Ground-Water Aquifers in West-Central Florida (After Miller, 1986; Swancar and Hutchinson, 1992)

The Floridan aquifer is located near the land surface in the northern Polk, Pasco and Hernando Counties, and dips down in the Pinellas and Hillsborough areas (Ryder, 1985). The surficial and intermediate aquifers are absent beneath most of the Tampa/St. Petersburg and Tampa Bay (Campbell, 1983; Ryder, 1985). The upper Floridan aquifer underlies the intermediate aquifers in other parts of west-central Florida and supplies freshwater (in addition to feeding the rivers) into Tampa Bay (Hutchinson, 1983; Brooks et al. 1993).

The hydraulic head of ground water (potentiometric highs), and the hydraulic conductivity of the aquifer structures as well as their thickness govern the transmissivity[6] of the upper Floridan water. The higher the transmissitivity, the higher the potential water withdrawal can be. In the recharge area the transmissitivity is lowest, while the potentiometric surface is the highest (e.g. Stringfield, 1936; Ryder, 1985; Bush and Johnston, 1988). The transmissivities of the upper Floridan in the west-central Florida range from 20,000 to 250,000 ft^2/day (0.0215 - 0.269 m^2/s; Bush and Johnston, 1988).

Rainwater recharges the aquifers through the surficial aquifer, sinkholes, and rock fractures which, subsequently, feed into the upper Floridan aquifer. Since the Green Swamp is located at the highest elevation ($\approx$ 42 m above the national geodetic vertical datum [NGVD]; highest hydraulic potential), it is considered the most important recharge area (Stringfield, 1936; Pride et al., 1966; Figure 17). However, in a recent study based on tritium in ground water, Swancar and Hutchinson (1992) suggested that the perimeter of the Green Swamp was the major recharge area. This freshwater reacts with the host rocks which alter the water chemistry along the flow paths. The bicarbonate-calcium rich phase (ground water enriched in Ca^{2+} and HCO_3^-) is the dominant ground water type in the region, except near the west coasts where the

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6. Transmissivity is the rate at which the ground water flows through a unit thickness of aquifer. The flow is caused by the hydraulic conductivity (head of water/distance of flow). 1 m^2/s transmissivity is equivalent to 1 $m^3/s/m$ or 6.96 x 10^6 gal/day/ft.

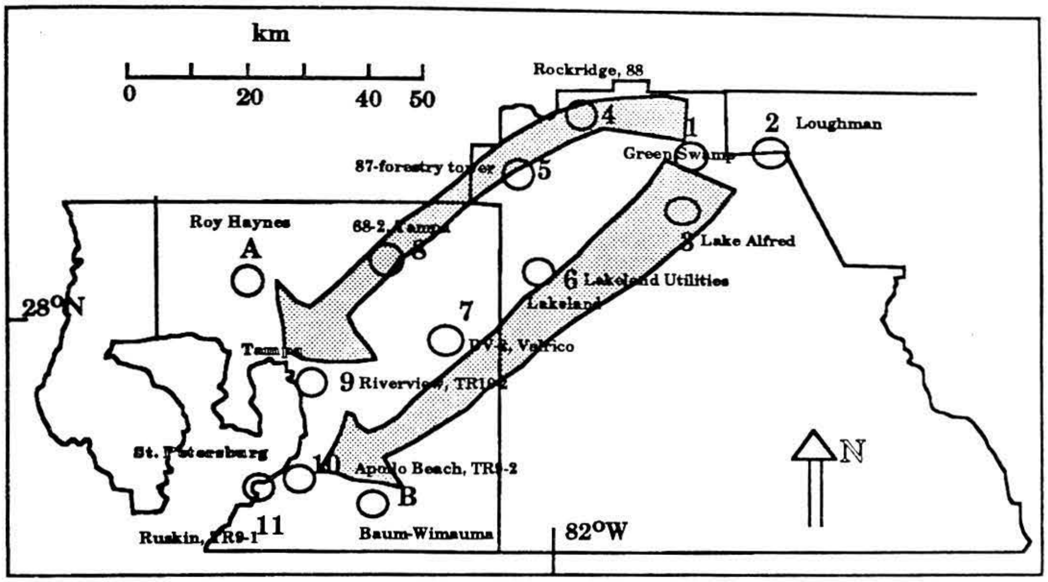

Figure 17. Schematic of Flow Paths of Ground Waters from the Recharge Area Close to the Green Swamp to the Coastal Discharge Area in the Tampa Bay

sodium chloride-rich phase is more important (Back and Hanshaw, 1970; Upchurch, 1992). The upper Floridan water is in equilibrium or slightly supersaturated with solid calcium carbonate in south Hillsborough Counties (Jones et al., 1993). The average pH of the upper Floridan water is 7.5, while the average temperature is 25 °C (Upchurch, 1992). Total dissolved inorganic solids increase along the flow paths in the confined aquifer from the recharge area (Green Swamp - 175 mg/L) to the coastal discharge ($\approx$ 600 mg/L) in west-central Florida (Sprinkle, 1989; Upchurch, 1992; Jones et al. 1993; unpublished SWFWMD data).

According to Jones et al. (1993), the calculated ion fluxes along stream tubes of the flow paths of ground waters in west-central Florida did not show a significant supersaturation with respect to the calcite and dolomite. This finding was contradictory to previous studies, especially to the Plummer group (Plummer, 1977; Plummer et al., 1983).

$\delta^{18}O$ and $\delta^{13}C$ (Inorganic) in Ground Waters and Carbonate Aquifers

Behavior Along the Flow Paths

The upper Floridan aquifer flow paths are arbitrarily divided into northern and southern directions according to its confined Hawthorn boundary (Scott, 1991; Figure 17). The northern flow path is located in the area where the Hawthorn Group was not well developed or absent. In contrast, the southern flow path is bounded by the Hawthorn confining unit. The northern flow paths are supposed to follow the potentiometric highs to lows (Figure 17), beginning at the Green Swamp (location 1) and flowing through the 88 Rockridge (4), the 87 (5 - Forestry Tower), the 68-2 (8 - north Tampa), and coastal Riverview (9 - TR10-2) wells. The southern flow paths begin in the Green Swamp (1), and flow through the Lake Alfred (3), Lakeland (6), Valrico (7 - DV-2), Apollo Beach (10 - TR9-2) and coastal Ruskin areas (11, TR9-1). The TR9- 1 site is an artesian well. The Loughman (2) is not considered for ground water chemistry because of the unusual heavier $\delta^{18}O$ and $\delta^{13}C_{DIC}$ in its ground water. The Loughman's Floridan well is likely to receive water from the surface, intermediate, and Floridan aquifers as a result of collapse of well casing even though the well was drilled to Avon Park Limestone depths (Table 1, Chapter 2). However, its carbonate aquifer samples, obtained at the time of well drilling, are thought to be unaffected.

For $\delta^{18}O$ (vs SMOW) in the upper Floridan water, the major recharge areas are located in the Green Swamp (-4.5 o/oo), Lake Alfred (-4.4 o/oo), and Lakeland (-4.2 o/oo) areas (Figures 18a and 18b). This assumes that the recharge water has a similar $\delta^{18}O$ to today's rainwater (weighted mean = -4.4 o/oo). Along the flow paths the upper Floridan waters have $\delta^{18}O$ ranging from -2.43 to - 3.36 o/oo with an average of -2.83 o/oo (by ignoring the Green Swamp, Lake Alfred, and Lakeland sites; Figure

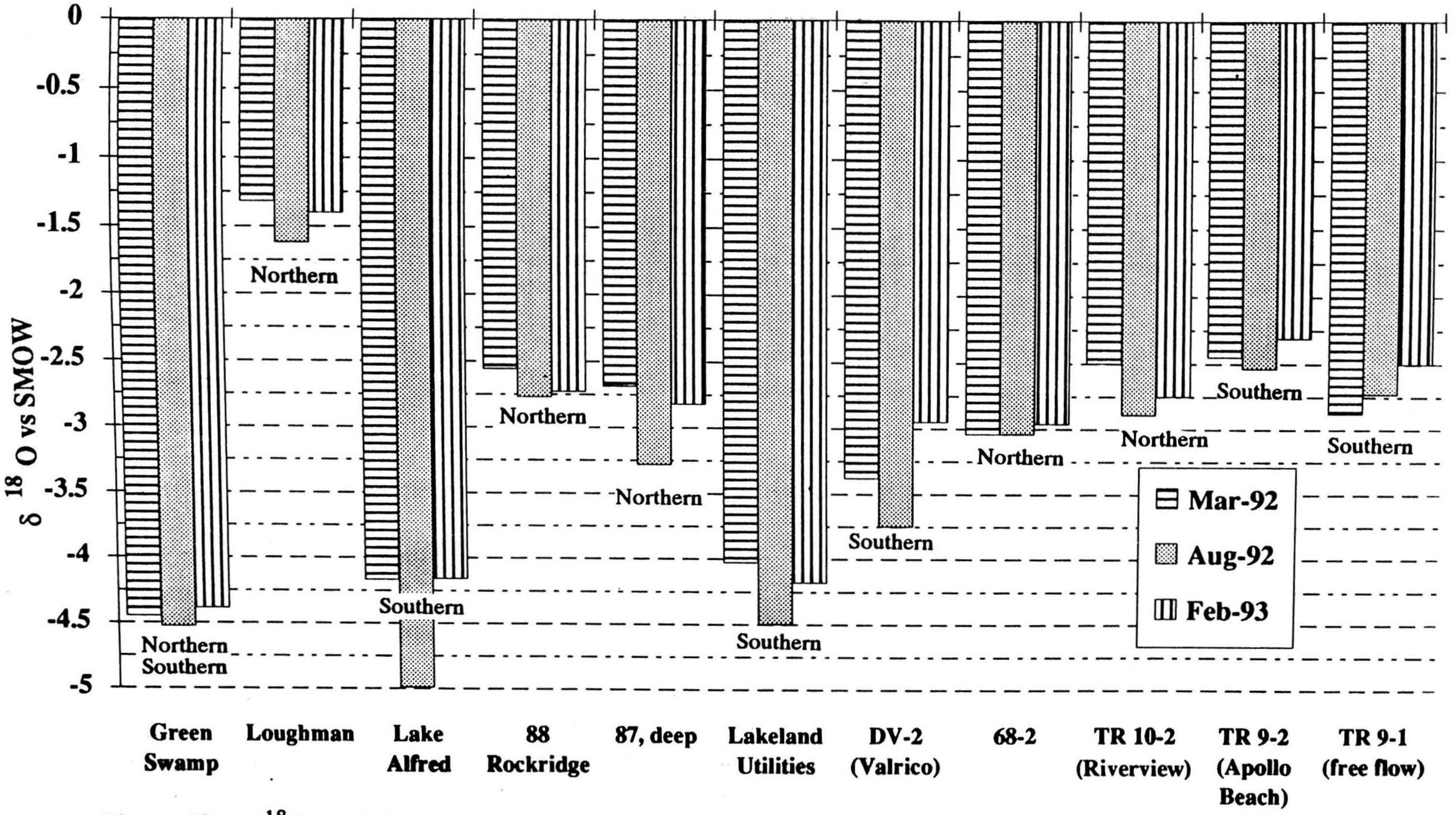

Figure 18a. $\delta^{18}O$ Variation during the Semi-Annual Studies of Ground Waters from the Recharge to Discharge Areas

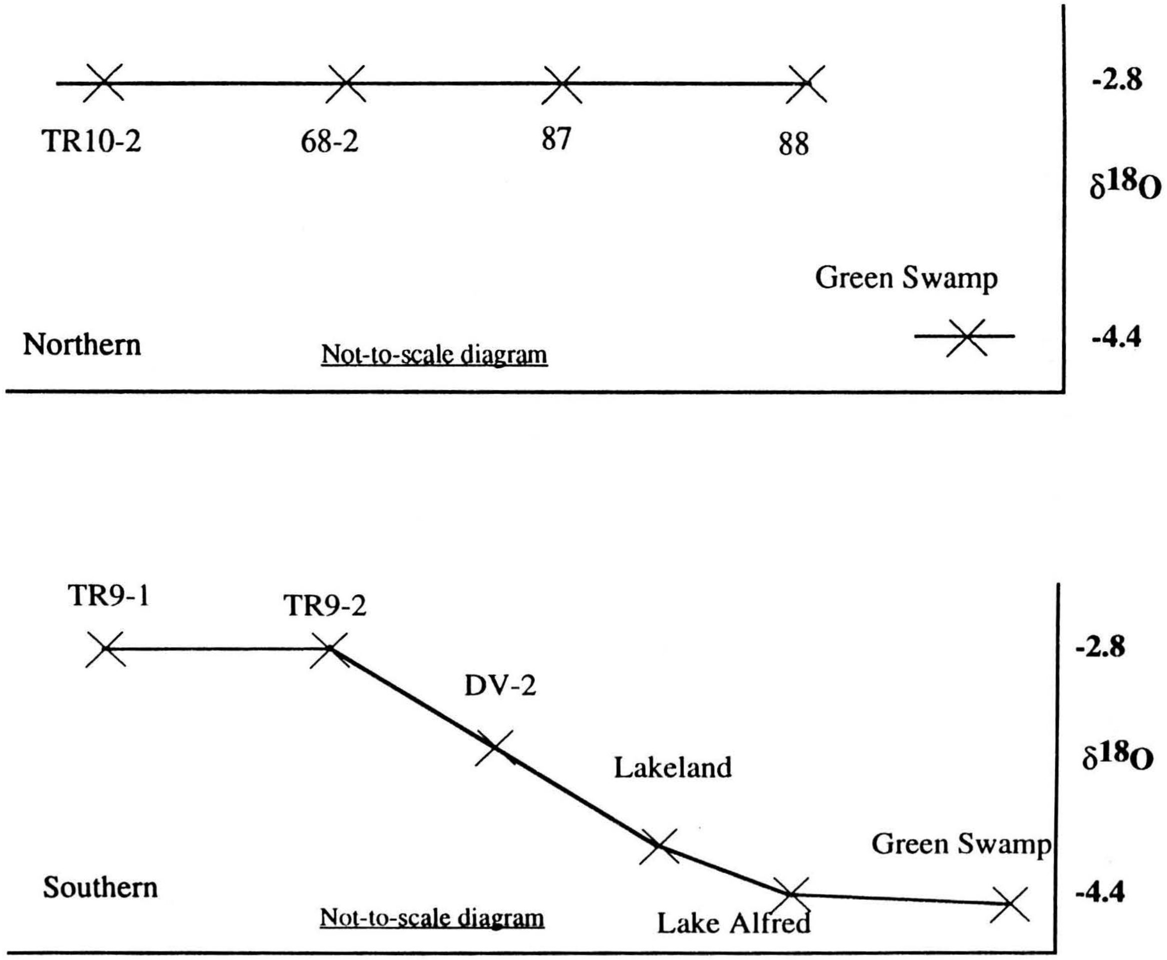

Figure 18b. Distribution of $\delta^{18}O$ Along the Northern and Southern Flow Paths from the Green Swamp to Coastal West-Central Florida

18a). This average $\delta^{18}O$ is similar to the regional -2.82 o/oo (Swancar and Hutchinson, 1992; for the Pinellas, Pasco, Hillsborough, and Polk counties).

The $\delta^{18}O$ of upper Floridan water, if followed along northern and southern flow paths, has 2 endmembers: the recharge area ($\approx$ -4.4 o/oo), and characteristic upper Floridan signature (-2.8 o/oo). The unconfined nature of the northern flow path could allow (today's) rainwater $\delta^{18}O$ (-4.4 o/oo) to modify the $\delta^{18}O$ of ground water along the path. The rather invariant $\delta^{18}O$ in the northern flow path (Figure 18b; other than the Green Swamp) indicates that there are extensive water-rock reactions through time or the source water feeding into these aquifers was different from today's rainwater. For the southern flow path (Figure 18b), the confining nature of aquifers define and control the evolution of $\delta^{18}O$ in the upper Floridan water. The recharge and discharge areas must constrain two major $\delta^{18}O$ endmembers in this southern flow path. The expected linear trend of mixing of these two endmembers was found only from Lake Alfred to TR 9-2 (Figures 18a and 18b). It is possible that the TR 9-1 and TR 9-2 wells are located within the same ground-water circulation cell.

$\delta^{13}C_{DIC}$ (vs PDB) of the upper Floridan water is dependent on the nature of water-rock interaction and changes in source of organic-derived CO_2. In general, there are two extreme $\delta^{13}C_{DIC}$ values in the two flow paths with values of $\approx$ -10.5 and -15 o/oo (Figures 19a and 19b). In the northern flow path, where the confining layer is absent, there is a decreasing trend of $\delta^{13}C_{DIC}$ along the travel path from the Green Swamp to TR 10-2 (Figure 19b). This trend may be attributable to immediate input of organic-derived CO_2 from shallower aquifers. On the contrary, the confining aquifers of the southern flow path has the $\delta^{13}C_{DIC}$ close to isotopic equilibrium value that there is no trend in $\delta^{13}C_{DIC}$ along the path. Figure 19b illustrates the deviation of $\delta^{13}C_{DIC}$ at Lake Alfred, Lakeland, and DV-2 sites which is probably caused by excessive water pumping in DV-2 and Lakeland sites, and a large extent of oxidation of dissolved organic carbon in Lake Alfred site.

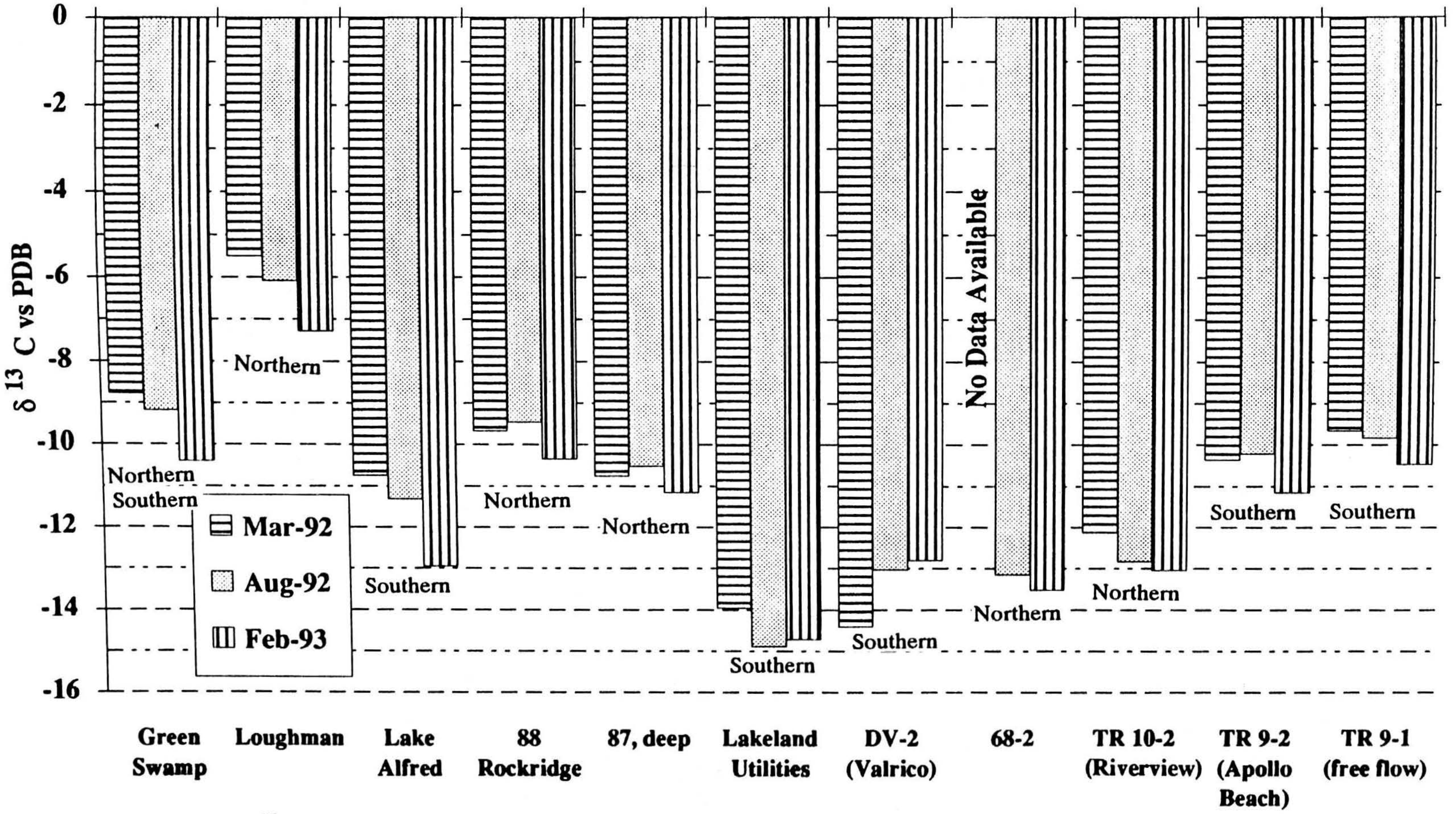

Figure 19a. $\delta^{13}C$ Variation during the Semi-Annual Studies of Ground Waters from the Recharge to Discharge Areas

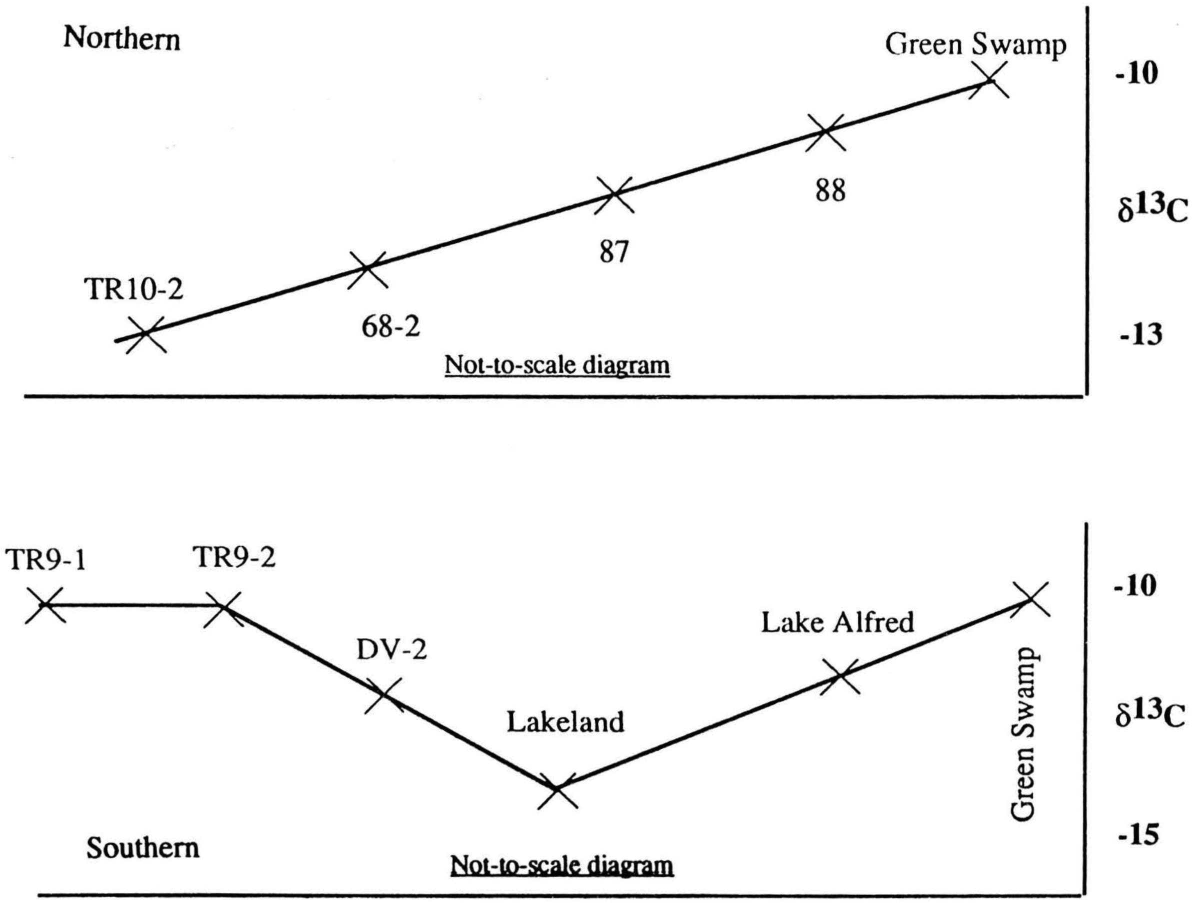

Figure 19b. Distribution of $\delta^{13}C$ Along the Northern and Southern Flow Paths from the Green Swamp to Coastal West-Central Florida

Figure 20 illustrates the variation of $\delta^{13}C$ and $\delta^{18}O$ of carbonate aquifer samples collected according to their casing depths (Table 1 and Figure 5, Chapter 2). The exception is Lake Alfred 2 site which the carbonate sample was taken from shallower depths. The carbonates close to the recharge area have $\delta^{18}O$ ranging from -1.46 to -1.17 o/oo vs PDB, and $\delta^{13}C$ ranging from +1.91 to +0.70 o/oo vs PDB. The upper values of these carbonates are close to the unaltered (marine) carbonate platform (e.g. Gross, 1964). The carbonates in the discharge area (Ruskin - TR9-1; Hawthorn group) have $\delta^{18}O$ and $\delta^{13}C$ equal to -2.09 and -5.97 o/oo vs PDB, respectively. The Roy Haynes (A; unknown carbonate depths), Valrico (7), and Apollo Beach (10) wells are not considered by the author to be representative aquifers in the discharge area since they fall on different endmembers of the $\delta^{13}C_{DIC}$ vs $\delta^{18}O$ plot, and could be a result of alteration by meteoric water. The alteration process causes a negative shift of the $\delta^{18}O$ of carbonates. Mineralogically, the carbonates in the selected sections of aquifers are pure calcite, with only minor traces of quartz and dolomite. The exception is the Wimauma site, which contains mostly dolomite (Appendix 2). A linear correlation is found between the $\delta^{13}C$ in the carbonate and percentage of carbonate ($r^2=0.795$; Figure 21). The percent carbonate was calculated from manometer-calibrated CO_2 obtained from the reaction between H_3PO_4 and carbonate rock sample of known weight. The extrapolated $\delta^{13}C$ of carbonate sample to 100 % equivalent carbonate is +1.8 o/oo vs PDB.

Assuming, for the confined aquifers, the southern flow path of ground water starts in the Green Swamp and flows to the coastal Ruskin area, and applying a mass isotopic balance suggested by Taylor (1974):

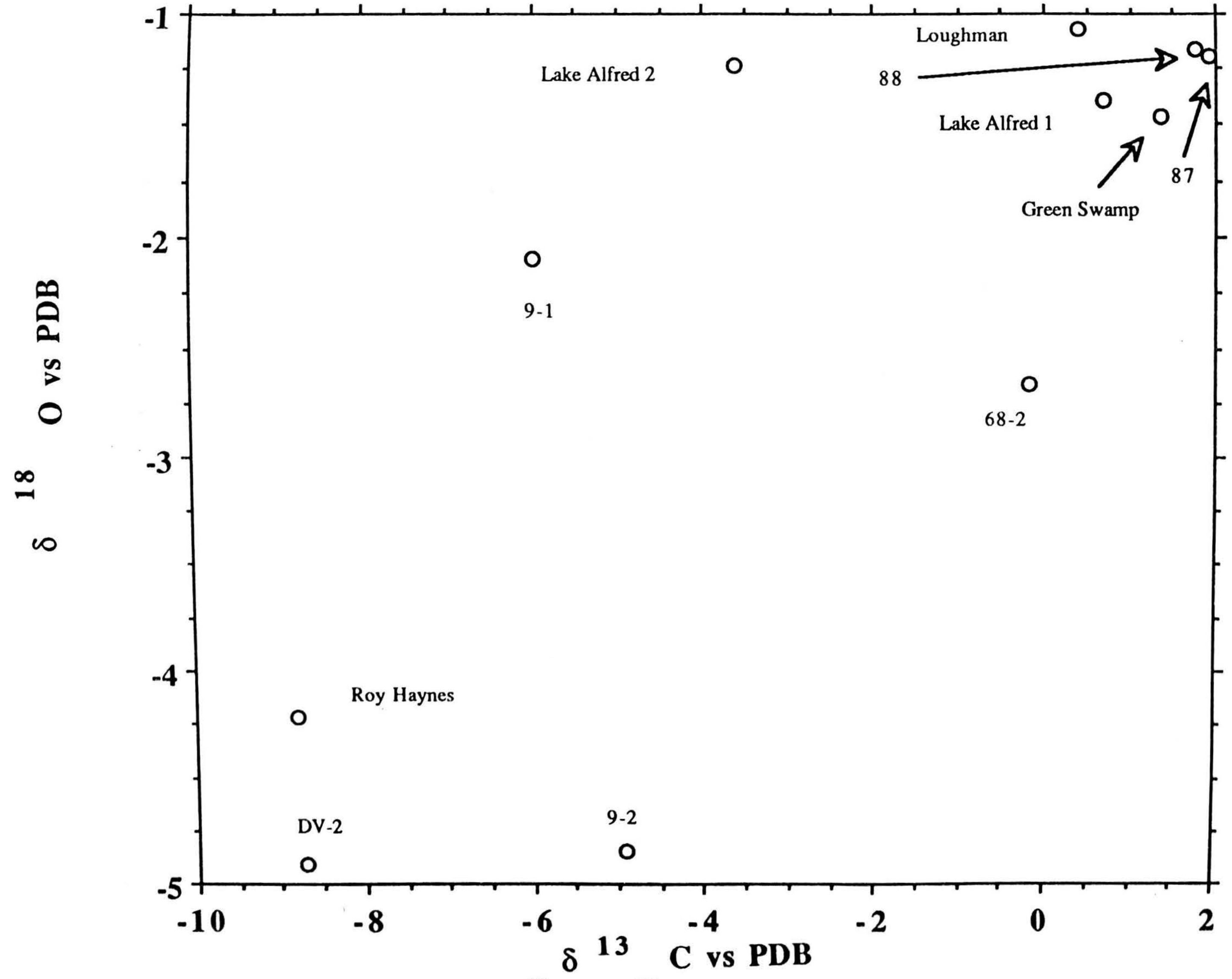

Figure 20. A Scatter Diagram of δ^{13}C and δ^{18}O for Aquifer Carbonates from West-Central Florida

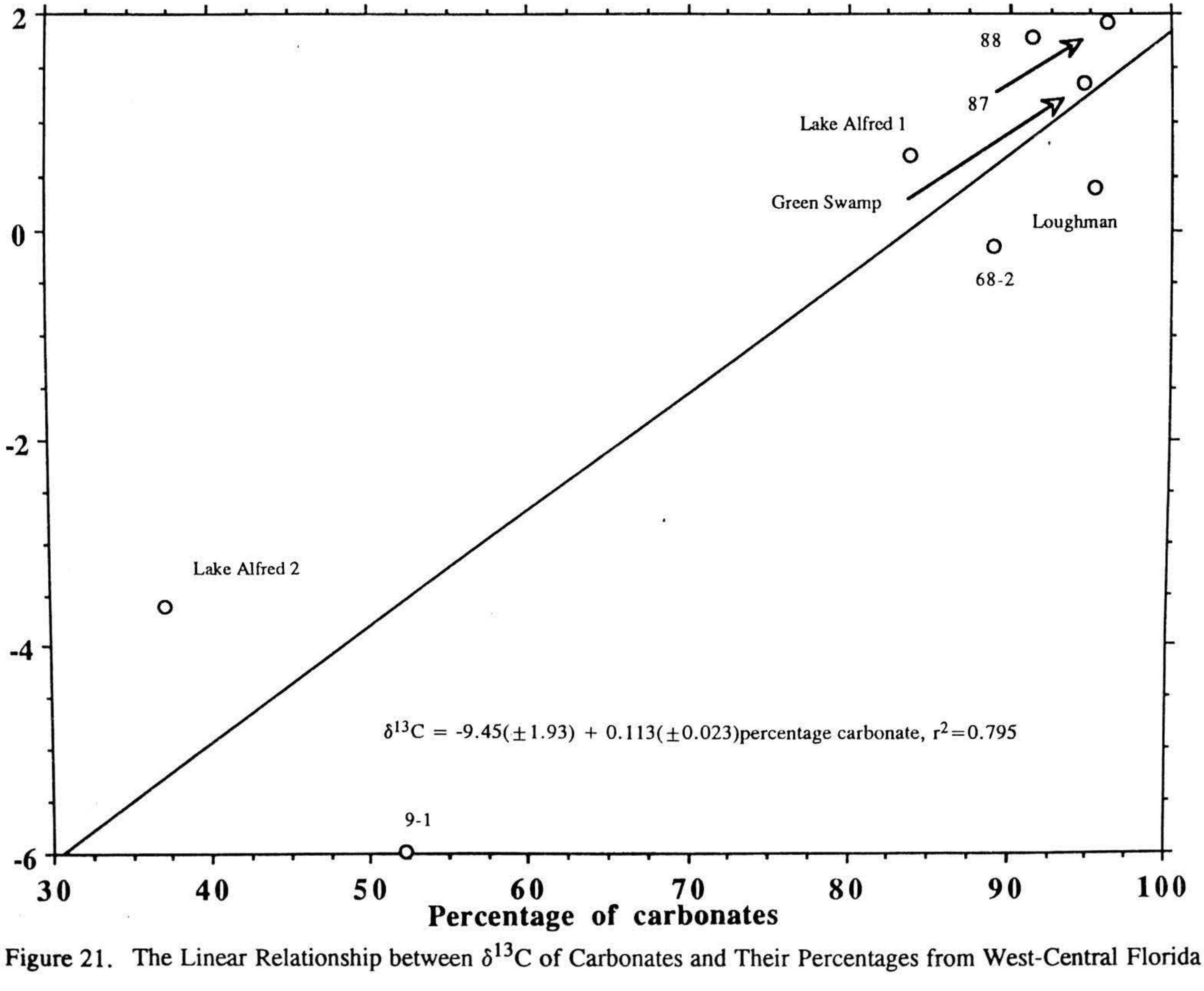

Figure 21. The Linear Relationship between $\delta^{13}C$ of Carbonates and Their Percentages from West-Central Florida

$$w\delta_{i\text{-water}} + r\delta_{i\text{-rock}} = w\delta_{f\text{-water}} + r\delta_{f\text{-rock}} \tag{25a}$$

where	w=mass of water;	r=mass of rock
$\delta_{i\text{-water}}$	=initial $\delta^{18}O$ of water	=-4.46o/oo vs SMOW
$\delta_{i\text{-rock}}$	=initial $\delta^{18}O$ of carbonate rock	=-1.43 o/oo vs PDB (=+29.39 o/oo vs SMOW)
$\delta_{f\text{-water}}$	=final $\delta^{18}O$ of water	=-2.70 o/oo vs SMOW
$\delta_{f\text{-rock}}$	=final $\delta^{18}O$ of carbonate rock	=-2.09 o/oo vs PDB (=+28.71 o/oo vs SMOW)

Note: $\delta^{18}O_{SMOW} = 1.03086\delta^{18}O_{PDB} + 30.86$
for the water equilibration and phosphoric-carbonate reactions performed at 25 °C

the calculated water/rock ratio is 0.375. If the p is the porosity of carbonate aquifer in volume/volume unit,

the w/r = p(density of water)/[(1-p)density of rock] (25b).

Assuming the densities of water and carbonate rocks are 1.0 and 2.7 g/cm^3, respectively, the calculated porosity of the rock is 0.503. The computed porosity is similar to the initial value suggested by Budd et al. (1993). It should be cautioned that this effective porosity is an average over a geological time (to reach an isotopic equilibrium), and other geological and climatic conditions have not greatly altered the primary carbonates to secondary carbonates, or not modified the recharge water from today's rainwater.

Figure 22 shows the intersection of two linearly-regressed lines from the rainwater (present study) and the ground water (Swancar and Hutchinson, 1992) with the crossing points of $\delta^{18}O$ of -4.23 (± 0.73) o/oo vs SMOW and δD of -21.8 (± 5.7) o/oo vs SMOW. Below the intersection coordinate, there is no ground-water data point. The intersection point, thus, represents the possible minimum set of $\delta^{18}O$ ($\approx$ -4.2 o/oo) and δD ($\approx$ -22 o/oo). This confirms that the local ground water in west-central

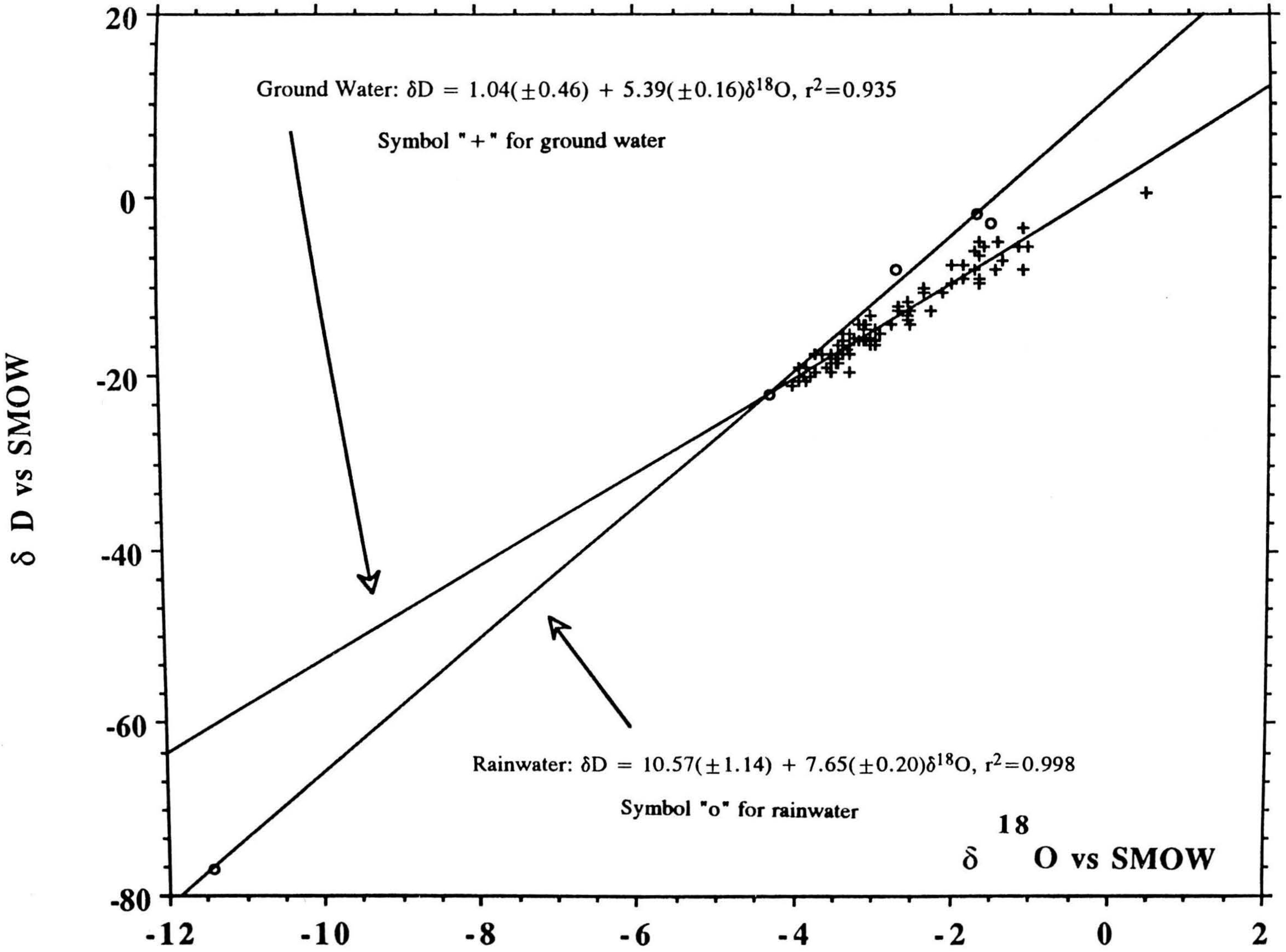

Figure 22. $\delta^{18}O$ and δD of Rainwater (This Study) and Local Ground Water (from Swancar and Hutchinson, 1992). The Intercept between the Two Best-Fitted Lines is the Original Source of Ground Water in West-Central Florida.

Florida is originated from the rainwater ($\delta^{18}O$ = - 4.4 o/oo). If the most depleted set of data ($\delta^{18}O$ = 11.6 o/oo, δD = -77 o/oo) was removed, the intersection of two lines would be at $\delta^{18}O$ of -4.8 o/oo and δD of -24.7 o/oo. A slight change in the intersection does not preclude the hypothesis that rainwater recharges ground water.

A Time-Series Study of $\delta^{18}O$ and $\delta^{13}C$ in Ground Waters at the Roy Haynes and Baum-Wimauma Sites

This time-series study was designed to test and monitor the temporal changes of $\delta^{18}O$ and $\delta^{13}C$ variations and their consistencies in ground waters, both at the unconfined and confined aquifer sites. The Roy Haynes (location A in Figure 17) is considered an unconfined aquifer well; while the Baum-Wimauma is located in the confined aquifer (location B in Figure 17). Figure 23 illustrates the consistent of $\delta^{18}O$ of the upper Floridan water in Roy Haynes (symbol O18RFl) with an average of -2.74 o/oo through sampling intervals (Table 9). This Roy Haynes average is close to the average regional $\delta^{18}O$ (-2.8 o/oo) of the upper Floridan waters (Swancar and Hutchinson, 1992). The consistent stable isotopic chemistry of the upper Floridan (Roy Haynes) and the intermediate waters (Baum-Wimauma) is reflected also in $\delta^{13}C$ (inorganic, symbols C13RFl, C13WInt; Figure 24). However, it takes a long time for total dissolved CO_2 to stabilize even after monitoring for many months (may be up to 5 months or longer based on Figure 25). The regular monitoring of ground waters is needed to purge enough water to achieve a representation of the chemistry of oxygen-18 and carbon-13. The intermediate water's $\delta^{18}O$ in Baum-Wimauma site (symbol O18WInt) is between those of the upper Floridan and surficial waters of Roy Haynes (Figure 23). The total dissolved CO_2 in the Roy Haynes's surficial water correlates linearly with the $\delta^{13}C$ (inorganic; r^2=0.701; Figure 26).

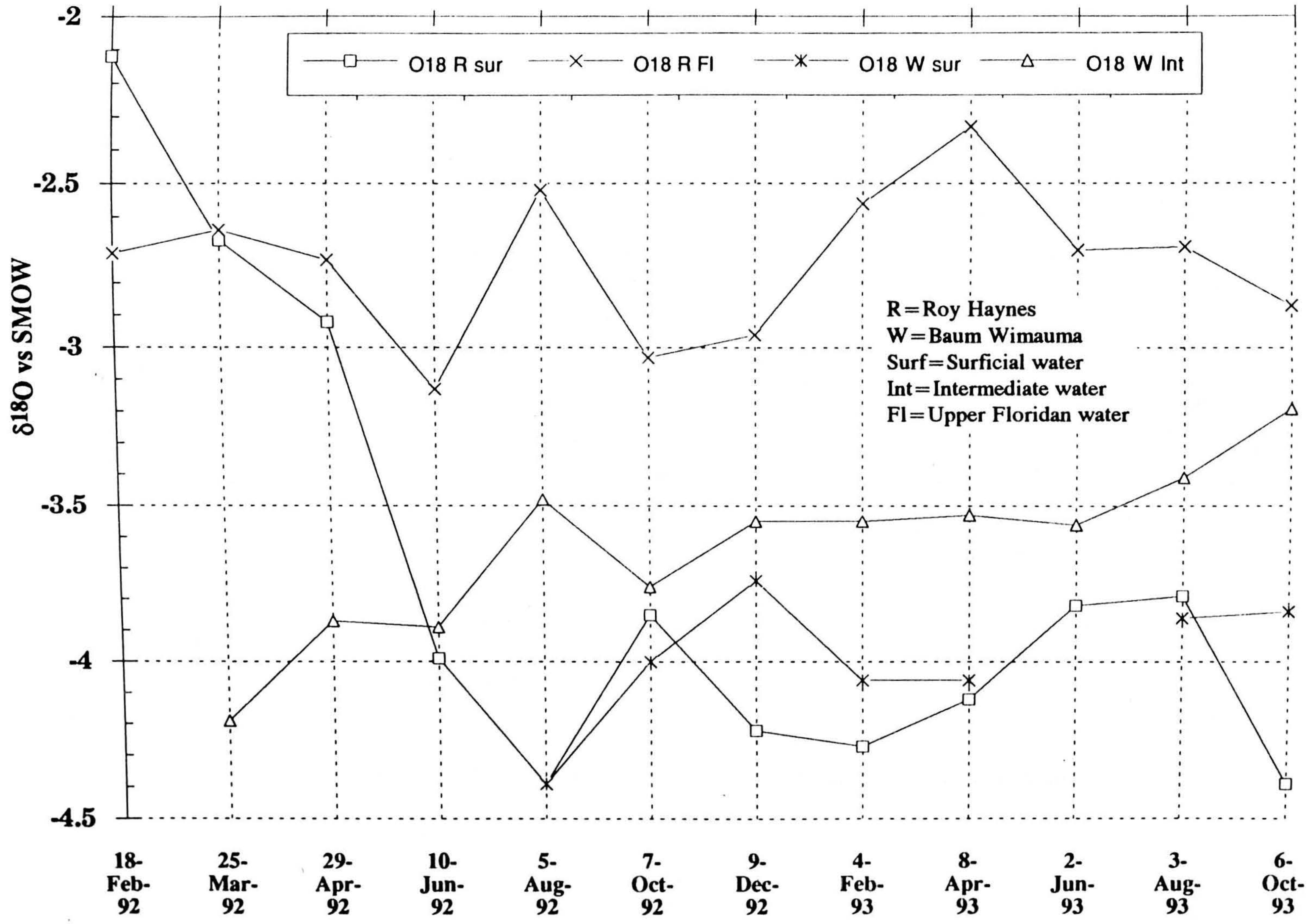

Figure 23. Temporal Variation of $\delta^{18}O$ in Ground Waters at Roy Haynes (R) and Baum-Wimauma (W) Sites

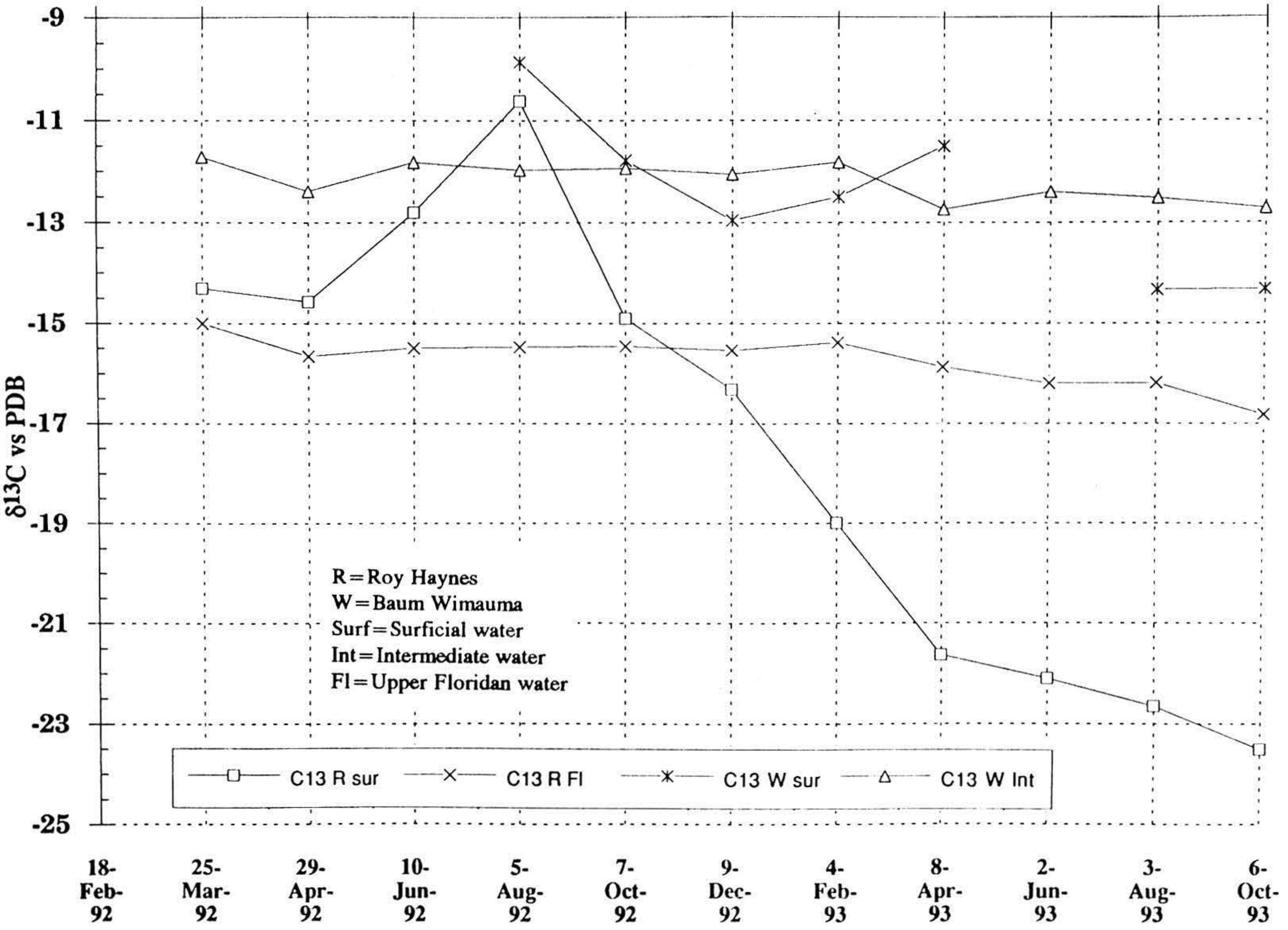

Figure 24. Temporal Variations of $\delta^{13}C$ in Ground Waters at Roy Haynes (R) and Baum-Wimauma (W) Sites

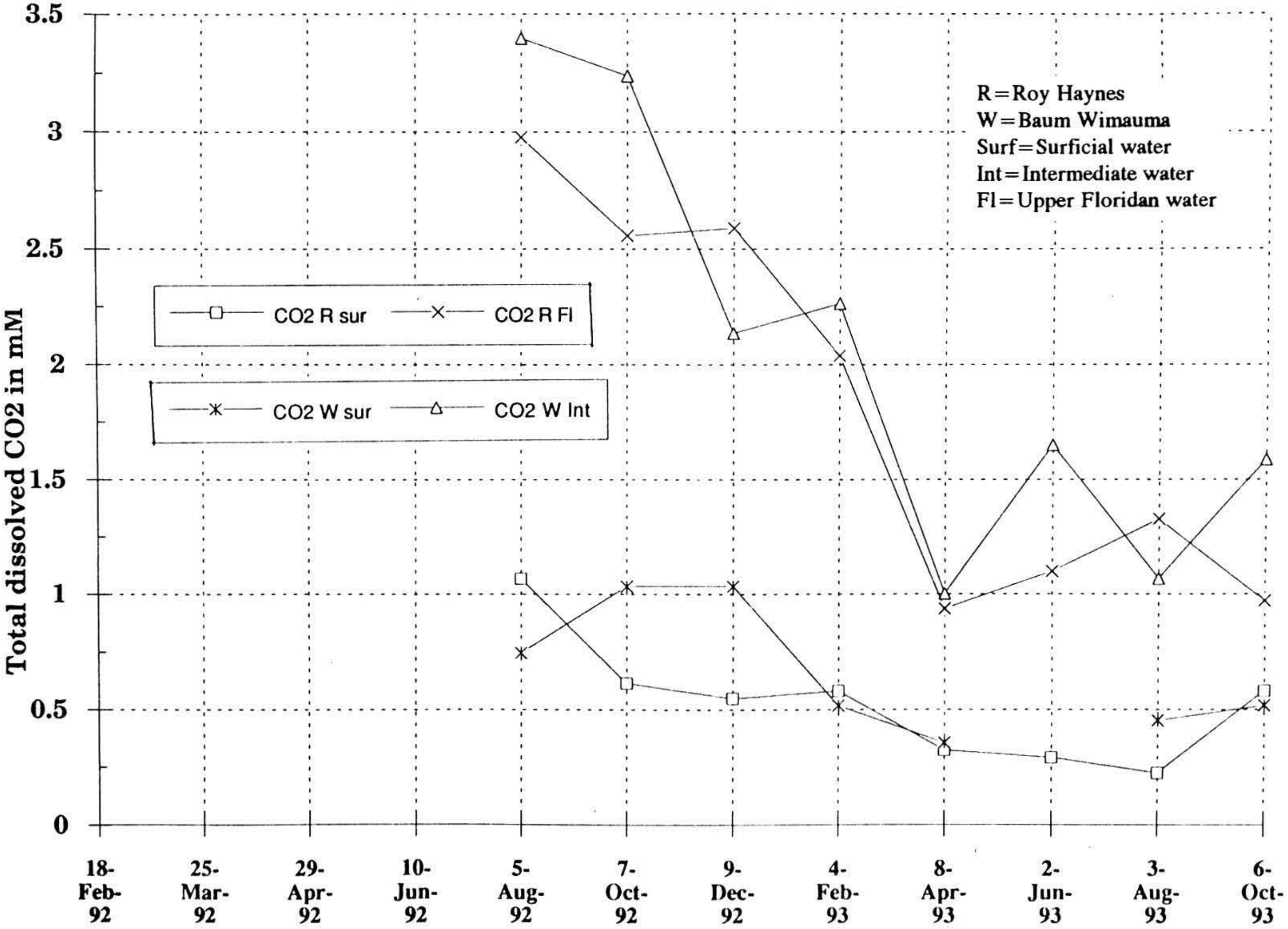

Figure 25. ΣCO_2 Changes during the Sampling Intervals for the Roy Haynes and Baum-Wimauma sites

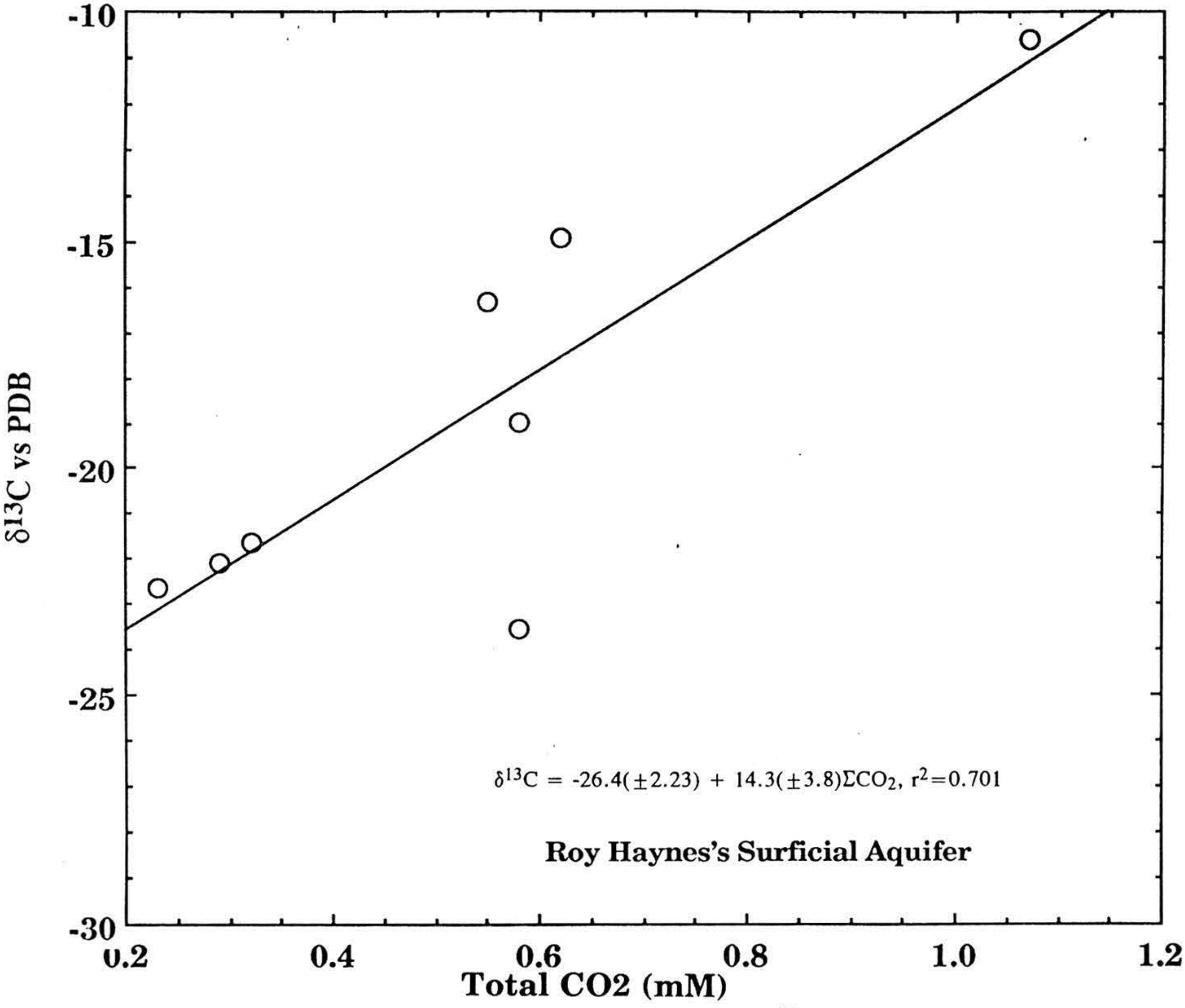

Figure 26. Linear Correlation between the ΣCO_2 and the $\delta^{13}C_{DIC}$ in Roy Haynes's Surficial Water

Table 9. Averages of $\delta^{18}O$ and $\delta^{13}C_{DIC}$ of Ground Waters in the Roy Haynes and Baum-Wimauma sites

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$\delta^{18}O$ of ground waters (vs SMOW, ± 1 standard deviation)

	Surficial	Intermediate	Floridan
Roy Haynes	-4.09 (± 0.24)	N/A	-2.74 (± 0.23)
Wimauma	-3.95 (± 0.21)	-3.63 (± 0.27)	N/A

$\delta^{13}C_{DIC}$ of ground waters (vs PDB, ± 1 standard deviation)

Roy Haynes	-17.5 *	N/A	-15.7 (± 0.50)
Wimauma	-13.0 (± 1.59)	-12.2 (± 0.38)	N/A

* See Figure 24 for a decreasing trend, the -17.5 o/oo $\delta^{13}C$ is an average

---

The average $\delta^{18}O$ of the surficial aquifer water in the Roy Haynes and Baum-Wimauma (Table 9) is -4.02 o/oo, which is almost 0.4 o/oo heavier than the average regional $\delta^{18}O$ of rainwater (Chapter 3). By using equations 18 and 19 described earlier in Chapter 3, δ_0 = -4.4 o/oo, $\delta_{measured}$ = -4.02 o/oo, and the (α^*-1) factor of -10.27 o/oo, the fraction of liquid (of the infiltration) remaining in the reservoir is 96.35 % (volume/volume). The fraction of liquid which evaporates into the atmosphere is thus equal to 3.64 % [=(1 - 0.9635)*100]. This 4% loss of water is very small and, as a first approximation, the infiltration water (portion from rainwater) recharges almost 100 % into the surficial aquifer.

Evaporation affects the δD as well, but the extent is, unfortunately, smaller than the $\delta^{18}O$ within analytical error. Assuming the equation: $\delta D = 5.393\delta^{18}O + 1.037$ (Figure 22) applies to the local ground water, the corresponding δD (for $\delta^{18}O$ = -4.02 o/oo) is -20.6 (± 5.4) o/oo. This δD deviates by only 0.46 o/oo from the computed δD from the local meteoric water line ($\delta D = 7.649\delta^{18}O + 10.569$). This means that the δD in water is not a good indicator for the small evaporation (normal analytical errors for the $\delta^{18}O$ and δD are 0.20 and 1.5 o/oo, respectively).

Major Ion Chemistry in Ground Waters of West-Central Florida

Back and Hanshaw (1970) illustrated the usefulness of major-ion chemistry in delineating the chemical evolution and types of ground waters in central Florida. More recently, Sprinkle (1989), Upchurch (1992), and Katz (1992) summarize the trend and evolution of chemistry of the upper Floridan waters in west-central Florida. Generally, the major cations of ground water are calcium, magnesium, sodium and potassium. The predominant anions are bicarbonate, chloride and sulfate (Figures 27a and 27b). The concentrations of dissolved salts are in milli-molar levels. By following the northern flow path (defined earlier in the study) of the upper Floridan water, there is no clear trend of dissolved salts. In contrast, the southern flow path shows an increasing trend of many dissolved constituents, with the exception of K^+ in the Valrico (7 - DV-2) and Ca^{2+} in the Green Swamp (1). This could be a result of the confining aquifer along which ground water travels from the recharge to discharge areas as illustrated in $\delta^{18}O$ data (Figure 18b).

A summary of concentrations (in mM) of major constituents and their ratios is tabulated in Table 10 (see also Figures 27a and 27b). For the northern flow path, one can find:

1. Ca^{2+} molar concentration is enriched in ground water by a factor of 4 over the Mg^{2+} (Figure 27a).
2. Total Ca^{2+} molar concentration can account for the forming of (if any) calcite ($CaCO_3$), dolomite ($Ca\{Mg\}\{CO_3\}_2$), and anhydrite ($CaSO_4$). The trend is shown also in the southern flow path except for Lakeland, TR9-1, and TR9-2.

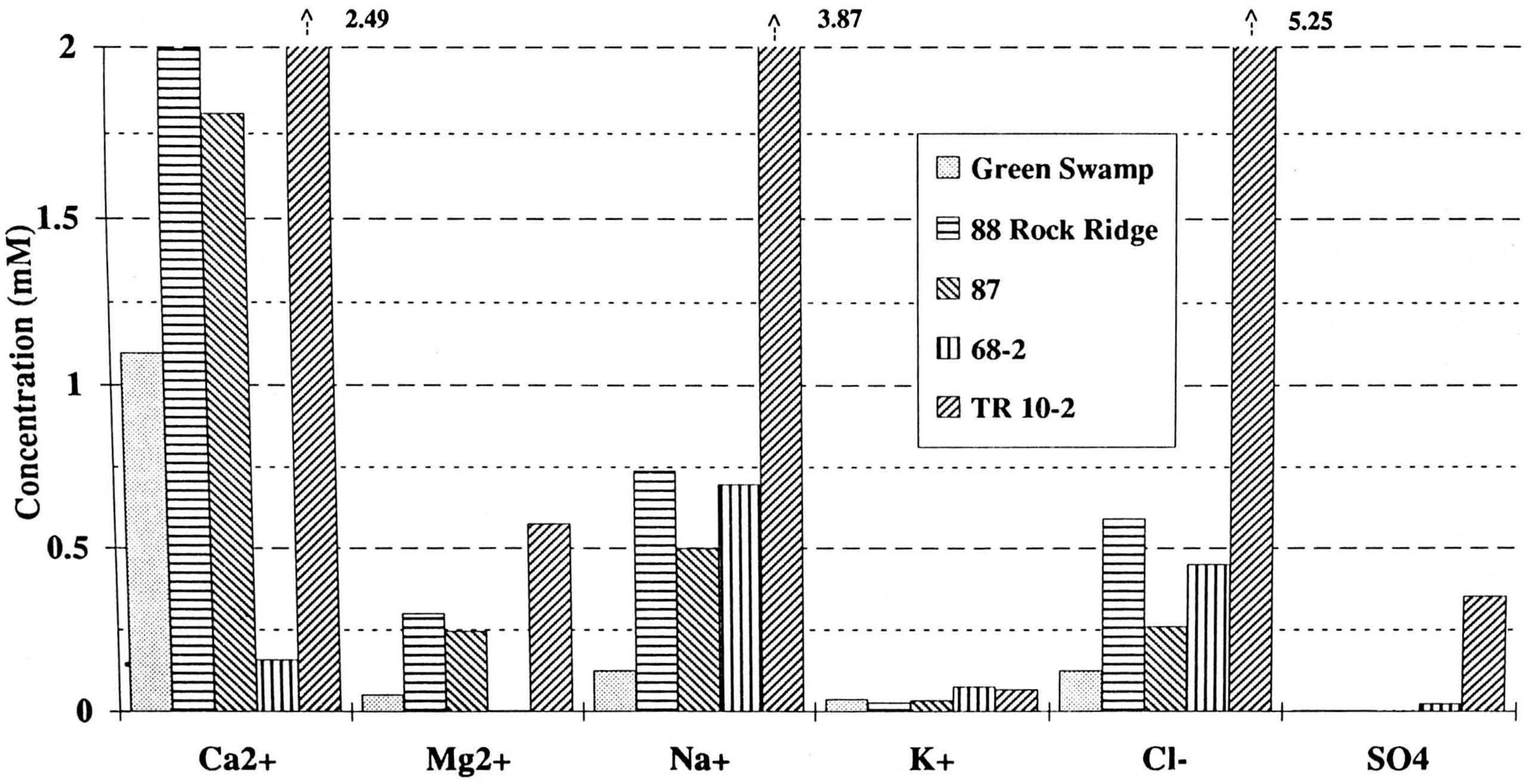

Figure 27a. Major Ion Concentrations in Ground Waters in the Northern Flow Path of West-Central Florida

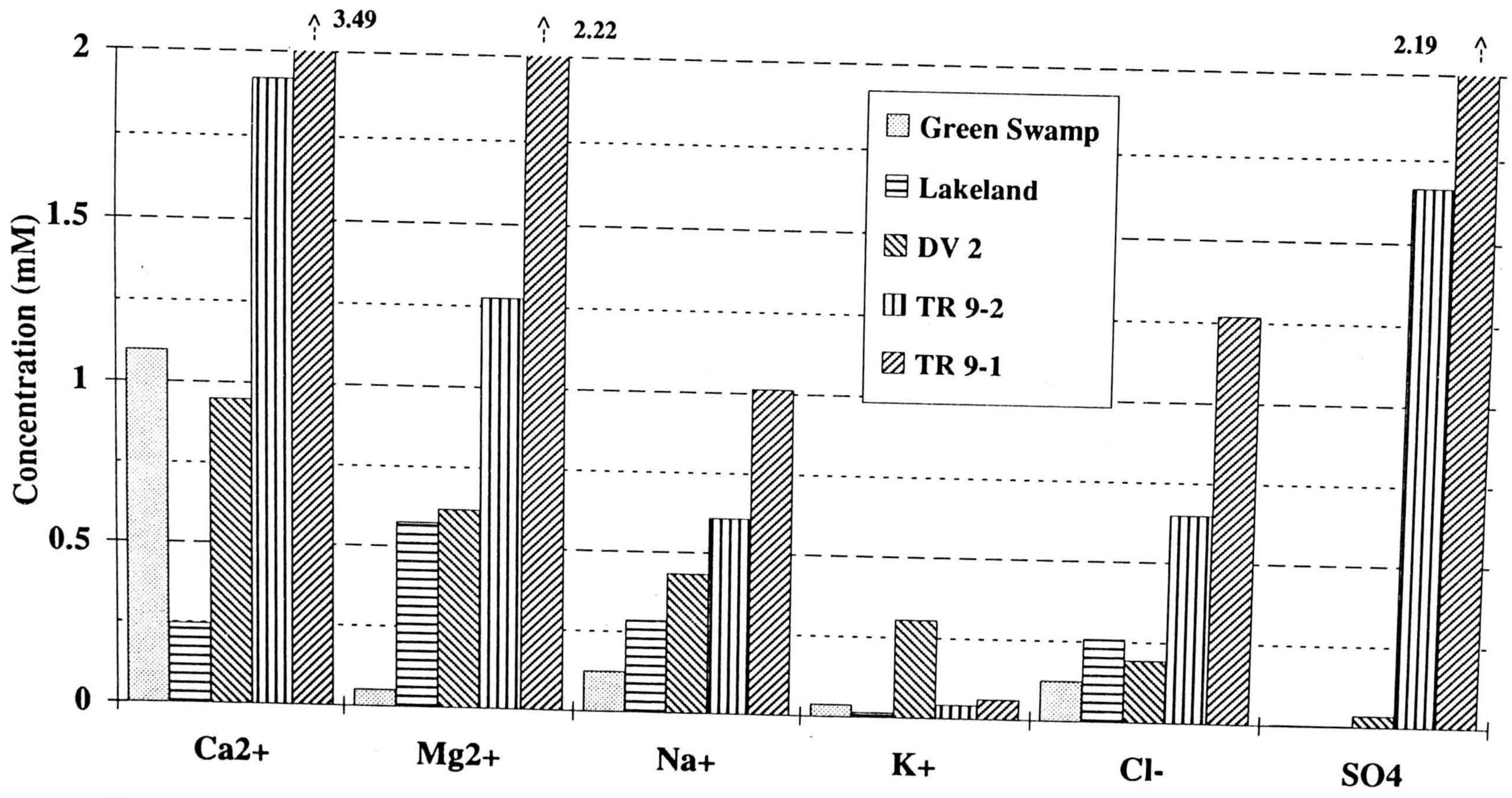

Figure 27b. Major Ion Concentrations in Ground Waters in the Southern Flow Path of West-Central Florida

3. The molar concentration ratios of Ca/Mg and Ca/SO_4 are higher in the northern flow path than in the southern path.

As mentioned previously the $\delta^{13}C_{DIC}$ (Figure 19b) of the ground water in the northern flow path decreases in a fashion which parallels the increase in Ca^{2+} concentration. There may be extra sources of isotopically light CO_2, which reacts with carbonate rocks, and subsequently releases more Ca^{2+} and lower the $\delta^{13}C_{DIC}$ in the travel path.

In southern flow path, the total Ca^{2+} molar concentration is slightly higher than the Mg^{2+} (Table 10, Figure 27b). The lower Ca/Mg ratio and almost invariant trend in $\delta^{13}C_{DIC}$ (Figure 19b) also help suggest that the upper Floridan water is more or less in equilibrium with aquifer carbonates. Surprisingly, the SO_4^{2-} concentration in rainwater may account for SO_4^{2-} concentration in the upper Floridan water, with the exception of 68-2, DV-2, TR10-2, TR9-1, and TR9-2 (Table 10).

Mirror Lake

Mirror Lake is located near downtown of St. Petersburg, and is a land-locked body of water used currently to retain storm water on a temporary basis. Its area is 12 acres (4.856×10^4 m^2), while the volume is 55×10^6 gallons ($= 2.082 \times 10^5$ m^3). The lake has a circular shape, and was 18 feet deep (5.6 m) during the excavation in the 1920s (1925 blue prints from the Engineering Department of the City of St. Petersburg; Dickinson et al., 1969). For over 10 years early in the history of Lake, the lake water was withdrawn for public use. In the center of the lake, a water fountain was installed to help add oxygen to the water. The lake water level remained constant throughout the weekly water samplings for $\delta^{18}O$ analyses during 1991. The lake stores the storm water and re-directs it over a weir to another outflow system into the Tampa Bay.

The average $\delta^{18}O$ of Mirror Lake water was -0.85 o/oo ($\pm$ 0.4; n=51) during the year 1991 (Figure 28). The temporal variations of $\delta^{18}O$ in lake water were small

Table 10. A Summary of Concentrations (mM) of Major Constituents in Upper Floridan Water along Northern and Southern Flow Paths, and of Major Ions in Rainwater of Central Florida (After SWFWMD [unpublished data], and Hendry and Brezonik [1980] and Junge and Werby [1958])

	Ca2+	Mg2+	Na+	K+	Cl-	SO4	Ca/Mg	Na/K	Cl/SO4	Na/Cl	Ca/SO4
Northern Flow Path											
Green Swamp	1.10E+00	5.35E-02	1.26E-01	3.84E-02	1.27E-01	3.12E-03	21	3.3	41	0.99	352
88 Rock Ridge	2.00E+00	3.00E-01	7.39E-01	2.81E-02	5.92E-01	3.12E-03	6.7	26	190	1.2	639
Romp 87	1.81E+00	2.47E-01	5.00E-01	3.45E-02	2.61E-01	2.08E-03	7.3	15	125	1.9	869
68-2	1.60E-01	4.11E-03	6.96E-01	7.67E-02	4.51E-01	2.50E-02	39	9.1	18	1.5	6.4
TR 10-2	2.50E+00	5.76E-01	3.87E+00	6.91E-02	5.25E+00	3.54E-01	4.3	56	15	0.74	7
Southern Flow Path											
Green Swamp	1.10E+00	5.35E-02	1.26E-01	3.84E-02	1.27E-01	3.12E-03	21	3.3	41	0.99	352
Lakeland	2.50E-01	5.76E-01	2.87E-01	1.56E-02	2.60E-01	3.12E-03	0.43	18	83	1.1	80
DV 2	9.48E-01	6.17E-01	4.35E-01	3.07E-01	1.95E-01	3.64E-02	1.5	1.4	5.3	2.2	26
TR 9-2	1.92E+00	1.28E+00	6.09E-01	4.35E-02	6.49E-01	1.67E+00	1.5	14	0.39	0.94	1.2
TR 9-1	3.49E+00	2.22E+00	1.01E+00	6.39E-02	1.27E+00	2.19E+00	1.6	16	0.58	0.79	1.6
Rainwater											
Hendry and Brezonik (1980)											
wet	1.02E-02	4.94E-03	1.91E-02	5.12E-03	2.76E-02	2.13E-02	2.1	3.7	1.3	0.69	0.48
bulk	2.02E-02	7.41E-03	3.57E-02	6.65E-03	5.30E-02	2.36E-02	2.7	5.4	2.2	0.67	0.86
Junge and Werby (1958)											
wet	1.35E-02	N/A	2.74E-02	3.58E-03	2.26E-02	1.55E-02	N/A	7.7	1.5	1.2	0.87

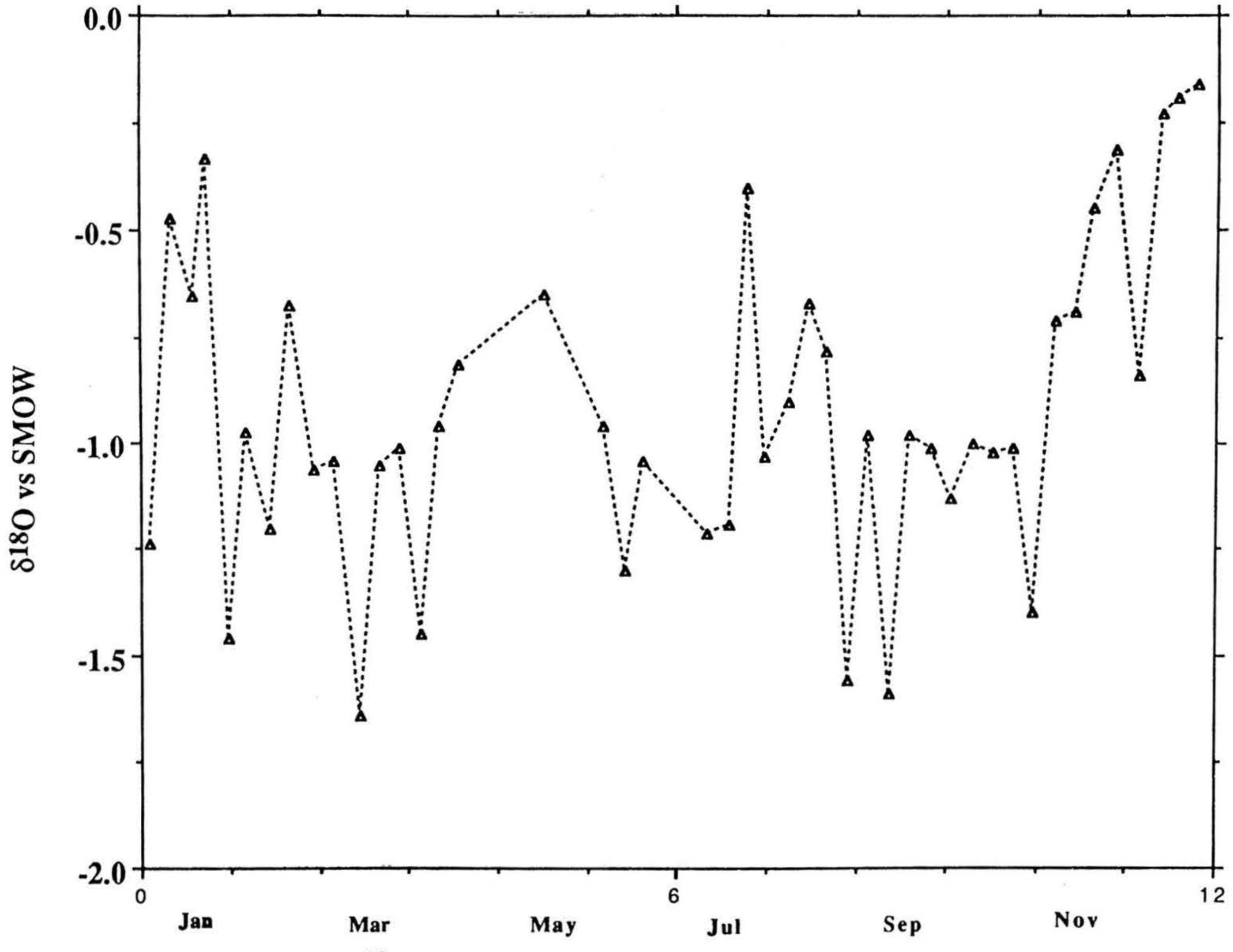

Figure 28. $\delta^{18}O$ Variation in Mirror-Lake Water during the Year 1991

(Figure 28). The calculated δ_E from equation 11 (in Chapter 3), using $m = 1.041$, $\delta_s = +12.22$ o/oo and $\delta^{18}O_{lake} = -0.85$ o/oo, is -14.46 o/oo. This computed δ_E is close to -13.9 o/oo obtained from the constant-feeding pan experiment. Similarity in isotopic compositions between $\delta^{18}O$ of calculated evaporative water from the Lake and from pan experiments suggests that the controlling parameters should be almost identical for the pan experiments and Mirror Lake.

An average replacement time varying from 36 to 43 days may be calculated assuming that the flow volume of storm water into the lake ($V_{st[\text{incoming storm water}]}$) equals the outflow of the storm water from the lake ($V_{st[\text{over the weir}]}$) in order to remain level and the input waters spends the same time in the Lake as the output waters (Figure 29), two following equations are set up:

$$V_{st(\text{over the weir})} + V_E = V_p + V_g + V_{st(\text{incoming storm water})} \qquad (26) \quad \text{and}$$

$$\delta_L T_L/(\delta_g V_g + \delta_{st} V_{st} + \delta_p V_p) = \delta_L T_L/(\delta_E V_E + V_{st}\delta_L) \qquad (27)$$

V_{st}=storm-water flow volume=unknown

V_E=evaporative flow volume=50"/year on 4.856×10^4 m^2 = 1.956×10^{-3} m^3/s

V_p=precipitation flow volume=1.33 m/year on 4.856×10^4 m^2
= 2.048×10^{-3} m^3/s

V_g=ground-water flow volume=unknown

δ_{st}=storm-water's $\delta^{18}O \approx$ -4.4 o/oo (assuming same as rainwater)

δ_E=evaporation's $\delta^{18}O$= -13.9 o/oo (measured, Chapter 3)

δ_p=rainwater's $\delta^{18}O$= -4.4 o/oo (measured, Chapter 3)

δ_g=ground water's $\delta^{18}O$= -2.8 o/oo (measured, and assumed to be from Floridan aquifer)

δ_L=Mirror Lake's $\delta^{18}O$= -0.85 o/oo (average from weekly sampling for one year)

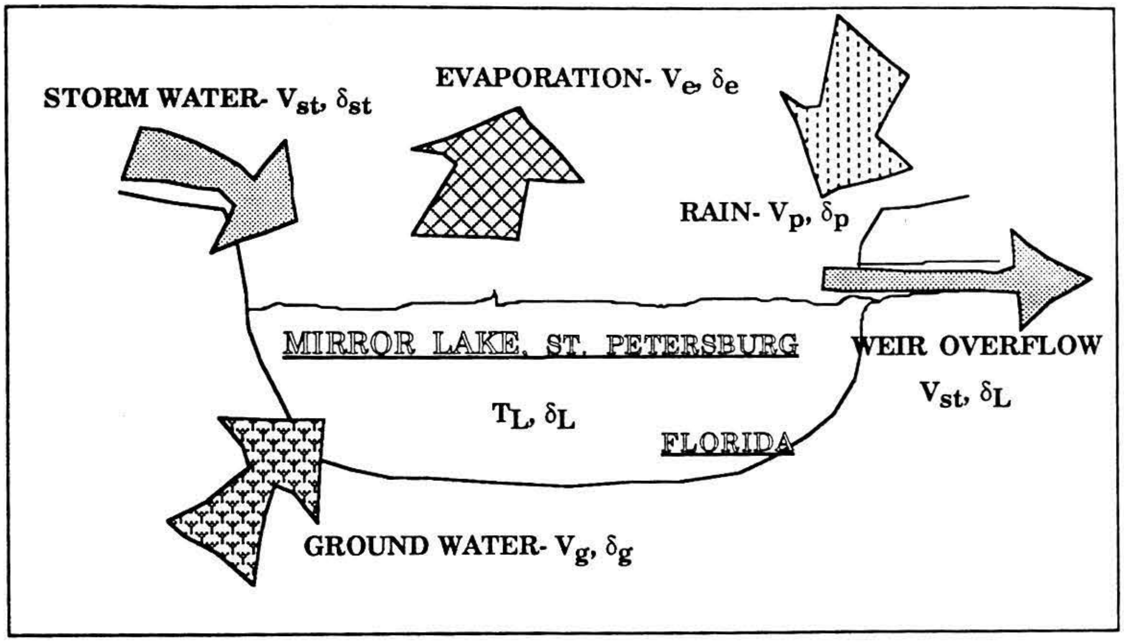

Figure 29. A Box Diagram for Various Inputs and Outputs of Waters in Mirror Lake, St. Petersburg, Florida

T_L=volume of Mirror Lake=(2/3)(2.08x10^5)m^3=1.39x10^5 m^3 (2/3 of the 1920's volume)

The calculated V_{st} and V_g are 5.19 x 10^{-3} and -9.20 x 10^{-5} m^3/s, respectively. The direction of V_g is opposite the one shown in the diagram above (the lake water recharges into ground-water aquifer). The replacement time of water in Mirror Lake can be computed by dividing the $\delta_L T_L$ by ($\delta_g V_g + \delta_{st} V_{st} + \delta_p V_p$) which is equal to 43 days. At higher evaporation rate (60"/year or 2.347x10^{-3} m^3/s for the Mirror Lake) and keeping other parameters the same, the computed V_{st} and V_g are 6.42 x 10^{-3}, and 2.99 x 10^{-4} m^3/s. The ground water seeps into the lake at higher evaporation rate as the sign of V_g is positive. At higher evaporation rate, the replacement time is only 36 days.

Chapter Discussion

Ground Water and Carbonate Aquifers

Assuming the average soil-derived $\delta^{13}C_{DIC}$ of -24 o/oo in central Florida (Rightmire and Hanshaw, 1973) and the $\delta^{13}C$ of starting calcitic aquifers of +2.0 o/oo vs PDB (from this study), the resulting ground water's $\delta^{13}C$ should be -11.0 o/oo (={[-24][1] + [+2.0][1]}/{[1 + 1]}; see equation 22, Chapter 4), which is close to the observed -10.4 o/oo value.

The buffering capacity of calcite and dolomite in confined aquifers helps maintain both the pH ($\approx$ 7.5) and $\delta^{13}C_{DIC}$ ($\approx$ -10.4 o/oo vs PDB) in ground waters along the southern flow paths that receive no additional inputs of organic-derived CO_2. The rather constant Ca/Mg ratio of the southern flow path also indicates that the carbonate aquifer is in near chemical equilibrium with the $HCO_3^-{}_{(aq)}$. This finding may not preclude the use of isotopic mass balance to compute the water-rock ratio and effective porosity.

There is still an unanswered question as to why in the unconfined aquifer (the northern flow path) the $\delta^{18}O$ of upper Floridan water does not show a similar trend as in $\delta^{13}C$ (Figures 18b and 19b). Could this phenomenon mean that the surficial or intermediate ground waters play a role in those changes, or was there a more extensive water-rock interaction, or did the upper Floridan water in this area originate from rainwater much different from today's? One possibility is that the source of this upper Floridan water comes from 2 sources: the Green Swamp and the Pasco High areas. Further isotopic and major ion studies could help identify the source and processes involved in the northern flow path.

For $\delta^{18}O$ in ground waters of the confined aquifer (southern flow path), the progressive enrichment of $\delta^{18}O$ from the recharge to discharge areas depicts a simple mixing of younger and older (rock-altered) waters. By knowing the recharge's $\delta^{18}O$ in carbonates and the temperature at which the equilibration of dissolved carbonate takes place, the modified $\delta^{18}O$ of carbonate can be calculated. Assuming that

1. The temperature of recharge water of 23 °C in the Green Swamp area (similar to the average air temperature), and
2. Accepting that the average temperature of upper Floridan water is 25 °C, and
3. The palaeotemperature vs degree celsius relationship is -0.24 o/oo per °C [Epstein et al., 1953],

the calcite that is reprecipitated in aquifers during the water/rock interaction should be 0.48 more depleted in $\delta^{18}O$ than the original calcite ($\delta^{18}O$ = -1.43 o/oo) in the recharge zone. The calculated δ^{18} of calcite at 25 °C is -1.91 o/oo vs PDB (= [(- 0.48) - 1.43]), which is close to a value of -2.09 o/oo observed at the Ruskin area (TR9-1, Figure 20). This finding further supports the idea that the water/rock interaction is responsible for the alteration of $\delta^{18}O$ in both carbonate rocks and ground waters in the confined aquifers. However, the conclusion would be correct only if the rates of dissolution and precipitation are fast enough to maintain chemical equilibrium, and the contact time is long enough for isotopic equilibrium to take place.

The infiltration portion of rainwater into surficial aquifer ($\approx$ 2" of water level) does not show evidence of excessive evaporation at all (less than 5 % volume loss) based on $\delta^{18}O$ data. It is possible that the transpiration process transfers the remaining water of 50" high into the atmosphere annually (from 52" rainwater). The isotopic data on transpiration over large scale of west-central Florida is needed for further understanding of the effect of transpiration on the water budget.

Mirror Lake

From the stable isotopic viewpoint, evaporation rate plays a major role in directing the flow of lake water out or into the ground water. However, the average flow volume of storm water, out of the lake, is 5×10^{-3} m^3/s over a one-year period based on model calculations given earlier.

Summary

$\delta^{18}O$ and $\delta^{13}C_{DIC}$ of the upper Floridan water were followed along 2 flow paths from the recharge to discharge areas. The northern flow path (along unconfined aquifers) has an invariant $\delta^{18}O$ in ground water, whereas the $\delta^{13}C_{DIC}$ decreases in a linear fashion. The southern flow path (along confined aquifers) shows an increasing $\delta^{18}O$ trend; however, the $\delta^{13}C_{DIC}$ seems to be constant except for the DV-2, Lakeland, and Lake Alfred areas.

High Ca/Mg ratios in the upper Floridan water of the northern flow path can be caused by excessive water-rock interaction. The reaction coupling with sources of light CO_2 results in the decreasing $\delta^{13}C_{DIC}$ along the travel path.

Time-series study of ground water at Roy Haynes and Baum-Wimauma indicates the necessity of adequate purging of wells before collecting samples for isotopic analyses. The upper Floridan water for each site has consistent $\delta^{13}C_{DIC}$ and $\delta^{18}O$. These isotope data did not vary much during repeated studies during a 15-month period. For surficial water the $\delta^{13}C_{DIC}$ can be affected by local shallow water input. The ΣCO_2 is also dependent on the frequency of well purges.

Calculations using isotopic mass balance of $\delta^{18}O$ in carbonate and ground water in the recharge and discharge areas of the confined aquifers (southern flow path) gives a porosity ($\approx$ 0.5) similar to a previous study, and also effective water/rock ratio of 0.38. This water/rock ratio assumes that air pockets are absent.

The intersection value (-4.23 ± 0.73) of linear-regressed lines of δD and $\delta^{18}O$ of rainwater (St. Petersburg) and ground water (upper Floridan water) suggests that the water recharging upper Floridan water has a similar $\delta^{18}O$ to today's rainwater (of -4.4 o/oo).

Further computation using isotopic mass balance of $\delta^{18}O$ in Mirror Lake, downtown St. Petersburg, shows that the replacement time of Lake water is 43 days. This replacement time depends upon the evaporation rate.

The small loss of infiltration water before recharging surficial aquifer suggests that the entire evaporation process is predominantly the transpiration process of various plants for the inland areas.

CHAPTER 6

GENERAL DISCUSSION

Methodology and Standard

The inter-laboratory calibration with the USGS (Menlo Park)'s Kendall laboratory revealed that the USF working $\delta^{18}O$ standard from the Gulf of Mexico was 0.3 o/oo heavier than the Kendall's standard. The slight difference was within the analytical uncertainties in the USF laboratory (± 0.3 o/oo vs SMOW). Figure 30 illustrates a plot of adjusted USF $\delta^{18}O$ data against the USGS $\delta^{18}O$ data. The adjustment of USF data is done because the USF working standard is about 0.3 o/oo vs SMOW heavier than international SMOW standard. The correlation equation suggests that the reproducibility of USF laboratory is comparable to the USGS laboratory.

For unknown reasons, the sealed IAEA standard ampoule, which was stored on a shelf for 2 years before breaking open for calibration with the working USF standard, was -1.35 o/oo relatively lighter (in $\delta^{18}O$ term) than the USF working SMOW standard.

Implications on the Modelling of the Hydrological Cycle of West-Central Florida

Attempts to estimate the replacement time of the entire water volume of both Tampa Bay and Mirror Lake suggested that both water bodies had comparable replacement times (43-67 days). For Tampa Bay, the dredging of shipping lanes may possibly alter the hydraulic properties of the Bay (Galperin et al., 1991), and the replacement time accordingly. In the near future, the replacement time of Tampa Bay

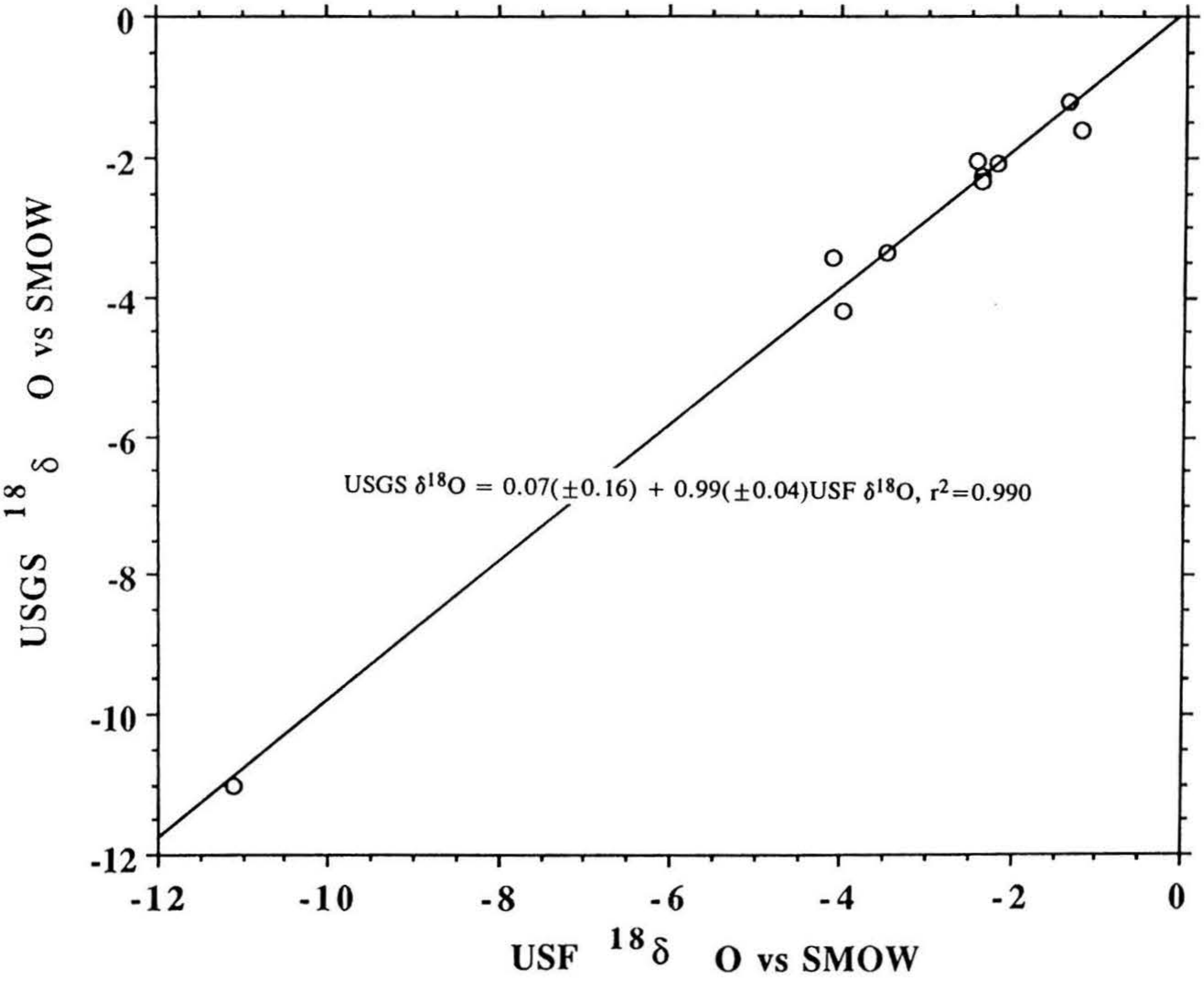

Figure 30. Linear Correlation between the Adjusted USF's $\delta^{18}O$ and the USGS's $\delta^{18}O$ Data

using the isotopic balance model will be validated by 3-dimensional modelling using the temperature, wind, salinity, and tides, which is still in progress.

As shown in the study of $\delta^{18}O$ of rainwater, the surface air temperature did not covary at all with the $\delta^{18}O$ in rainwater (Figure 11c, Chapter 3). Questions remain whether the assumption of linear correlation between the $\delta^{18}O$ of rainwater and air temperature which are normally used for palaeo-climatic studies are correct for the subtropics. Generally, the correlation breaks down at surface air temperature above 15 °C (Jacob and Sonntag, 1991). This temperature effect is secondary as the real condensation of precipitation occurs inside the rain clouds. The primary temperature effect involves water in liquid, solid and vapor forms (Dansgaard, 1953; Jouzel, 1986). The surface air temperature (secondary effect) correlates with the $\delta^{18}O$ in precipitation as if it were primary effect only when

1. The exchange with atmospheric water vapor is minimal during falling down to the ground (Woodcock and Friedman, 1963; Craig and Gordon, 1965),
2. The re-evaporation of droplets of precipitation is small (Stewart, 1975),
3. Evaporation of precipitation at ground surface is minimal.

In subtropic and equatorial areas the secondary temperature effect would not strongly correlate with the primary temperature effect, so the correlation between the $\delta^{18}O$ in precipitation and surface air temperature is very weak or absent as exemplified in rainwater of west-central Florida.

Precipitation (or re-precipitation) of carbonate minerals in aquifers records the water temperature at which the chemical and isotopic reactions take place (Epstein et al., 1953). Thus, the old carbonate aquifers in Florida may offer a potential to estimate the palaeo-temperature of the ground water (and of surface average air temperature), and extent of water-rock interactions. The surface air temperature can then be estimated from the ground water temperatures derived from carbonate aquifers.

The agreement of the inferred porosity (≈ 0.5) using mass balance calculations of the $\delta^{18}O$ of ground water and carbonate aquifers with previous study (Budd et al., 1993) indicates that the confined, southern flow path (see Chapter 5) of upper Floridan water is more or less in equilibrium with the carbonate rocks as suggested by Jones et al. (1993). In addition, the confining boundary of aquifers influences the evolution of isotopic chemistry of ground water along the flow paths.

Lack of $\delta^{18}O$ data in soil water precludes the complete connection of interactions between soil water and surficial aquifer water. $\delta^{18}O$ study of surficial aquifer water here compared with rainwater's $\delta^{18}O$ suggests a minimal evaporation of infiltration portion of rainwater before recharging aquifers. It may suggest that transpiration would predominate over evaporation of open water body in terms of total evaporation rate. Until further studies of $\delta^{18}O$ profiles in soil water are done, the extent of transpiration over free-water evaporation in the total evaporation budget remains uncertain.

There is still a room for further studies of partitioning of water in soil, atmospheric water vapor, and direct transpiration for inland stations compared with free water evaporation using the isotopic methods since this dissertation focusses on the coastal environment. The known partitioning of water fluxes and isotopes can be further used to calculate the changes in transpired O_2 and uptake of CO_2 by plants in Florida.

The heavy freshwater demand in the 21st century from the wells in the Pasco High, and west of the Green Swamp will help emphasize the needs for a better understanding of the ground water residence time, the recharge zones, and the water sources other than in the upper Floridan water.

A diagrammatic summary of $\delta^{18}O$ in various water types which is the main theme of this paper is shown in Figure 31. It should be noted also that the intermediate ground water is still not well understood in terms of both stable oxygen and carbon isotopes.

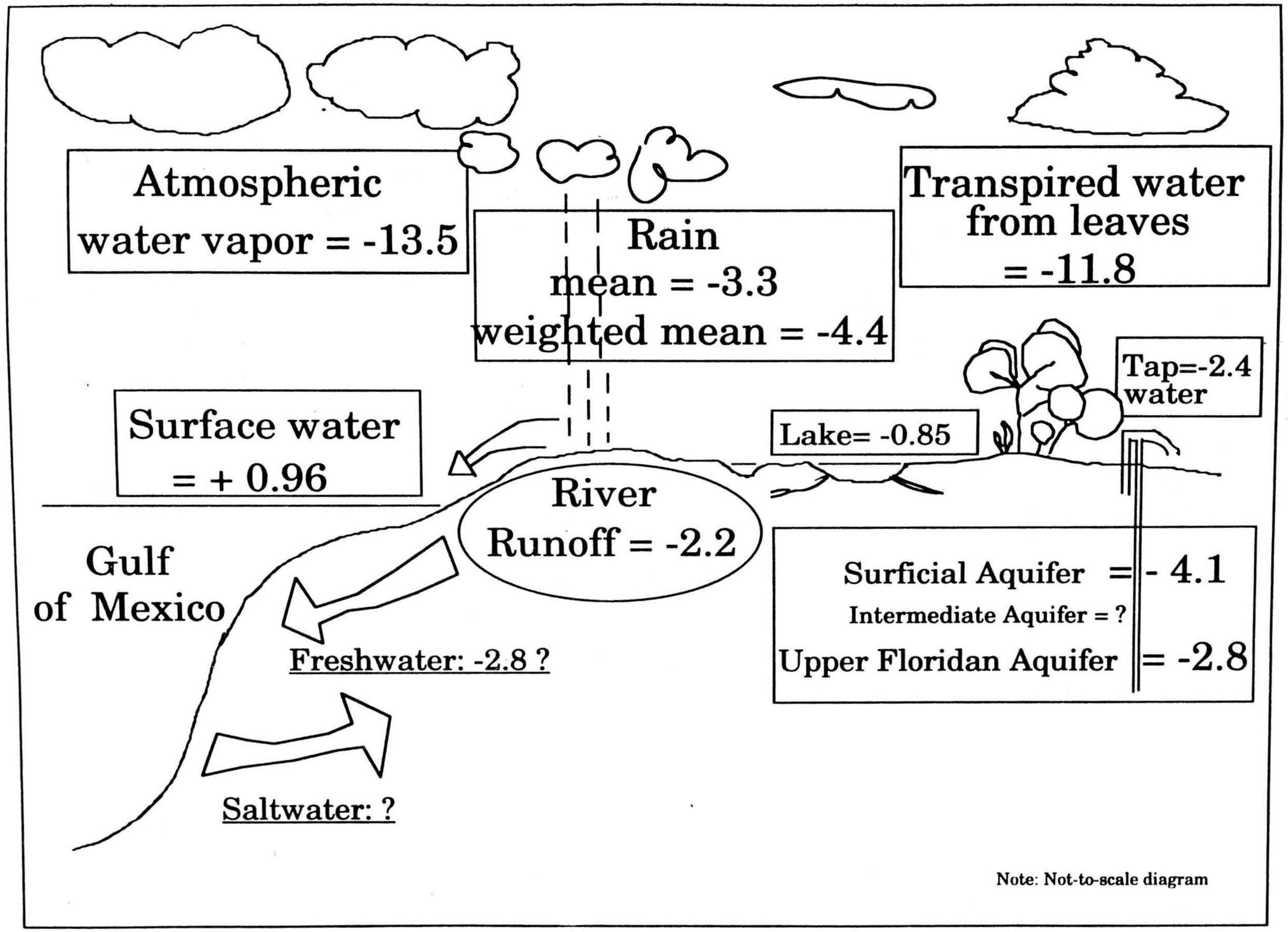

Figure 31. A Schematic Summary of $\delta^{18}O$ of Various Water Types in West-Central Florida

CHAPTER 7

CONCLUSIONS

1. For rainwater in St. Petersburg, Florida, the mean and weighted mean $\delta^{18}O$ are -3.3 and -4.4 o/oo vs SMOW, respectively. The weighted mean takes into account the fact that the $\delta^{18}O$ of rainfall becomes more negative as it rains heavier.

2. For west-central Florida, the $\delta^{18}O$ of rainwater does not covary with the surface air temperature (Figure 11c). Therefore, palaeo-temperature calculations, based on the $\delta^{18}O$ of surficial water and temperature relationship in Florida, without supporting data from isotopic studies of aquifer rocks, should be approached with caution.

3. The west-central Florida's meteoric water line is

$$\delta D = 7.65(\pm 0.20)\ \delta^{18}O + 10.6(\pm 1.1) \qquad r^2=0.998,\ n=5.$$

This equation is similar to the Global Meteoric Water Line of Craig (1961).

4. The $\delta^{18}O$ of atmospheric water vapor is -13.5 o/oo vs SMOW, based on short-term studies, while the transpired water from oak trees is -11.8 o/oo. The evaporative water vapor from a pan experiment has a $\delta^{18}O$ of -13.9 o/oo.

5. The $\delta^{18}O$ of transpired water correlates linearly with the specific humidity in the air. The correlation equation is $\delta^{18}O = -18.9(\pm 1.09) + 0.482(\pm 0.145)q$, where q is the specific humidity ($r^2=0.581$, $n= 10$).

6. During transpiration of water from leaves, calculations show that the leaf water is kinetically in equilibrium with the source stem water and the atmospheric water vapor. In addition, diffusion predominates during the transpiration processes.

7. The observed $\delta^{18}O$ of evaporative water vapor (δ_E, -13.9 o/oo vs SMOW) is similar to the calculated one (-14.1 o/oo) from pan experiments; the calculated $\delta^{18}O$ (+10.5

o/oo vs SMOW) of the remaining liquid (δ_s) is close to the regressed $\delta^{18}O$ (+12.2 o/oo) obtained from pan experiments.

8. The apparent fractionation factor of free water evaporation ($-\epsilon^*$ or approximately = $-[(\alpha^+-1)1000]$) is equal to -10.27 o/oo for m = 1.04. The slightly heavier ϵ^* value relative to the equilibrium value is attributed to an additional kinetic fractionation factor ($\Delta\epsilon$). This evaporation parameters can be used to calculate the fraction of remaining liquid during evaporation, δ_E, and δ_L in local and adjacent bodies of water.

9. $\delta^{18}O$ and $\delta^{13}C$ behave conservatively along salinity gradients. The behavior suggests there are 2 major water endmembers: freshwater and saline waters. The correlation equations are

March, 1990 $\delta^{18}O = -2.2(\pm0.2) + 0.108(\pm0.010)\text{salinity}, r^2=0.841, n=24,$

January, 1993 $\delta^{18}O = -2.4(\pm0.2) + 0.099(\pm0.010)\text{salinity}, r^2=0.913, n=14,$

March, 1990 $\delta^{13}C = -10.4(\pm0.79) + 0.239(\pm0.039)\text{salinity } r^2=0.660, n=24,$

January, 1993 $\delta^{13}C = -10.6(\pm0.43) + 0.254(\pm0.019)\text{salinity } r^2=0.945, n=14.$

The river endmember has similar $\delta^{13}C_{DIC}$ (-10.5 o/oo vs PDB) to the upper Floridan water (-10.4 o/oo vs PDB). However, the river endmember's $\delta^{18}O$ (-2.3 o/oo vs SMOW) is 0.5 o/oo heavier than the Floridan water's $\delta^{18}O$ (-2.8 o/oo). The difference in $\delta^{18}O$ in the river endmember may be due to a local evaporation effect. Ground water is likely to contribute freshwater to Tampa Bay in terms of river flows. However, the freshwater volume of rivers discharging into Tampa Bay accounts for 56 % of total freshwater inputs. The rainwater that falls directly on Tampa Bay contributes the remaining 44 % of the freshwater volume in the Bay.

10. The average $\delta^{18}O$ of the upper Floridan water is -2.8 o/oo vs SMOW, while the average $\delta^{13}C_{DIC}$ of the Floridan water is -10.4 o/oo vs PDB.

11. Based on a mass isotopic balance in the confined aquifers of southern flow path, the calculated effective upper Floridan water/carbonate rock mass ratio is 0.375, and the effective porosity is 0.503.

12. The intersection points of δD and $\delta^{18}O$ of rainwater and local Floridan water are for δD of -21.8 o/oo and $\delta^{18}O$ of -4.23 o/oo vs SMOW. The -4.23 o/oo intersection point represents the most depleted $\delta^{18}O$ composition that ground water can receive isotopic signature from rainwater. The ground water with $\delta^{18}O$ value of -4.2 o/oo must be located in the recharge area.

13. Calculations, based on observed $\delta^{18}O$ in surficial aquifer, suggest that the infiltration water from rainwater seeps into the aquifer with little evaporation. Addition $\delta^{18}O$ profile data of soil water will help confirm the idea that transpiration process predominates over free-water evaporation in the total evaporation budget for the inland areas.

14. The purging time required before collecting ground-water samples in the unconfined and confined aquifers varies depending the type of stable isotopes. For $\delta^{18}O$ the upper Floridan water seems to be unaffected by the number and frequency of purges. Inputs of surface water and frequency of purges during ground-water sampling can affect the $\delta^{13}C_{DIC}$ in surficial aquifer.

15. Based on similar physical conditions, pan evaporation experiments can be used to infer the isotopic parameters of nearby lakes (e.g. Mirror Lake).

16. Based on simple mass-balance calculations using oxygen isotopes and flow rates of water inputs and outputs, the replacement time of Tampa-Bay water is on the order of 67 days, while that for the Mirror Lake is 43 days.

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APPENDICES

APPENDIX 1. THE CALCULATION OF SPECIFIC HUMIDITY (q)

$$q = \epsilon e/p \qquad (28)$$

(McIlveen, 1992)

q = specific humidity (g of water vapor per kg of air)

ϵ = 0.622

e = water vapor pressure (mbar)

p = atmospheric pressure (mbar)

$$RH = 100e/e_s \qquad (29)$$

(McIlveen, 1992)

RH = relative humidity

e = water vapor pressure (mbar)

e_s = saturated water vapor pressure (mbar at a given temperature)

$$e_s = 6.11 * 10^{7.5t/(t+237.3)} \qquad (30)$$

(Bolton, 1980)

e_s = saturated water vapor pressure (mbar)

t = degree Celsius

The e_s is calculated from the observed temperature (eq. 30), and substituted into eq. 29. The calculated e is then substituted into eq. 28.

Example:

At 25 °C, and 60 % relative humidity ----> e_s = 31.79 mbar

atmospheric pressure = 1,013 mbar (1 atm.) e = 19.01 mbar

q = 0.01168 (or = 11.7 g of water per 1 kg of air)

At pumping air rate of 1.5 L/min. for 5 hours, MW of air ≈ 29

--> mass of air = 0.5826 kg, the condensed water = 6.8 g.

APPENDIX 2. DESCRIPTIVE MINERALOGY OF THE CARBONATE SAMPLES OBTAINED FOR THE δ^{18}O AND δ^{13}C ANALYSES

4990 Lake Alfred 2:	Calcite	trace: quartz, aragonite, cholorapatite
5471 Loughman:	Calcite (pure)	
5473 Green Swamp:	Calcite	trace: quartz, fluorite
13052 Lake Alfred 2:	Calcite	trace: quartz, dolomite, chlorapatite
13515 TR 9-1:	Calcite	trace: dolomite, quartz, aragonite
14887 68-2:	Calcite	trace: quartz
14889 87:	Calcite (pure)	
15650 88:	Calcite	trace: quartz
16268 Baum-Wimauma:	Dolomite	trace: quartz, analcime?, calcite
16428 Roy Haynes:	Calcite	trace: quartz
16577 DV-2:	Calcite	trace: quartz
16618 TR9-2:	Calcite	trace: quartz

The first 4 or 5 digit numbers are the Florida Geological Survey's ID numbers for the cores. The following name is for the SWFWMD's ID. The trace minerals are listed in the decreasing order of abundance. The major mineral comprises ≥ 75 % of total abundances. The identification was based on the peak readings from the X-ray diffractogram generated from a diffractometer in the Department of Marine Science (see Netratanawong [1990] for a detailed discussion on the methodology).

APPENDIX 3. THE PREPARATION OF 100% H_3PO_4 FROM 85% (w/w) H_3PO_4 and P_2O_5

1. First, the following chemical equation is established:

$$P_2O_5 + 3H_2O \text{ ---» } 2H_3PO_4 \qquad (30).$$

Note that the maximum amount of water absorbed by P_2O_5 is 3 times the molar concentration of P_2O_5.

2. Determine the given P_2O_5 size (mw = 141.94)

3. In 1 gram of 85% H_3PO_4 there is $15(1)/\{(100)(18.015)\}$ moles of water.

4. Calculate the amount of 85% H_3PO_4 needed for a given P_2O_5

   e.g. Given 100 g P_2O_5 and 85% H_3PO_4

   4.1 Maximum of water amount taken up by the P_2O_5

   $= 3\{[(100gP_2O_5)(1 \text{ mole of } P_2O_5)]/[(141.94\ gP_2O_5)]\}$

   4.2 Amount of H_3PO_4 required $= 100(18.015)(3)(100)/\{(15)(1)(141.94)\}$

   $= 253.8$ g of 85%H_3PO_4

5. If one needs to measure the volume, use the density appropriate for the 85% H_3PO_4 (= 1.689 g/cm^3).

APPENDIX 4. REGRESSED VALUES OF m AND δ_s FROM PAN EXPERIMENTS

The equation given by Welhan and Fritz (1977) is used:

$$f^m = (\delta-\delta_s)/(\delta_0-\delta_s) \text{ or } f^m = (\delta_s-\delta)/(\delta_s-\delta_0) \qquad \text{(Chapter 3)} \quad (10).$$

Upon the manipulation,

$$m\ln f = \ln(\delta_s-\delta) - \ln(\delta_s-\delta_0)$$
$$\ln f = (1/m)\ln(\delta_s-\delta) - (1/m)\ln(\delta_s-\delta_0)$$

$$y = b^*x + a$$

$$y=\ln f;\ b=1/m;\ \delta_s=\delta_0+e^{-am};\ \delta_0=-2.42 \text{ o/oo}.$$

The algorithm is to minimize the difference between the guessed δ_s and the observed δ for all the data points. The slope and the intercept are iterated until the best r is obtained. Xuewu Liu helped write the following BASIC code for used in the QBasic under the DOS computer. Since this QBasic cannot generate the final .EXE file, therefore the code will always be seen during the translation by the QBasic compiler.

	δ_s	m
pan3	+12.22	+1.041
pan1	+14.19	+0.8074

PAN 3

```
DIM x(8), y(8)
x0 = -2.42
n = 8
LPRINT "guessed;calculated;difference;m;r"
FOR i = 1 TO n
      READ y(i), mx(i)
            y(i) = LOG(y(i))
                  NEXT i
FOR p = 0 TO 6 STEP .025
      x1 = 7.3 + p
            FOR i = 1 TO n
                  x(i) = x1 - mx(i): x(i) = LOG(x(i))
                        NEXT i
                  GOSUB 1000
                  m = 1 / b
                  x11 = x0 + EXP(-a * m)
            LPRINT x1, x11, x1 - x11, m, r
```

APPENDIX 4. (Continued)

```
NEXT p
END
1000 xx = 0: x = 0: yy = 0: y = 0: xy = 0
    FOR i = 1 TO n
        x = x + x(i)
        y = y + y(i)
        xx = xx + x(i) * x(i):
        yy = yy + y(i) * y(i):
        xy = xy + x(i) * y(i)
    NEXT i
    xx = xx - x * x / n:
    yy = yy - y * y / n:
    xy = xy - x * y / n
b = xy / xx
a = (y - b * x) / n
r = xy / SQR(xx * yy)
RETURN
DATA  1,-2.42,0.9287,-1.06,0.9064,-
0.49,0.7771,0.804,0.7503,0.94,0.5943,4.08,0.4293,6.14,0.3579,7.29
```

PAN 1

```
DIM x(8), y(8)
x0 = -2.42
n = 8
LPRINT "guessed;calculated;difference;m;r"
FOR i = 1 TO n
    READ y(i), mx(i)
        y(i) = LOG(y(i))
            NEXT i
FOR p = 0 TO 4 STEP .025
    x1 = 11.7 + p
        FOR i = 1 TO n
            x(i) = x1 - mx(i): x(i) = LOG(x(i))
                NEXT i
            GOSUB 1000
            m = 1 / b
            x11 = x0 + EXP(-a * m)
        LPRINT x1, x11, x1 - x11, m, r
NEXT p
END
1000 xx = 0: x = 0: yy = 0: y = 0: xy = 0
    FOR i = 1 TO n
        x = x + x(i)
        y = y + y(i)
        xx = xx + x(i) * x(i):
        yy = yy + y(i) * y(i):
        xy = xy + x(i) * y(i)
    NEXT i
    xx = xx - x * x / n:
    yy = yy - y * y / n:
```

APPENDIX 4. (Continued)

```
      xy = xy - x * y / n
b = xy / xx
a = (y - b * x) / n
r = xy / SQR(xx * yy)
RETURN
DATA  1,-2.42,0.9002,-0.09,0.8669,
0.36,0.7339,1.623,0.6342,1.816,0.6176,2.88,0.4347,6.05,0.1021,11.69
```