Technical Publication SJ2003-1

# WATER QUALITY AND ISOTOPE CONCENTRATIONS FROM SELECTED SPRINGS IN THE ST. JOHNS RIVER WATER MANAGEMENT DISTRICT
## PART 2

by

David J. Toth, Ph.D., P.G.

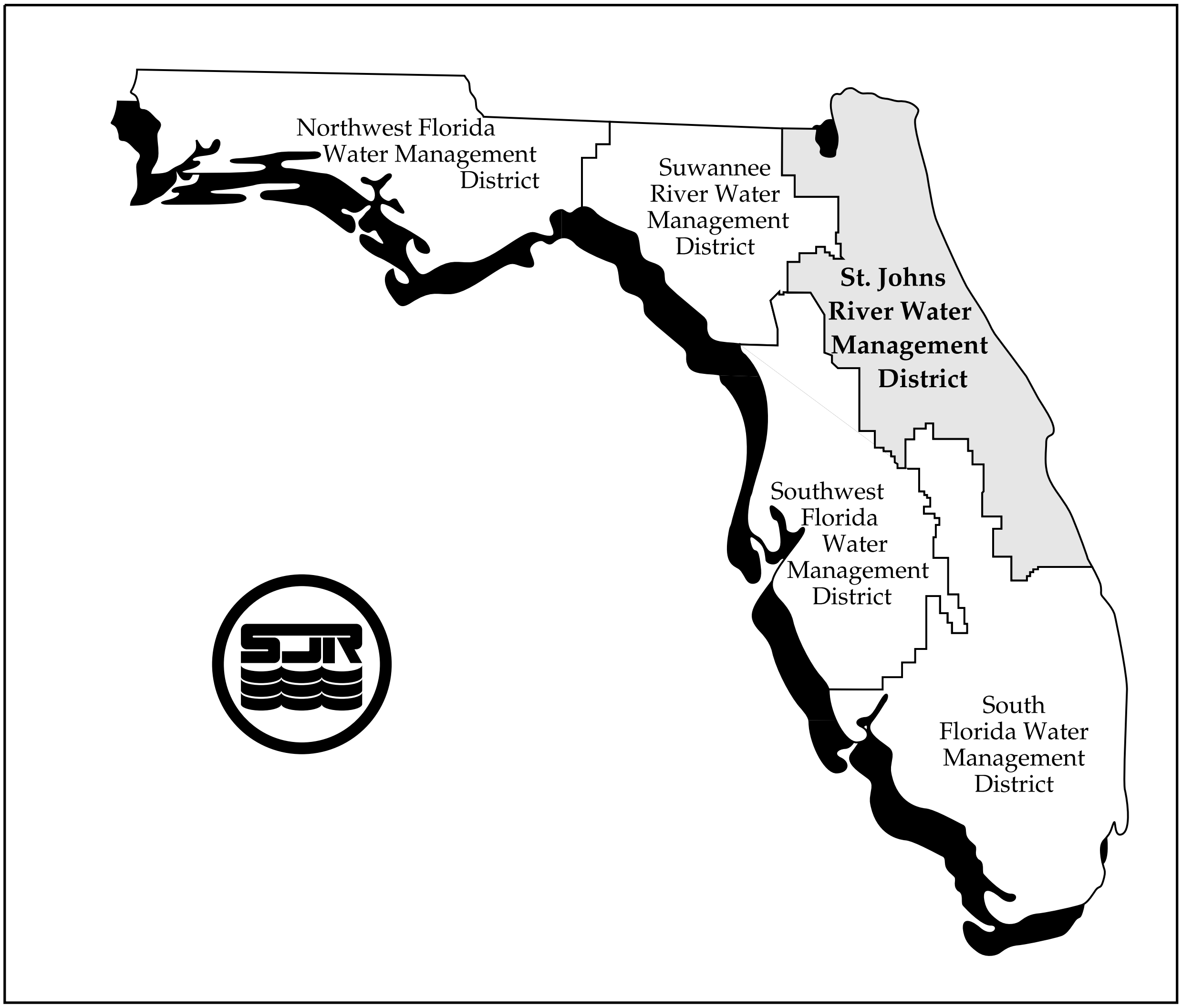
David J. Toth

David J. Toth
Professional Geologist
License No. 110
June 20, 2003

Seal

St. Johns River Water Management District
Palatka, Florida

2003



The St. Johns River Water Management District (SJRWMD) was created by the Florida Legislature in 1972 to be one of five water management districts in Florida. It includes all or part of 18 counties in northeast Florida. The mission of SJRWMD is to manage water resources to ensure their continued availability while maximizing environmental and economic benefits. SJRWMD accomplishes its mission through regulation; applied research; assistance to federal, state, and local governments; operation and maintenance of water control works; and land acquisition and management.

This document is published to disseminate information collected by SJRWMD in pursuit of its mission. Copies of this document can be obtained from:

Library
St. Johns River Water Management District
4049 Reid Street
Palatka, FL 32177

Phone: (386) 329-4132

# EXECUTIVE SUMMARY

Water quality and stable and radioactive isotope concentrations were determined for selected springs in the St. Johns River Water Management District. Seventeen springs (three of which are submerged) were sampled to assess water quality and stable and radioactive isotope concentrations. The purposes of the sampling were (1) to document water quality, (2) to determine the isotopic characteristics of spring water, (3) to determine the age of spring water and to evaluate the nature of the spring flow system, and (4) to determine the source of nitrogen in springs with nitrate-nitrogen concentrations above 0.2 milligrams per liter (mg/L).

Water quality was highly variable for the springs sampled. Chloride, sulfate, and total dissolved solids (TDS) concentrations ranged from 5 to 1,520 mg/L for chloride, from 8 to 64 mg/L for sulfate, and from 409 to 3,020 mg/L for TDS. For comparison, the drinking water standard for chloride, sulfate, and TDS is 250 mg/L, 250 mg/L, and 500 mg/L, respectively.

Water discharging from all springs is undersaturated with respect to common aquifer minerals calcite, dolomite, gypsum, and celestite. The fact that spring waters are undersaturated with respect to the various aquifer minerals suggests that the spring waters have not had sufficient time to reach mineral equilibrium. It also suggests that the spring waters are young.

Two different ages were determined for each spring: a tritium age and a carbon-14 ($^{14}C$) age. The tritium age for most springs was less than 48 years old. Two different models were used to determine the $^{14}C$ age. One model represents a confined aquifer. Its $^{14}C$ ages ranged from 1,824 to 19,491 years before 1950. The other model represents a leaky aquifer. Its $^{14}C$ ages range from less than 50 years before 1950 to 14,397 years before 1950. Because it agrees more closely with the tritium age than $^{14}C$ ages from a confined aquifer model, it is assumed to represent the true $^{14}C$ age.

The isotope data indicate that the flow system for all of these springs ranges from shallow to deep. It also indicates that water discharging from the springs consists of a mixture of ages—some water is less than 48 years old, some 75 years old, and some hundreds to thousands of years old. This age difference supports the concept that these springs have complex flow systems.

The delta-nitrogen-15 ($\delta^{15}N$) values for nitrate-nitrogen in spring water indicate that several springs have been contaminated by a mixture of nitrogen from inorganic and organic sources. The $\delta^{15}N$ values suggest that the elevated nitrate levels in Apopka, Bugg, Silver, Blue at Yalaha, and Holiday springs are probably due to contamination by a mixture of synthetic fertilizers and animal waste or sewage. Apopka, Blue at Yalaha, and Holiday springs have the lowest $\delta^{15}N$ values and are probably the springs most influenced by synthetic fertilizers. These springs also have the highest nitrate-nitrogen concentrations.

# CONTENTS

# FIGURES

# TABLES

# INTRODUCTION

Springs are a significant natural resource of Florida. They augment the flow of many rivers, provide habitat for wildlife, and provide recreation for Florida's residents. They contain crystal-clear water, colorful fish, turtles, and alligators. They also provide a winter refuge for manatees. The majority of springs in the St. Johns River Water Management District (SJRWMD) (Figure 1) are located along the St. Johns, Ocklawaha, and Wekiva rivers (Figure 2). About 90 springs occurred in SJRWMD in 2001. They discharged an estimated 690 million gallons per day in 2001 (SJRWMD database). Past and present sampling only involved the major springs. Seventeen springs were sampled in 1995 and 1996 to assess their water quality and age (Figure 3; Toth 1999). Seventeen springs (including three submerged springs) were sampled during this study to assess their water quality and age (Figure 4).

## PURPOSES

The purposes of this study were (1) to document water quality, (2) to determine the stable and radioactive isotope concentrations for selected springs in SJRWMD, (3) to determine the age of spring water and to evaluate the nature of the spring flow systems, and (4) to determine the source of nitrogen in springs with nitrate-nitrogen concentrations above 0.2 milligrams per liter (mg/L). Most of the remaining first-, second-, and third-magnitude springs in SJRWMD (Rosenau et al. 1977) that were not sampled in Toth (1999) were sampled in this study. Because rainfall during the winter and spring of 2001 was below normal, the discharge for five sampled springs was below 1 cubic foot per second (cfs).

## BENEFITS

Determination of the stable and radioactive isotope concentrations increases the knowledge and understanding of the chemical concentrations of spring water. Determination of the age of spring water identifies discharge as part of a shallow, rapid flow system or a deep, slow flow system. Information on flow systems is needed to clarify the way springs are conceptualized in groundwater flow models developed by SJRWMD. Finally, determination of the source of nitrogen in spring water indicates if spring water is being polluted. Possible sources of nitrogen are fertilizers, septic tanks, animal waste, and stormwater discharge.

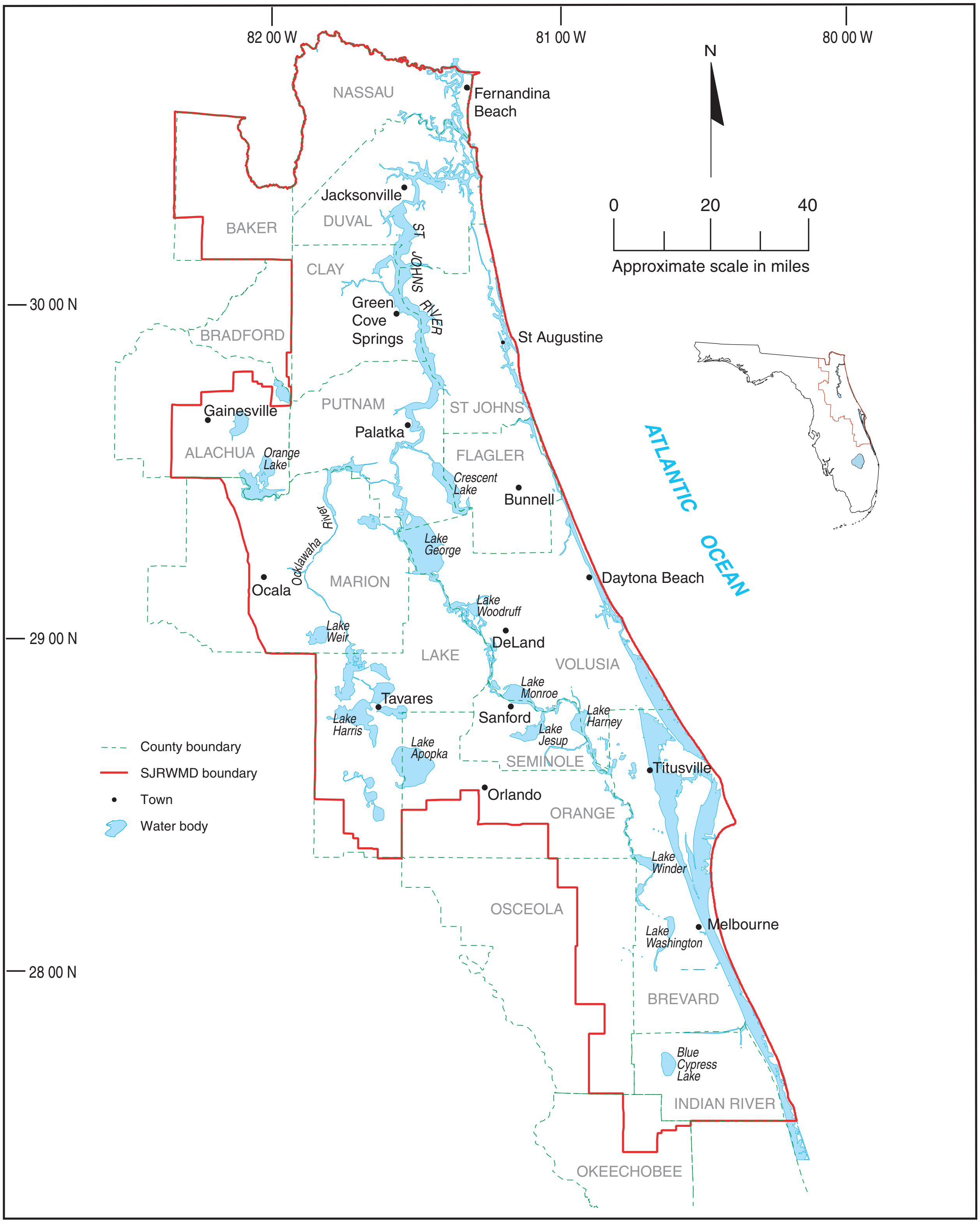


Figure 1. The St. Johns River Water Management District

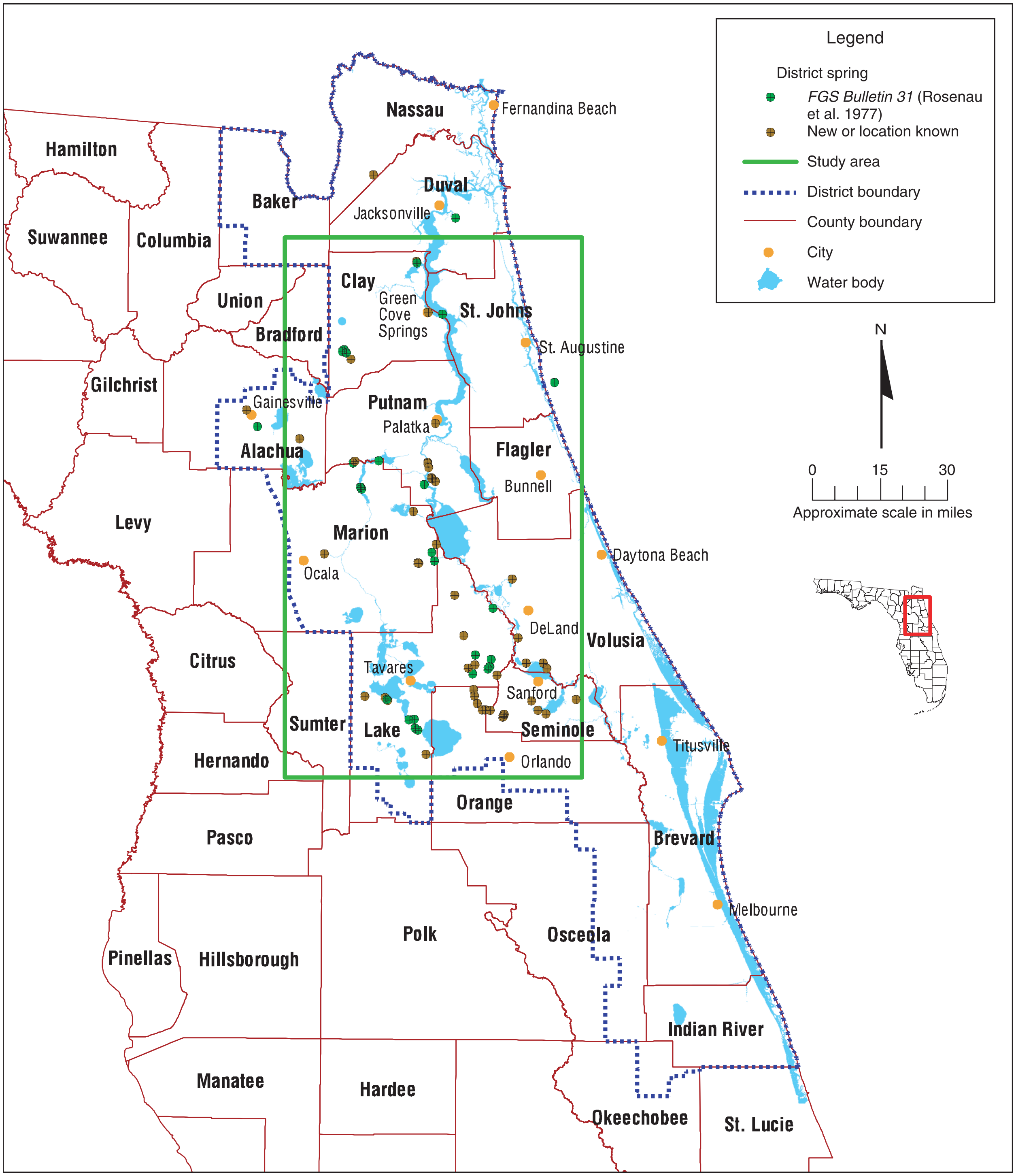


Figure 2. Study area

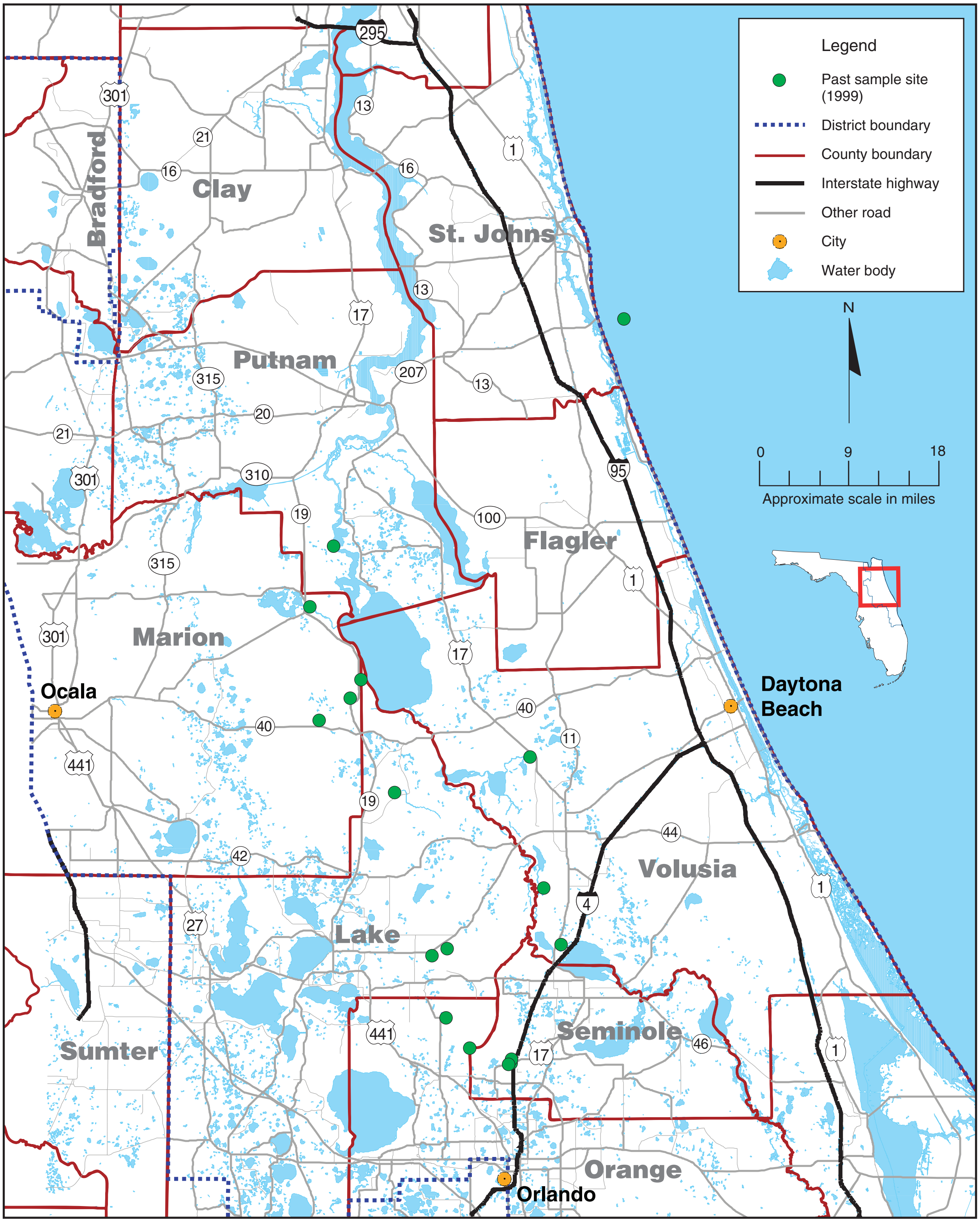


Figure 3. Location of past sampled springs

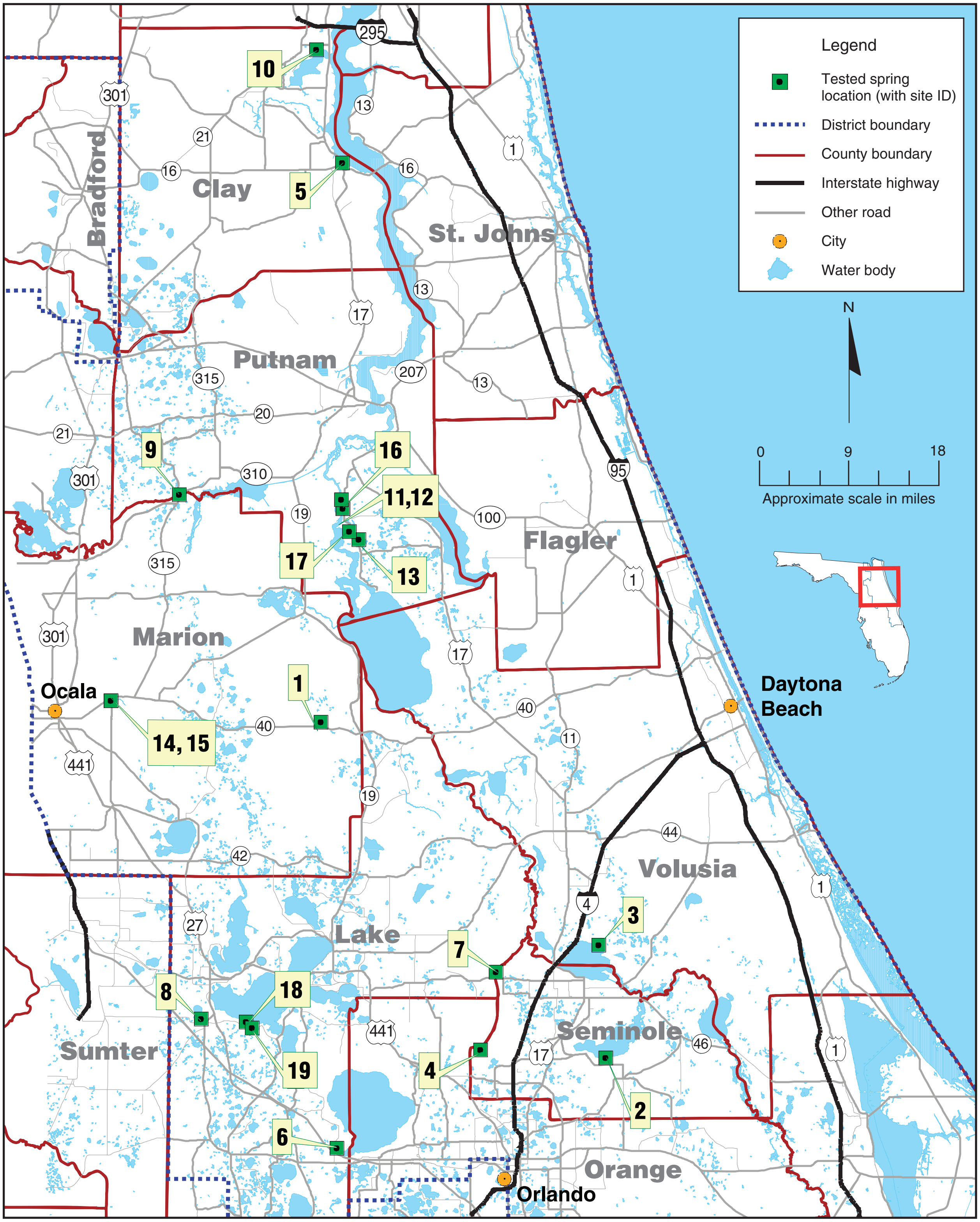


Figure 4. Location of sampled springs

## SPRINGS

Springs are classified by magnitude, from one to eight, on the basis of their volume of flow, or discharge (Rosenau et al. 1977). Seventeen springs were sampled in this study: one first-magnitude, two second-magnitude, nine third-magnitude, four fourth-magnitude, and one eighth-magnitude. First-magnitude springs have an average flow, or discharge, of 100 cfs (64.6 million gallons per day) or more. The first-magnitude spring sampled in this study is Silver Springs in Marion County. The discharge of second- and third-magnitude springs ranges between 10–100 cfs and 1–10 cfs, respectively. The second-magnitude springs sampled are Fern Hammock Springs in Marion County and Apopka Spring in Lake County. The third-magnitude springs are Clifton, Miami, and Island springs in Seminole County; Green Cove Spring in Clay County; Bugg Spring and Blue Springs at Yalaha in Lake County; Orange Spring in Marion County; and Welaka and Beecher springs in Putnam County. The discharge of fourth- and eighth-magnitude springs ranges between 0.223 cfs (100 gallons per minute [gpm]) and 1 cfs (448 gpm) and less than 0.000279 cfs (1 pint per minute), respectively. Fourth-magnitude springs are Wadesboro Spring in Clay County; Satsuma and Mud springs in Putnam County; and Holiday Springs in Lake County. The eighth-magnitude spring is Green Springs in Volusia County. The average discharge in Rosenau et al. 1977 of the fourth- and eighth-magnitude springs sampled in this study would make them third- and fourth-magnitude springs, respectively. However, because rainfall was below normal during the winter and spring of 2001, when the springs were sampled, the discharge for these springs fell in the range of fourth- and eighth-magnitude.

Three of the above springs are submerged. Apopka Spring is located in Lake Apopka, Island Spring lies in the Wekiva River, and Welaka Spring lies in the St. Johns River.

# STUDY AREA

The study area is located in east-central Florida in the St. Johns River Water Management District and includes St. Johns, Clay, Putnam, Flagler, Volusia, Seminole, and parts of Marion and Lake Counties (Figure 4). The springs that were sampled are in Lake, Marion, Putnam, Clay, Seminole, and Volusia counties (Figure 4). The submerged springs are in Lake, Seminole, and Putnam counties, in Lake Apopka, the Wekiva River, and the St. Johns River.

## TOPOGRAPHY

The topography ranges from rolling highlands in Orange, Lake, Marion, Clay, and western Volusia and Putnam counties to flat, swampy lowlands along the St. Johns River floodplain in Seminole, Lake, Marion, Putnam, Clay, and Volusia counties. Land-surface altitudes in the rolling highlands generally range from 100 to 200 feet (ft) above sea level, but may be as high as 310 ft west of Lake Apopka. In coastal areas and along the St. Johns River, altitudes are generally less than 35 ft.

Karst topography occurs near many springs and is present in all counties. Karst is a term applied to topography that describes any landscape conspicuously influenced by subsurface dissolution of rock. Such areas are characterized by high relief, a lack of surface drainage features, and the presence of subsurface drainage, sinkholes, and sinkhole-related lakes. Conduit/fracture flow occurs in this karst terrain. The discharge at many springs may result from conduit/fracture flow.

## CLIMATE

The climate of the study area is humid subtropical, with a mean annual temperature of 71°F. Most years have a few days of freezing temperatures, but the minimum temperature rarely falls below 20°F. The maximum temperature generally rises above 90°F from May through September, but 100°F is rarely reached.

Rainfall is unevenly distributed throughout the area, and the amount varies during the year. Most of the summer rainfall is a result of local, convective thunderstorms, which prevail from June through September. May is generally dry. The normal summer rainfall can be substantially augmented by tropical storms and hurricanes that pass through the area from time to time. Winters are typically drier than summers. Most of the rainfall in winter results from frontal activity rather than from convective thunderstorms. The average annual rainfall is about 52 inches over most of the study area (Tibbals 1990).

## HYDROGEOLOGIC FRAMEWORK

The hydrogeologic units in the study area are the surficial aquifer system, the intermediate aquifer system or intermediate confining unit, and the Floridan aquifer system (Table 1). Detailed information about the geology and hydrology of these systems can be found in Puri and Vernon (1959), Stringfield (1966), Miller (1982a, b), Miller (1986), and Tibbals (1990).

Table 1. Hydrogeologic framework for the study area

| Hydrogeologic Unit | Epoch | Stratigraphic Unit | General Lithology |
|---|---|---|---|
| Surficial aquifer system | Holocene<br>Pleistocene | Surficial sands and terrace deposits | Sand, clayey sand, and clay, with some shell locally |
| Intermediate aquifer system, or intermediate confining unit | Pliocene | Undifferentiated deposits | Sand, silt, clay, and shell |
| | Miocene | Hawthorn Group | Phosphatic clay, silt, sand, dolomite, and limestones |
| Upper Floridan aquifer | Oligocene | Suwannee Limestone | Limestone |
| | Eocene | Ocala Limestone | Limestones and dolomitic limestones |
| | | Avon Park Formation | Limestones and dolomite |
| Middle semi-confining unit | | | Soft to hard, porous to dense limestones and dolomite |
| Lower Floridan aquifer | | | Limestones and dolomite |
| | | Oldsmar Formation | |
| | Paleocene | Cedar Keys Formation | Dolomite, some limestone; anhydrite occurs in lower two-thirds of formation |
| Sub-Floridan confining unit | | | |

### Surficial Aquifer System

The first water-bearing unit is the surficial aquifer system, which is composed of Holocene and Pleistocene sand, clayey sand, clay, and some shell. The sand and shell layers vary in thickness, extending from the land surface down to the uppermost areally extensive clay layer, which is less permeable. The lithology, texture, and thickness of deposits in the surficial aquifer system vary laterally as well as vertically. The sediments range from unconsolidated to poorly consolidated and generally grade from sand to clayey sand to clay. Shell beds, where present, may have a matrix of sand and/or clay. The clay layers can vary in extent, thickness, and permeability, but do not significantly retard the downward movement of water.

Water in the surficial aquifer system is generally unconfined, and its level is free to rise and fall. In the swampy lowlands, the water table is generally near land surface throughout most of the year. In the rolling highlands, the water table is generally a subdued reflection of the topography but can be several tens of feet below land surface.

The surficial aquifer system is recharged primarily by rainfall. In coastal areas, the surficial aquifer system is also recharged by upward movement of water from underlying aquifers. Some lakes, streams, irrigation ditches, septic tank effluents, and stormwater retention ponds also recharge the surficial aquifer. Water leaves the system through evapotranspiration, seepage to some lakes, discharge to some streams and wetlands, leakage to underlying aquifers, and pumpage from wells. The surficial aquifer system is generally tapped by wells for small to moderate amounts of water that is widely used for lawn and garden irrigation. In St. Johns County, the surficial aquifer system is also tapped for public supply.

### Intermediate Aquifer System

Directly below the surficial aquifer system lies the intermediate aquifer system. The intermediate aquifer system in the study area consists of undifferentiated deposits of Pliocene sand, silt, and clay as well as the phosphatic sand, silt, clay, limestone, and dolomite of the Hawthorn Group of the Miocene Epoch. The intermediate aquifer system is composed of thin, discontinuous layers, or lenses, of sand, shell, or limestone and yields moderate amounts of water to domestic wells. Water in the intermediate aquifer system is confined. The intermediate aquifer system is recharged from the overlying surficial aquifer system or the underlying Floridan aquifer system, depending on hydraulic pressure relationships and the degree of confinement of the intermediate aquifer and Floridan aquifer systems.

The clays within the Pliocene sediments and the Hawthorn Group act as confining units and retard the vertical movement of water between the surficial aquifer, the intermediate aquifer, and the Floridan aquifer system. The thickness of the upper confining unit is variable throughout much of the study area (Figure 5). It is less than 50 ft thick throughout much of Volusia, Lake, and Marion counties and thickens to the north, where it is more than 400 ft thick in northern Clay County. Throughout much of Volusia County, the Hawthorn Group is absent. No information is available on the thickness of Pliocene deposits or of clays within the upper confining unit. The upper confining unit is generally thin where springs are located.

### Faults

A fault is a fracture in the rock along which displacement has occurred. It can facilitate the exchange of water between aquifer systems by providing an avenue along which water can move. Miller (1986) mapped two faults in the study area: One occurs along the St. Johns River in Clay County and the other occurs along the St. Johns River in southern Volusia County (Figure 5). Green Cove Spring occurs near the fault in Clay County. The thickness of the upper confining unit is 250 ft at Green Cove Spring. The fault may allow water from the Upper Floridan aquifer to discharge at the spring.

## Floridan Aquifer System

The Floridan aquifer system lies directly beneath the intermediate aquifer system. It consists of a thick sequence of limestone and dolomitic limestone. The top of the Floridan aquifer is defined as the first occurrence of vertically persistent, permeable, consolidated, carbonate rocks. The top of the Floridan aquifer system is highest in east Marion, Lake, central Volusia, west Seminole, and west Orange counties (Figure 6). In these areas the top is at or slightly above sea level.

The Floridan aquifer system is the principal source of fresh groundwater in SJRWMD and is capable of supplying large quantities of water to wells. Wells drilled into the Floridan aquifer system derive water from fissures and cavities created by the dissolution and fracturing of limestones. Throughout much of the study area, the Floridan aquifer is confined. The Floridan aquifer is unconfined in western Marion and Lake counties.

The Floridan aquifer system consists of the Suwannee Limestone (where present) of the Oligocene epoch, the Ocala Limestone (where present) and the Avon Park and Oldsmar formations of the Eocene epoch, and part of the Cedar Keys Formation of the Paleocene epoch. The Ocala Limestone constitutes the top of the

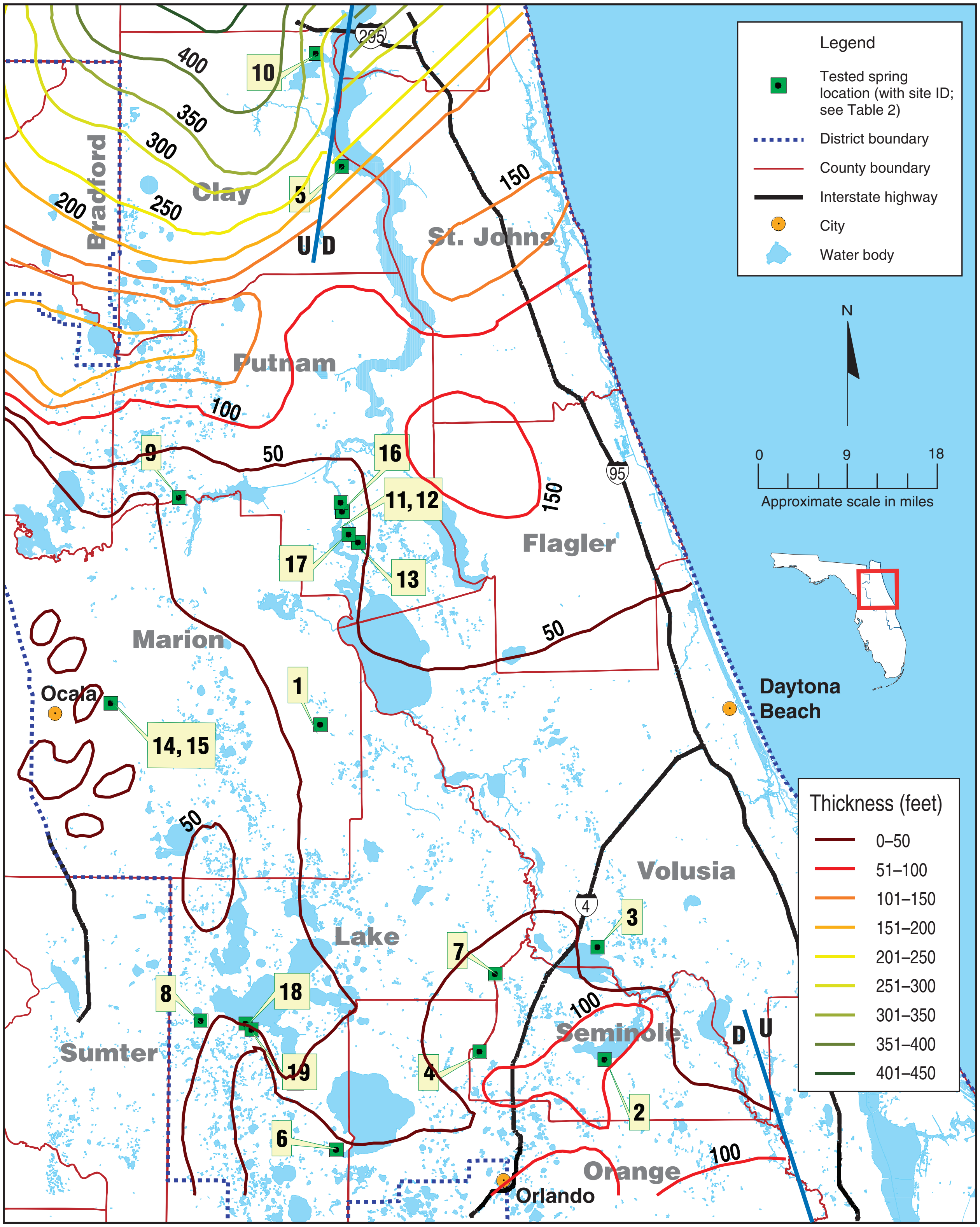


Figure 5. Thickness of the upper confining unit in the study area. D/U represents the normal fault (vertical): U = upthrown side, D = downthrown side (adapted from Miller 1986)

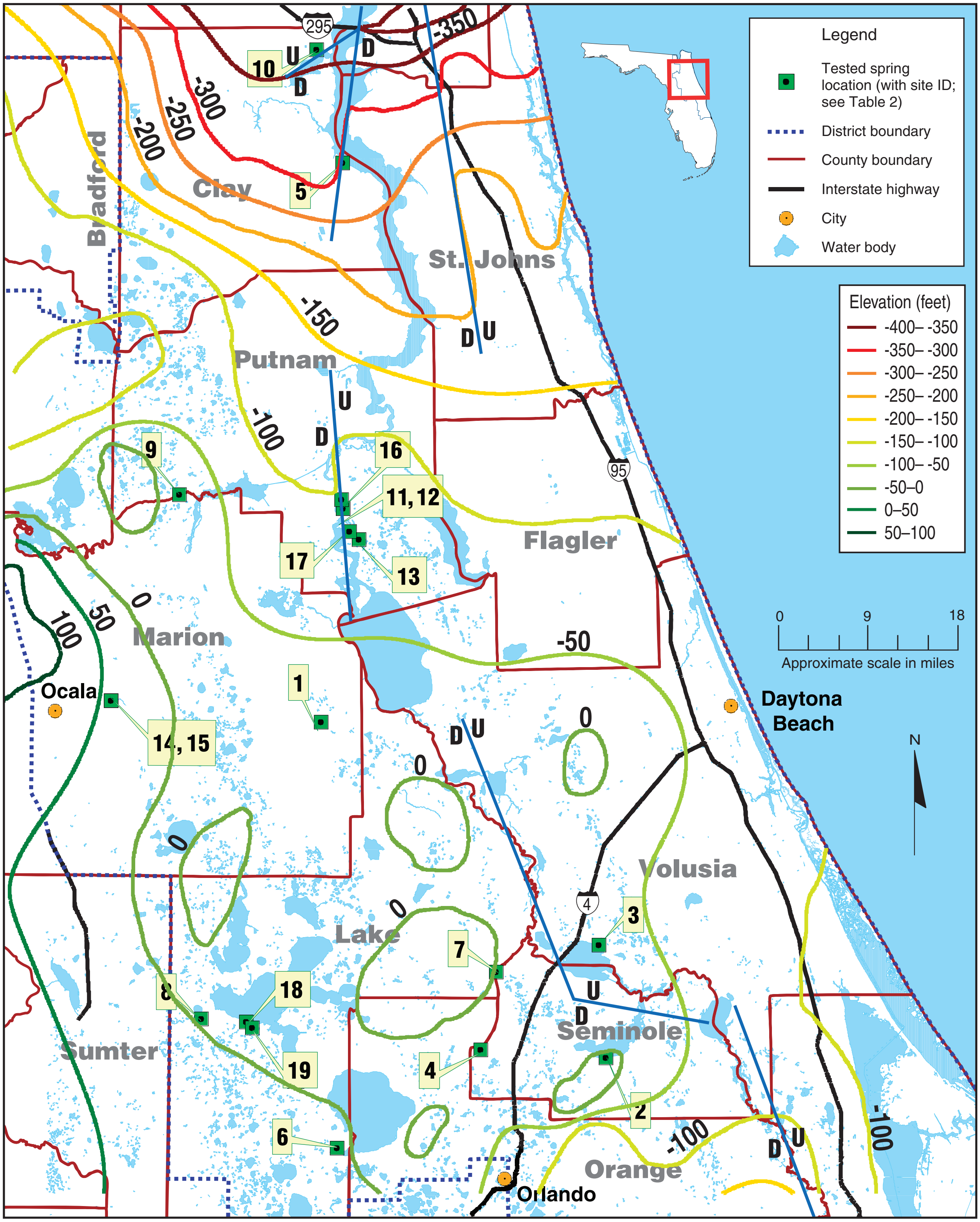


Figure 6. Elevation of the top of the Floridan aquifer system in the study area. D/U represents the normal fault (vertical): U = upthrown side, D = downthrown side (adapted from Miller 1986)

Floridan aquifer system over much of the study area. The Ocala Limestone is absent and the Avon Park Formation constitutes the top of the Floridan aquifer in southwest Volusia, north Seminole, and extreme northeast Lake counties. The Suwannee Limestone forms the top of the Floridan aquifer system in parts of southeastern SJRWMD.

The Floridan aquifer is divided vertically into three zones on the basis of permeability. Two zones contain relatively high permeability and are referred to as the Upper Floridan and Lower Floridan aquifers. Both zones are separated by a zone of less-permeable dolomitic limestone referred to as the middle semiconfining unit. The Upper Floridan aquifer consists of the Suwannee Limestone, the Ocala Limestone, and the upper part of the Avon Park Formation. It generally contains potable water and is a major source of water for public supply. The Lower Floridan aquifer consists of the lower part of the Avon Park Formation, the Oldsmar Formation, and part of the Cedar Keys Formation. It generally contains poor-quality water and is not a major source of water for public supply in much of the study area. However, in Orlando and western Seminole County, the Lower Floridan aquifer is tapped for public supply. The middle semiconfining unit consists of part of the Avon Park Formation. The discharge for most springs comes from the Upper Floridan aquifer.

The thickness of the Upper Floridan aquifer varies throughout the study area and ranges between 200 and 500 ft at most of the springs sampled (Figure 7).

The depth to the top of the Lower Floridan aquifer also varies throughout the study area and ranges from about 400 to 900 ft below sea level at the springs sampled (Figure 8). The depth to the top of the Lower Floridan aquifer increases from west to east in the study area.

## Faults

Miller (1986, 1982c) mapped several faults on the top of the Floridan aquifer system in the study area (Figure 6). They occur along the St. Johns River and Doctors Lake in Clay County, in central St. Johns County, along the St. Johns River in southern Putnam County, and along the St. Johns River in western and southern Volusia County and northern Seminole County. Wadesboro Spring, Green Cove Spring, Satsuma Spring, Welaka Spring, Mud Spring, and Beecher Springs occur on or near these faults. The faults may partially be responsible for the occurrence of the above springs.

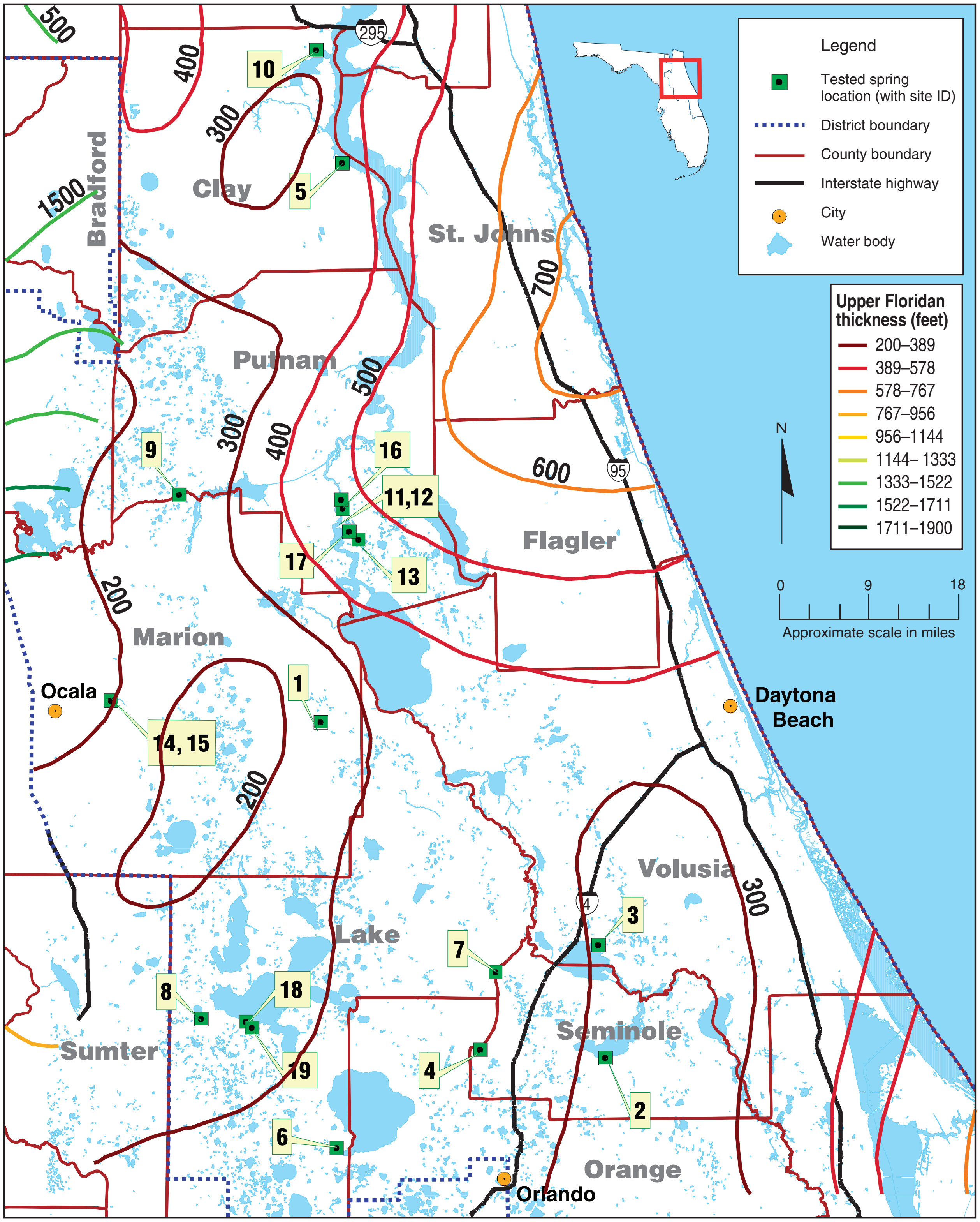


Figure 7. Thickness of the Upper Floridan aquifer in the study area

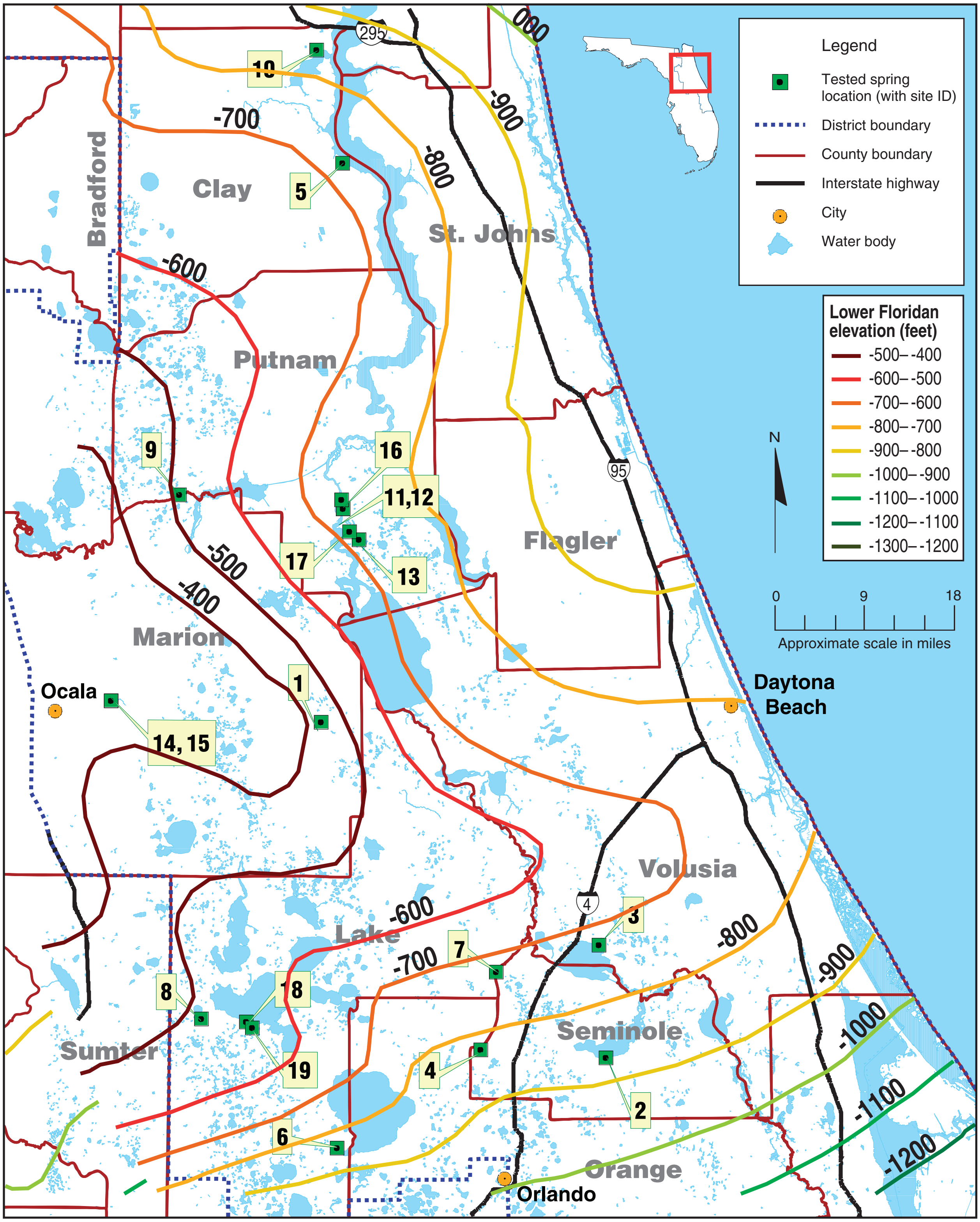


Figure 8. Top of the Lower Floridan aquifer in the study area

## Recharge and Discharge

Recharge to the Floridan aquifer occurs wherever water levels in the surficial and intermediate aquifers are higher than the potentiometric surface of the underlying Floridan aquifer. The rate of recharge depends on the difference between water levels in overlying aquifers and the potentiometric surface of the Floridan aquifer and on the thickness and permeability of the confining bed. Recharge rates are directly proportional to head differences and confining bed permeability and inversely proportional to confining bed thickness. Recharge rates of 12 or more inches per year are common in many portions of the study area (Figure 9).

Discharge from the Floridan aquifer occurs wherever the potentiometric surface of the Floridan aquifer is higher than water levels in overlying aquifers and surface water bodies. Discharge can occur directly through springs or as diffuse flow. Discharge areas are also common in the study area (Figure 9).

Most of the springs sampled in this study occur within less than 4 miles of high (12 or more inches per year) recharge areas. This suggests that the waters discharging from each spring may be locally derived.

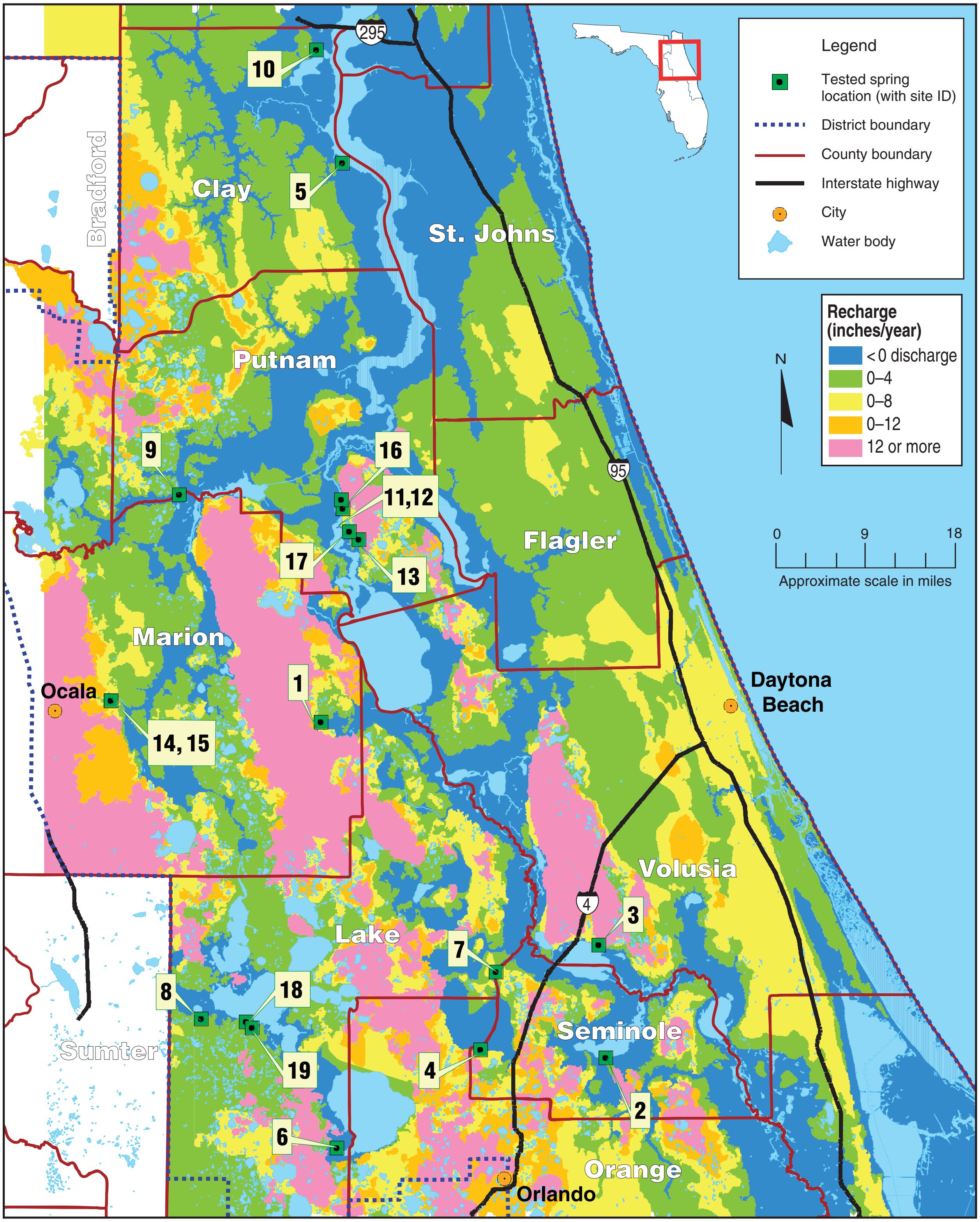


Figure 9. Recharge rates to the Floridan aquifer in the study area (from Boniol 1993)

# PROCEDURES

In this study, the procedures involved sampling nonsubmerged and submerged springs.

## SAMPLING SPRINGS—NONSUBMERGED

All springs were sampled by inserting a weighted, clear vinyl tubing in the spring vent and extending the tubing to shore. The end of the tubing which was placed in the spring vent was equipped with a screen which prevented sand-sized particles in and around the spring vent from entering the tubing. The tubing on shore was attached to a peristaltic pump. The discharge from the pump was passed through a Hydrolab meter and the parameters of temperature, pH, and conductivity were noted. The tubing was purged until the discharge was clear and the above parameters stabilized, after which samples were collected. Unfiltered samples were collected first, followed by filtered samples. The filtered samples were passed through 0.45-micron filters.

## SAMPLING SPRINGS—SUBMERGED

Divers from Karst Environmental Services assisted in the sampling of Island and Welaka springs. For Island Spring, the divers inserted the weighted, clear vinyl tubing with a screen attached into the spring vent to a depth of about 40 ft, and the tubing was extended to the surface where it was attached to a peristaltic pump on board a canoe. The discharge from the pump was passed through a Hydrolab meter and the parameters of temperature, pH, and conductivity were noted. The tubing was purged until the above parameters stabilized, after which samples were collected. For Welaka Spring, the divers inserted the weighted, clear vinyl tubing with a screen attached into the spring vent to a depth of about 11 ft, and the tubing was extended to shore where it was attached to a peristaltic pump. The same procedure as for Island Spring was followed.

Apopka Spring was sampled by SJRWMD staff. An airboat was positioned above the spring and weighted Teflon tubing was lowered into the spring vent at a depth of about 45 ft. On the airboat, the tubing was attached to a peristaltic pump and the same procedure as for Island Spring was followed.

## SAMPLE COLLECTION

Samples from nonsubmerged and submerged springs were collected by procedures approved by SJRWMD and the U.S. Geological Survey (USGS). With a Hydrolab meter, all samples were measured for dissolved oxygen, temperature, and specific conductance. Samples for metals (calcium, magnesium, sodium, potassium, strontium, and iron), TDS, fluoride (F), dissolved $SiO_2$, dissolved nutrients ($NO_x$ and $PO_4$), dissolved ammonia ($NH_4$), dissolved Kjeldahl nitrogen (TKN), dissolved phosphorus (P), dissolved organic carbon (DOC), $^{87}Sr/^{86}Sr$, and $^{15}N$ were filtered. Samples for D, $^{18}O$, $^{13}C$, $^{14}C$, tritium (T), and $^{34}S$ were not filtered. Total chemical samples were not filtered either. The collection of samples for $^{34}S$ depended on the sulfate concentration. If the past sulfate concentration was above 40 milligrams per liter (mg/L), the sample was collected in a liter bottle and acidified to pH 2 by adding concentrated hydrochloride (HCl), then ultra pure nitrogen gas was bubbled through the solution for 30 minutes to expel any hydrogen sulfide gas. If the past sulfate concentration was less than 40 mg/L, the sample was collected in a churn and acidified to pH 2 by adding concentrated HCl, then ultra pure nitrogen gas was bubbled through the solution for 30 minutes to expel any hydrogen sulfide gas. The sulfate was then concentrated by passing 10 liters of acidified, degassed solution through an ion exchange resin.

Samples were analyzed for the following:

| | |
|---|---|
| Specific conductance | Total and dissolved ammonia nitrogen ($NH_4$) |
| Temperature | Total and dissolved Kjeldahl nitrogen (TKN) |
| pH | Total and dissolved total phosphorus (TP) |
| Lab alkalinity | Iron (Fe) |
| Calcium (Ca) | Dissolved silicon dioxide |
| Magnesium (Mg) | Total and dissolved nitrate and nitrite nitrogen |
| Sodium (Na) | Total and dissolved orthophosphate phosphorus |
| Potassium (K) | |
| Strontium (Sr) | Delta-deuterium ($\delta^2H$ or D) |
| Chloride (Cl) | Delta-oxygen-18 ($\delta^{18}O$) |
| Fluoride (F) | Strontium 87/86 ($^{87}Sr/^{86}Sr$) |
| Sulfate ($SO_4$) | Delta-carbon-13 ($\delta^{13}C$) |
| Total dissolved solids | Delta-sulfur-34 ($\delta^{34}S$) |
| Dissolved oxygen | Delta-nitrogen-15 ($\delta^{15}N$) |
| Total and dissolved organic carbon (TOC and DOC) | Tritium ($^3H$ or T) |
| | Carbon-14 ($^{14}C$) |

Samples for deuterium, oxygen-18, and sulfur 34 were sent to the USGS lab in Reston, Virginia, for analysis. Samples for tritium and strontium 87/86 were sent to the USGS lab in Menlo Park, California, for analysis. Nitrogen-15, carbon-13, and carbon-14 analyses were performed by contract labs for USGS: Global Geochemistry in Los Angeles, California, for nitrogen-15 and the University of Waterloo in Ottawa, Ontario, Canada, for carbon-13 and carbon-14. Carbon-14 was determined by accelerated mass spectrometry. The remaining analyses were performed by the SJRWMD laboratory.

Excluding the submerged springs, discharge measurements were made by SJRWMD. Discharge measurements at the submerged springs were made by Karst Environmental Services ( 2001a, b, and c).

# WATER QUALITY

Water quality is a measurement of chemical and physical parameters of water in a flow system. The parameters consist of dissolved oxygen (DO), metals, anions, nutrients, $SiO_2$, organic carbon, and TDS.

Water quality was highly variable for the springs sampled in this study (Table 2). Chloride concentrations ranged from 5 mg/L at Fern Hammock Springs to 1,520 mg/L at Island Spring. Similarly, sulfate and TDS concentrations ranged from 8 and 64 mg/L, respectively, at Fern Hammock Springs to 409 and 3,020 mg/L, respectively, at Island Spring. For comparison, the secondary drinking water standard (FDER 1989) for chloride, sulfate, and TDS is 250 mg/L, 250 mg/L, and 500 mg/L, respectively.

The water discharging from springs can be classified by the use of Stiff diagrams. Stiff diagrams illustrate the major chemical compositions of water. The water discharging from most springs was a calcium-bicarbonate type (Figure 10). Calcium-magnesium-sulfate-bicarbonate water discharged from Green Cove Spring. Calcium-bicarbonate-sodium-chloride water discharged from Clifton and Beecher springs. Sodium-chloride water discharged from Green, Island, Welaka, Satsuma, and Mud springs. Young water generally has a calcium-bicarbonate composition. Old water in the aquifer generally has a sodium-chloride signature.

Dissolved oxygen was highest (5.72 mg/L) at Fern Hammock Springs and lowest (0.15 mg/L) at Green Cove Spring. The median DO concentration was 0.63 mg/L. Dissolved oxygen generally is an indication of young water. Old water contains little or no DO because microbes consume oxygen early.

There is little or no difference between total and dissolved nitrate plus nitrite nitrogen ($NO_x$) concentrations. For that reason, further discussion will only deal with total nitrate plus nitrite nitrogen.

Five springs had total nitrate plus nitrite concentrations above 0.2 mg/L, a maximum concentration reported for five springs in the Ocala National Forest (SJRWMD database) and considered to represent background $NO_3$ concentrations. The highest concentration, 4.93 mg/L, occurred at Apopka Spring. Other “elevated” concentrations occurred at Bugg Spring (0.64 mg/L), Silver Springs (0.65 mg/L), Holiday Springs (3.94 mg/L), and Blue Springs at Yalaha (4.31 mg/L). The presence of elevated nitrate levels in spring water suggests a shallow to intermediate flow system for the springs.

Table 2. Physical and chemical parameters for water from springs sampled in this study

| Site No. | Site Name | Sample Collection Date | Water Temperature (ºC) | Discharge (date) (cfs) | Specific Conductance (lab) (µmhos/cm) | pH (mg/L) | Dissolved Oxygen | Alk-lab $CaCO_3$ (mg/L) | Ca-D (mg/L) | Mg-D (mg/L) | Na-D (mg/L) | K-D (mg/L) | Sr-D (µg/L) | Fe-D (µg/L) | Cl (mg/L) | F (mg/L) | $SO_4$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Fern Hammock Springs | 1/16/2001 | 21.35 | 10.2 | 116 | 8.16 | 5.72 | 45 | 13 | 4.9 | 3 | 0.3T | 103 | 2.4T | 5 | 0.07 | 8 |
| 2 | Clifton Springs | 1/17/2001 | 22.80 | 1.2 | 581 | 7.14 | 1.33 | 112 | 43 | 13.8 | 59 | 2.4 | 429 | 7.2T | 109 | 0.18 | 36 |
| 3 | Green Springs | 1/17/2001 | 18.16 | 0.0 | 1,340 | 6.87 | 0.96 | 163 | 71 | 22.6 | 183 | 6.7 | 1,042 | 6.0T | 321 | 0.08 | 51 |
| 4 | Miami Springs | 1/18/2001 | 24.12 | 4.2 | 267 | 7.11 | 0.62 | 115 | 36 | 9.6 | 6 | 0.9T | 188 | 8.1T | 10 | 0.15 | 10 |
| 5 | Green Cove Spring | 3/15/2001 | 25.06 | 2.7 | 293 | 7.59 | 0.15 | 81 | 28 | 15.3 | 4 | 1.5 | 1,251 | 1.0T | 6 | 0.27 | 57 |
| 6 | Apopka Spring | 3/21/2001 | 22.68 | 24.8 | 239 | 7.30 | 2.46 | 73 | 30 | 8.1 | 5 | 1.0 | 61 | 2.5T | 11 | 0.07 | 10 |
| 7 | Island Spring | 3/22/2001 | 23.61 | 7.4 | 5,350 | 6.75 | 0.63 | 128 | 195 | 91.8 | 789 | 21.4 | 4,765 | 1.5T | 1,520 | 0.23 | 409 |
| 8 | Bugg Spring | 4/9/2001 | 23.26 | 6.9 | 285 | 7.30 | 2.11 | 119 | 48 | 3.2 | 6 | 1.2 | 62 | 3.1T | 10 | 0.06 | 10 |
| 9 | Orange Spring | 4/10/2001 | 24.10 | 2.4 | 271 | 7.39 | 0.33 | 127 | 7 | 6.7 | 4 | 2.0 | 66 | 36.8T | 6 | 0.15 | 10 |
| 10 | Wadesboro Spring | 4/11/2001 | 22.78 | 0.9<br>(4/12/01) | 351 | 6.52 | 0.22 | 125 | 46 | 8.9 | 10 | 1.1 | 205 | 463 | 17 | 0.18 | 22 |
| 11 | Welaka Spring | 4/12/2001 | 23.15 | 7.9 | 1,047 | 7.11 | 0.26 | 79 | 39 | 17.8 | 140 | 4.5 | 557 | 5.2T | 260 | 0.13 | 41 |
| 12 | Welaka Spring (duplicate) | 4/12/2001 | 23.15 | 7.9 | 1,056 | 7.11 | 0.26 | 79 | 39 | 17.6 | 139 | 4.4 | 550 | 2.0T | 259 | 0.13 | 42 |
| 13 | Beecher Springs | 5/7/2001 | 22.93 | 7.3 | 391 | 6.96 | 0.29 | 100 | 35 | 7.5 | 28 | 1.3 | 170 | 40.7T | 51 | 0.14 | 10 |
| 14 | Silver Springs | 5/8/2001 | 23.23 | 396.0 | 448 | 6.65 | 1.26 | 189 | 74 | 9.1 | 6 | 0.5T | 466 | 0.8T | 10 | 0.21 | 28 |
| 15 | Silver Springs (duplicate) | 5/8/2001 | 23.23 | 396.0 | 447 | 6.65 | 1.26 | 189 | 74 | 9.2 | 6 | 0.5T | 477 | 2.2T | 10 | 0.21 | 28 |
| 16 | Satsuma Spring | 5/9/2001 | 24.49 | 0.9<br>(5/7/01) | 4,660 | 7.03 | 0.55 | 95 | 102 | 73.4 | 691 | 23.5 | 2,408 | 2.2T | 1,366 | 0.34 | 213 |
| 17 | Mud Spring | 5/10/2001 | 22.52 | 0.9<br>(5/8/01) | 1,010 | 7.27 | 0.36 | 83 | 37 | 16.8 | 125 | 4.1 | 570 | 0.6T | 238 | 0.16 | 39 |
| 18 | Blue Springs at Yalaha | 5/14/2001 | 23.80 | 1.6 | 272 | 7.19 | 3.52 | 98 | 40 | 6.2 | 6 | 0.7T | 68 | 5.4T | 10 | 0.10 | 10 |
| 19 | Holiday Springs | 5/14/2001 | 23.90 | 0.9 | 293 | 7.08 | 1.11 | 106 | 43 | 6.7 | 6 | 0.7T | 68 | 3.0T | 12 | 0.11 | 10 |

Note:
cfs = cubic feet per second
mg/L = milligrams per liter
µg/L = micrograms per liter
µmhos/cm = microohms per centimeter

T signifies that value reported is less than the laboratory method detection limit

Table 2—*Continued*

| Site No. | Site Name | Sample Collection Date | TDS (mg/L) | $SiO_2$-D (mg/L) | $NO_x$-T (mg/L) | $NO_x$-D (mg/L) | $NH_4$-T (mg/L) | $NH_4$-D (mg/L) | TKN-T (mg/L) | TKN-D (mg/L) | $PO_4$-T (mg/L) | $PO_4$-D (mg/L) | TP-T (mg/L) | TP-D (mg/L) | TOC (mg/L) | DOC (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Fern Hammock Springs | 1/16/2001 | 64 | 9.28 | 0.09 | 0.09 | 0.006 | 0.007 | 0.000T | 0.000T | 0.017 | 0.018 | 3.253 | 0.016 | 1.57 | 0.81T |
| 2 | Clifton Springs | 1/17/2001 | 361 | 10.41 | 0.01T | 0.01T | 0.113 | 0.111 | 0.277 | 0.212 | 0.034 | 0.036 | 0.054 | 0.043 | 1.73 | 1.72 |
| 3 | Green Springs | 1/17/2001 | 746 | 8.66 | 0.16 | 0.16 | 0.197 | 0.192 | 0.322 | 0.297 | 0.057 | 0.056 | 0.066 | 0.060 | 2.07T | 2.32 |
| 4 | Miami Springs | 1/18/2001 | 149 | 9.16 | 0.04 | 0.04 | 0.016 | 0.020 | 0.061 | 0.087 | 0.070 | 0.075 | 0.099 | 0.097 | 0.41T | 1.02T |
| 5 | Green Cove Spring | 3/15/2001 | 165 | 13.55 | 0.00T | 0.00T | 0.029 | 0.031 | 0.079T | 0.082T | 0.005T | 0.005T | 0.003 | 0.004 | 0.10T | 0.13 |
| 6 | Apopka Spring | 3/21/2001 | 137 | 10.39 | 4.93 | 4.96 | 0.002T | 0.001 | 0.017T | 0.007 | 0.020 | 0.021 | 0.031 | 0.027 | 0.20T | 0.22T |
| 7 | Island Spring | 3/22/2001 | 3,020 | 11.03 | 0.00T | 0.00T | 0.234 | 0.232 | 0.558 | 0.414 | 0.068 | 0.072 | 0.506 | 0.082 | 1.65 | 1.43T |
| 8 | Bugg Spring | 4/9/2001 | 173 | 8.17 | 0.64 | 0.66 | 0.011 | 0.010 | 0.075T | 0.065T | 0.068 | 0.063 | 0.105 | 0.091 | 1.56 | 0.87T |
| 9 | Orange Spring | 4/10/2001 | 150 | 12.22 | 0.01 | 0.01 | 0.133 | 0.084 | 0.190 | 0.140 | 0.048 | 0.054 | 0.154 | 0.096 | 1.36T | 1.53T |
| 10 | Wadesboro Spring | 4/11/2001 | 192 | 9.34 | 0.00T | 0.00T | 0.049 | 0.050 | 0.139 | 0.108 | 0.126 | 0.128 | 0.144 | 0.150 | 2.37 | 1.19T |
| 11 | Welaka Spring | 4/12/2001 | 559 | 7.43 | 0.03 | 0.03 | 0.00T | 0.00T | 0.197 | 0.064T | 0.049 | 0.046 | 0.055 | 0.062 | 0.77T | 0.72T |
| 12 | Welaka Spring (duplicate) | 4/12/2001 | 584 | 7.19 | 0.04 | 0.04 | 0.00T | 0.00T | 0.191 | 0.073T | 0.046 | 0.046 | 0.055 | 0.061 | 0.57T | 0.83T |
| 13 | Beecher Springs | 5/7/2001 | 202 | 8.29 | 0.00T | 0.00T | 0.163 | 0.161 | 0.225 | 0.229 | 0.106 | 0.112 | 0.132 | 0.123 | 2.19 | 1.37T |
| 14 | Silver Springs | 5/8/2001 | 253 | 10.91 | 0.65 | 0.67 | 0.009 | 0.010 | 0.028T | 0.011T | 0.033 | 0.034 | 0.038 | 0.018 | 1.98 | 2.63 |
| 15 | Silver Springs (duplicate) | 5/8/2001 | 220 | 10.63 | 0.65 | 0.66 | 0.006 | 0.008 | 0.006T | 0.024T | 0.035 | 0.034 | 0.058 | 0.020 | 2.93 | 0.47T |
| 16 | Satsuma Spring | 5/9/2001 | 2,550 | 8.60 | 0.00T | 0.00T | 0.142 | 0.159 | 1.090 | 1.080 | 0.025 | 0.024 | 0.025 | 0.007T | 1.33T | 0.52T |
| 17 | Mud Spring | 5/10/2001 | 527 | 7.95 | 0.03 | 0.03 | 0.004T | 0.005 | 0.221 | 0.184 | 0.070 | 0.068 | 0.077 | 0.071 | 0.58T | 0.22T |
| 18 | Blue Springs at Yalaha | 5/14/2001 | 200 | 1.14T | 4.31 | 4.31 | 0.00T | 0.00T | 0.039T | 0.023T | 0.026 | 0.024 | 0.028 | 0.022 | 0.31T | 0.00T |
| 19 | Holiday Springs | 5/14/2001 | 200 | 10.62 | 3.94 | 4.00 | 0.00T | 0.00T | 0.108 | 0.048 | 0.041 | 0.027 | 0.093 | 0.028 | 0.00T | 0.00T |

Note: mg/L = milligrams per liter

T signifies that value reported is less than the laboratory method detection limit

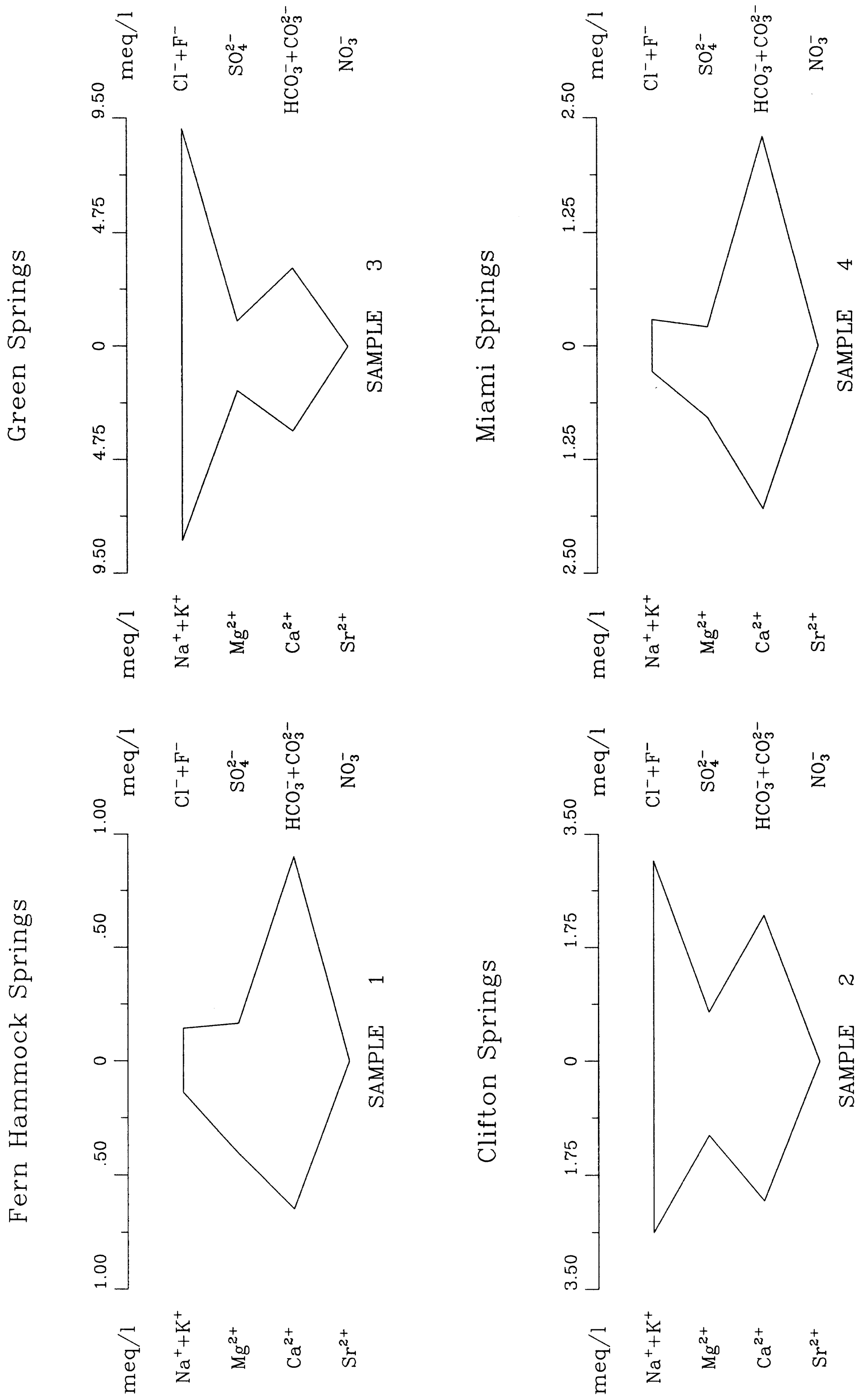


Figure 10. Water types for sampled springs

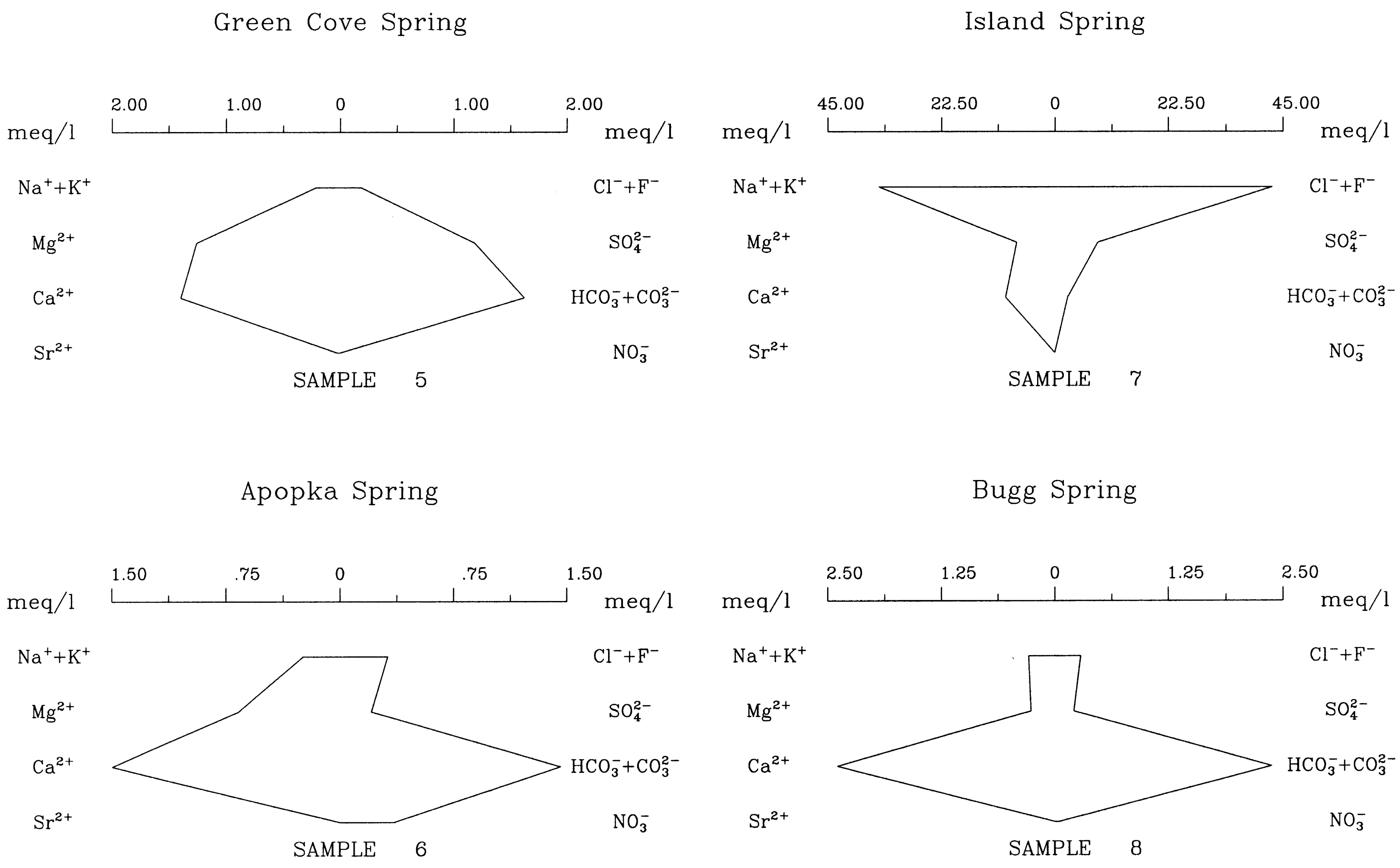


Figure 10. Water types for sampled springs—*continued*

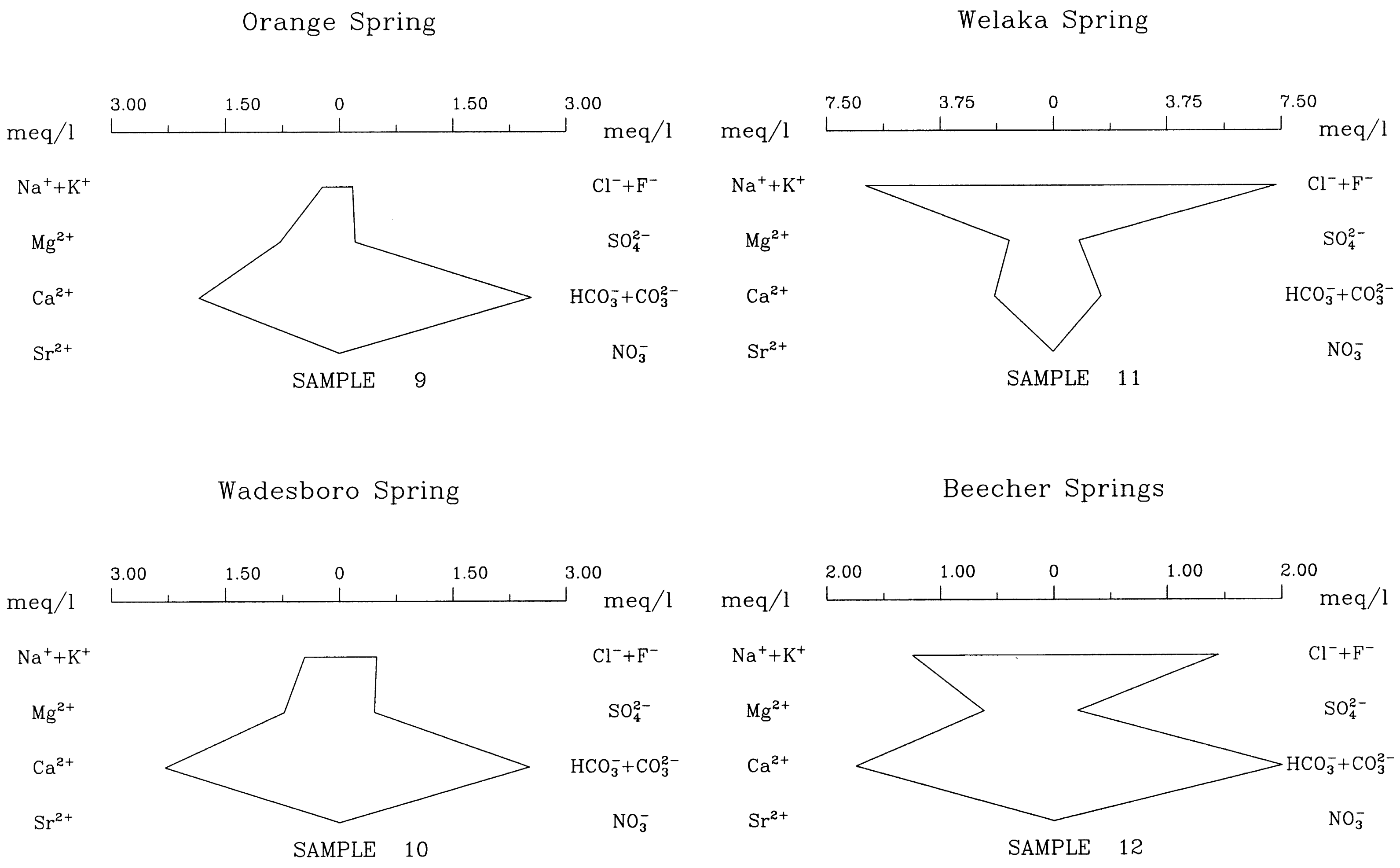


Figure 10. Water types for sampled springs—*continued*

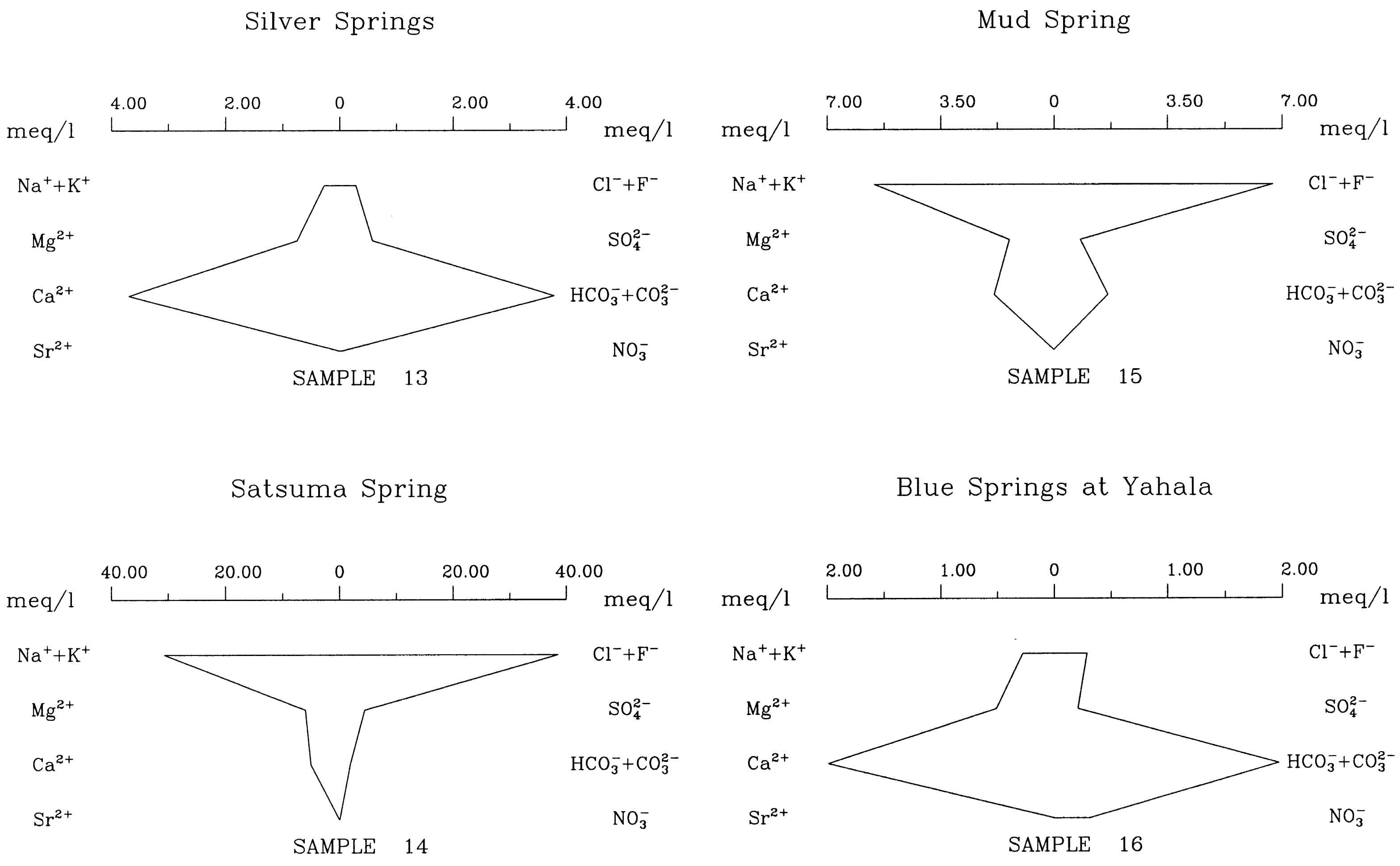


Figure 10. Water types for sampled springs—*continued*

## Holiday Springs

| Ion | meq/l | meq/l |
|---|---|---|
| $Na^+ + K^+$ | .28 | |
| $Mg^{2+}$ | .55 | |
| $Ca^{2+}$ | 2.15 | |
| $Sr^{2+}$ | .00 | |
| $Cl^- + F^-$ | | .34 |
| $SO_4^{2-}$ | | .21 |
| $HCO_3^- + CO_3^{2-}$ | | 2.11 |
| $NO_3^-$ | | .29 |
| | ------ | ------ |
| | 2.98 | 2.95 |

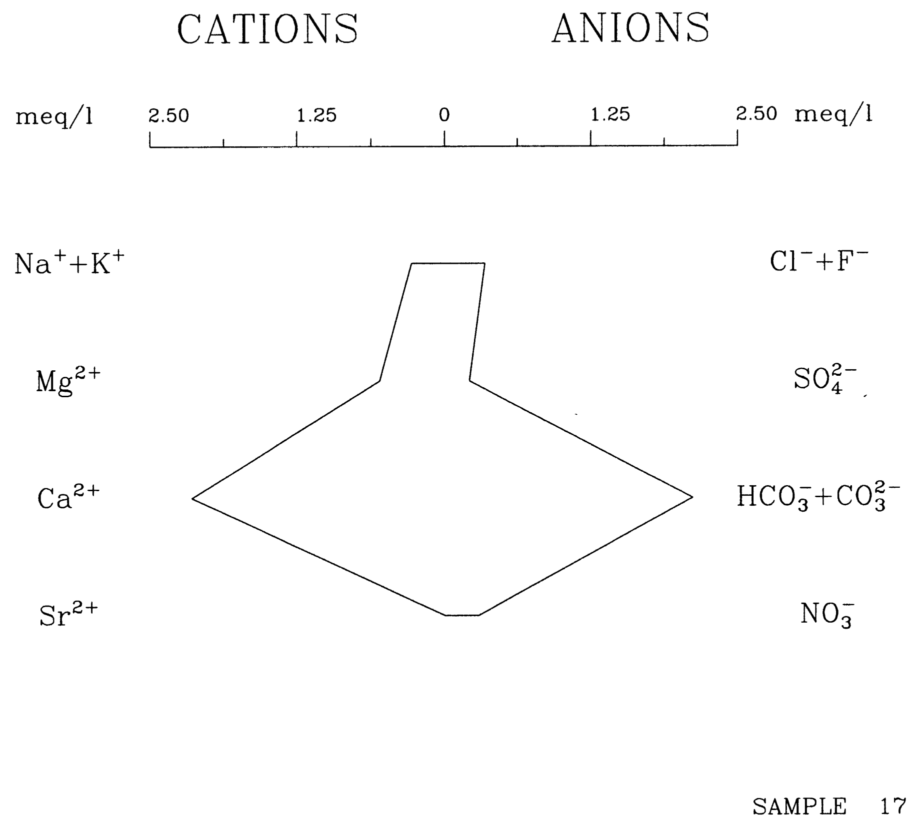


Figure 10. Water types for sampled springs—*continued*

The primary drinking water standard (FDER 1989) for nitrate-nitrogen is 10 mg/L as N. Concentrations above 10 mg/L can cause oxygen deprivation, a condition known as “blue baby syndrome.” This condition is especially hazardous in infants and young children (Hersh 1968; Hem 1985). However, “anecdotal evidence and field observations suggest nitrate levels of less than 1 mg/L cause a significant shift in the balance of spring ecological communities, leading to intensified degradation of biological systems” (Florida Springs Task Force 2000). The major cause of concern is algal growth and eutrophication, both of which will cause the clarity of spring water to diminish.

In addition to nitrate and nitrite nitrogen, nitrogen can also be present as ammonia ($NH_4$) and Kjeldahl nitrogen. Ammonia nitrogen is generally present under reducing conditions, while nitrate nitrogen is the predominant nitrogen form under oxidizing conditions. Both total and dissolved ammonia-nitrogen is low in all the sampled springs. The highest concentration of total ammonia nitrogen was 0.234 mg/L and occurred in Island Spring. The highest concentration of total Kjeldahl nitrogen as nitrogen was 1.090 mg/L and occurred in Satsuma Spring.

Total organic carbon was 1.33 mg/L in this spring. The highest concentration of total organic carbon was 2.93 mg/L, which occurred in Silver Springs.

Total and dissolved orthophosphate ($PO_4$) phosphorus concentrations are low. The highest total orthophosphate concentration was 0.126 mg/L, which occurred in Wadesboro Spring. Total and dissolved total phosphorus (TP) concentrations as phosphorus are generally low. The highest TP-T concentration was 3.253 mg/L and occurred in Fern Hammock Spring.

Dissolved iron concentrations are low for all springs except Wadesboro Spring (463 micrograms per liter), where it is above the secondary drinking water standard of 300 micrograms per liter (FDER 1989).

Water quality data for the springs sampled in this study were plotted on a Piper diagram (Figure 11). A Piper diagram plots the cation and anion composition of water on separate triangular diagrams and projects the resulting locations onto a diamond-shaped area. Different water types occur in different regions of this diamond-shaped area (Frazee 1982). Fern Hammock, Miami, Apopka, Bugg, Orange, Wadesboro, Silver, Blue at Yalaha, and Holiday springs plotted together and are located in a recharge area (Frazee 1982; compare Figures 11 and 12). These springs are high in calcium and bicarbonate, and their water “probably travels along relatively short, lateral flow paths that originate in high-rate

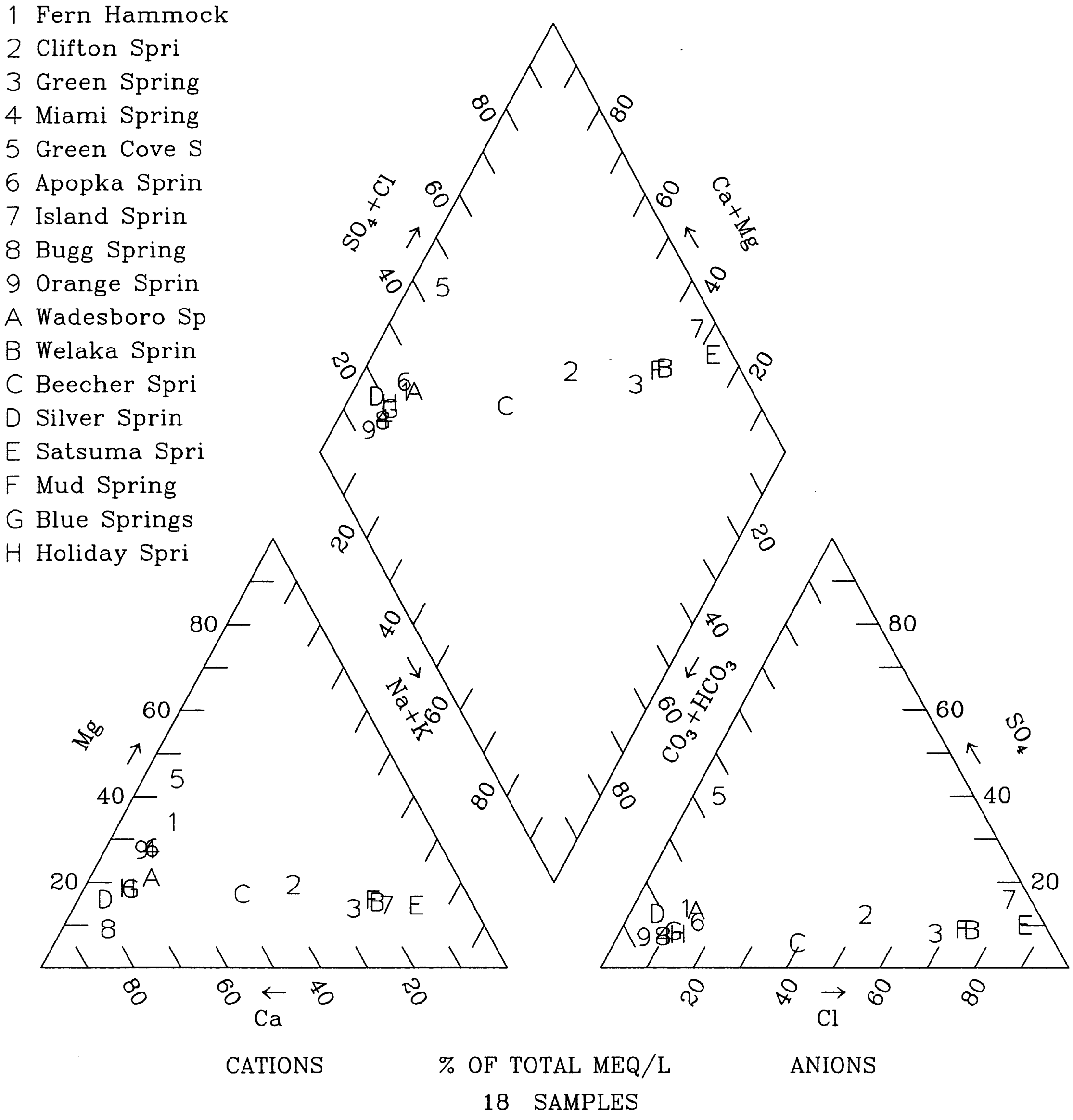


Figure 11. Piper diagram (diamond-shaped area) of spring water sampled

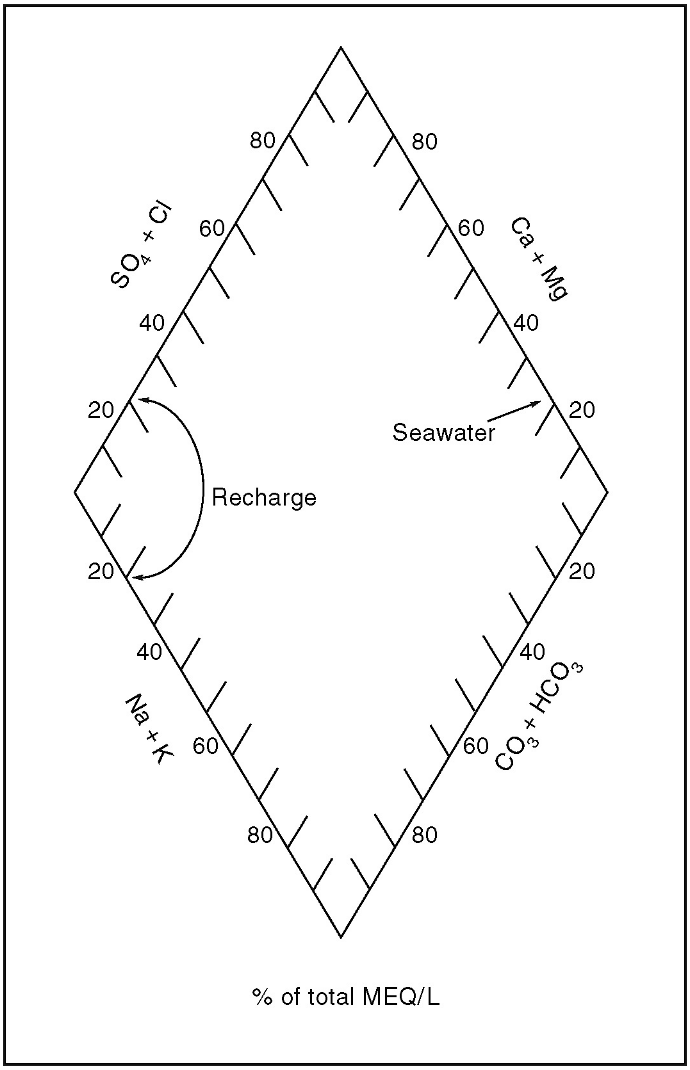


Figure 12. Piper diagram of recharge water and seawater (Toth 1999, based on Frazee 1982). Arrows indicate sample locations.

recharge areas" (Murray and Halford 1996). Green Cove Spring plotted in an area of the diagram that indicates the spring is enriched in calcium and sulfate. "This calcium sulfate type water results from the dissolution of a calcium sulfate aquifer matrix and probably travels along longer and deeper flow paths" than the fresh recharge type springs discussed above (Murray and Halford 1996). Island Spring and Satsuma Spring plotted together and are located very close to where seawater would plot on the diagram. These springs are enriched in sodium and chloride, probably from the mixing of freshwater with entrapped relict seawater or from the upwelling of deeper brackish water through fractures or faults. Based on the water type, these springs contain old water. Other springs that plotted near the seawater region are Green Spring, Welaka Spring, and Mud Spring. Both Clifton Springs and Beecher Springs plotted in the transitional region of the diagram between fresh recharge water and seawater. These springs are enriched in sodium plus potassium, calcium, chloride, and bicarbonate, probably from the mixing of freshwater with entrapped relict seawater.

## MINERAL SATURATION STATE

The mineral saturation state of groundwater changes with flow along a flowpath from recharge to discharge areas. Recharge and young waters are generally undersaturated with respect to aquifer minerals whereas old waters are generally saturated. Common aquifer minerals are calcite, dolomite, gypsum, and celestite. The saturation index (SI) is a measure of the departure from equilibrium of the water with respect to various mineral phases. An SI value of zero indicates that the water is at equilibrium (saturated) with respect to the mineral phase. A negative value indicates undersaturation (dissolution of the mineral), and a positive value indicates supersaturation (precipitation is possible). SIs for spring water samples (Table 3) were calculated using the aqueous speciation model in NETPATH (Plummer et al. 1994):

$$SI = \log(IAP / K_T) \qquad \textbf{(1)}$$

where

IAP = the ion activity product of the components of the mineral phase
KT = the solid phase solubility equilibrium product at the specified temperature

The determination of whether or not carbonate minerals are at equilibrium is dependent upon the accuracy of the chemical analysis and pH and water temperature measurements (Sacks and Tihansky 1996). Hence, equilibrium is defined to occur within a range of SI values and not at a specific value.

Table 3. Saturation indexes of sampled spring water for selected minerals

| Site | Calculated Saturation Indexes | | | |
|---|---|---|---|---|
| | Calcite | Dolomite | Gypsum | Celestite |
| Fern Hammock Springs | -0.401 | -0.923 | -3.189 | -3.584 |
| Clifton Springs | -0.582 | -1.337 | -2.215 | -2.509 |
| Green Springs | -0.613 | -1.465 | -1.974 | -2.106 |
| Miami Springs | -0.606 | -1.448 | -2.761 | -3.334 |
| Green Cove Spring | -0.399 | -0.714 | -2.142 | -1.780 |
| Apopka Spring | -0.698 | -1.645 | -2.811 | -3.796 |
| Island Spring | -0.537 | -1.066 | -1.009 | -0.908 |
| Bugg Spring | -0.292 | -1.432 | -2.638 | -3.819 |
| Orange Spring | -0.965 | -1.611 | -3.393 | -3.710 |
| Wadesboro Spring | -1.088 | -2.569 | -2.343 | -2.987 |
| Welaka Spring | -0.838 | -1.690 | -2.257 | -2.394 |
| Welaka Spring (duplicate) | -0.838 | -1.695 | -2.246 | -2.388 |
| Beecher Springs | -0.853 | -2.053 | -2.782 | -3.389 |
| Silver Springs | -0.597 | -1.778 | -2.094 | -2.588 |
| Silver Springs (duplicate) | -0.597 | -1.773 | -2.094 | -2.578 |
| Satsuma Spring | -0.600 | -0.996 | -1.479 | -1.392 |
| Mud Spring | -0.681 | -1.387 | -2.287 | -2.392 |
| Blue Springs at Yalaha | -0.549 | -1.573 | -2.709 | -3.770 |
| Holiday Springs | -0.599 | -1.671 | -2.688 | -3.780 |

For calcite, equilibrium is assumed for SI values between –0.15 and 0.15, and for dolomite, the range is –0.30 to 0.30 (Sacks and Tihansky 1996).

All of the springs sampled in this study are undersaturated with respect to calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$ , gypsum ($CaSO_4 \bullet 2H_2O$), and celestite ($SrSO_4$) (Table 3). The mineral closest to saturation is calcite. The springs closest and furthest from calcite saturation are Bugg Spring and Wadesboro Spring, respectively. Green Cove Spring and Wadesboro Spring are closest and furthest from dolomite saturation. Island Spring is closest to gypsum and celestite saturation, whereas Fern Hammock Spring and Bugg Spring are furthest from gypsum and celestite saturation, respectively. The fact that spring waters are undersaturated with respect to the various aquifer minerals suggests that the spring waters have not had sufficient time to reach mineral equilibrium. It also suggests that the spring waters are young relative to waters that are thousands of years old.

There is a strong relation between the gypsum and celestite saturation index and sulfate concentration (Figures 13a, b). This implies that gypsum and celestite dissolution is the primary source of sulfate in many of the sampled springs. Other sources of sulfate are connate water and seawater.

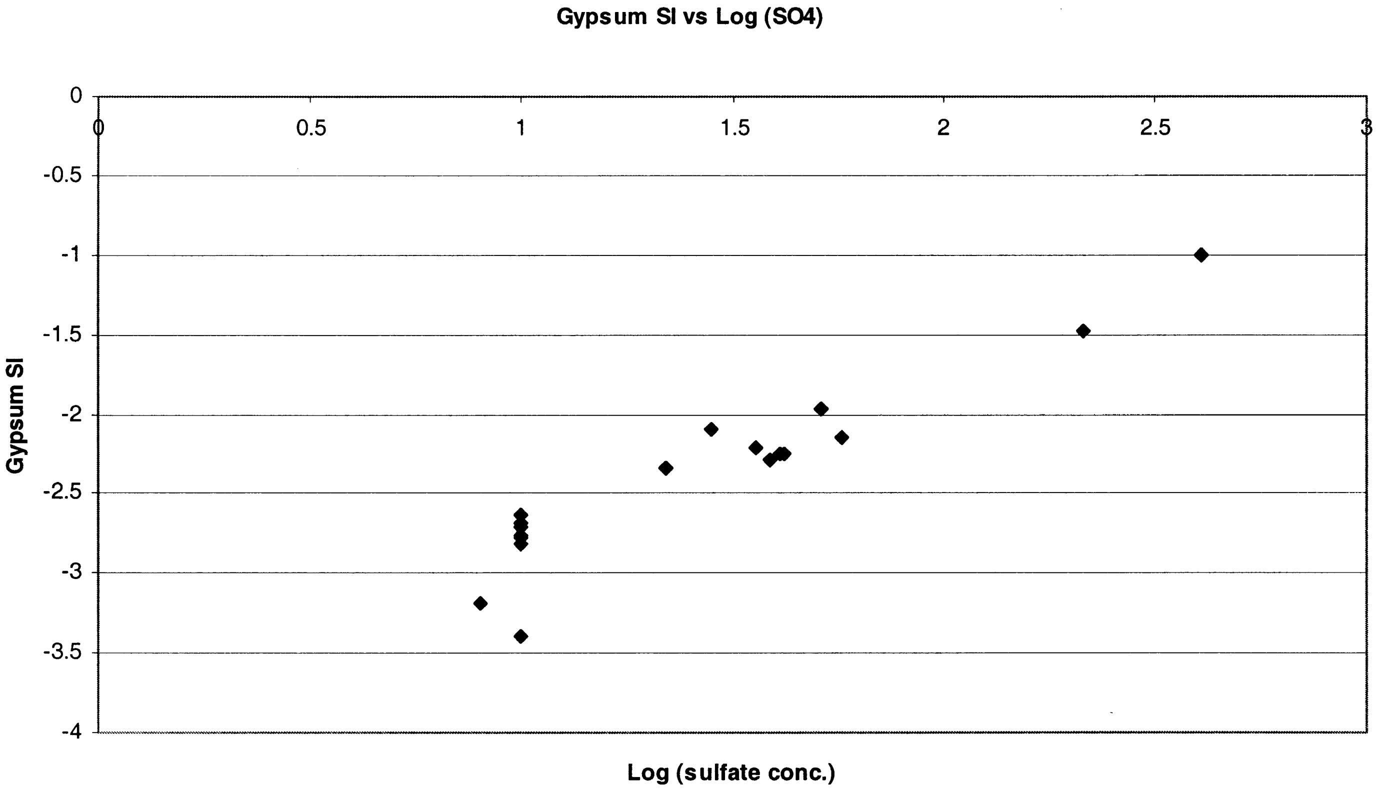


Figure 13a. Relationship between the gypsum saturation index and the log of sulfate concentrations

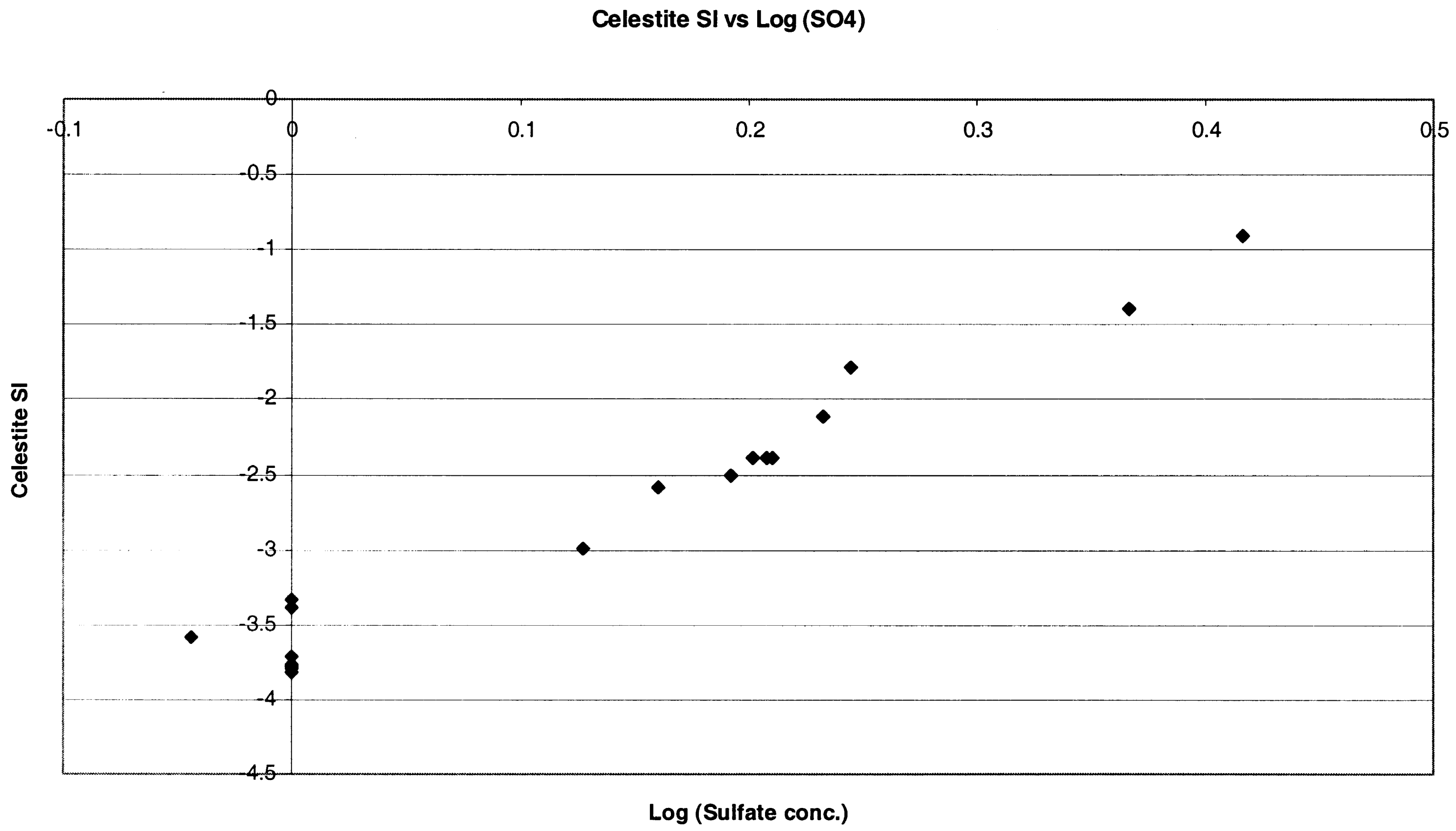


Figure 13b. Relationship between the celestite saturation index and the log of sulfate concentrations

# ISOTOPES

Isotopes are atoms of the same element that differ in mass because of a difference in the number of neutrons in the nucleus. There are two types of isotopes: stable and radioactive. Stable isotopes, such as D and $^{18}$O, are used in hydrologic studies to identify sources of water and to learn more about hydrologic processes such as recharge, evaporation, mixing, and water-rock interactions. The stable isotopes monitored in this study are D, $^{13}$C, $^{15}$N, $^{18}$O, $^{34}$S, $^{86}$Sr and $^{87}$Sr. Radioactive isotopes are generally used for age-dating water because these isotopes decay over a period of time at a known rate. The radioactive isotopes monitored in this study are $^{3}$H and $^{14}$C.

## STABLE ISOTOPES

The variation in the abundance of the stable isotopes of the elements hydrogen, carbon, nitrogen, oxygen, and sulfur in natural substances is small. For most studies, only the relative ratio of the rare isotope to the common isotope needs to be considered. This is important because the relative ratio of two isotopes can be determined about an order of magnitude more accurately than the absolute ratio of two isotopes (Coplen 1993).

The stable isotope content of samples generally is measured as a ratio and reported as a delta (δ) value (Gonfiantini 1981); that is, these isotopes are compared to a standard (Equation 2).

$$\delta_{\xi} = (R_x / R_{standard} - 1)1{,}000 \qquad \textbf{(2)}$$

where

$\delta_{\xi}$ = delta values for a given stable isotope *x* in parts per thousand or per mil (‰), relative to a standard

$R_x$ = ratio of isotope *x* in the sample (e.g., $^{2}H / ^{1}H$, $^{13}C / ^{12}C$, $^{15}N / ^{14}N$, $^{18}O / ^{16}O$, $^{34}S / ^{32}S$, or $^{87}Sr / ^{86}Sr$)

$R_{standard}$ = ratio of isotope *x* in the standard (e.g., $^{2}H / ^{1}H$, $^{13}C / ^{12}C$, $^{15}N / ^{14}N$, $^{18}O / ^{16}O$, $^{34}S / ^{32}S$, or $^{87}Sr / ^{86}Sr$)

A water sample that had been analyzed for oxygen isotopes, for example, might have a $\delta^{18}$O value of +2‰. The positive δ value means that the sample is enriched in $^{18}$O relative to the standard; in other words, the sample is isotopically “heavy” relative to the standard. A negative δ value indicates that the sample is depleted in the isotope relative to the standard; that is, the sample is isotopically ‘light’ relative to the standard.

Isotope standards represent the concentrations found in specific substances. The standard used for oxygen and hydrogen isotopic values of water is the Vienna Standard Mean Ocean Water (VSMOW). By convention, $\delta^{2}$H and $\delta^{18}$O of VSMOW are assigned a value of 0‰. Carbon-isotope ratios are reported relative to the PeeDee belemnite (PDB) or Vienna PDB (VPDB) carbonate standard. Nitrogen in air is well mixed and is the nitrogen isotope standard. Sulfur isotope values are reported relative to troilite from the Canyon Diablo meteorite. Strontium isotope ratios are reported relative to seawater or as the direct ratio $^{87}$Sr / $^{86}$Sr; in this paper, strontium isotopes are reported as the ratio of $^{87}$Sr / $^{86}$Sr. The precision attainable in the USGS laboratories for sample preparation and analysis of stable isotope samples is 2‰ for $\delta^{2}$H, 0.2‰ for $\delta^{13}$C, $\delta^{15}$N, $\delta^{18}$O, and $\delta^{34}$S, and 0.00002‰ for $^{87}$Sr / $^{86}$Sr (Coplen, USGS, pers. com. 1993).

## Deuterium and Oxygen-18

Deuterium and oxygen-18 are stable isotopes of hydrogen and oxygen. Because stable hydrogen and oxygen are intimately associated in the water molecule, they are discussed together here.

Deuterium and $^{18}$O generally are used to determine the origin of water or to learn more about hydrologic processes. For different hydrologic processes, such as evaporation, silicate hydrolysis, and geothermal exchange, the relationship between $\delta^{2}$H and $\delta^{18}$O changes.

The global meteoric water (GMW) line is an average of $\delta^{2}$H and $\delta^{18}$O values for precipitation and freshwater worldwide. Equation 3 represents the GMW line (Craig 1961).

$$\delta^{2}H = (8 \times \delta^{18}O) + 10 \qquad \textbf{(3)}$$

where

$\delta^{2}$H = delta value for deuterium
$\delta^{18}$O = delta value for oxygen-18

If values for samples fall on or near this line, the water originated from rainwater.

Evaporation, geothermal reactions, and low-temperature silicate hydrolysis produce different $\delta^2$H and $\delta^{18}$O relationships compared to the GMW line (Coplen 1993). Evaporation from surface water bodies is a nonequilibrium process that enriches $^2$H and $^{18}$O in the remaining water. Evaporation causes the plot of $\delta^2$H versus $\delta^{18}$O to diverge from the GMW line. The slope of the resulting evaporation line generally ranges from 3 to 6, compared to a slope of 8 for the GMW line (Coplen 1993). Because of the difference in mass between water containing $^2$H and $^{18}$O and water not containing these isotopes, evaporation preferentially transfers water containing the light isotopes H and $^{16}$O into the atmosphere, thus enriching the remaining water in the heavier $^2$H and $^{18}$O. Of the above processes, evaporation is most likely the only process that has affected the $\delta^2$H and $\delta^{18}$O relationship in groundwater samples in Florida.

Most of the springs sampled in this study plot near the GMW line (Figure 14). This indicates that climatic conditions probably did not vary substantially during the time period that spring waters were recharged. The sample from Clifton Springs (no. 2 on Figure 14) is furthest from the GMW line. It is below the GMW line and suggests that the water recharging Clifton Springs may have been evaporated (for example, lake leakage). This sample plots directly on an evaporation trend line for lakes in central Florida (Sacks, in press).

## Carbon-13

Carbon-13 is a stable isotope of carbon. Processes that affect its composition ($\delta^{13}$C) in groundwater include carbonate mineral dissolution and precipitation, microbially mediated processes that oxidize organic carbon and generate carbon dioxide ($CO_2$), and mixing of waters (Sacks and Tihansky 1996). It is often used to identify the possible reactions which occur along a flow path. It is also used to correct the $^{14}$C concentration for the addition of $HCO_3$ resulting from limestone dissolution. Limestone dissolution results in the addition of dead carbon to the system. Dead carbon does not contain any $^{14}$C. By adding dead carbon to the system, the $^{14}$C concentration is diluted, which, if uncorrected, would yield an older calculated age for the sample. A general equation for carbonate dissolution is:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \qquad \textbf{(4)}$$

Values of $\delta^{13}$C depend on the source of the carbon. Organically derived carbon ($CO_2$ and organic matter) tends to be light, with $\delta^{13}$C values averaging about –25‰ (Deines et al. 1974). Dissolution of carbonate minerals ($\delta^{13}$C averages about 1‰; Phelps 2001) adds heavier $^{13}$C to the system. According to Equation 4, calcite

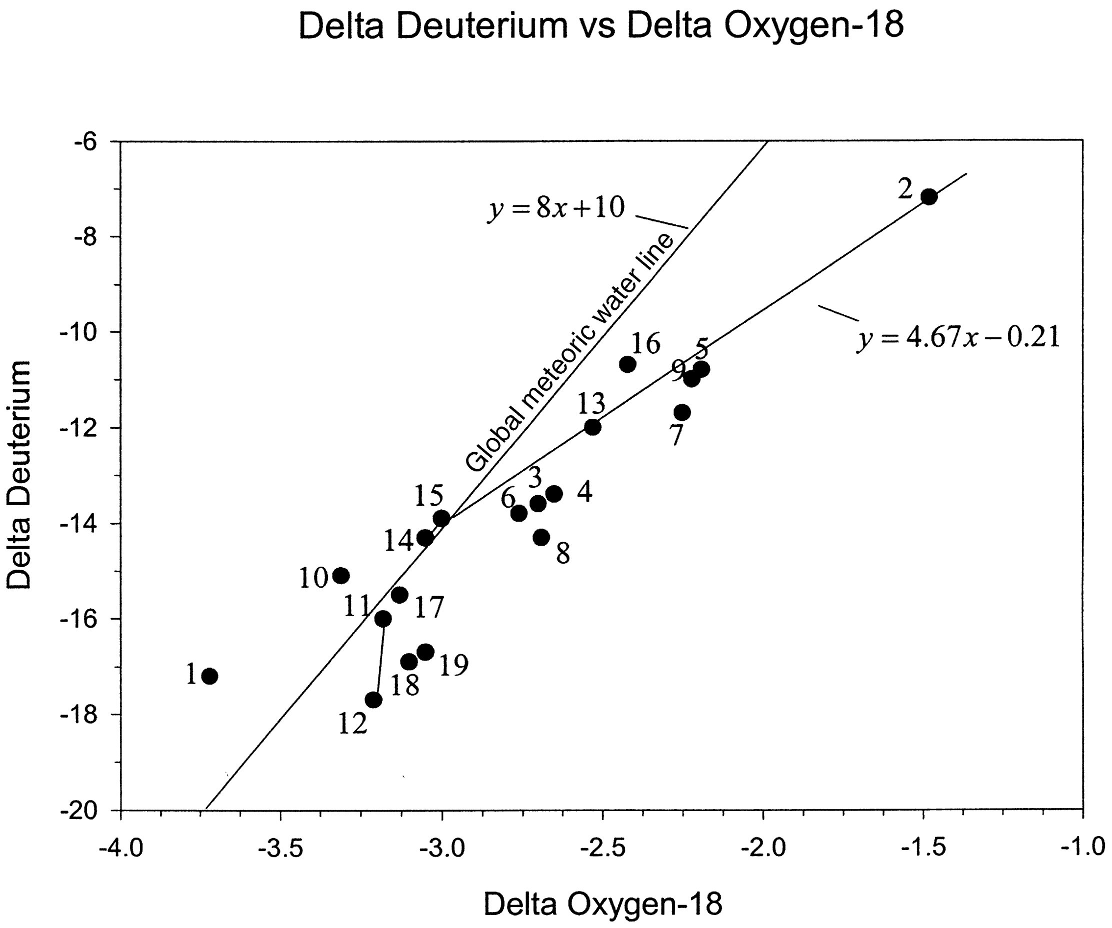


Figure 14. Relationship between delta-deuterium and delta-oxygen-18 for samples analyzed in this study (see Table 4 for spring names and numbers)

having a $\delta^{13}C$ value of 1‰ reacting with $CO_2$ having a $\delta^{13}C$ value of –25‰ would produce a $\delta^{13}C$ value of –12‰.

The $\delta^{13}C$ values for the springs sampled in this study ranged from –11.41 at Wadesboro Spring to –7.01 at Satsuma Spring (Table 4 and Figure 15). For most of the samples, $\delta^{13}C$ ranged between –10.3‰ and –8.40‰. The generally heavier (less negative) $\delta^{13}C$ values indicate that a larger proportion of the dissolved inorganic carbon was derived from carbonate minerals. The difference between duplicate samples at Silver and Welaka springs indicates the precision of the analyses. The $\delta^{13}C$ values for Silver and Welaka springs and their duplicates differ by 0.01‰ and 0.24‰, respectively. For comparison, the $\delta^{13}C$ values for 17 springs in east-central Florida ranged from –10.86‰ to –5.22‰ (Toth 1999).

The $\delta^{13}C$ values in west-central Florida in the Upper Floridan aquifer were less than –8‰ in recharge areas and greater than –5‰ in discharge areas and generally increased with depth in the aquifer (Sacks and Tihansky 1996). The $\delta^{13}C$ value in the Keystone Heights recharge area was –12‰ (Plummer 1997).

## Nitrogen-15

Nitrogen-15 is a stable isotope of nitrogen. It is generally used to identify sources of nitrate contamination (e.g., synthetic fertilizers versus animal wastes) or to document oxidation and reduction reactions involving nitrogen species (e.g., denitrification). In this study, it will be used to identify possible sources of nitrate contamination.

The $\delta^{15}N$ value of nitrate has been used to identify the source of nitrate contamination (Heaton 1986). Low $\delta^{15}N$ values (0–3‰) generally indicate an inorganic nitrate source (artificial or synthetic fertilizer), whereas higher $\delta^{15}N$ values (above 10‰) typically indicate an organic source of nitrate (animal waste or sewage). Values of $\delta^{15}N$ that fall between 3 and 10‰ likely are indicative of mixed inorganic and organic sources of nitrate (Katz et al. 1999).

As stated previously, nitrate concentrations above 0.2 mg/L are considered elevated. Nitrogen-15 was determined on all samples where the nitrate concentration was above 0.2 mg/L. Springs where the nitrate concentration is above 0.2 mg/L are Apopka, Bugg, Silver, Blue at Yalaha, and Holiday (Table 2).

The $\delta^{15}N$ value of nitrate for all samples analyzed in this study is positive. It ranges from 4.3 at Apopka Spring to 8.7 at Silver Springs (Table 4).

Table 4. Stable and radioactive isotope values for samples collected in this study

| Site No. | Site Name | Delta-deuterium (‰) | Delta-oxygen-18 (‰) | $Strontium^{87}/strontium^{86}$ | Delta-carbon-13 (‰) | Carbon-14 (pmc) | Delta-sulfur-34 (‰) | Tritium (TU) | Delta-nitrogen-15 (‰) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Fern Hammock Springs | -17.2 | -3.72 | 0.70797 | -8.40 | 26.00 | 17.6 | 2.45 | |
| 2 | Clifton Springs | -7.2 | -1.48 | 0.70802 | -9.40 | 22.90 | 22.3 | 0.11 | |
| 3 | Green Springs | -13.6 | -2.70 | 0.70806 | -9.90 | 49.10 | 20.1 | 2.48 | |
| 4 | Miami Springs | -13.4 | -2.65 | 0.70801 | -10.3 | 35.70 | 14.6 | 1.35 | |
| 5 | Green Cove Spring | -11.0 | -2.22 | 0.70780 | -7.32 | 4.97 | 21.0 | 0.00 | |
| 6 | Apopka Spring | -13.8 | -2.76 | 0.70843 | -9.20 | 35.00 | 4.9 | 2.73 | 4.3 |
| 7 | Island Spring | -11.7 | -2.25 | 0.70790 | -8.45 | 22.99 | 21.4 | 0.55 | |
| 8 | Bugg Spring | -14.3 | -2.69 | 0.70810 | -9.95 | 41.75 | 8.6 | 2.44 | 7.0 |
| 9 | Orange Spring | -10.8 | -2.19 | 0.70794 | -9.93 | 22.12 | 33.6 | 0.09 | |
| 10 | Wadesboro Spring | -15.1 | -3.31 | 0.70866 | -11.41 | 51.87 | 11.0 | 2.85 | |
| 11 | Welaka Spring | -16.0 | -3.18 | 0.70802 | -8.95 | 38.19 | 19.6 | 2.91 | |
| 12 | Welaka Spring (duplicate) | -17.7 | -3.21 | 0.70798 | -9.19 | 39.43 | 19.8 | 2.74 | |
| 13 | Beecher Springs | -12.0 | -2.53 | 0.70811 | -8.98 | 43.71 | 15.7 | 2.64 | |
| 14 | Silver Springs | -14.3 | -3.05 | 0.70783 | -10.00 | 46.98 | 18.5 | 3.51 | 8.7 |
| 15 | Silver Springs (duplicate) | -13.9 | -3.00 | 0.70784 | -10.01 | 47.12 | 18.5 | 3.33 | 8.5 |
| 16 | Satsuma Spring | -10.7 | -2.42 | 0.70798 | -7.01 | 19.88 | 22.1 | 0.85 | |
| 17 | Mud Spring | -15.5 | -3.13 | 0.70797 | -8.98 | 33.51 | 19.3 | 2.69 | |
| 18 | Blue Springs at Yalaha | -16.9 | -3.10 | 0.70809 | -8.97 | 34.72 | 1.1 | 2.38 | 4.5 |
| 19 | Holiday Springs | -16.7 | -3.05 | 0.70812 | -9.35 | 34.09 | 3.3 | 2.60 | 4.4 |

Note: Blank cells signify not measured

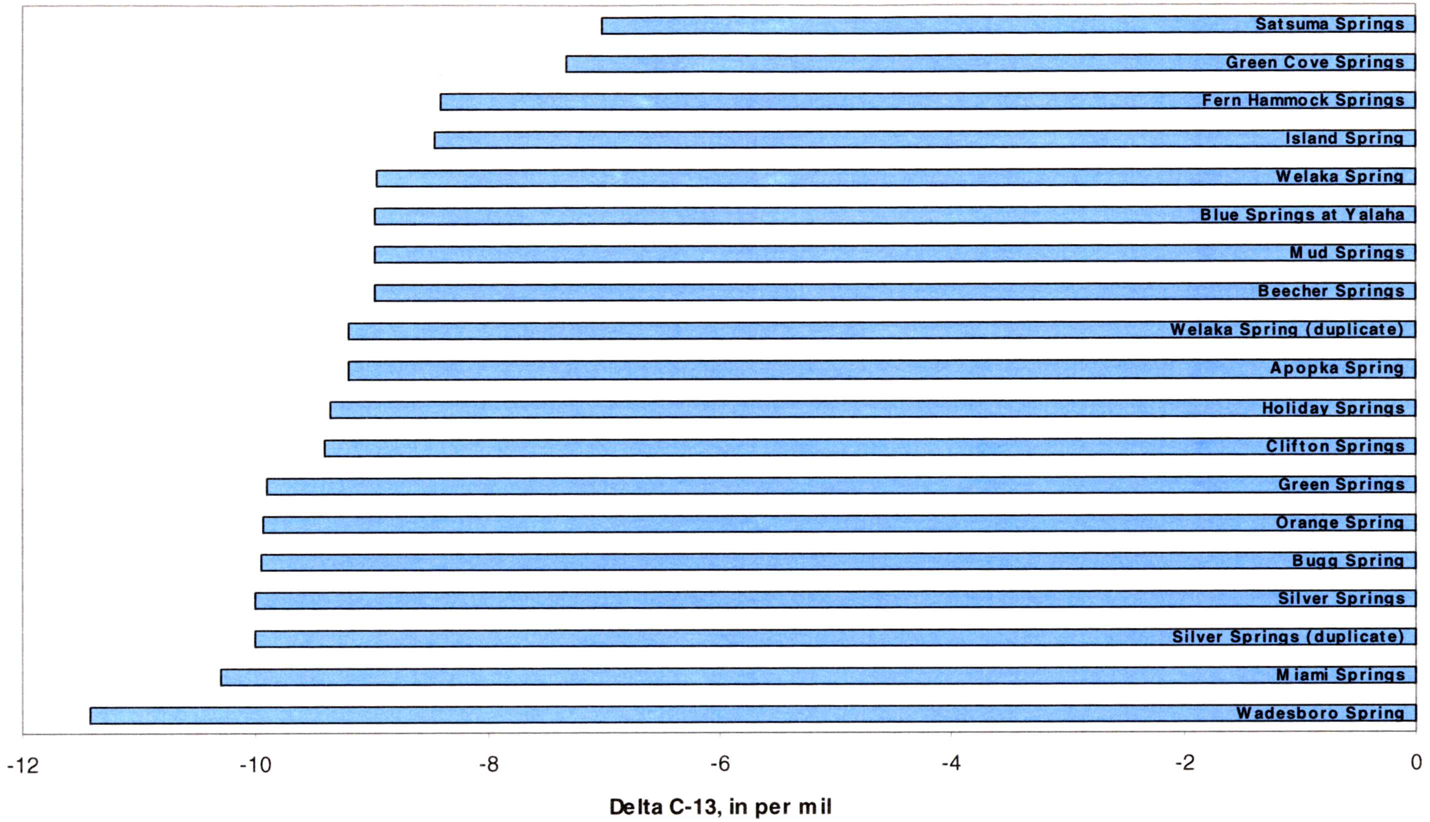


Figure 15. Distribution of delta-carbon-13 values for samples collected in this study

On the basis of the above discussion, it can be concluded that the elevated nitrate levels in Apopka, Bugg, Silver, Blue at Yalaha, and Holiday springs are probably due to contamination by a mixture of synthetic fertilizers and animal waste or sewage. Apopka, Blue at Yalaha, and Holiday springs have the lowest $\delta^{15}N$ values and are probably the springs most influenced by synthetic fertilizers. These springs also have the highest nitrate nitrogen concentrations (Table 2).

## Sulfur-34

Sulfur-34 is a stable isotope of sulfur. It is generally used to evaluate the sources of sulfur in groundwater and to test various geochemical reaction models along a flow path. Sulfur-34 and $^{13}C$ isotope data are often used to eliminate one or more reaction models. Possible sources of sulfur in groundwater are atmospheric precipitation, gypsum or celestite dissolution, and seawater. Atmospheric sulfur and most fresh waters have sulfur isotopic compositions ranging from 0 to about +15‰ (Long et al. 1988). The sulfur isotope composition of rainwater in north-central Florida ranged from 3.4 to 5.9‰ (Katz et al. 1995). For comparison, the $\delta^{34}S$ value of contemporary dissolved oceanic sulfate and modern sulfate evaporite minerals is +20‰ (Coplen 1993).

If the source of sulfur in groundwater is from dissolution of sulfate minerals in the aquifer, the isotopic composition would reflect the composition of the various minerals. Evaporites from the middle semiconfining unit of the Floridan aquifer system in southwestern Florida had an average $\delta^{34}S$ value of 23.4‰. Gypsum from the Lower Floridan aquifer and the lower confining unit had lighter values, averaging 20.1‰ (Sacks and Tihansky 1996).

The sulfur isotopic composition cannot be used to differentiate ancient from modern seawater. In fact, the $\delta^{34}S$ of seawater probably has not changed substantially since the middle Miocene, about 15 million years ago (Claypool et al. 1980).

The $\delta^{34}S$ values for samples collected during this study ranged from 1.07‰ at Blue Springs at Yalaha to 33.6‰ at Orange Spring (Table 4). The light values at Apopka Spring (4.90‰), Holiday Springs(3.29‰), and Blue Springs at Yalaha (1.07‰) probably indicate an atmospheric source for the sulfur, more fresh recharge water, or oxidation of reduced S, such as $FeS_2$. The sulfate concentration at these springs was 10 mg/L (Table 2). The $\delta^{34}S$ value for springs with a sulfate concentration at or above 28 mg/L is at or above 18.49‰ (compare Tables 2 and 4; see also Figure 16). Springs in this category are Clifton Springs, Green Springs, Green Cove Spring, Island Spring, Welaka Spring, Silver Springs, Satsuma

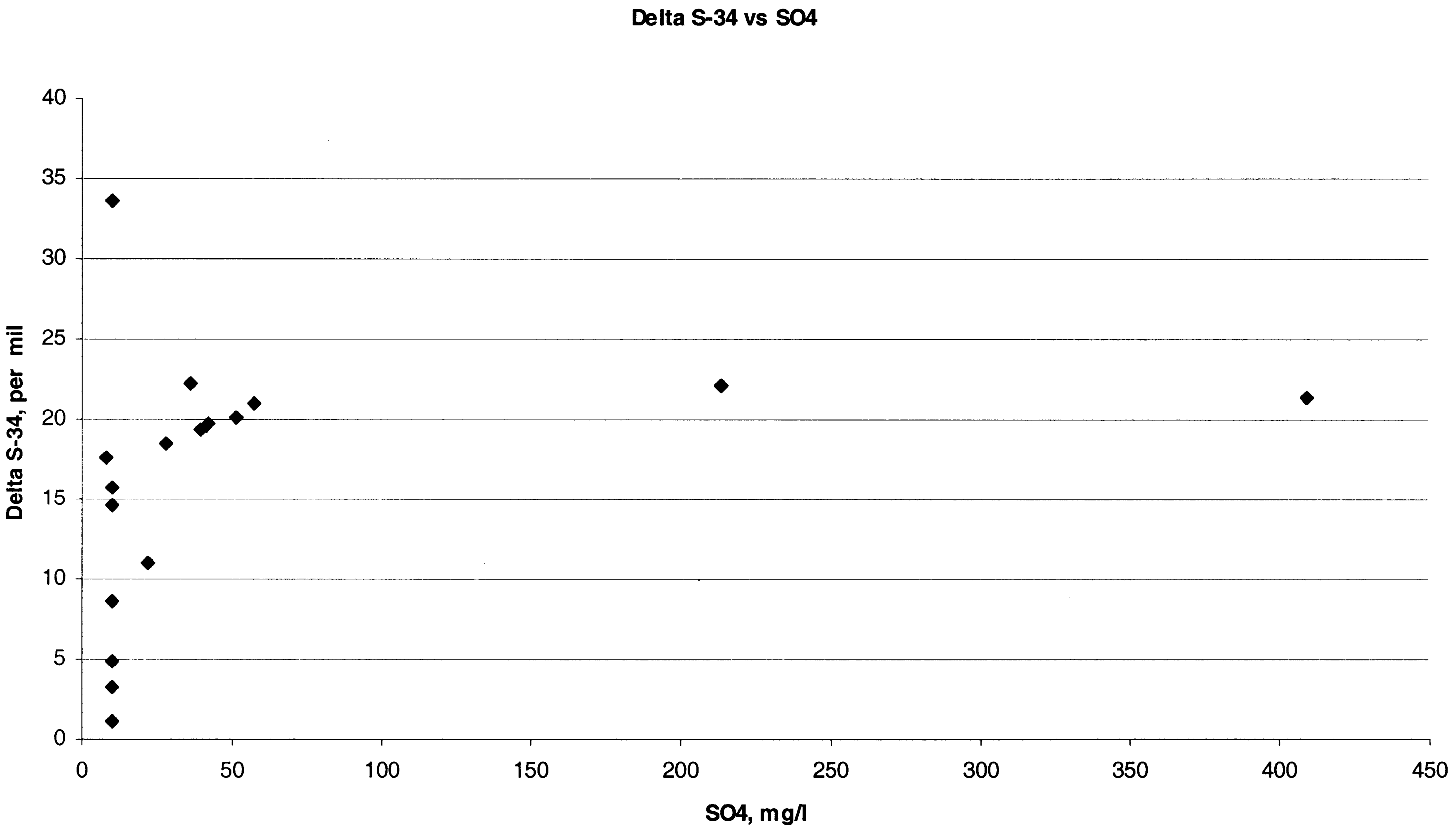


Figure 16. Relationship between delta-sulfur-34 and $SO_4$ for samples collected in this study

Spring, and Mud Spring. These values are near those for modern sulfate evaporite minerals (+20‰). For comparison, the median $\delta^{34}$S value for groundwater samples from the Upper Floridan aquifer in northeast Florida was 23.5‰, with values ranging from 16.9 to 28.2‰ (Phelps 2001). Toth (1999) reported $\delta^{34}$S values for 17 springs in east-central Florida of 5.7 to 21.0‰.

Orange Spring had the highest $\delta^{34}$S value (33.6). It also had one of the lowest concentrations of sulfate (10 mg/L). This suggests that sulfate in groundwater at Orange Spring was altered by bacterial sulfate reduction. A sulfur odor was noted while sampling.

## Strontium-87

Strontium-87 is a radiogenic isotope of strontium. It is produced by the radioactive decay of rocks rich in rubidium-87. Strontium-87 is normally reported as a ratio of strontium-87 to strontium-86, $^{87}$Sr/$^{86}$Sr. This ratio is a good tracer in the hydrologic cycle because strontium obtains its isotopic ratio by dissolution of or exchange with strontium-bearing minerals along a flow path. During the Tertiary period, the $^{87}$Sr/$^{86}$Sr values of marine carbonates were distinctive. The $^{87}$Sr/$^{86}$Sr value increases as the age decreases. Limestones in the Floridan aquifer system from the Paleocene epoch have $^{87}$Sr/$^{86}$Sr values between 0.7076 and 0.70775 and from the Eocene epoch, $^{87}$Sr/$^{86}$Sr values between 0.70775 and 0.7079. Limestones from the Oligocene epoch have $^{87}$Sr/$^{86}$Sr values between 0.7079 and 0.7083, and limestones from the Miocene epoch have $^{87}$Sr/$^{86}$Sr values above 0.7083. For comparison, present-day seawater has a $^{87}$Sr/$^{86}$Sr value of 0.70925 (Kendall et al. 1995). The Floridan aquifer system consists of Eocene-age and Paleocene-age limestones (Table 1).

There are two possible sources for strontium in the springs sampled in this study. First, strontium can come from the dilution of seawater, as evidenced by the linear relation between log(strontium concentration) and log(chloride concentration) (Figure 17). Second, strontium can come from the dissolution of strontium-bearing minerals, as evidenced by the samples above this linear trend. These samples are enriched in strontium because they lie above the linear trend. The chloride concentration in these springs is low, less than 17 mg/L—the log(chloride concentration) for these springs is below 1.5. All springs are undersaturated with respect to celestite (strontium sulfate) and strontianite (strontium carbonate), common strontium-bearing minerals in the Floridan aquifer.

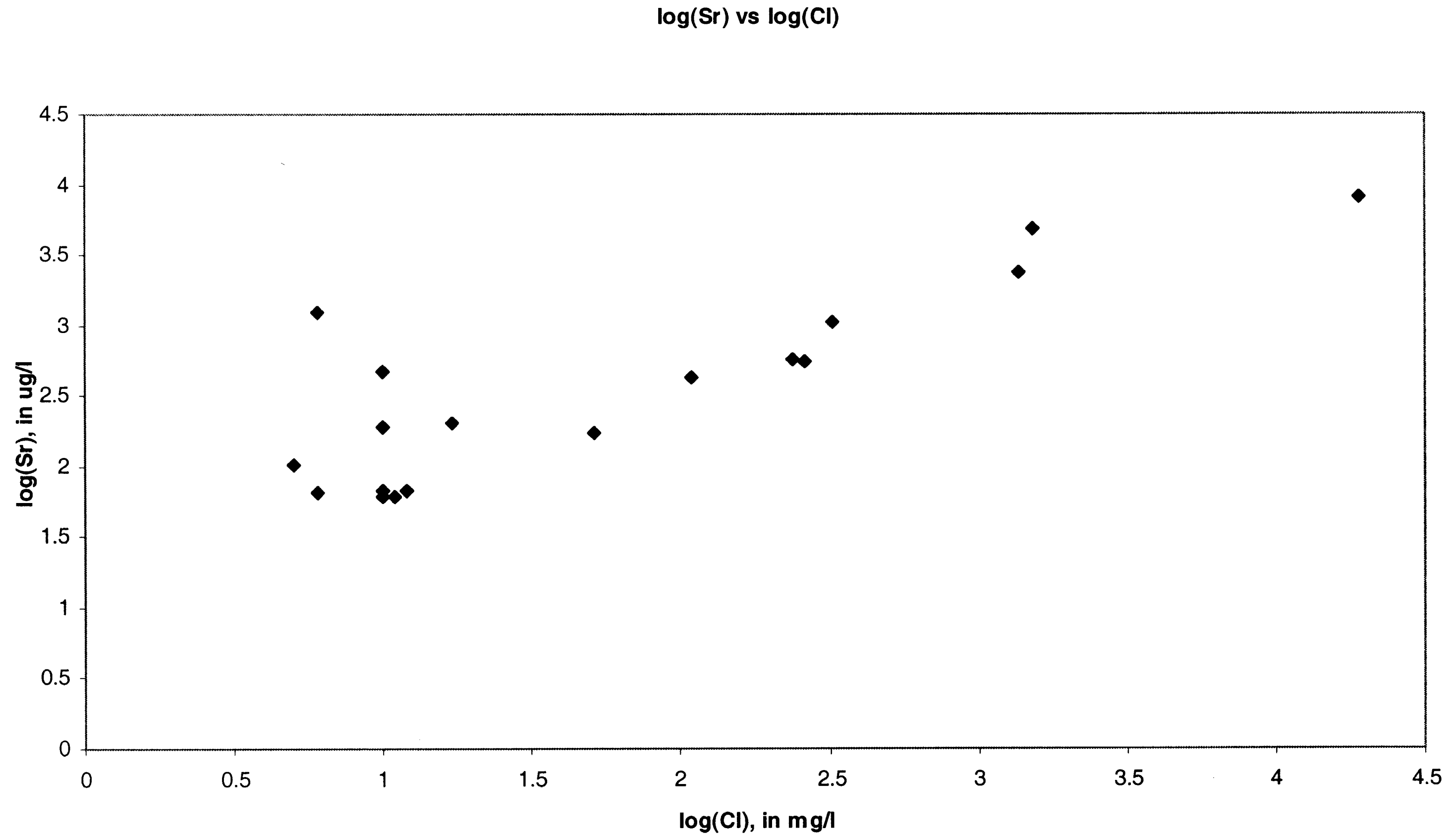


Figure 17. Relationship between log(strontium concentration) versus log(chloride concentration)

The $^{87}Sr/^{86}Sr$ values for the samples collected during this study ranged from 0.70780 at Green Cove Spring to 0.70866 at Wadesboro Spring (Table 4, Figure 18). Based on the $^{87}Sr/^{86}Sr$ values, water from Green Cove Spring and Silver Springs appears to be in equilibrium with Eocene-age limestones. Water from Island Spring has a $^{87}Sr/^{86}Sr$ value of 0.70790. This ratio lies at the boundary between the Eocene and Oligocene epochs. Water from a majority of the samples appears to be in equilibrium with Oligocene-age limestones. Water from Apopka Spring and Wadesboro Spring appears to be in equilibrium with Miocene-age limestones.

However, the young age (Miocene and Oligocene) for most of the water from springs suggests that the water is not in equilibrium with the Eocene-age limestones in the Floridan aquifer system. In fact, there are no Oligocene-age limestones in the study area (Miller 1986). Most springs are located within 4 miles of high recharge areas. This short distance between recharge and discharge areas may not allow sufficient time for the water in the Floridan aquifer system to reach equilibrium. Water from the recharge areas dissolve post-Miocene-age sediments overlying the Floridan aquifer system. This water then enters the Floridan aquifer system. The Oligocene age for most of the samples is assumed to result from a mixing of waters with strontium signatures from the post-Miocene and Eocene ages. All of the springs sampled are undersaturated with respect to calcite, a common mineral in the rocks of the Floridan aquifer system. Undersaturation with respect to calcite supports the conclusion that water from the Floridan aquifer system at most springs is not in equilibrium (calcite saturation was determined for all samples using NETPATH [Plummer et al. 1994]).

The scatter of the samples in Figure 17 supports the mixing hypothesis presented above. Mixing is occurring between many different source waters (for example, strontium from relict seawater, strontium from recharge waters, or strontium from limestones of Eocene age).

The young age of the strontium for the majority of these springs suggests that the springs have a shallow flow system. Age can be equated with depth. Springs with an Eocene age have deeper flow systems than those with an Oligocene age. Also, shallow flow systems have a smaller area of influence than deeper flow systems.

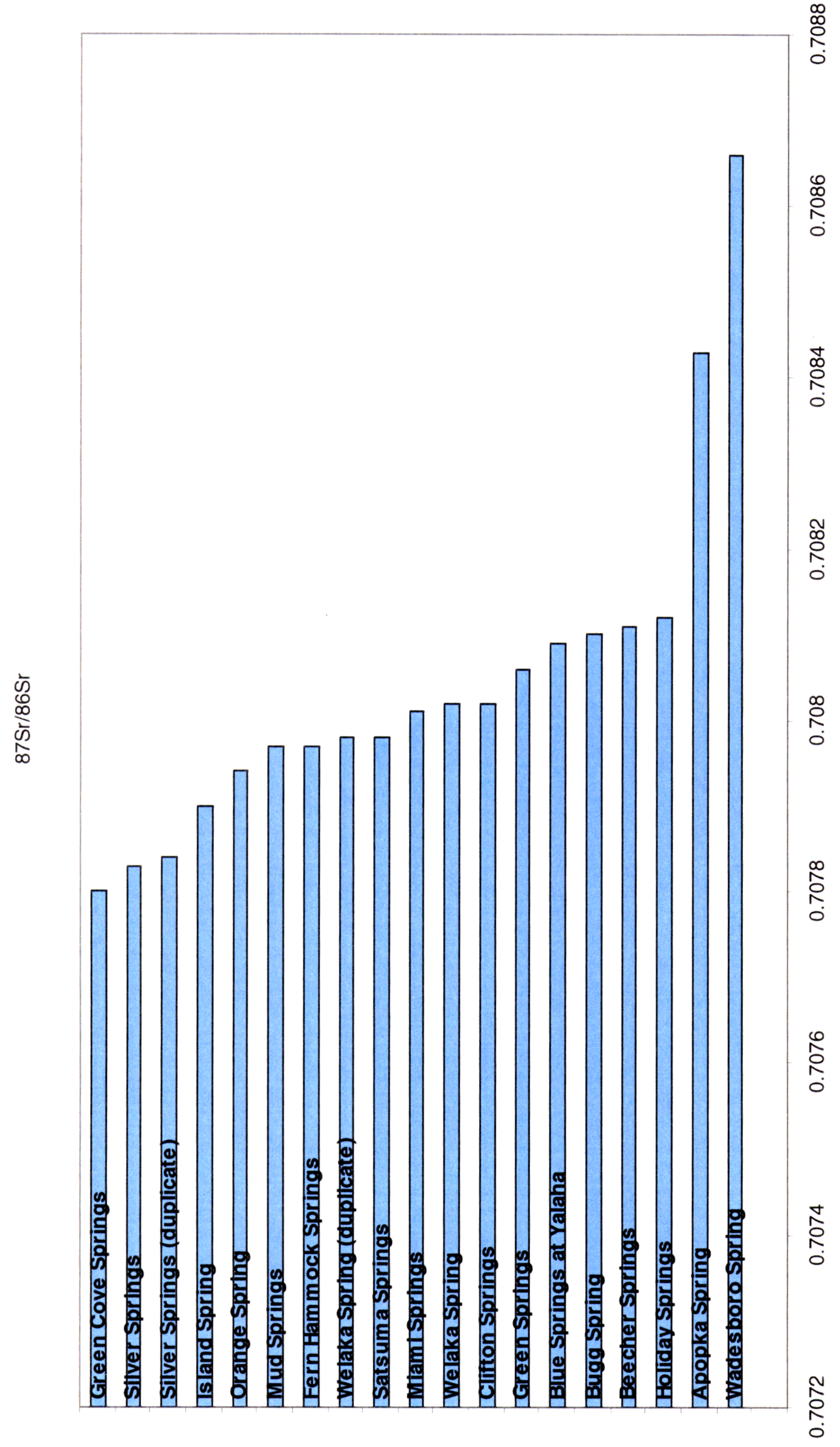


Figure 18. Distribution of strontium-87/strontium-86 values for samples collected in this study

## RADIOACTIVE ISOTOPES

In this study, the age of groundwater is determined by measuring the radioactive isotopes $^3$H and $^{14}$C. Tritium was used because it can identify water that is less than 70 years old (Swancar and Hutchinson 1992). Carbon-14 was used because it can identify water that is less than 50,000 years old (Coplen 1993).

Half-life is a fundamental property of radioactive isotopes. Half-life is a measure of decay rate (the time for a concentration of the isotope to decrease by one-half) and is unique for each radioactive isotope. The longer the half-life, the older the age that can be determined; the half-life of an isotope determines its utility as a measure of the age of groundwater.

### Tritium

Tritium ($^3$H) is a radioactive isotope of hydrogen which is produced naturally in small amounts by the interaction of cosmic rays with the earth’s atmosphere. Cosmogenic $^3$H enters groundwater by way of rainfall at a concentration of approximately 3–5 tritium units (TU—a tritium unit is one $^3$H atom in $10^{18}$ atoms of hydrogen, or 3.2 picocuries/liter) (Kaufman and Libby 1954; Robertson and Cherry 1989). With the onset of atmospheric nuclear testing in 1953, the $^3$H concentration in rainfall began to increase. At Ocala, Florida, the $^3$H concentration in rainfall increased to as high as 700 TU in 1963 (Katz et al. 1995). In 1988, the $^3$H concentration in rain at Ocala was not measurably different from the estimated pre-1953 concentration (Katz et al. 1995). Because of the difference in $^3$H concentration in rainwater before and after 1953, $^3$H has been used as a hydrologic tracer to age-date recent groundwater (Coplen 1988). The half-life of $^3$H is 12.43 years, which means that the $^3$H concentration decreases by a half every 12.43 years.

In this study, no $^3$H was detected in the sample from Green Cove Spring. For the remainder of the samples, $^3$H concentrations ranged from 0.09 TU at Orange Spring to 3.51 TU at Silver Springs (Table 4, Figure 19.). The $^3$H concentration in most springs was above 1.00 TU. Similar findings reported in Toth (1999) indicated that the $^3$H concentration in most springs was above 1.00 TU. This suggests that most springs contain young water derived from rapid recharge waters of a more localized groundwater flow system.

Except for Green Cove Spring, Orange Spring, and Clifton Springs, the $^3$H concentration of all samples was above 0.32 TU. Tritium concentrations above 0.32 TU are assumed to be appreciable and represent samples that were

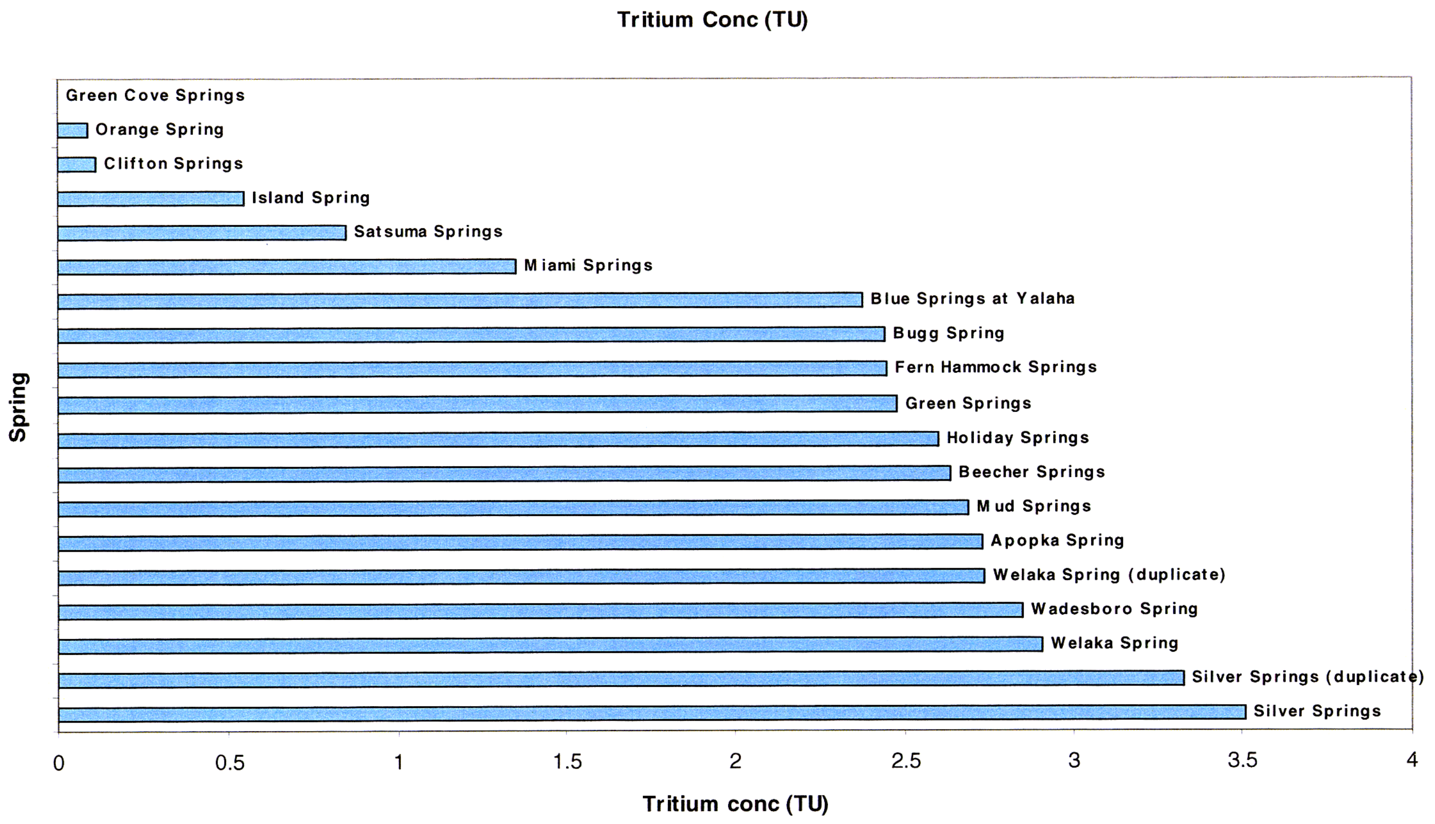


Figure 19. Distribution of tritium values for samples collected in this study. Samples without tritium values represent old water.

recharged after 1953. (Assuming a pre-1953 $^3$H concentration of 5.00 TU, decay of four half-lives of about 50 years yields 0.32 TU.) Because of the variability in the $^3$H concentration of rainfall with time since 1953, a more precise age could not be determined. The three samples where the $^3$H concentration was below 0.32 TU, however, were most likely recharged with water prior to 1953. The samples with $^3$H concentrations of 0.11 and 0.09 TU are probably 75 years old. The sample with no $^3$H is probably older than 75 years.

The young age for many of the samples confirms that the flow system for many of the springs is shallow. Conduit/fracture flow may predominate in springs with high $^3$H, whereas flow through porous medium may occur in springs where the $^3$H concentration is low (below 1.00 TU).

## Carbon-14

Carbon-14 is a radioactive isotope of carbon formed by the reaction between cosmic rays and nitrogen in the atmosphere. Carbon-14 combines with oxygen to form $CO_2$, which is taken up by plants or absorbed by rain and is found in surface water bodies. When plants, animals, and groundwater are no longer exposed to atmospheric $CO_2$, the $^{14}$C content begins to decline through radioactive decay. The radiocarbon content of groundwater decreases at a rate equal to the half-life of $^{14}$C, which is 5,730 years (Plummer et al. 1994). Therefore, water that has been underground for an extended period of time will have a lower concentration of $^{14}$C than will water that has only recently entered the ground.

The measured $^{14}$C content of groundwater is expressed as a percentage of the modern $^{14}$C content of groundwater, or percent modern carbon (pmc). Because the content of $^{14}$C in the atmosphere increased after 1953, the base year for modern $^{14}$C is 1950. The standard for modern $^{14}$C represents 95% of the activity (reactive concentration) of oxalic acid, as measured by the National Institute of Standards and Technology (Coplen 1993).

The $^{14}$C content of samples collected during this study ranged from 4.97 pmc for a sample from Green Cove Spring to 51.87 pmc at Wadesboro Spring (Table 4, Figure 20). The $^{14}$C content for most springs is above 20 pmc. In general, the higher the $^{14}$C content of the sample, the younger the water.

The $^{14}$C content of samples collected during this study is inversely related to the $\delta^{13}$C content of the samples (Figure 21), but proportional to the $^{87}$Sr/$^{86}$Sr ratio (Figure 22). Samples with high concentrations of $\delta^{14}$C have lighter (more

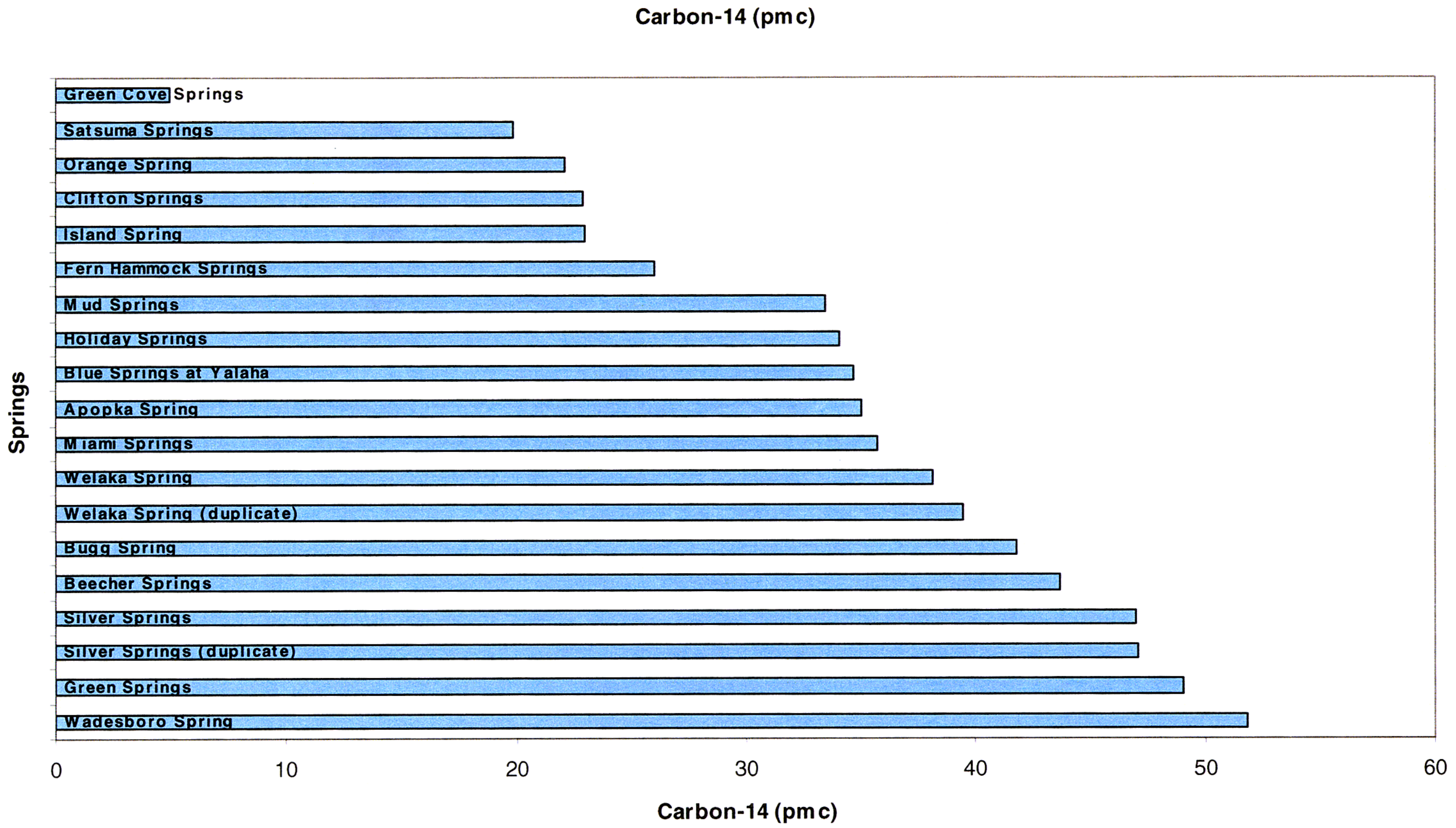


Figure 20. Distribution of carbon-14 values for samples collected in this study. Samples are arranged in descending order: oldest samples are at the top and youngest samples are at the bottom.

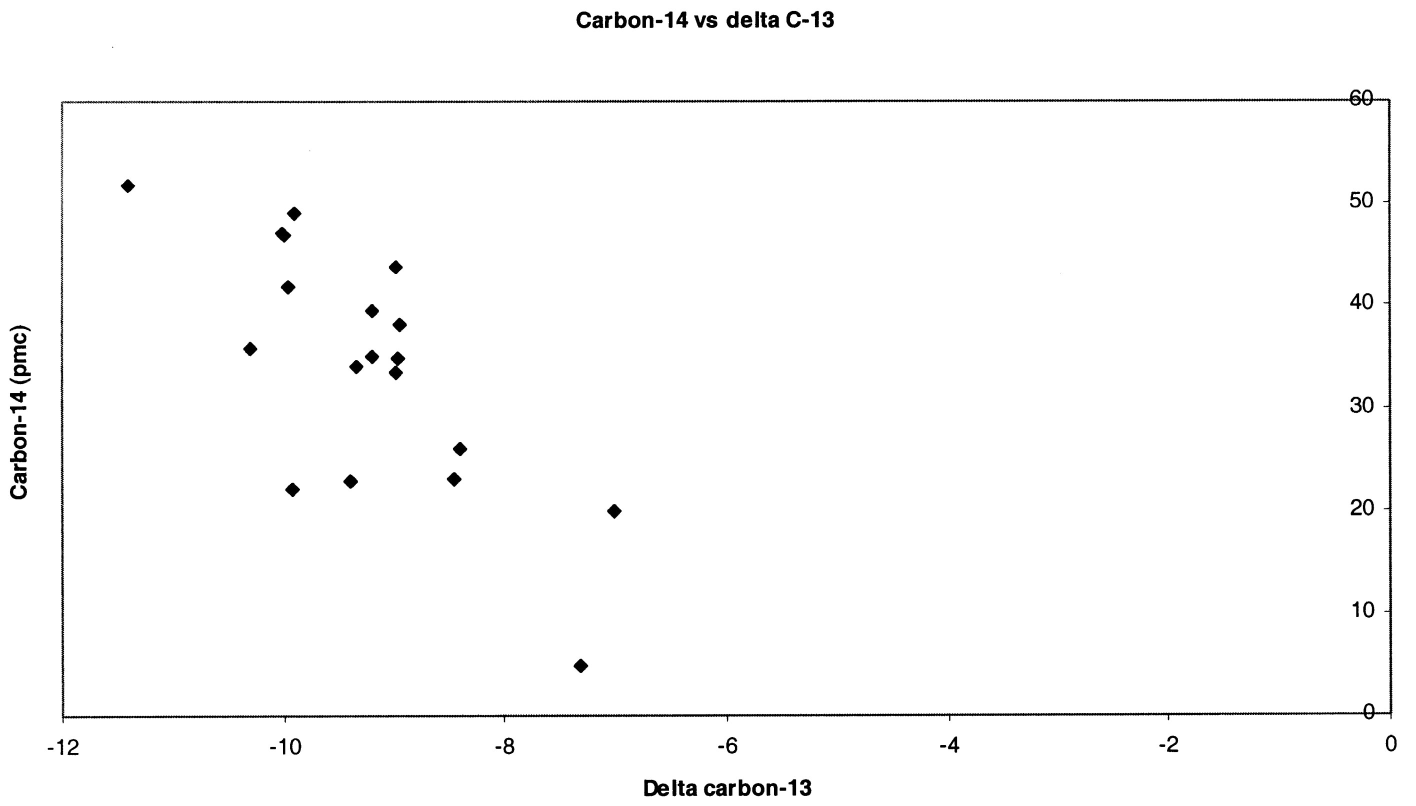


Figure 21. Plot of carbon-14 versus delta-carbon-13 for samples collected in this study

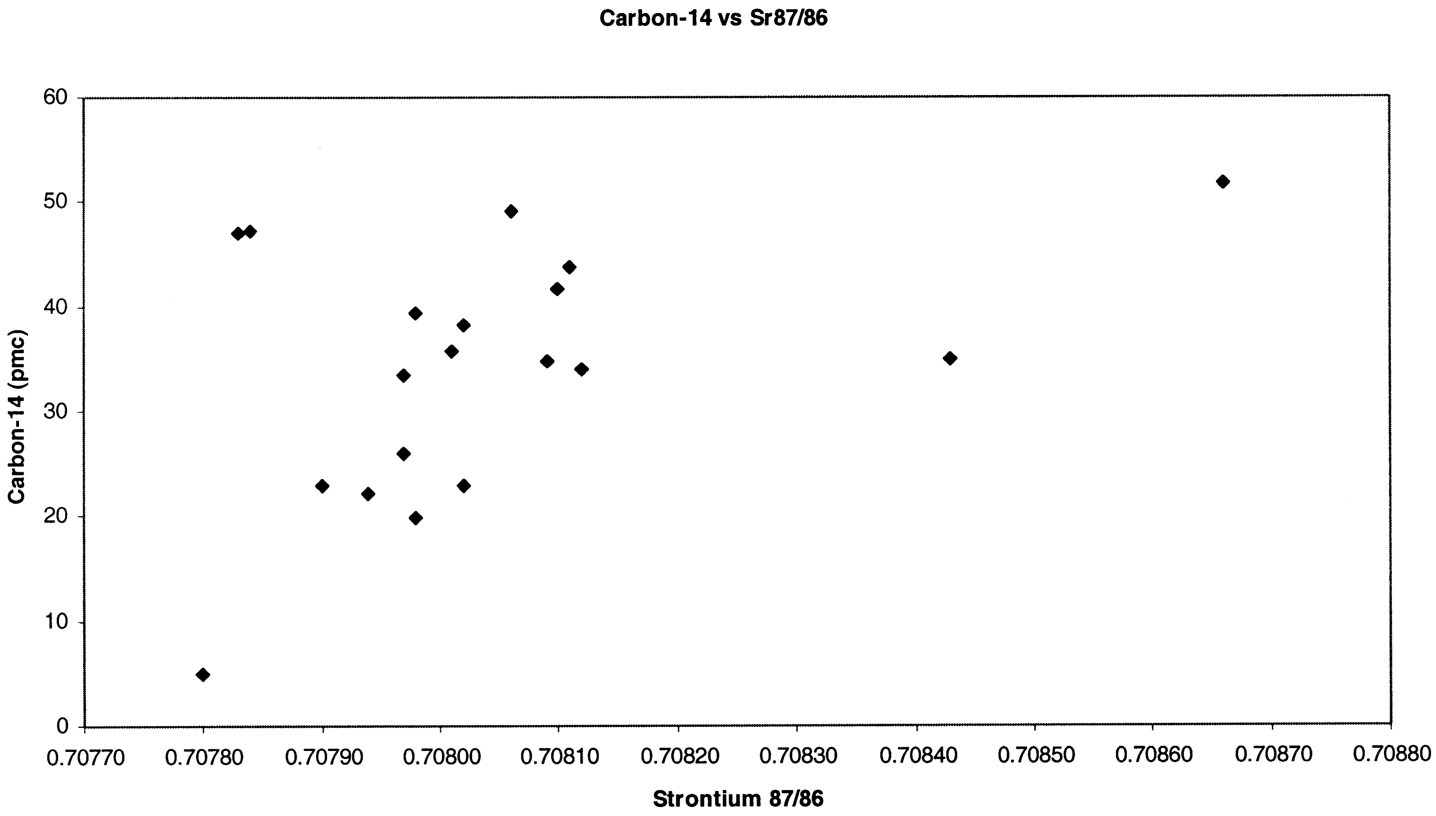


Figure 22. Plot of carbon-14 versus strontium-87/strontium-86 for samples collected in this study

negative) values of $\delta^{13}C$ than those with low concentrations of $^{14}C$. This relationship may be due to the fact that samples with high concentrations of $^{14}C$ are younger and are therefore closer to recharge areas, while samples with low concentrations of $^{14}C$ are older and are more distant from recharge areas. Landmeyer and Stone (1995) noted a similar relationship for samples from the Upper Floridan aquifer on and around Hilton Head Island. Toth (1999) noted a similar relationship for springs in east-central Florida.

The proportional trend between $^{14}C$ and $^{87}Sr/^{86}Sr$ (Figure 22) supports the conclusion that samples with a high value for $^{87}Sr/^{86}Sr$ are generally younger than those with a low value. The two samples from Silver Springs are the exception. Samples from this spring have low values for $^{87}Sr/^{86}Sr$ but relatively high values for $^{14}C$.

# AGE

Two different ages were determined for groundwater samples collected during this study: a tritium age and a carbon-14 age.

## TRITIUM AGE

The $^3H$ age for the samples can be obtained by subtracting 1953 from the last year samples were collected. Except for samples from Green Cove, Orange, and Clifton springs, the $^3H$ concentration suggests that all samples contain post-1953 water. Samples were collected in 2001. Hence the $^3H$ age for most samples would be 2001 – 1953, or less than 48 years old. The sample from Green Cove Spring, which contains no $^3H$, is older than 75 years. The $^3H$ age for samples from Orange and Clifton springs is probably about 75 years old because the $^3H$ concentration of these springs is greater than 0 and less than 0.32 TU.

## CARBON-14 AGE

Because most of the samples collected in this study had measurable $^3H$, they also contain $^{14}C$ arising from atmospheric testing of atomic bombs. However, because the $^3H$ content of all samples is low, bomb $^{14}C$ is assumed to be low. No attempt was made to correct for bomb $^{14}C$. The presence of bomb $^{14}C$ means the true age is older than that calculated.

Two different models were used to calculate the $^{14}C$ age for each sample: the Tamers (1967, 1975) model and a Fontes and Garnier (1979) model (Table 5). The Tamers (1967, 1975) model is for a system closed to $CO_2$. It represents the age for a confined aquifer. The Fontes and Garnier (1979) model is for a system open to $CO_2$. It represents the age for a leaky aquifer or an aquifer near a recharge area.

There is quite a large difference between the ages calculated by each model. The $^{14}C$ ages for each sample were calculated using NETPATH (Plummer et al. 1994). The age represents the time since water from each spring was last in contact with the atmosphere and is given relative to 1950.

The $^{14}C$ ages calculated using the Tamers (1967, 1975) model ranged from 1,824 years before 1950 for Green Springs to 19,491 years before 1950 for Green Cove Spring. The $^{14}C$ age (Tamers model) for Silver Springs was about 2,800 years, for Apopka Spring about 3,700 years, for Orange Spring about 7,400 years, and for Island Spring about 8,200 years before 1950.

Table 5. Calculated carbon-14 ages before 1950 for samples collected in this study

| Site No. | Site Name | Carbon-14 Age | |
|---|---|---|---|
| | | Tamers (1967, 1975) | Fontes and Garnier (1979) |
| 1 | Fern Hammock Springs | 5,531 | 1,985 |
| 2 | Clifton Springs | 7,474 | 3,953 |
| 3 | Green Springs | 1,824 | <50 |
| 4 | Miami Springs | 3,868 | 1,065 |
| 5 | Green Cove Spring | 19,491 | 14,397 |
| 6 | Apopka Spring | 3,717 | 274 |
| 7 | Island Spring | 8,184 | 2,932 |
| 8 | Bugg Spring | 2,248 | <50 |
| 9 | Orange Spring | 7,380 | 4,727 |
| 10 | Wadesboro Spring | 2,419 | <50 |
| 11 | Welaka Spring | 3,284 | <50 |
| 12 | Welaka Spring (duplicate) | 3,020 | <50 |
| 13 | Beecher Springs | 2,541 | <50 |
| 14 | Silver Springs | 2,790 | <50 |
| 15 | Silver Springs (duplicate) | 2,765 | <50 |
| 16 | Satsuma Spring | 8,727 | 2,507 |
| 17 | Mud Spring | 4,093 | 423 |
| 18 | Blue Springs at Yalaha | 3,950 | 99 |
| 19 | Holiday Springs | 4,312 | 600 |

The $^{14}C$ ages calculated using the Fontes and Garnier (1979) model ranged from less than 50 years before 1950 for Green Springs, Bugg Spring, Wadesboro Spring, Welaka Spring, Beecher Springs, and Silver Springs to 14,397 years before 1950 for Green Cove Spring. The $^{14}C$ age (Fontes and Garnier model) for Apopka Spring is about 300 years, for Orange Spring about 4,700 years, and for Island Spring about 2,900 years before 1950.

Errors in the determination of $^{14}C$ will affect the ages calculated. Duplicate samples were collected at Silver Springs and Welaka Spring. The maximum difference in $^{14}C$ ages is about 300 years for duplicate samples from Welaka Spring (Tamers model, Table 5). To be conservative, $^{14}C$ ages could be considered to be accurate to ±150 years.

## COMPARISON OF AGES—TRITIUM VERSUS CARBON-14

Different age estimates for samples collected during this study were obtained using $^{3}H$ and $^{14}C$. Based on $^{3}H$ analyses of groundwater, the water in many samples is less than 48 years old. The $^{14}C$ analyses of samples indicate that the waters from some springs are from hundreds to thousands of years old. Because the $^{14}C$ age of the Fontes and Garnier (1979) model agree more closely with the tritium age, the Fontes and Garnier model is assumed to represent the true $^{14}C$ age. The difference between $^{3}H$ and $^{14}C$ ages indicates that the springs contain a mixture of water of different ages traveling along different flow paths. The amount of $^{3}H$ and $^{14}C$ originally in the surficial aquifer system, which recharges the Upper Floridan aquifer, has been diluted by mixing with older water from deep in the Upper Floridan aquifer. The apparent $^{14}C$ age of this water provides information about mixing.

The presence of both young water (post-1953) and old water (hundreds to thousands of years old) suggests that the flow systems are complex for many of the springs in the study area.

The flow system and the area of contribution for the springs sampled in this study are inferred from the $^{14}C$ content of the springs (Toth 1999; Table 6, Figure 23). Springs with a $^{14}C$ above 40 pmc are inferred to have a shallow flow system and a local area of contribution. Springs with a $^{14}C$ between 25 and 40 pmc are inferred to have an intermediate flow system and a subregional area of contribution. Finally, springs with a $^{14}C$ below 25 pmc are inferred to have a deep flow system and a regional area of contribution.

Table 6. Flow system and area of contribution for springs sampled in this study

| Spring | Carbon-14 (pmc) | Flow System | Area of Contribution |
|---|---|---|---|
| Fern Hammock Springs | 26.00 | Intermediate | Subregional |
| Clifton Springs | 22.90 | Deep | Regional |
| Green Springs | 49.10 | Shallow | Local |
| Miami Springs | 35.70 | Intermediate | Subregional |
| Green Cove Spring | 4.97 | Deep | Regional |
| Apopka Spring | 35.00 | Intermediate | Subregional |
| Island Spring | 22.99 | Deep | Regional |
| Bugg Spring | 41.75 | Shallow | Local |
| Orange Spring | 22.12 | Deep | Regional |
| Wadesboro Spring | 51.87 | Shallow | Local |
| Welaka Spring | 38.19 | Intermediate | Subregional |
| Welaka Spring (duplicate) | 39.43 | Intermediate | Subregional |
| Beecher Springs | 43.71 | Shallow | Local |
| Silver Springs | 46.98 | Shallow | Local |
| Silver Springs (duplicate) | 47.12 | Shallow | Local |
| Satsuma Spring | 19.88 | Deep | Regional |
| Mud Spring | 33.51 | Intermediate | Subregional |
| Blue Springs at Yalaha | 34.72 | Intermediate | Subregional |
| Holiday Springs | 34.09 | Intermediate | Subregional |

Note: pmc = percent modern carbon

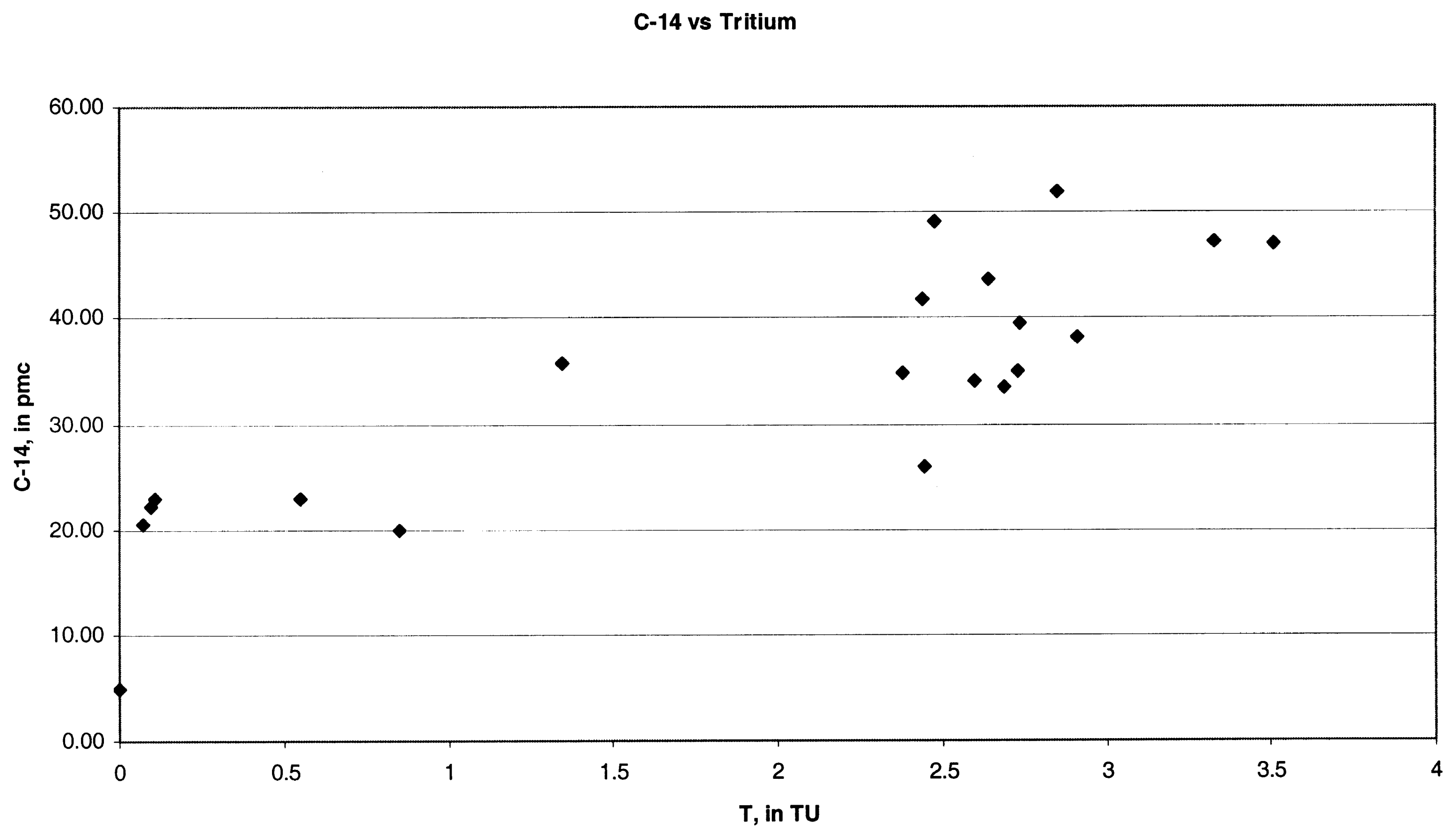


Figure 23. Carbon-14 versus tritium for springs sampled in this study

# CONCLUSION

Seventeen springs (three of which are submerged) were sampled to assess water quality and stable and radioactive isotope concentrations. The purposes of the sampling were (1) to document water quality, (2) to determine the isotopic characteristics of spring water, (3) to determine the age of spring water and to evaluate the nature of the spring flow system, and (4) to determine the source of nitrogen in springs with nitrate-nitrogen concentrations above 0.2 mg/L.

Water quality was highly variable for the springs sampled. Chloride concentrations ranged from 5 mg/L at Fern Hammock Springs to 1,520 mg/L at Island Spring. Similarly, sulfate and TDS concentrations ranged from 8 and 64 mg/L at Fern Hammock Springs to 409 and 3,020 mg/L at Island Spring. For comparison, the secondary drinking water standards (FDER 1989) for chloride, sulfate, and TDS are 250 mg/L, 250 mg/L, and 500 mg/L, respectively.

All of the sampled springs are undersaturated with respect to calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$, gypsum ($CaSO_4 \bullet 2H_2O$), and celestite ($SrSO_4$). The fact that spring waters are undersaturated with respect to the various aquifer minerals suggests that the spring waters have not had sufficient time to reach mineral equilibrium. It also suggests that the spring waters are young.

Two different ages were determined for groundwater samples collected during this study: a $^{3}$H age and a $^{14}$C age. The $^{3}$H age for most springs was less than 48 years old, but was 75 years old for two springs and greater than 75 years for one spring. Two different models were used to calculate the $^{14}$C ages: a Tamers (1967, 1975) model and a Fontes and Garnier (1979) model. There is a large difference between the $^{14}$C ages calculated by these two models. The $^{14}$C ages calculated with the Tamers (1967, 1975) model ranged from 1,824 years to 19,491 years before 1950. The $^{14}$C ages calculated with the Fontes and Garnier (1979) model ranged from less than 50 years before 1950 to 14,397 years before 1950. Because the $^{14}$C age from the Fontes and Garnier (1979) model agree more closely with the tritium age than the $^{14}$C ages from the Tamers (1967, 1975) model, the Fontes and Garnier model is assumed to represent the true $^{14}$C age.

Different age estimates for samples collected during this study indicate that the springs contain a mixture of waters of different ages representing water traveling along different flow paths. The presence of both relatively young water (post-1953) and old water (hundreds to thousands of years old) suggests that the flow systems for most of the springs in this study range from shallow to deep. However, the $^{14}C$ data indicate the relative importance of shallow, intermediate, and deep flow systems for given springs. Five springs are dominated by shallow, local flow systems, seven by intermediate subregional flow systems, and five by deep, regional flow systems. The shallow nature of the flow system also is supported by $^{87}Sr/^{86}Sr$ data.

The $\delta^{15}N$ values for the springs sampled in this study suggest that the elevated nitrate levels are due to a mixture of inorganic and organic sources. The elevated nitrate levels in Apopka, Bugg, Silver, Blue at Yalaha, and Holiday springs are probably due to contamination by a mixture of synthetic fertilizers and animal waste or sewage. Apopka, Blue at Yalaha, and Holiday springs have the lowest $\delta^{15}N$ values and are probably the springs most influenced by synthetic fertilizers. These springs also have the highest nitrate nitrogen concentrations.

# REFERENCES

Boniol, D., M. Williams, and D. Munch. 1993. *Mapping recharge to the Floridan aquifer using a geographic information system*. Technical Publication SJ93-5. Palatka, Fla.: St. Johns River Water Management District.

Claypool, G.E., W.T. Holser, I.R. Kaplan, H. Sakai, and I. Zak. 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chem. Geol.* 28:199–260.

Coplen, T.B. 1988. Environmental isotopes in groundwater studies. In *Handbook on hydrogeology*, S.C. Csallany and R.A. Kanivetsky, eds. New York: McGraw-Hill.

———. 1993. Uses of environmental isotopes. In *Regional groundwater quality*, W. Alley, ed. New York: Van Nostrand Reinhold.

Craig, H. 1961. Standard for reporting concentrations of deuterium and oxygen-18 in natural water. *Science* 133:1833–1834.

Deines, P., D.L. Langmuir, and R.S. Harmon. 1974. Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate groundwaters. *Geochimica et Cosmochimica Acta*. 38:1147–1164.

[FDER] Florida Department of Environmental Regulation. 1989. *Florida groundwater guidance concentrations.* Tallahassee, Fla.

Fontes, J.-C., and J.-M. Garnier. 1979. Determination of the initial $^{14}$C activity of the total dissolved carbon: A review of the existing models and a new approach. *Water Resources Research* 15(2):399–413.

Frazee, J.M., Jr. 1982. Geochemical pattern and analysis: Method of describing the southeastern limestone regional aquifer system. In *Studies of the hydrogeology of the southeastern United States*, B.F. Becks, ed. Special Publication 1. Americus, Ga.: Georgia Southeastern College.

Gonfiantini, R. 1981. The δ-notation and the mass-spectrometric measurement techniques. In *Stable isotope hydrology: Deuterium and oxygen-18 in the water cycle*, J.R. Gat and R. Gonfiantini, eds. International Atomic Energy Agency, Vienna, Austria 4:35–84.

Heaton, T.H.E. 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere—A review. *Chem. Geol.* 59:87–102.

Hem, J.D. 1985. *Study and interpretation of the chemical characteristics of natural water.* Water-Supply Paper 2254, 3d ed. Washington, D.C.: U.S. Geological Survey.

Hersh, C.K. 1968. Nitrogen. In *The encyclopedia of the chemical elements*, C.A. Hampel, ed. New York: Van Nostrand Reinhold.

Karst Environmental Services, Inc. 2001a. Results of discharge measurements of Lake Apopka Gourdneck Spring, Lake County, Florida; March 21, 2001. High Springs, Fla.

———. 2001b. Results of discharge measurements of Island Spring, Seminole County, Florida; March 22, 2001. High Springs, Fla.

———. 2001c. Results of discharge measurement of Welaka Spring, Putnam County, Florida; April 12, 2001. High Springs, Fla.

Katz, B.G., H.D. Hornsby, J.F. Bohlke, and M.F. Mokray. 1999. *Sources and chronology of nitrate contamination in spring waters, Suwannee River Basin, Florida.* Water Resources Investigations Report 99-4252. Tallahassee, Fla.: U.S. Geological Survey.

Katz, B.G., T.M. Lee, L.N. Plummer, and E. Busenberg. 1995. Chemical evolution of groundwater near a sinkhole lake, northern Florida: 1. Flow patterns, age of groundwater, and influence of lake water leakage. *Water Resources Research* 31(6):1549–64.

Kaufman, S., and W.F. Libby. 1954. The natural distribution of tritium. *Physical Review* 93:1337–44.

Kendall, C., B. Michel, T. Bullen, J.K. Bohlke, P. McMahon, J. Turk, and R. Wanty. 1995. Isotope hydrology (GO192)—course offered by the U.S. Geological Survey at their National Training Center in Denver, Colo.

Landmeyer, J.E., and P.A. Stone. 1995. Radiocarbon and $\delta^{13}$C values related to groundwater recharge and mixing. *Groundwater* 33(2):227–34.

Miller, J.A. 1982a. *Configuration of the base of the upper permeable zone of the Tertiary limestone aquifer system, southeastern United States.* Water-Resources Investigations Open-File Report 81-1177. Atlanta, Ga.: U.S. Geological Survey.

———. 1982b. *Thickness of the upper permeable zone of the Tertiary limestone aquifer system, southeastern United States.* Water-Resources Investigations Open-File Report 81-1179. Atlanta, Ga.: U.S. Geological Survey.

——— 1982c. *Geology and configuration of the top of the Tertiary limestone aquifer system, southeastern United States.* Water-Resources Investigations Open-File Report 81-1178. Atlanta, Ga.: U.S. Geological Survey.

———. 1986. *Hydrogeologic framework of the Floridan aquifer system in Florida and in parts of Georgia, Alabama, and South Carolina.* Professional Paper 1403-B. Washington D.C.: U.S. Geological Survey.

Murray, L.C., and K.J. Halford. 1996. *Hydrologic conditions and simulation of groundwater flow in the greater Orlando metropolitan area, east-central Florida.* Water-Resources Investigations Report 96-4181. Tallahassee, Fla.: U.S. Geological Survey.

Phelps, G.G. 2001. *Geochemistry and origins of mineralized waters in the Floridan aquifer system, northeastern Florida.* Water-Resources Investigations Report 01-4112. Tallahassee, Fla.: U.S. Geological Survey.

Plummer, L.N. 1997. Radiocarbon dating of dissolved inorganic carbon in groundwater from confined portions of the Upper Floridan aquifer, Florida. Geological Society of America Abstracts with programs 29(7):A-287.

Plummer, L.N., E.C. Prestemon, and D.L. Parkhurst. 1994. *An interactive code (NETPATH) for modeling net geochemical reactions along a flow path.* Version 2.0. Water-Resources Investigations Report 94-4169. Reston, Va.: U.S. Geological Survey.

Puri, H.S., and R.O. Vernon. 1959. *Summary of the geology of Florida and a guide to the classic exposures.* Special Publication 5. Tallahassee, Fla.: Florida Geological Survey.

Robertson, W.D., and J.A. Cherry. 1989. Tritium as an indicator of recharge and dispersion in a groundwater system in central Ontario. *Water Resources Research* 25(6):1097–1109.

Rosenau, J.C., G.L. Faulkner, C.W. Hendry Jr., and R.W. Hull. 1977. *Springs of Florida* (revised). Bulletin 31. Tallahassee, Fla.: Florida Bureau of Geology.

Sacks, L.A. Estimating ground-water inflow to lakes in central Florida using the isotope mass-balance approach. U.S. Geological Survey, Tallahassee, Fla. In press.

Sacks, L.A., and A.B. Tihansky. 1996. *Geochemical and isotopic composition of groundwater, with emphasis on sources of sulfate, in the Upper Floridan aquifer and intermediate aquifer system in southwest Florida.* Water-Resources Investigations Report 96-4146. Tallahassee, Fla.: U.S. Geological Survey.

Stringfield, V.T. 1966. *Artesian water in Tertiary limestone in the southeastern states.* Professional Paper 517. Washington D.C.: U.S. Geological Survey.

Swancar, A., and C.B. Hutchinson. 1992. *Chemical and isotopic composition and potential for contamination of water in the Upper Floridan aquifer, west-central Florida, 1986–89.* Open-File Report 92-47. Tallahassee, Fla.: U.S. Geological Survey.

Tamers, M.A. 1967. Surface-water infiltration and groundwater movement in arid zones of Venezuela. In *Isotopes in Hydrology*. International Atomic Energy Agency: Vienna, 339–351.

———. 1975. Validity of radiocarbon dates on groundwater. *Geophysical Surveys* 2:217–239.

Florida Springs Task Force. 2000. Florida's springs, strategies for protection and restoration. Department of Environmental Protection. Tallahassee, Fla.

Tibbals, C.H. 1990. *Hydrology of the Floridan aquifer system in east-central Florida.* Professional Paper 1403-E. Washington, D.C.: U.S. Geological Survey.

Toth, D.J. 1999. *Water quality and isotope concentrations from selected springs in the St. Johns River Water Management District.* Technical Publication SJ99-2. Palatka, Fla.: St. Johns River Water Management District.