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

by

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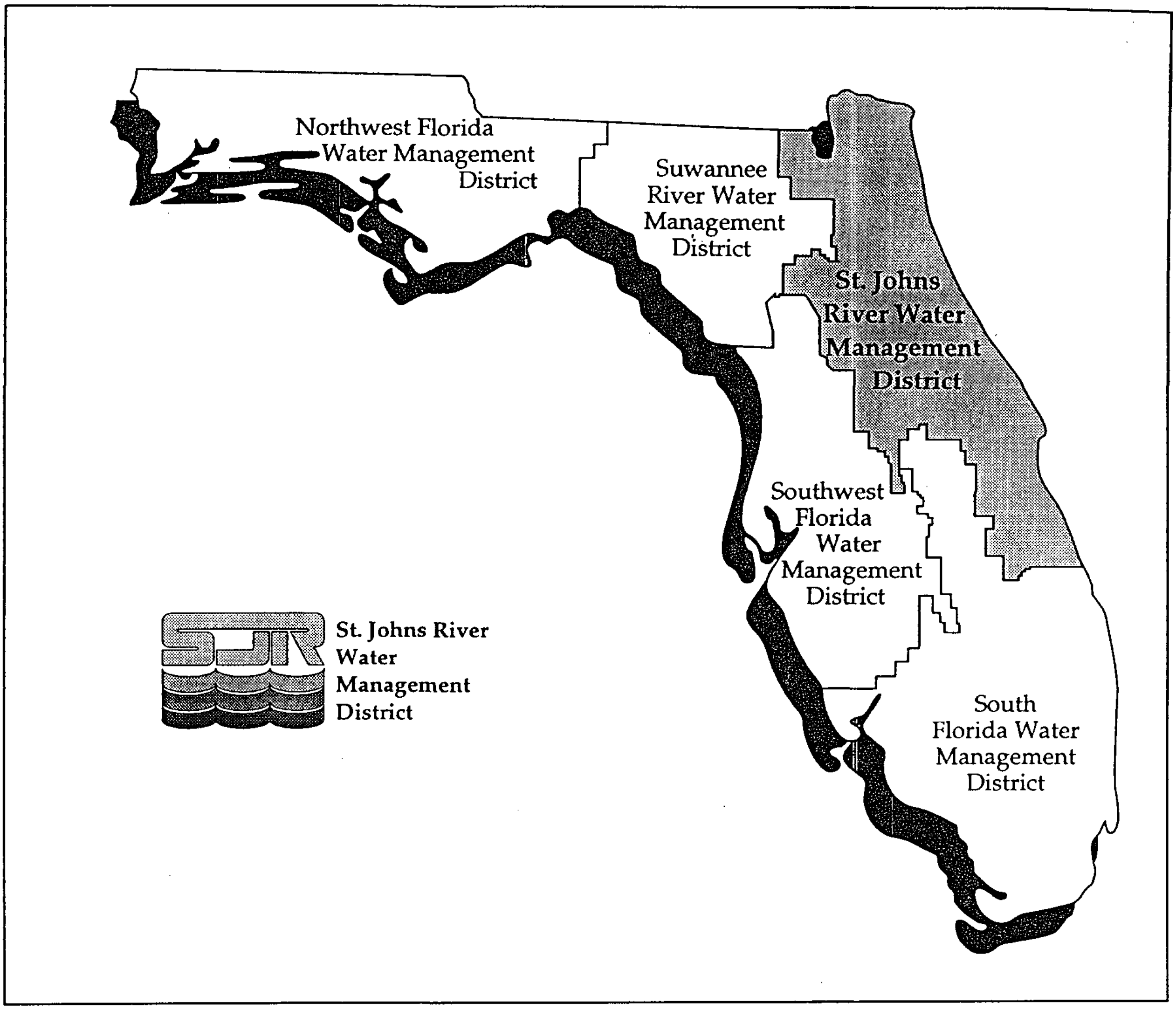

The **St. Johns River Water Management District** (SJRWMD) was created by the Florida Legislature in 1972 to be one of five water management districts in Florida. It includes all or part of 19 counties in northeast Florida. The mission of SJRWMD is to manage water resources to ensure their continued availability while maximizing both environmental and economic benefits. It 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.

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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 (two of which are submerged), eight wells in the Upper Floridan aquifer, and one well in the Lower Floridan aquifer 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 source of spring water, (4) to determine the age of spring water and to evaluate the nature of the spring flow system, and (5) to determine the sources of elevated nitrate-nitrogen concentrations in these springs.

Water quality was highly variable for the springs sampled. Water quality in the springs compared favorably with that in the sampled wells with the exception of Blue and Ponce de Leon springs in Volusia County.

The data indicate that the source of spring discharge is from the Upper Floridan aquifer. The data further indicate that the flow system for all of these springs ranges from shallow to deep. Water discharging from the springs consists of a mixture of ages; some water is less than 43 years old, and some is hundreds to thousands of years old. This age difference supports the concept that these springs have complex flow systems.

The delta-nitrogen-15 values for water from the springs sampled in this study indicate that the springs have been polluted. The available data do not provide a distinction between past and present nitrate contamination. Additional studies are required to determine when contamination occurred.

The source of nitrate differs by location of the spring. The elevated nitrate levels in Sanlando, Starbuck, Wekiva, and Ponce de Leon springs are probably due to contamination by animal waste and/or sewage. The elevated nitrate level in Palm Springs is probably due to contamination by animal waste and/or sewage and perhaps mixing with nitrates derived from soil organic nitrogen. Finally, the elevated nitrate levels in Rock and Seminole springs are probably due to contamination by nitrates from fertilizers mixing with nitrates from soil organic nitrogen. The presence of elevated nitrate levels in spring water suggests a shallow to intermediate flow system for these springs.

CONTENTS

FIGURES

TABLES

INTRODUCTION

Springs are a major natural resource of Florida. They feed and augment the flow of many rivers, provide a habitat for wildlife, and provide recreation for Florida's residents. Seventeen springs (including two submerged springs) were sampled during this study to assess their water quality, source, and age.

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 the St. Johns River Water Management District (SJRWMD), (3) to compare the isotope concentrations from spring samples with concentrations from nearby wells in the Upper and Lower Floridan aquifers, (4) to determine the age of spring water and to evaluate the nature of the spring flow systems, and (5) to determine the source of nitrogen in springs with nitrate-nitrogen concentrations above 0.2 milligrams per liter (mg/L).

BENEFITS

Determination of the stable and radioactive isotope concentrations increases the knowledge and understanding of the chemical concentrations of spring water. Comparison of the isotope concentrations from springs with those from nearby wells in the Upper and Lower Floridan aquifers helps identify the sources of spring water. The resulting data help determine whether the discharge is derived from the Upper Floridan aquifer or the Lower Floridan aquifer or is a mixture of both. 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 whether spring water is being polluted. Possible sources of nitrogen are fertilizers, septic tanks, animal waste, and stormwater discharge.

SPRINGS

All of the springs sampled in this study discharge from the Floridan aquifer system. Springs are classified by magnitude, from one to eight, on the basis of their volume of flow, or discharge (Rosenau et al. 1977). Excluding the submerged springs in this study, 15 springs were sampled: 2 first-magnitude, 12 second-magnitude, and 1 third-magnitude. First-magnitude springs have an average flow, or discharge, of 100 cubic feet per second (ft^3/s) or more. The first-magnitude springs sampled in this study are Silver Glen Springs in Marion County and Blue Spring in Volusia County. The discharges of second- and third-magnitude springs range between 10 to 100 ft^3/s and 1 to 10 ft^3/s, respectively. The second-magnitude springs sampled were Wekiva and Rock springs in Orange County; Ponce de Leon and Gemini springs in Volusia County; Alexander, Messant, and Seminole springs in Lake County; Sanlando and Starbuck springs in Seminole County; and Salt, Juniper, and Sweetwater springs in Marion County. The third-magnitude spring was Palm Springs in Seminole County.

Many springs contain more than one vent. The water discharging from each vent may be discernible as a boil on the water surface of the spring pool. There are four discernible boils at Salt Springs, and each vent was sampled. There are three boils at Gemini Springs, but only two vents were sampled. One of the vents sampled had been converted to a well in September 1991. This well, V-0564, is 153 feet (ft) deep. For the remainder of the springs sampled in this study, the major vent was the only one sampled, even though more than one boil may have been present.

In addition to the above springs, two submerged springs were sampled. One submerged spring, Croaker Hole Spring, occurs in the St. Johns River north of Lake George and south of the mouth of the Ocklawaha River. It is a second-magnitude spring (Tibbals 1990). The other submerged spring, Crescent Beach Submarine Spring (Crescent Beach Spring), occurs in the Atlantic Ocean off the northeast coast of Florida approximately 2.5 miles east of Crescent Beach. It is estimated to be either a first- or second-magnitude spring (Rosenau et al. 1977).

WELLS

Wells in the Upper and Lower Floridan aquifers (six and one, respectively) that occur near the above springs also were sampled for water quality parameters and isotope concentrations. Wells in the Upper Floridan aquifer are OR0548 in Wekiwa Springs State Park, V-1030 in Ponce De Leon Springs State Park, OR0170 in Dr. Howard A. Kelly County Park (Rock Springs), L-0066 in Alexander Springs recreation area, V-0083 in Blue Spring State Park, and V-0564 in Gemini Springs (Table 1). In addition, two wells in the Upper Floridan aquifer also were sampled for water quality parameters: SJ0432 at Crescent Beach, 1 mile north of Crescent Beach Spring, and SJ0516 at Dupont Center, about 8 miles west of Crescent Beach Spring. These two wells were sampled to compare Upper Floridan aquifer water quality with water quality of the Crescent Beach Spring discharge. The well in the Lower Floridan aquifer, OR0547, occurs in Wekiwa Springs State Park.

Table 1. Well characteristics for the wells sampled in this study

Well	Total Depth (feet)	Casing Depth (feet)	Aquifer
L-0066	102	74	Upper Floridan
OR0170	365	143	Upper Floridan
OR0547	645	440	Lower Floridan
OR0548	155	100	Upper Floridan
SJ0432	210	100	Upper Floridan
SJ0516	238	204	Upper Floridan
V-0083	432	84	Upper Floridan
V-0564	153	—	Upper Floridan
V-1030	200	120	Upper Floridan

Note: — = no data

PARAMETERS MEASURED

Water quality parameters measured were specific conductance, temperature, pH, laboratory alkalinity, dissolved calcium, dissolved magnesium, dissolved sodium, dissolved potassium, dissolved strontium, chloride, fluoride, sulfate, total dissolved solids (TDS), dissolved silicon dioxide (SiO_2), total and dissolved nitrogen oxides (NO_x), and total and dissolved phosphate (PO_4). Excluding the two submerged springs, discharge measurements were made at all springs by the U.S. Geological Survey (USGS) or SJRWMD.

Stable isotopes measured were deuterium (^2H or D), oxygen-18 (^{18}O), carbon-13 (^{13}C), nitrogen-15 (^{15}N), sulfur-34 (^{34}S), strontium-87/strontium 86 (as a ratio) ($^{87}Sr/^{86}Sr$), helium-3 (^3He), helium-4 (^4He), and neon (Ne).

Radioactive isotopes measured were tritium (^3H or T) and carbon-14 (^{14}C).

STUDY AREA

The study area is in east-central Florida and includes Lake, Marion, Orange, Putnam, Seminole, St. Johns, and Volusia, counties (Figure 1). Excluding the two submerged springs, the springs that were sampled occur in Lake, Marion, Orange, Seminole, and Volusia counties (Figure 2). One of the submerged springs occurs in Putnam County and the other in the Atlantic Ocean off the coast of St. Johns County. Wells in the Upper Floridan aquifer were sampled in Lake, Orange, St. Johns, and Volusia counties. A well in the Lower Floridan aquifer was sampled in Orange County.

TOPOGRAPHY

The topography ranges from rolling highlands in Orange, Lake, Marion, and western Volusia and Putnam counties to flat, swampy lowlands along the coast of Volusia and St. Johns counties and along the St. Johns River floodplain in Seminole, Lake, Marion, Putnam, and Volusia counties. Land-surface altitudes in the rolling highlands generally range from 100 to 200 ft above sea level. In the 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 in the study area except St. Johns. 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.

CLIMATE

The climate of the study area is humid subtropical, with a mean annual temperature of 71 degrees Fahrenheit (°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,

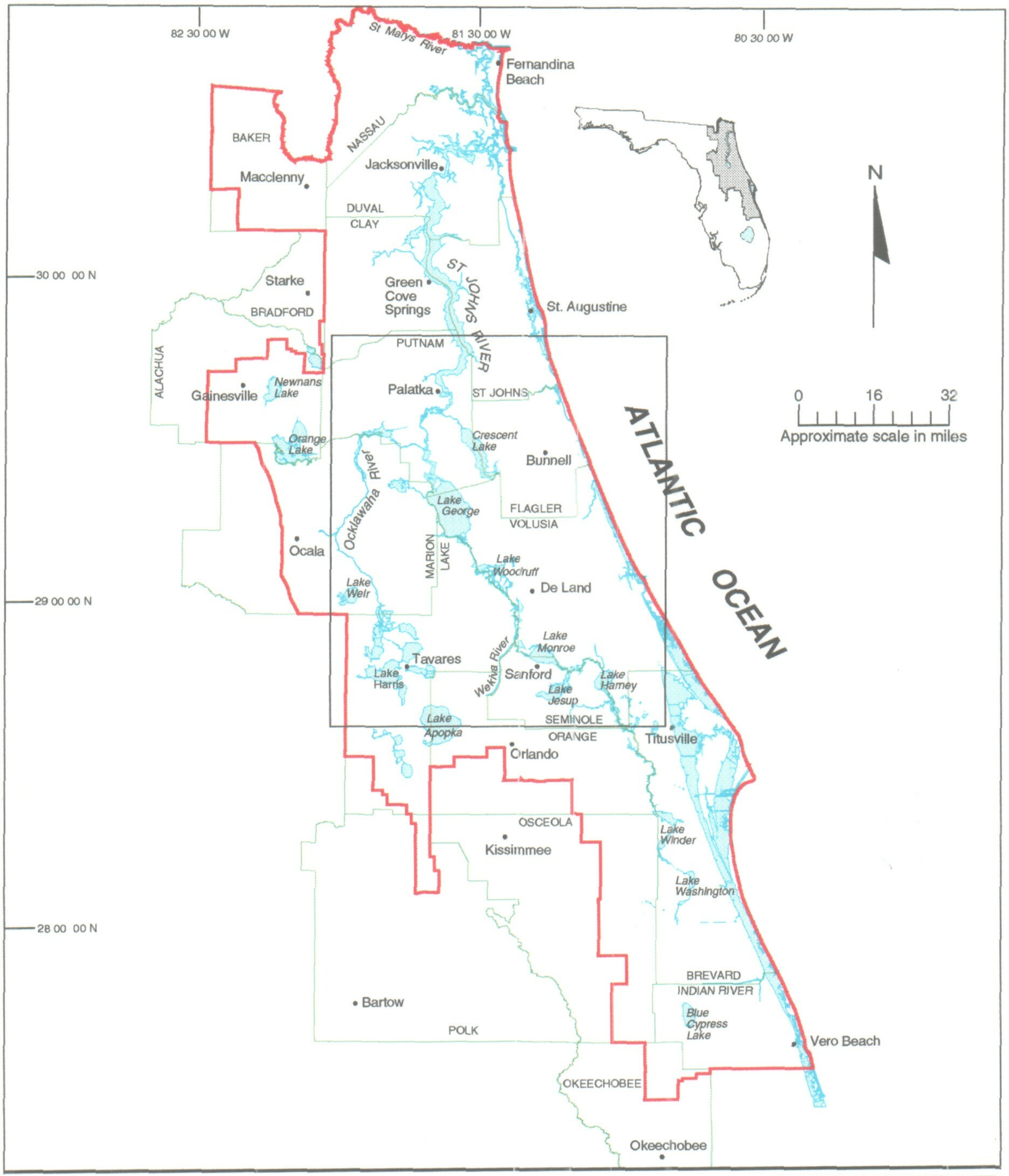

Figure 1. Study area in relationship to the St. Johns River Water Management District

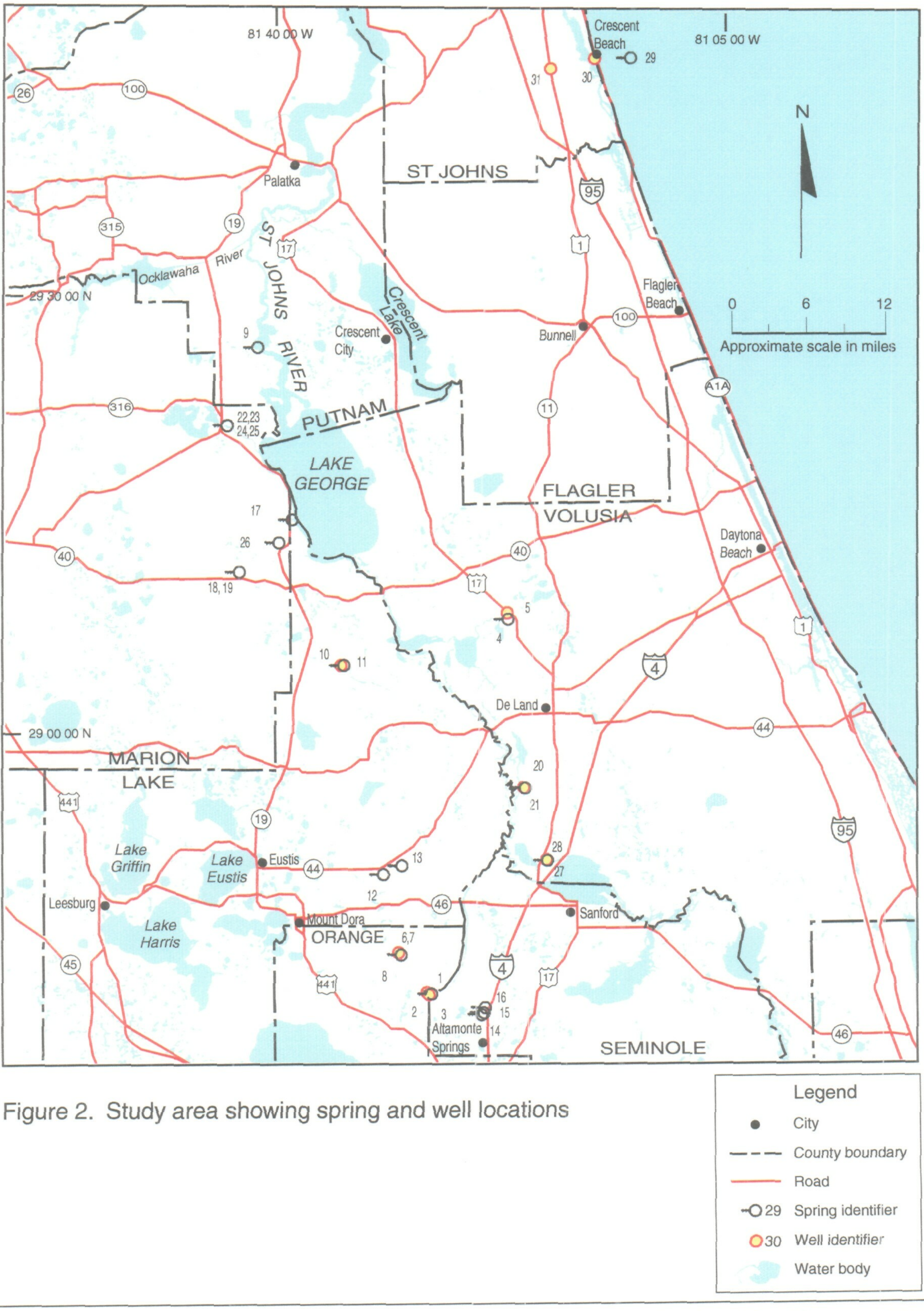

Figure 2. Study area showing spring and well locations

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 2). Detailed information about the geology and hydrology of these systems can be found in Puri and Vernon (1959), Stringfield (1966), Miller (1982a, b; 1986), and Tibbals (1990).

Table 2. Hydrogeologic framework for the study area

Hydrogeologic Unit	Epoch	Stratigraphic Unit	General Lithology
Surficial aquifer system	Holocene 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
Floridan aquifer system	Eocene	Ocala Limestone	Limestones and dolomitic limestones
		Avon Park Formation	Limestones and dolostone
		Oldsmar Formation	Limestones and dolostone
	Paleocene	Cedar Keys Formation	Dolostone, some limestone; anhydrite occurs in lower two-thirds of formation
Lower confining unit			

SURFICIAL AQUIFER SYSTEM

The uppermost 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.

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 it can be several tens of feet below land surface.

The surficial aquifer system is recharged primarily by rainfall. In coastal areas and along the St. Johns River, the surficial aquifer system also is recharged by upward movement of water from underlying aquifers. Some lakes, streams, and irrigation ditches; septic tank effluent; and stormwater retention ponds also recharge the surficial aquifer system. 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 tapped by wells for small to moderate amounts of water that are widely used for lawn and garden irrigation.

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 they do not significantly retard the downward movement of water.

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, shell, and clay and the phosphatic sand, silt, clay, limestone, and dolostone of the Miocene Hawthorn Group. The intermediate aquifer system is composed of thin, discontinuous layers, or lenses, of sand, shell, or limestone within the Hawthorn Group, which yield 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 the Floridan aquifer systems.

The clays within the Pliocene sediments and the Hawthorn Group act as the upper confining unit for the Floridan aquifer system and retard the vertical movement of water between the surficial and intermediate aquifer systems and between the intermediate and Floridan aquifer systems. The thickness of the upper confining unit for the Floridan aquifer system is variable throughout much of the study area (Figure 3). No information is available on the thickness of Pliocene deposits or of clays within the upper confining unit.

Miocene and post-Miocene deposits make up the sediments above the Floridan aquifer system. These sediments vary in thickness throughout the study area, but are consistently thin where nonsubmerged springs are located (Figure 4).

FLORIDAN AQUIFER SYSTEM

The Floridan aquifer system lies directly beneath the intermediate aquifer system. It consists of a thick sequence of limestone, dolomitic limestone, and dolostone. The thickness of the Floridan aquifer system increases from approximately 1,600 ft in the northwest part of the study area to 2,300 ft in the southeast (Miller 1986). The top of the Floridan aquifer system is defined as the first occurrence of vertically persistent, permeable, consolidated, carbonate rocks. The top of the Floridan aquifer system is highest in eastern Marion County, Lake County, central Volusia County, western and northern Orange County, and western Seminole County (Figure 5). 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 both from the porous limestones and from fissures and cavities created by the dissolution and fracturing of limestones and dolostones. Throughout much of the study area, the Floridan aquifer system is

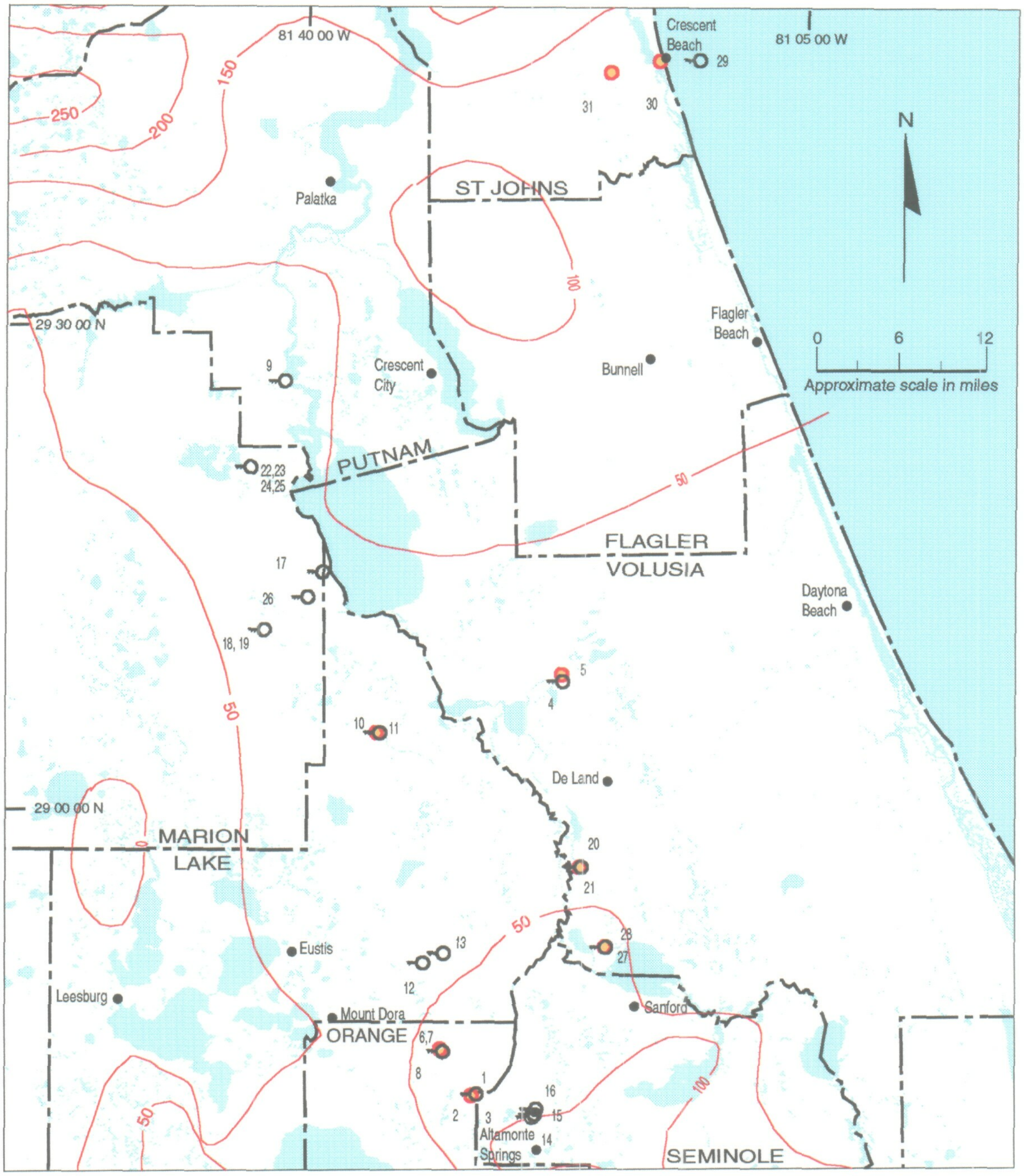

Figure 3. Thickness of the upper confining unit for the Floridan aquifer system in the study area (from Miller 1986)

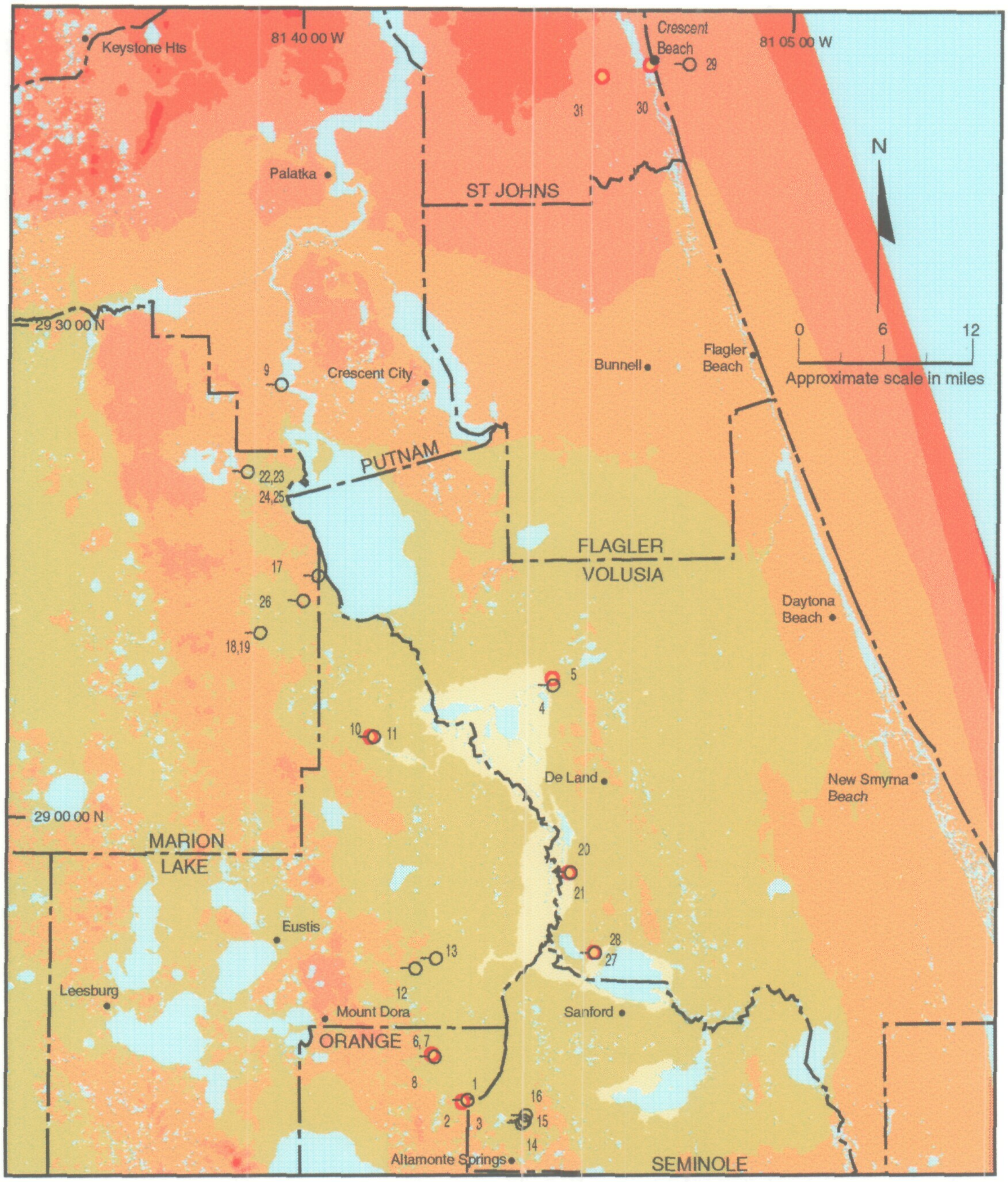

Figure 4. Thickness of sediments above the Floridan aquifer system in the study area

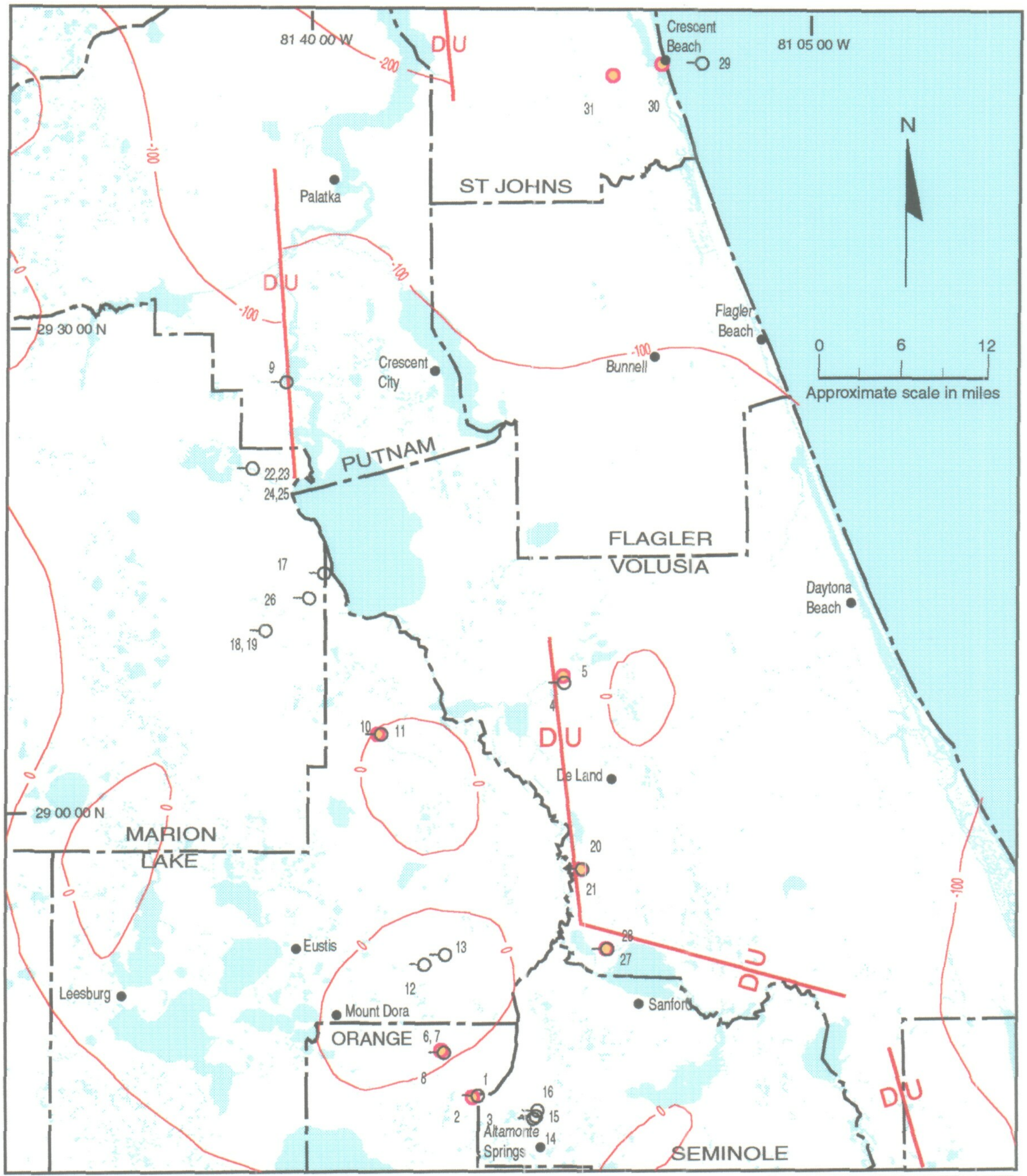

Figure 5. Elevation of the top of the Floridan aquifer system in the study area—D|U represents the normal fault (vertical): U=upthrown side, D=downthrown side (adapted from Miller 1982c)

confined. This aquifer system is unconfined in western Marion and Lake counties.

The Floridan aquifer system consists of 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 Floridan aquifer system across much of the study area. The Ocala Limestone is absent and the Avon Park Formation constitutes the top of the Floridan aquifer system in southwestern Volusia County, northern Seminole County, and the extreme northeastern portion of Lake County.

The Floridan aquifer system is divided vertically into three zones on the basis of permeability. Two zones have relatively high permeability and are referred to as the Upper and Lower Floridan aquifers. These zones are separated by a less-permeable dolomitic limestone referred to as the middle semiconfining unit. The Upper Floridan aquifer consists of 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. The middle semiconfining unit consists of part of the Avon Park Formation.

The thickness of the Upper Floridan aquifer varies throughout the study area and ranges between 200 and 400 ft at most of the springs and between 400 and 800 ft at the submerged springs (Figure 6).

The depth to the top of the Lower Floridan aquifer also varies throughout the study area and ranges from 400 to 1,000 ft below sea level at the springs sampled (Figure 7).

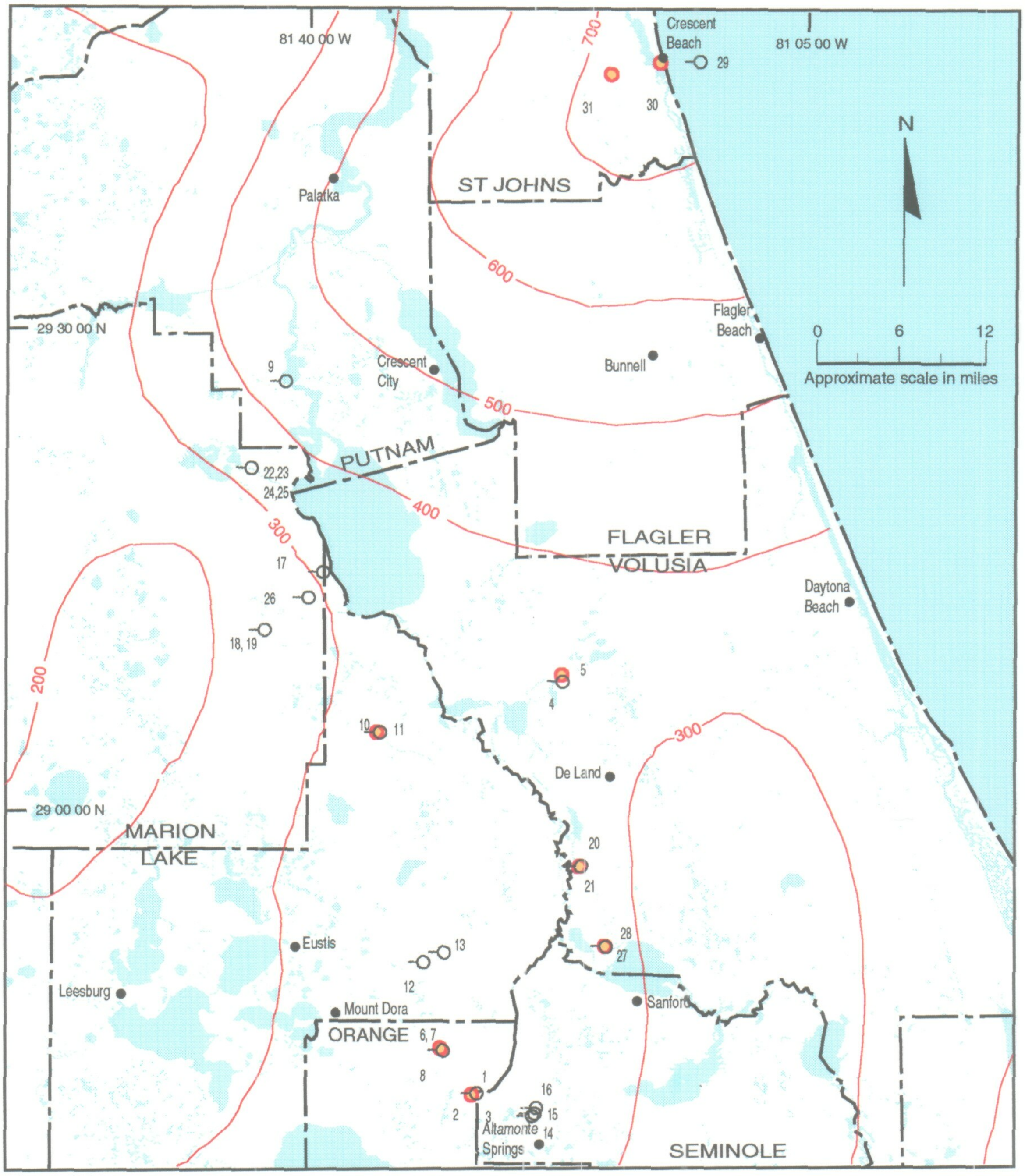

Figure 6. Thickness of the Upper Floridan aquifer in the study area

Legend

- ● City
- — — County boundary
- —200— Thickness of Upper Floridan aquifer (feet)
- -○29 Spring identifier
- ● 30 Well identifier
- Water body

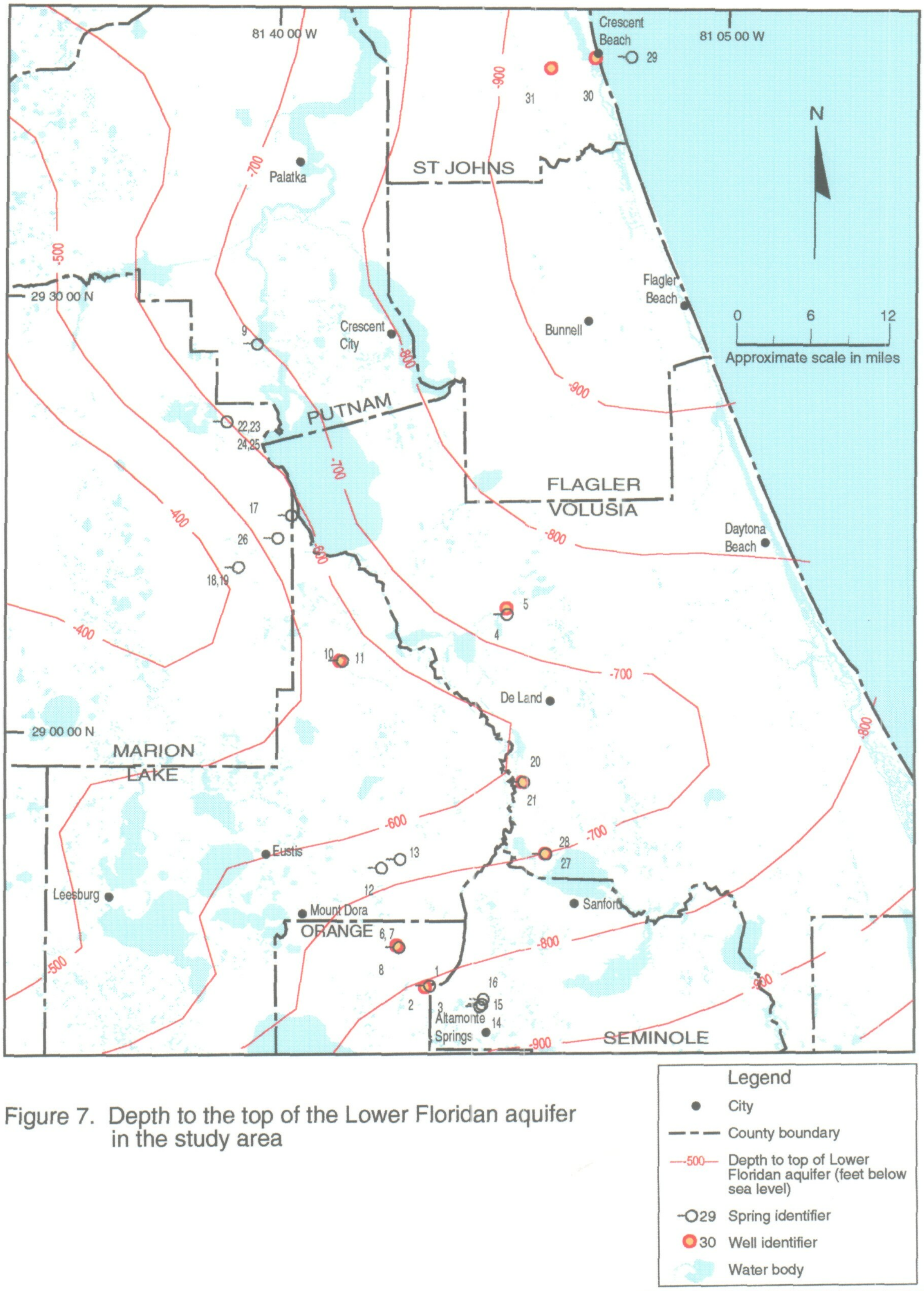

Figure 7. Depth to the top of the Lower Floridan aquifer in the study area

RECHARGE AND DISCHARGE

Recharge to the Floridan aquifer system occurs wherever water levels in the surficial and intermediate aquifer systems are higher than the potentiometric surface of the underlying Floridan aquifer system. The rate of recharge depends on the difference between water levels in overlying aquifers and surface water and the potentiometric surface of the Floridan aquifer system 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 8).

Discharge from the Floridan aquifer system occurs wherever the potentiometric surface of the Floridan aquifer system 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 8).

Except for Crescent Beach Spring, all of the springs sampled in this study area occur within less than 4 miles of high recharge areas (12 or more inches per year). This short distance suggests that the waters discharging from each spring are locally derived. Water discharging from Crescent Beach Spring originates in the recharge areas of Keystone Heights in Clay County (Brooks 1961).

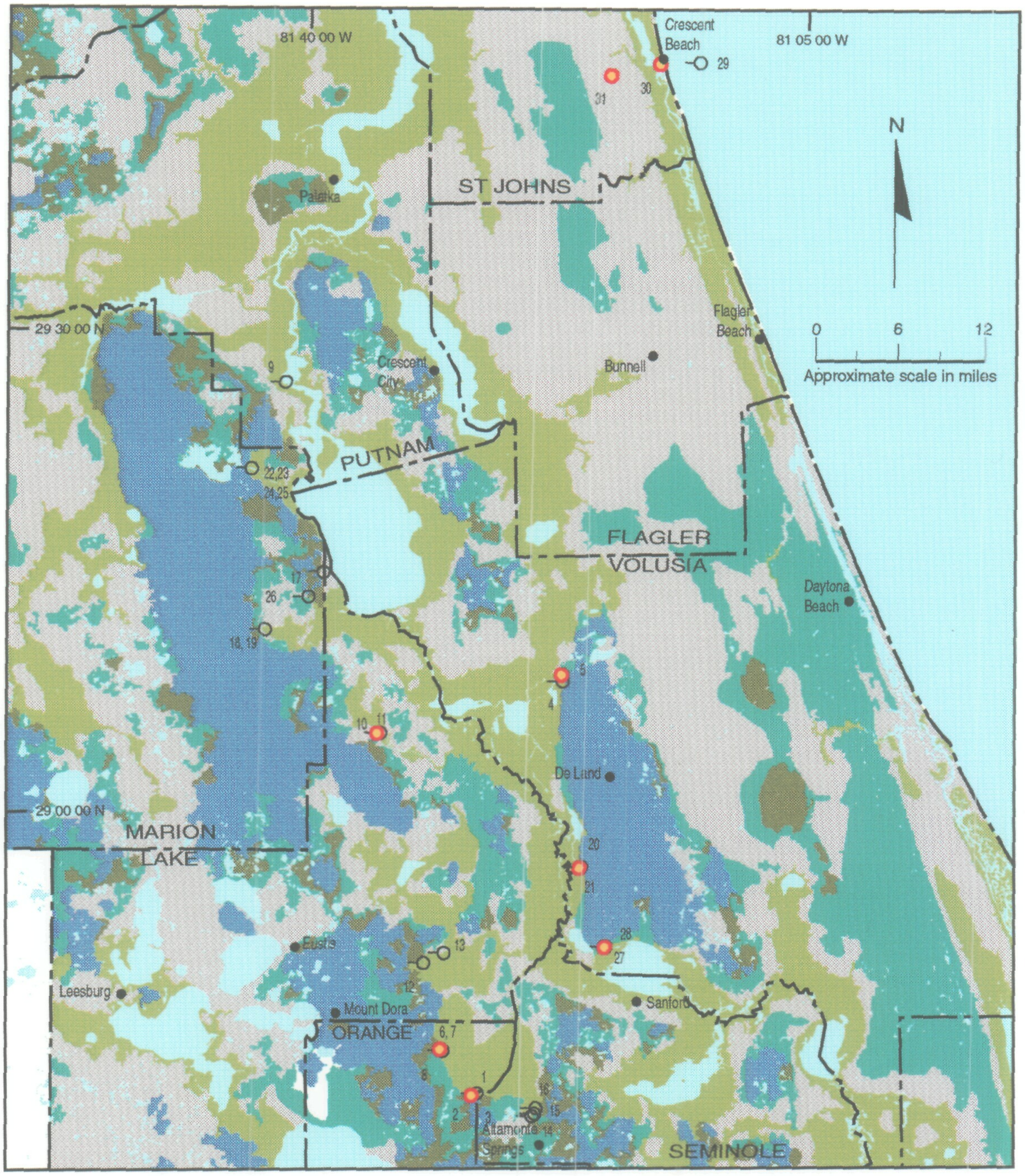

Figure 8. Amount of recharge to the Floridan aquifer system in the study area (Boniol et al. 1993)

PROCEDURES

In this study, the procedures involved sampling springs—nonsubmerged and submerged—and groundwater from wells near the springs. These wells tap the Floridan aquifer system.

SAMPLING SPRINGS—NONSUBMERGED

All springs were sampled by inserting weighted, clear vinyl tubing in the spring vent and extending the tubing to shore. The end of the tubing that 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, and temperature, pH, and specific conductance were measured. The tubing was purged until the discharge was clear and the parameters were stabilized, after which samples were collected. Unfiltered samples were collected first, followed by filtered samples, which were passed through 0.45-micron filters.

SAMPLING SPRINGS—SUBMERGED

Divers from USGS assisted in the sampling of Croaker Hole Spring. The divers inserted the weighted, clear vinyl tubing with a screen attached into the spring vent. The tubing was extended to the surface, where it was attached to a peristaltic pump on board a boat. The discharge from the pump was passed through a Hydrolab, and temperature, pH, and specific conductance were noted. The tubing was purged until the parameters were stabilized, after which samples were collected.

Divers from the Jacksonville Reef Research Team, Continental Shelf Associates, and USGS assisted in the sampling of Crescent Beach Spring. A "sand point" (used in well sampling) was attached to the weighted, clear vinyl tubing, and the divers inserted the sand point into sediments at the bottom of the spring. The tubing was extended to the surface, where it was attached to a peristaltic pump on board a boat. The discharge from the pump was passed through a Hydrolab, and temperature, pH, and specific conductance were measured. The tubing was purged until the parameters were stabilized and the specific conductance was significantly less than that of seawater. Samples then were collected.

SAMPLING GROUNDWATER

Each well was purged prior to sampling. Purging continued until the temperature, pH, and specific conductance did not change by more than 10% between two successive well volumes. The number of well volumes taken during the purging generally varied between three and five.

Purging and sampling were done with the same pump. A submersible pump was used when the depth to the water was greater than or equal to 15 ft. A centrifugal pump was used when the depth to the water was less than 15 ft.

After purging, unfiltered and filtered water samples were collected. The filtered samples were passed through 0.45-micron filters.

SAMPLE COLLECTION

Samples from all springs and wells were collected using procedures approved by SJRWMD and USGS. Samples for metals (calcium, magnesium, sodium, potassium, and strontium), TDS, dissolved SiO_2, dissolved nutrients (NO_x and PO_4), $^{87}Sr/^{86}Sr$, and ^{15}N were filtered. Samples for ^{2}H, ^{18}O, ^{13}C, ^{14}C, ^{3}H, ^{34}S, ^{3}He, ^{4}He, and Ne were not filtered. All samples for ^{34}S were collected in a churn (a Teflon tub holding 15–20 liters) and acidified to pH 2 by adding concentrated hydrochloric acid. Ultra-pure nitrogen gas was bubbled through the solution for 30 minutes to expel any hydrogen sulfide gas. If the samples were suspected to contain less than 20 mg/L of sulfate, the sulfate was concentrated by passing 10 to 15 liters of acidified, degassed solution through an ion exchange resin. Samples for ^{3}He, ^{4}He, and Ne were collected in special pinch-off copper tubes (with a diameter of 3/8 inch and a length of 30 inches, and containing about 40 cubic centimeters of water). The sample tubes were supplied by USGS.

Samples were analyzed for the following:

Specific conductance		Temperature	
pH		Delta-deuterium	$\delta ^2H$ or δD
Lab alkalinity		Delta-oxygen-18	$\delta ^{18}O$
Magnesium	Mg^{2+}	Delta-carbon-13	$\delta ^{13}C$
Sodium	Na^+	Delta-sulfur-34	$\delta ^{34}S$
Potassium	K^+	Delta-nitrogen-15	$\delta ^{15}N$
Calcium	Ca^{2+}	Helium-3	^3He
Chloride	Cl^-	Helium-4	^4He
Fluoride	F^-	Neon	Ne
Sulfate	SO_4^{-2}	Tritium	^3H or T
Total dissolved solids	TDS	Carbon-14	^{14}C
Total and dissolved nitrate and nitrite nitrogen	NO_x	Dissolved silicon dioxide	SiO_2
Strontium	Sr^{2+}	Strontium-87/strontium-86	$^{87}Sr/^{86}Sr$
Total and dissolved orthophosphate phosphorus	PO_4		

Samples for ^2H, ^{18}O, and ^{34}S were sent to the USGS laboratory in Reston, Virginia, for analysis. Samples for ^3H and $^{87}Sr/^{86}Sr$ were sent to the USGS laboratory in Menlo Park, California, for analysis. Nitrogen-15, ^{13}C, ^{14}C, ^3He, ^4He, and Ne analyses were performed by contract laboratories for USGS (Global Geochemistry in Los Angeles for ^{15}N; University of Waterloo in Ottawa, Ontario, for ^{13}C and ^{14}C; and Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York, for ^3He, ^4He, and Ne). Carbon-14 was determined by accelerated mass spectrometry. The remaining analyses were performed by the SJRWMD laboratory.

WATER QUALITY

Water quality is a measurement of chemical and physical parameters of water in a flow system. The primary parameters consist of metals, anions, nutrients, SiO_2, and TDS. Sampling results for this study are discussed separately for springs and wells.

SPRINGS

Water quality was highly variable for the springs sampled in this study. Chloride concentrations ranged from 4 mg/L at Juniper Springs to 3,630 mg/L at Crescent Beach Spring (Table 3). Similarly, sulfate and TDS concentrations ranged from 6 and 65 mg/L at Juniper Springs to 816 and 7,460 mg/L at Crescent Beach Spring.

The four vents at Salt Springs have different water quality, suggesting that the discharge from the Floridan aquifer system at Salt Springs is probably mixing with varying amounts of water from the surficial aquifer system or with water from different depths in the Floridan aquifer system. The chloride concentrations ranged from 1,610 mg/L at the southeast vent to 2,130 mg/L at the northwest vent. The northwest vent is over the main vent at Salt Springs. Similarly, sulfate and TDS concentrations ranged from 414 and 3,230 mg/L at the southeast vent to 511 and 4,170 mg/L at the northwest vent.

Nitrate-nitrogen concentrations in groundwater are generally below 0.2 mg/L (SJRWMD database). Concentrations above this value imply a source of nitrogen. Total nitrate-nitrogen concentrations were above the "elevated" threshold of 0.2 mg/L in Wekiva Springs (1.92 mg/L as nitrogen [N]), Ponce de Leon Springs (0.948 mg/L), Rock Springs (1.62 mg/L), Seminole Springs (1.41 mg/L), Sanlando Springs (0.782 mg/L), Palm Springs (0.703 mg/L), Starbuck Spring (0.447 mg/L), Blue Spring (0.617 mg/L), and Gemini Springs (0.633 mg/L). The presence of elevated nitrate levels in spring water suggests a shallow to intermediate flow system for the springs.

The primary drinking water standard (FDER 1989) for nitrate-nitrogen is 10 mg/L as N. In addition, there is a health advisory for nitrate at 1 mg/L as N. The major cause of concern is nitrate-nitrogen levels

above 10 mg/L, which 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).

Water quality data for the springs sampled in this study were plotted on a Piper diagram (Figure 9). Wekiva, Rock, Palm, Starbuck, Juniper, and Sanlando springs plotted together and are located in a recharge area (Frazee 1982) (compare Figures 9 and 10). These springs are high in calcium and bicarbonate, and their water "probably travels along relatively short, lateral flow paths that originate in high-rate recharge areas" (Murray and Halford 1996). Messant and Seminole springs plotted together in an area of the diagram that indicates the springs are 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). Sweetwater Spring, Crescent Beach Spring, and the four vents at Salt Springs 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. These springs contain old water. Other springs that plotted near the seawater region are Croaker Hole, Silver Glen, Alexander, and Gemini springs. Both Ponce de Leon Springs and Blue Spring 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 also from the mixing of freshwater with entrapped relict seawater.

WELLS

Water quality was highly variable for wells sampled in the Upper Floridan aquifer during this study. Chloride concentrations in these wells ranged from 8 mg/L in OR0170 at Rock Springs to 3,200 mg/L in SJ0432 at Crescent Beach (Table 3). Similarly, sulfate concentrations ranged from 3 mg/L in V-1030 at Ponce de Leon Springs to 794 mg/L in SJ0432. TDS concentrations ranged from 145 mg/L in OR0170 to 7,491 mg/L in SJ0432. Chloride, sulfate, and TDS concentrations in the well (OR0547) in the Lower Floridan aquifer at Wekiva Springs were 6, 15, and 147 mg/L, respectively. Except for well V-0564, the nitrate-

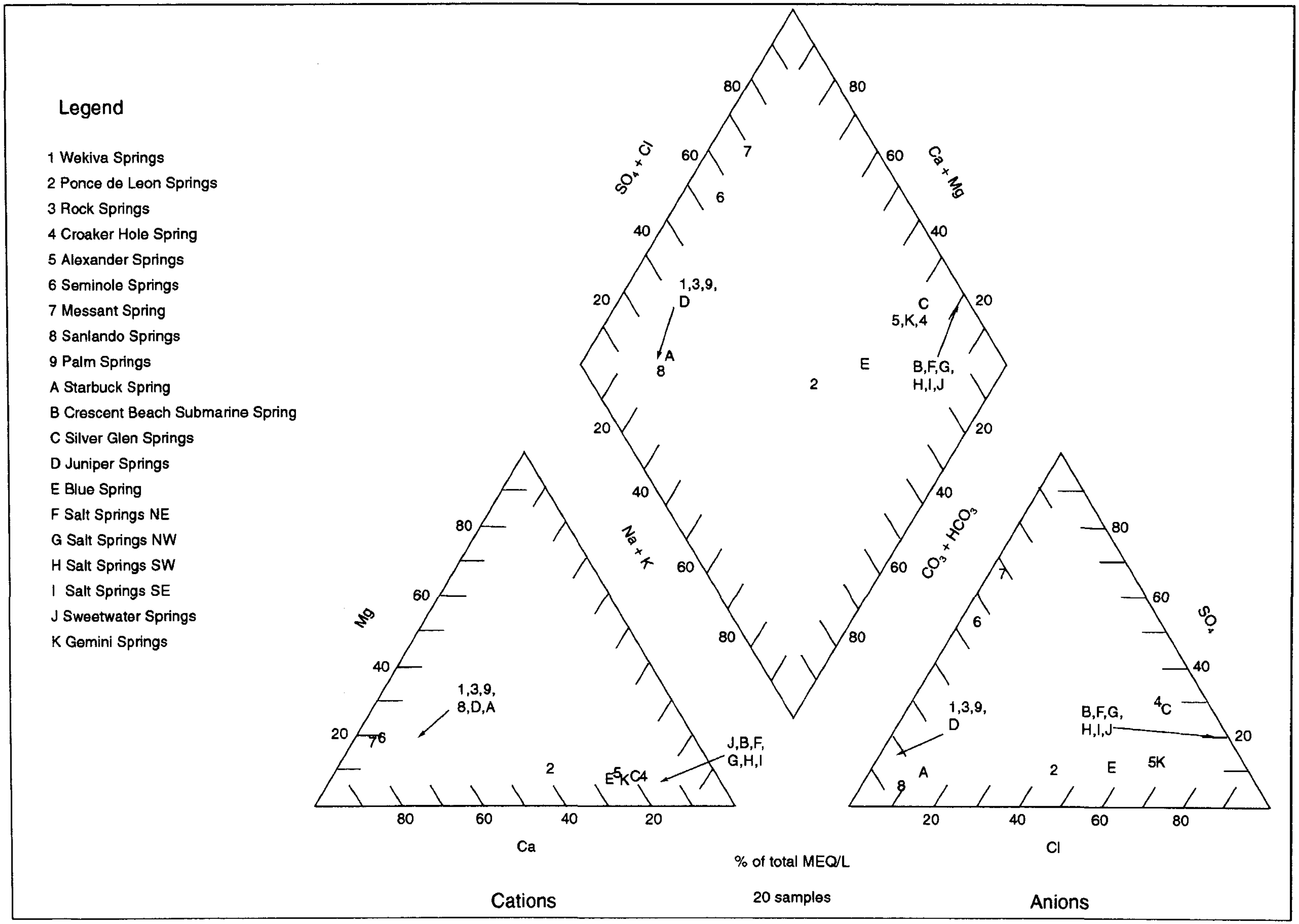

Figure 9. Piper diagram (diamond shaped area) of spring water sampled. *Arrows indicate sample locations.*

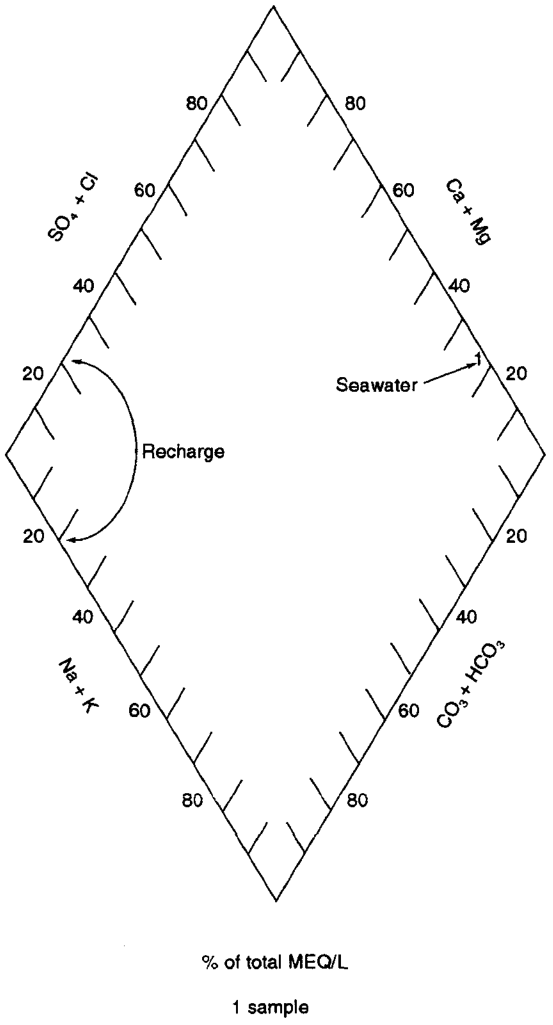

Figure 10. Piper diagram of recharge water and seawater (based on Frazee 1982). *Arrows indicate sample locations.*

nitrogen concentrations for all wells in the Upper and Lower Floridan aquifers were below 0.2 mg/L. The nitrate-nitrogen concentration for V-0564 was 0.672 mg/L.

Comparing water quality from wells in the Upper and Lower Floridan aquifers with that of the springs, water quality at Wekiva Springs is most similar to that from well OR0548 in the Upper Floridan aquifer. Both have similar conductivities and dissolved calcium, magnesium, sodium, chloride, sulfate, and TDS concentrations. This similarity suggests that the water discharging from Wekiva Springs is derived from the Upper Floridan aquifer.

The pH is lower in water from Wekiva Springs compared to water in wells of both the Upper and Lower Floridan aquifers because spring water is continually discharging. Water from the wells moves much slower than spring water and hence has a longer time to equilibrate with limestone.

A comparison of water quality from three other wells in the Upper Floridan aquifer with that of the springs indicates similar water quality at OR0170 and Rock Springs, SJ0432 and Crescent Beach Spring, and V-0564 and Gemini Springs. It is not surprising for V-0564 to have water quality similar to Gemini Springs because V-0564 is one of three vents that make up Gemini Springs. The similar water quality between these springs and wells in the Upper Floridan aquifer suggests that the spring discharge is derived from the Upper Floridan aquifer.

Water quality at well V-1030 in the Upper Floridan aquifer is very different from that at Ponce de Leon Springs. The specific conductance and the chloride, sulfate, TDS, magnesium, and sodium concentrations are much lower in the well than in the spring. The data suggest that the water tapped by the well is mixing with water of a higher mineral content in the drainage basin for the spring. Rutledge (1982, Figure 28) defined the drainage area for Ponce de Leon Springs. The drainage basin contains an area where the chloride concentration in the Upper Floridan aquifer varies between 250 and 1,000 mg/L (Rutledge, Figure 29).

Water quality at well L-0066 in the Upper Floridan aquifer is slightly different from that at Alexander Springs. The specific conductance and the sodium, chloride, sulfate, and TDS concentrations are higher in the well than in the spring, which suggests that most of the discharge from the spring originates at a slightly shallower depth than well L-0066. The well is only 102 ft deep.

Water quality in well V-0083 in the Upper Floridan aquifer at Blue Spring is very different from that of water in the spring. Specific conductance, calcium, magnesium, sodium, potassium, chloride, sulfate, and TDS are much higher in the well than in the spring. This difference suggests that water from the well is probably stagnant, and water in the area of the well contributes very little, if any, discharge by lateral flow to the spring.

Major constituents of water from the wells sampled in this study also were plotted on a Piper diagram (Figure 11). Wells OR0548, V-1030, and OR0170 in the Upper Floridan aquifer and well OR0547 in the Lower Floridan aquifer are plotted in a recharge area (Frazee 1982) (compare Figures 10 and 11). Water in these wells is high in calcium and bicarbonate and probably has traveled along relatively short, lateral flow paths. Wells SJ0432 and V-0083 in the Upper Floridan aquifer plotted very close to where seawater would plot on the diagram. Water from these wells is 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. Other wells in the Upper Floridan aquifer that plotted near the seawater region of the diagram are L-0066 and V-0564.

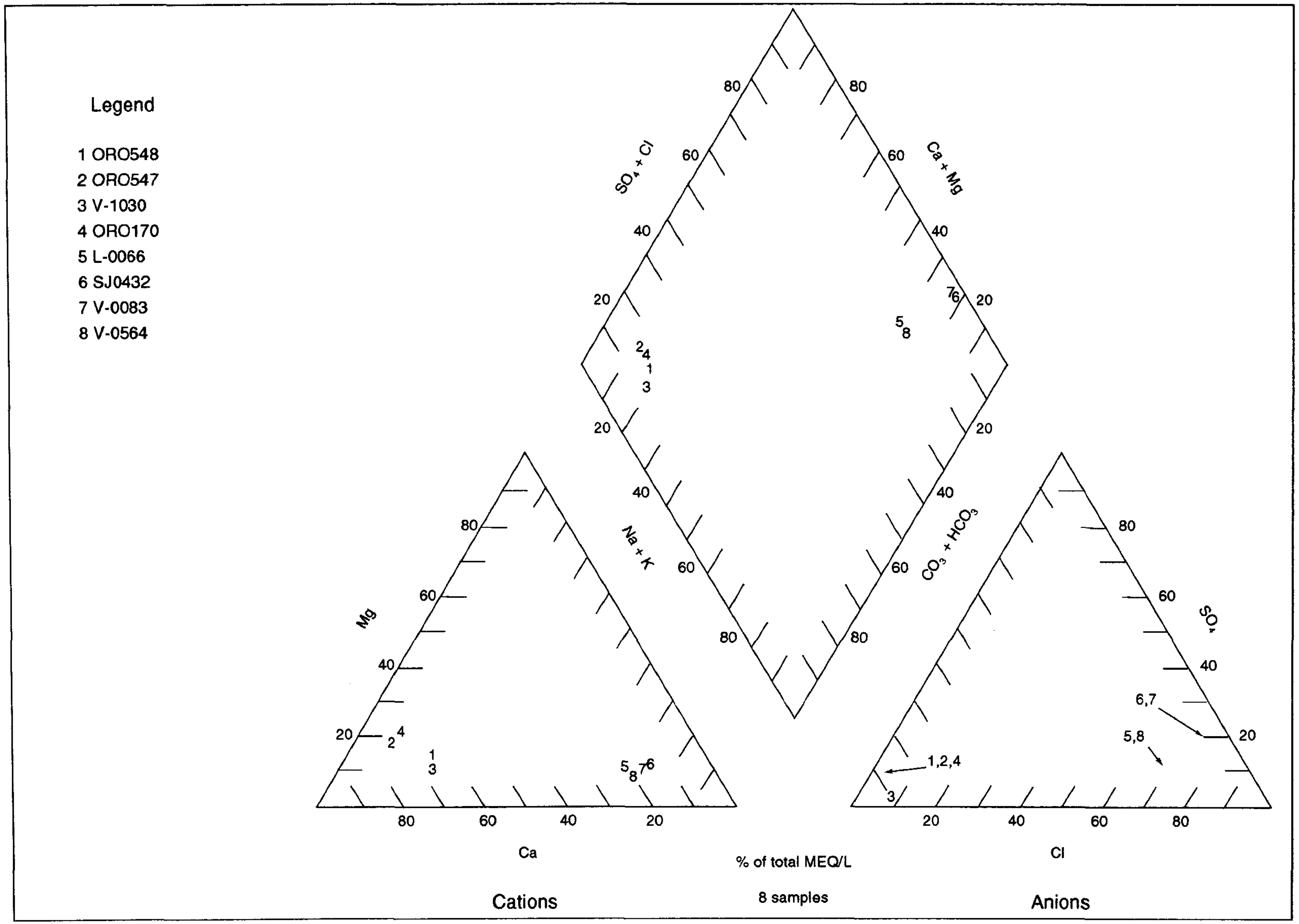

Figure 11. Piper diagram (diamond shaped area) of well water sampled. *Arrows indicate sample locations.*

ISOTOPES

Isotopes are atoms of the same chemical 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 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. Stable isotopes monitored in this study are ^{2}H, ^{3}He, ^{4}He, Ne, ^{13}C, ^{15}N, ^{18}O, ^{34}S, and $^{87}Sr/^{86}Sr$. 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. The average terrestrial abundance of the sampled isotopes varies (Table 4).

Table 4. The average terrestrial abundance and half-life of some common isotopes

Element	Isotope	Average Terrestrial Abundance (atom %)	Radioactive Half-Life (years)
Carbon	^{12}C	98.90	
	^{13}C	1.10	
	^{14}C	$<10^{-10}$	5,730*
Helium	^{3}He	0.00014	
	^{4}He	99.99986	
Hydrogen	^{1}H	99.985	
	^{2}H (D)	0.015	
	^{3}H (T)	$<10^{-14}$	12.43
Neon	Ne	†	
Nitrogen	^{14}N	99.63	
	^{15}N	0.37	
Oxygen	^{16}O	99.762	
	^{18}O	0.200	
Strontium	^{86}Sr	9.86	
	^{87}Sr	7.00	
Sulfur	^{32}S	95.02	
	^{34}S	4.21	

Source: Coplen 1993

Note: Blank cells indicate stable isotopes.

*From Plummer et al. 1994
†Not available

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. The relative ratio needs to be considered 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; that is, these isotopes are compared to a standard (Equation 1).

$$\delta_x = \left(\frac{R_x}{R_{standard}} - 1 \right) 1{,}000 \qquad (1)$$

where

δ_x = delta values for a given stable isotope x in parts per thousand (‰), 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 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 or

Vienna Peedee belemnite 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 ^{4}He; 1% for $^{3}He/^{4}He$; 4% for Ne (Plummer USGS, pers. com. 1996); 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 ^{18}O 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 (Figure 12).

The global meteoric water (GMW) line represents the relationship between $\delta^{2}H$ and $\delta^{18}O$ values contained in meteoric water worldwide. Equation 2 represents the GMW line (Craig 1961).

$$\delta^{2}H = \left(8 \times \delta^{18}O\right) + 10 \tag{2}$$

where

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

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

Evaporation, evapotranspiration, geothermal reactions, and low-temperature silicate hydrolysis produce different $\delta^{2}H$ and $\delta^{18}O$ relationships compared with the GMW line. Evaporation from surface water bodies is a nonequilibrium process that enriches ^{2}H and ^{18}O in

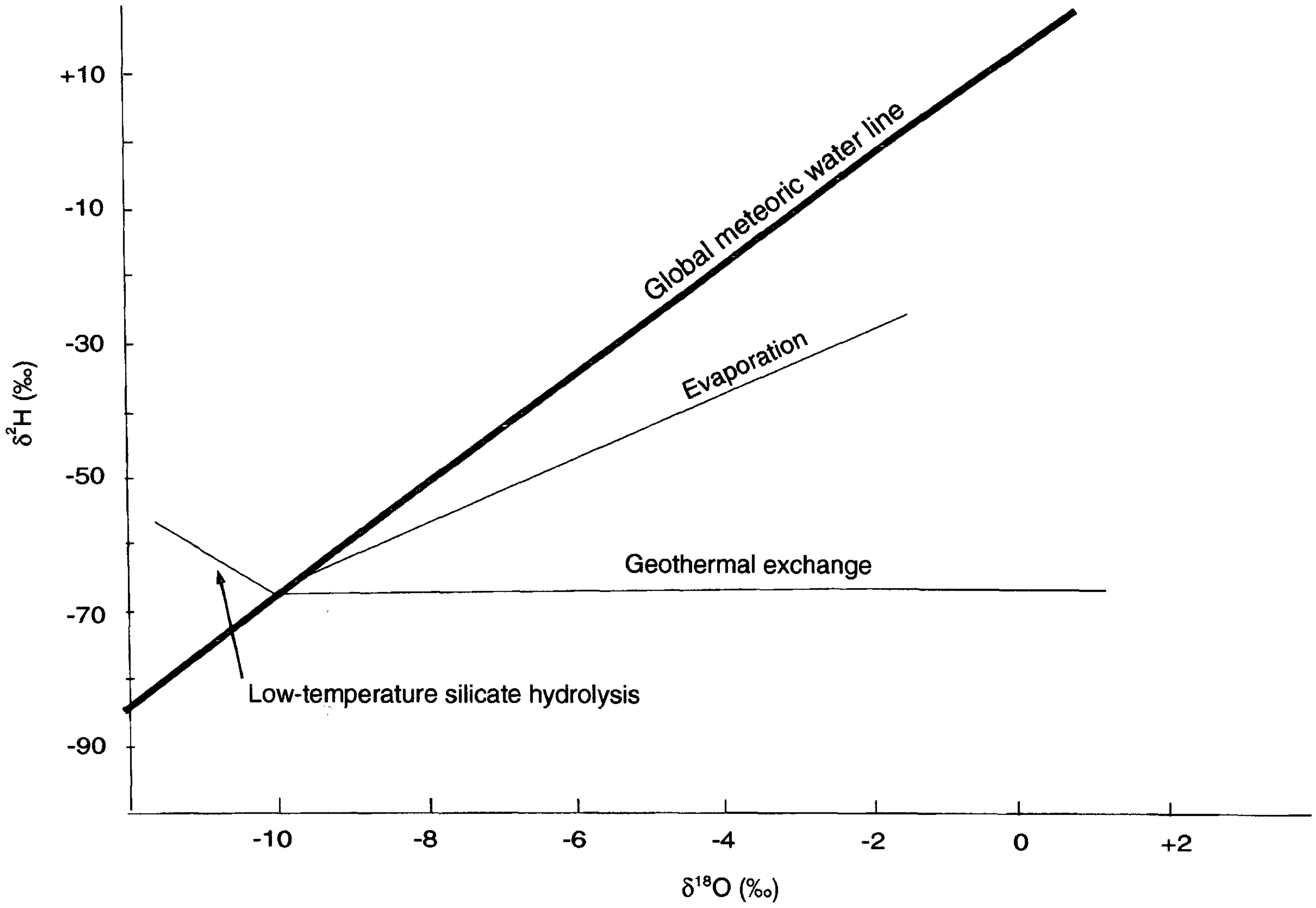

Figure 12. Schematic relationship between delta-deuterium (δ^2H) and delta-oxygen-18 ($\delta^{18}O$) for different hydrologic processes (modified from Coplen 1993)

the remaining water. Evaporation causes the plot of ^{2}H versus ^{18}O to diverge from the GMW line (Figure 12). 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, evapotranspiration 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. The enrichment of groundwater in ^{2}H and ^{18}O because of evapotranspiration is similar to that of evaporation. Of the above processes, evaporation and evapotranspiration are most likely the only major processes that have affected the $\delta^{2}H$ and $\delta^{18}O$ relationship in groundwater samples in Florida.

The relationship between $\delta^{2}H$ and $\delta^{18}O$ can be used to identify spring waters that have similar histories, such as source, flow paths, and mixing. If $\delta^{2}H$ and $\delta^{18}O$ values plot near or next to one another, the samples have a similar history (Figure 13). Samples that are separated have different values and therefore have different histories. The precision of the analyses is indicated by the relative position of duplicate samples (sites 6 and 7 for Rock Springs, sites 18 and 19 for Juniper Springs).

Springs with water that has similar $\delta^{2}H$ and $\delta^{18}O$ values are Palm (site 15) and Starbuck (site 16), Silver Glen (site 17) and Sweetwater (site 26), and Seminole (site 12), Blue (site 20), and the northwest vent of Salt (site 23) and Gemini (site 27) (Figure 13 and Table 5). It is not surprising for Palm and Starbuck springs or Silver Glen and Sweetwater springs to have similar $\delta^{2}H$ and $\delta^{18}O$ values because they occur near each other. However, it is surprising for Seminole, Blue, the northwest vent of Salt, and Gemini springs to have similar $\delta^{2}H$ and $\delta^{18}O$ values because they are so far apart.

Inspection of Figure 13 indicates that water samples from the four vents at Salt Springs (site 22–25) have different $\delta^{2}H$ and $\delta^{18}O$ values, suggesting that they have different histories. Other differences occur between Seminole (site 12) and Messant (site 13) springs and between Palm (site 15), Starbuck (site 16), and Sanlando (site 14) springs. Palm and Starbuck springs have similar $\delta^{2}H$ and $\delta^{18}O$ values, as do Seminole and the northwest boil of Salt Springs (site 23). The other boils at Salt

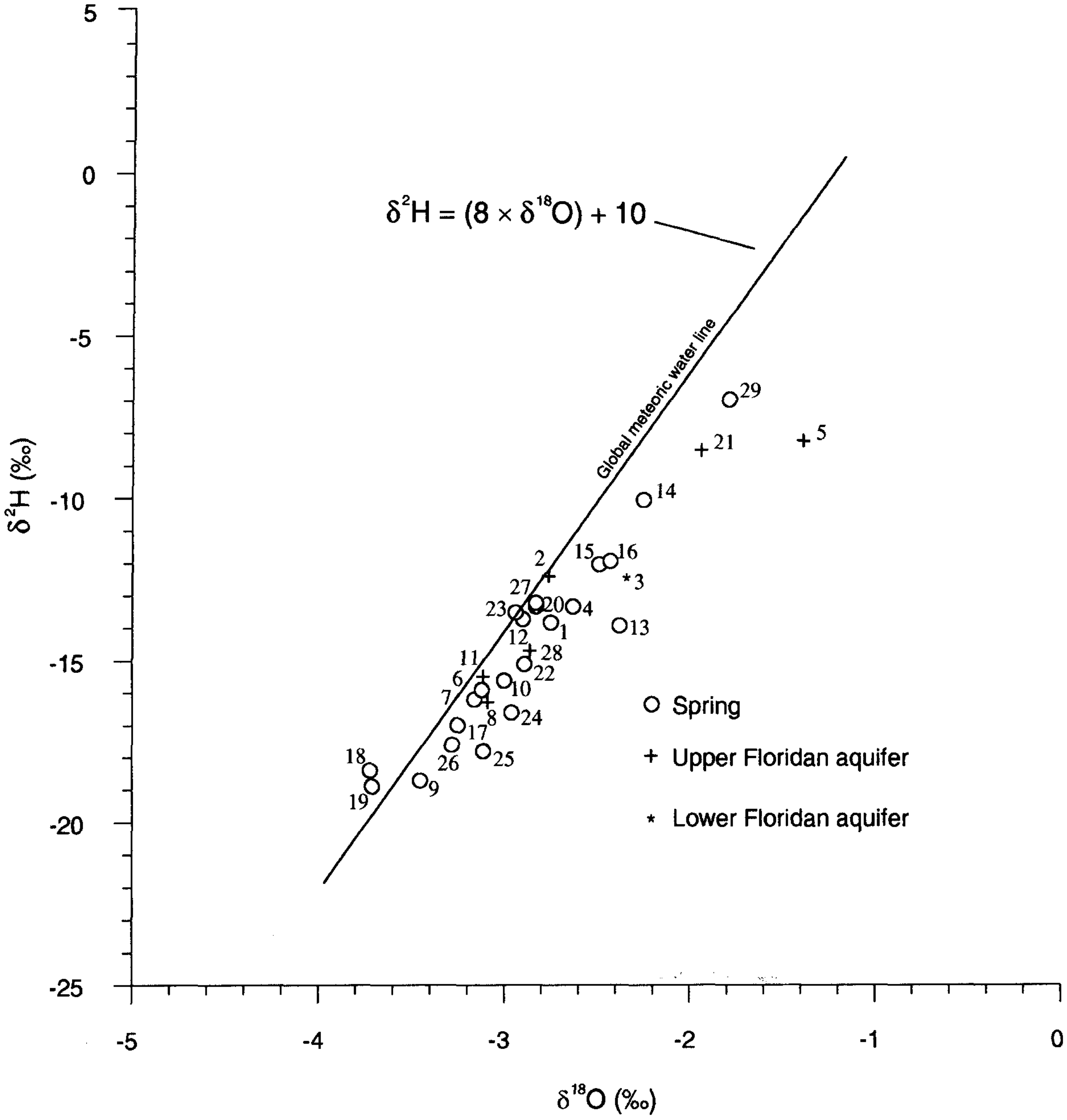

Figure 13. Relationship between delta-deuterium (δ^2H) and delta-oxygen-18 (δ^{18}O) for samples analyzed in this study (see Table 5 for spring names and well numbers)

Springs (sites 22, 24, 25), along with Seminole, Messant, and Sanlando springs, have different δ^2H and $\delta^{18}O$ values and suggest that they have different histories.

Comparing δ^2H and $\delta^{18}O$ values for springs and wells in Figure 13 reveals similarities and differences. Rock Springs (sites 6 and 7) water is similar to water from well OR0170 (site 8) in the Upper Floridan aquifer. Alexander Springs (site 10) water is similar to water from well L-0066 (site 11) in the Upper Floridan aquifer. Gemini Springs (site 27) water is similar to water from well V-0564 (site 28). Wekiva Springs (site 1) water also is most similar to water from well OR0548 (site 2) in the Upper Floridan aquifer, but different from water from well OR0547 (site 3) in the Lower Floridan aquifer. Ponce de Leon Springs and Blue Spring waters are very different from waters from wells near these springs. Well V-1030 (site 5) is near Ponce de Leon Springs (site 4) and well V-0083 (site 21) is near Blue Spring (site 20).

Carbon-13

Carbon-13 is a stable isotope of carbon. In groundwater, the fraction of ^{13}C is generally a function of the $\delta^{13}C$ of the rocks that make up the aquifer, the $\delta^{13}C$ of the total dissolved carbon dioxide (CO_2) in the system, and the extent of the reaction of CO_2 with the rocks and soils with which the water is in contact. Carbon-13 often is used to identify possible reactions that occur along a flow path. It also is used to correct the ^{14}C concentration for the addition of bicarbonate resulting from limestone dissolution, which results in the addition of nonradioactive (stable) carbon to the system. The addition of stable carbon to the system causes the ^{14}C concentration to be diluted. If uncorrected, the ^{14}C concentration would yield an older calculated age for the sample.

The $\delta^{13}C$ values for the spring and well samples in this study ranged from -5.22‰ at Crescent Beach Spring to -10.90‰ at well V-0564 (Table 5 and Figure 14). For most of the samples, $\delta^{13}C$ ranged between -7.43‰ and -10.90‰. The difference between duplicate samples and spring samples at Rock and Juniper springs indicates the precision of the analyses. The $\delta^{13}C$ results for samples from Rock and Juniper springs and their duplicates differ by 0.21‰ and 0.30‰, respectively.

Table 5. Stable and radioactive isotope values for samples collected in this study

Site Number	Site Name	$\delta^{2}H$ (‰)	$\delta^{18}O$ (‰)	$^{87}Sr/^{86}Sr$	$\delta^{13}C$ (‰)	^{14}C (pmc)	$\delta^{34}S$ (‰)	^{3}H or T (TU)	$\delta^{15}N$* (‰)
1	Wekiva Springs	-13.8	-2.75	0.70826	-10.14	50.04	5.7	3.0	8.6
2	OR0548	-12.3	-2.76	0.70812	-9.22	43.51	12.0	2.6	6.0
3	OR0547	-12.6	-2.34	0.70790	-9.02	20.88	33.9	0.0	5.2
4	Ponce de Leon Springs	-13.3	-2.63	0.70860	-7.96	34.91	13.9	2.1	8.9
5	V-1030	-8.1	-1.39	0.70873	-7.43	34.43	†	4.0	1.4
6	Rock Springs	-15.9	-3.12	0.70807	-9.08	41.25	9.4	3.1	5.8
7	Rock Springs (duplicate)	-16.2	-3.16	0.70803	-9.29	41.17	9.4	3.0	5.9
8	OR0170	-16.2	-3.09	0.70807	-7.78	33.99	2.1	2.3	9.4
9	Croaker Hole Spring	-18.7	-3.45	0.70792	-8.47	31.07	20.9	4.5	
10	Alexander Springs	-15.6	-3.00	0.70795	-9.50	28.43	21.0	2.7	
11	L-0066	-15.4	-3.11	0.70788	-9.18	23.98	21.0	2.5	
12	Seminole Springs	-13.7	-2.90	0.70790	-9.31	26.33	18.9	2.5	5.1
13	Messant Spring	-13.9	-2.38	0.70788	-8.57	22.60	20.8	0.2	
14	Sanlando Springs	-10.0	-2.25	0.70839	-10.49	57.01	10.7	2.9	11.7
15	Palm Springs	-12.0	-2.49	0.70797	-10.86	42.79	17.8	1.6	7.8
16	Starbuck Spring	-11.9	-2.43	0.70799	-10.51	45.82	15.3	2.4	12.9
17	Silver Glen Springs	-17.0	-3.25	0.70796	-7.70	20.30	20.2	2.4	
18	Juniper Springs	-18.4	-3.72	0.70799	-9.50	30.70	17.0	4.2	
19	Juniper Springs (duplicate)	-18.9	-3.71	0.70799	-9.80	31.30	16.9	4.0	
20	Blue Spring	-13.3	-2.83	0.70825	-10.10	45.20	18.1	3.8	
21	V-0083	-8.4	-1.94	0.70790	-8.10	6.71	20.8	0.0	
22	Salt Springs northeast vent	-15.1	-2.89	0.70799	-8.30	22.40	20.6	3.4	
23	Salt Springs northwest vent	-13.5	-2.94	0.70799	-8.30	21.50	20.7	3.3	
24	Salt Springs southwest vent	-16.6	-2.96	0.70799	-7.70	22.50	‡	3.0	
25	Salt Springs southeast vent	-17.8	-3.11	0.70798	-8.40	22.00	20.8	3.5	
26	Sweetwater Springs	-17.6	-3.28	0.70797	-8.10	16.00	20.3	1.2	
27	Gemini Springs	-13.2	-2.83	0.70798	-10.40	40.90	§	3.3	
28	V-0564	-14.6	-2.86	0.70797	-10.90	40.70	20.7	3.5	

Table 5—*Continued*

Site Number	Site Name	δ^2H (‰)	$\delta^{18}O$ (‰)	$^{87}Sr/^{86}Sr$	$\delta^{13}C$ (‰)	^{14}C (pmc)	$\delta^{34}S$ (‰)	^3H or T (TU)	$\delta^{15}N$* (‰)
29	Crescent Beach Submarine Spring	-6.9	-1.79	0.70798	-5.22	14.13	20.8		
30	SJ0432								
31	SJ0516								

Note: Blank cells indicate not measured.

*In nitrate
†Laboratory error
‡Bottle broke
§Sample lost

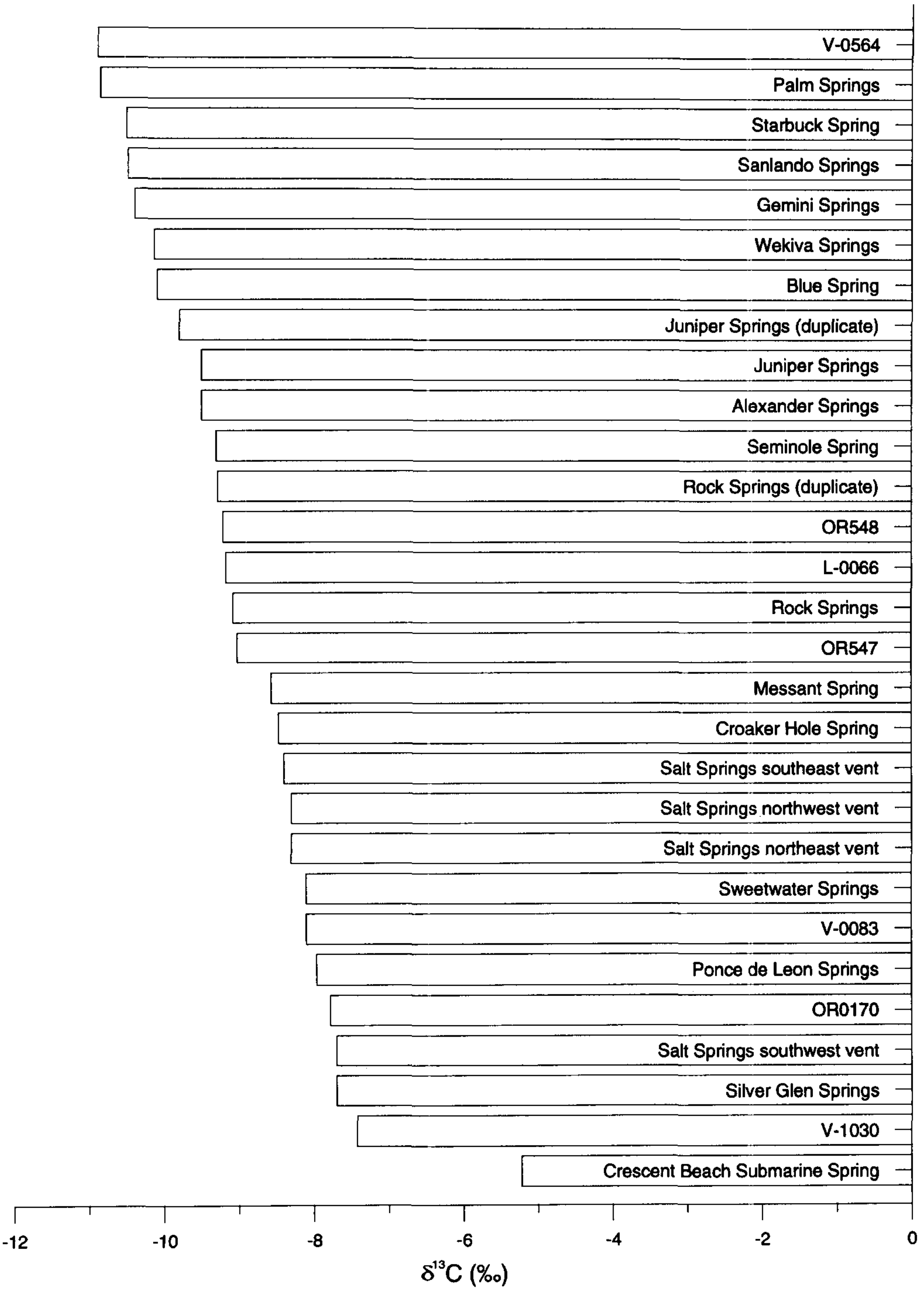

Figure 14. Distribution of delta-carbon-13 ($\delta^{13}C$) values for samples collected in this study

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. Metabolic processes tend to favor lighter isotopes (e.g., ^{14}N). As a consequence, the heavier isotope (^{15}N) is left behind. In this study, ^{15}N was used to identify possible sources of nitrate contamination.

The $\delta^{15}N$ value generally is used to identify the source of the nitrogen. The $\delta^{15}N$ values for soil organic nitrogen generally range between +3‰ and +9‰ (Heaton 1986) (Figure 15). The $\delta^{15}N$ value of nitrate in fertilizers ranges between -1‰ and +6‰, but is generally less than +3‰. The $\delta^{15}N$ value of nitrate from animal waste and/or sewage has a value above +8‰.

As stated previously (p. 23), nitrate concentrations above 0.2 mg/L were considered elevated in this study. The $\delta^{15}N$ value was determined on all samples in which the nitrate concentration was above 0.2 mg/L, with the exception of Blue Spring, Gemini Springs, and well V-0564. The $\delta^{15}N$ value was also determined for water from wells OR0548, OR0547, V-1030, and OR0170, even though the nitrate concentrations were below 0.2 mg/L (Tables 3 and 5). Springs with nitrate concentrations above 0.2 mg/L are Wekiva, Ponce de Leon, Rock, Seminole, Sanlando, Palm, Starbuck, Blue, and Gemini. The $\delta^{15}N$ values for all samples analyzed in this study ranged from 1.4‰ for water from well V-1030 to 12.9‰ for a sample from Starbuck Spring.

The source of nitrate differs by location of the spring. The elevated nitrate levels in Sanlando ($\delta^{15}N$ = +11.7‰), Starbuck ($\delta^{15}N$ = +12.9‰), Wekiva ($\delta^{15}N$ = +8.6‰), and Ponce de Leon ($\delta^{15}N$ = +8.9‰) springs, based on $\delta^{15}N$, are probably due to contamination by animal waste and/or sewage. The elevated nitrate level in Palm Springs ($\delta^{15}N$ = +7.8‰) is probably due to contamination by animal waste and/or sewage, perhaps mixing with nitrates derived from soil organic nitrogen. Finally, the elevated nitrate levels in Rock Springs ($\delta^{15}N$ = +5.8‰) and Seminole springs ($\delta^{15}N$ = +5.1‰) are probably due to contamination by nitrates from fertilizers mixing with nitrates from

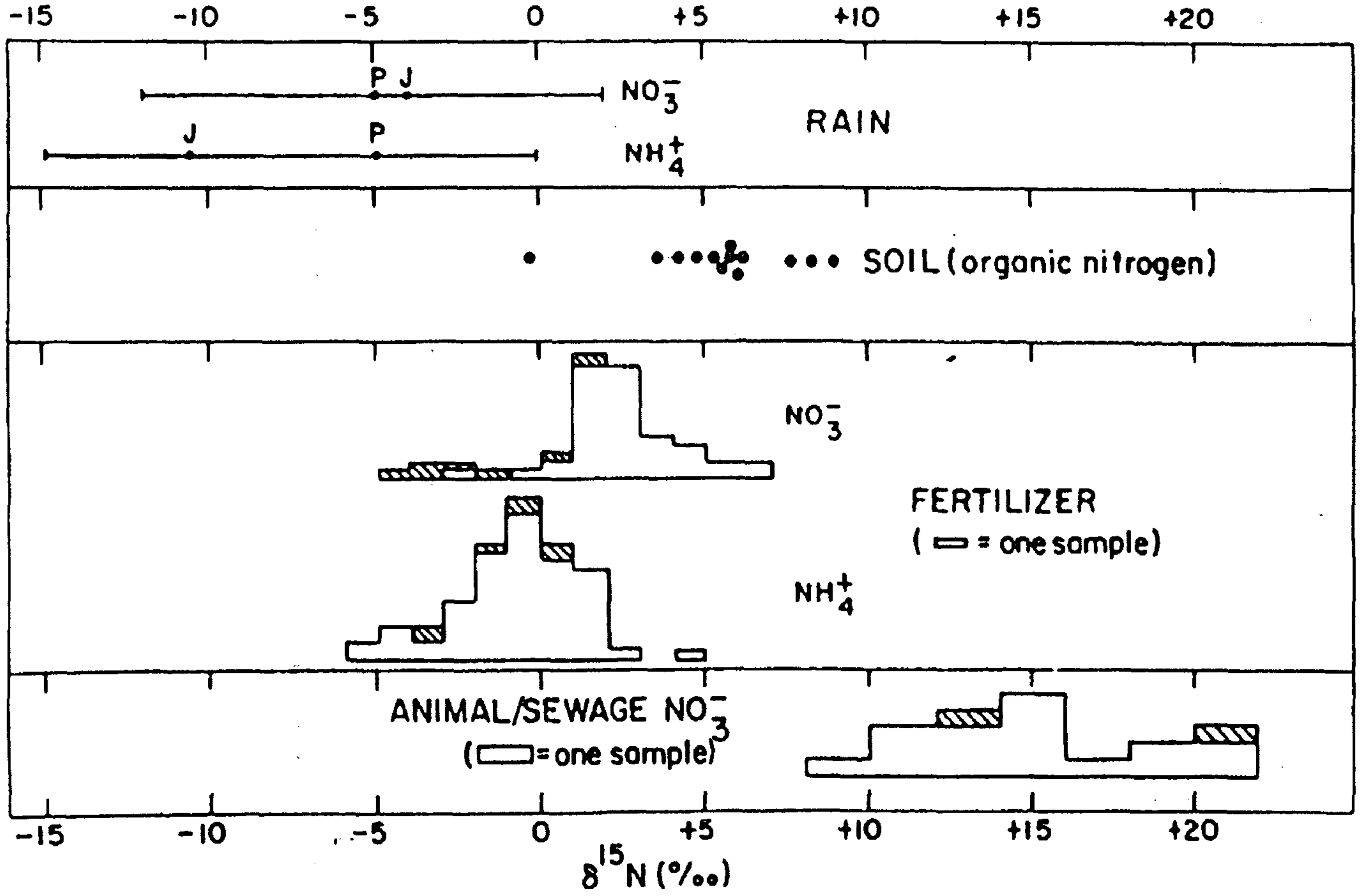

Figure 15. Sources of nitrogen in ground and surface waters and their delta-nitrogen-15 ($\delta^{15}N$) content (Heaton 1986)

soil organic nitrogen. The presence of elevated nitrate levels in spring water suggests a shallow to intermediate flow system for the springs.

The available data do not provide a distinction between nitrate contamination which occurred in 1995 (sampling time period) and nitrate contamination which occurred prior to that date. Additional studies are required of land use practices and historical concentrations of nitrate in groundwater to determine when contamination occurred.

Sulfur-34

Sulfur-34 is a stable isotope of sulfur. Analysis for $\delta^{34}S$ generally is used to test various geochemical reaction models along a flow path. Sulfur-34 and ^{13}C isotope data are often used to constrain one or more reaction models. Under favorable conditions, $\delta^{34}S$ can be used to identify the particular evaporite formation being dissolved (Coplen 1993). The $\delta^{34}S$ content of ancient evaporites ranges between +10‰ and +35‰ (Claypool et al. 1980) and there is no isotopic fractionation during dissolution. For comparison, the $\delta^{34}S$ value of contemporary, dissolved, oceanic sulfate and modern sulfate evaporite minerals is +20‰ (Coplen 1993).

The $\delta^{34}S$ values for samples collected during this study ranged from +2.1‰ for a sample from well OR0170 in the Upper Floridan aquifer to +33.9‰ for a sample from well OR0547 in the Lower Floridan aquifer (Table 5). For samples in which the sulfate concentration was above approximately 150 mg/L, the $\delta^{34}S$ values were approximately constant at about +20.8‰ (Figure 16). This value is approximately the same as that for modern sulfate evaporite minerals. For samples in which the sulfate concentration was below approximately 50 mg/L, the $\delta^{34}S$ values vary. There is essentially no difference in the $\delta^{34}S$ values for the water samples from the vents at Salt Springs (Table 5), because the sulfate concentrations for water were above 150 mg/L (Table 3). The samples from wells OR0548 (Upper Floridan aquifer) and OR0547 (Lower Floridan aquifer) at Wekiva Springs and the samples from well OR0170 (Upper Floridan aquifer) at Rock Springs and from Rock Springs have distinctly different $\delta^{34}S$ values. The $\delta^{34}S$ values also differ between Rock and Wekiva springs samples and between OR0548 and OR0170 samples, because the sulfate levels in these samples were low

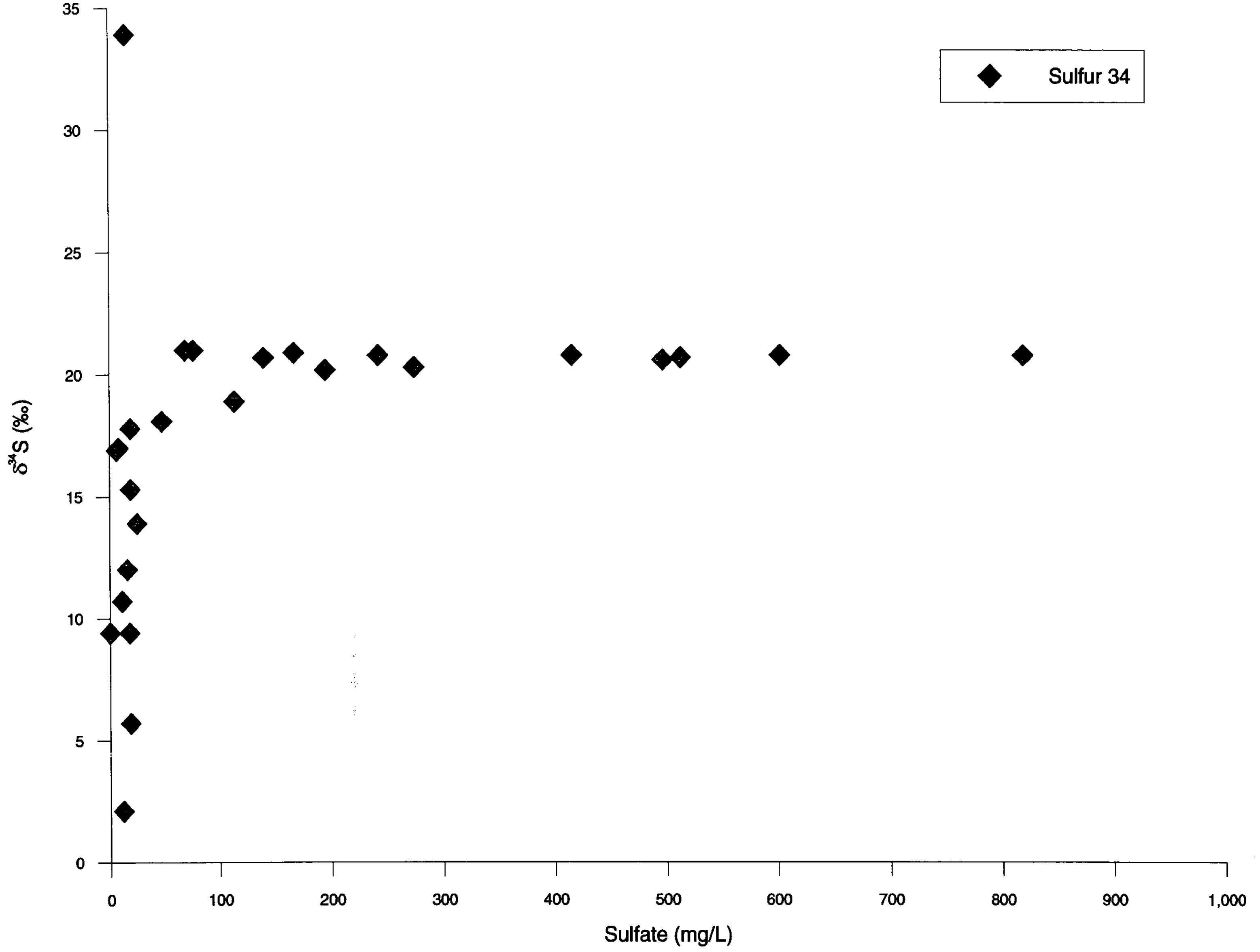

Figure 16. Variation of delta-sulfur-34 ($\delta^{34}S$) with sulfate content for samples collected in this study

(below 50 mg/L; Table 3). When sulfate levels are low, $\delta^{34}S$ generally reflects the net results of the $\delta^{34}S$ levels in rainfall, which can be variable, and differences in $\delta^{34}S$ resulting from geochemical reactions that occur along the flow path.

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. Limestones from the Eocene epoch have $^{87}Sr/^{86}Sr$ 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 2).

The $^{87}Sr/^{86}Sr$ values for the samples collected during this study ranged from 0.70788 for Messant Springs and well L-0066 (Upper Floridan aquifer) at Alexander Springs to 0.70873 for well V-1030 (Upper Floridan aquifer) at Ponce de Leon Springs (Table 5, Figure 17). Based on the $^{87}Sr/^{86}Sr$ values, water from Messant Spring and from well L-0066 (Upper Floridan aquifer) at Alexander Springs appears to be in equilibrium with Eocene-age limestones. Water from well OR0547, Seminole Springs, and well V-0083 has a $^{87}Sr/^{86}Sr$ value of 0.7079. 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 Sanlando and Ponce de Leon springs and well V-1030 appears to be in equilibrium with Miocene-age limestones.

However, the young age (Miocene and Oligocene) for most of the water from springs and wells suggests that the water is not in

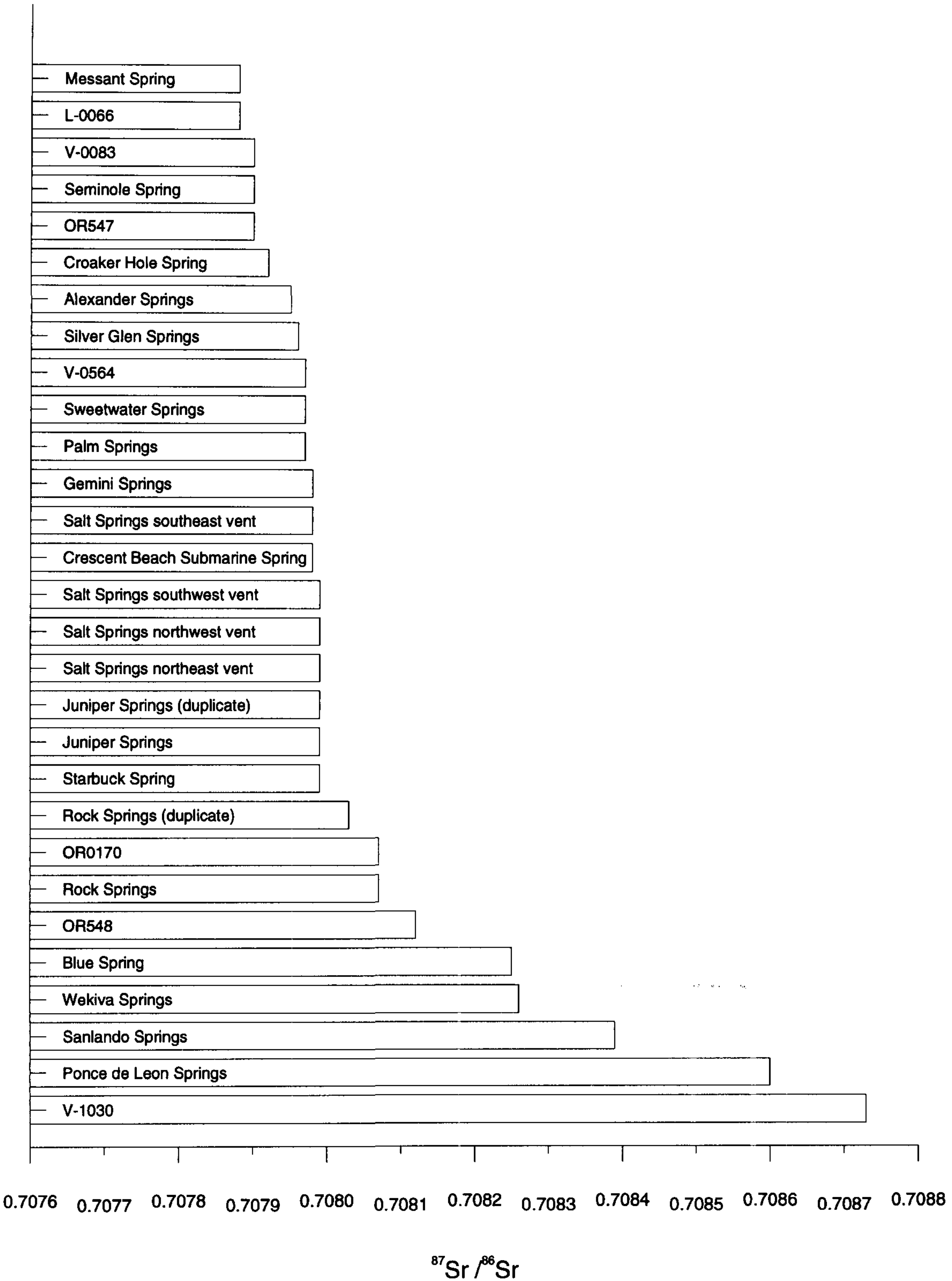

Figure 17. Distribution of strontium-87/strontium-86 ($^{87}Sr/^{86}Sr$) values for samples collected in this study

equilibrium with the Eocene-age limestones in the Floridan aquifer system. All but one of the springs and wells are located within 4 miles of high recharge areas. This short distance between recharge and discharge areas may not allow for sufficient time for the water in the Floridan aquifer system to reach equilibrium. Water from the recharge areas dissolve Miocene-age limestones 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 Miocene and Eocene ages. Most of the springs and wells 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 sampled sites is not in equilibrium. Only samples from wells OR0548, OR0547, and V-1030 and Messant Spring are saturated with respect to calcite (calcite saturation was determined for all samples using NETPATH [Plummer et al. 1994]).

The young age 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 that those with an Oligocene age. Also, shallow flow systems have a smaller area of influence than deeper flow systems.

Helium-3, Helium-4, and Neon

Concentrations of ^{3}He and ^{4}He can be used to determine an age for a water sample. Helium-3 is a radiogenic isotope of helium (He). It is produced by the radioactive decay of ^{3}H. Both ^{3}He and ^{4}He are stable isotopes of helium. Helium-3 was measured to calculate the tritium/helium-3 (^{3}H/^{3}He) age of the sample. Helium-4 was measured to correct the ^{3}He concentration for ^{3}He due to atmospheric sources—that is, ^{3}He concentrations arising from equilibration with air during recharge and entrainment of air bubbles. Neon is a noble gas. Neon was measured to correct ^{4}He for helium produced through the uranium and thorium decay series (Schlosser et al. 1989).

The ^{3}He in the water is assumed to be of atmospheric and tritogenic origin. This condition usually prevails in shallow aquifers containing predominantly young waters occurring in sediments and rocks of relatively low uranium and thorium content. Additional He sources may be present in aquifers where the rocks are enriched in uranium or thorium, or in groundwater samples in which young water has mixed with relatively old water containing radiogenic He. In these cases, the measured Ne content can be used to calculate the additional He (Schlosser et al. 1989).

As part of a pilot study, waters from three springs, Wekiva, Rock, and Ponce de Leon, were sampled for ^{3}He, ^{4}He, and Ne. The purpose of the pilot study was to examine the feasibility of ^{3}H/^{3}He age-dating. Because the purpose of measuring ^{3}He, ^{4}He, and Ne concentrations in waters from three springs was to correct the ^{3}H/^{3}He ages, only the ^{3}H/^{3}He ages were reported by the USGS laboratory (see Tritium/Helium-3 Age, p. 57).

RADIOACTIVE ISOTOPES

Radioactive isotopes measured in this study were ^{3}H and ^{14}C. The error attainable in the USGS laboratories for sample preparation and analysis of radioactive isotope samples is less than 15% for ^{3}H, except for the sample from Messant Spring, and 1.4% for ^{14}C (Ann Bradner, USGS, pers. com., December 1996). The error in the ^{3}H analysis for the sample from Messant Spring may be as high as 100% because the ^{3}H value was low.

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 (Table 4). 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.

In this study, the age of groundwater was determined by measuring the radioactive isotopes ^{3}H and ^{14}C and the stable isotopes ^{3}He and ^{4}He. Helium-3 and ^{4}He were used because they can, in combination with ^{3}H, accurately identify water that is less than 30 years old (Plummer, USGS, pers. com. 1996). 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).

Tritium

Tritium is a radioactive isotope of hydrogen that 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) (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 date recent groundwater (Coplen 1988). The half-life of ^{3}H is 12.43 years, which means that the ^{3}H concentration decreases by one-half every 12.43 years.

In this study, no ^{3}H was detected in two samples: from well OR0547 in the Lower Floridan aquifer and from well V-0083 in the Upper Floridan aquifer (Table 5). Tritium was not measured on the sample from Crescent Beach Spring. For the remainder of the samples, ^{3}H concentrations ranged from 0.2 TU at Messant Spring to 4.5 TU at Croaker Hole Spring (Figure 18). Even the four vents from Salt Springs had an appreciable ^{3}H concentration (3.0–3.5 TU). These values suggest that the vents from Salt Springs contain young water based on the presence of ^{3}H.

Except for Messant Spring, Sweetwater Springs, well OR0547, and well V-0083, the ^{3}H concentration of each sample was above 1.6 TU (Table 5, Figure 18). Tritium concentrations of 1.6 TU or above are assumed to be significant and represent samples that were recharged after 1953 (the date when ^{3}H began to increase in rainfall) (Plummer et al. 1993). Because of the variability in the ^{3}H concentration of rainfall with time since 1953, a more precise age could not be determined. The four samples in which the ^{3}H concentration was below 1.6 TU, however, were most likely recharged with water prior to 1953. The samples with no ^{3}H are probably more than 70 years old (Swancar and Hutchinson 1992).

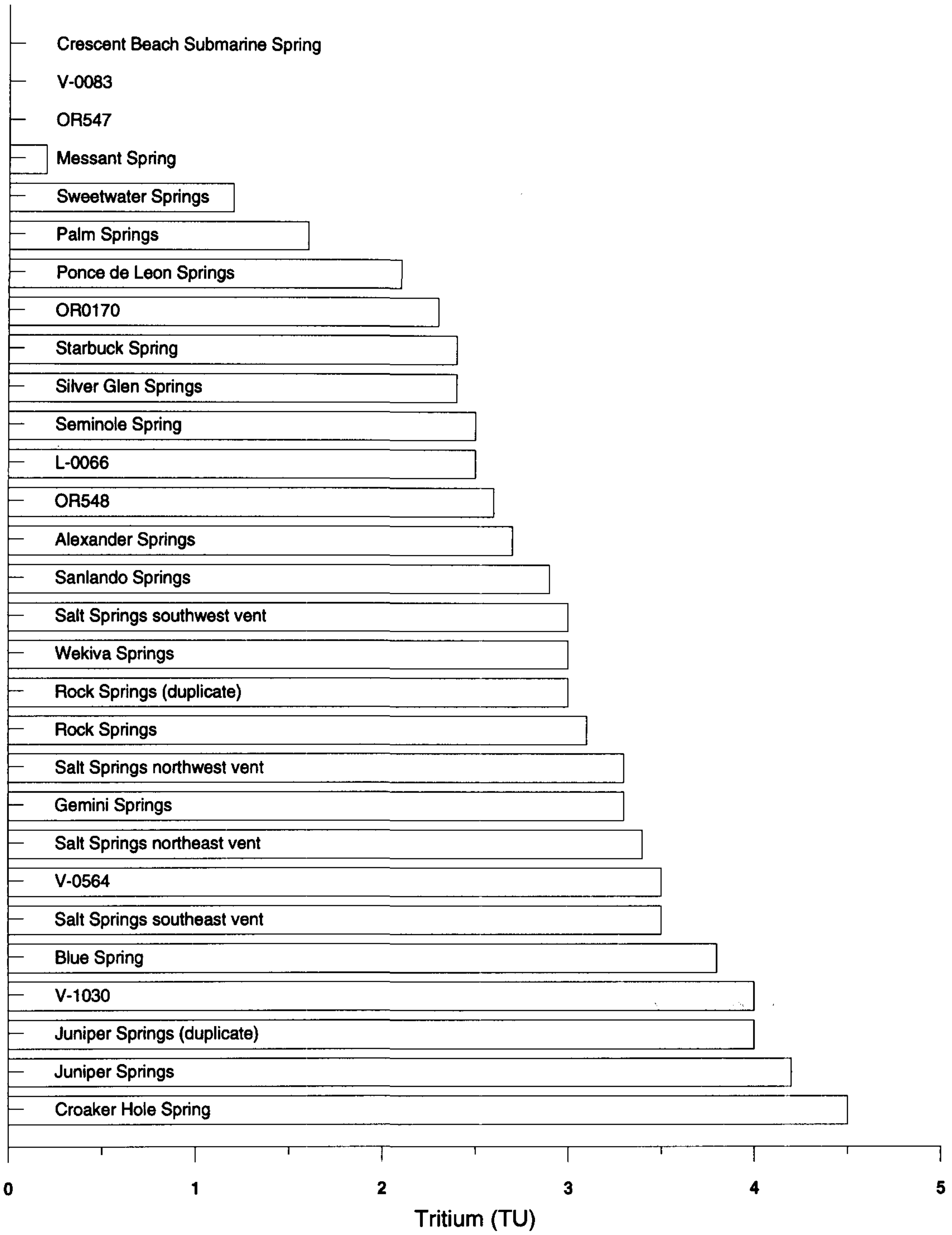

Figure 18. Distribution of tritium values for samples collected in this study. *Samples without tritium values represent old water (except for Crescent Beach Submarine Spring which was not sampled.*

The young age for many of the samples confirms that the flow system for many of the springs is shallow.

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 6.71 pmc for well V-0083 in the Upper Floridan aquifer to 57.01 pmc at Sanlando Springs (Table 5, Figure 19). The four vents from Salt Springs had a ^{14}C content ranging from 21.5 to 22.5 pmc. Crescent Beach Spring had a ^{14}C content of 14.13 pmc. Wekiva Springs had a ^{14}C content of 50.04 pmc. In general, the higher the ^{14}C content of the sample, the younger the water.

Water from Sanlando Springs had an anomalously high ^{14}C content. The ^{14}C content of Floridan aquifer water is generally less than 55 pmc (Toth 1995). The high ^{14}C content of Sanlando Springs is postulated to be due to inflow of water from the spring pool during reconstruction of the pool. Therefore, water from Wekiva Springs, with a ^{14}C content of 50.04 pmc, is considered to be the youngest for the samples collected during this study.

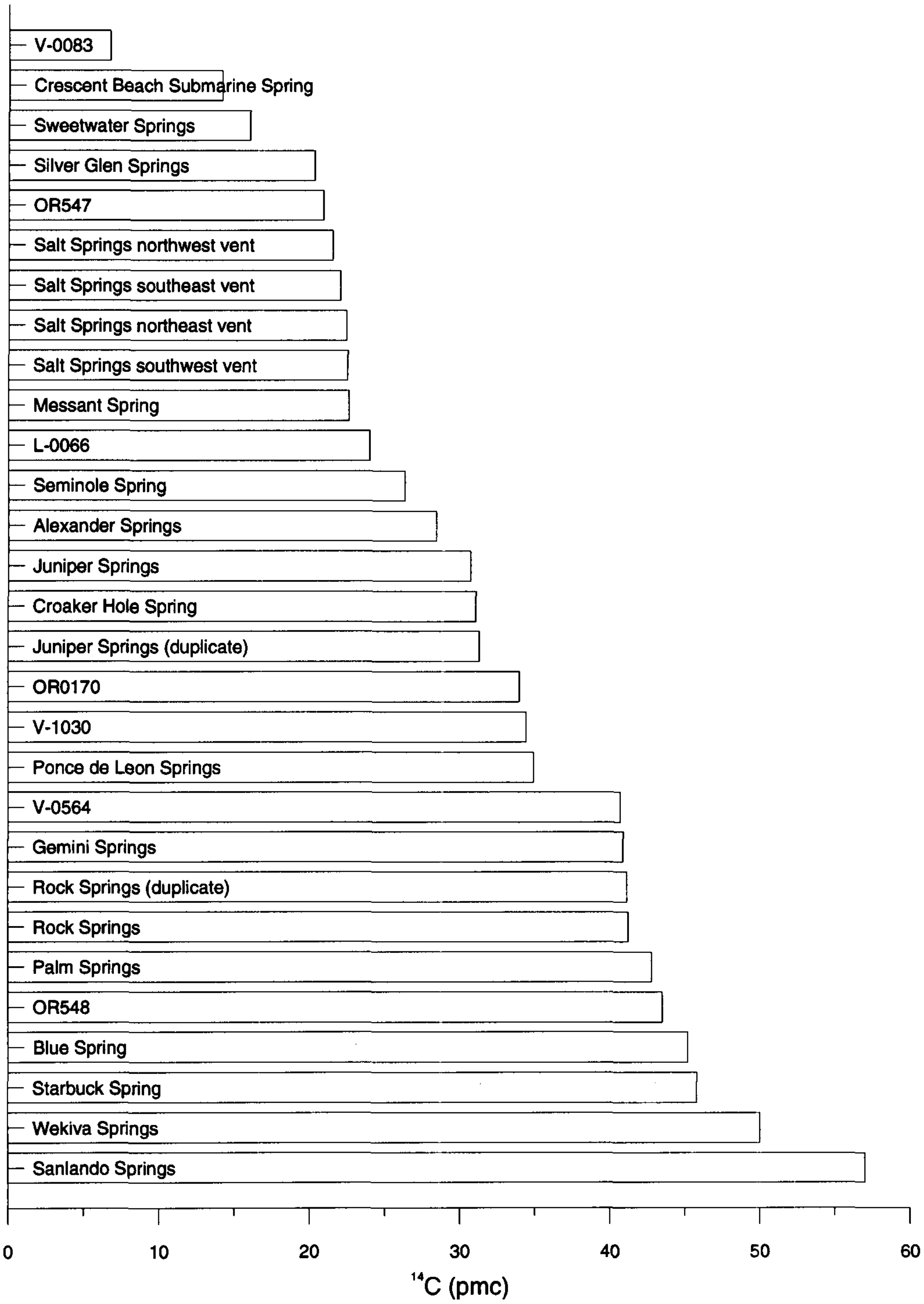

Figure 19. Distribution of carbon-14 (^{14}C) values for samples collected in this study. *Samples are arranged in descending order: oldest samples are at the top and youngest samples are at the bottom.*

Comparing the ^{14}C content of springs with that from wells near the springs (Upper Floridan aquifer), the ^{14}C content is always greater in the spring than in the well. This pattern indicates that water in the springs is younger than water in the wells.

There is also a significant difference in the ^{14}C content of well water from the Upper and Lower Floridan aquifers. The ^{14}C content of water from well OR0548 in the Upper Floridan aquifer is 43.51 pmc, while the ^{14}C content of well OR0547 in the Lower Floridan aquifer is 20.88 pmc. In a discharge area, water in the Lower Floridan aquifer would be expected to be older than water in the Upper Floridan aquifer.

The ^{14}C content of samples collected during this study is inversely related to the ^{13}C content of the samples (Figure 20), but proportional to the $^{87}Sr/^{86}Sr$ ratio (Figure 21). Samples with high concentrations of ^{14}C have lighter (more negative) values of ^{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.

The proportional trend between ^{14}C and $^{87}Sr/^{86}Sr$ (Figure 21) supports the conclusion that samples with a high value for $^{87}Sr/^{86}Sr$ are generally younger than those with a low value. Samples from Ponce de Leon Springs and well V-1030 are the exception. Samples from this spring and well have the highest values for $^{87}Sr/^{86}Sr$, but only contain 34.91 and 34.43 pmc, respectively.

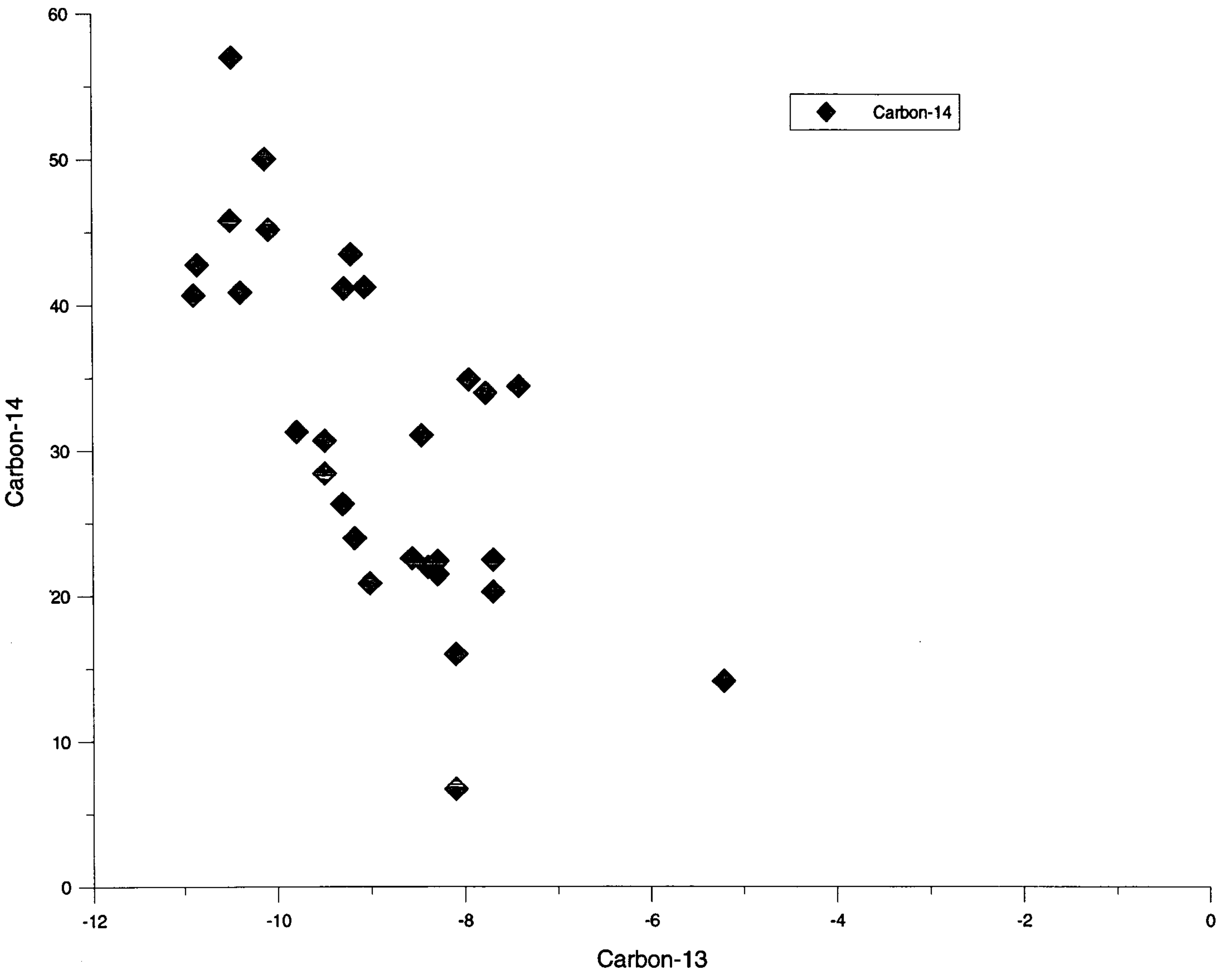

Figure 20. Plot of carbon-14 versus carbon-13 for the samples collected in this study

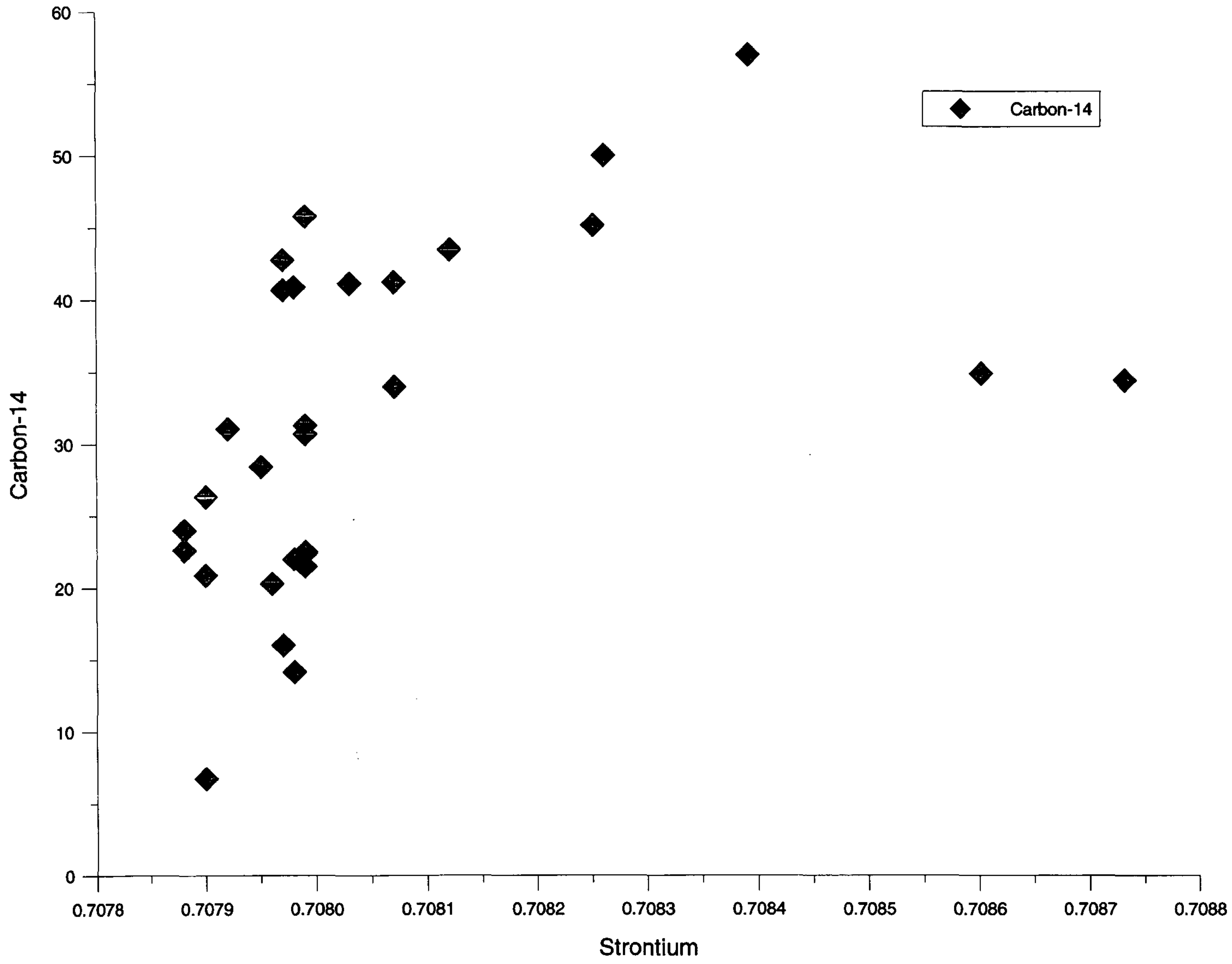

Figure 21. Plot of carbon-14 versus strontium-87/strontium-86 for the samples collected in this study

AGE

Three different ages were determined for groundwater samples collected during this study: a ^{3}H age, a ^{3}H/^{3}He age, and a ^{14}C age. A ^{3}H age was determined for all but one of the samples in this study (Crescent Beach Spring). A ^{14}C age was not determined for samples from Wekiva and Sanlando springs. A ^{3}H/^{3}He age was only determined for samples from Wekiva, Rock, and Ponce de Leon springs. The ^{3}H concentration for these three springs suggested that they contained post-1953 water.

TRITIUM AGE

The maximum possible ^{3}H age for a sample can be calculated by subtracting 1953 from the last year that a sample was collected. The ^{3}H concentrations suggest that all samples except those from Messant and Sweetwater springs and wells OR0547 and V-0083 contain post-1953 water. Samples were collected in 1995 and 1996. Hence, the ^{3}H age for most samples would be 1996 minus 1953, or less than 43 years old. Samples from wells OR0547 and V-0083, which contain no ^{3}H, are more than 70 years old. The ^{3}H age for samples from Messant and Sweetwater springs is probably less than 70 years old because their ^{3}H concentration is greater than 0 and less than 1.6 TU.

TRITIUM/HELIUM-3 AGE

The ^{3}H/^{3}He age of groundwater is an indicator of the time elapsed since recharge and isolation from the atmosphere. The method is based on the radioactive decay of ^{3}H to ^{3}He. Because these substances are virtually inert in groundwater and are unaffected by contamination from anthropogenic sources, ^{3}H/^{3}He dating can be applied to a wide range of hydrologic investigations.

The ^{3}H/^{3}He age of water samples from Wekiva, Rock, and Ponce de Leon springs is 17.1 ± 0.5 years, 19.8 ± 0.5 years, and 28.6 ± 0.7 years, respectively (Plummer, USGS, pers. com., September 1997). The relatively young age of the water from these springs supports the conclusion that their flow systems are very shallow. The use of ^{3}H/^{3}He techniques for measuring age was successful and is therefore a valid technique for measuring age.

However, $^3H/^3He$ ages can have an error of about 10% due to ^3H confinement and its incomplete mixing with older water (Plummer et al. 1993). Therefore, the samples from both Wekiva and Rock springs are statistically the same with regard to $^3H/^3He$ age, even though they have different values for ^{14}C. This difference could result from the fact that the $^3H/^3He$ age gives the apparent age of the youngest component of a mixed sample. The ratio of $^3H/^3He$ does not change as the water is mixed and diluted with older water, but the concentration of ^{14}C does change. This response to mixing suggests that the true age of the oldest component of a mixed sample is older than its ^{14}C age. The source for the youngest component of a mixed sample is lateral flow from recharge areas. The source for the oldest component is vertical flow from depth.

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.

Because most of the samples collected in this study are undersaturated with respect to calcite, dead-carbon probably has been added to most, if not all, samples. Dead-carbon contains no ^{14}C and arises from the dissolution of limestone. The presence of dead-carbon would make the samples appear older than they really are. In this study, all samples are assumed to contain the same amount of dead-carbon.

The ^{14}C age for samples collected during this study can be calculated from Equation 3 (Plummer et al. 1994):

$$Age^{14}C = \left(\frac{5730}{\ln 2}\right) \ln \left(\frac{A_0}{A}\right) \tag{3}$$

where

$Age^{14}C$ = carbon-14 age
Ao = initial carbon-14 concentration of the sample, in percent modern carbon
A = measured carbon-14 concentration of the sample, in percent modern carbon

Several models calculate the age of groundwater from its ^{14}C content. The age represents the time since water was last in contact with the atmosphere and is given relative to 1950.

In this study, *Ao* is assumed to be equivalent to the ^{14}C content of Wekiva Springs, or 50.04 pmc. The ^{3}H content of Wekiva Springs suggests that it contains post-1953 water. Except for Sanlando Springs, Wekiva Springs has the highest ^{14}C content (see p. 51).

The ^{14}C ages for the samples collected during this study ranged from 728 years before 1950 at Starbuck Spring to 16,610 years before 1950 in well V-0083, at Blue Spring State Park (Table 6). In this calculation, the age for Wekiva Springs is assumed to be recent. An age was not calculated for Sanlando Springs because the ^{14}C content is assumed to be contaminated by water from the spring pool.

Other ^{14}C ages are 3,940 years before 1950 for Croaker Hole Spring, 6,608–6,983 years before 1950 for the four vents at Salt Springs, and 10,453 years before 1950 for Crescent Beach Spring. Water from well OR0548 (Upper Floridan aquifer) at Wekiva Springs has a ^{14}C age of 1,156 years before 1950, and water from well OR0547 (Lower Floridan aquifer) has a ^{14}C age of 7,225 years before 1950.

The relatively young age (<1,900 years) for many of the springs confirms that they represent the discharge from shallow flow systems.

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 43 years old. The ^{14}C analyses of samples indicate the waters are from hundreds to thousands of years

Table 6. Carbon-14 age for samples collected in this study. *Samples are arranged in the same order as site names in Table 5.*

Sample	^{14}C Age (years before 1950)
Wekiva Springs	*
OR0548	1,156
OR0547	7,225
Ponce de Leon Springs	2,976
V-1030	3,091
Rock Springs	1,597
Rock Springs (duplicate)	1,613
OR0170	3,197
Croaker Hole Spring	3,940
Alexander Springs	4,674
L-0066	6,081
Seminole Springs	5,308
Messant Spring	6,571
Sanlando Springs	†
Palm Springs	1,294
Starbuck Spring	728
Silver Glen Springs	7,458
Juniper Springs	4,039
Juniper Springs (duplicate)	3,879
Blue Spring	841
V-0083	16,610
Salt Springs northeast vent	6,644
Salt Springs northwest vent	6,983
Salt Springs southwest vent	6,608
Salt Springs southeast vent	6,793
Sweetwater Springs	9,426
Gemini Springs	1,667
V-0564	1,708
Crescent Beach Submarine Spring	10,453
SJ0432	not measured
SJ0516	not measured

*Wekiva Springs is the baseline; age assumed to be recent.
†Not calculated

old. The difference between ^{3}H and ^{14}C ages indicates that the springs and the wells in the Upper Floridan aquifer contain a mixture of water of different ages. 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 area of influence for the springs sampled in this study are inferred from ^{14}C content of the springs (Table 7). Springs with a ^{14}C above 40 pmc are inferred to have a shallow flow system and a local area of influence. Springs with a ^{14}C between 25 and 40 pmc are inferred to have an intermediate flow system and a subregional area of influence. Finally, springs with a ^{14}C below 25 pmc are inferred to have a deep flow system and a regional area of influence.

Table 7. Flow system and area of influence for the springs sampled in this study

Spring	^{14}C (pmc)	Age (years)	Flow System	Area of Influence
Alexander	28.43	4,674	Intermediate	Subregional
Blue	45.20	841	Shallow	Local
Crescent Beach Submarine	14.13	10,453	Deep	Regional
Croaker Hole	31.07	3,940	Intermediate	Subregional
Gemini	40.90	1,667	Shallow	Local
Juniper	30.70	4,039	Intermediate	Subregional
Messant	22.60	6,571	Deep	Regional
Palm	42.79	1,294	Shallow	Local
Ponce de Leon	34.91	2,976	Intermediate	Subregional
Rock	41.25	1,597	Shallow	Local
Salt—northeast vent	22.40	6,644	Deep	Regional
Salt—northwest vent	21.50	6,983	Deep	Regional
Salt—southeast vent	22.00	6,793	Deep	Regional
Salt—southwest vent	22.50	6,608	Deep	Regional
Sanlando	57.01	*	Shallow	Local
Seminole	26.33	5,308	Intermediate	Subregional
Silver Glen	20.30	7,458	Deep	Regional
Starbuck	45.82	728	Shallow	Local
Sweetwater	16.00	9,426	Deep	Regional
Wekiva	50.04	†	Shallow	Local

*Not calculated

†Wekiva Springs is the baseline; age assumed to be recent.

CONCLUSIONS

Seventeen springs (two of which are submerged), eight wells in the Upper Floridan aquifer, and one well in the Lower Floridan aquifer 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 source of spring water, (4) to determine the age of spring water and to evaluate the nature of the spring flow system, and (5) to determine the sources of elevated nitrate-nitrogen concentrations in these springs.

Water quality was highly variable for the springs sampled. Water quality in the springs compared favorably with that in the sampled wells with the exception of Blue and Ponce de Leon springs in Volusia County.

The source of spring discharge is the Upper Floridan aquifer. Water quality and the stable-isotope signatures of most of the springs and wells in the Upper Floridan aquifer are similar. However, water samples from Ponce de Leon and Blue springs are very different from samples from nearby wells. This data suggest that water represented by the well near Ponce de Leon Springs is mixing with water with higher mineral content in the drainage basin for the spring. The data also suggest that water from a nearby well at Blue Spring is stagnant and that water in the area of the well contributes very little, if any, discharge by lateral flow to the spring.

Three different ages were determined for groundwater samples collected during this study: a ^{3}H age, a ^{3}H/^{3}He age, and a ^{14}C age. The ^{3}H age for most samples was less than 43 years old. The ^{3}H /^{3}He age for three springs ranged between 17.1 and 28.6 years old. The ^{14}C age ranged from 728 years to 16,610 years before 1950. Different age estimates for samples collected during this study indicate that the springs and the wells in the Upper Floridan aquifer contain a mixture of waters of different ages. 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 area range from shallow to deep. The shallow nature of the flow system also is supported by $^{87}Sr/^{86}Sr$ data.

In this study, nitrate levels above 0.2 mg/L nitrate-nitrogen were considered to be elevated. Nitrate-nitrogen concentrations in groundwater are generally below 0.2 mg/L. Concentrations above this value imply a source of nitrogen. The ^{15}N isotope data for the springs sampled in this study suggest that the elevated nitrate levels in Sanlando, Starbuck, Wekiva, and Ponce de Leon springs are probably due to contamination by animal waste and/or sewage. The elevated nitrate level in Palm Springs is probably due to contamination by animal waste and/or sewage and perhaps mixing with nitrates derived from soil organic nitrogen. Finally, the elevated nitrate levels in Rock and Seminole springs are probably due to contamination by nitrates from fertilizers mixing with nitrates from soil organic nitrogen. The presence of elevated nitrate levels in spring water suggests a shallow to intermediate flow system for these springs.

The available data do not provide a distinction between past and present nitrate contamination. Additional studies are required to determine when contamination occurred.

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