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Sources of Groundwater and Characteristics of Surface-Water Recharge at Bell, White, and Suwannee Springs, Florida, 2012–13

Open-File Report 2016–1190

U.S. Department of the Interior
U.S. Geological Survey

Cover. Photograph of White Springs and wall of the Spring House.
Photograph by Alan Cressler, U.S. Geological Survey.

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By John F. Stamm and W. Scott McBride

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U.S. Department of the Interior
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U.S. Geological Survey
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U.S. Geological Survey, Reston, Virginia: 2016

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
inch (in.)	2.54×10^4	micrometer (µm)
inch (in.)	25.4	millimeter (mm)
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Volume	
ounce, fluid (fl. oz)	0.02957	liter (L)
	Flow rate	
foot per second (ft/s)	0.3048	meter per second (m/s)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
	Mass	
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F = (1.8 \times °C) + 32.$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C = (°F - 32) / 1.8.$$

Datum

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L), micrograms per liter (µg/L), or milliequivalents per liter.

Activities for radioactive constituents in water are given in picocuries per liter (pCi/L).

Abbreviations

C_0	initial concentration of tritium
C_t	concentration of tritium at t years
D	deuterium
DOT	Department of Transportation
Ma	mega-annum, or million years ago
NWIS	National Water Information System
RGDL	Reston Groundwater Dating Laboratory
RSIL	Reston Stable Isotope Laboratory
SCUBA	self-contained underwater breathing apparatus
SRWMD	Suwannee River Water Management District
UFA	Upper Floridan aquifer
USGS	U.S. Geological Survey
VCDT	Vienna Canyon Diablo Troilite
VSMOW	Vienna Standard Mean Ocean Water

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Sources of Groundwater and Characteristics of Surface-Water Recharge at Bell, White, and Suwannee Springs, Florida, 2012–13

By John F. Stamm and W. Scott McBride

Abstract

Discharge from springs in Florida is sourced from aquifers, such as the Upper Floridan aquifer, which is overlain by an upper confining unit that locally can have properties of an aquifer. Water levels in aquifers are affected by several factors, such as precipitation, recharge, and groundwater withdrawals, which in turn can affect discharge from springs. Therefore, identifying groundwater sources and recharge characteristics can be important in assessing how these factors might affect flows and water levels in springs and can be informative in broader applications such as groundwater modeling. Recharge characteristics include the residence time of water at the surface, apparent age of recharge, and recharge water temperature.

The groundwater sources and recharge characteristics of three springs that discharge from the banks of the Suwannee River in northern Florida were assessed for this study: Bell Springs, White Springs, and Suwannee Springs. Sources of groundwater were also assessed for a 150-foot-deep well finished within the Upper Floridan aquifer, hereafter referred to as the UFA well. Water samples were collected for geochemical analyses in November 2012 and October 2013 from the three springs and the UFA well. Samples were analyzed for a suite of major ions, dissolved gases, and isotopes of sulfur, strontium, oxygen, and hydrogen. Daily means of water level and specific conductance at White Springs were continuously recorded from October 2012 through December 2013 by the Suwannee River Water Management District. Suwannee River stage at White Springs was computed on the basis of stage at a U.S. Geological Survey streamgage about 2.4 miles upstream. Water levels in two wells, located about 2.5 miles northwest and 13 miles southeast of White Springs, were also used in the analyses.

Major ion concentrations were used to differentiate water from the springs and Upper Floridan aquifer into three groups: Bell Springs, UFA well, and White and Suwannee Springs. When considered together, evidence from water-level, specific conductance, major-ion concentration, and isotope data indicated that groundwater at Bell Springs and the UFA well was a mixture of surface water and groundwater from the upper confining unit, and that groundwater at White and Suwannee Springs was a mixture of surface water, groundwater from the upper confining unit, and groundwater from the Upper Floridan aquifer. Higher concentrations of magnesium in groundwater samples at the UFA well than in samples at Bell Springs might indicate less mixing with surface water at the UFA well than at Bell Springs. Characteristics of surface-water recharge, such as residence time at the surface, apparent age, and recharge water temperature, were estimated on the basis of isotopic ratios, and dissolved concentrations of gases such as argon, tritium, and sulfur hexafluoride. Oxygen and deuterium isotopic ratios were consistent with rapid recharge by rainwater for samples collected in 2012, and longer residence time at the surface (ponding) for samples collected in 2013. Apparent ages of groundwater samples, computed on the basis of tritium activity and sulfur hexafluoride concentration, indicated groundwater recharge occurred after the late 1980s; however, the estimated apparent ages likely represent the average of ages of multiple sources. Recharge since the 1980s is consistent with groundwater from shallow sources, such as the upper confining unit and Upper Floridan aquifer. Recharge water temperature computed for the three springs and UFA well averaged 20.1 degrees Celsius, which is similar to the mean annual air temperature of 20.6 degrees Celsius at a nearby weather station for 1960–2014.

Introduction

Establishment of minimum flows and levels for springs, rivers, and lakes is required by the State of Florida pursuant to section Subsection 373.041(2), Florida Statutes (Suwannee River Water Management District, 2014), to protect water resources. Discharge from Florida springs is sourced from aquifers, such as the Floridan aquifer system, and springs provide a “window” into the aquifer’s geochemistry (Scott and others, 2004). The Floridan aquifer system is composed of several Tertiary-age (66–3 million years ago [Ma]) formations (Johnson and Bush, 1988; Williams and Kuniansky, 2015). Discharge from springs might be sourced from other aquifers such as the intermediate aquifer system. For example, the Hawthorn Group, which overlies the Floridan aquifer system, is referred to as the intermediate aquifer system where it exhibits characteristics of an aquifer.

Water levels in aquifers are affected by several factors, such as precipitation and groundwater withdrawals, which in turn can affect flow from springs that discharge groundwater from these aquifers (Spechler and Schiffer, 1995; Currell, 2016). Therefore, identifying groundwater sources and recharge characteristics (residence time at the surface, apparent age of recharge, and recharge water temperature) can be important in assessing how these factors might affect minimum flows and water levels in springs, and can be informative in broader applications such as groundwater modeling and water resources management. To address this need, the U.S. Geological Survey (USGS), in cooperation with the Suwannee River Water Management District, initiated a study in 2010 to identify sources of groundwater and recharge characteristics in springs. The study focused on White Springs, and included nearby springs and one well.

Purpose and Scope

The purpose of this report is to assess sources of groundwater discharge and characteristics of surface-water recharge at Bell, White, and Suwannee Springs, Florida, during 2012–13. Sources of groundwater and characteristics of surface-water recharge are also assessed for a nearby Upper Floridan aquifer well, hereafter referred to as the UFA well. The springs are located along the banks of the Suwannee River, which delineates the border between Suwannee, Hamilton, and Columbia Counties in northern Florida; the UFA well is about 0.2 mile (mi) east of White Springs and the Suwannee River. The springs and UFA well are within the Suwannee River Water Management District (SRWMD; fig. 1).

Sampling and monitoring was directed more at White Springs than at other sites. Continuous daily mean water level and specific conductance were monitored by the SRWMD at White Springs from October 1, 2011, through December 9, 2013, hereinafter referred to as the study period. Samples were collected from all sites during November 2012 and from all sites except Bell Springs during October 2013.

The geochemistry of water samples was used to determine the potential sources of groundwater and characteristics of recharge at the four sites. Geochemical tracers assessed in water samples included isotopes of sulfur (^{34}S, ^{32}S) dissolved in water as sulfate (SO_4^{2-}) and sulfide (S^{2-}), strontium (^{87}Sr, ^{86}Sr) dissolved in water, and oxygen (^{18}O, ^{16}O) and hydrogen (^{2}H, ^{1}H) in water; the isotope ^{2}H is referred to as deuterium (D). Source of groundwater also might be reflected in the age of the water, as indicated by the presence of tritium (^{3}H) and sulfur hexafluoride (SF_6). The combination of isotopic ratios and age dating have been shown to be effective in understanding current and past flow conditions and potential changes in water quality (Sanford and others, 2011).

Limitations

A limitation of this study was the small sample size, which totaled seven samples. Groundwater flow in karst systems can be spatially and temporally variable, commonly responding to variations in seasonal rainfall (Fetter, 2001; Scott and others, 2004); therefore, a more extensive sampling effort would be required to more accurately determine the geochemistry of groundwater discharged at these sites.

Springs

Bell Springs (fig. 2) is the most upstream of the springs sampled and is located about 1,000 feet (ft) south of the Suwannee River on its left (south) bank. Bell Springs should not be confused with Bell Spring; the latter was described by Rosenau and others (1977) and Scott and others (2004). White Springs discharges from the right (north) bank of the Suwannee River, immediately adjacent to the river channel. The spring is enclosed by a bath house known as the Spring House (fig. 3), located within Stephen Foster Folk Culture Center State Park. Spring flow is discharged to the river through a weir in the foundation wall at the south end of the Spring House (Scott and others, 2004). The top of the weir has a minimum (invert) elevation of 52.8 ft. Discharge from White Springs was reported by Rosenau and others (1977) for seven instantaneous observations from 1907 through 1946, and ranged from a maximum of 72 cubic feet per second (ft^3/s) to a minimum of 36.4 ft^3/s. Scott and others (2004) indicated that there were several years (not specified) when rangers at the state park reported that flow had stopped. Suwannee Springs comprises at least six spring orifices along the left (south) bank of the Suwannee River, and the main spring is enclosed by a bath house built in the 1800s (fig. 4; Scott and others, 2004). Discharge from Suwannee Springs was measured 52 times from 1906 through 1973 and averaged 23.4 ft^3/s, and ranged from a maximum of 71.5 ft^3/s to a minimum of 2.35 ft^3/s (Rosenau and others, 1977).

Hydrogen sulfide (H_2S) odor has been reported at White and Suwannee Springs (Scott and others, 2004). Previous investigations have attributed the presence of H_2S in the Upper Floridan aquifer, where overlain by a confining unit, to reduction of sulfate, and alternately, to available organic matter (Meyer, 1962; Ceryak and others, 1983; Sprinkle, 1989). At White Springs, sulfate content was reported as 19 and 16 milligrams per liter (mg/L) in 1923 and 1946, respectively (Rosenau and others, 1977). At Suwannee Springs, sulfate concentration was reported as 27, 18, 17, and 7.4 mg/L in 1924, 1966, 1973, and 2002, respectively (Scott and others, 2004). Dissolved sulfate in Florida groundwater is derived from several sources, including dissolution of gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$), oxidation of pyrite (FeS_2), decomposition of organic matter, seawater, and rainwater (Sacks, 1996; Sacks and Tihansky, 1996). Dissolution of gypsum is typically associated with deep sources of groundwater, and decomposition of organic matter is associated with shallow sources of groundwater. Water at depth is associated with the Floridan aquifer system, which is subdivided into the Upper and Lower Floridan aquifers (Johnson and Bush, 1988; Williams and Kuniansky, 2015).

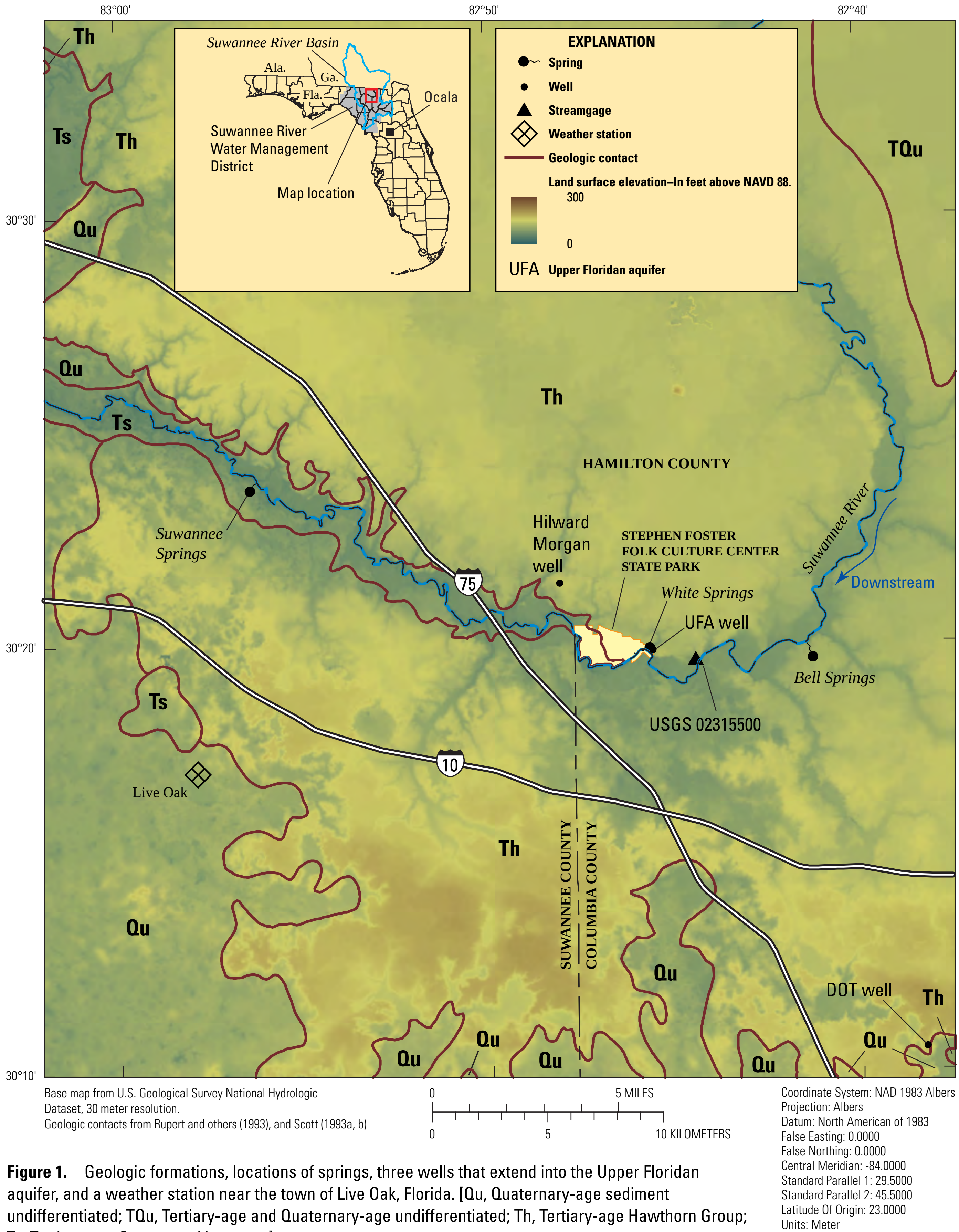

Figure 1. Geologic formations, locations of springs, three wells that extend into the Upper Floridan aquifer, and a weather station near the town of Live Oak, Florida. [Qu, Quaternary-age sediment undifferentiated; TQu, Tertiary-age and Quaternary-age undifferentiated; Th, Tertiary-age Hawthorn Group; Ts, Tertiary-age Suwannee Limestone]

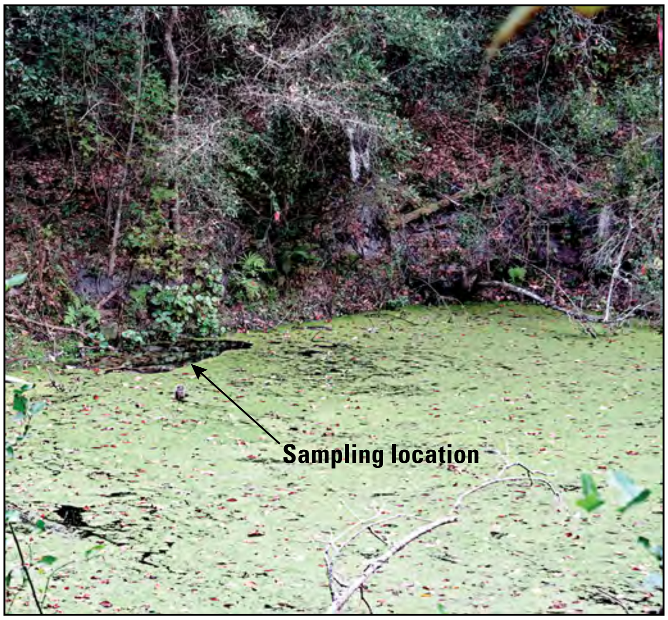

Figure 2. Sampling site at Bell Springs. The spring vent that was sampled is located at a section of pool that was not covered by floating vegetation as shown in the photo. The spring flows approximately 1,000 feet before it discharges into the Suwannee River. (Photo by Patricia Metz, U.S. Geological Survey)

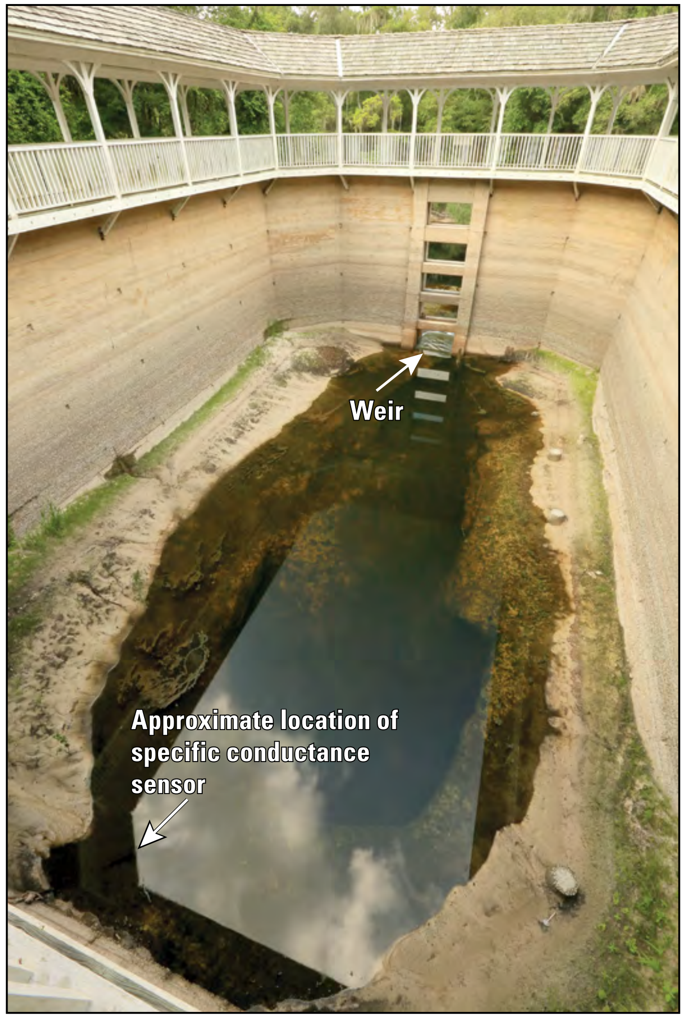

Figure 3. White Springs and the remains of the Spring House. The spring vent is located in the lower right corner of the pool, and the base of the vent at the time the photograph was taken was about 45 feet below the water surface. The spring discharges to the Suwannee River through a weir at the wall opening at the far side of the spring (south end), as viewed in this photo. The Suwannee River Water Management District installed a water-level and specific conductance sensor at the location shown. (Photo by Alan Cressler, U.S. Geological Survey)

Hydrogeologic Setting

The oldest unit exposed at the surface in the study area (fig. 1) is the Eocene- to Oligocene-age Suwannee Limestone, a fossiliferous limestone and dolostone that was deposited between 38 and 28 Ma (Rupert and others, 1993). The top of the unit lies as much as 150 ft below the land surface in Suwannee County and unit thickness ranges from 45 to 180 ft (Rupert, 2003). Suwannee Springs developed in surface exposures of the Suwannee Limestone. In this region, the Suwannee Limestone is the uppermost formation of the Upper Floridan aquifer, including the Eocene-age Ocala Limestone, which underlies the Suwannee Limestone. The base of the Upper Floridan aquifer in this region is referred to as the middle confining unit III (Miller, 1986), and was recently redefined as the Lisbon-Avon Park composite unit (Williams and Kuniansky, 2015, fig. 32). Middle confining unit III is described by Miller (1986) as a low permeability, dense, fossiliferous, gypsiferous, dolomitic limestone within the lower and middle parts of rocks of Eocene age. Williams and Kuniansky (2015) generally describe the lithology of the Lisbon-Avon Park composite unit for north-central Florida as limestone, dolomitic limestone, and dolostone.

The Suwannee Limestone is overlain by the Oligocene- to Miocene-age Hawthorn Group, which was deposited from 25 to 5 Ma, and is composed of sandy clays, silt, and some carbonates (Rupert, 2003; Rupert and others, 1993). The area in the vicinity of White and Bell Springs is underlain by the Hawthorn Group (fig. 1). White Springs developed in unmapped exposures of Suwannee Limestone along the banks of the Suwannee River (Rupert, 1989). Meyer (1962) indicated that limestone is exposed along the Suwannee River up to 6 mi east-northeast of White Springs. Bell Springs is located about 4 mi east of White Springs but is located 1,000 ft south of the Suwannee River. Given that it is located away from the main channel of the Suwannee River, it is possible that Bell Springs developed in exposures of the Hawthorn Group. The Hawthorn Group generally acts as a confining unit to the Upper Floridan aquifer and is referred to as the upper confining unit (Williams and Kuniansky, 2015). In Columbia, Hamilton, and Suwannee Counties, the Hawthorn Group locally has permeable beds that have properties of an aquifer (Meyer, 1962; Rupert, 1989, 2003) that is referred to as the intermediate aquifer system (Williams and Kuniansky, 2015). The

Figure 4. Suwannee Springs and the remains of the bath house walls. Water discharges to the Suwannee River through the wall opening in the far right corner of the spring pool. A spring vent is in the center of the pool, and a second vent is located in the lower left side of the spring as viewed in this photo, marked by an arch opening in the wall. The Suwannee River appears in the upper right corner of the photo, and is flowing away from view. (Photo by Scott McBride, U.S. Geological Survey).

term "intermediate" is used because the intermediate aquifer system is deeper than aquifers composed of Quaternary-age (3–0 Ma) formations and shallower than the Floridan aquifer system; however, the Hawthorn Group is not used extensively as a source of fresh water in Hamilton and Suwannee Counties (Rupert, 1989; 2003).

Quaternary-age, undifferentiated sand and clay overlay Tertiary-age units and locally act as a nonartesian, freshwater aquifer referred to as the surficial aquifer system. The aerial extent of this aquifer system corresponds to that of the relict Okefenokee Terrace sands (Rupert, 1989). Quaternary-age deposits are generally less than 50 ft thick in Hamilton and Suwannee Counties (Rupert, 1989, 2003), and were not mapped in the vicinity of Bell, White, or Suwannee Springs (fig. 1) by Rupert and others (1993) and Scott (1993a, b).

Climate

The climate of Suwannee and White Springs was estimated on the basis of data from the weather station at Live Oak, Fla. (fig. 1), located about 13 mi southwest of White Springs. This weather station is part of the Global Historical Climatology Network (http://www.ncdc.noaa.gov/cdo-web/search), station number USC00085099. The weather station is at an elevation of 120 ft and is located at latitude 30°17'00"N. longitude 82°58'0.01"E. (fig. 1). Estimated mean annual air temperature at the Live Oak weather station was 20.6 degrees Celsius (°C) for 1960–2015. Standard error of estimated mean annual air temperature was 0.09 °C, with a 95-percent confidence of mean annual air temperature of 20.4 to 20.8 °C. Median annual precipitation at the Live Oak weather station was 1,289 millimeters (mm; 50.75 inches [in.]) for 1960–2015. The 2000–13 period was relatively dry with 11 out of 14 years having annual precipitation less than the median (fig. 5). Annual precipitation was less than the median for the 6-year period preceding sampling (2006–11). Annual precipitation for 2012 was 1,750 mm (68.90 in.) and for 2013 was 1,095 mm (43.11 in.).

Methods of Investigation

The methods used in this study include those followed in the field and laboratory, as well as subsequent methods of analyses. The field methods include water-sample collection, laboratory analyses, and continuous monitoring and data collection of water levels and specific conductance. Laboratory methods are discussed for analyses of isotopes, dissolved gases, and estimates of the temperature and age of water that recharged the aquifers in the area of White Springs.

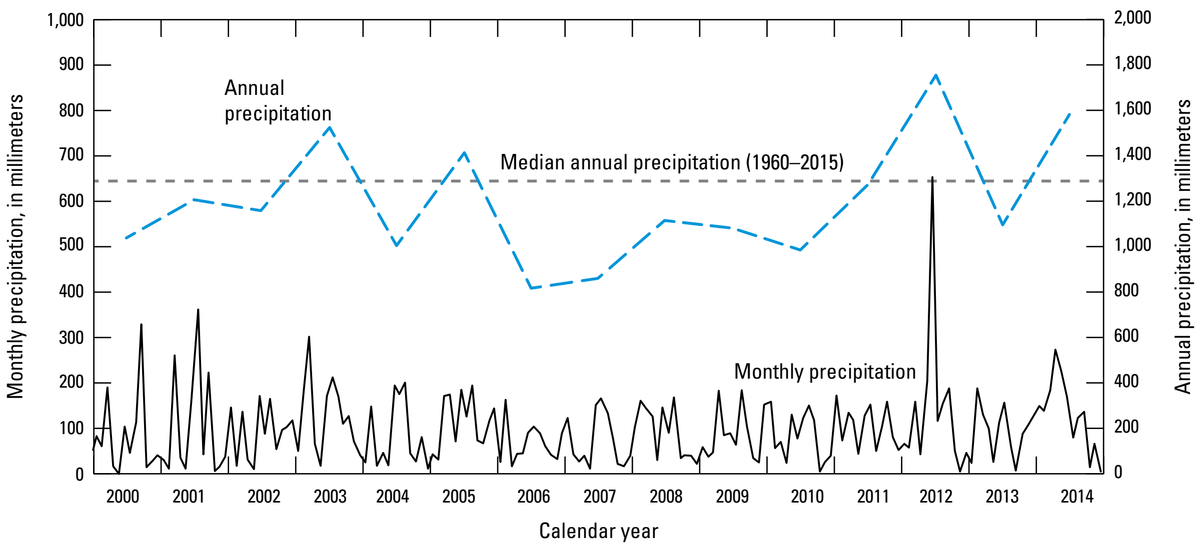

Figure 5. Monthly and annual precipitation during 2000–14 at the Global Historical Climatology Network weather station at Live Oak, Florida (station number USC00085099).

Sample Collection, Laboratory Analyses, and Continuous Data Collection

Spring water and groundwater samples were collected from Bell Springs, White Springs, Suwannee Springs, and the 150-ft-deep UFA well (fig. 1). The well is designated in the USGS National Water Information System (NWIS) as USGS site number 301949082452801 (http://waterdata.usgs.gov/nwis/inventory?agency_code=USGS&site_no=301949082452801), and is described as being completed within the Ocala Limestone and Upper Floridan aquifer. Samples were collected on November 28 and 29, 2012, from all four sites and collected on October 23 and 24, 2013, at White Springs, Suwannee Springs, and the UFA well. Samples were not collected at Bell Springs on October 23 and 24, 2013, because the spring was not flowing. Samples were analyzed for major ions, stable isotopes, ^{3}H, SF_6, and dissolved gases.

Water samples for analyses of sulfur isotopes (^{34}S, ^{32}S) in dissolved SO_4^{2-} and S^{2-} were collected using USGS protocols described by Carmody and others (1998). Water samples from Bell Springs were not analyzed for sulfur isotopes from sulfide. Water samples for other geochemical analyses were collected using protocols described in the National Field Manual for collection of water-quality data (U.S. Geological Survey, variously dated). All water samples were filtered using a 0.45-micrometer (µm) pore-size, hydrophilic, polyethersulfone filter. Water samples were analyzed for major ions by the USGS National Water Quality Laboratory in Denver, Colorado (http://nwql.usgs.gov/); for stable isotopes (sulfur, and oxygen and hydrogen in water) by the USGS Reston Stable Isotope Laboratory (RSIL) in Reston, Virginia (http://isotopes.usgs.gov/); for strontium isotopes by the USGS Isotope Geochemistry Laboratory in Menlo Park, California; for tritium at the USGS Tritium Laboratory in Menlo Park, California; and for sulfur hexafluoride and dissolved gases by the USGS Reston Groundwater Dating Laboratory (RGDL) in Reston, Virginia (http://water.usgs.gov/lab/). At all field sites, hydrogen sulfide was measured using a portable spectrophotometer (Hach Company, 2009). Other physical properties, such as pH, specific conductance, dissolved oxygen, and water temperature, were measured in the field by either inserting a multiparameter sonde directly into the spring vent (Bell and Suwannee Springs), or through a closed flow-through sampling chamber (White Springs and UFA well).

Water samples at Bell and Suwannee Springs were collected using a Fultz groundwater sampling pump with Teflon tubing that was lowered into the spring vent by hand. Water samples at the UFA well were collected using the existing pump in the well, which is used for domestic supply. Water-sample collection at White Springs required installation of plastic tubing that transmits water from a submerged vent to the surface via a peristaltic pump. A SCUBA (self-contained underwater breathing apparatus) diver installed tubing that extended from a vent at a depth of about 45 ft below the water surface on November 1, 2012. A local datum was available that allowed conversion of water level to elevation relative to NAVD 88. The vent corresponds to an elevation of about 7 ft. A screen was installed on the end of the tube in the spring vent to prevent material from blocking the opening to the tube. A peristaltic pump brought water through the tubing to the surface, where samples were collected. The tubing was installed on November 1, 2012, and remains at White Springs to date (2016).

Continuous water-level and specific conductance data for White Springs were available from sensors installed by the SRWMD (Suwannee River Water Management District, 2016a). The water-level and specific conductance sensors were installed in a solution feature in the rock adjacent to the main pool, with the sensors at an elevation of about 44 ft (T. Rodgers, Suwannee River Water Management District,

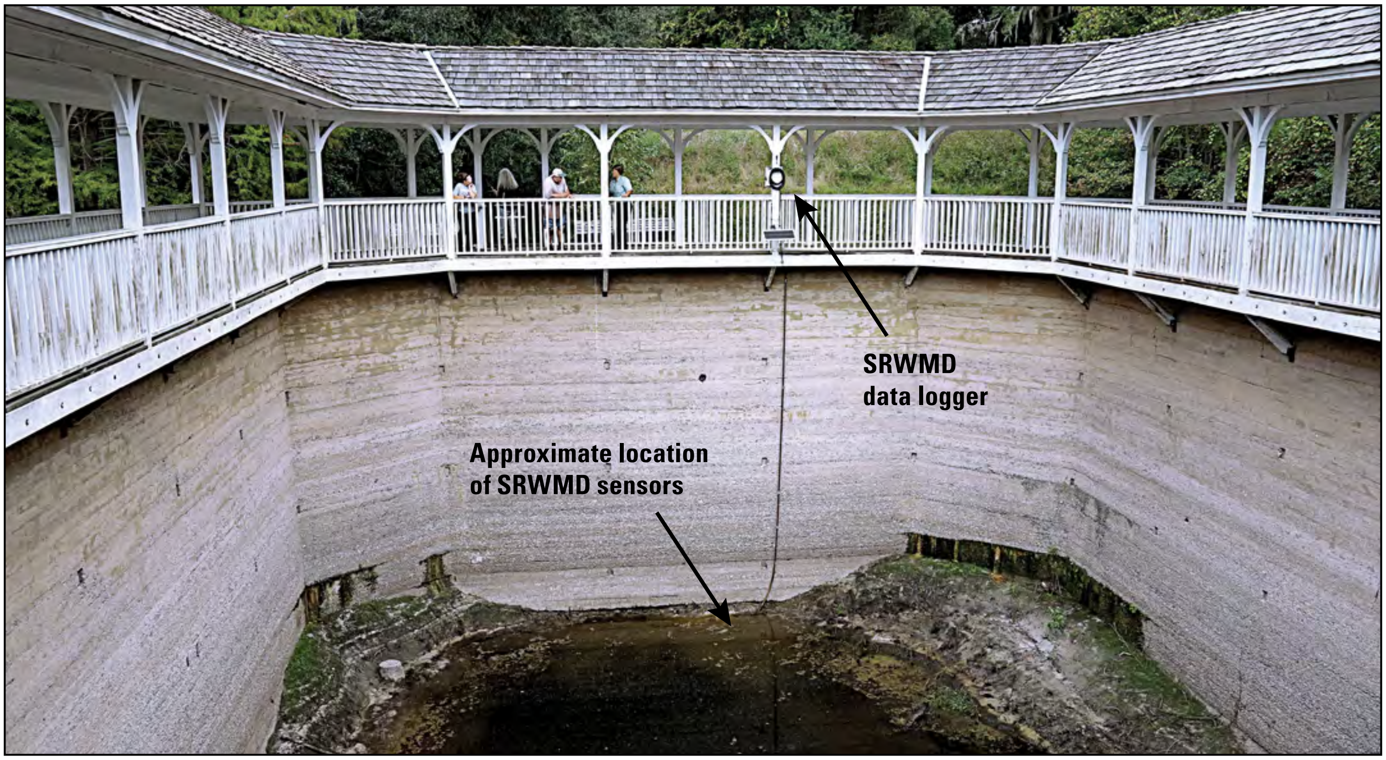

Figure 6. White Springs and remains of the Spring House, showing location of data logger and cables for continuous water-level and specific conductance sensors installed and operated by Suwannee River Water Management District (SRWMD).

written commun., 2016), which is about 5 ft below the invert elevation of the weir that drains the spring pool into the Suwannee River (figs. 3, 6). Therefore, specific conductance was continuously measured by SRWMD at approximately 37 ft above the vent from which water samples were collected.

There were some issues with the records of water level and specific conductance at White Springs. Water level and specific conductance had a gap in the record from June 28, 2012, through July 12, 2012, and June 27, 2012, through July 12, 2012, respectively. There was a large discrepancy in the discrete and continuous measurement of specific conductance for November 28, 2012. The SRWMD took a discrete measurement in the pool on January 9, 2013, of 275 microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C) (T. Rodgers, Suwannee River Water Management District, written commun., 2016), which differs substantially from the continuous reading of 104 µS/cm for that day from the sensor location (solution feature adjacent to the main pool). A second discrete reading was taken by the SRWMD on February 22, 2013, of 110.8 µS/cm, which was similar to the continuous reading of 104.6 µS/cm for that same day. In this case, the discrete reading was not from the pool but from the solution feature in which the sensor was installed. The discrepancy between continuous sensor data and discrete readings on November 28, 2012, and January 9, 2013, could be a result of instrumentation error. However, similar specific conductance measurements on February 22, 2013, make this explanation less likely. Specific conductance readings were anomalous from November 16, 2012, through February 25, 2013. During this period, specific conductance changed when there were no changes in river stage and no precipitation events. It was determined that readings in the solution feature in which the sensor was installed might not be representative of the specific conductance of the pool during this time period; therefore, the period November 16, 2012, through February 25, 2013, is excluded from subsequent analyses and discussions herein.

Water levels at two wells and one streamgage in the Suwannee River were also assessed for this study (fig. 1). One well is located about 13 mi southeast of White Springs (USGS 301031082381085, DOT - Columbia; SRWMD well number S041705001), and is hereinafter referred to as the DOT well. This well has a total depth of 836 ft below land surface and is finished in the Floridan aquifer system. The second well is located about 2.5 mi northwest of White Springs (USGS 302127082475801, Hilward Morgan well near Facil FL; SRWMD well number S011534001). This well has a depth of 260 ft, is also completed in the Floridan aquifer system, and is referred to hereinafter as the Hilward Morgan well. Data for the two wells are available from the Suwannee River Water Management District (2016b, c).

Suwannee River stage data are available at USGS streamgage 02315500, named “Suwannee River at White Springs, Fla. Bridge,” located about 1.4 mi east-southeast of White Springs and about 2.4 river mi upstream from White Springs (fig. 1). Streamflow records for this gage extend back to 1927. To compare hydrographs at White Springs and the Suwannee River, stage measured at the Suwannee River USGS streamgage at the bridge was adjusted downward by

1.61 ft (the gage is upstream from the spring; fig. 1), computed as the mean difference between the water level at White Springs and stage of the Suwannee River when the water level at White Springs was 62.8 ft or greater (at least 1 ft above the weir separating the spring and river).

Stable Isotopes

Isotopes of strontium, sulfur, and oxygen and hydrogen in water were measured for this study. Several previous groundwater studies in Florida have used sulfur isotopes (^{34}S, ^{32}S) of SO_4^{2-} and S^{2-} to differentiate between sources of dissolved sulfur in the Upper Floridan aquifer (Sacks, 1996; Phelps, 2001). Isotopic signatures are expressed in terms of the ratio of two isotopes relative to that ratio in a standard, and use delta notation represented by the symbol "δ". Stable isotopic ratios are reported as per mil, or parts per thousand relative to the standard $^{34}S/^{32}S$ ratio taken from a USGS laboratory standard SO_2, and corrected to match the accepted Vienna Canyon Diablo Troilite (VCDT) standard, defined by the International Atomic Energy Agency in Vienna, Austria (Coplen and Krouse, 1998). The formula used to compute delta values for $^{34}S/^{32}S$ is

$$\delta\,^{34}S=\left(\left[\frac{(^{34}S/^{32}S)_{sample}}{(^{34}S/^{32}S)_{standard}}\right]-1\right)\cdot 1{,}000\,. \qquad (1)$$

The $\delta\,^{34}S$ was determined separately for sulfur isotopes in dissolved SO_4^{2-} and S^{2-}. Seawater has a typical $\delta^{34}S$ from sulfate of about 20 per mil, rainwater in unindustrialized areas typically has a $\delta^{34}S$ from sulfate range of 3.2 to 8.2 per mil (Östlund, 1959; Jensen and Nakai, 1961; Sacks, 1996), and rainwater in north-central Florida is reported to range from 3.4 to 5.9 per mil (Katz and others, 1995).

Equations similar in form to equation 1 are used to compute isotopic abundances of oxygen ($\delta^{18}O$) and deuterium ($\delta^{18}D$) relative to the Vienna Standard Mean Ocean Water (VSMOW):

$$\delta\,^{18}O=\left(\left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{VSMOW}}\right]-1\right)\cdot 1{,}000\,, \qquad (2)$$

$$\delta\,D=\left(\left[\frac{(D/^{1}H)_{sample}}{(D/^{1}H)_{VSMOW}}\right]-1\right)\cdot 1{,}000\,. \qquad (3)$$

There is a relation between $\delta^{18}O$ and δD referred to as the "global meteoric water line" (Craig, 1961; Rozanski and others, 1993). The linear relation (in units of per mil) indicates that in meteoric water (rainwater), as $\delta^{18}O$ changes, δD changes by a factor of 8. Katz and others (1998) identified a "local meteoric water line" for the region of northern Florida, which differs from the global meteoric water line by a shift in the intercept and a small decrease in slope (from 8 to 7.92). Evaporation causes a reduction in slope and a shift in the intercept relative to the global meteoric line, resulting in an evaporation trend line. A graphical representation of $\delta^{18}O$ relative to δD can be used to determine whether water samples fall along the global or local meteoric line, indicating a short residence time at the surface, or that the water has been enriched by surface processes that cause fractionation of the isotopes, indicating a longer residence time (Katz and others, 1997). Locally, evaporation from standing bodies of surface water is the most common cause of fractionation; transpiration does not partition these isotopes. Clusters of observations of $\delta^{18}O$ and δD can also indicate different populations, or sources, of water.

Strontium isotopic ratios were used as a tracer of the geologic formation from which groundwater was potentially sourced. In contrast to other isotopes discussed, the strontium isotopic ratio ($^{87}Sr/^{86}Sr$) is not commonly reported as a delta value. Strontium isotopic ratios in seawater are assumed to be uniform in ocean water at any given point in time, but the ratio changes in seawater over geological time periods because of changes in strontium influx from sources such as hydrothermal activity, rivers, and carbonate formation and weathering (Hess and others, 1986). The strontium isotopic ratio of seawater at a given point in geologic time is preserved within limestone and gypsum; however, diagenetic change to dolomite can change the ratio (Sacks and Tihansky, 1996). There has been an upward trend in strontium isotopic ratios in seawater since the beginning of the Cenozoic (DePaolo and Ingram, 1985; Hess and others, 1986).

Noble Gases and Recharge Water Temperature

Noble gases that are dissolved in groundwater, such as argon (Ar), can be used to estimate the water temperature at the time of recharge (Mazor, 1972; Solomon and others, 1998). The recharge water temperature is commonly assumed to be the temperature at which groundwater equilibrates with the gas phase at the top of the capillary fringe of the groundwater table (Solomon and others, 1998). In this case, the recharge water temperature is commonly the mean annual air temperature (Solomon and others, 1998). High recharge water temperatures could be associated with recharge during warmer years (Shanley and others, 1998) or during warmer seasons. For example, recharge that occurs during summer months could result in elevated recharge water temperature. The conceptual model of equilibration of groundwater temperature with that of the capillary fringe might not be applicable to karst regions. Recharge in karst regions can be rapid, and water temperature can vary over short periods of time. For example, water temperature in the fractured zone of a well in a karst area of southern France exhibited diurnal variations of about 2 °C, associated with diurnal variations of about 5 °C observed in a nearby creek (Mahler and others, 2000). Therefore, recharge temperature might be associated with surface-water temperature during recharge events, rather than annual or seasonal air temperatures.

Groundwater-Age Estimates

The age of groundwater (that is, the amount of time that has elapsed since recharge) can be estimated from measurements of SF_6 and ^3H in samples of groundwater. Ages determined from SF_6 and ^3H measurements were based on the assumption of "piston-flow" conditions, which assumes no mixing of groundwater sources. Such conditions are not likely in karst settings, and ages probably reflect the mean age of a mixture of water sources, and are therefore apparent ages.

Sulfur hexafluoride, whose production began in 1953, is accumulating in the atmosphere; this chemical is used mainly as an electrical insulator in high-voltage switches and in the melting of magnesium (Busenberg and Plummer, 2000; Maiss and Brenninkmeijer, 1998). Groundwater can be dated with SF_6 under the assumption that SF_6 in water was in equilibrium with SF_6 in the atmosphere at the time of recharge. Recharge dates can be estimated back as far as about 1970 (Busenberg and Plummer, 2000). Tritium is a product of atmospheric tests of nuclear bombs (Sanford and others, 2011) and has a half-life of 12.32 years (Plummer and Friedman, 1999). Therefore, the presence of tritium in groundwater indicates that recharge occurred more recently than 1950.

A measure of the uncertainty of apparent age calculated on the basis of the SF_6 concentrations was determined using tritium concentrations. The apparent age of recharge was assumed to be that computed on the basis of SF_6 concentration. The concentration of tritium at the time of recharge (C_0) was estimated as a function of a decay constant (λ), the concentration of tritium when sampled in 2012 or 2013 (C_t), and the number of years (t) since recharge computed on the basis of SF_6 apparent age (Allègre, 2008):

$$C_0 = C_t e^{\lambda t} . \tag{4}$$

The decay constant is computed as

$$\lambda = \frac{\ln(2)}{12.32} . \tag{5}$$

Where 12.32 is the half-life of tritium in years. Observed concentrations of tritium at Ocala, Fla. (fig. 1) (International Atomic Energy Agency, 2014) were used for comparison with the calculated concentration. The year during which observed concentrations matched those calculated were then used to estimate uncertainty in SF_6 apparent ages. This methodology was applied by McBride and Wacker (2014) to corroborate SF_6 ages in water samples in Tallahassee, Fla.

Sources of Groundwater

Major ions, water level, specific conductance, stable isotopes, strontium isotopes, and recharge water temperature were used to assess the potential groundwater sources of Bell Springs, White Springs, Suwannee Springs, and the UFA well. Potential sources of groundwater are river water, rainwater, the shallow aquifer (Quaternary-age deposits), the upper confining unit (Hawthorn Group), and units in the Upper Floridan aquifer (Suwannee and Ocala Limestones).

Major Ions

Geochemical analyses of major ions (table 1) were used to distinguish water sources at sites. Major ions in natural waters include sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), nitrite (NO_2^-) plus nitrate (NO_3^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-). Note that carbonate is not reported in table 1; pH of samples was less than 7.7 and carbonate ions occur at pH values greater than about 8.5 (Fetter, 2001, table 9.5). Piper diagrams were used to distinguish differences in water chemistry among sites (November 2012, October 2013) (fig. 7). The use of Piper diagrams as discussed by Fetter (2001) is summarized herein. The lower left graph shows percent of cations and the lower right graph shows percent of anions. Percent is computed on the basis of the cation or anion concentration relative to total cation or anion concentration in milliequivalents per liter, respectively. Points on the cation and anion graph are projected onto the diamond-shaped graph along lines that parallel the magnesium and sulfate axes, respectively.

In general, although the Piper diagram does not indicate large differences in geochemistry by site or sampling event, some differences were observed. Values generally fall within the fields of calcite-dolomite type, calcium type, and bicarbonate type. The Piper diagram distinguishes the Bell Springs November 2012 sample from other samples, primarily because of the elevated nitrate plus nitrite concentration relative to other sites. Elevated nitrate plus nitrite relative to other sites might indicate a greater contribution from surface water at Bell Springs than at other sites, or might indicate local differences in land use. Analysis of differences in land use was beyond the scope of this study. Katz and Bohlke (2000) discuss sources of nitrate in groundwater beneath areas of mixed agricultural land use in Suwannee County. Elevated magnesium concentrations distinguish the Bell Springs and UFA well from other sites. Elevated magnesium might indicate (1) the upper confining unit as a groundwater source, because of the presence of magnesium in clay minerals and dolomite in the Hawthorn Group (Upchurch, 1992), or (2) an extended residence time of groundwater, allowing groundwater-rock interaction. The higher concentrations of magnesium at the UFA well distinguish this site from Bell Springs, and given

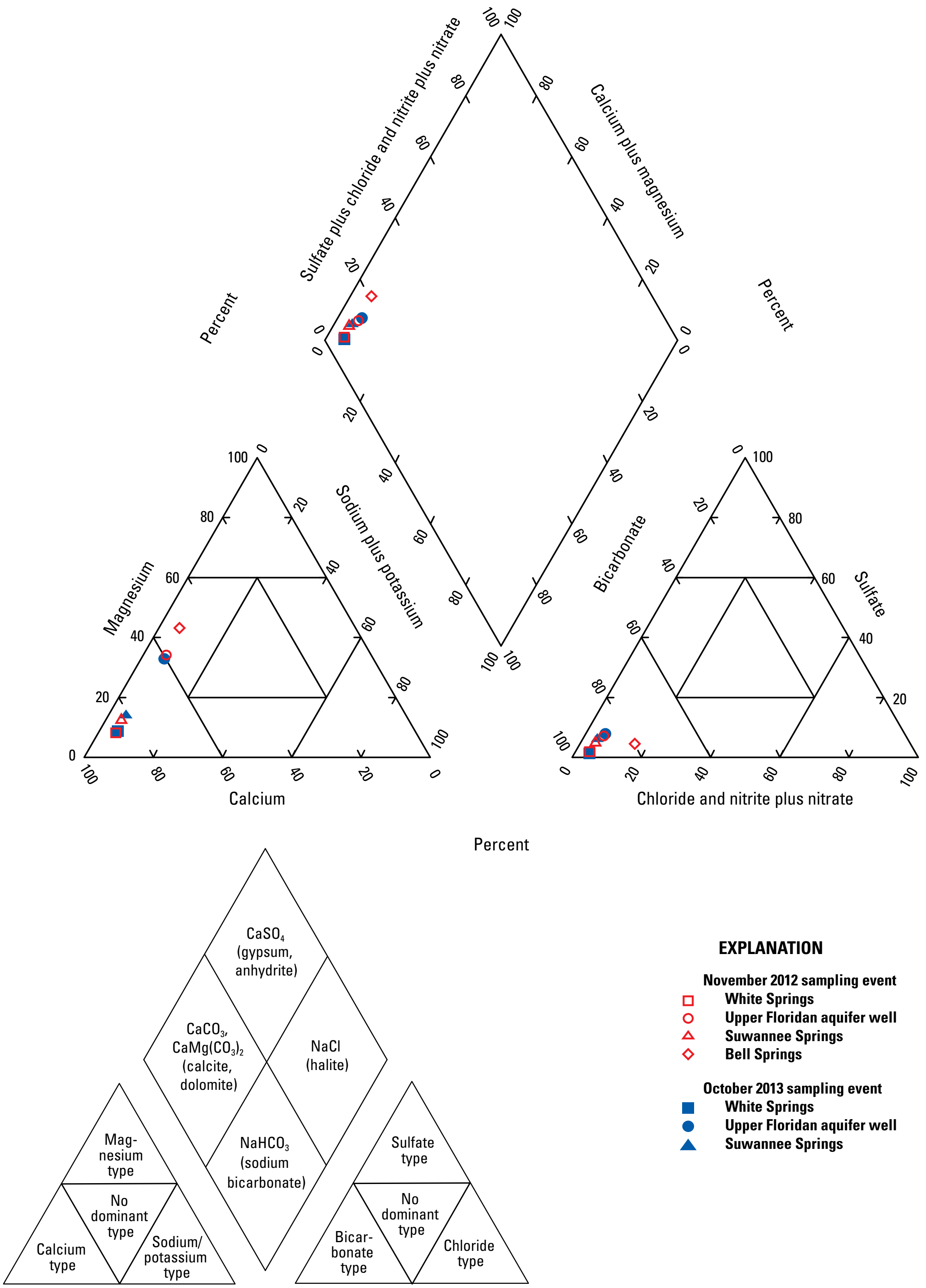

Figure 7. Piper diagram showing major ion species in water samples collected during November 2012 and October 2013 in the study area. Bell Springs was not sampled in October 2013.

Table 1. Spring water and groundwater samples collected, dates of collection, and chemical analyses completed.

[Groundwater and surface-water data for each USGS site are available online through the National Water Information System for Florida (http://nwis.waterdata.usgs.gov/fl/nwis/nwis). USGS, U.S. Geological Survey; yyyy, year; mm, month; dd, day; EST, Eastern Standard Time; µs/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; mg, milligram; L, liter; NTRU, nephelometric turbidity ratio unit; $CaCO_3$, calcium carbonate; µg, microgram; Fla., Florida; ft, foot; UFA, Upper Floridan aquifer; na, not applicable]

USGS site identification number	Station name	Date (yyyy/mm/dd)	Time (EST)	Temperature, water (degrees Celsius)	Specific conductance (µs/cm at 25 °C field)	Oxygen concentration, dissolved, field (mg/L)	Field pH	Turbidity (NTRU)	Alkalinity (mg/L as $CaCO_3$)	Bicarbonate concentration (mg/L)	Organic carbon concentration, dissolved (mg/L)
November 2012 sampling event											
02315503	White Sulphur Springs at White Springs, Fla.	2012/11/28	1200	19.4	282	0.6	7.2	3.2	140	170	7
301949082452801	White Springs Methodist 150 ft UFA well at White Springs, Fla.	2012/11/28	1700	19.7	448	0.2	7.3	4	209	283	0.69
02315600	Suwannee Springs near Live Oak, Fla.	2012/11/29	1200	19.8	311	0.3	7.3	0.4	152	185	4.37
301945082411800	Bell Springs near White Springs, Fla.	2012/11/29	1700	20.7	212	5.2	7.7	0.2	86	105	< 0.23
October 2013 sampling event											
02315503	White Sulphur Springs at White Springs, Fla.	2013/10/23	1300	21.5	257	0.2	7.2	0.7	129	158	13.7
301949082452801	White Springs Methodist 150 ft UFA well at White Springs, Fla.	2013/10/23	1900	21.7	441	0.1	7.3	1.9	208	254	0.57
02315600	Suwannee Springs near Live Oak, Fla.	2013/10/24	1100	20.6	318	0.2	7.4	0.8	155	188	5.45

Table 1. Spring water and groundwater samples collected, dates of collection, and chemical analyses completed.—Continued

[Groundwater and surface-water data for each USGS site are available online through the National Water Information System for Florida (http://nwis.waterdata.usgs.gov/fl/nwis/nwis). USGS, U.S. Geological Survey; yyyy, year; mm, month; dd, day; EST, Eastern Standard Time; µs/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; mg, milligram; L, liter; NTRU, nephelometric turbidity ratio unit; $CaCO_3$, calcium carbonate; µg, microgram; Fla., Florida; ft, foot; UFA, Upper Floridan aquifer; na, not applicable]

USGS site identification number	Station name	Date (yyyy/mm/dd)	Time (EST)	Boron concen-tration, dissolved (µg/L)	Calcium concen-tration, dissolved (mg/L)	Magnesium concen-tration, dissolved (mg/L)	Potassium concen-tration, dissolved (mg/L)	Sodium concen-tration, dissolved (mg/L)	Bromide concen-tration, dissolved (mg/L)	Chloride concen-tration, dissolved (mg/L)	Fluoride concen-tration, dissolved (mg/L)
November 2012 sampling event											
02315503	White Sulphur Springs at White Springs, Fla.	2012/11/28	1200	12	53.4	3.01	0.75	3.26	0.015	4.48	0.14
301949082452801	White Springs Methodist 150 ft UFA well at White Springs, Fla.	2012/11/28	1700	20	58.9	20.4	0.73	6.98	0.044	10.9	0.18
02315600	Suwannee Springs near Live Oak, Fla.	2012/11/29	1200	12	56.9	5.18	0.47	3.29	0.016	4.94	0.16
301945082411800	Bell Springs near White Springs, Fla.	2012/11/29	1700	11	22.9	11.8	0.25	2.95	0.022	6.67	0.46
October 2013 sampling event											
02315503	White Sulphur Springs at White Springs, Fla.	2013/10/23	1300	11	48.1	2.89	0.61	3.28	0.021	4.46	0.13
301949082452801	White Springs Methodist 150 ft UFA well at White Springs, Fla.	2013/10/23	1900	17	59.2	19.4	0.72	7.33	0.058	10	0.18
02315600	Suwannee Springs near Live Oak, Fla.	2013/10/24	1100	10	55.4	5.8	0.49	3.76	0.032	5.06	0.16

Table 1. Spring water and groundwater samples collected, dates of collection, and chemical analyses completed.—Continued

[Groundwater and surface-water data for each USGS site are available online through the National Water Information System for Florida (http://nwis.waterdata.usgs.gov/fl/nwis/nwis). USGS, U.S. Geological Survey; yyyy, year; mm, month; dd, day; EST, Eastern Standard Time; µs/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; mg, milligram; L, liter; NTRU, nephelometric turbidity ratio unit; $CaCO_3$, calcium carbonate; µg, microgram; Fla., Florida; ft, foot; UFA, Upper Floridan aquifer; na, not applicable]

USGS site identification number	Station name	Date (yyyy/mm/dd)	Time (EST)	Silica concen-tration, dissolved (mg/L)	Sulfate concen-tration, dissolved (mg/L)	Sulfide concen-tration, field (mg/L)	Strontium concen-tration, dissolved (µg/L)	Ammonia + organic nitrogen concen-tration (mg/L as nitrogen)	Ammonia concen-tration (mg/L as nitrogen)	Nitrate + nitrite concen-tration (mg/L as nitrogen)	Orthophosphate concentration (mg/L as phosphate)
November 2012 sampling event											
02315503	White Sulphur Springs at White Springs, Fla.	2012/11/28	1200	10.8	2.37	0.09	50.8	0.34	0.12	< 0.04	0.179
301949082452801	White Springs Methodist 150 ft UFA well at White Springs, Fla.	2012/11/28	1700	22.7	17.8	0.12	74.7	< 0.07	0.013	< 0.04	0.039
02315600	Suwannee Springs near Live Oak, Fla.	2012/11/29	1200	9.75	7.87	0.56	60.6	0.3	0.159	< 0.04	0.162
301945082411800	Bell Springs near White Springs, Fla.	2012/11/29	1700	13.8	4.74	na	27.0	0.09	< 0.01	2.15	0.065
October 2013 sampling event											
02315503	White Sulphur Springs at White Springs, Fla.	2013/10/23	1300	9.57	1.4	0.19	42.7	0.41	0.136	< 0.04	0.185
301949082452801	White Springs Methodist 150 ft UFA well at White Springs, Fla.	2013/10/23	1900	21	17.8	0.05	64.0	< 0.07	0.012	< 0.04	0.047
02315600	Suwannee Springs near Live Oak, Fla.	2013/10/24	1100	9.96	10.2	0.8	58.7	0.26	0.133	< 0.04	0.127

the depth of the sample (150 ft), might indicate less mixing with surface water at the UFA well than at Bell Springs. Bell Springs is located 1,000 ft from the channel of the Suwannee River, and the Hawthorn Group (upper confining unit) is mapped as exposed at the surface at this location. Therefore, the elevated concentration of magnesium in groundwater at Bell Springs and the UFA well relative to other sites implies that the upper confining unit is a source of water at both locations.

Sulfate and chloride concentrations at the UFA well were elevated relative to those at other sites (table 1). Elevated sulfate is commonly associated with dissolution of evaporite minerals at the base of the Floridan aquifer system and locally can be associated with waters from the Hawthorn Group (Upchurch, 1992). Elevated chloride might be associated with the release of local connate water, which is saltwater that was trapped in pores when the sediment was originally deposited, or it might be associated with evaporation and transpiration at land surface (Upchurch, 1992). Given that the UFA well is located within an area overlain by the Hawthorn Group (fig. 1), it is more likely that the chloride is derived from groundwater associated with the Hawthorn Group than the base of the Floridan aquifer system.

Plots of concentrations of sodium and chloride in groundwater (fig. 8) and magnesium and calcium in groundwater (fig. 9) show clustered values for White Springs and Suwannee Springs. Bell Springs and UFA well plot separately from these clusters and separately from each other. Bell Springs concentrations are farthest from the 1:1 line of chloride to sodium (fig. 8). Enrichment of chloride relative to sodium can result from movement of water through the aquifer, which would decrease sodium concentration through

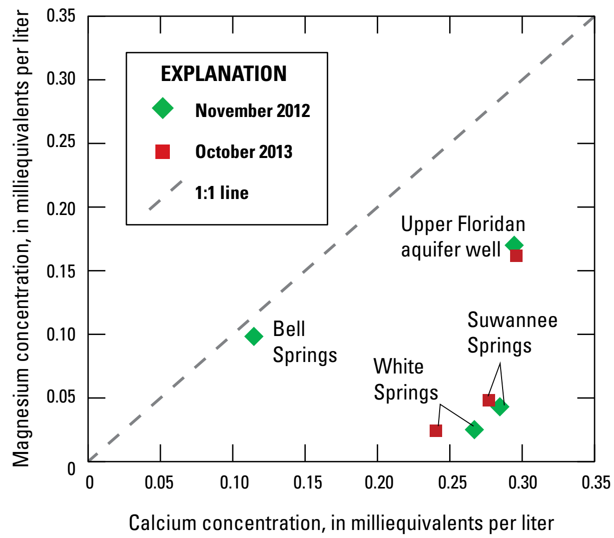

Figure 9. Calcium and magnesium in water samples collected November 2012 and October 2013 in the study area. Bell Springs was not sampled in October 2013.

cation exchange (Srinivasamoorthy and others, 2011). The UFA well has higher concentrations of chloride and sodium than Bell Springs but plots along the 1:1 line.

Water samples from Bell Springs and the UFA well have higher concentrations of magnesium in groundwater (fig. 9) relative to those from White and Suwannee Springs. This might reflect groundwater enrichment with magnesium from the Hawthorn Group (upper confining unit) at Bell Springs and the UFA well, or it might indicate longer residence time and associated groundwater-rock interaction. Plots of bicarbonate

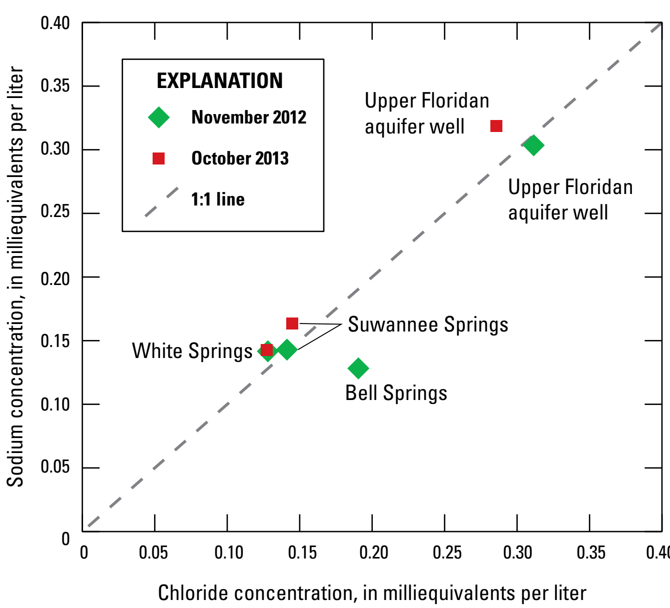

Figure 8. Sodium and chloride in water samples collected during November 2012 and October 2013 in the study area. Bell Springs was not sampled in October 2013.

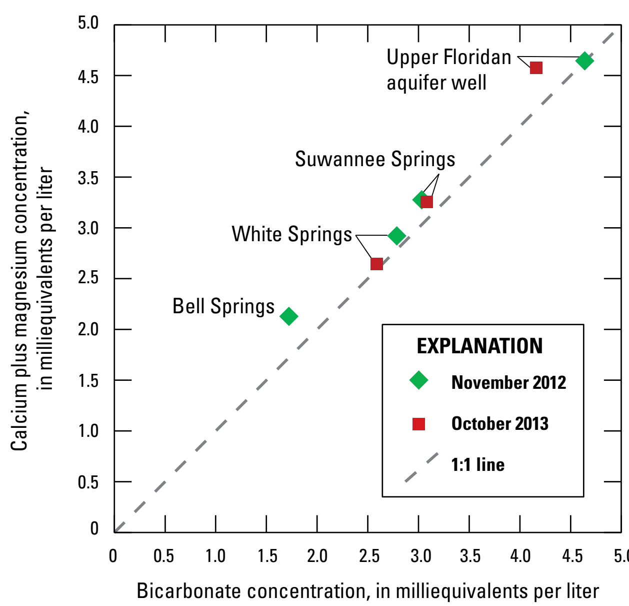

Figure 10. Calcium plus magnesium, and bicarbonate in water samples collected during November 2012 and October 2013 in the study area. Bell Springs was not sampled in October 2013.

and calcium-plus-magnesium concentration (fig. 10) provide information about the relative importance of carbonate species dissolution versus weathering of other rock types, such as silicates and gypsum (Srinivasamoorthy and others, 2011). Values plotting along the 1:1 line would indicate dissolution as the dominant process. All values plot near and slightly above the 1:1 line (fig. 10), indicating dissolution of carbonate minerals rather than calcium or magnesium derived from other sources, such as weathering of silicates or gypsum. As with other major-ion plots (figs. 8, 9), values are separated into three groups: Bell Springs, White and Suwannee Springs, and the UFA well. These results may indicate that groundwater sources differ among these three groups.

Water Level

Continuous daily mean water level was monitored by SRWMD at White Springs during the study period. Comparison of water levels in the pool and the stage of the Suwannee River indicates that water flowed from the pool to the river during 10 percent of the study period and followed periods of inundation of White Springs by the Suwannee River. During 43 percent of the study period, there was no surface-water connection between the pool and river, during which the elevation of the pool and stage often differed. During periods of inundation at White Springs, the Suwannee River potentially recharges groundwater through this karst feature. Meyer (1962) indicated that groundwater systems recharge through White Springs during periods of high flow. To support this finding, Meyer (1962) presented a piezometric surface for Columbia County for June 1957 that shows a piezometric high in the region around White Springs, extending approximately 5 mi to the southeast.

Water level in the Hilward Morgan well (fig. 11) during 2012–13 was similar to water level at White Springs when the Suwannee River experienced low flow, but during periods of high river flow, the groundwater level in the well did not rise as high as the White Springs pool level. In contrast, the water level in the DOT well (fig. 11) rose beginning in late June 2012, concurrent with a rise in Suwannee River stage but without the temporal variability observed at the Suwannee River, White Springs, and the Hilward Morgan well. This difference in temporal patterns of groundwater level might indicate that groundwater near the Suwannee River has a more direct connection to the river and responds more rapidly to changes in river level than does groundwater level farther from the Suwannee River. This inference is based on a limited number of wells, however, and other wells that are more distant from the Suwannee River might respond more variably and rapidly to changes in streamflow.

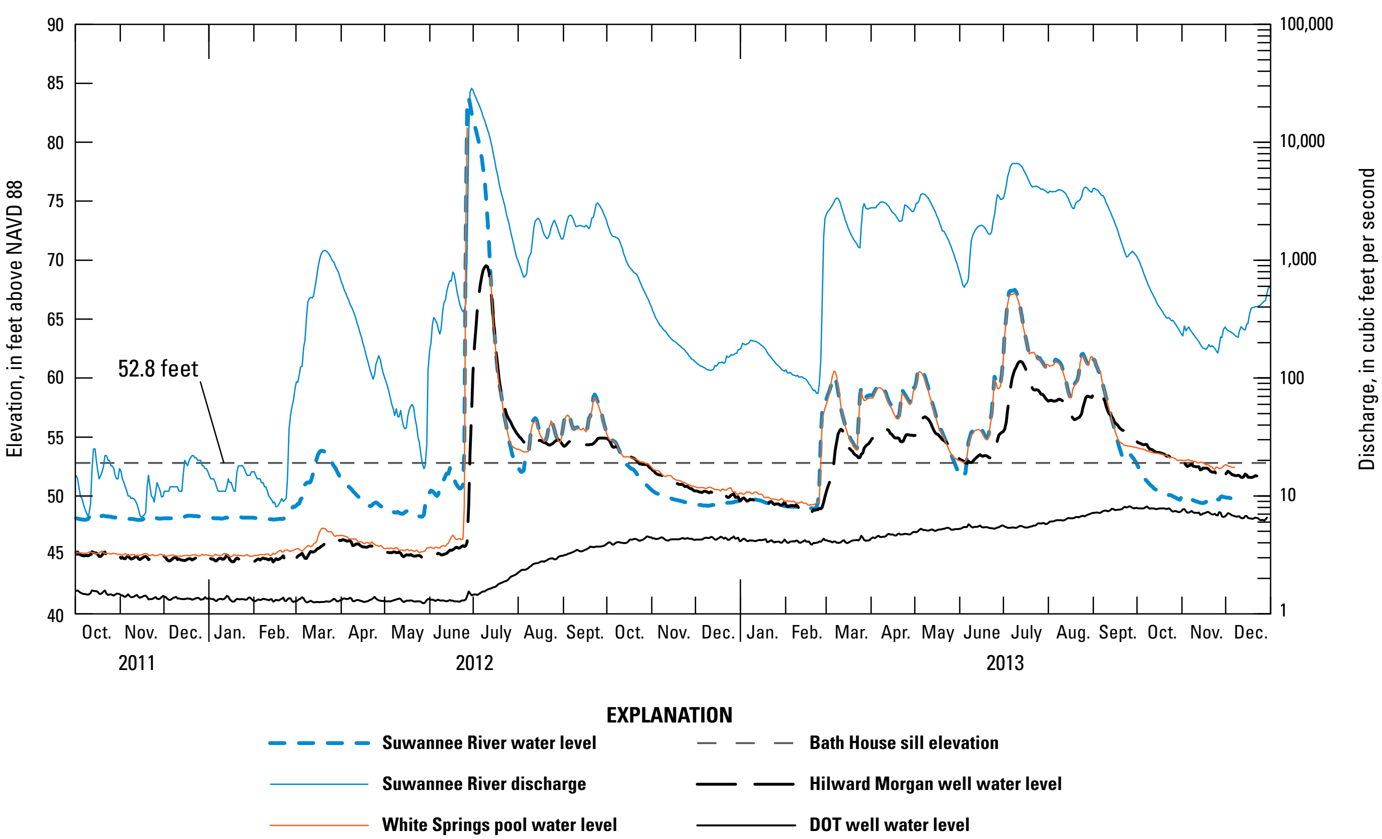

Figure 11. Water levels in the pool at White Springs, at the Suwannee River at White Springs, Fla. (U.S. Geological Survey streamgage 02315500), and at the Hilward Morgan and DOT wells, for October 2011–January 2014.

Specific Conductance

Specific conductance is a measure of the ability of water to conduct an electrical current through a unit length and unit cross section at a given temperature and is a function of the concentration of dissolved solids in the water sample (Hem, 1985). As a result, specific conductance values are typically lower in surface water than in groundwater, which contains dissolved solids resulting from contact with soil and rock. Specific conductance is commonly used as a tracer of meteoric water or river water and can change in a matter of hours in response to rainfall and recharge events (Ryan and Meiman, 1996; Desmarais and Rojstaczer, 2002). Inundation of White Springs by the Suwannee River is reflected by a decrease in the specific conductance of spring discharge (fig. 12). During water sampling visits on November 28, 2012, and October 23, 2013, Suwannee River stage was below the weir elevation and spring water was discharging from the spring to the river.

When Suwannee River stage exceeded the weir elevation and river water flowed into the spring pool, specific conductance values were considered to be representative of river water. Under such conditions during the study period (exclusive of November 16, 2012, through February 25, 2013), continuous specific conductance ranged from 33 to 236 µS/cm, with a mean and median of 72 and 62 µS/cm, respectively. When Suwannee River stage was below the weir elevation, continuous specific conductance values were considered to be representative of groundwater. Under such conditions, specific conductance ranged from 87 to 344 µS/cm, with mean and median of 272 µS/cm. There were four periods when the water level in White Springs was higher than in the Suwannee River, so that water was flowing from the pool to the river: July 31 to August 5, 2012; October 15 to October 27, 2012; May 30 to June 6, 2013; and October 2 to November 16, 2013. During these events, the median specific conductance, as recorded by SRWMD, was 228, 269, 197, and 246 µS/cm, respectively. The short duration of the May 30 to June 6, 2013 event, with inundation of the spring by the river both before and after the event, probably explains why specific conductance was lower during that event than during the other three. Specific conductance during these events is closer to values representative of groundwater than of river water. This finding indicates that river water recharging the system might be displacing groundwater, leading to later discharge of mixed river/groundwater from the spring. Displacement of groundwater by recharging surface water was proposed by Desmarais and Rojtaczer (2002) as a mechanism for spring discharge in Tennessee. In contrast to specific conductance measured in White Springs, specific conductance measured by the USGS in the UFA well was 448 and 441 µS/cm in November 2012 and October 2013, respectively. Specific conductance in White Springs (when not inundated by the Suwannee River) is intermediate between that in the UFA well and river water. This finding indicates an alternate model for White Springs is plausible involving

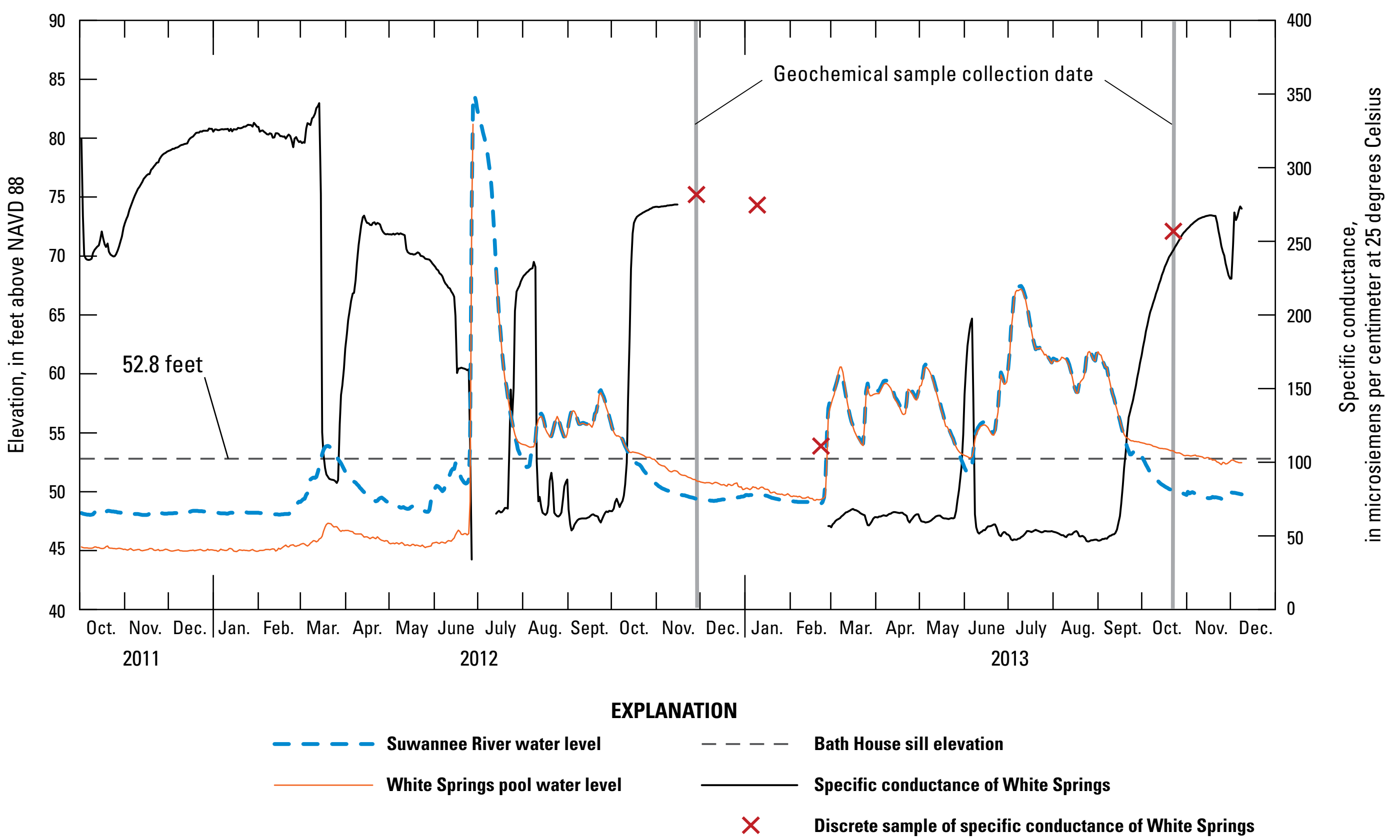

Figure 12. Specific conductance and water levels at White Springs.

subsurface mixing of deeper groundwater from Upper Floridan aquifer with surface water or shallow groundwater.

The water level in White Springs was below that of the Suwannee River prior to June 2012 (fig. 11). Streamflow in the Suwannee River during this period was low, with a median discharge of 18 ft^3/s from October 1, 2011, to May 31, 2012 (fig. 11). The elevated levels of specific conductance during this period (fig. 12), however, indicate little contribution of river water to water in White Springs during periods of low flow.

During both USGS sampling periods, upstream sites had lower specific conductance than downstream sites, possibly indicating a spatial trend in specific conductance. Upstream to downstream, the underlying geology transitions from the Hawthorn Group to the Suwannee Limestone (fig. 1). The Hawthorn Group is composed of silicic sediment that acts as a confining unit to the Upper Floridan aquifer and might perch groundwater that is recharged by rainfall and streamflow having lower specific conductance. Additional data are required, however, to corroborate the observation of a spatial trend in specific conductance.

Sulfur Isotopes

Isotopic ratios of sulfur in dissolved sulfate have been used to identify sources of groundwater in aquifers and confining units in Florida. A water sample from the surficial aquifer system had a $\delta^{34}S$ from sulfate of 8.3 per mil (Sacks and Tihansky, 1996). Isotopically light sulfate ($\delta^{34}S$ less than 18 per mil) in the Upper Floridan aquifer has been attributed to atmospheric precipitation and isotopically heavy sulfate ($\delta^{34}S$ greater than 22 per mil) has been attributed to gypsum dissolution (Sacks and Tihansky, 1996). Reported $\delta^{34}S$ from sulfate from the middle confining unit (base of the Upper Floridan aquifer) is commonly between 21 and 25 per mil, in the Upper Floridan aquifer ranges from 13.8 to 44.2 per mil, and in the upper confining unit ranges from –8.0 to 31.0 per mil (Sacks and Tihansky, 1996). Isotopically light values (more negative) have also been attributed to sources of sulfur from pyrite and organic matter (Sacks and Tihansky, 1996). Pyrite is present within the upper confining unit (Upchurch, 1992).

Values of $\delta^{34}S$ from sulfate at all sites ranged from 19.1 to –8.0 per mil. Values were predominantly isotopically light (less than 18 per mil), which indicates rainwater, and pyrite or organic matter as possible sources of sulfate (Sacks and Tihansky, 1996). The range of $\delta^{34}S$ in sulfate in rainwater in Florida was reported to be 3.2–8.2 per mil by Katz and others (1995). Values of $\delta^{34}S$ at Suwannee Springs are within the ranges expected for groundwater from the Upper Floridan aquifer (13.8–44.2 per mil) and the upper confining unit (–8.0–31.0 per mil). Mixing of water from these two groundwater sources, therefore, is possible at Suwannee Springs. The $\delta^{34}S$ from sulfate values of 4.37 and 6.31 per mil for White Springs and Bell Springs, respectively, for November 2012 samples are within the range of rainfall values for north-central Florida (fig. 13). However, samples collected at other

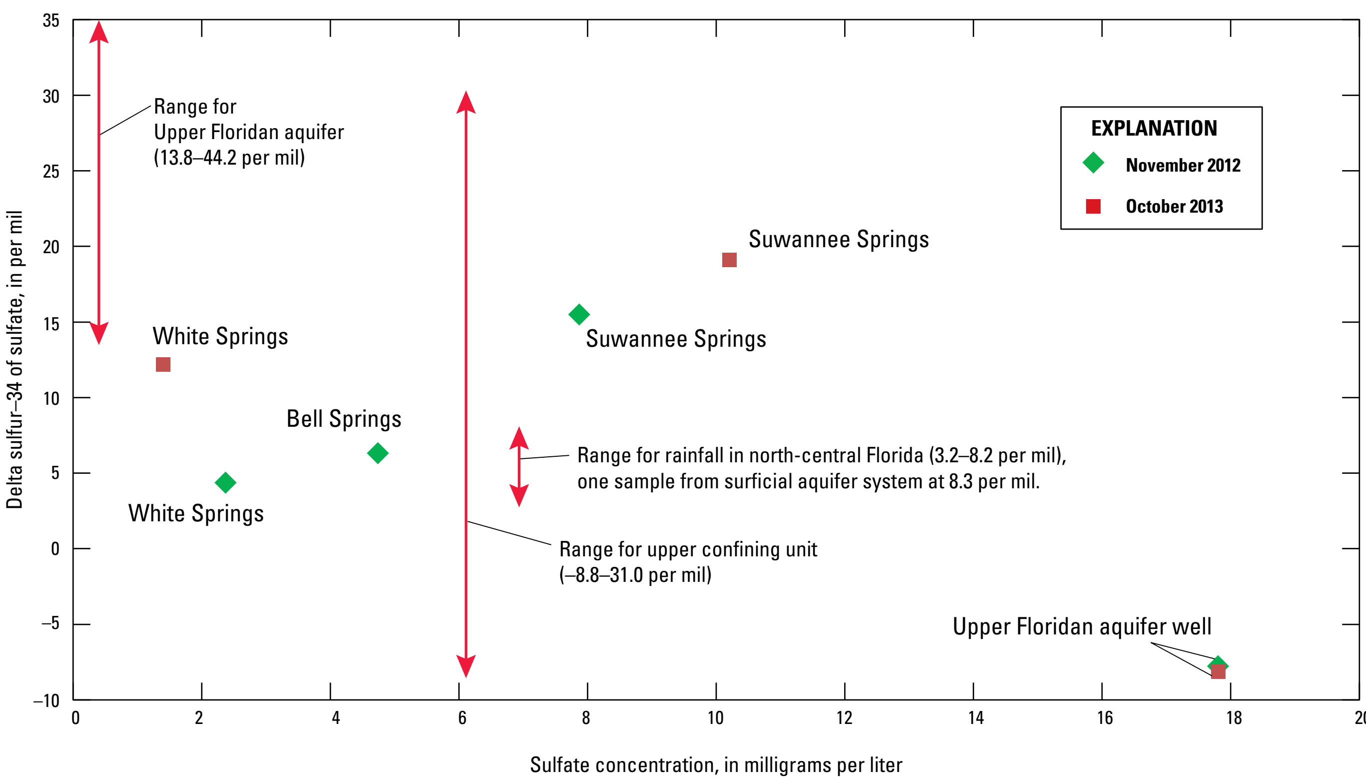

Figure 13. Sulfur isotopic ratios from sulfate compared to sulfate concentration in water samples collected during November 2012 and October 2013 from sites in the study area. Bell Springs was not sampled in October 2013.

sites and the sample collected at White Springs in October 2013 did not have $\delta^{34}S$ values similar to those of rainwater. (A sample was not collected at Bell Springs in October 2013 because it was not flowing.) Values of $\delta^{34}S$ in samples collected in 2012 and 2013 at White Springs, Bell Springs, and the UFA well also fell within the range of $\delta^{34}S$ from sulfate values for the upper confining unit, and the isotopic signature in the samples from the UFA well was isotopically the lightest among samples from all of the sites. Isotopically light sources of sulfur, such as pyrite, have been associated with the upper confining unit (Upchurch, 1992). Water in the UFA well would not be expected to have an isotopic signature of the upper confining unit. The UFA well description and a generalized geologic cross section by Rupert (1989) through a nearby well (designated W–190 in his report) indicate that the UFA well penetrates into the Suwannee Limestone and Ocala Limestone of the Upper Floridan aquifer. Drilling logs for the UFA well were not available (Kevin Wright, Suwannee River Water Management District, written commun., 2015). Because the UFA well penetrates units of the Upper Floridan aquifer, the water in UFA well might be expected to have an isotopic signature of the Upper Floridan aquifer; however, this does not appear to be the case. In summary, $\delta^{34}S$ from sulfate values indicated a mixture of groundwater from the upper confining unit and Upper Floridan aquifer at Suwannee Springs, a mixture of rainfall and groundwater from the upper confining unit at White and Bell Springs, and groundwater from the upper confining unit at the UFA well.

Dissolved sulfide in water is commonly associated with H_2S, and emits a rotten-egg smell in what is colloquially referred to as “sulfur” springs. Dissolved S^{2-} is a product of reduction of SO_4^{2-} in parts of the aquifer that become oxygen depleted (Hem, 1985). Others sources of H_2S and S^{2-} include petroleum and decay of organic material. The $\delta^{34}S$ of sulfide in southwest Florida ranges from –42.0 to 12.4 per mil in the Upper Floridan aquifer and from –50.5 to –6.5 per mil in the upper confining unit (Sacks and Tihansky, 1996). Therefore, $\delta^{34}S$ in sulfide might be used to distinguish the upper confining unit as a source if values are relatively high (greater than –6.5 per mil). Lighter $\delta^{34}S$ values might also be associated with oxidation of isotopically light sulfate, such as would be expected in water from the upper confining unit and rainfall, or also could be associated with short residence time in an aquifer (Sacks and Tihansky, 1996).

The $\delta^{34}S$ from sulfide (S^{2-}) values for White Springs and Suwannee Springs ranged from –6.4 to –17.7 per mil and were in the range or close to within the range (-6.4 per mil) typical for both the upper confining unit and Upper Floridan aquifer (Sacks and Tihansky, 1996); $\delta^{34}S$ from sulfide values, therefore, are not useful for distinguishing sources of groundwater. Sulfide concentrations were lower at White Springs and the UFA well than at Suwannee Springs (table 1), indicating a shallower source of water or shorter residence time for groundwater in samples from White Springs and the UFA well. Water samples for Bell Springs were not analyzed for $\delta^{34}S$ from sulfide.

Strontium Isotopes

Strontium isotopic ratios for Cenozoic-age carbonates in Florida were estimated by Katz and Bullen (1996), Sacks and Tihansky (1996), Katz and others (1997), Phelps (2001), and Tihansky (2005). Tihansky (2005) estimated a strontium isotopic ratio of 0.7092 for modern seawater. Ranges in strontium isotopic ratio for geologic units and aquifers were 0.7079–0.7083 for the Suwannee and Ocala Limestones, which compose the Upper Floridan aquifer in the study area; 0.7083–0.7088 for the Hawthorn Group, which composes the upper confining unit; and 0.7100–0.7109 for Quaternary-age deposits that compose the surficial aquifer. Katz and others (1997) reported strontium isotopic ratios in rainfall and surface water in the range of 0.7090 to 0.7107, which falls within the range for the surficial aquifer.

White Springs and Suwannee Springs (fig. 14) have strontium isotopic ratios that are transitional between groundwater sourced from the upper confining unit (Hawthorn Group) and the Upper Floridan aquifer (Suwannee and Ocala Limestones), indicating groundwater at White and Suwannee Springs might be a mixture of groundwater from these two sources. Strontium isotopic ratios and concentrations at White Springs and Suwannee Springs were similar for both samples collected (November 2012, October 2013). Water samples from the UFA well and Bell Springs had strontium isotopic ratios that were within the upper range associated with the upper confining unit. A cross-plot of strontium isotopic ratios and magnesium-calcium ratios (fig. 15) shows the three groupings of sites previously identified: Bell Springs, UFA well, and White and Suwannee Springs.

Summary of Water Sources

Water levels of the Suwannee River and wells in the study area, specific conductance, and isotopes were used to identify possible sources of groundwater at Bell Springs, White Springs, Suwannee Springs, and the UFA well (table 2). Water levels, sulfur isotopes, and specific conductance were used as indicators of surface-water sources. Surface water, either from rainfall or by inundation of springs by the Suwannee River during high-flow events, was identified as a source of water at all sites. Major ions, sulfur isotopes, and strontium isotopes in groundwater samples indicated that the upper confining unit was a source of groundwater at Bell Springs and the UFA well. Sulfur and strontium isotopes in groundwater samples indicated a mixture of groundwater from the upper confining unit and Upper Floridan aquifer, as well as surface water, were sources of water to White and Suwannee Springs. A mixture of sources at White Springs is consistent with the observation by Meyer (1962) that White Springs was a discrete point of recharge to the Upper Floridan aquifer by the Suwannee River. A limitation of the current study is that springs and the UFA well were sampled only one time per year over 2 years. A more extensive sampling effort, over several

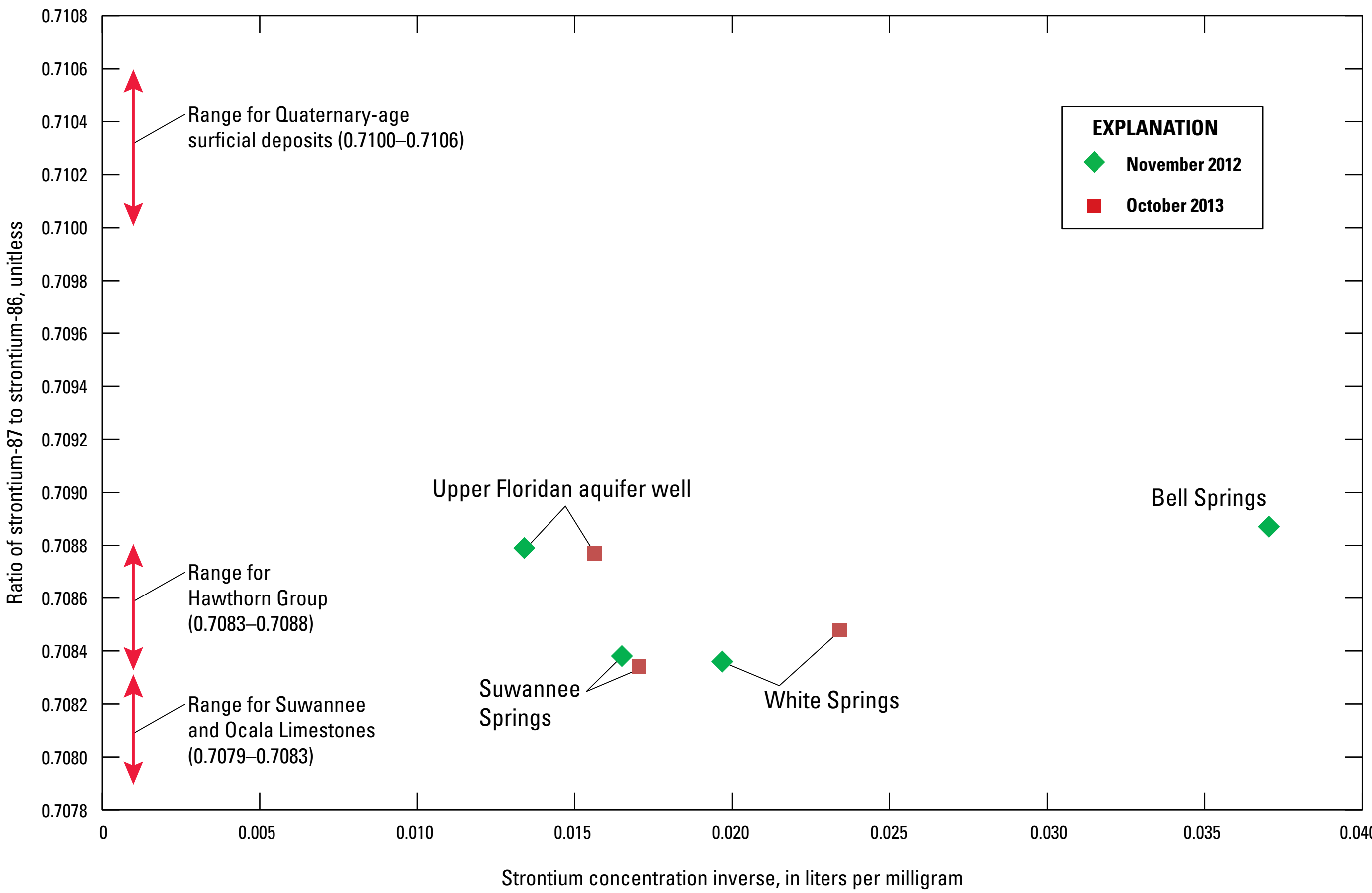

Figure 14. Strontium isotopic ratios and strontium (Sr) concentration in water samples collected during November 2012 and October 2013 from sites in the study area. Bell Springs was not sampled in October 2013.

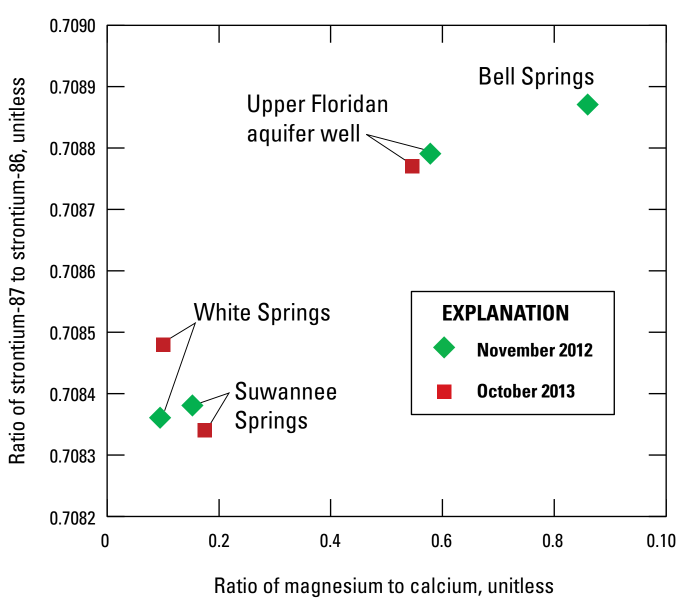

Figure 15. Ratios of concentration of magnesium to calcium in strontium isotopic ratios in water samples collected during November 2012 and October 2013 from sites in the study area. Bell Springs was not sampled in October 2013.

years with samples collected several times per year, would increase confidence in the conclusions reached.

Characteristics of Recharge

The residence time, apparent age of recharge, and temperature of surface water at the time of recharge can be estimated using isotopic ratios for oxygen and hydrogen, and concentration of gases dissolved in water samples (table 3). Although residence time, age, and temperature are not indicators of sources of groundwater, they provide information about the characteristics of recharge at the surface from precipitation and streamflow.

Oxygen and Deuterium Isotopes

Oxygen and deuterium isotopic ratios ($\delta^{18}O$, δD) generally fall along the local meteoric water line (defined by Katz and others, 1998) for samples collected in November 2012 and along the evaporation trend line for samples collected in October 2013 (fig. 16). These contrasting trends

Table 2. Summary of evidence of surface water and groundwater sources at sites.

[Evidence of a source of surface water and groundwater are listed for each source, and includes water levels of the Suwannee River and in wells, specific conductance (continuous measurements and discrete samples), and sulfur and strontium isotopes in discrete water samples. UFA, Upper Floridan aquifer; --, findings do not indicate aquifer to be a major source of groundwater at the site]

Sites	Source of groundwater		
	Surface water	Upper confining unit	Upper Floridan aquifer
Bell Springs	Water levels, sulfur isotopes	Major ions, sulfur isotopes, strontium isotopes	--
UFA well	Water levels	Major ions, sulfur isotopes, strontium isotopes	--
White and Suwannee Springs	Water levels, specific conductance, sulfur isotopes	Sulfur isotopes, strontium isotopes	Sulfur isotopes, strontium isotopes

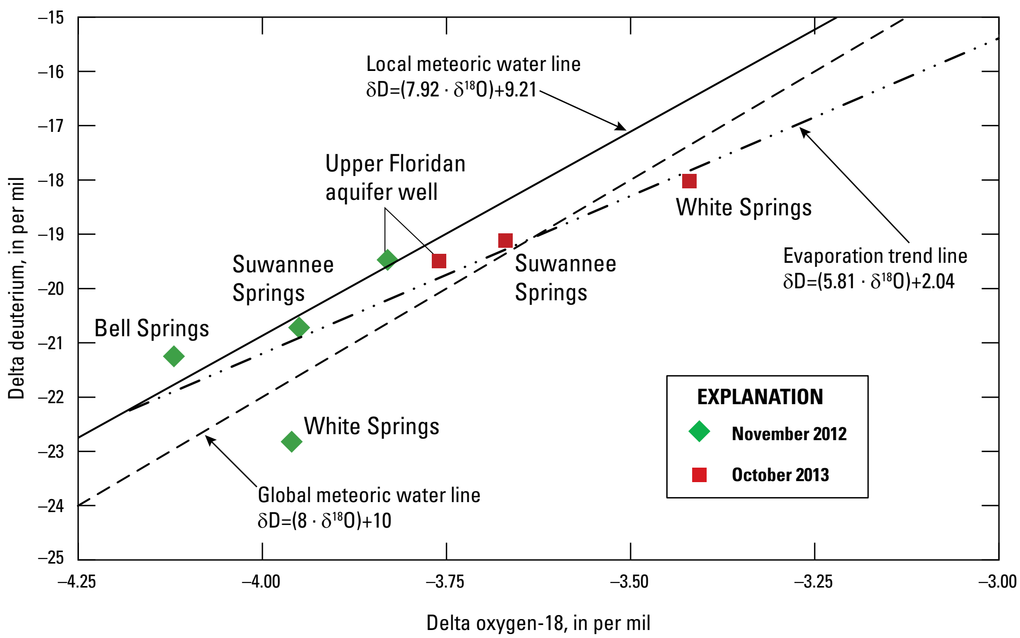

Figure 16. Oxygen and deuterium isotopic ratios (^{18}O and δD, respectively) in water samples collected during November 2012 and October 2013 at sites in the study area. Global meteoric water line from Craig (1961). Local meteoric water line from Katz and others (1998).

indicate that rainwater probably infiltrated rapidly for samples collected in 2012 and had a longer residence time near the surface (either by ponding or remaining in the soil unsaturated zone) for samples collected in 2013, resulting in relatively greater evaporation. This result is consistent with climatic conditions for 2011 and 2012, in that 2011 was a dry year during which recharge would be rapid, and 2012 was a wet year where water may have had more residence time at the surface (fig. 5); however, samples might represent much older water. The sample collected at White Springs in November 2012 falls below the local meteoric water line and evaporation trend line (fig. 16). The reason for this deviation could not be determined.

Apparent Age of Water Samples

Sulfur hexafluoride and tritium were detected in all water samples (table 3), and the presence of each indicates a recharge contribution that occurred after the 1950s. The approximate years of recharge from rainwater determined on the basis of sulfur hexafluoride concentration ranged from 1988 to 2001 for water samples collected in November 2012 and from 1989 to 1994 for water samples collected in October 2013 (table 3). Apparent ages computed on the basis of tritium concentration ranged from 1988 to 1993 for water samples collected in November 2012 and from 1988 to 1995 for water samples collected in October 2013. Recharge ages estimated

Table 3. Geochemical analyses of gases and tracers, and estimated ages of water samples based on tritium and sulfur hexafluoride concentrations. Groundwater and surface-water data for each USGS site are available online through the National Water Information System for Florida (http://nwis.waterdata.usgs.gov/fl/nwis/nwis).

[USGS, U.S. Geological Survey; yyyy, year; mm, month; dd, day; EST, Eastern Standard Time; mg, milligram; L, liter; fg, femtogram; kg, kilogram; pCi, picocurie; Fla., Florida; na, not applicable; ft, foot; UFA, Upper Floridan aquifer]

USGS site identification number	Station name	Date (yyyy/mm/dd)	Time (EST)	Argon concentration (mg/L)	Recharge temperature (degrees Celsius)	Oxygen concentration, dissolved, lab (mg/L)	Carbon dioxide concentration (mg/L)	Dinitrogen concentration (mg/L)	Methane concentration (mg/L)
November 2012 sampling event									
02315503	White Sulphur Springs at White Springs, Fla.	2012/11/28	1200	na	na	na	na	na	na
			1201	0.515	26.4	0.2	12.1	14.81	0.566
			1202	0.520	26.4	0.2	12.6	15.14	0.479
301949082452801	White Springs Methodist 150 ft UFA well at White Springs, Fla.	2012/11/28	1700	na	na	na	na	na	na
			1701	0.610	19.1	0.2	15.9	17.89	0.038
			1702	0.606	19.1	0.2	15.7	17.72	0.036
02315600	Suwannee Springs near Live Oak, Fla.	2012/11/29	1200	na	na	na	na	na	na
			1201	0.645	17.2	0.2	12.4	19.33	0.479
			1202	0.650	17.2	0.2	12.6	19.42	0.471
301945082411800	Bell Springs near White Springs Fla.	2012/11/29	1700	na	na	na	na	na	na
			1701	0.623	17.1	3.1	5.7	17.9	0.001
			1702	0.625	17.1	3.4	5.3	17.96	0.001
October 2013 sampling event									
02315503	White Sulphur Springs at White Springs, Fla.	2013/10/23	1300	na	na	na	na	na	na
			1301	0.620	21.0	0.2	13.4	19.22	1.39
			1302	0.624	21.1	0.2	13	19.48	1.39
301949082452801	White Springs Methodist 150 ft UFA well at White Springs, Fla.	2013/10/23	1900	na	na	na	na	na	na
			1901	0.594	21.9	0.2	17.8	17.98	0.013
			1902	0.601	21.5	0.2	17.6	18.26	0.013
02315600	Suwannee Springs near Live Oak, Fla.	2013/10/24	1100	na	na	na	na	na	na
			1101	0.637	18.3	0.3	13.1	19.19	0.388
			1102	0.633	18.1	0.3	13.3	18.86	0.385

Table 3. Geochemical analyses of gases and tracers, and estimated ages of water samples based on tritium and sulfur hexafluoride concentrations. Groundwater and surface-water data for each USGS site are available online through the National Water Information System for Florida (http://nwis.waterdata.usgs.gov/fl/nwis/nwis). —Continued

[USGS, U.S. Geological Survey; yyyy, year; mm, month; dd, day; EST, Eastern Standard Time; mg, milligram; L, liter; fg, femtogram; kg, kilogram; pCi, picocurie; Fla., Florida; na, not applicable; ft, foot; UFA, Upper Floridan aquifer]

USGS site identification number	Station name	Date (yyyy/mm/dd)	Time (EST)	Sulfur-hexafluoride concentration (fg/kg)	Sulfur-hexafluoride age, as calendar year	Tritium activity (pCi/L)	Computed initial tritium activity (pCi/L)	Calendar year initial tritium concentration observed at Ocala, Florida	Difference in sulfur-hexafloride age and tritium age (years)
				November 2012 sampling event					
02315503	White Sulphur Springs at White Springs, Fla.	2012/11/28	1200	na	na	6.2	17.0	1990	5
			1201	146.7	1995	na	na	na	na
			1202	155	1996	na	na	na	na
301949082452801	White Springs Methodist 150 ft UFA well at White Springs, Fla.	2012/11/28	1700	na	na	6.6	21.0	1988	5
			1701	176.8	1993	na	na	na	na
			1702	157.1	1992	na	na	na	na
02315600	Suwannee Springs near Live Oak, Fla.	2012/11/29	1200	na	na	5.0	20.9	1988	-1
			1201	129.1	1988	na	na	na	na
			1202	128.4	1988	na	na	na	na
301945082411800	Bell Springs near White Springs Fla.	2012/11/29	1700	na	na	6.4	12.9	1993	8
			1701	283.3	2001	na	na	na	na
			1702	271.6	2000	na	na	na	na
				October 2013 sampling event					
02315503	White Sulphur Springs at White Springs, Fla.	2013/10/23	1300	na	na	5.5	21.6	1988	2
			1301	162	1990	na	na	na	na
			1302	159.9	1990	na	na	na	na
301949082452801	White Springs Methodist 150 ft UFA well at White Springs, Fla.	2013/10/23	1900	na	na	5.3	16.2	1991	3
			1901	203.6	1994	na	na	na	na
			1902	203	1994	na	na	na	na
02315600	Suwannee Springs near Live Oak, Fla.	2013/10/24	1100	na	na	2.9	12.0	1995	-7
			1101	139.8	1989	na	na	na	na
			1102	141.5	1989	na	na	na	na

Table 3. Geochemical analyses of gases and tracers, and estimated ages of water samples based on tritium and sulfur hexafluoride concentrations. Groundwater and surface-water data for each USGS site are available online through the National Water Information System for Florida (http://nwis.waterdata.usgs.gov/fl/nwis/nwis). —Continued

[USGS, U.S. Geological Survey; yyyy, year; mm, month; dd, day; EST, Eastern Standard Time; mg, milligram; L, liter; fg, femtogram; kg, kilogram; pCi, picocurie; Fla., Florida;
na, not applicable; ft, foot; UFA, Upper Floridan aquifer]

USGS site identification number	Station name	Date (yyyy/mm/dd)	Time (EST)	$\delta^{18}O$ (per mil)	δD (per mil)	$^{87}Sr/^{86}Sr$ (per mil)	$\delta^{34}S$ in sulfate (per mil)	$\delta^{34}S$ in sulfide (per mil)
			November 2012 sampling event					
02315503	White Sulphur Springs at White Springs, Fla.	2012/11/28	1200	-3.96	-22.8	0.70836	4.37	-11.69
			1201	na	na	na	na	na
			1202	na	na	na	na	na
301949082452801	White Springs Methodist 150 ft UFA well at White Springs, Fla.	2012/11/28	1700	-3.83	-19.5	0.70879	-7.76	-39.11
			1701	na	na	na	na	na
			1702	na	na	na	na	na
02315600	Suwannee Springs near Live Oak, Fla.	2012/11/29	1200	-3.95	-20.7	0.70838	15.5	-17.63
			1201	na	na	na	na	na
			1202	na	na	na	na	na
301945082411800	Bell Springs near White Springs Fla.	2012/11/29	1700	-4.12	-21.3	0.70887	6.31	na
			1701	na	na	na	na	na
			1702	na	na	na	na	na
			October 2013 sampling event					
02315503	White Sulphur Springs at White Springs, Fla.	2013/10/23	1300	-3.42	-18	0.70848	12.18	-6.36
			1301	na	na	na	na	na
			1302	na	na	na	na	na
301949082452801	White Springs Methodist 150 ft UFA well at White Springs, Fla.	2013/10/23	1900	-3.76	-19.5	0.70877	-7.96	-37.33
			1901	na	na	na	na	na
			1902	na	na	na	na	na
02315600	Suwannee Springs near Live Oak, Fla.	2013/10/24	1100	-3.67	-19.1	0.70834	19.12	-17.67
			1101	na	na	na	na	na
			1102	na	na	na	na	na

using both methodologies were similar, having a maximum age difference of 8 years (Bell Springs, November 2012 water sample). Therefore, the residence time of groundwater since recharge is estimated to be as much as 24 years. Given that there might be several potential sources of groundwater (such as rainfall, the upper confining unit, and the Upper Floridan aquifer), this age reflects the average age of the mixture of these groundwater sources. Surface water could be mixed with groundwater more than 24 years old that might predate the presence of atmospheric deposition of hexafluoride and tritium, and actual recharge age could therefore be younger than apparent age. Groundwater recharge since the 1980s is consistent with groundwater from shallow sources, such as the upper confining unit and Upper Floridan aquifer.

Recharge Water Temperature

Recharge water temperatures, as computed from noble gas concentrations determined in water samples, indicate that water temperature at the time of recharge ranged from a minimum of 17.1 °C to a maximum of 26.4 °C, with a mean of 20.1 °C (table 3). Mean annual air temperature at the Live Oak weather station (fig. 1) for 1960–2014 was 20.6 °C. Recharge temperature for the water sample collected at White Springs in November 2012 (26.4 °C) is elevated relative to recharge temperatures for other samples. Elevated recharge water temperature might be associated with recharge that occurred during a warm year and (or) a warm time of the year (such as summer). In Florida, summers are associated with convective storms and high streamflow. This pattern is illustrated by the hydrograph for the Suwannee River near the White Springs streamgage, which indicates peaks in flow in 2012 and 2013 during summer months (fig. 11). Samples collected at White Springs in November 2012 therefore might be associated with summer recharge events.

Summary

Discharge from springs of Florida is sourced from aquifers, such as the Upper Floridan aquifer, which is overlain by the upper confining unit. The upper confining unit is within the Hawthorn Group and locally can have properties of an aquifer. Water levels in aquifers are affected by precipitation, recharge, and groundwater withdrawals, which in turn can affect spring discharge. Therefore, the identification of sources of groundwater can be important in assessing how these factors might affect flows and levels in springs and can be informative in broader applications such as groundwater modeling.

Sources of groundwater in three springs that discharge from the banks of the Suwannee River in northern Florida were assessed in this study: Bell Springs, White Springs, and Suwannee Springs. Sources of groundwater were also assessed for a 150-foot-deep well finished within the Upper Floridan aquifer, referred to as the UFA well. Seven discrete water samples were collected for geochemical analyses on November 2012 and October 2013 from the three springs and the UFA well, and were analyzed for a suite of major ions, dissolved gases, and isotopes of sulfur, strontium, oxygen, and hydrogen. Daily means of water level and specific conductance were continuously recorded at White Springs from October 2012 through December 2013. Suwannee River stage at White Springs was estimated on the basis of stage at a U.S. Geological Survey streamgage about 2.4 miles (mi) upstream. Water level in two wells, located about 2.5 mi northwest and 13 mi southeast of White Springs, were also used in the analyses.

During the November 2012 and October 2013 sampling periods, water flowed from White Springs to the Suwannee River, but this was not always the case at White Springs. White Springs and the Suwannee River were disconnected from October 2011 through June 2012, during which time the water level in the Suwannee River was higher than the water level in the pool of White Springs. This indicates little hydrologic connection of river water and spring water at that time; otherwise, the river and spring would have been at the same elevation. The Suwannee River inundated White Springs during June–October 2012 and during much of 2013. During these inundation events, groundwater levels in a well 2.5 mi from White Springs had short-term fluctuations similar to those measured in the Suwannee River, indicating the river as a likely source of groundwater recharge. Water levels in the well 13 mi from White Springs and the Suwannee River did not exhibit the same short-term fluctuations as those at the river and in the well 2.5 mi from the river, but instead rose smoothly over several months.

Multiple lines of evidence, when available, were considered to determine sources of groundwater for the three springs and UFA well: water levels, specific conductance, major ion concentrations, and isotopic ratios. Water levels in the pool at White Springs periodically were below the water level of the river, indicating little contribution of river water to the spring. However, when stage in the Suwannee River is high, river water inundates White Springs. Inundation of White Springs by the Suwannee River was also indicated by a drop in specific conductance. Groundwater levels in wells indicate that the river recharges the groundwater system during periods of high flow, with wells more distant from the river having a less variable response.

Major ion concentrations in groundwater samples were used to differentiate water from the springs and UFA into three groups: Bell Springs, the UFA well, and White and Suwannee Springs. Nitrate and nitrite at Bell Springs was elevated relative to other sites, indicating a surface-water source at this site. Slightly elevated magnesium in Bell Springs and the UFA well might indicate sources of groundwater from the upper confining unit. Higher concentrations of magnesium at the UFA well might indicate less mixing with surface water at this site than the others. Isotopes of sulfur and strontium were used to identify sources of groundwater. Isotopically light values for sulfur have been attributed to sources of sulfur from pyrite and organic matter; pyrite is present within the upper confining unit. Isotopic ratios of sulfur from sulfate indicated (1) groundwater from Bell Springs was a mixture

of surface water and groundwater from the upper confining unit, (2) groundwater from the UFA well was from the upper confining unit, (3) groundwater from White Springs was a mixture of surface water and groundwater from the upper confining unit, and (4) groundwater at Suwannee Springs was a mixture of groundwater from the upper confining unit and Upper Floridan aquifer. Strontium isotopic ratios in groundwater samples from Bell Springs and the UFA well were consistent with groundwater originating from the upper confining unit, whereas ratios for Suwannee and White Springs were consistent with groundwater from the Upper Floridan aquifer.

When considered together, evidence from water-level, specific conductance, major ion, and isotope data indicated that groundwater at Bell Springs and the UFA well was a mixture of surface water and groundwater from the upper confining unit. Higher concentrations of magnesium in groundwater samples at the UFA well than in samples at Bell Springs might indicate less mixing with surface water at the UFA well than at Bell Springs. Evidence indicated that groundwater at White and Suwannee Springs was a mixture of surface water and groundwater from the upper confining unit and Upper Floridan aquifer. Mixing of water from all three sources at White Springs is consistent with an observation from an earlier study that White Springs is a point of recharge for the Upper Floridan aquifer. A limitation of the current study is that the three springs and UFA well were sampled once per year over 2 years. A more extensive sampling effort lasting several years, with samples collected several times per year, would increase confidence of conclusions regarding sources of groundwater.

Characteristics of surface-water recharge, such as the residence time at the surface, apparent age, and recharge water temperature, were estimated for discrete groundwater samples from springs and the UFA well. Oxygen and deuterium isotopic ratios were consistent with a meteoric-water source of recharge for samples collected in 2012, and enrichment of isotopic ratios for samples collected in 2013 potentially indicates a longer residence time at the surface (ponding) prior to infiltration. Apparent ages of samples, computed on the basis of concentrations of tritium and sulfur hexafluoride, indicated groundwater recharge occurred after the late 1980s; however, the estimated apparent ages likely represent the average of ages of multiple sources. Groundwater recharge since the 1980s is consistent with groundwater from shallow sources, such as the upper confining unit and Upper Floridan aquifer. Recharge water temperatures, as computed from argon concentrations in water samples, indicate that water temperature at the time of recharge ranged from a minimum of 17.1 degrees Celsius (°C) to a maximum of 26.4 °C, with a mean of 20.1 °C, which is similar to the mean annual air temperature of 20.6 °C at a nearby weather station for 1960–2014. Elevated recharge water temperature (26.4 °C for the White Springs, November 2012 sample) might be associated with recharge that occurred during a warm year and (or) warm time of year (such as summer).

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