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NITRATE CONCENTRATIONS IN THE WEKIVA GROUNDWATER BASIN WITH EMPHASIS ON WEKIWA SPRINGS

by

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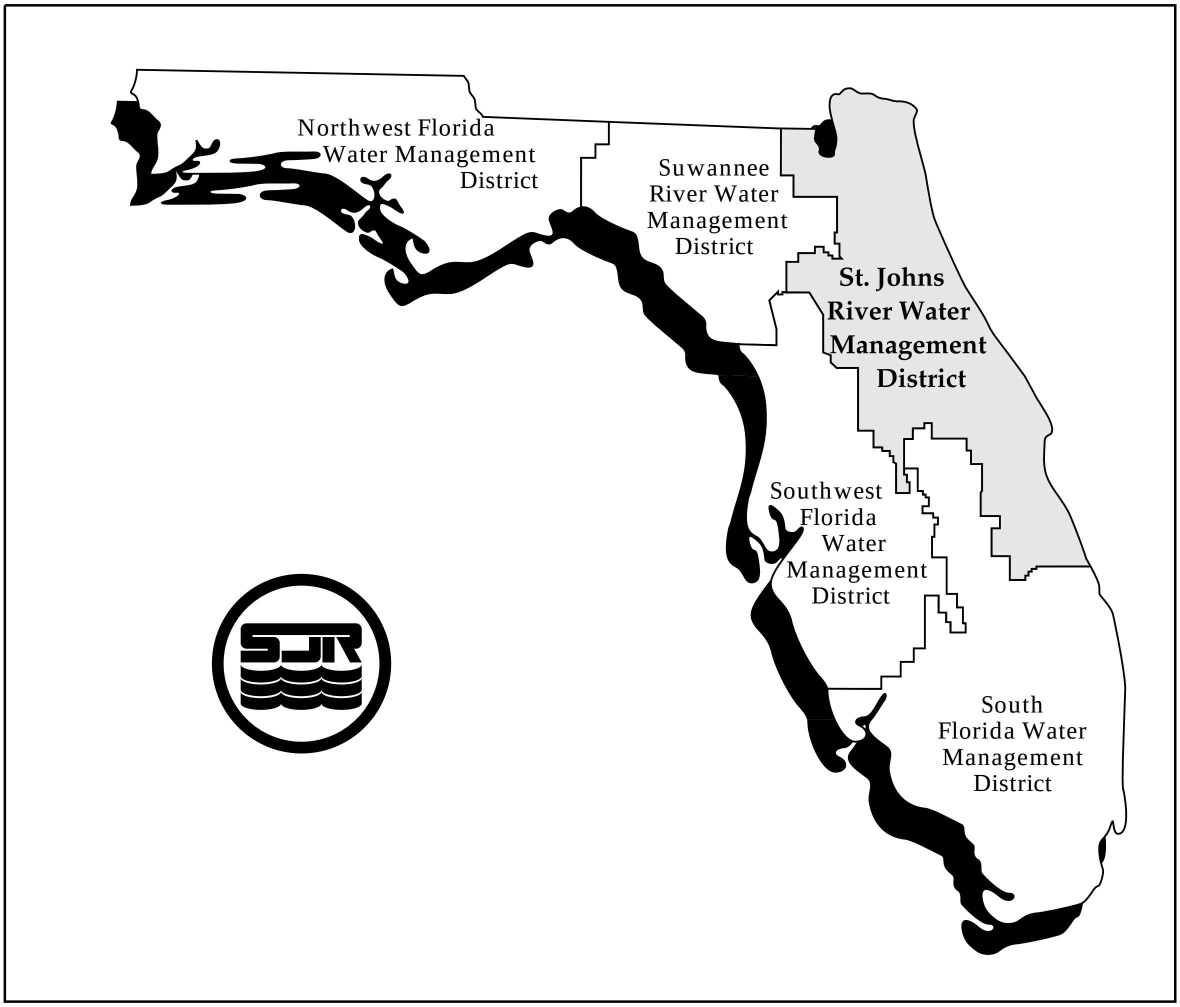

The St. Johns River Water Management District (SJRWMD) was created by the Florida Legislature in 1972 to be one of five water management districts in Florida. It includes all or part of 19 counties in northeast Florida. The mission of SJRWMD is to manage water resources to ensure their continued availability while maximizing environmental and economic benefits. SJRWMD accomplishes its mission through regulation; applied research; assistance to federal, state, and local governments; operation and maintenance of water control works; and land acquisition and management.

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ABSTRACT

Nitrate nitrogen (N) concentrations have been measured in Wekiwa Springs since 1961 and increased during the 1980s to a maximum in 1995 of 2.00 milligrams per liter (mg/L). Since 1995, nitrate N concentrations have decreased. In August 1999, the nitrate N concentration at Wekiwa Springs was measured at 1.30 mg/L. At this concentration, Wekiwa Springs discharges approximately 458 pounds of nitrogen per day, or 84 tons of nitrogen per year.

In a previous investigation (Toth 1999), the St. Johns River Water Management District (SJRWMD) determined that the delta nitrogen-15 value for Wekiwa Springs was +8.6 parts per thousand. This suggests that the source of the nitrates in Wekiwa Springs is a mixture of leachate from septic tanks and recharge water from fertilized lawns. In an effort to better locate the source of the nitrates, in 1999, SJRWMD, with the cooperation of the U.S. Geological Survey, sampled 50 sites in the Wekiva groundwater basin for nitrate N and 11 sites for isotopes (deuterium, oxygen-18, nitrogen-15, tritium, helium-3, helium-4, and neon). Twenty-two samples contained “elevated” concentrations of nitrate N above the background concentration of 0.2 mg/L. The highest concentration (7.5 mg/L) occurred to the west of Lake Apopka. N isotope concentrations indicated a piston flow fertilizer source for these nitrates, and tritium and helium-3 indicated a piston flow median age of 27.4 years for the water. The highest nitrate N concentrations corresponded to a cropland land use category in 1973 and are probably due to citrus fertilization.

The data indicate that the areas of the highest nitrate N concentrations probably do not contribute to the nitrate N discharging from Wekiwa Springs. Land use changes between 1973 and 1990 suggest that the sources for the nitrates at Wekiwa Springs are septic tanks and lawn fertilizers. The more locally developed flow of the Upper Floridan aquifer in the vicinity of the spring results in a more direct influence and source of the nitrate N contamination displayed at the spring. The contamination occurred by processes that took place approximately 17 years ago.

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INTRODUCTION

Nitrate nitrogen (N) is a nutrient essential for plant and algal growth. High concentrations of nitrate N are detrimental to water bodies because it causes eutrophication. The St. Johns River Water Management District (SJRWMD) is charged with protecting the quality of its springs and therefore is concerned about concentrations of nitrate N in the springs. This paper focuses on Wekiwa Springs because it had the highest concentration of nitrate N among the 17 springs sampled in 1995–96 (Toth 1999).

Many springs in the Wekiva groundwater basin are known to have elevated concentrations (greater than 0.2 milligrams per liter [mg/L]) of nitrate N (Toth 1999). Total nitrate N concentrations were detected above the “elevated” threshold of 0.2 mg/L in Wekiwa Springs (1.92 mg/L as nitrogen), Rock Springs (1.62 mg/L), Seminole Springs (1.41 mg/L), Sanlando Springs (0.782 mg/L), Palm Springs (0.703 mg/L), and Starbuck Spring (0.447 mg/L). No nitrate N was detected in Messant Spring. Nitrate N was not measured in Gemini Springs in 1995 or 1996, but it was measured (0.8 mg/L) in this study.

The source of the nitrates differed by location of the springs (Toth 1999). The source was determined by measuring the delta nitrogen-15 ($\delta^{15}N$) content of the nitrate N. The elevated nitrate levels in Sanlando ($\delta^{15}N$ = +11.7‰ [parts per thousand]) and Starbuck ($\delta^{15}N$ = +12.9‰) springs, based on $\delta^{15}N$, are probably due to contamination by animal waste and/or sewage. The elevated nitrate levels in Palm Springs ($\delta^{15}N$ = +7.8‰) and Wekiwa Springs ($\delta^{15}N$ = +8.6‰) are probably due to contamination by animal waste and/or sewage, perhaps mixing with nitrates derived from fertilizers. Finally, the elevated nitrate levels in Rock ($\delta^{15}N$ = +5.8‰) and Seminole springs ($\delta^{15}N$ = +5.1‰) are probably due to contamination by nitrates from fertilizers. Concentrations of soil organic nitrogen are assumed to be low.

The nitrate concentrations in all springs are below the primary drinking water standard (FDER 1989) of 10 mg/L as N. However, there is concern that concentrations of “less than 1 mg/L cause a significant shift in the balance of spring ecological communities, leading to intensified degradation of biological systems" (FDEP 2000). Both algal growth and eutrophication will cause the clarity of spring water to diminish.

PURPOSE

The purpose of this study was to determine the nitrate N concentrations in the Wekiva groundwater basin, the sources responsible for the elevated nitrate N concentrations, and the age of the water. Special emphasis was placed on Wekiwa Springs because it had one of the highest concentrations of nitrate N among the springs in the basin.

STUDY AREA

The study area occurs in SJRWMD (Figure 1) in east-central Florida. It occurs in what Tibbals (1990) defined as the Wekiva groundwater basin and includes western Seminole and Orange counties, a large part of Lake County, and a small portion of western Volusia and northern Polk counties (Figure 2). The boundaries of the Wekiva groundwater basin are based on the May 1980 potentiometric map for the Floridan aquifer. The study area includes most of the Wekiwa Springs groundwater basin (B. McGurk, SJRWMD, pers. com. 2000). The Wekiwa Springs groundwater basin lies in western Orange County and includes small portions of Seminole, Lake, and Polk counties (Figure 3). The Wekiwa Springs groundwater basin was defined on the basis of the 1995 average potentiometric map for the Floridan aquifer. The basin boundaries are approximate and may change from year to year.

The boundaries for the Wekiva groundwater basin and the Wekiwa Springs groundwater basin differ because they were defined by two different individuals who used two different potentiometric surface maps for the Floridan aquifer. In reality, they are the same. The Wekiwa Springs surface water basin is smaller than the groundwater basin. It occurs in western Orange and Seminole counties and eastern Lake County (Figure 4).

Land surface elevation is variable throughout the Wekiva groundwater basin (Figure 5). Elevations are above 150 feet mean sea level (ft msl) in the middle and western part of the groundwater basin, but are generally less than 100 ft msl in the surface water basin, and at Wekiwa Springs.

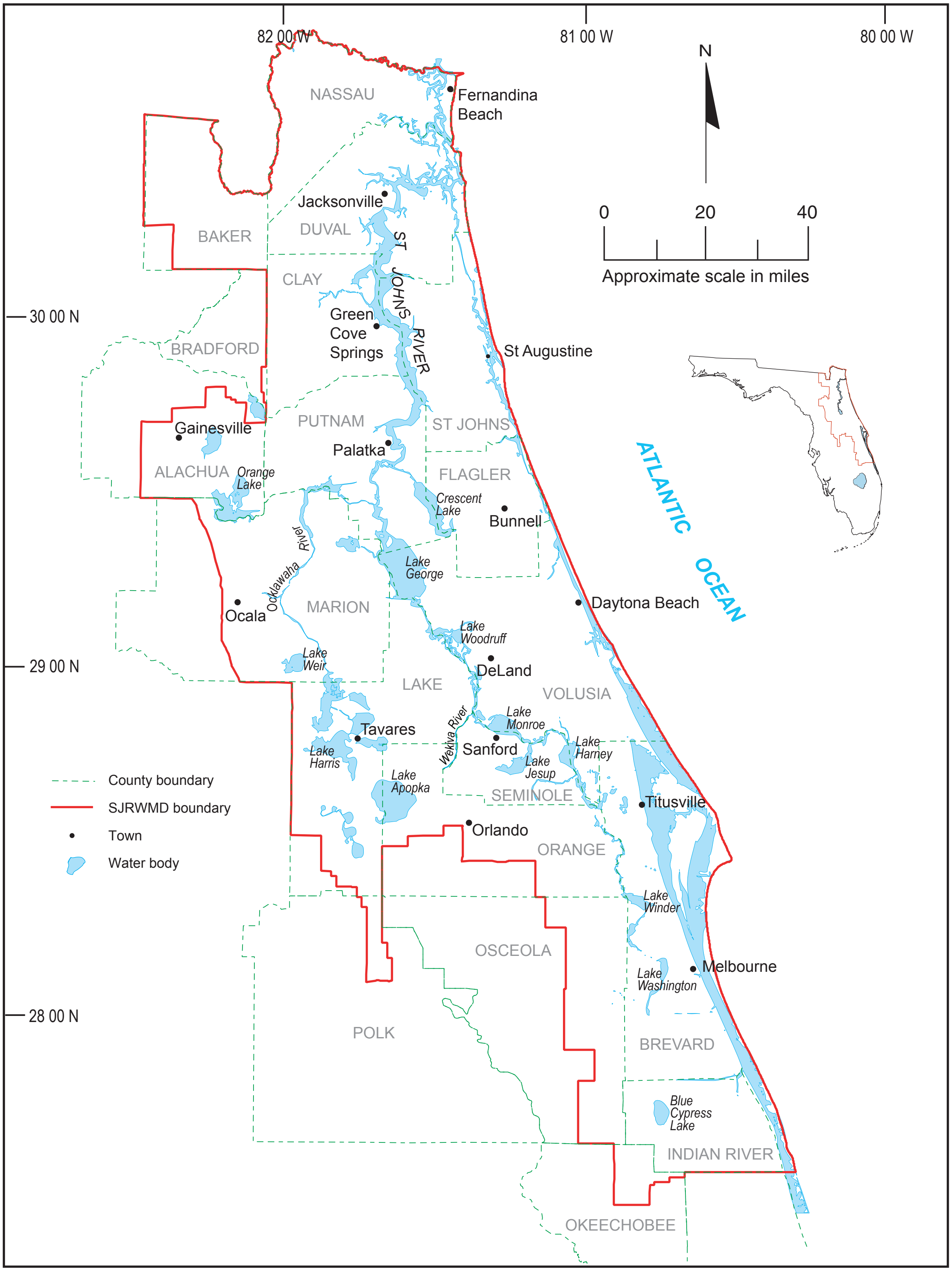


Figure 1. The St. Johns River Water Management District

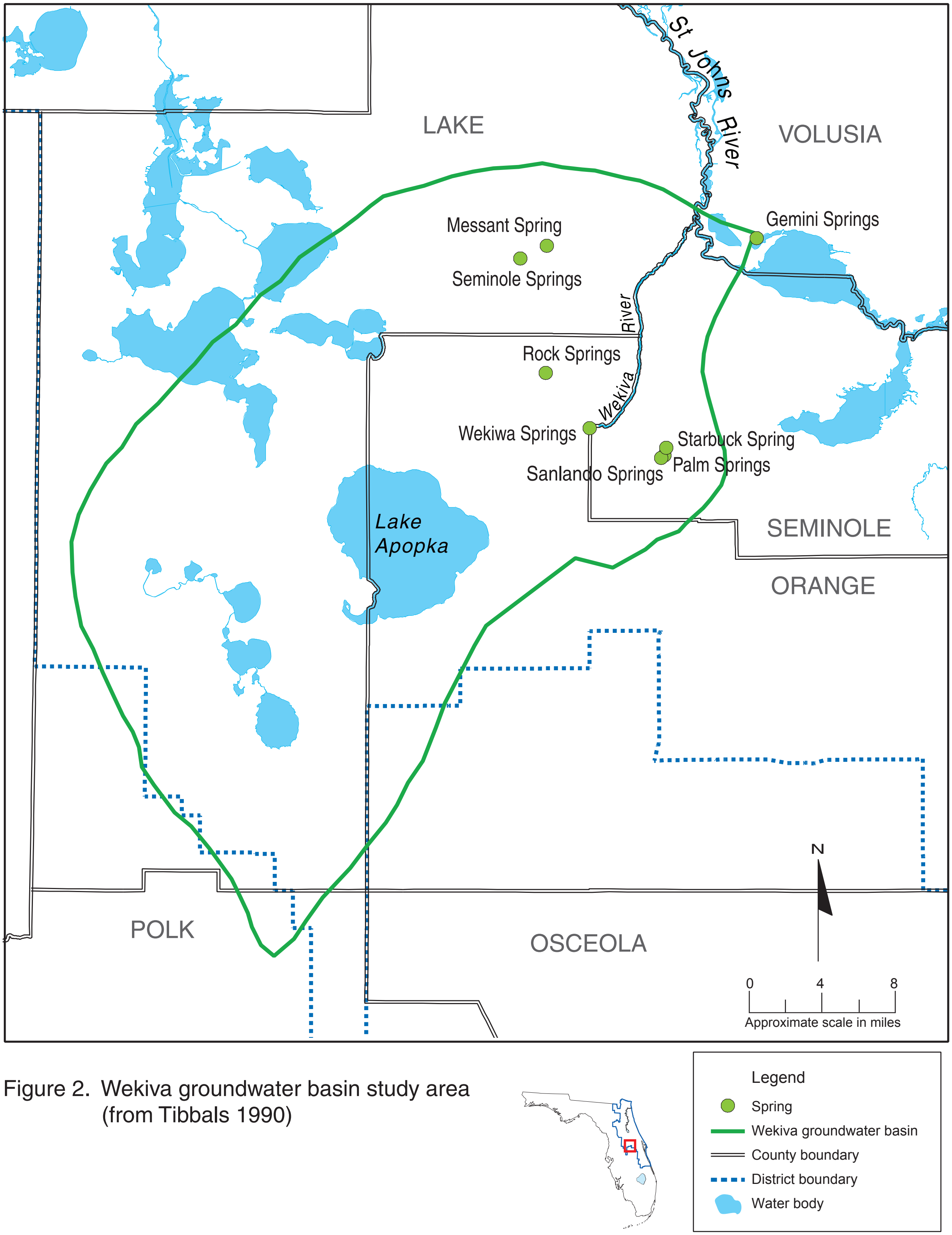
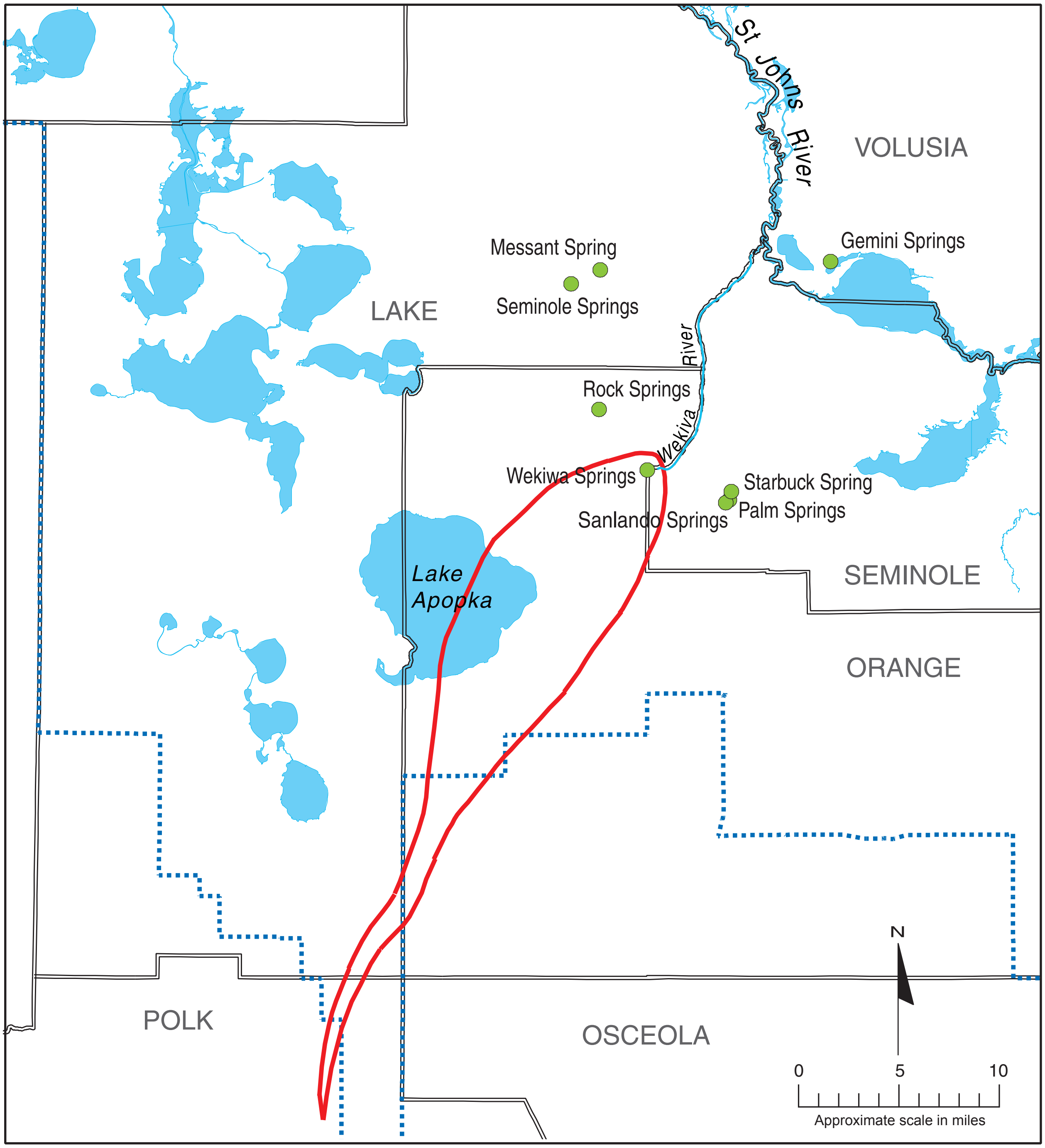


Figure 2. Wekiva groundwater basin study area (from Tibbals 1990)



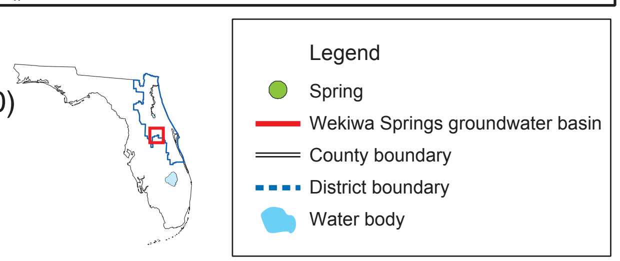


Figure 3. Wekiwa Springs groundwater basin (B. McGurk, SJRWMD, pers. com. 2000)

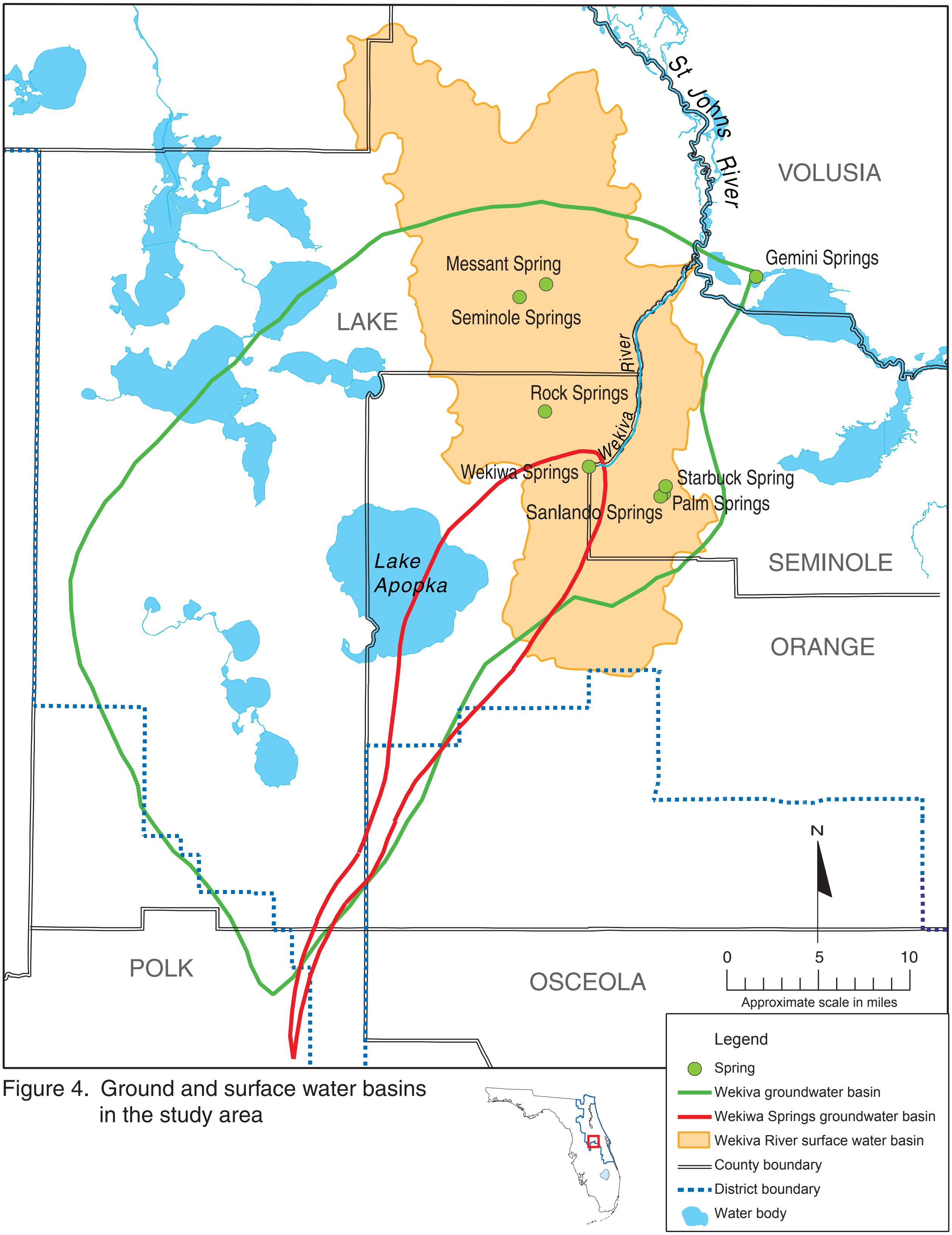


Figure 4. Ground and surface water basins in the study area

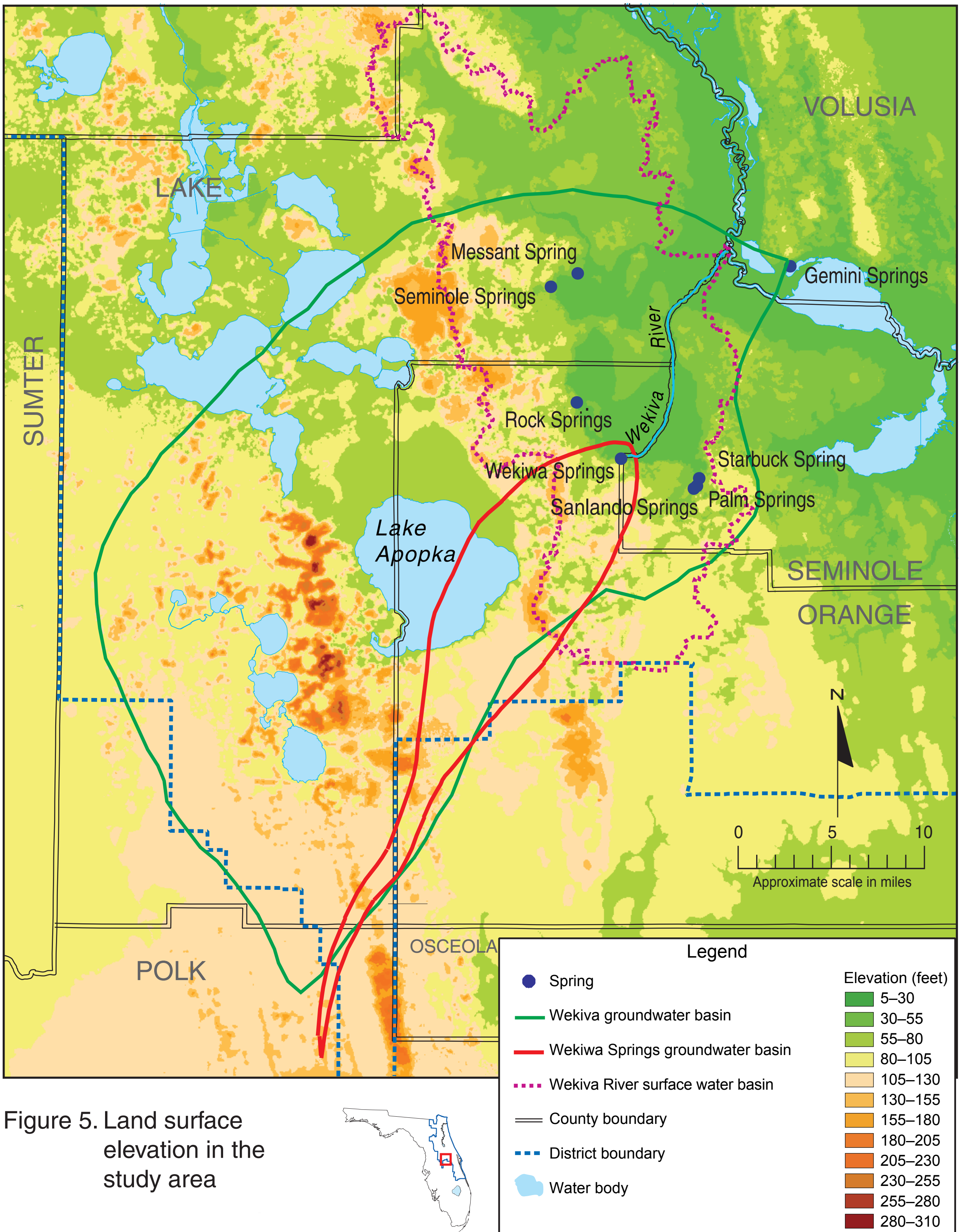


Figure 5. Land surface elevation in the study area

METHOD

Fifty water samples were collected from Upper Floridan aquifer wells, springs, and sinks in or close to the Wekiva groundwater basin for water quality analysis (Figure 6; Appendix A). Using standard sampling procedures, the samples were collected by SJRWMD with the cooperation of the U.S. Geological Survey (USGS) and analyzed in the USGS Ocala laboratory for total dissolved nitrate and nitrite nitrogen and total organic and ammonia nitrogen. In addition, eleven of the above samples were analyzed for deuterium (^{2}H), oxygen-18 (^{18}O), nitrogen-15 (^{15}N), tritium (^{3}H), helium-3 (^{3}He), helium-4 (^{4}He), and neon (Ne). The above isotopes were measured in contract laboratories for USGS. Tritium, helium-3, helium-4, and neon were measured in the Noble Gas Laboratory, Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York. All samples were collected in August and September 1999.

Results from the water quality analyses of the 50 water samples were used to prepare contour maps. The contours were generated using ArcView. In addition to the 50 samples, results from 35 other samples were included in the preparation of the contour maps. The other samples were collected from Upper Floridan aquifer wells and springs in the study area during 1996–99. Some of the other samples only reported total nitrate and nitrite nitrogen. However, it is assumed that there is little difference between total and dissolved nitrate and nitrite nitrogen. It is further assumed that nitrite concentrations are low to zero. Hence, future discussions will mention only nitrate.

Total nitrate as N was also plotted from Florida Department of Health (FDH)-sampled wells in Orange, Seminole, and Lake counties. FDH sampled domestic wells that are in the surficial and Floridan aquifers. For many wells, the total depth and casing depth were unknown. If a well was sampled more than once, the average concentration was plotted. The wells were sampled between 1994 and 2000. Over 3,000 wells were sampled. The total nitrate as N was plotted from all FDH wells to give an indication of the distribution of total nitrate in the Wekiva groundwater basin. Finally, 1973 and 1990 land use maps were compared to an Upper Floridan aquifer recharge map of the basin (Boniol et al. 1993) to identify potential sources for nitrate N.

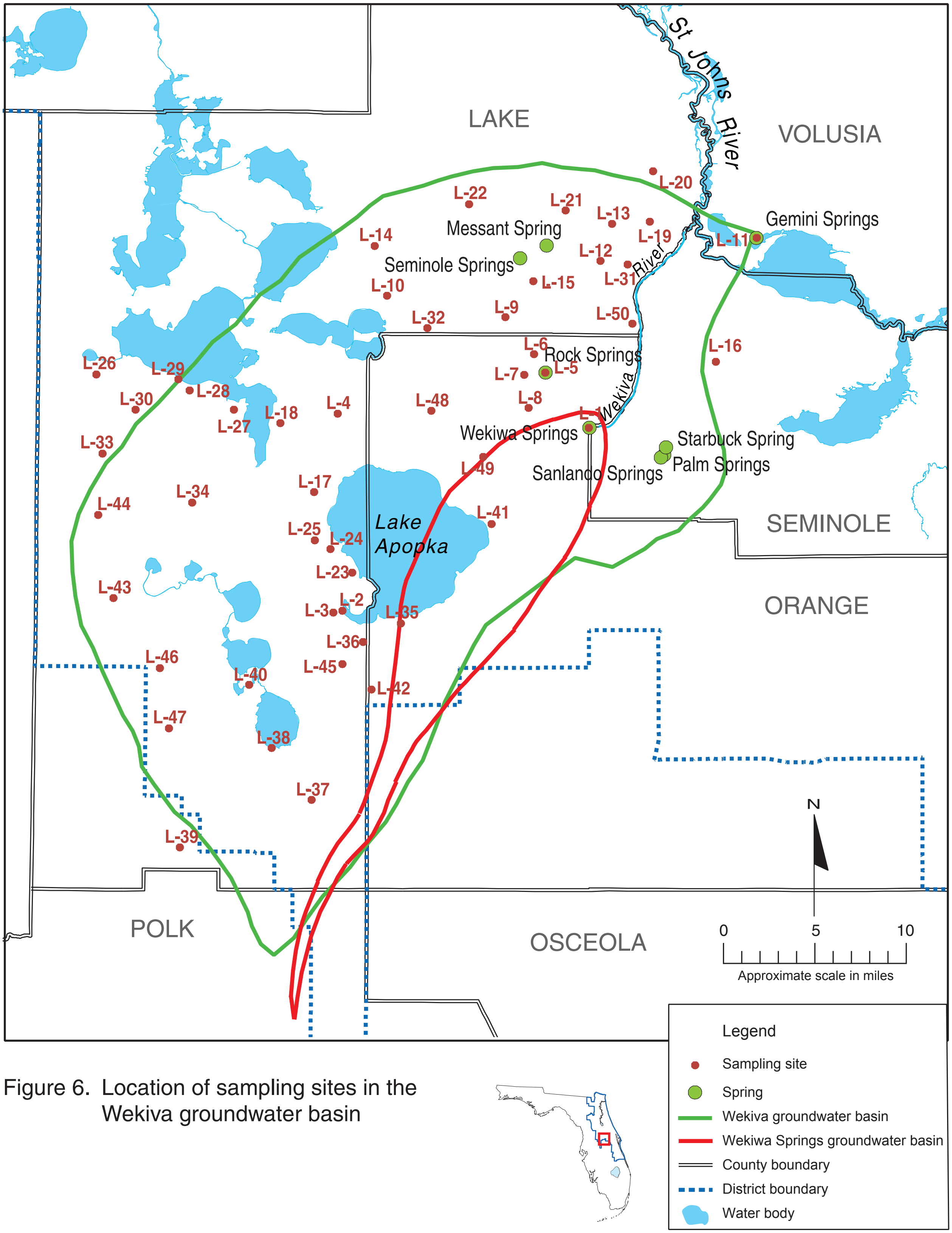


Figure 6. Location of sampling sites in the Wekiva groundwater basin

HYDROGEOLOGIC FRAMEWORK

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

Table 1. Hydrogeologic framework for the study area

<table>
<tr><th>Hydrogeologic Unit</th><th>Epoch</th><th>Stratigraphic Unit</th><th>General Lithology</th></tr>
<tr><td>Surficial aquifer system</td><td>Holocene
Pleistocene</td><td>Surficial sands and terrace deposits</td><td>Sand, clayey sand, and clay, with some shell locally</td></tr>
<tr><td rowspan="2">Intermediate aquifer system, or intermediate confining unit</td><td>Pliocene</td><td>Undifferentiated deposits</td><td>Sand, silt, clay, and shell</td></tr>
<tr><td>Miocene</td><td>Hawthorn Group</td><td>Phosphatic clay, silt, sand, dolostone, and limestones</td></tr>
<tr><td rowspan="4">Floridan aquifer system</td><td rowspan="3">Eocene</td><td>Ocala limestone</td><td>Limestones and dolomitic limestones</td></tr>
<tr><td>Avon Park Formation</td><td>Limestones and dolostone</td></tr>
<tr><td>Oldsmar Formation</td><td>Limestones and dolostone</td></tr>
<tr><td rowspan="2">Paleocene</td><td rowspan="2">Cedar Keys Formation</td><td rowspan="2">Dolostone, some limestone; anhydrite occurs in lower two-thirds of formation</td></tr>
<tr><td>Lower confining unit</td></tr>
</table>

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. Generally, the water table is 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. 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 the 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 7). The upper confining unit is absent over much of western Lake County, and its

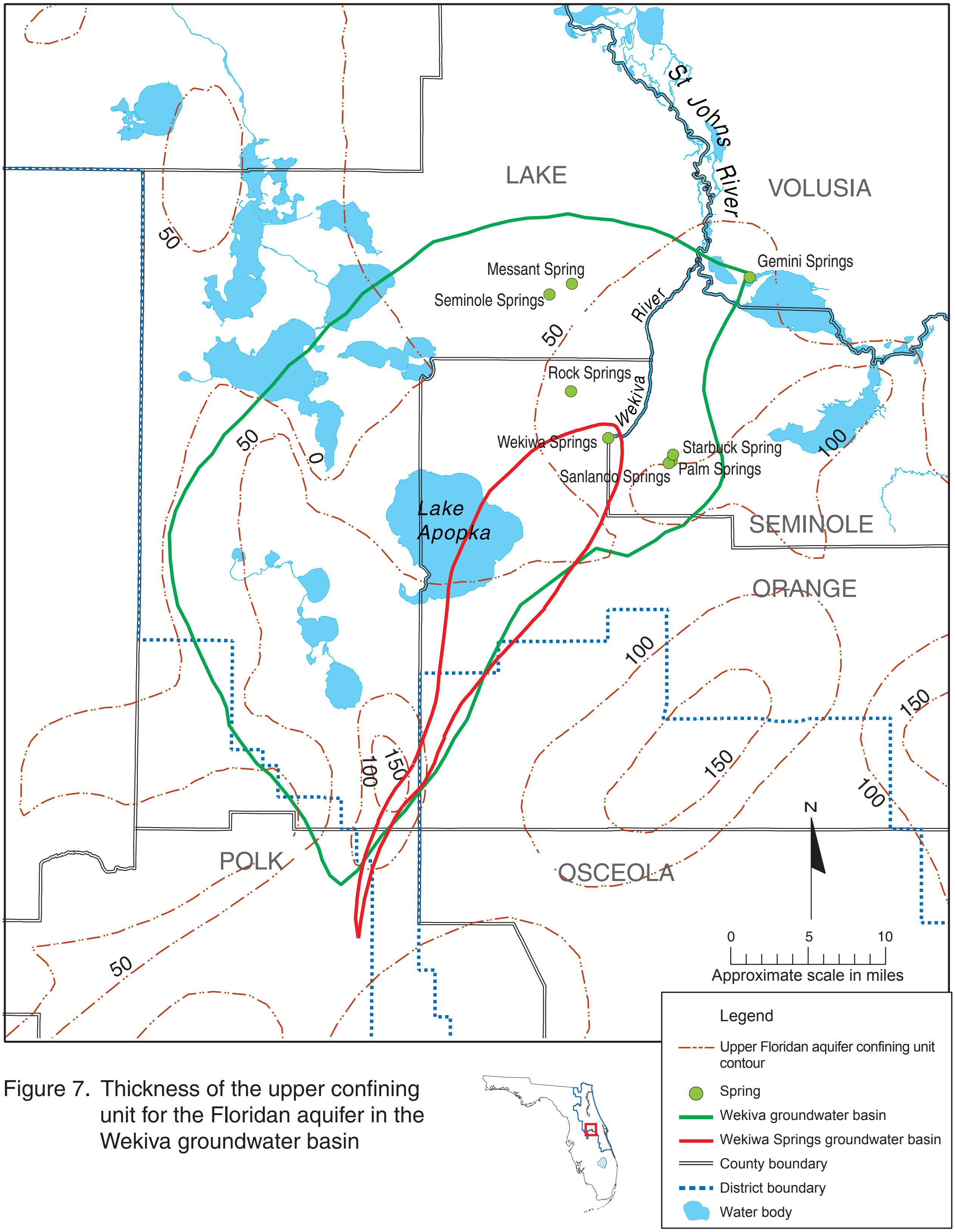


Figure 7. Thickness of the upper confining unit for the Floridan aquifer in the Wekiva groundwater basin

thickness is less than 50 feet near Lake Apopka and over much of the Wekiva groundwater basin. At Wekiwa Springs, the thickness of the upper confining unit is between 50 and 100 feet. No information is available on the thickness of Pliocene deposits or of clays within the upper confining unit.

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 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 Lake County, central Volusia County, western and northern Orange County, and western Seminole County. In those areas, the top is at, or slightly above, sea level.

The Floridan aquifer system is the principal source of fresh groundwater in the St. Johns River Water Management District (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 confined. This aquifer system is unconfined in western Lake County.

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 and northern Seminole 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. Near Orlando in Orange County, drainage wells are located in this aquifer. The city of Orlando and much of Orange County get their drinking water from the Lower Floridan aquifer. This paper only deals with the Upper Floridan aquifer.

High-rate (11–22 inches per year) recharge areas for the Upper Floridan aquifer generally occur in the center and western part of the Wekiva groundwater basin (Figure 8). High-rate recharge areas also occur near Wekiwa Springs in the Wekiwa Springs groundwater basin. The highest rate recharge areas in the Wekiwa Springs groundwater basin generally occur less than 5 miles from Wekiwa Springs. Some occur just to the south and southwest of Wekiwa Springs.

The potentiometric surface of the Upper Floridan aquifer ranged from less than 20 to greater than 120 ft msl in the study area for May 1995 (Figure 9). The potentiometric surface is the level to which water in the Floridan aquifer will rise in tightly cased wells in the aquifer. The level declines from the southwest to the northeast. At Wekiwa Springs, the level was about 25 ft msl in May 1995. Water flows at right angles to the potentiometric contours from areas of higher head to areas of lower head. Most water at Wekiwa Springs flows from the southwest.

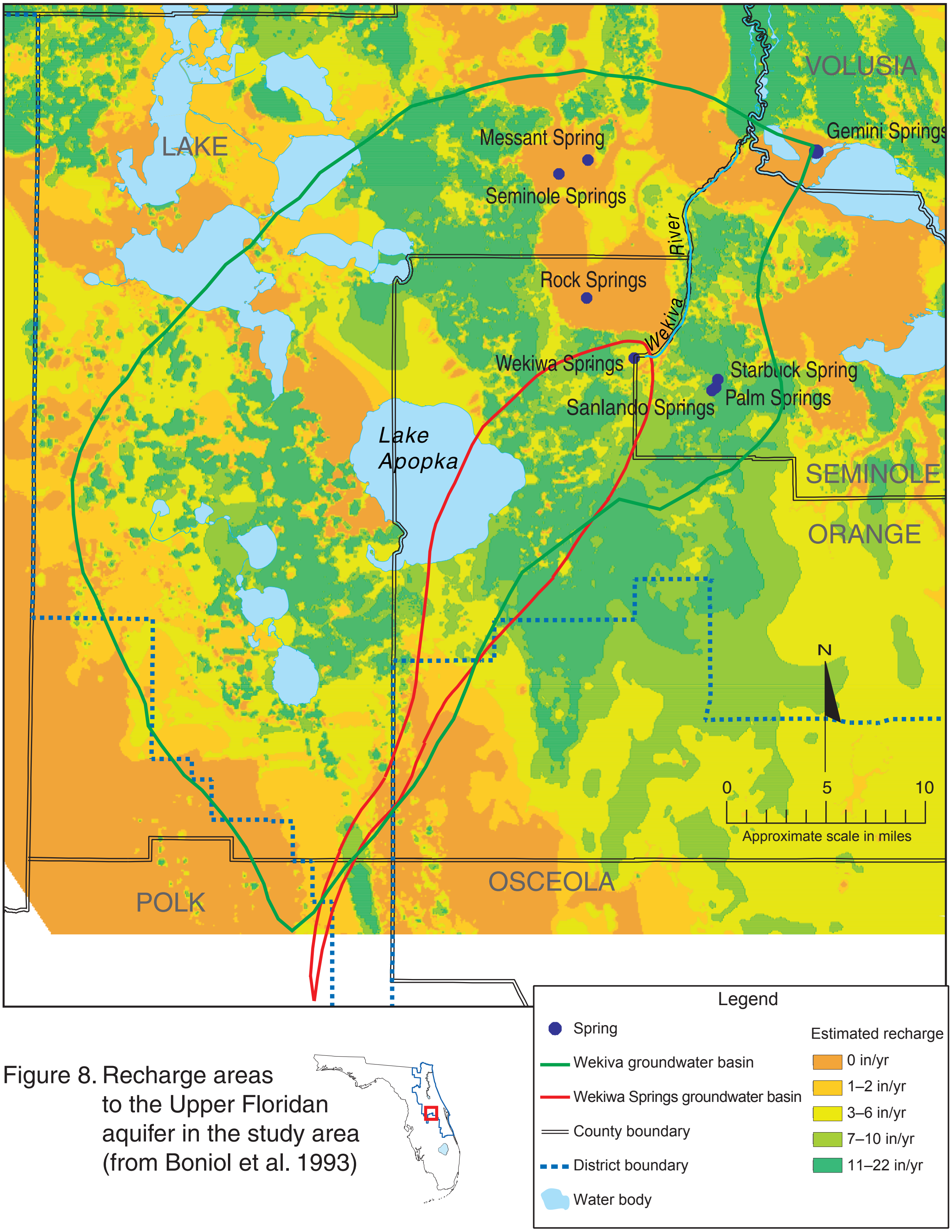


Figure 8. Recharge areas to the Upper Floridan aquifer in the study area (from Boniol et al. 1993)

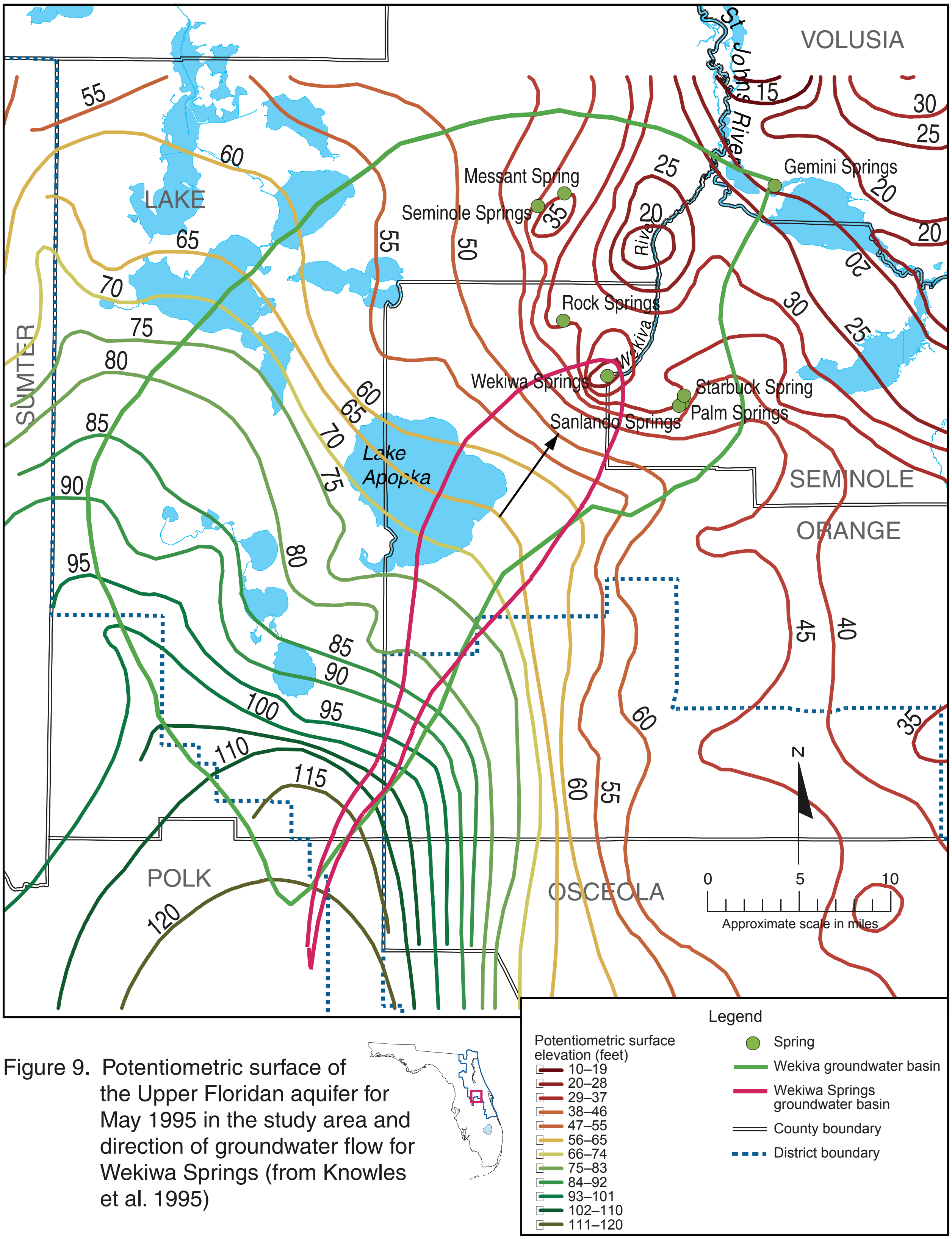


Figure 9. Potentiometric surface of the Upper Floridan aquifer for May 1995 in the study area and direction of groundwater flow for Wekiwa Springs (from Knowles et al. 1995)

WATER QUALITY

The water quality parameters analyzed for in this study are total and dissolved nitrate nitrogen and total organic and ammonia nitrogen. Total nitrate as N was also plotted from FDH-sampled wells.

NITRATE NITROGEN

Nitrate N concentrations are variable throughout the Wekiva groundwater basin. Concentrations are highest west and southwest of Lake Apopka, where concentrations above 5 mg/L occur (Figure 10). The highest concentration measured was 7.5 mg/L (at L-25, see Figure 6; Appendix A). Twenty-two samples had concentrations above the "elevated" concentration of 0.2 mg/L. This concentration was the maximum measured nitrate N concentration for five springs in the Ocala National Forest. Nitrate N concentrations for springs in the Ocala National Forest are assumed to not be affected by man. A sampled well near Wekiwa Springs was above 0.2 mg/L. The concentration of nitrate N at Wekiwa Springs was 1.3 mg/L (Appendix A).

The concentration of dissolved nitrate N in Wekiwa Springs has varied with time (Figure 11). It was 0.61 mg/L in 1961, peaked at 2.00 mg/L in 1995, and was 1.30 mg/L in August 1999. Using a discharge of 65.39 cubic feet per second measured on July 14, 1999, and a concentration of 1.30 mg/L, Wekiwa Springs discharged 458 pounds of nitrogen per day, or 84 tons of nitrogen per year in 1999. This concentration is diluted as it flows down the Wekiva River and enters the St. Johns River. Median nitrate N concentrations for six samples from a station in the Wekiva River near Sanford and a station in the St. Johns River near DeLand are 0.44 and 0.04 mg/L, respectively.

Nitrate N concentrations in Wekiwa Springs do not appear to be related to either discharge or monthly rainfall (Figure 11). Discharge measurements generally were made on the same day the spring was sampled for nitrate. Since 1995, nitrate N has generally declined. Discharge peaked in 1994 and was low in 1998, but was generally high between 1995 and 1999. However, both nitrate N and discharge decline for the last three measurements, which corresponds to the time period November 1999 to March 2000. Monthly rainfall was also low during that period. Yearly rainfall was significantly below average in 1998. Yearly rainfall was 45.18 inches in

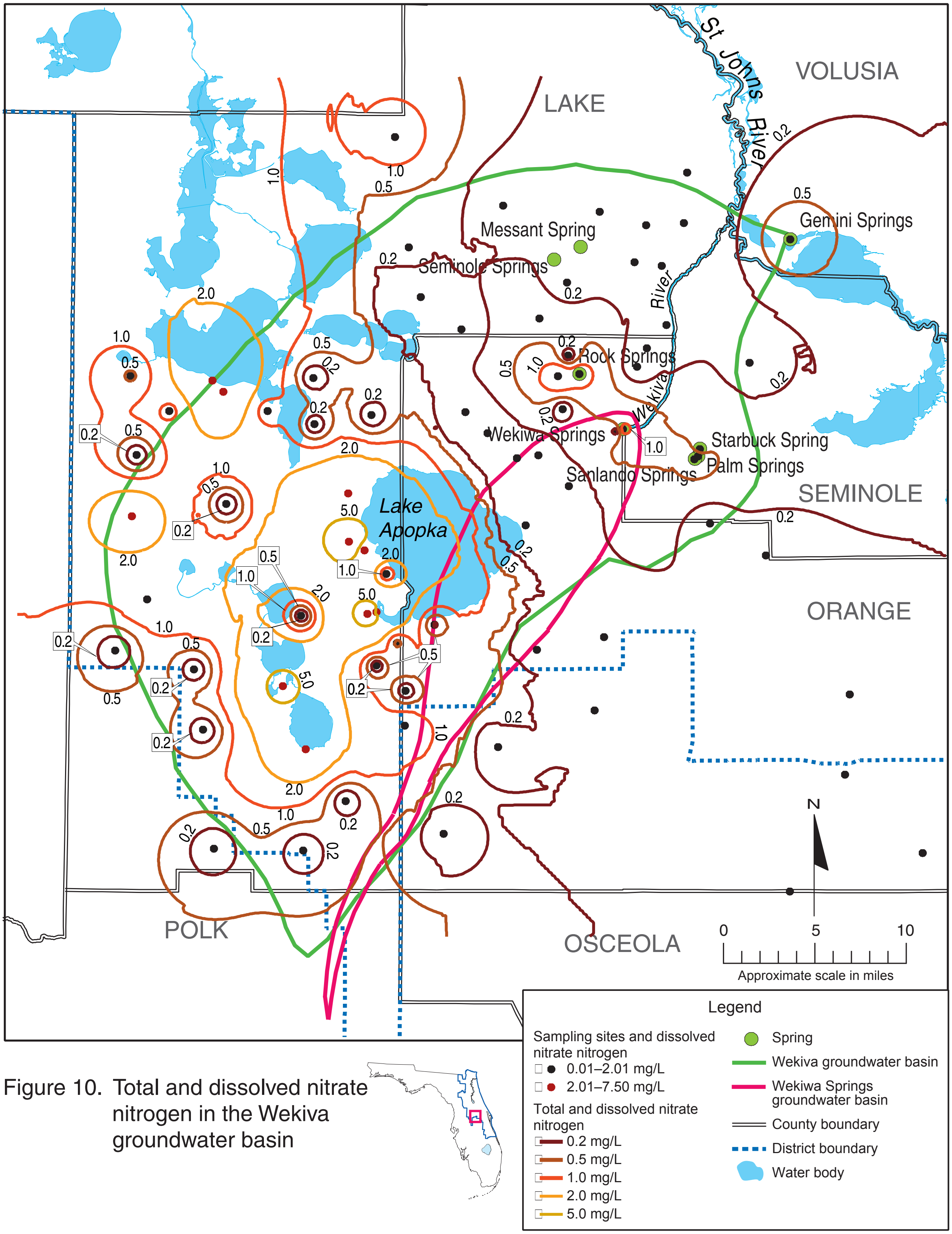


Figure 10. Total and dissolved nitrate nitrogen in the Wekiva groundwater basin

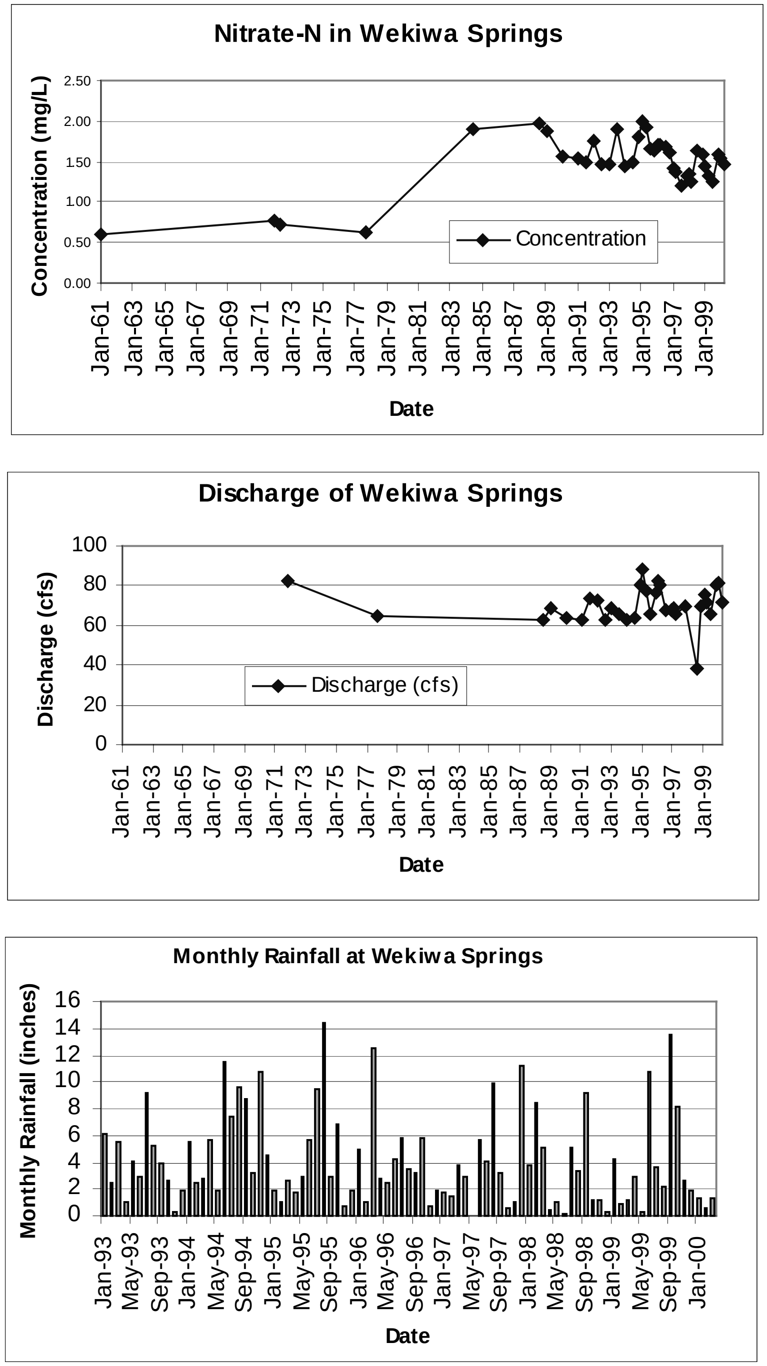


Figure 11. (A) variation in the concentration of dissolved nitrate nitrogen in Wekiwa Springs, with time; (B) variation in the discharge of Wekiwa Springs, with time; (C) monthly rainfall at Wekiwa Springs

1993, 74.17 inches in 1994, 52.20 inches in 1995, 49.15 inches in 1996, 45.69 inches in 1997, 38.96 inches in 1998, and 52.25 inches in 1999.

Total nitrate as N from FDH wells is also variable throughout the basin (Figure 12). Concentration ranges of total nitrate N as high as 10–30 mg/L occur. These are generally located to the south and west of Lake Apopka. Concentrations near Wekiwa Springs fall in the range between 0.2 and 2 mg/L.

ORGANIC AND AMMONIA NITROGEN

Besides nitrate N, nitrogen can also be present in organic and ammonia nitrogen. In oxygenated waters, nitrogen is present as nitrate. In reducing waters, nitrogen is present as nitrite and ammonia.

Concentrations of total organic and ammonia nitrogen are generally below 0.2 mg/L throughout the basin (Figure 13). Concentrations are above 0.8 mg/L to the southeast of Wekiwa Springs. The low concentrations of organic and ammonia nitrogen suggest that most of the nitrogen is present as nitrate.

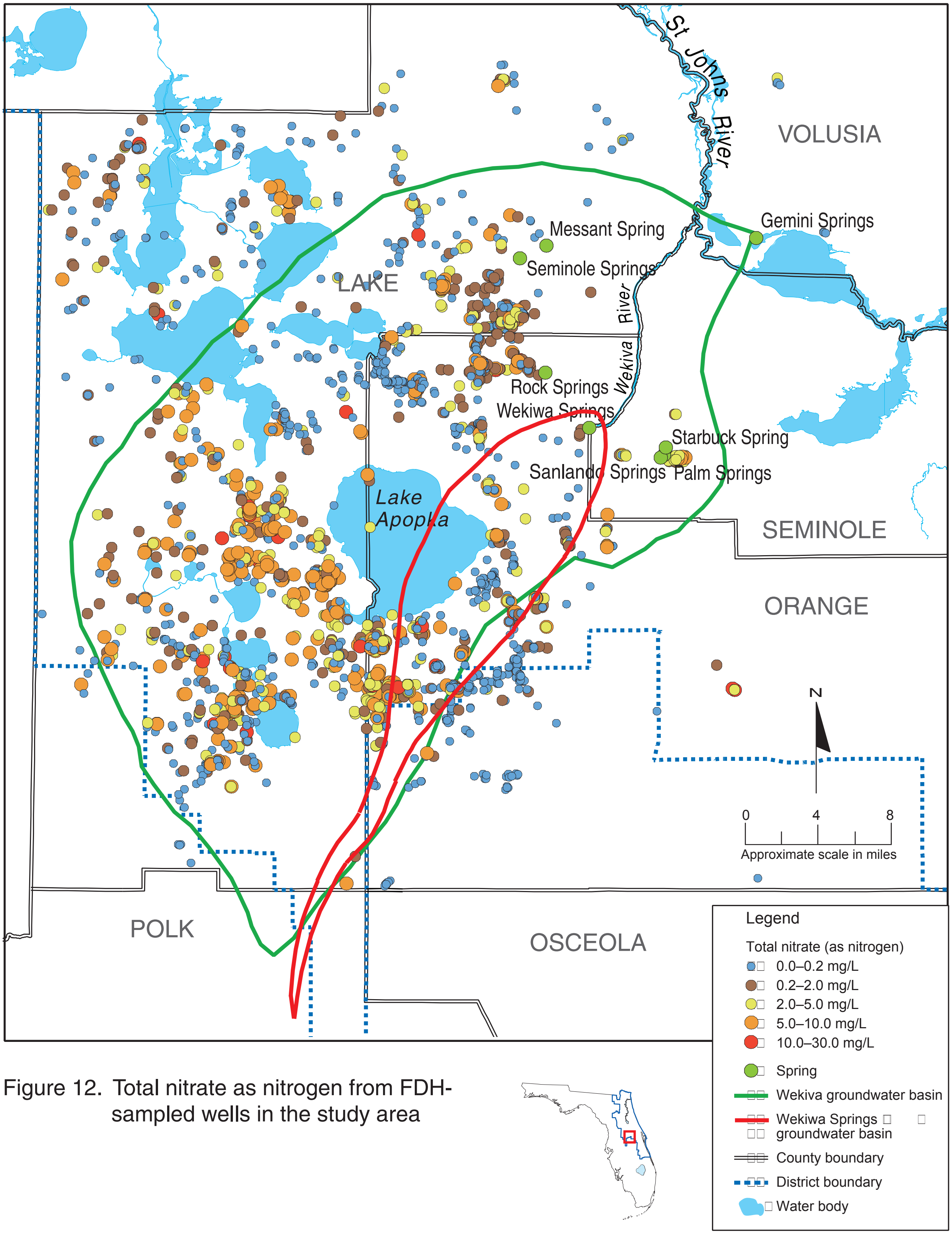


Figure 12. Total nitrate as nitrogen from FDH-sampled wells in the study area

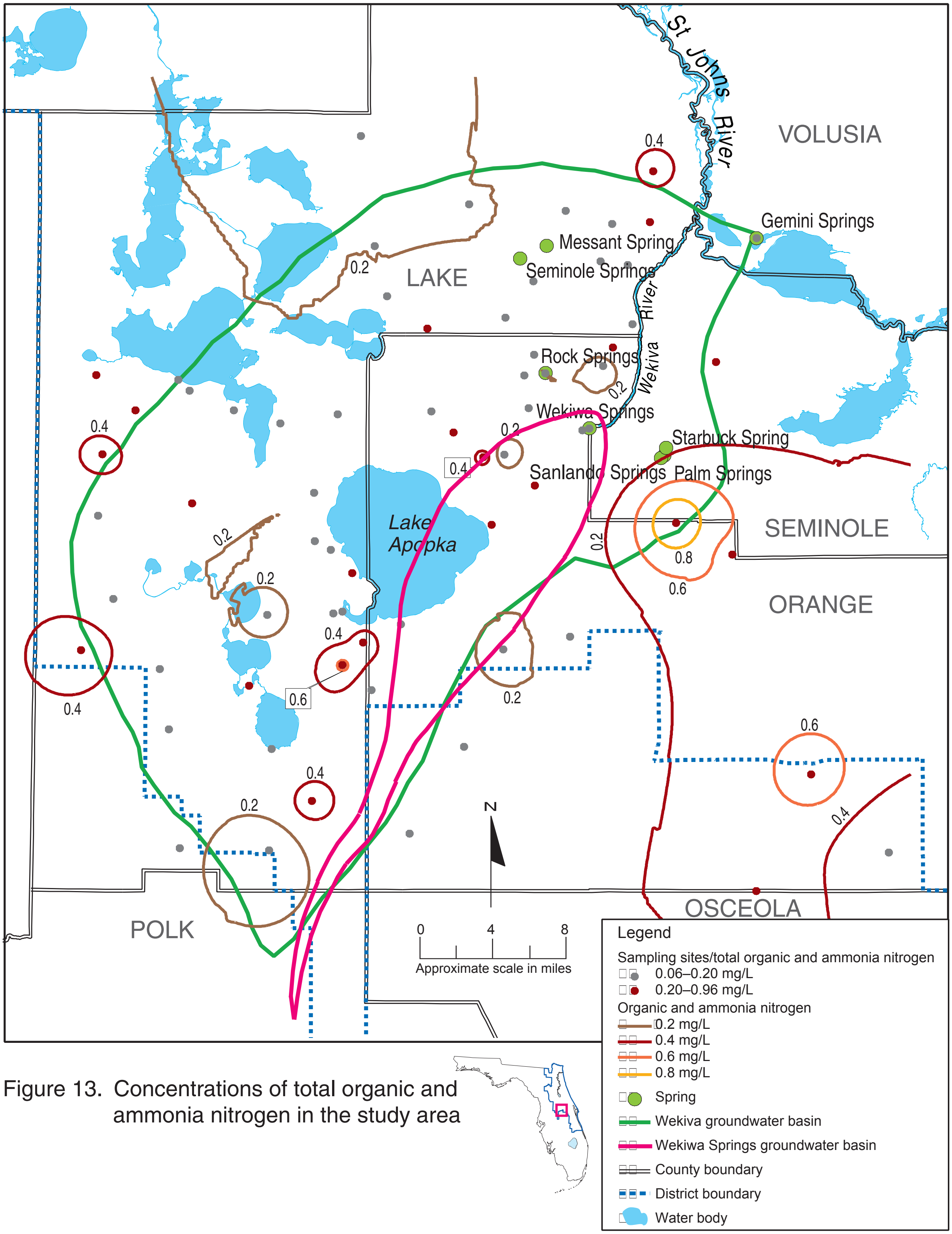


Figure 13. Concentrations of total organic and ammonia nitrogen in the study area

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, age of water recharge, and water-rock interactions. Stable isotopes monitored in this study are ^{2}H, ^{3}He, ^{4}He, Ne, ^{15}N, and ^{18}O. Radioactive isotopes are generally used for age-dating water because these isotopes decay over a period of time at a known rate. The radioactive isotope monitored in this study is ^{3}H.

STABLE ISOTOPES

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, Gonfiantini 1981):

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

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., $^{2}H/^{1}H$, $^{15}N/^{14}N$, $^{18}O/^{16}O$)

$R_{standard}$ = ratio of isotope *x* in the standard (e.g., $^{2}H/^{1}H$, $^{15}N/^{14}N$, $^{18}O/^{16}O$)

A water sample that had been analyzed for oxygen isotopes, for example, might have a $\delta^{18}O$ value of +2‰. The positive delta 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 delta 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, δ^2H and δ^{18}O of VSMOW are both assigned a value of 0‰. Nitrogen in air is well mixed and is the nitrogen isotope standard. Its value is 0‰. The precision attainable in contract laboratories of USGS for sample preparation and analysis of stable isotope samples is 2% for ^{4}He; 1% for ^{3}He / ^{4}He; 4% for Ne (L.N. Plummer, USGS, pers. com. 1996); 2% for δ^2H; and 0.2% for δ^{15}N and δ^{18}O (T.B. Coplen, USGS, pers. com. 1993).

Deuterium and Oxygen-18

Deuterium and ^{18}O are stable isotopes of hydrogen and oxygen. Because 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 δ^2H and δ^{18}O changes.

The global meteoric water (GMW) line represents the relationship between δ^2H and δ^{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 the GMW line, the water originated from rainwater.

Evaporation, evapotranspiration, geothermal reactions, and low-temperature silicate hydrolysis produce different δ^2H and δ^{18}O relationships compared with the GMW line. Evaporation from surface water bodies, such as lakes, is a non-equilibrium process that enriches ^{2}H and ^{18}O in the remaining water. Evaporation causes the plot of δ^2H versus $\delta^{18}O$ to diverge from the GMW line. The slope of the resulting evaporation line generally ranges from 3 to 6, compared to a slope of 8 for the GMW line (Coplen 1993). Because of the difference in mass between water containing ^2H and ^{18}O and water not containing these isotopes, evapotranspiration preferentially transfers water containing the light isotopes ^1H and ^{16}O into the atmosphere, thus enriching the remaining water in the heavier ^2H and ^{18}O. The enrichment of groundwater in ^2H and ^{18}O because of evapotranspiration is assumed to be similar to that of evaporation. Of the above processes, evaporation and evapotranspiration are most likely the only major processes that have affected the δ^2H and $\delta^{18}O$ relationship in groundwater samples in the study area.

The relationship between the eleven samples of delta deuterium and delta oxygen-18 collected in this study do not plot along the GMW line (Figure 14). However, many samples, including that from Wekiwa Springs (Toth 1999), falls on a local meteoric water line. The local meteoric water line has a slope of 8 but a different intercept than the GMW line. The line signifies that the samples originate from local rainfall. Several samples fall on an evaporation trend line ($\delta^2H = 4.51\ \delta^{18}O - 0.41$), as defined by Sacks et al. (1998) for ten lakes in ridge areas of Polk and Highlands counties. This suggests that the Floridan aquifer in the study area is being recharged by evaporated water. The most likely sources for the evaporated water are Lake Apopka, karst lakes, and solution features in the study area. The sample in the lower left-hand corner to the left of the GMW line in Figure 14 is anomalous. It was collected from a Floridan aquifer well (L-38) in Lake Louisa State Park. Well L-38 is located next to a sinkhole lake.

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, $\delta^{15}N$ was used to identify possible sources of nitrate contamination.

The $\delta^{15}N$ values for soil organic nitrogen generally range between +3‰ and +9‰ (Heaton 1986). However, the soils in the study area are assumed to have low concentrations of soil organic nitrogen. The $\delta^{15}N$ value of

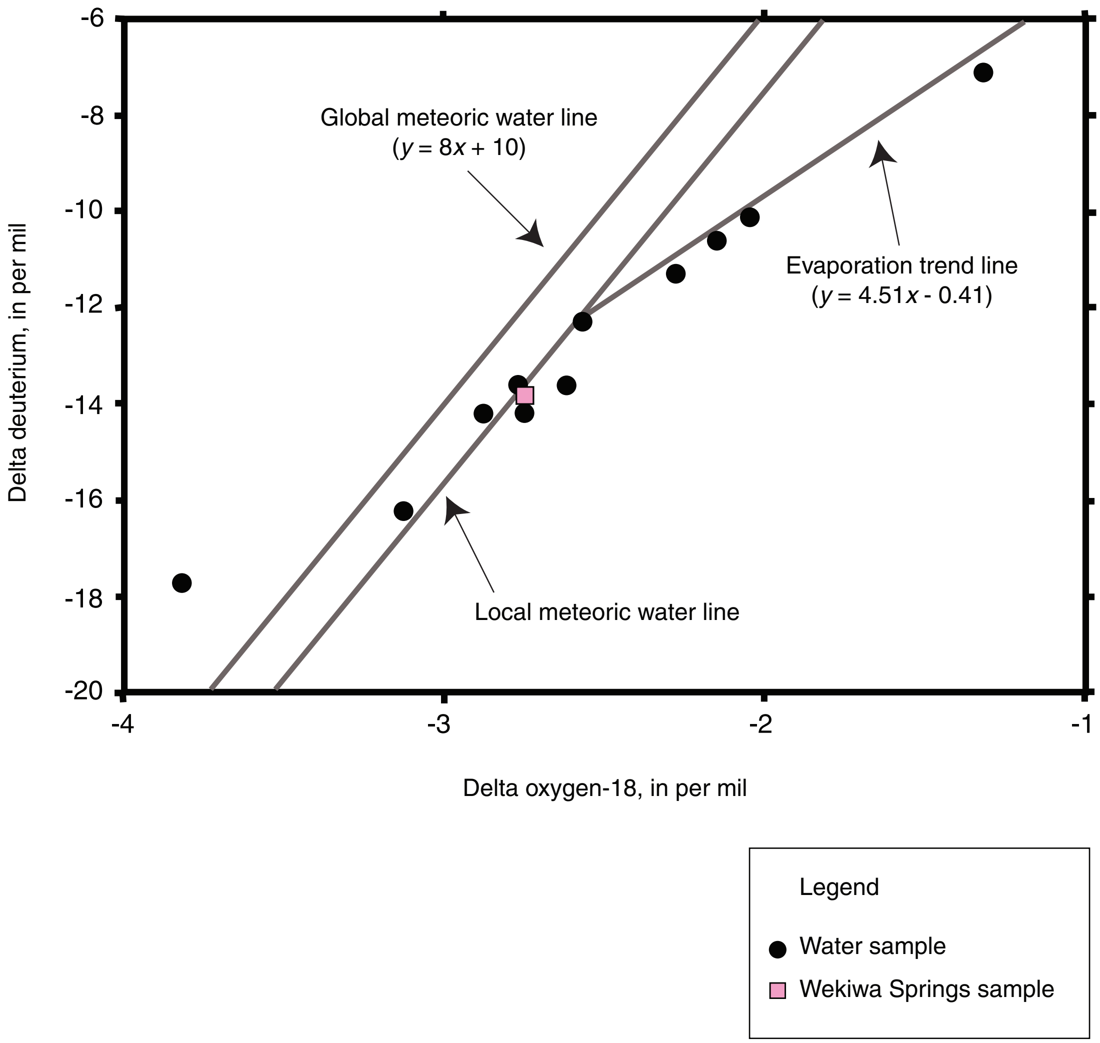


Figure 14. Relationship between delta deuterium and delta oxygen-18 for samples collected in this study

nitrate in synthetic 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 is generally above +10‰. The $\delta^{15}N$ value of the ammonium ion (NH_4^+) has a range similar to nitrate for fertilizers, animal waste, and sewage.

In this study, the $\delta^{15}N$ value was determined for nine nitrate samples and two ammonium samples (L-16 and L-33) (Table 2). Nitrate N was insufficient in the two ammonium samples to measure $\delta^{15}N$. The 11 $\delta^{15}N$ values determined in this study ranged from 3.0‰ to 11.2‰, with eight of the values falling below 5.3‰ (Figure 15). Only three samples had $\delta^{15}N$ values above +8‰. The $\delta^{15}N$ values suggest that most of the nitrates in the study area are due to synthetic fertilizers.

Table 2. Total dissolved nitrate nitrogen, delta nitrogen-15, and tritium/helium-3 age for samples collected in this study

Sampling Site ID	Station Name	Total Dissolved Nitrate Nitrogen	Delta Nitrogen-15	Tritium/ Helium-3 Age
L-2	Apopka Spring	4.9	3.9	24.5
L-40	Country Garden nursery	6.1	4.8	23.4
L-14	City of Eustis water plant	0.26	10.9	24.7
L-11	Gemini Springs	0.8	5.3	18.6
L-33	Groveland Tower	0.02	5.2 (NH_4)	32.4
L-27	Town of Howey-in-the-Hills	0.71	8.6	26.2
L-38	Lake Louisa State Park	3.8	3.6	29.6
L-16	Lake Mary	0.02	3.0 (NH_4)	27.4
L-43	City of Mascotte	1.4	11.2	28.7
L-44	Sunset Lakes Ski Center	3.3	4.4	29.9
L-3	Turnpike, site 38	6.7	4.1	27.5

Note: NH_4 = ammonium

The $\delta^{15}N$ value for Wekiwa Springs is +8.6‰ (Toth 1999). This suggests that the nitrates in Wekiwa Springs are a mixture of those from septic tanks and those from synthetic fertilizers applied to lawns. The data suggest that the areas of highest nitrate N concentrations do not contribute to the nitrate N discharging from Wekiwa Springs. However,

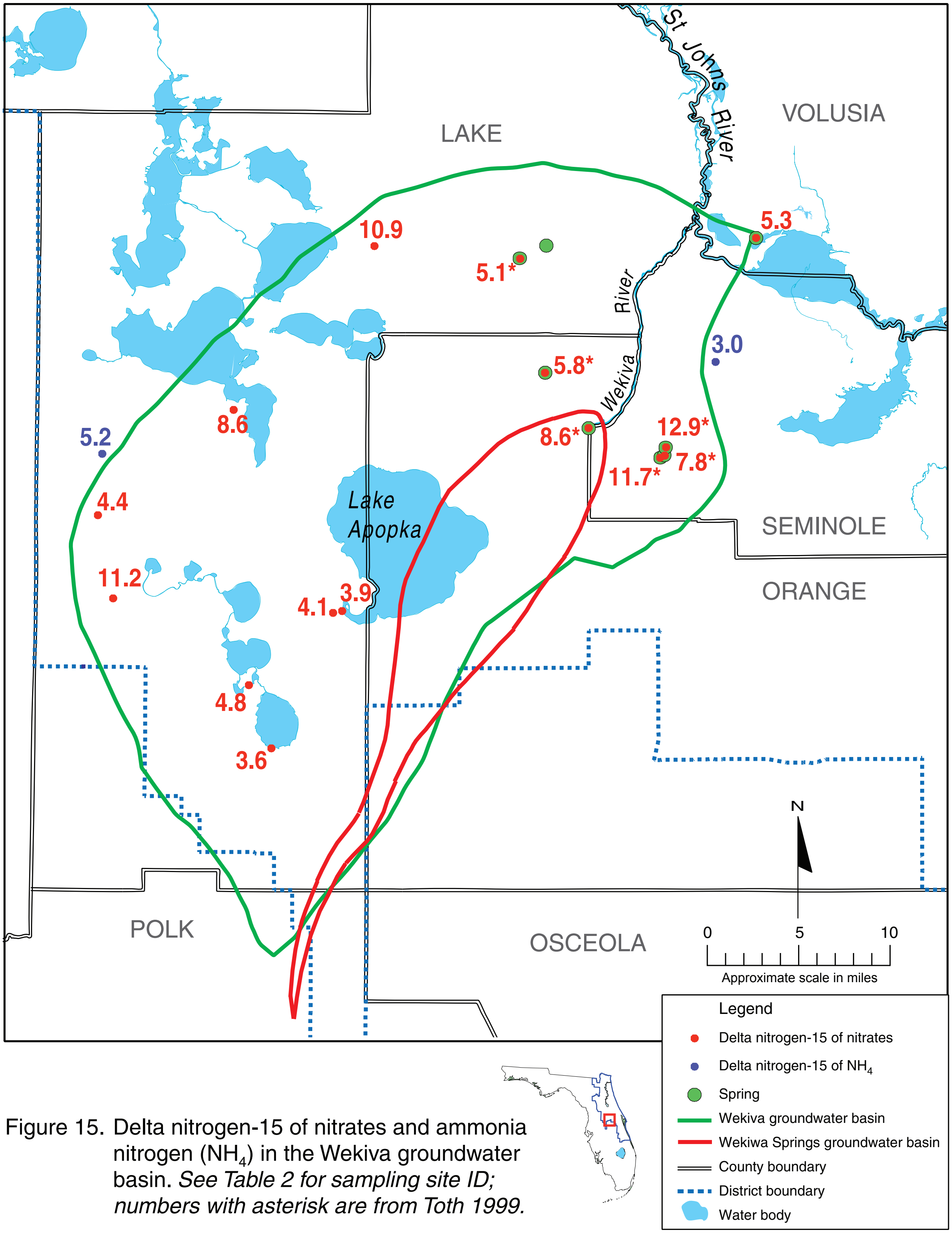


Figure 15. Delta nitrogen-15 of nitrates and ammonia nitrogen (NH_4) in the Wekiva groundwater basin. *See Table 2 for sampling site ID; numbers with asterisk are from Toth 1999.*

the more locally developed flow of the Upper Floridan aquifer in the vicinity of the spring results in a more direct influence and source of the nitrate N contamination displayed at the spring.

However, the nitrates at the city of Eustis water plant (L-14) and the city of Mascotte (L-43) are probably due to animal waste and / or sewage because their $\delta^{15}N$ values are above 10‰. The nitrates for the town of Howey in the Hills (L-27) are probably due to a mixture resulting from synthetic fertilizers and animal waste and / or sewage because their $\delta^{15}N$ value is 8.6‰. The most likely source for sewage is septic tanks.

Helium-3, Helium-4, and Neon

Concentrations of ^{3}He, ^{3}H, and ^{4}He can be used to determine an age for a water sample (Appendix B). Helium-3 is a radiogenic isotope of helium (He). It is produced by the radioactive decay of tritium (^{3}H or T). 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 mainly to atmospheric sources—that is, ^{3}He concentrations arising from equilibration with air during recharge and entrainment of air bubbles. Both helium and neon are noble gases. 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 such cases, the measured neon content can be used to calculate the additional sources of He (Schlosser et al. 1989). In this study, most of the ^{3}He has a tritogenic origin.

RADIOACTIVE ISOTOPES

The radioactive isotope measured in this study was tritium (^{3}H). Tritium decays to helium-3. The error in the tritium analysis is listed in Appendix B.

Half-life is a fundamental property of radioactive isotopes. Half-life is a measure of decay rate (the time for a concentration of the isotope to decrease by one-half) and is unique for each radioactive isotope. The half-life for tritium is 12.43 years (Coplen 1993). 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 isotope ^3H and the stable isotopes ^3He, ^4He, and Ne. Groundwater generally contains a mixture of waters of different age (Toth 1999). The tritium / helium-3 age of groundwater is the age of the young fraction. Tritium, helium-3, helium-4, and neon can generally identify water that is less than 30 years old (L.N. Plummer, USGS, pers. com. 1996). Carbon-14 can be used to determine the age of the old fraction of groundwater. Carbon-14 can be used to identify water that is less than 50,000 years old (Coplen 1993). Most of the tritium / helium-3 ages of groundwater in this study are less than 30 years.

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 ^3H enters groundwater by way of rainfall at a concentration of approximately 3 to 5 tritium units (TU; 1 TU = 3.2 picocuries / liter). With the onset of atmospheric nuclear testing in 1953, the ^3H concentration in rainfall began to increase. At Ocala, Florida, the ^3H concentration in rainfall increased to as high as 700 TU in 1963 (Katz et al. 1995). In 1988, the ^3H concentration in rain at Ocala was not measurably different from the estimated pre-1953 concentration (Katz et al. 1995). Because of the difference in ^3H concentration in rainwater before and immediately after 1953 (i.e., before 1953 and after 1988), ^3H has been used as a hydrologic tracer to date recent groundwater (Coplen 1988). The half-life of ^3H is 12.43 years, which means that the ^3H concentration decreases by one-half every 12.43 years.

In this study, tritium concentrations ranged from 1.92 TU to 4.65 TU (Appendix B). For comparison, the tritium concentration in Wekiwa Springs was 3.0 TU in 1995 (Toth 1999). Since tritium was present in all samples, all samples contain some fraction of water that is less than 46 years old (1953 to 1999).

AGE

Groundwater generally contains a mixture of waters of different age (Toth 1999). The tritium / helium-3 age of groundwater is the age of the young fraction. Tritium / helium-3 age can generally identify water that is less than 30 years old. The carbon-14 age of groundwater likely represents the age of the old fraction and can generally identify water that is less than 50,000 years old. In Toth 1999, the carbon-14 age of groundwater ranged between 728 and 10,500 years old. Carbon-14 was not measured in this study.

TRITIUM/HELIUM-3 AGE

The tritium / helium-3 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. However, $^{3}H / ^{3}He$ can be affected by dispersion processes. No attempt was made to correct for dispersion in this study.

The $^{3}H / ^{3}He$ age of water samples collected in the Wekiva groundwater basin ranged from 18.6 years at Gemini Springs (L-11) to 32.4 years at the Groveland Tower (L-33) (Figure 16 and Table 2; Appendix B). The median age was 27.4 years. For comparison, the $^{3}H / ^{3}He$ age of Wekiwa Springs was 17.1 years (Toth 1999). This age suggests that all samples in the study area contain some fraction of young water and that the age is less than 32 years old.

The youngest age occurs at Wekiwa Springs. This suggests that a significant fraction of spring water is coming from nearby sources. High-rate recharge areas occur just to the south of the spring (see Figure 8) and are the most likely source of the water discharging from the spring. This conclusion is consistent with a local meteoric origin for the waters discharging from Wekiwa Springs.

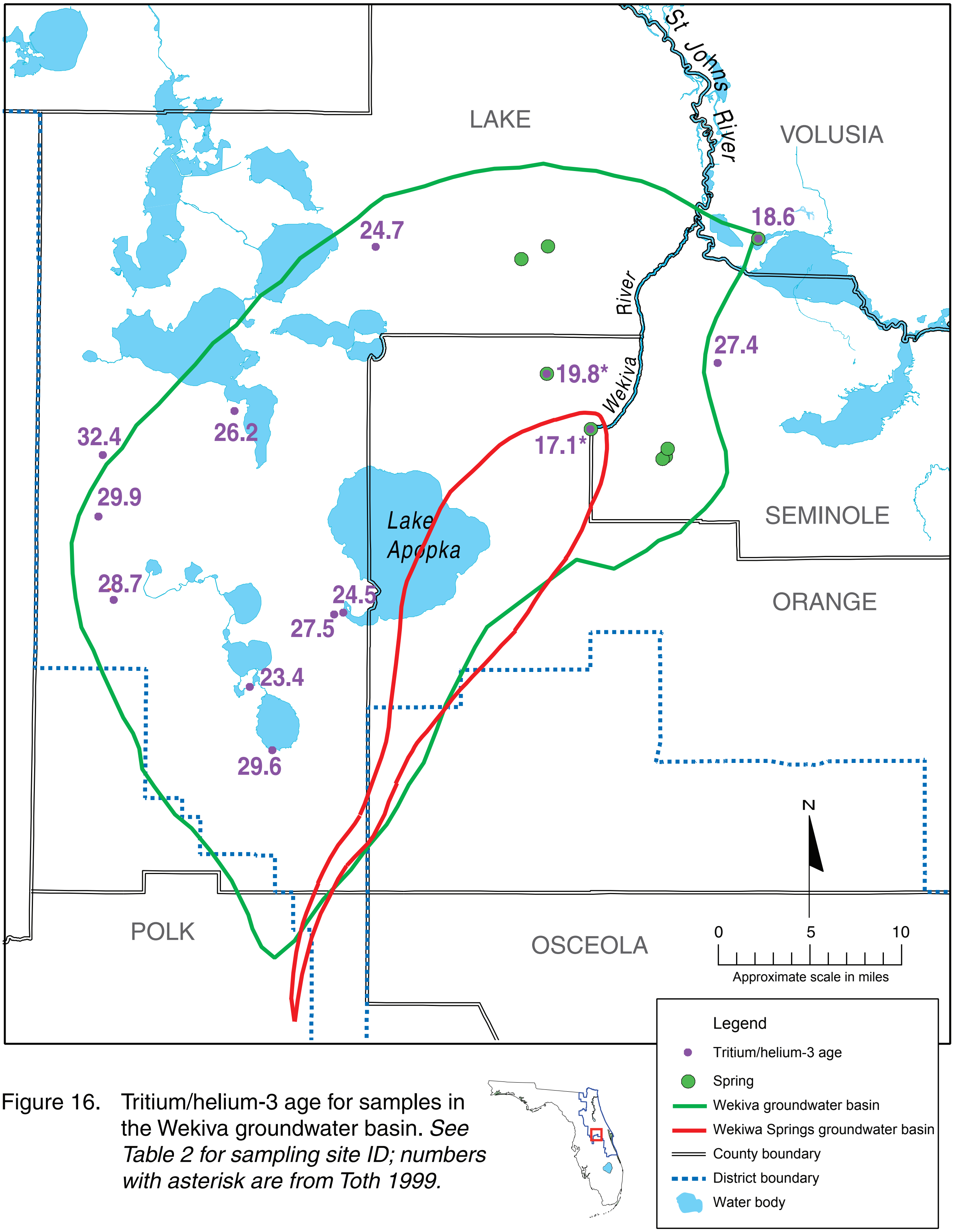


Figure 16. Tritium/helium-3 age for samples in the Wekiva groundwater basin. *See Table 2 for sampling site ID; numbers with asterisk are from Toth 1999.*

LAND USE

Because the median age of the wells sampled for tritium/helium-3 age dating was 27.4 years, the total nitrate N contours were superimposed on a map of 1973 land use (Figure 17). The three areas where total nitrate N is above 5 mg/L coincide with cropland land use and occur south and west of Lake Apopka. Lower nitrate N values also correspond to cropland areas. Hence, not all cropland areas have high nitrate N values.

This land use probably corresponds to citrus cultivation. Hence, the high nitrate N in groundwater is probably a result of citrus fertilization (prior to 1973). Citrus acreage in Lake and Orange counties peaked in 1968 (Figure 18). Acreage dropped significantly after 1984, a year of a severe freeze. No data are available for 1984.

The land use category in 1973 near Wekiwa Springs was pasture and urban. By 1990, most of the land use category south of Wekiwa Springs was urban and residential (Figure 19). In fact, urban areas in the Wekiwa Springs groundwater basin increased from 9.3% to 21.1% between 1973 and 1990. During this period, nitrate N increased in Wekiwa Springs. This indicates that the sources of the nitrates in Wekiwa Springs are likely a mixture of leachate from septic tanks and recharge from fertilized lawns. The urban areas are also high-rate recharge areas for the Upper Floridan aquifer (compare Figures 19 and 8), which suggests that young water is a substantial fraction of the mixture.

Because the $\delta^{15}N$ content of Wekiwa Springs suggests that the nitrates are mostly mixtures from animal waste and/or sewage and lawn fertilizers, the location of sewage treatment plants was examined. The nearest sewage treatment plant to Wekiwa Springs is in Seminole County (Figure 20). It was built in 1973, and may be responsible for the decline in nitrates at Wekiwa Springs. As urban areas continued to expand in close proximity to the spring, these developments have been brought on-line to the wastewater treatment facilities. This action and the more localized sources of recharge to the spring could account for the lower concentrations of nitrate and younger age of the water at the spring.

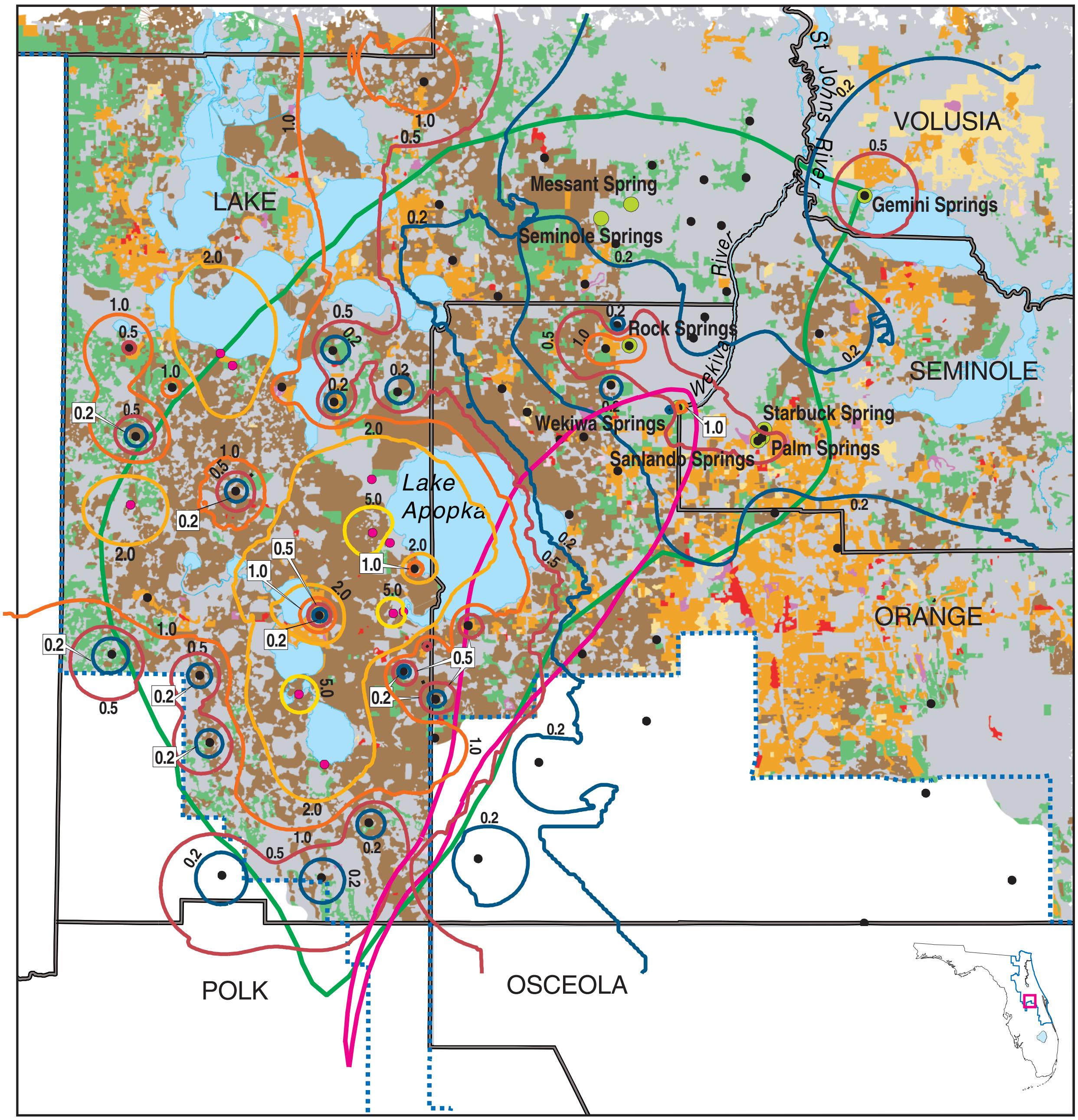


Figure 17. Relationship between total and dissolved nitrate nitrogen and 1973 land use in the study area

Legend

Sampling sites/total and dissolved nitrate nitrogen
- 0.01–2.0 mg/L
- 2.01–7.5 mg/L
- Spring
- Wekiva groundwater basin
- Wekiwa Springs groundwater basin
- 0.2 mg/L nitrogen
- 0.5 mg/L nitrogen
- 1.0 mg/L nitrogen
- 2.0 mg/L nitrogen
- 5.0 mg/L nitrogen
- County boundary
- District boundary
- Water body

Land use
- Open land
- Recreation
- Residential
- Industrial/mining
- Nurseries
- Cropland
- Pasture
- Other

N

0 4 8
Approximate scale in miles

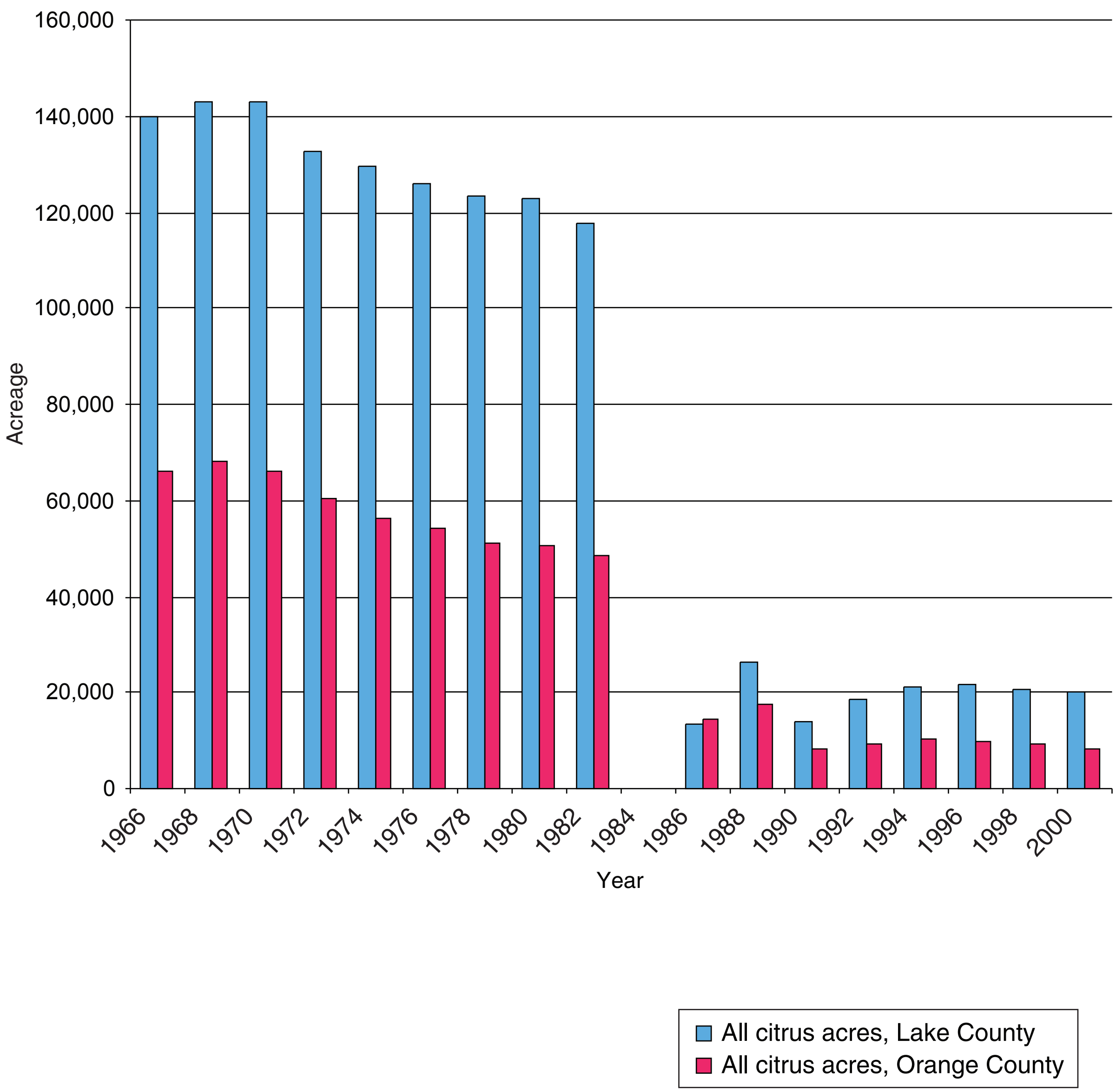


Figure 18. Citrus acreage by year for Lake and Orange counties (R. Johnson, Florida Agricultural Statistics Service, pers. comm., July 11, 2001)

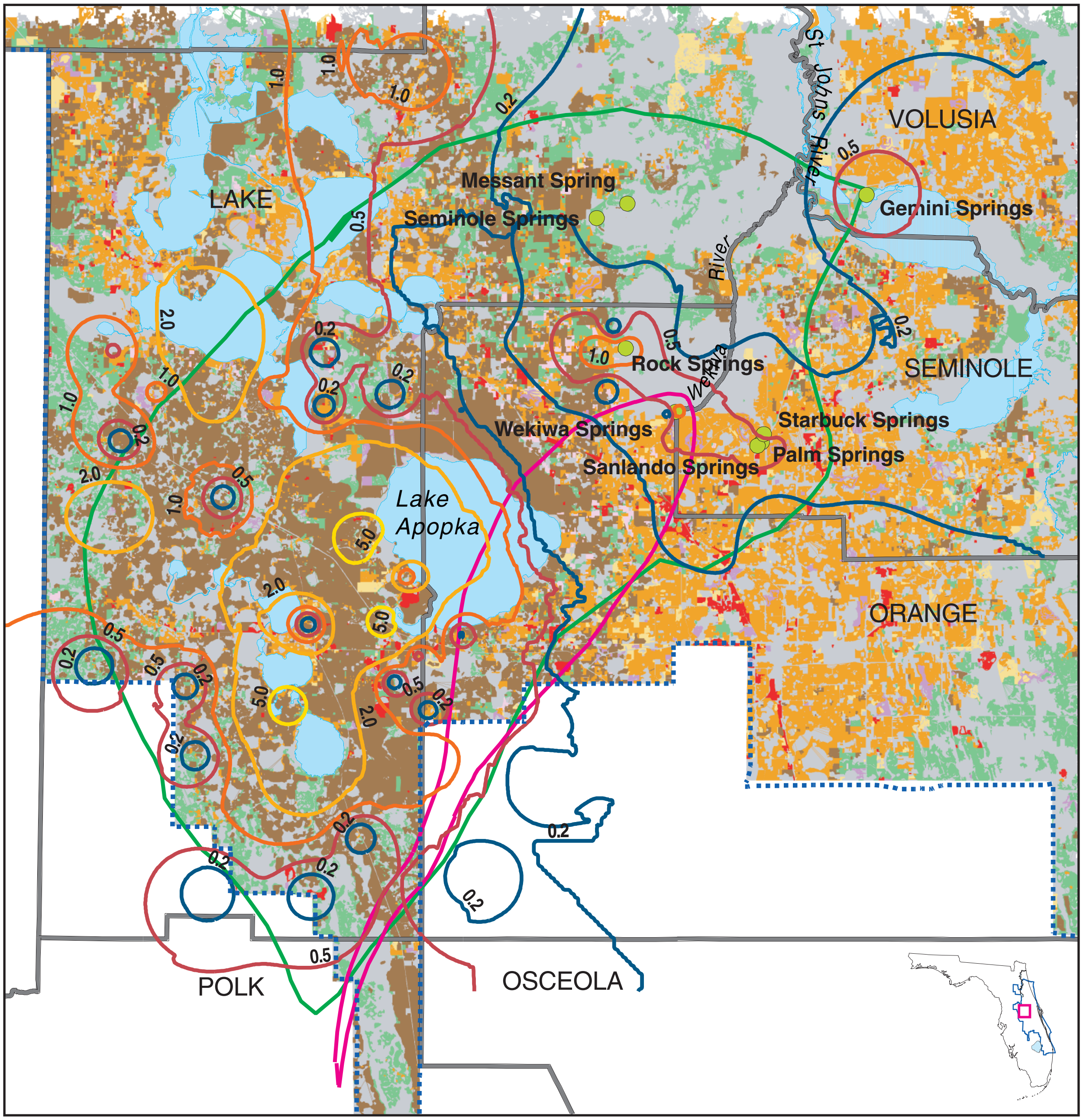


Figure 19. Relationship between total and dissolved nitrate nitrogen and 1990 land use in the study area

Legend

- Spring
- Wekiva groundwater basin
- Wekiwa Springs groundwater basin
- County boundary
- District boundary
- Water body
- 0.2 mg/L nitrogen
- 0.5 mg/L nitrogen
- 1.0 mg/L nitrogen
- 2.0 mg/L nitrogen
- 5.0 mg/L nitrogen

Land use

- Open land
- Recreation
- Residential
- Industrial/mining
- Nurseries
- Cropland
- Pasture
- Other

N

0 4 8

Approximate scale in miles

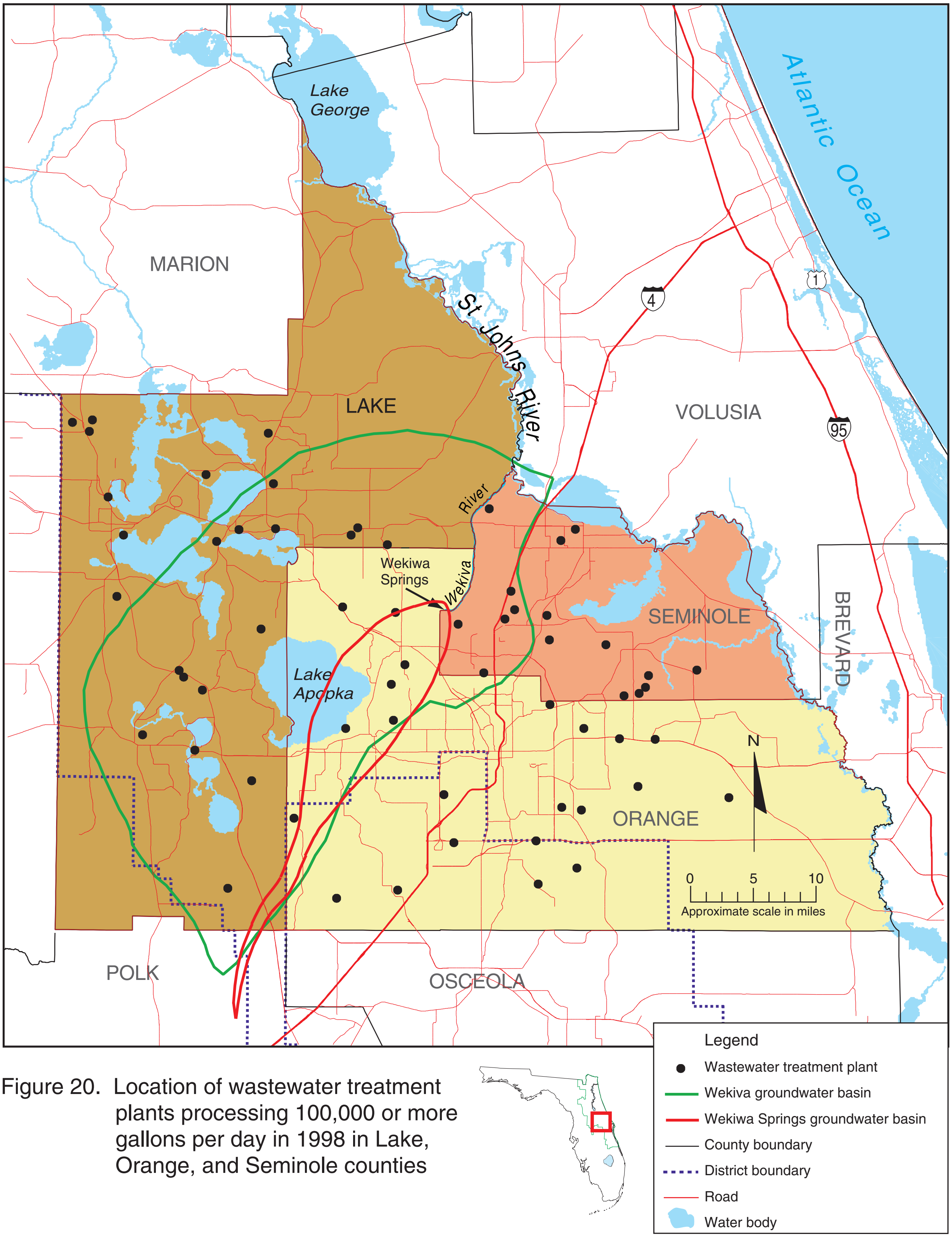


Figure 20. Location of wastewater treatment plants processing 100,000 or more gallons per day in 1998 in Lake, Orange, and Seminole counties

CONCLUSION

Areas where the nitrate N concentrations are highest (above 5 mg/L) occur to the south and west of Lake Apopka. These concentrations occur in the cropland land use category for 1973 and likely are due to fertilizers applied in citrus production. The median age for groundwater in the Wekiva groundwater basin, based on 11 samples, is 27.4 years.

Based on its stable isotopic composition, groundwater in the Wekiva groundwater basin is being recharged by local precipitation and evaporated water. The most likely source for the evaporated water is the lakes within the study area.

Nitrate N concentrations at Wekiwa Springs increased during the 1980s. The $\delta^{15}N$ value at the spring suggests that the source of the nitrogen is from a mixture of animal waste or sewage and lawn fertilizers. Between 1973 and 1990, the urban land use category south of Wekiwa Springs increased. Land use changed from pasture to residential in high-recharge areas for the Upper Floridan aquifer during this period. This confirms that the source of the nitrates in Wekiwa Springs is a mixture of leachate from septic tanks and recharge water from fertilized lawns. The age of water discharging from Wekiwa Springs is 17 years. This suggests that past practices are affecting Wekiwa Springs today.

Nitrate N concentrations at Wekiwa Springs peaked at a value of 2.00 mg/L in 1995. Since 1995, nitrate N concentrations have declined. The decline in nitrates at Wekiwa Springs may be due to the construction of a wastewater treatment plant in Seminole County in 1973 or to lower discharge that might represent water from a deeper part of the aquifer. Rainfall at Wekiwa Springs was significantly below normal in 1998 and 2000. In 1999, Wekiwa Springs discharged 458 pounds of nitrogen per day or 84 tons of nitrogen per year.

The ^{15}N data suggest that the areas of the highest nitrate N concentrations do not contribute to the nitrate N discharging from Wekiwa Springs because the $\delta^{15}N$ of the highest nitrate N areas are below 5.0‰ but the $\delta^{15}N$ of Wekiwa Springs is 8.6‰. However, the more locally developed flow of the Upper Floridan aquifer in the vicinity of the spring results in a more direct influence and source of the nitrate N contamination displayed at the spring. Most of the water at Wekiwa Springs flows from the southwest.

The source of the nitrates is from the high-rate recharge areas just south and southwest of the spring.

Since the tritium / helium-3 age of Wekiwa Springs water is 17 years (Toth 1999), it is assumed that the processes that contaminated Wekiwa Springs occurred approximately 17 years ago. The groundwater discharging at Wekiwa Springs is a mixture of ages representing water traveling along many different flow paths. The young age suggests that most of the flow was from shallow flow paths in 1996 when the age was determined.

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APPENDIX A—STATION NAME, LOCATION, WELL CHARACTERISTICS, WATER QUALITY, AND ISOTOPE DATA FOR SAMPLES COLLECTED IN THIS STUDY

Appendix A

Sampling Site ID	Measured D.O. [mg/L]	Total Organic + Ammonia N [mg/L]	Total Dis. Nitrate + Nitrite N [mg/L]	Total P [mg/L]	N14/N15 NO3 Fraction (NH4 in red) [per mil]	(Oxygen/ Deuterium) Delta H-2/ Delta O-18 [per mil]		Station ID	Station Name	Quad	Latitude_dd	Longitude_dd	Map ID	County	LSD, ft msl	Station Type	Stickup	Casing Depth (ft)	Well Depth (ft)	Data Frequency	Data Source	GeoLog Type	QW Source
L-39	0.0	0.2	0.02	0.07				282245081492601	Eva 6" UFL	Lake Nellie	28.37917	-81.82389	53	69	113.47	UF	-3.40	105	192	Monthly	USGS (Mike)	Geol/Drill/ Gamma	SJRWMD/ DEP
L-37	0.0	0.47	0.02	0.11				282502081422301	Lykes Bros. replacement 4" UFL (S Burger) near Keene Lake	Lake Louisa	28.41722	-81.70639	68	69	120	UF	-0.80	-9999	-9999	Semiannual	USGS (Mike)	-9999	USGS
L-38	—	0.2	3.8	0.02	3.6	-17.7	-3.82	282729081443301	Lake Louisa State Park 4" UFL (L-0053)	Lake Louisa	28.45806	-81.74250	97	69	100.87	UF	-0.40	70	85	Monthly	SJRWMD (Mike)	-9999	SJRWMD/ DEP
L-47	0.0	0.2	0.04	0.06				282823081500401	D Patton 6" UFL (prev. DD Gaffney) near Eva firetower	Lake Nellie	28.47306	-81.83444	103	69	119.20	UF	-0.63	96	390	Semiannual	USGS (Mike)	-9999	USGS
L-40	1.7	0.22	6.1	0.1	4.8	-12.3	-2.57	283028081454701	Country Garden Nursery 4" UFL, Clermont	Clermont West	28.50778	-81.76306	123	69	122	UF	-1	-9999	-9999	Not sampled	USGS	-9999	USGS
L-46	—	0.2	0.05	0.08				283114081503401	Bernard DuFrene 2" UFL, SR 33 south of Groveland	Clermont West	28.52056	-81.84278	137	69	120	UF	0.00	-9999	-9999	Not sampled	USGS	-9999	USGS
L-45	0.0	0.63	0.02	0.17				283128081404701	Johns Lake 4" UFL (L-0052)	Clermont East	28.52444	-81.67972	141	69	97.73	UF	-1	73	155	Semiannual	USGS (Mike)	Gamma	USGS
L-36	0.8	0.49	0.4	0.14				283232081394101	83213902 22S26E25 Edgewater Beach UFL near (East) Johns Lake	Clermont East	28.54222	-81.66139	149	69	135.00	UF	2.18	-9999	-9999	Semiannual	USGS (Mike)	-9999	USGS
L-3	—	0.2	6.7	0.02	4.1	-16.2	-3.13	283355081411701	Site 38 Turnpike—Waits Junction 4" UFL (L-0199)	Clermont East	28.56528	-81.68806	173	69	94.00	UF	-4.24	110	146	Continuous	SJRWMD (Mike)	Gamma/Calip	SJRWMD/ DEP
L-2	1.7	0.2	4.9	0.03	3.9	-14.2	-2.88	283400081405100	Apopka (Gourd Neck) Spring near Oakland	Clermont East	28.56667	-81.68000	176	69	66	SP	40	-9999	-9999	Quarterly	SJRWMD	Geol	USGS
L-43	0.0	0.2	1.4	0.04	11.2	-13.6	-2.62	283432081530601	(City of) Mascotte 8" UFL	Mascotte	28.57556	-81.88500	185	69	130.63	UF	-1.80	143	291	Not sampled	USGS	Drill	USGS
L-23	0.0	0.22	0.52	0.02				283549081401701	Montverde School 6" freeflow	Clermont East	28.59694	-81.67139	201	69	72	UF	-1.75	-9999	120	Not sampled	USGS	-9999	USGS
L-24	2.2	0.2	4.3	0.02				283655081412701	Freeflow 4" UFL, Ferndale	Clermont East	28.61528	-81.69083	222	69	71.41	UF	0.00	-9999	123	Not sampled	USGS	-9999	USGS
L-25	3.5	0.2	7.5	0.02				283720081421801	Ferndale Baptist Church 4" UFL	Clermont East	28.62222	-81.70500	228	69	128.61	UF	-1.49	-9999	-9999	Not sampled	USGS	-9999	USGS
L-44	1.1	0.2	3.3	0.24	4.4	-14.2	-2.75	283828081535701	Sunset Lakes Ski Center 4" UFL, north of Mascotte	Center Hill	28.64111	-81.89917	246	69	95	UF	0.00	-9999	-9999	Not sampled	USGS	-9999	USGS
L-34	0.0	0.22	0.02	0.04				283905081485401	Novelty Crystal Plant 4" UFL, O'Brien Road 0.1 mile south of the Florida Turnpike	Howey in the Hills	28.65139	-81.81500	258	69	90	UF	-1.00	-9999	-9999	QW only	USGS	-9999	USGS

Sampling Site ID	Measured D.O. [mg/L]	Total Organic + Ammonia N [mg/L]	Total Dis. Nitrate + Nitrite N [mg/L]	Total P [mg/L]	N14/N15 NO3 Fraction (NH4 in red) [per mil]	(Oxygen/ Deuterium) Delta H-2/ Delta O-18 [per mil]		Station ID	Station Name	Quad	Latitude_dd	Longitude_dd	Map ID	County	LSD, ft msl	Station Type	Stickup	Casing Depth (ft)	Well Depth (ft)	Data Frequency	Data Source	GeoLog Type	QW Source
L-17	—	0.2	4.3	0.02				283937081422101	Lake Apopka Restoration Area (SJRWMD) 4" iIntermittent, Clay Island	Astatula	28.66028	-81.70583	265	69	68.70	UF	-2.66	-9999	141	Not sampled	USGS	-9999	USGS
L-33	0.0	0.49	0.02	0.13	5.2	-7.1	-1.32	284122081534401	Groveland Tower 4" UFL (L-0095), SR 33 south of Okahumpka	Center Hill	28.68944	-81.89556	293	69	134.70	UF	-2.93	148	368	Continuous/ monthly	SJRWMD (Mike)	Gamma/Calip	SJRWMD/ DEP
L-18	—	0.2	0.02	0.02				284253081441101	Astatula (J. Swaffer Park) 4" UFL	Astatula	28.71472	-81.73639	318	69	100	UF	-0.50	-9999	-9999	QW only	USGS	-9999	USGS
L-4	—	0.2	0.02	0.02				284320081410701	Apopka-Beauclair Canal 4" (lower) UFL (L-0139) near SR 48	Astatula	28.72222	-81.68528	322	69	70.51	UF	-1.90	575	650	Semiannual	USGS	-9999	USGS
L-30	0.0	0.21	0.88	0.07				284328081515901	Creek Farms 8" UFL	Howey in the Hills	28.72444	-81.86639	324	69	103.29	UF	-0.5	145	539	Semiannual	USGS (Mike)	-9999	USGS
L-27	0.0	0.2	0.71	0.03	8.6	-10.6	-2.15	284330081464201	(Town of) Howey in the Hills 14" UFL #3 (L-0591)	Howey in the Hills	28.72500	-81.77833	326	69	135	UF	-1.30	162	350	Every 3 years	SJRWMD/ DEP	-9999	SJRWMD/ DEP
L-28	0.5	0.2	4.1	0.02				284424081490500	Holiday Springs at Yalaha	Howey in the Hills	28.74000	-81.81806	337	69	76	SP	0	-9999	-9999	Not sampled	USGS	-9999	USGS
L-29	1.0	0.2	5.0	0.03				284455081494100	Blue Springs, Park Drive near Yalaha	Howey in the Hills	28.74861	-81.82806	347	69	65	SP	0	-9999	-9999	Not sampled	USGS	-9999	USGS
L-26 L-26 Dup	0.0	0.24	0.46	0.09				284507081540600	Bugg Spring near Okahumpka	Leesburg West	28.75194	-81.90167	353	69	76	SP	0	-9999	170	Not sampled	Branham, Joe	-9999	USGS
L-32	0.0	0.26	0.02	0.11				284725081361901	Wolf Sink (LCWA) 6" deep (L-0600) near Sorrento	Sorrento	28.79028	-81.60528	374	69	139.07	UF	-2.69	160	205	Logged	USGS	-9999	USGS
L-50	0.0	0.2	0.02	0.03				284740081251700	Wekiva Falls Resort	Sanford SW	28.79444	-81.42139	381	69	22	SP	14.2	84.5	120	Not sampled	USGS	-9999	USGS
L-9 L-9 Dup	0.1	0.2	0.35	0.08				284757081320701	L Knowles 4" UFL, 30845 CR 435, Mt. Plymouth	Sorrento	28.79917	-81.53528	391	69	86.50	UF	-1.00	-9999	170	Not sampled	USGS	-9999	USGS
L-10	—	0.2	0.02	0.06				284856081383001	(City of) Mount Dora 20" UFL #3	Eustis	28.81556	-81.64167	431	69	163.39	UF	-1.77	155	752	Semiannual	USGS (Mike)	Geol/Drill	USGS
L-15	—	0.2	0.02	0.11				284940081303800	Droty Springs near Sorrento	Sorrento	28.82778	-81.51056	461	69	18	SP	0	-9999	-9999	Not sampled	USGS	-9999	USGS
L-31	0.0	0.2	0.02	0.03				285028081253301	Seminole State Forest 4" UFL #1 (L-0037)	Sanford SW	28.84111	-81.42583	484	69	38.99	UF	-1.60	102	364	Monthly	USGS (Jerry and Mike)	Gamma/Calip	-9999
L-12	0.2	0.2	0.02	0.04				285038081270100	Palm Springs, Seminole State Forest	Sanford SW	28.84389	-81.45028	488	69	12	SP	0	-9999	-9999	Not sampled	USGS	-9999	USGS
L-14	—	0.2	0.26	0.04	10.9	-10.1	-2.05	285118081391001	(City of) Eustis water plant 16" UFL (L-0593), CR 44A	Eustis	28.85500	-81.65278	511	69	140	UF	-9999	274	750	Every 3 years	SJRWMD/ DEP	-9999	SJRWMD/ DEP

Sampling Site ID	Measured D.O. [mg/L]	Total Organic + Ammonia N [mg/L]	Total Dis. Nitrate + Nitrite N [mg/L]	Total P [mg/L]	N14/N15 NO3 Fraction (NH4 in red) [per mil]	(Oxygen/ Deuterium) Delta H-2/ Delta O-18 [per mil]		Station ID	Station Name	Quad	Latitude_dd	Longitude_dd	Map ID	County	LSD, ft msl	Station Type	Stickup	Casing Depth (ft)	Well Depth (ft)	Data Frequency	Data Source	GeoLog Type	QW Source
L-13	—	0.2	0.04	0.05				285224081262400	Shark's Tooth Spring, Seminole State Forest	Sanford SW	28.87333	-81.44000	534	69	12	SP	0	-9999	-9999	Not sampled	USGS	-9999	USGS
L-19	0.0	0.31	0.02	0.06				285230081242201	Lower Wekiva River State Preserve 2" freeflow #2 (south)	Sanford SW	28.87500	-81.40611	538	69	19.61	UF	-2.70	102	109	Not sampled	USGS	-9999	USGS
L-21	0.0	0.2	0.02	0.10				285301081285401	Reese 4" UFL near Cassia	Pine Lakes	28.88361	-81.48167	550	69	64.5	UF	0.63	-9999	-9999	Semiannual	USGS (Mike)	-9999	USGS
L-22	0.0	0.2	0.02	0.11				285318081340601	Eustis Sand Co. 12" UFL (L-0375)	Paisley	28.88833	-81.56833	557	69	120.84	UF	-0.10	-9999	350	Semiannual	USGS (Mike)	-9999	USGS
L-20	0.1	0.46	0.02	0.10				285454081241201	Lower Wekiva River State Preserve 2" intermittent flow #1 (north)	Pine Lakes	28.91500	-81.40333	582	69	26.67	UF	-0.50	-9999	65	Not sampled	USGS	-9999	USGS
L-42	0.0	0.2	0.02	0.03				283017081391301	(17830) Davenport Road 4" UFL south of Oakland	Clermont East	28.50472	-81.65361	1028	95	108.06	UF	-1.30	-9999	-9999	Semiannual	USGS (Jerry)	-9999	USGS
L-35	0.0	0.2	0.17	0.05				283325081374001	(Town of) Oakland 12" UFL #2	Clermont East	28.55694	-81.62778	1029	95	123.18	UF	-1.00	148.0	370	Semiannual	USGS (Jerry)	Geol	-9999
L-41	0.0	0.22	0.02	0.04				283809081324801	Magnolia Park 6" UFL near Ocoee	Apopka	28.63583	-81.54694	1049	95	96	UF	-2.90	105	117	Not sampled	USGS	Drill	-9999
L-49 L-49 Dup	—	0.44	0.02	0.35				284120081331701	Minute Maid/Plymouth Prod. 12" UFL #1	Apopka	28.68889	-81.55472	1091	95	120.9	UF	-1.20	192	565	Not sampled	USGS	Drill	-9999
L-1	0.1	0.2	1.3	0.12				284243081273600	Wekiwa Springs, Wekiwa Springs State Park	Forest City	28.71194	-81.46000	1093	95	19.82	SP	5.28	-9999	-9999	Monthly	USGS (David)	-9999	USGS
L-48	—	0.2	0.02	0.02				284330081360501	World Foliage Resource, Inc. 8" UFL near Zellwood	Apopka	28.72500	-81.60139	1096	95	83	UF	-2	127	403	Not sampled	USGS	-9999	USGS
L-8	0.1	0.2	0.02	0.03				284340081305101	James Owens UFL, 132 W. Ponkan Road, 3.9 miles north of Apopka	Apopka	28.72778	-81.51417	1098	95	91	UF	-0.65	-9999	150	Not sampled	USGS	Apopka Well and Pump	USGS
L-7	0.7	0.2	1.8	0.09				284513081310601	Blue Sink, Orange Co. near Rock Springs	Sorrento	28.75361	-81.51833	1105	95	45	UF	0	-9999	-9999	Not sampled	USGS	-9999	USGS
L-5	0.2	0.2	1.4	0.08				284520081295800	Rock Springs near Apopka	Sorrento	28.75556	-81.49944	1106	95	28	SP	0.57	-9999	-9999	Monthly	USGS (David)	-9999	USGS
L-6	0.0	0.2	0.02	0.03				284612081303400	Sulphur (Camp) Springs near Mt. Plymouth	Sorrento	28.77000	-81.50944	1114	95	25	SP	0	-9999	-9999	Not sampled	USGS	-9999	USGS
L-16 L-16 Dup	—	0.26	0.02	0.10	3.0	-11.3	-2.28	284553081204801	S-0972 Lake Mary UFL #2	Sanford	28.76472	-81.34667	1331	117	67	UF	-3	-9999	-9999	Every 3 years	SJRWMD/ DEP	-9999	SJRWMD/ DEP
L-11 L-11 Dup	0.2	0.2	0.8	0.06	5.3	-13.6	-2.77	285144081183900	Gemini Springs near DeBary	Sanford	28.86250	-81.31056	1493	127	2	SP	0	-9999	80	Bimonthly	USGS/ SJRWMD	-9999	USGS

APPENDIX B—TRITIUM, HELIUM-3, HELIUM-4, AND NEON MEASUREMENTS AND TRITIUM/HELIUM-3 AGE DETERMINATIONS FOR SAMPLES COLLECTED IN THIS STUDY

USGS-FL-Knowles

Item	USGS Lab ID #	Field ID #	Tritium (TU)	^{4}He cm^{3}STPg^{-1}	δ^3He	Ne cm^{3}STPg^{-1}
1	992780001	Apopka Spring/992780001	2.94 3.03	5.3746E-08	29.04	2.1419E-07
2	992780009	Country garden/992780009	2.79 3.02	5.3195E-08	26.1	2.1463E-07
3	992780004	Eustis/992780004	2.32	5.3367E-08	23.17	2.1308E-07
4	992780003	GeminiSpring/992780003	2.53 2.21	6.0696E-08	3.26	2.1839E-07
5	992780007	Groveland/992780007	1.95 2.01	5.1108E-08	32.19	2.0161E-07
6	992780006	Howey/992780006	2.23 1.92	5.2442E-08	21.23	2.0304E-07
7	992780008	Lake Louisa/992780008	3.93 4.12	5.5318E-08	55.7	2.2465E-07
8	992780005	Lake Mary/992780005	2.95 2.71	5.1249E-08	41.77	2.1482E-07
9	992780010	Mascotte/992780010	4.01 3.64	5.2863E-08	53.83	2.1237E-07
10	992780011	Sunset lakes/992780011	4.65 4.13	5.2897E-08	66.24	2.0953E-07
11	992780002	Turnpike/992780002	3.06 2.75	5.3634E-08	35.6	2.1121E-07

SampleID	Sampling Date	Tritium	± 1σ TU	δ^3He	±1σ (%)	Ratio 10^{-6}	± 1σ (%)	^{4}He (10^{-8}	Ne ccSTP/g)	%He (terrigen.)	Age ±1σ (yrs) (uncorrected)	Age ±1σ (yrs) (corrected)	published comments
Apopka Spring/992780001	8/11/99	2.94	0.12	29.04	0.24	1.786	0.47	5.37	21.42	-1.71	25.3 ± 0.6	24.5 ± 1.1	
Alternate tritium used for age calc.								Δ^4He 22.8	ΔNe 21.5				
Apopka Spring/992780001	8/11/99	3.03	0.08										
Alternate tritium used for age calc.								Δ^4He	ΔNe		Tritium data from bottle sample		
Country garden/992780009	9/8/99	2.79	0.14	26.10	0.24	1.745	0.47	5.32	21.46	-2.29	24.5 ± 0.7	23.4 ± 1.2	
Alternate tritium used for age calc.								Δ^4He 20.9	ΔNe 20.2				
Country garden/992780009	9/8/99	3.02	0.08										
Alternate tritium used for age calc.								Δ^4He	ΔNe		Tritium data from bottle sample		
Eustis/992780004	8/17/99	2.32	0.11	23.17	0.24	1.705	0.47	5.34	21.31	-1.37	25.5 ± 0.7	24.7 ± 1.2	
Alternate tritium used for age calc.								Δ^4He 21.5	ΔNe 19.9				
GeminiSpring/992780003	8/17/99	2.53	0.11	3.26	0.24	1.429	0.47	6.07	21.84	9.27	8.5 ± 0.5	18.6 ± 0.8	
Alternate tritium used for age calc.								Δ^4He 36.9	ΔNe 20.5		Terrigenic He		
GeminiSpring/992780003	8/17/99	2.21	0.08										
Alternate tritium used for age calc.								Δ^4He	ΔNe		Tritium data from bottle sample		
Groveland/992780007	9/1/99	1.95	0.20	32.19	0.24	1.830	0.47	5.11	20.16	1.21	31.8 ± 1.5	32.4 ± 1.8	
Alternate tritium used for age calc.								Δ^4He 16.0	ΔNe 12.5				
Groveland/992780007	9/1/99	2.01	0.06										
Alternate tritium used for age calc.								Δ^4He	ΔNe		Tritium data from bottle sample		
Howey/992780006	8/30/99	2.23	0.11	21.23	0.24	1.678	0.47	5.24	20.30	2.61	24.7 ± 0.7	26.2 ± 1.2	
Alternate tritium used for age calc.								Δ^4He 19.2	ΔNe 13.7				
Howey/992780006	8/30/99	1.92	0.05										
Alternate tritium used for age calc.								Δ^4He	ΔNe		Tritium data from bottle sample		
Lake Louisa/992780008	9/7/99	3.93	0.24	55.70	0.23	2.155	0.46	5.53	22.47	-3.35	30.5 ± 0.9	29.6 ± 1.1	
Alternate tritium used for age calc.								Δ^4He 25.4	ΔNe 25.3				
Lake Louisa/992780008	9/7/99	4.12	0.08										
Alternate tritium used for age calc.								Δ^4He	ΔNe		Tritium data from bottle sample		
Lake Mary/992780005	8/18/99	2.95	0.12	41.77	0.24	1.962	0.47	5.12	21.48	-6.15	29.5 ± 0.6	27.4 ± 1.0	
Alternate tritium used for age calc.								Δ^4He 16.1	ΔNe 19.9				
Lake Mary/992780005	8/18/99	2.71	0.06										
Alternate tritium used for age calc.								Δ^4He	ΔNe		Tritium data from bottle sample		
Mascotte/992780010	9/22/99	4.01	0.14	53.83	0.23	2.129	0.46	5.29	21.24	-1.32	29.0 ± 0.5	28.7 ± 0.8	
Alternate tritium used for age calc.								Δ^4He 19.9	ΔNe 18.3				

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{H^3}= .05577yr.$^{-1}$; $^3He/^4He_{atmos}$ = 1.384 x10^{-6}; crustal terrigenic $^3He/^4He$ ratio: 2 x10^{-8}

SampleID	Sampling Date	Tritium	± 1σ TU	δ^3He	±1σ (%)	Ratio 10^{-6}	± 1σ (%)	^4He (10^{-8} ccSTP/g)	Ne	%He (terrigen.)	Age (uncorrected)	±1σ (yrs)	Age (corrected)	±1σ (yrs)	published comments
Mascotte/992780010	9/22/99	3.64	0.08												
Alternate tritium used for age calc.								Δ^4He	ΔNe		Tritium data from bottle sample				
Sunset lakes/992780011	9/22/99	4.65	0.14	66.24	0.23	2.301	0.46	5.29	20.95	0.45	29.8	± 0.5	29.9	± 0.7	
Alternate tritium used for age calc.								Δ^4He 19.8	ΔNe 16.4						
Sunset lakes/992780011	9/22/99	4.13	0.09												
Alternate tritium used for age calc.								Δ^4He	ΔNe		Tritium data from bottle sample				
Turnpike/992780002	8/11/99	3.06	0.12	35.60	0.24	1.877	0.47	5.36	21.12	0.18	27.4	± 0.6	27.5	± 0.9	
Alternate tritium used for age calc.								Δ^4He 22.2	ΔNe 18.9						
Turnpike/992780002	8/11/99	2.75	0.08												
Alternate tritium used for age calc.								Δ^4He	ΔNe		Tritium data from bottle sample				

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{H}= .05577yr.$^{-1}$; $^3He/^4He_{atmos}$ = 1.384 x10^{-6}; crustal terrigenic $^3He/^4He$ ratio: 2 x10^{-8}

LDEO NGL

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

report: r

Sender: Knowles | Organization: USGS | Program: FL-Knowles

Sample ID: Apopka Spring/992780001

Channel No.: 1 | Tritium Bottle No.: | Date received: 10/7/99

Sample Date: 8/11/99 | Sampling Time: 1000 | Altitude: 55 m | Temp.: 25.7 °C | Salinity: 0

T Degas No. **14919** | T Degas Date | T Measurement Date 03/06/2000

Tritium: 2.940 ± 0.116 TU (1σ) 0.116

^{4}He bulb blank 0.887 $\times 10^{-9}$ cm^3STP
Ingrown $^3He_{trit}$ 5.82968 $\times 10^{-15}$ cm^3STP
$\%^3He_{trit}$ 78.8

Alternative tritium value: ± **TU (1σ)** comment:

He Extraction No. **14919** | He Extraction Date 11/11/1999 | He Measurement Date 12/13/99

δ^3He: 29.04 ± 0.240 % (1σ) | δ^3He_{cor} from other T (see above): 29.04 % | δ^3He_{uncor}: 29.179 ± 0.238 % (1σ)

$^3He_{trit}$: 9.107 ± 0.080 TU (1σ) | ^{3}He: 9.599 $\times 10^{-14}$ cm^3 STP/g

Sample weight: 40.0 g

^{4}He: 5.375 ± 0.014 $\times 10^{-8}$ cm^3STP/g (1σ) | **Δ^4He: 22.84** %

Ne: 21.419 ± 0.294 $\times 10^{-8}$ cm^3STP/g (1σ) | **ΔNe: 21.47** %

Uncorrected
Age ±1σ (y)
25.3 ± 0.6

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 $\times 10^{-8}$:

δ^3He_{cor}: 26.894 %

$^3He_{cor}$: 8.603 TU | **$^3He_{cor}$: 9.600** $\times 10^{-14}$ cm^3STP/g

$^4He_{cor}$: 5.467 $\times 10^{-8}$ cm^3STP/g | % Terrigenic ^{4}He **-1.7**

$^4He_{terrigenic}$: -0.092 $\times 10^{-8}$ cm^3STP/g

Corrected for terrigenic He
Age ±1σ (y)
24.5 ± 1.1

Site specific terrigenic ^{3}He/^{4}He ratio:

δ^3He_{cor} 26.894 %

$^3He_{cor}$ 8.603 TU | **$^3He_{cor}$ 9.600** $\times 10^{-14}$ cm^3STP/g

Corrected for terrigenic He
Age ±1σ (y)
±

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; $^3He/^4He_{atmos}$ = 1.384 $\times 10^{-6}$

published comments

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

report: r	Sender: Knowles	Organization: USGS	Program: FL-Knowles		
Sample ID: Apopka Spring/992780001					
Channel No.:	Tritium Bottle No.: 1	Date received: 10/7/99			
Sample Date: 8/11/99	Sampling Time: 1000	Altitude: 55 m	Temp.: 25.7 °C	Salinity: 0	

T Degas No. **1006288** T Degas Date 11/12/1999 T Measurement Date 02/21/2000

Tritium: 3.030 ± 0.076 TU (1σ) 0.076

^{4}He bulb blank 1.920 x10^{-9} cm^{3}STP
Ingrown $^3He_{trit}$ 13.2280 x10^{-15} cm^{3}STP
%$^3He_{trit}$ 79.9

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. He Extraction Date He Measurement Date

δ^3He: ± % (1σ) δ^3He_{cor} from other T (see above): % δ^3He_{uncor}: ± % (1σ)
$^3He_{trit}$: ± TU (1σ) ^{3}He: x10^{-14} cm^3 STP/g
Sample weight: g

^{4}He: ± x10^{-8} cm^{3}STP/g (1σ) **Δ^4He:** %
Ne: ± x10^{-8} cm^{3}STP/g (1σ) **ΔNe:** %
Uncorrected **Age** ±1σ (y)

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 x10^{-8}:
δ^3He_{cor}: %
$^3He_{cor}$: TU **$^3He_{cor}$:** x10^{-14} cm^{3}STP/g
$^4He_{cor}$: x10^{-8} cm^{3}STP/g % Terrigenic ^{4}He
$^4He_{terrigenic}$: x10^{-8} cm^{3}STP/g
Corrected for terrigenic He **Age** ±1σ (y)

Site specific terrigenic ^{3}He/^{4}He ratio:
δ^3He_{cor} % **$^3He_{cor}$** x10^{-14} cm^{3}STP/g
$^3He_{cor}$ TU
Corrected for terrigenic He **Age** ±1σ (y)

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; $^3He/^4He_{atmos.}$= 1.384 x10^{-6}

published comments Tritium data from bottle sample

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

report: r	Sender	Knowles	Organization	USGS	Program	FL-Knowles	
	Sample ID	Country garden/992780009					
	Channel No.	1	Tritium Bottle No.		Date received	10/7/99	
Sample Date	9/8/99	Sampling Time	1330	Altitude	40 m	Temp. 24.2 °C	Salinity 0

T Degas No. 14909 | T Degas Date | T Measurement Date 03/07/2000

Tritium: 2.792 ± 0.137 TU (1σ) 0.137

^4He bulb blank 1.103 $x10^{-9}$ cm^3STP
Ingrown $^3He_{trit}$ 5.97019 $x10^{-15}$ cm^3STP
$\%^3He_{trit}$ 74.3

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. 14909 | He Extraction Date 11/9/1999 | He Measurement Date 12/14/99

δ^3He:	26.10	± 0.240	% (1σ)	δ^3He_{cor} from other T (see above): 26.1 %
$^3He_{trit}$:	8.150	± 0.070	TU (1σ)	

δ^3He_{uncor}: 26.188 ± 0.240 % (1σ)
^3He: 9.284 $x10^{-14}$ cm^3STP/g
Sample weight: 39.4 g

^4He:	5.320	± 0.014 $x10^{-8}$ cm^3STP/g (1σ)	Δ^4He:	20.87 %	Uncorrected Age	±1σ (y)
Ne:	21.463	± 0.276 $x10^{-8}$ cm^3STP/g (1σ)	ΔNe:	20.21 %	24.5	± 0.7

Average crustal terrigenic $^3He/^4He$ ratio: 2 $x10^{-8}$:

δ^3He_{cor}:	23.310	%		
$^3He_{cor}$:	7.483	TU	$^3He_{cor}$: 9.286	$x10^{-14}$ cm^3STP/g
$^4He_{cor}$:	5.441	$x10^{-8}$ cm^3STP/g	% Terrigenic ^4He	-2.3
$^4He_{terrigenic}$:	-0.122	$x10^{-8}$ cm^3STP/g		

Corrected for terrigenic He — Age ±1σ (y): 23.4 ± 1.2

Site specific terrigenic $^3He/^4He$ ratio:

δ^3He_{cor}	23.310	%	$^3He_{cor}$ 9.286	$x10^{-14}$ cm^3STP/g
$^3He_{cor}$	7.483	TU		

Corrected for terrigenic He — Age ±1σ (y): ±

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; $^3He/^4He_{atmos.}$ = 1.384 $x10^{-6}$

published comments

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

report	Sender	Knowles	Organization	USGS	Program	FL-Knowles
r	Sample ID	Country garden/992780009				
	Channel No.		Tritium Bottle No.	1	Date received	10/7/99
Sample Date	9/8/99	Sampling Time	1330	Altitude 40 m	Temp. 24.2 °C	Salinity 0

T Degas No. 1006282	T Degas Date 10/29/1999	T Measurement Date	02/22/2000
Tritium: 3.024 ± 0.079 TU (1σ) 0.079		^{4}He bulb blank 1.711	x10^{-9} cm^{3}STP
		Ingrown ^{3}He$_{trit}$ 14.6398	x10^{-15} cm^{3}STP
		%^{3}He$_{trit}$ 83.8	
Alternative tritium value: ± TU (1σ)	comment:		

He Extraction No. He Extraction Date He Measurement Date

δ^{3}He: ± % (1σ) δ^{3}He$_{cor}$ from other T (see above): % δ^{3}He$_{uncor}$: ± % (1σ)

^{3}He$_{trit}$: ± TU (1σ) ^{3}He: x10^{-14} cm^3 STP/g

Sample weight: g

^{4}He: ± x10^{-8} cm^{3}STP/g (1σ) **Δ^{4}He:** % Uncorrected **Age** ±1σ (y)

Ne: ± x10^{-8} cm^{3}STP/g (1σ) **ΔNe:** %

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 x10^{-8}: Corrected for terrigenic He

δ^{3}He$_{cor}$: %

^{3}He$_{cor}$: TU **^{3}He$_{cor}$:** x10^{-14} cm^{3}STP/g

^{4}He$_{cor}$: x10^{-8} cm^{3}STP/g % Terrigenic ^{4}He **Age** ±1σ (y)

^{4}He$_{terrigenic}$: x10^{-8} cm^{3}STP/g

Site specific terrigenic ^{3}He/^{4}He ratio: Corrected for terrigenic He

δ^{3}He$_{cor}$ % **^{3}He$_{cor}$** x10^{-14} cm^{3}STP/g **Age** ±1σ (y)

^{3}He$_{cor}$ TU

constants: δ^{3}He$_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; ^{3}He/^{4}He$_{atmos.}$ = 1.384 x10^{-6}

published comments Tritium data from bottle sample

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

report: r	Sender: Knowles	Organization: USGS	Program: FL-Knowles		
Sample ID: Eustis/992780004					
Channel No.: 1	Tritium Bottle No.:	Date received: 10/7/99			
Sample Date: 8/17/99	Sampling Time: 1630	Altitude: 48 m	Temp.: 24.7 °C	Salinity: 0	

T Degas No. 14915 | T Degas Date | T Measurement Date 03/06/2000

Tritium: 2.322 ± 0.110 TU (1σ) 0.110

^{4}He bulb blank 1.295 x10^{-9} cm^{3}STP
Ingrown $^3He_{trit}$ 5.51831 x10^{-15} cm^{3}STP
%$^3He_{trit}$ 67.4

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. 14915 | He Extraction Date 11/9/1999 | He Measurement Date 12/14/99

δ^3He:	23.17	± 0.240	% (1σ)
$^3He_{trit}$:	7.305	± 0.070	TU (1σ)

δ^3He_{cor} from other T (see above): 23.17 %

δ^3He_{uncor}: 23.267 ± 0.241 % (1σ)

^{3}He: 9.097 x10^{-14} cm^{3}STP/g

Sample weight: 39.3 g

^{4}He:	5.337	± 0.014 x10^{-8} cm^{3}STP/g (1σ)	Δ^4He:	21.54	%	Uncorrected Age ±1σ (y)
Ne:	21.308	± 0.268 x10^{-8} cm^{3}STP/g (1σ)	ΔNe:	19.88	%	25.5 ± 0.7

Average crustal terrigenic $^3He/^4He$ ratio: 2 x10^{-8}:

δ^3He_{cor}:	21.530	%	
$^3He_{cor}$:	6.905	TU	$^3He_{cor}$: 9.099 x10^{-14} cm^{3}STP/g
$^4He_{cor}$:	5.410	x10^{-8} cm^{3}STP/g	% Terrigenic ^{4}He -1.4
$^4He_{terrigenic}$:	-0.073	x10^{-8} cm^{3}STP/g	

Corrected for terrigenic He
Age ±1σ (y)
24.7 ± 1.2

Site specific terrigenic $^3He/^4He$ ratio:

δ^3He_{cor}	21.530	%	$^3He_{cor}$ 9.099 x10^{-14} cm^{3}STP/g
$^3He_{cor}$	6.905	TU	

Corrected for terrigenic He
Age ±1σ (y)
±

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; $^3He/^4He_{atmos.}$ = 1.384 x10^{-6}

published comments

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

report: r	Sender: Knowles	Organization: USGS	Program: FL-Knowles		
	Sample ID: GeminiSpring/992780003				
	Channel No.: 1	Tritium Bottle No.:		Date received: 10/7/99	
Sample Date: 8/17/99	Sampling Time: 1130	Altitude: 15 m	Temp.: 22.6 °C	Salinity: 0	

T Degas No. **14918** T Degas Date T Measurement Date 03/06/2000

Tritium: 2.531 ± 0.108 TU (1σ) 0.108

^{4}He bulb blank 0.507 x10^{-9} cm^{3}STP
Ingrown ^{3}He$_{trit.}$ 4.69447 x10^{-15} cm^{3}STP
%^{3}He$_{trit}$ 84.9

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. **14918** He Extraction Date 11/11/1999 He Measurement Date 12/9/99

δ^{3}He: 3.26 ± 0.240 % (1σ) δ^{3}He$_{cor}$ from other T (see above): 3.26 % δ^{3}He$_{uncor}$: 3.362 ± 0.241 % (1σ)

^{3}He$_{trit}$: 1.532 ± 0.080 TU (1σ) ^{3}He: 8.674 x10^{-14} cm^3 STP/g

Sample weight: 39.9 g

^{4}He: 6.070 ± 0.026 x10^{-8} cm^{3}STP/g (1σ) Δ^{4}He: 36.89 %

Ne: 21.839 ± 0.138 x10^{-8} cm^{3}STP/g (1σ) ΔNe: 20.54 %

Uncorrected Age ±1σ (y): 8.5 ± 0.5

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 x10^{-8}:

δ^{3}He$_{cor}$: 13.667 %
^{3}He$_{cor}$: 4.617 TU ^{3}He$_{cor}$: 8.663 x10^{-14} cm^{3}STP/g
^{4}He$_{cor}$: 5.507 x10^{-8} cm^{3}STP/g % Terrigenic ^{4}He 9.3
^{4}He$_{terrigenic}$: 0.563 x10^{-8} cm^{3}STP/g

Corrected for terrigenic He — Age ±1σ (y): 18.6 ± 0.8

Site specific terrigenic ^{3}He/^{4}He ratio:

δ^{3}He$_{cor}$ 13.667 % ^{3}He$_{cor}$ 8.663 x10^{-14} cm^{3}STP/g
^{3}He$_{cor}$ 4.617 TU

Corrected for terrigenic He — Age ±1σ (y): ±

constants: δ^{3}He$_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; ^{3}He/^{4}He$_{atmos}$ = 1.384 x10^{-6}

published comments: Terrigenic He

Comments:

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report: r

Sender: Knowles | Organization: USGS | Program: FL-Knowles

Sample ID: GeminiSpring/992780003

Channel No.: | Tritium Bottle No.: 1 | Date received: 10/7/99

Sample Date: 8/17/99 | Sampling Time: 1130 | Altitude: 15 m | Temp. 22.6 °C | Salinity: 0

T Degas No. **1006279** | T Degas Date 10/29/1999 | T Measurement Date 02/22/2000

Tritium: 2.214 ± 0.076 TU (1σ) 0.076

^{4}He bulb blank 1.022 x10^{-9} cm^{3}STP
Ingrown ^{3}He$_{trit}$ 9.70668 x10^{-15} cm^{3}STP
%^{3}He$_{trit}$ 85.4

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. | He Extraction Date | He Measurement Date

δ^3He: ± % (1σ) | δ^3He$_{cor}$ from other T (see above): % | δ^3He$_{uncor}$: ± % (1σ)

^{3}He$_{trit}$: ± TU (1σ) | ^{3}He: x10^{-14} cm^3 STP/g

Sample weight: g

^{4}He: ± x10^{-8} cm^{3}STP/g (1σ) | **Δ^4He:** %

Ne: ± x10^{-8} cm^{3}STP/g (1σ) | **ΔNe:** %

Uncorrected **Age ±1σ (y)**

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 x10^{-8}:

δ^3He$_{cor}$: %
^{3}He$_{cor}$: TU | ^{3}He$_{cor}$: x10^{-14} cm^{3}STP/g
^{4}He$_{cor}$: x10^{-8} cm^{3}STP/g | % Terrigenic ^{4}He
^{4}He$_{terrigenic}$: x10^{-8} cm^{3}STP/g

Corrected for terrigenic He **Age ±1σ (y)**

Site specific terrigenic ^{3}He/^{4}He ratio:

δ^3He$_{cor}$ % | ^{3}He$_{cor}$ x10^{-14} cm^{3}STP/g
^{3}He$_{cor}$ TU

Corrected for terrigenic He **Age ±1σ (y)**

constants: δ^3He$_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; ^{3}He/^{4}He$_{atmos}$ = 1.384 x10^{-6}

published comments Tritium data from bottle sample

Comments:

LDEO NGL

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report: r | Sender: Knowles | Organization: USGS | Program: FL-Knowles

Sample ID: Groveland/992780007

Channel No. 1 | Tritium Bottle No. | Date received 10/7/99

Sample Date 9/1/99 | Sampling Time 1200 | Altitude 48 m | Temp. 23.5 °C | Salinity 0

T Degas No. **14912** | T Degas Date | T Measurement Date 03/06/2000

Tritium: 1.953 ± 0.202 TU (1σ) 0.202

^{4}He bulb blank 10.372 x10^{-9} cm^{3}STP
Ingrown ^{3}He$_{trit}$ 17.5619 x10^{-15} cm^{3}STP
%^{3}He$_{trit}$ 18.2

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. **14912** | He Extraction Date 11/9/1999 | He Measurement Date 12/15/99

δ^3He: 32.19 ± 0.240 % (1σ) δ^3He$_{cor}$ from other T (see above): 32.19 % | δ^3He$_{uncor}$: 32.257 ± 0.240 % (1σ)

^{3}He$_{trit}$: 9.579 ± 0.070 TU (1σ) | ^{3}He: 9.350 x10^{-14} cm^3 STP/g

Sample weight: 40.1 g

^{4}He: 5.111 ± 0.013 x10^{-8} cm^{3}STP/g (1σ) | **Δ^4He: 16.01 %**

Ne: 20.161 ± 0.241 x10^{-8} cm^{3}STP/g (1σ) | **ΔNe: 12.46 %**

Uncorrected **Age ±1σ (y)**: **31.8 ± 1.5**

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 x10^{-8}:

δ^3He$_{cor}$: 33.789 %

^{3}He$_{cor}$: 9.917 TU | **^{3}He$_{cor}$: 9.349** x10^{-14} cm^{3}STP/g

^{4}He$_{cor}$: 5.049 x10^{-8} cm^{3}STP/g | % Terrigenic ^{4}He **1.2**

^{4}He$_{terrigenic}$: 0.062 x10^{-8} cm^{3}STP/g

Corrected for terrigenic He **Age ±1σ (y)**: **32.4 ± 1.8**

Site specific terrigenic ^{3}He/^{4}He ratio:

δ^3He$_{cor}$ 33.789 % | **^{3}He$_{cor}$ 9.349** x10^{-14} cm^{3}STP/g

^{3}He$_{cor}$ 9.917 TU

Corrected for terrigenic He **Age ±1σ (y)**: ±

Constants: δ^3He$_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; ^{3}He/^{4}He$_{atmos.}$ = 1.384 x10^{-6}

published comments

Comments:

LDEO NGL

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

report r

Sender: Knowles | Organization: USGS | Program: FL-Knowles

Sample ID: Groveland/992780007

Channel No.: | Tritium Bottle No.: 1 | Date received: 10/7/99

Sample Date: 9/1/99 | Sampling Time: 1200 | Altitude: 48 m | Temp. 23.5 °C | Salinity: 0

T Degas No. **1006281** | T Degas Date 10/29/1999 | T Measurement Date 02/21/2000

Tritium: 2.006 ± 0.057 TU (1σ) 0.057

^{4}He bulb blank 0.793 x10^{-9} cm^{3}STP
Ingrown $^3He_{trit}$ 8.37876 x10^{-15} cm^{3}STP
%$^3He_{trit}$ 86.8

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. | He Extraction Date | He Measurement Date

δ^3**He:** ± % (1σ) δ^3He_{cor} from other T (see above): % δ^3He_{uncor}: ± % (1σ)

^{3}**He**$_{trit}$: ± TU (1σ) ^{3}He: x10^{-14} cm^3 STP/g

Sample weight: g

^{4}**He:** ± x10^{-8} cm^{3}STP/g (1σ) Δ^4**He:** %

Ne: ± x10^{-8} cm^{3}STP/g (1σ) Δ**Ne:** %

Uncorrected **Age** ±1σ (y)

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 x10^{-8}:

δ^3He_{cor}: %

$^3He_{cor}$: TU $^3He_{cor}$: x10^{-14} cm^{3}STP/g

$^4He_{cor}$: x10^{-8} cm^{3}STP/g % Terrigenic ^{4}He

$^4He_{terrigenic}$: x10^{-8} cm^{3}STP/g

Corrected for terrigenic He **Age** ±1σ (y)

Site specific terrigenic ^{3}He/^{4}He ratio:

δ^3He_{cor} %

$^3He_{cor}$ TU $^3He_{cor}$ x10^{-14} cm^{3}STP/g

Corrected for terrigenic He **Age** ±1σ (y)

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; $^3He/^4He_{atmos.}$ = 1.384 x10^{-6}

published comments: Tritium data from bottle sample

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

report: r	Sender: Knowles	Organization: USGS	Program: FL-Knowles		
	Sample ID: Howey/992780006				
	Channel No.: 1	Tritium Bottle No.:		Date received: 10/7/99	
Sample Date: 8/30/99	Sampling Time: 1130	Altitude: 40 m	Temp.: 24.2 °C	Salinity: 0	

T Degas No. **14914** T Degas Date T Measurement Date 03/06/2000

Tritium: 2.233 ± 0.108 TU (1σ) 0 103

^{4}He bulb blank 1.276 $\times10^{-9}$ cm^3STP
Ingrown $^3He_{trit}$ 5.44762 $\times10^{-15}$ cm^3STP
$\%^3He_{trit}$ 67.4

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. **14914** He Extraction Date 11/9/1999 He Measurement Date 12/15/99

δ^3He: 21.23 ± 0.240 % (1σ) δ^3He_{cor} from other T (see above): 21.23 % δ^3He_{uncor}: 21.317 ± 0.242 % (1σ)

$^3He_{trit}$: 6.621 ± 0.070 TU (1σ) ^{3}He: 8.799 $\times10^{-14}$ cm^3 STP/g

Sample weight: 39.8 g

^{4}He: 5.244 ± 0.016 $\times10^{-8}$ cm^3STP/g (1σ) Δ^4He: 19.16 %

Ne: 20.304 ± 0.241 $\times10^{-8}$ cm^3STP/g (1σ) ΔNe: 13.72 %

Uncorrected Age ±1σ (y): 24.7 ± 0.7

Average crustal terrigenic $^3He/^4He$ ratio: 2 $\times10^{-8}$:

δ^3He_{cor}: 24.444 %
$^3He_{cor}$: 7.372 TU $^3He_{cor}$: 8.796 $\times10^{-14}$ cm^3STP/g
$^4He_{cor}$: 5.107 $\times10^{-8}$ cm^3STP/g % Terrigenic ^{4}He 2.6
$^4He_{terrigenic}$: 0.137 $\times10^{-8}$ cm^3STP/g

Corrected for terrigenic He — Age ±1σ (y): 26.2 ± 1.2

Site specific terrigenic $^3He/^4He$ ratio:

δ^3He_{cor} 24.444 % $^3He_{cor}$ 8.796 $\times10^{-14}$ cm^3STP/g
$^3He_{cor}$ 7.372 TU

Corrected for terrigenic He — Age ±1σ (y): ±

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; $^3He/^4He_{atmos.}$= 1.384 $\times10^{-6}$

published comments

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

LDEO NGL

report: r	Sender: Knowles	Organization: USGS	Program: FL-Knowles		
	Sample ID: Howey/992780006				
	Channel No.:	Tritium Bottle No.: 1		Date received: 10/7/99	
Sample Date: 8/30/99	Sampling Time: 1130	Altitude: 40 m	Temp.: 24.2 °C	Salinity: 0	

T Degas No. **1006285** T Degas Date 10/29/1999 T Measurement Date 02/21/2000

Tritium: 1.919 ± 0.050 TU (1σ) 0.050

^{4}He bulb blank 0.958 $\times 10^{-9}$ cm^{3}STP
Ingrown $^3He_{trit.}$ 10.9872 $\times 10^{-15}$ cm^{3}STP
%$^3He_{trit}$ 87.9

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. He Extraction Date He Measurement Date

δ^3He: ± % (1σ) δ^3He_{cor} from other T (see above): % δ^3He_{uncor}: ± % (1σ)

$^3He_{trit}$: ± TU (1σ) ^{3}He: $\times 10^{-14}$ cm^3 STP/g

Sample weight: g

^{4}He: ± $\times 10^{-8}$ cm^{3}STP/g (1σ) **Δ^4He:** %

Ne: ± $\times 10^{-8}$ cm^{3}STP/g (1σ) **ΔNe:** %

Uncorrected **Age** ±1σ (y)

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 $\times 10^{-8}$:

δ^3He_{cor}: %

$^3He_{cor}$: TU **$^3He_{cor}$:** $\times 10^{-14}$ cm^{3}STP/g

$^4He_{cor}$: $\times 10^{-8}$ cm^{3}STP/g % Terrigenic ^{4}He

$^4He_{terrigenic}$: $\times 10^{-8}$ cm^{3}STP/g

Corrected for terrigenic He **Age** ±1σ (y)

Site specific terrigenic ^{3}He/^{4}He ratio:

δ^3He_{cor} % **$^3He_{cor}$** $\times 10^{-14}$ cm^{3}STP/g

$^3He_{cor}$ TU

Corrected for terrigenic He **Age** ±1σ (y)

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; ^{3}He/$^4He_{atmos.}$= 1.384 $\times 10^{-6}$

published comments: Tritium data from bottle sample

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

LDEO NGL

report: r	Sender: Knowles	Organization: USGS	Program: FL-Knowles
Sample ID: Lake Louisa/992780008			
Channel No.: 1	Tritium Bottle No.:		Date received: 10/7/99
Sample Date: 9/7/99	Sampling Time: 1730	Altitude: 35 m	Temp.: 23.7 °C; Salinity: 0

T Degas No. **14913** T Degas Date T Measurement Date 03/06/2000

Tritium: 3.929 ± 0.242 TU (1σ) 0.242

^{4}He bulb blank 1.512 $\times 10^{-9}$ cm^3STP
Ingrown $^3He_{trit}$ 8.24727 $\times 10^{-15}$ cm^3STP
%$^3He_{trit}$ 74.5

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. **14913** He Extraction Date 11/9/1999 He Measurement Date 12/14/99

δ^3**He:** 55.70 ± 0.230 % (1σ) δ^3He_{cor} from other T (see above): 55.7 % δ^3He_{uncor}: 55.821 ± 0.232 % (1σ)

$^3He_{trit}$: 17.567 ± 0.080 TU (1σ) ^{3}He: 11.920 $\times 10^{-14}$ cm^3 STP/g

Sample weight: 39.4 g

^{4}**He:** 5.532 ± 0.014 $\times 10^{-8}$ cm^3STP/g (1σ) Δ^4**He:** 25.44 %

Ne: 22.465 ± 0.291 $\times 10^{-8}$ cm^3STP/g (1σ) Δ**Ne:** 25.3 %

Uncorrected Age ±1σ (y): 30.5 ± 0.9

Average crustal terrigenic $^3He/^4He$ ratio: 2 $\times 10^{-8}$:

δ^3He_{cor}: 50.702 %
$^3He_{cor}$: 16.551 TU $^3He_{cor}$: 11.924 $\times 10^{-14}$ cm^3STP/g
$^4He_{cor}$: 5.717 $\times 10^{-8}$ cm^3STP/g % Terrigenic ^{4}He -3.3
$^4He_{terrigenic}$: -0.185 $\times 10^{-8}$ cm^3STP/g

Corrected for terrigenic He — Age ±1σ (y): 29.6 ± 1.1

Site specific terrigenic $^3He/^4He$ ratio:

δ^3He_{cor} 50.702 % $^3He_{cor}$ 11.924 $\times 10^{-14}$ cm^3STP/g
$^3He_{cor}$ 16.551 TU

Corrected for terrigenic He — Age ±1σ (y): ±

constants: $\delta^3He_{equilibrium}$: -1.8 %; $\lambda_{1/2}$= .05577yr.$^{-1}$; $^3He/^4He_{atmos.}$= 1.384 $\times 10^{-6}$

published comments

Comments:

LDEO NGL

Noble Gas Laboratory
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report: r	Sender: Knowles	Organization: USGS	Program: FL-Knowles				
	Sample ID: Lake Louisa/992780008						
	Channel No.:	Tritium Bottle No.: 1		Date received: 10/7/99			
Sample Date: 9/7/99	Sampling Time: 1730	Altitude: 35 m	Temp.: 23.7 °C	Salinity: 0			

T Degas No. **1006284** T Degas Date 10/29/1999 T Measurement Date 02/21/2000

Tritium: 4.122 ± 0.082 TU (1σ) 0.079

^{4}He bulb blank 0.724 x10^{-9} cm^{3}STP
Ingrown ^{3}He$_{trit}$ 19.7434 x10^{-15} cm^{3}STP
%^{3}He$_{trit}$ 94.9

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. He Extraction Date He Measurement Date

δ^{3}He: ± % (1σ) δ^{3}He$_{cor}$ from other T (see above): % δ^{3}He$_{uncor}$: ± % (1σ)

^{3}He$_{trit}$: ± TU (1σ) ^{3}He: x10^{-14} cm^3 STP/g

Sample weight: g

^{4}He: ± x10^{-8} cm^{3}STP/g (1σ) **Δ^{4}He:** %

Ne: ± x10^{-8} cm^{3}STP/g (1σ) **ΔNe:** %

Uncorrected **Age** ±1σ (y)

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 x10^{-8}:

δ^{3}He$_{cor}$: %

^{3}He$_{cor}$: TU ^{3}He$_{cor}$: x10^{-14} cm^{3}STP/g

^{4}He$_{cor}$: x10^{-8} cm^{3}STP/g % Terrigenic ^{4}He

^{4}He$_{terrigenic}$: x10^{-8} cm^{3}STP/g

Corrected for terrigenic He **Age** ±1σ (y)

Site specific terrigenic ^{3}He/^{4}He ratio:

δ^{3}He$_{cor}$ % ^{3}He$_{cor}$ x10^{-14} cm^{3}STP/g

^{3}He$_{cor}$ TU

Corrected for terrigenic He **Age** ±1σ (y)

constants: δ^{3}He$_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; ^{3}He/^{4}He$_{atmos}$ = 1.384 x10^{-6}

published comments: Tritium data from bottle sample

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

report: r	Sender: Knowles	Organization: USGS	Program: FL-Knowles		
	Sample ID: Lake Mary/992780005				
	Channel No.: 1	Tritium Bottle No.:	Date received: 10/7/99		
Sample Date: 8/18/99	Sampling Time: 0900	Altitude: 20 m	Temp.: 24 °C	Salinity: 0	

T Degas No. **14916** T Degas Date T Measurement Date 03/06/2000

Tritium: 2.946 ± 0.117 TU (1σ) 0.117

^{4}He bulb blank 1.211 x10^{-9} cm^{3}STP
Ingrown ^{3}He$_{trit}$ 6.47657 x10^{-15} cm^{3}STP
%^{3}He$_{trit}$ 74.0

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. **14916** He Extraction Date 11/9/1999 He Measurement Date 12/14/99

δ^{3}He: 41.77 ± 0.240 % (1σ) δ^{3}He$_{cor}$ from other T (see above): 41.77 % δ^{3}He$_{uncor}$: 41.898 ± 0.237 % (1σ)

^{3}He$_{trit}$: 12.336 ± 0.070 TU (1σ) ^{3}He: 10.056 x10^{-14} cm^3 STP/g

Sample weight: 39.9 g

^{4}He: 5.125 ± 0.013 x10^{-8} cm^{3}STP/g (1σ) **Δ^{4}He:** 16.1 %

Ne: 21.482 ± 0.274 x10^{-8} cm^{3}STP/g (1σ) **ΔNe:** 19.86 %

Uncorrected
Age ±1σ (y)
29.5 ± 0.6

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 x10^{-8}:

δ^{3}He$_{cor}$: 33.642 %
^{3}He$_{cor}$: 10.609 TU **^{3}He$_{cor}$:** 10.062 x10^{-14} cm^{3}STP/g
^{4}He$_{cor}$: 5.440 x10^{-8} cm^{3}STP/g % Terrigenic ^{4}He **-6.1**
^{4}He$_{terrigenic}$: -0.315 x10^{-8} cm^{3}STP/g

Corrected for terrigenic He
Age ±1σ (y)
27.4 ± 1.0

Site specific terrigenic ^{3}He/^{4}He ratio:

δ^{3}He$_{cor}$ 33.642 % **^{3}He$_{cor}$** 10.062 x10^{-14} cm^{3}STP/g
^{3}He$_{cor}$ 10.609 TU

Corrected for terrigenic He
Age ±1σ (y)
±

constants: δ^{3}He$_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; ^{3}He/^{4}He$_{atmos}$ = 1.384 x10^{-6}

published comments

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

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report: r	Sender: Knowles	Organization: USGS	Program: FL-Knowles		
	Sample ID: Lake Mary/992780005				
	Channel No.:	Tritium Bottle No.: 1		Date received: 10/7/99	
Sample Date: 8/18/99	Sampling Time: 0900	Altitude: 20 m	Temp.: 24 °C	Salinity: 0	

T Degas No. **1006283** T Degas Date 10/29/1999 T Measurement Date 02/21/2000

Tritium: 2.715 ± 0.057 TU (1σ) 0.057

^{4}He bulb blank 0.593 x10^{-9} cm^3STP
Ingrown $^3He_{trit}$ 14.3343 x10^{-15} cm^3STP
%$^3He_{trit}$ 94.2

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. He Extraction Date He Measurement Date

δ^3He: ± % (1σ) δ^3He_{cor} from other T (see above): % δ^3He_{uncor}: ± % (1σ)

$^3He_{trit}$: ± TU (1σ) ^{3}He: x10^{-14} cm^3 STP/g

Sample weight: g

^{4}He: ± x10^{-8} cm^3STP/g (1σ) **Δ^4He:** %

Ne: ± x10^{-8} cm^3STP/g (1σ) **ΔNe:** %

Uncorrected **Age** ±1σ (y)

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 x10^{-8}:

δ^3He_{cor}: %

$^3He_{cor}$: TU $^3He_{cor}$: x10^{-14} cm^3STP/g

$^4He_{cor}$: x10^{-8} cm^3STP/g % Terrigenic ^{4}He

$^4He_{terrigenic}$: x10^{-8} cm^3STP/g

Corrected for terrigenic He **Age** ±1σ (y)

Site specific terrigenic ^{3}He/^{4}He ratio:

δ^3He_{cor} % $^3He_{cor}$ x10^{-14} cm^3STP/g

$^3He_{cor}$ TU

Corrected for terrigenic He **Age** ±1σ (y)

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; ^{3}He/$^4He_{atmos.}$ = 1.384 x10^{-6}

published comments Tritium data from bottle sample

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

report: r	Sender: Knowles	Organization: USGS	Program: FL-Knowles		
	Sample ID: Mascotte/992780010				
	Channel No.: 1	Tritium Bottle No.:		Date received: 10/7/99	
Sample Date: 9/22/99	Sampling Time: 1030	Altitude: 40 m	Temp.: 23.4 °C	Salinity: 0	

T Degas No. **14910** T Degas Date T Measurement Date 03/06/2000

Tritium: 4.014 ± 0.138 TU (1σ) 0.138

^{4}He bulb blank 1.839 x10^{-9} cm^{3}STP
Ingrown $^3He_{trit}$ 8.96508 x10^{-15} cm^{3}STP
%$^3He_{trit}$ 71.5

Alternative tritium value: ± **TU (1σ)** comment:

He Extraction No. **14910** He Extraction Date 11/9/1999 He Measurement Date 12/14/99

δ^3He: 53.83 ± 0.230 % (1σ) δ^3He_{cor} from other T (see above): 53.83 % δ^3He_{uncor}: 53.930 ± 0.233 % (1σ)

$^3He_{trit}$: 16.256 ± 0.080 TU (1σ) ^{3}He: 11.255 x10^{-14} cm^{3}STP/g

Sample weight: 40.1 g

^{4}He: 5.286 ± 0.016 x10^{-8} cm^{3}STP/g (1σ) **Δ^{4}He: 19.85 %**

Ne: 21.237 ± 0.277 x10^{-8} cm^{3}STP/g (1σ) **ΔNe: 18.26 %**

Uncorrected **Age** ±1σ (y): **29.0 ± 0.5**

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 x10^{-8}:

δ^3He_{cor}: 51.847 %
$^3He_{cor}$: 15.874 TU $^3He_{cor}$: 11.256 x10^{-14} cm^{3}STP/g
$^4He_{cor}$: 5.356 x10^{-8} cm^{3}STP/g % Terrigenic ^{4}He -1.3
$^4He_{terrigenic}$: -0.070 x10^{-8} cm^{3}STP/g

Corrected for terrigenic He **Age** ±1σ (y): **28.7 ± 0.8**

Site specific terrigenic ^{3}He/^{4}He ratio:

δ^3He_{cor} 51.847 % $^3He_{cor}$ 11.256 x10^{-14} cm^{3}STP/g
$^3He_{cor}$ 15.874 TU

Corrected for terrigenic He **Age** ±1σ (y): ±

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; $^3He/^4He_{atmos.}$ = 1.384 x10^{-6}

published comments

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

report: r	Sender: Knowles	Organization: USGS	Program: FL-Knowles		
	Sample ID: Mascotte/992780010				
	Channel No.:	Tritium Bottle No.: 1		Date received: 10/7/99	
Sample Date: 9/22/99	Sampling Time: 1030	Altitude: 40 m	Temp.: 23.4 °C	Salinity: 0	

T Degas No. **1006280** T Degas Date 10/29/1999 T Measurement Date 02/21/2000

Tritium: 3.638 ± 0.078 TU (1σ) 0.078

^4He bulb blank 0.657 $x10^{-9}$ cm^3STP
Ingrown $^3He_{trit}$ 13.9591 $x10^{-15}$ cm^3STP
$\%^3He_{trit}$ 93.4

Alternative tritium value: ± **TU (1σ)** comment:

He Extraction No. He Extraction Date He Measurement Date

δ^3He: ± % (1σ) δ^3He_{cor} from other T (see above): % δ^3He_{uncor}: ± % (1σ)

$^3He_{trit}$: ± TU (1σ) ^3He: $x10^{-14}$ cm^3 STP/g

Sample weight: g

^4He: ± $x10^{-8}$ cm^3STP/g (1σ) **Δ^4He:** %

Ne: ± $x10^{-8}$ cm^3STP/g (1σ) **ΔNe:** %

Uncorrected **Age** $\pm 1\sigma$ (y)

Average crustal terrigenic $^3He/^4He$ ratio: 2 $x10^{-8}$:

δ^3He_{cor}: %
$^3He_{cor}$: TU **$^3He_{cor}$:** $x10^{-14}$ cm^3STP/g
$^4He_{cor}$: $x10^{-8}$ cm^3STP/g % Terrigenic ^4He
$^4He_{terrigenic}$: $x10^{-8}$ cm^3STP/g

Corrected for terrigenic He **Age** $\pm 1\sigma$ (y)

Site specific terrigenic $^3He/^4He$ ratio:

δ^3He_{cor} % **$^3He_{cor}$** $x10^{-14}$ cm^3STP/g
$^3He_{cor}$ TU

Corrected for terrigenic He **Age** $\pm 1\sigma$ (y)

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; $^3He/^4He_{atmos}$ = 1.384 $x10^{-6}$

published comments Tritium data from bottle sample

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

report: r	Sender: Knowles	Organization: USGS	Program: FL-Knowles		
Sample ID: Sunset lakes/992780011					
Channel No.: 1	Tritium Bottle No.:		Date received: 10/7/99		
Sample Date: 9/22/99	Sampling Time: 1230	Altitude: 37 m	Temp.: 23.1 °C	Salinity: 0	

T Degas No. **14911** T Degas Date T Measurement Date 03/06/2000

Tritium: 4.654 ± 0.142 TU (1σ) 0.142

^{4}He bulb blank 1.189 x10^{-9} cm^{3}STP
Ingrown ^{3}He$_{trit}$ 8.97246 x10^{-15} cm^{3}STP
%^{3}He$_{trit}$ 81.6

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. **14911** He Extraction Date 11/9/1999 He Measurement Date 12/15/99

δ^3He: 66.24 ± 0.230 % (1σ) δ^3He$_{cor}$ from other T (see above): 66.24 % δ^3He$_{uncor}$: 66.360 ± 0.232 % (1σ)

^{3}He$_{trit}$: 19.918 ± 0.090 TU (1σ) ^{3}He: 12.170 x10^{-14} cm^3 STP/g

Sample weight: 39.4 g

^{4}He: 5.290 ± 0.014 x10^{-8} cm^{3}STP/g (1σ) Δ^4He: 19.78 %

Ne: 20.953 ± 0.251 x10^{-8} cm^{3}STP/g (1σ) ΔNe: 16.38 %

Uncorrected Age ±1σ (y): 29.8 ± 0.5

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 x10^{-8}:

δ^3He$_{cor}$: 66.978 %
^{3}He$_{cor}$: 20.047 TU ^{3}He$_{cor}$: 12.170 x10^{-14} cm^{3}STP/g
^{4}He$_{cor}$: 5.266 x10^{-8} cm^{3}STP/g % Terrigenic ^{4}He 0.4
^{4}He$_{terrigenic}$: 0.024 x10^{-8} cm^{3}STP/g

Corrected for terrigenic He — Age ±1σ (y): 29.9 ± 0.7

Site specific terrigenic ^{3}He/^{4}He ratio:

δ^3He$_{cor}$ 66.978 % ^{3}He$_{cor}$ 12.170 x10^{-14} cm^{3}STP/g
^{3}He$_{cor}$ 20.047 TU

Corrected for terrigenic He — Age ±1σ (y): ±

constants: δ^3He$_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; ^{3}He/^{4}He$_{atmos}$ = 1.384 x10^{-6}

published comments

Comments:

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report **r**	Sender	Knowles	Organization	USGS	Program FL-Knowles
	Sample ID	Sunset lakes/992780011			
	Channel No.		Tritium Bottle No.	1	Date received 10/7/99
Sample Date	9/22/99	Sampling Time	1230	Altitude 37 m	Temp. 23.1 °C Salinity 0

T Degas No. **1006286** T Degas Date 11/12/1999 T Measurement Date 02/21/2000

^{4}He bulb blank 1.061 x10^{-9} cm^3STP
Ingrown $^3He_{trit}$ 15.5774 x10^{-15} cm^3STP
%$^3He_{trit}$ 90.5

Tritium: 4.130 ± 0.089 TU (1σ) 0.089

Alternative tritium value: ± **TU (1σ)** comment:

He Extraction No. He Extraction Date He Measurement Date

δ^3He: ± % (1σ) δ^3He_{cor} from other T (see above): % δ^3He_{uncor}: ± % (1σ)

$^3He_{trit}$: ± TU (1σ) ^{3}He: x10^{-14} cm^3 STP/g

Sample weight: g

^{4}He: ± x10^{-8} cm^3STP/g (1σ) **Δ^4He:** % Uncorrected **Age ±1σ (y)**

Ne: ± x10^{-8} cm^3STP/g (1σ) **ΔNe:** %

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 x10^{-8}:

δ^3He_{cor}: %

$^3He_{cor}$: TU **$^3He_{cor}$:** x10^{-14} cm^3STP/g

$^4He_{cor}$: x10^{-8} cm^3STP/g % Terrigenic ^{4}He

$^4He_{terrigenic}$: x10^{-8} cm^3STP/g

Corrected for terrigenic He **Age ±1σ (y)**

Site specific terrigenic ^{3}He/^{4}He ratio:

δ^3He_{cor} % **$^3He_{cor}$** x10^{-14} cm^3STP/g

$^3He_{cor}$ TU

Corrected for terrigenic He **Age ±1σ (y)**

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; $^3He/^4He_{atmos.}$= 1.384 x10^{-6}

published comments Tritium data from bottle sample

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

report: r	Sender: Knowles	Organization: USGS	Program: FL-Knowles		
	Sample ID: Turnpike/992780002				
	Channel No.: 2	Tritium Bottle No.:	Date received: 10/7/99		
Sample Date: 8/11/99	Sampling Time: 1000	Altitude: 55 m	Temp.: 24.6 °C	Salinity: 0	

T Degas No. **14931** T Degas Date T Measurement Date 03/06/2000

Tritium: 3.056 ± 0.121 TU (1σ) 0.121

^{4}He bulb blank 1.012 $\times10^{-9}$ cm^3STP
Ingrown $^3He_{trit}$ 6.07394 $\times10^{-15}$ cm^3STP
$\%^3He_{trit}$ 76.8

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. **14931** He Extraction Date 11/15/1999 He Measurement Date 12/15/99

δ^3He: 35.60 ± 0.240 % (1σ) δ^3He_{cor} from other T (see above): 35.6 % δ^3He_{uncor}: 35.749 ± 0.237 % (1σ)

$^3He_{trit}$: 11.047 ± 0.080 TU (1σ) ^{3}He: 10.065 $\times10^{-14}$ cm^3 STP/g

Sample weight: 39.8 g

^{4}He: 5.363 ± 0.015 $\times10^{-8}$ cm^3STP/g (1σ) **Δ^4He:** 22.22 %

Ne: 21.121 ± 0.246 $\times10^{-8}$ cm^3STP/g (1σ) **ΔNe:** 18.85 %

Uncorrected Age ±1σ (y): 27.4 ± 0.6

Average crustal terrigenic $^3He/^4He$ ratio: 2 $\times10^{-8}$:

δ^3He_{cor}: 35.836 %
$^3He_{cor}$: 11.098 TU **$^3He_{cor}$:** 10.065 $\times10^{-14}$ cm^3STP/g
$^4He_{cor}$: 5.354 $\times10^{-8}$ cm^3STP/g % Terrigenic ^{4}He 0.2
$^4He_{terrigenic}$: 0.009 $\times10^{-8}$ cm^3STP/g

Corrected for terrigenic He: Age ±1σ (y): 27.5 ± 0.9

Site specific terrigenic $^3He/^4He$ ratio:

δ^3He_{cor} 35.836 % **$^3He_{cor}$** 10.065 $\times10^{-14}$ cm^3STP/g
$^3He_{cor}$ 11.098 TU

Corrected for terrigenic He: Age ±1σ (y): ±

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; $^3He/^4He_{atmos}$ = 1.384 $\times10^{-6}$

published comments:

Comments:

Noble Gas Laboratory
Lamont-Doherty Earth Observatory
Columbia University, New York

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report r	Sender	Knowles	Organization	USGS	Program	FL-Knowles	
	Sample ID	Turnpike/992780002					
	Channel No.		Tritium Bottle No.	1		Date received	10/7/99
Sample Date	8/11/99	Sampling Time	1000	Altitude	55 m	Temp. 24.6 °C	Salinity 0

T Degas No. **1006278** T Degas Date 10/29/1999 T Measurement Date 02/22/2000

Tritium: 2.752 ± 0.081 TU (1σ) 0.081

^{4}He bulb blank 0.817 x10^{-9} cm^{3}STP
Ingrown $^3He_{trit}$ 11.2069 x10^{-15} cm^{3}STP
%$^3He_{trit}$ 89.8

Alternative tritium value: ± TU (1σ) comment:

He Extraction No. He Extraction Date He Measurement Date

δ^3He: ± % (1σ) δ^3He_{cor} from other T (see above): % δ^3He_{uncor}: ± % (1σ)

$^3He_{trit}$: ± TU (1σ) ^{3}He: x10^{-14} cm^3 STP/g

Sample weight: g

^{4}He: ± x10^{-8} cm^{3}STP/g (1σ) **Δ^4He:** %

Ne: ± x10^{-8} cm^{3}STP/g (1σ) **ΔNe:** %

Uncorrected Age ±1σ (y)

Average crustal terrigenic ^{3}He/^{4}He ratio: 2 x10^{-8}:

δ^3He_{cor}: %
$^3He_{cor}$: TU **$^3He_{cor}$:** x10^{-14} cm^{3}STP/g
$^4He_{cor}$: x10^{-8} cm^{3}STP/g % Terrigenic ^{4}He
$^4He_{terrigenic}$: x10^{-8} cm^{3}STP/g

Corrected for terrigenic He
Age ±1σ (y)

Site specific terrigenic ^{3}He/^{4}He ratio:

δ^3He_{cor} % **$^3He_{cor}$** x10^{-14} cm^{3}STP/g
$^3He_{cor}$ TU

Corrected for terrigenic He
Age ±1σ (y)

constants: $\delta^3He_{equilibrium}$: -1.8 %; λ_{3H}= .05577yr.$^{-1}$; ^{3}He/$^4He_{atmos.}$= 1.384 x10^{-6}

published comments Tritium data from bottle sample

Comments: