

Case Study/

## Vulnerability of a Public Supply Well in a Karstic Aquifer to Contamination

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### Abstract

To assess the vulnerability of ground water to contamination in the karstic Upper Floridan aquifer (UFA), age-dating tracers and selected anthropogenic and naturally occurring compounds were analyzed in multiple water samples from a public supply well (PSW) near Tampa, Florida. Samples also were collected from 28 monitoring wells in the UFA and the overlying surficial aquifer system (SAS) and intermediate confining unit located within the contributing recharge area to the PSW. Age tracer and geochemical data from the earlier stage of the study (2003 through 2005) were combined with new data (2006) on concentrations of sulfur hexafluoride (SF<sub>6</sub>), tritium (<sup>3</sup>H), and helium-3, which were consistent with binary mixtures of water for the PSW dominated by young water (less than 7 years). Water samples from the SAS also indicated mostly young water (less than 7 years); however, most water samples from monitoring wells in the UFA had lower SF<sub>6</sub> and <sup>3</sup>H concentrations than the PSW and SAS, indicating mixtures containing high proportions of older water (more than 60 years). Vulnerability of the PSW to contamination was indicated by predominantly young water and elevated nitrate-N and volatile organic compound concentrations that were similar to those in the SAS. Elevated arsenic (As) concentrations (3 to 19 µg/L) and higher As(V)/As(III) ratios in the PSW than in water from UFA monitoring wells indicate that oxic water from the SAS likely mobilizes As from pyrite in the UFA matrix. Young water found in the PSW also was present in UFA monitoring wells that tap a highly transmissive zone (43- to 53-m depth) in the UFA.

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### Introduction

Recent studies have found that public supply wells (PSWs) in the United States are susceptible to contamination from various anthropogenic compounds, such as solvents, disinfection by-products, other volatile organic compounds (VOCs) (Ivahnenko and Zogorski 2006; Schaap

and Zogorski 2006; Zogorski et al. 2006), and pesticides (Gilliom et al. 2006). Ground water contamination from nutrients, such as nitrate, is widespread (Nolan et al. 1998), particularly in karstic aquifers (Katz 2004). In addition, other ground water studies have found that high levels of naturally occurring contaminants, such as radon (Sowerby et al. 2000) and arsenic (As) (Focazio et al. 1999; Welch et al. 2000), are detected in some drinking water wells.

In response to health concerns, the USGS National Water Quality Assessment (NAWQA) Program began a series of studies in 2001 to assess the vulnerability of PSWs to contamination. These studies of the transport of anthropogenic and naturally occurring contaminants (TANC) to PSWs have been conducted at regional and small scales at several sites in the United States (Eberts et al. 2005). The TANC studies were developed based on previous NAWQA studies that found low levels of mixtures of contaminants in ground water beneath urban areas across the United States (Hamilton et al. 2004).

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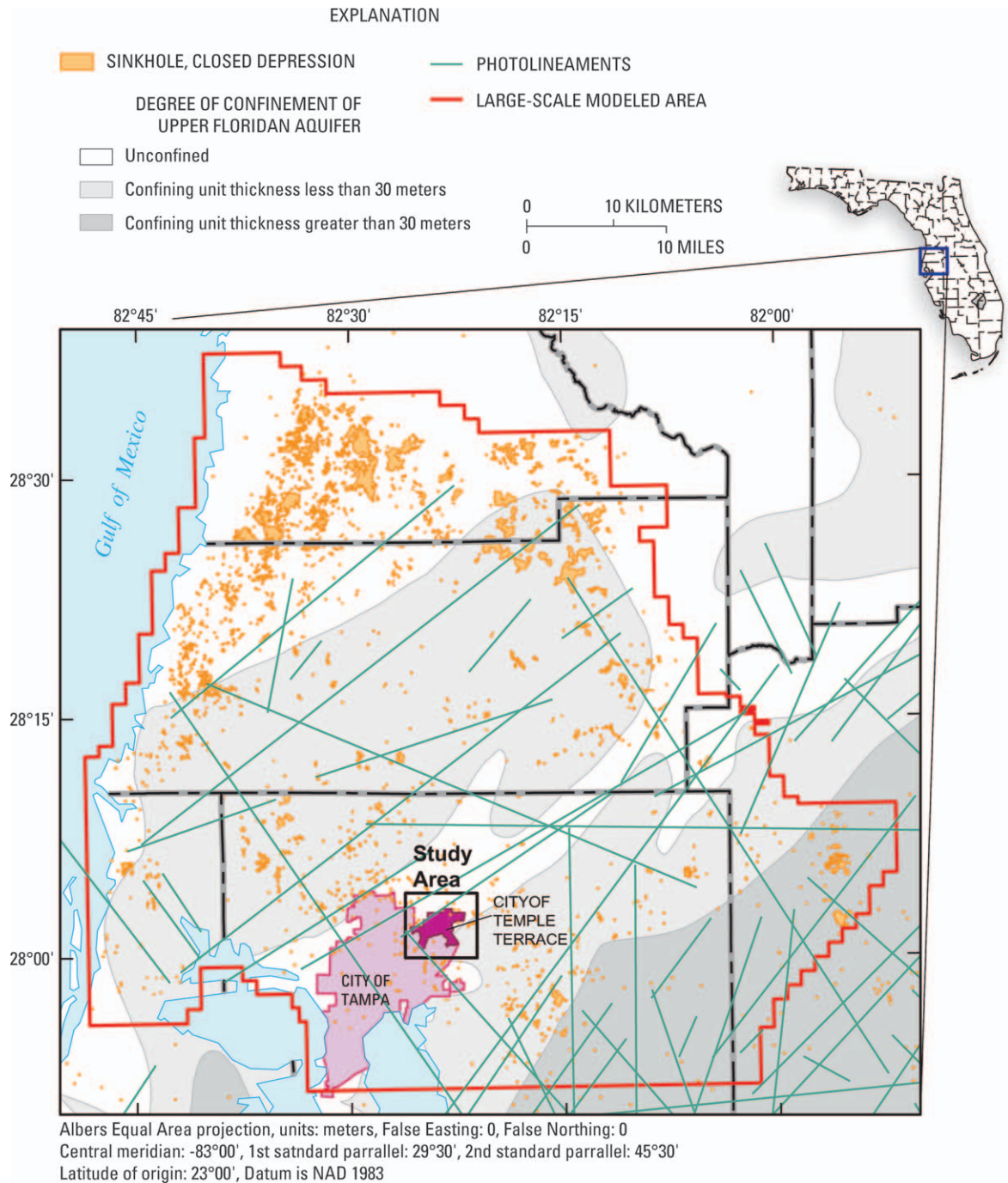
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The Floridan aquifer system provides drinking water to millions of people throughout the southeastern United States. The presence of numerous karst features, such as sinkholes, facilitates the downward movement of water from the land surface and from highly permeable units overlying the Upper Floridan aquifer (UFA). Solution features trending predominantly in a northeast-southwest direction have been mapped throughout west-central Florida, indicating a regionally extensive karst terrane (Knochenmus and Robinson 1996; Figure 1). The PSW near Tampa, Florida, selected for this TANC

study was sampled for a variety of chemical and bacteriological constituents as part of the USGS NAWQA Program in 2002 (Paschke 2006). Several contaminant groups were found in water from the PSW, including nitrate, VOCs, pesticides, uranium, and As, at concentrations less than maximum contaminant levels. Several of these compounds have been detected in other community water system wells in the northern Tampa Bay area (Metz et al. 2007). These studies did not address mechanisms of contaminant transport to PSWs in the karstic UFA.



**Figure 1. Map showing large- and small-scale study areas, photolineaments, degree of confinement of the UFA, and selected karst features in west-central Florida (modified from Katz et al. 2007).**

This article combines new information on ground water ages and geochemistry from 2006 with selected data (age tracers, nitrate, VOCs, and As) from the earlier stage of the study (2002 through 2005) (Katz et al. 2007) to assess the vulnerability of a PSW to contamination in the karstic UFA in west-central Florida. The combined use of ground water age dating with isotopic and other chemical tracers (such as nitrate, VOCs, and As) provides critical information on modes of contaminant transport to PSWs from anthropogenic sources at the land surface and from water-rock interactions. Construction and operational practices of the studied PSW are similar to many other community water system wells that supply water in the Tampa Bay region, and in other karstic aquifers in the United States.

## Description of Study Area

The study area is 86 km<sup>2</sup> and encompasses the city of Temple Terrace, which is located northeast of Tampa, Florida (Figure 1). PSWs in Temple Terrace tap the UFA, which underlies most of the southeastern United States and is a significant drinking water source for the Tampa Bay region, as well as about 9 million people living in parts of Alabama, Florida, Georgia, and South Carolina (Marella and Berndt 2005).

The population of Temple Terrace has grown exponentially during the past 50 years—with about 430 people in 1950, 10,751 people in 1974, and 20,918 people in 2000. The population density in 2000 was 1135 people per km<sup>2</sup>. The growth in population occurred while land use transitioned from agricultural in 1950 to commercial and residential in the 1970s and later. The average withdrawal rate for the selected PSW was 884 m<sup>3</sup>/d in 2000 (C. Crandall, USGS, written communication, 2007). Temple Terrace is located on a local topographic high, with land surface elevations close to 27 m along the western edge of the city to less than 6 m at the Hillsborough River. Urban drainage within Temple Terrace is routed to a series of stormwater retention basins.

Average annual rainfall in the Tampa area was 114 cm (1971 through 2000) at the National Oceanic and Atmospheric Administration station at the Tampa International Airport (National Climatic Data Center, National Oceanic and Atmospheric Agency 2004). On average, about 60% of the rainfall occurs from June through September. August is typically the wettest month, with about 17% of the annual rainfall. November is typically the driest month, with slightly less than 4% of the annual rainfall.

## Hydrogeology

The geology of the study area consists of sand, clay, and carbonate rocks that were deposited primarily in a marine environment. The geological framework is characterized by layers of sand to clayey sand to sandy clay that overlie a highly weathered limestone sequence. Interspersed throughout the study area are a number of localized surface or buried depressions called sinkholes that disrupt this layering. Numerous deep sinkholes are

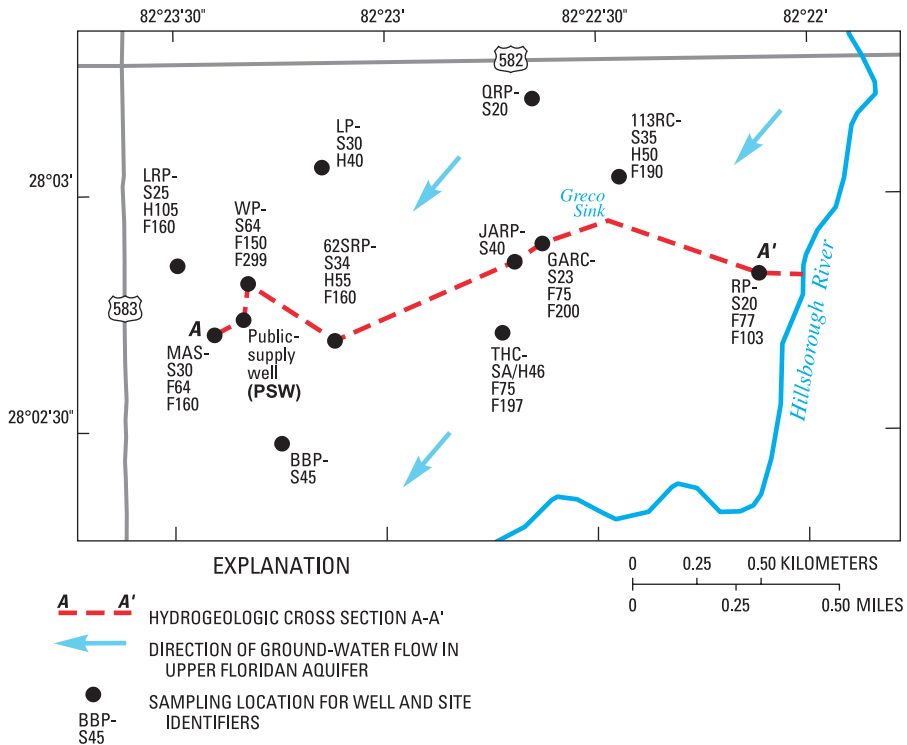
present in the floodplain of the Hillsborough River. The area north of Temple Terrace also contains large sinkholes; several are more than 60 m deep (Stewart et al. 1978). Some of these sinkholes are open to the UFA and may receive water from the Hillsborough River or wetland areas near the sinks.

Principal hydrogeologic units within the study area include the surficial aquifer system (SAS), intermediate confining unit (ICU), and the UFA, as shown in a generalized east-west section through the study area (Figures 2 and 3). A detailed description of the hydrogeology along with lithologic and mineralogical information obtained from analysis of core material from well drilling are compiled by Katz et al. (2007). This article briefly summarizes relevant hydrogeologic information that relates to ground water chemistry and age, and ground water flow patterns.

The SAS is a permeable hydrogeologic unit that is unconfined, is contiguous with land surface, and consists of unconsolidated to poorly indurated clastic deposits of the undifferentiated surficial deposits (Southeastern Geological Society 1986). Depth to the water table in the SAS ranges from about 3 to 15 m below land surface. The SAS is recharged by rainfall, and in some areas of the study area, recharge is relatively rapid because the surficial sands are highly permeable and the water table is relatively close to land surface. This hydrogeologic unit is not used as a major source of water supply because of the relatively low yields to wells (less than 19 L/min), high iron content, and the potential for contamination. Water table elevations in the SAS generally are above the potentiometric surface of the UFA (C. Crandall, USGS, written communication, 2007).

The ICU is a nonwater-yielding layer that controls the downward leakage between the SAS and the UFA (Figure 3). The ICU in the study area varies in color, composition, and permeability. This unit has varying amounts of sand, clay, and chert. The clay may be calcareous in places, particularly near the underlying limestone contact. The extent, thickness, and permeability of the clay unit are variable throughout the study area. Breaches form in this clay unit from localized subsidence activity that occurs when the underlying limestone dissolves and the overlying clay layers collapse. Generally, ground water moves laterally within the SAS and moves downward to the UFA through breaches in the ICU, where present. Many of these breaches in the ICU serve as preferential flow paths to the underlying UFA.

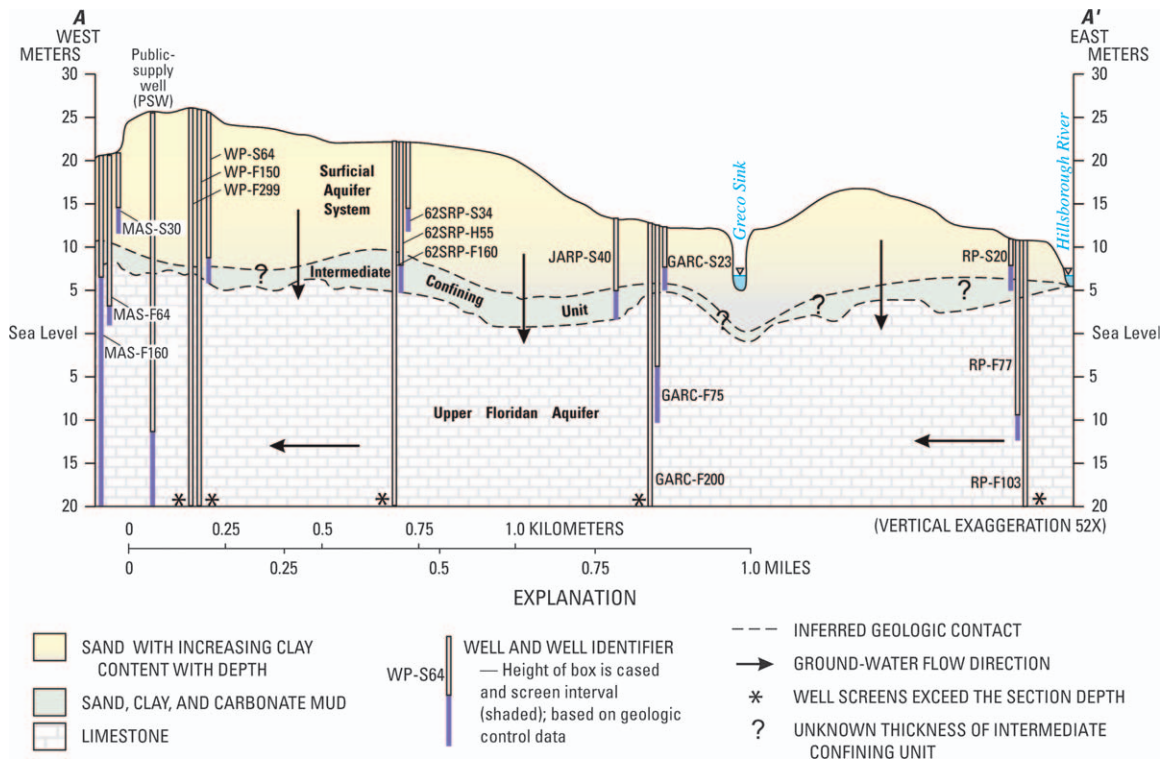
The UFA is the major source of water supply within the study area and consists of limestone and dolomite that contain many solution-enlarged fractures, which commonly yield large supplies of water to wells. Caliper logs of production and monitoring wells show sections of relatively large (larger than 1 m) borehole diameters (Stewart et al. 1978). The most productive water-yielding zone of the UFA in the Temple Terrace area is a cavernous zone ranging from 37 to 55 m below land surface (Stewart et al. 1978). Wells that tap this zone can yield as much as 5700 L/min.



**Figure 2. Map showing line of hydrogeologic section A to A', sampling site locations, and direction of ground water flow in the UFA in the study area (modified from Katz et al. 2007).**

As part of the earlier stage of the study (Katz et al. 2007), geophysical measurements were made in the open interval of the PSW borehole (36 to 53 m below land surface) in October 2004 (J.H. Williams, USGS, written

communication, 2007) to obtain detailed information on aquifer properties and dominant flow zones. Geophysical logs indicated that the PSW penetrates high-flow zones at 46.8 and 49.2 m below land surface (Katz et al. 2007).



**Figure 3. Generalized hydrogeologic cross section of the Temple Terrace, Florida, study area (modified from Katz et al. 2007).**

Borehole flow (electromagnetic and spinner flowmeter methods) was downward under ambient conditions from the upper to the lower zone. Under pumping conditions, the lower zone contributed 70% of the 1020 L/min discharged from the well. Flowmeter model analysis suggested that the lower zone had a transmissivity about three times higher than that of the upper zone, and there was about 0.09-m hydraulic head difference between the zones. Caliper and televiwer logs revealed large solution openings in the UFA limestone at depths greater than 47 m. Specific conductance decreased substantially in the 45- to 53-m zone, possibly indicating the downward movement of water from the SAS, which has lower conductance than water from the UFA.

Based on analyses of particle size distribution, bulk density, and moisture content of core material, estimates of recharge to the UFA range from 0.8 to 43 cm/year, with a median value of 13 cm/year (R. Healy, USGS, written communication, 2004). Based on data from an aquifer test conducted in March 1975 for a PSW cased to 28 m with an open hole to 146 m, with an average storage coefficient of  $3.4 \times 10^{-4}$ , transmissivity values for the UFA ranged from 2700 to 12,100 m<sup>2</sup>/d (Stewart et al. 1978). The regional ground water flow direction in the UFA is generally from the north-northeast to south-southwest in the study area (Figure 2).

## Methods

Wells were installed in the contributing recharge area of the PSW, which was delineated using a regional ground water flow model with particle-tracking software and a stochastic model that incorporated fracture flow (C. Crandall, USGS, written communication, 2007). Detailed information on well drilling, coring, and construction methods is described in other reports (Paschke 2006; Katz et al. 2007). During the first phase of well drilling, 15 wells were installed in five well nests. Each nest contained three wells that consisted of one shallow well screened in the SAS, one well screened near the top of the UFA, and one deep well in the UFA. Because the ICU was absent at many locations, only one well was installed in that unit during the first phase. During the second phase of well drilling, another 14 monitoring wells were installed.

## Collection and Analysis of Water Samples

Water samples were collected from monitoring wells and the PSW during 2003 through 2005 (Katz et al. 2007) according to NAWQA protocols (Koterba et al. 1995; Lapham et al. 1995). Each well was purged a minimum of three casing volumes, and water samples were collected after field properties (temperature, pH, specific conductance, turbidity, and dissolved oxygen) had stabilized. Alkalinity was measured in the field using fixed end point titration methods.

As part of the earlier stage of the study, samples of ground water and surface water were analyzed for major ions, nutrients, dissolved organic carbon, 128 pesticides

and pesticide degradates, 85 VOCs, stable isotopes (carbon, nitrogen, oxygen, hydrogen, and sulfur), dissolved gases (nitrogen, argon, carbon dioxide, methane, sulfur hexafluoride [SF<sub>6</sub>], and helium), trace elements, As speciation, uranium, and radon-222 (Katz et al. 2007). Detailed sampling and analytical methods are described by Katz et al. (2007) and in references contained therein. This article summarizes data for nitrate, VOCs, As, and redox indicators.

## Age Dating of Ground Water

Water samples were collected and analyzed from selected wells for the transient environmental tracer <sup>3</sup>H, its radioactive decay product (tritogenic <sup>3</sup>He [<sup>3</sup>He<sub>trit</sub>]), and SF<sub>6</sub>. Water samples from the earlier stage of the study were collected during 2003 through 2005 (Katz et al. 2007); however, selected sites were targeted for additional age dating in 2006 and are included in this article. Anthropogenic activities, such as industrial processes and atmospheric testing of thermonuclear devices, have released SF<sub>6</sub> and <sup>3</sup>H into the atmosphere in low but measurable concentrations (Figure 4). Precipitation that incorporates SF<sub>6</sub> and <sup>3</sup>H from the atmosphere infiltrates into the ground and carries a particular chemical or isotopic signature related to atmospheric conditions at the time of recharge to ground water. Tritium (<sup>3</sup>H) in rainfall was measured at the International Atomic Energy Agency precipitation monitoring station in Ocala, Florida, which is about 175 km northeast of the Temple Terrace study area. Atmospheric weapons testing beginning in the early 1950s increased <sup>3</sup>H concentrations in rainfall in this area to a maximum of several hundred <sup>3</sup>H units during the mid-1960s, followed by a nearly logarithmic decrease in concentrations to the present (Figure 4). Combined measurements of <sup>3</sup>H and its daughter product of radioactive decay, <sup>3</sup>He<sub>trit</sub>, define a relatively stable tracer of the initial <sup>3</sup>H input to ground water (Schlosser et al. 1988 1989; Solomon and Sudicky 1991). The recharge temperature and the quantity of dissolved excess air (Heaton and Vogel 1981) are determined from gas chromatography analyses of nitrogen gas and argon in the headspace of water samples collected in the field (Busenberg et al. 1993). An apparent age of the sampled water is determined from a comparison of the partial pressure of SF<sub>6</sub> in the sample, calculated from measured concentrations using solubility data, with the record of atmospheric partial pressures over the northern hemisphere at different times (Figure 4). The tritium/tritogenic helium-3 (<sup>3</sup>H/<sup>3</sup>He<sub>trit</sub>) and SF<sub>6</sub> dating methods assume that gas exchange between the unsaturated zone and air is fast but that shallow ground water remains closed to gas exchange after recharge (Schlosser et al. 1989; Plummer and Busenberg 1999; Busenberg and Plummer 2000).

Ground water samples for the determination of <sup>3</sup>H/<sup>3</sup>He<sub>trit</sub>, <sup>4</sup>He, and Ne were collected in pinched-off copper tubes while applying back pressure to prevent formation of gas bubbles (Katz et al. 2007) and analyzed using quantitative gas extraction followed by mass spectrometric techniques (Schlosser et al. 1989; Ludin et al. 1998;

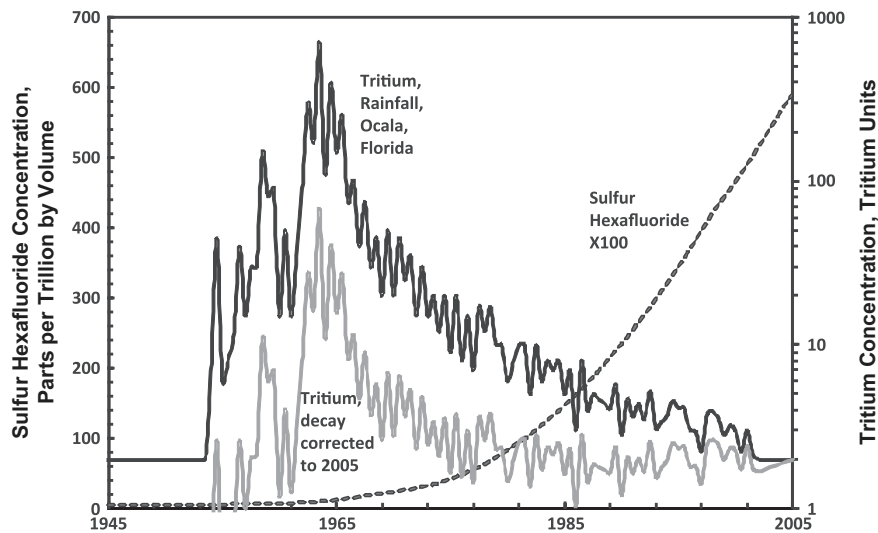


Figure 4. Plot showing input of SF<sub>6</sub> to the atmosphere in the northern hemisphere and <sup>3</sup>H concentrations in rainfall from Ocala, Florida, during 1950 through 2005. <sup>3</sup>H concentrations that are decay corrected to 2005 are also shown.

Bayer et al. 1989; Beyerle et al. 2000). Ground water samples for the SF<sub>6</sub> dating method were collected and analyzed using methods described by Busenberg and Plummer (2000).

#### Assessing Ground Water Age Distributions Using Lumped-Parameter Models

Although analytical methods are capable of determining extremely low concentrations of the tracers SF<sub>6</sub>, <sup>3</sup>H, and <sup>3</sup>He in ground water, the subsequent interpretation of age or mean residence time of ground water in complex karstic aquifer systems still is fraught with considerable uncertainty. In many previous studies where SF<sub>6</sub> and <sup>3</sup>H/<sup>3</sup>He<sub>trit</sub> have been used to date ground water, flow systems were relatively well characterized and water samples typically were collected from discrete depth intervals. Extending tracer age-dating techniques to wells with large open intervals in complex karstic systems requires an analysis of several possible ground water flow scenarios.

Lumped-parameter models are used in this study to estimate the mean residence time and age distribution of ground water in the SAS, ICU, and UFA. These models consider an aquifer system as a homogeneous compartment in which tracer input concentrations are converted to tracer output concentrations according to the system response function used (Zuber 1986; Maloszewski and Zuber 1996). By fitting measured tracer concentrations to modeled output curves, the response function accounts for the age distribution at a sampled site (Zuber et al. 2001). No detailed information is needed regarding the flow system, such as boundary conditions, porosity, and hydraulic conductivity, all of which are necessary for numerical models based on Darcy's law. Lumped-parameter models used in this study assume a steady-state flow system and assume that the selected tracers behave like a water molecule. Although this assumption typically is valid for <sup>3</sup>H, which is part of the water molecule, the gas

tracer SF<sub>6</sub> may or may not be transported in exactly the same way as the water.

Flow system characteristics can be described by two endmember lumped-parameter models: piston flow and exponential flow (Katz et al. 2007). The piston flow model assumes that after a tracer is isolated from the atmosphere at the time of ground water recharge, it becomes incorporated in a parcel of water that moves from the recharge area with the mean velocity of ground water. All flow lines are assumed to have similar velocities, and hydrodynamic dispersion and molecular diffusion of the tracer are assumed to be negligible. The exponential flow model represents an aquifer system in which the mean residence time of ground water is exponentially distributed. Ground water flow is composed of recharge from all past years. Ground water contributions to well discharge, however, decrease exponentially from the most recent recharge to that which has occurred in the distant past. Although the exponential model may provide a reasonable approximation of homogeneous unconsolidated aquifers, it may not be as useful in karst systems where ground water moves slowly through small openings in the carbonate matrix, fractures or fissures, and much more rapidly through large conduits or caverns (Wilson and Skiles 1988).

In addition to the aforementioned models, simple binary mixing models and combined binary models and exponential models are used to evaluate mixing scenarios that involve relatively young water (recharged within the past 7 years) and older water (recharged decades ago), presumably from deeper parts of the UFA. In principle, both endmembers of a binary mixture can be of any age, but the calculation is greatly simplified if it is assumed that one or both endmembers are either "young" (assumed to represent recharge that occurred after 1995) or "old" (recharged before 1940 with undetectable SF<sub>6</sub> concentrations). Ground water ages were determined using combinations of tracers including SF<sub>6</sub> and <sup>3</sup>H, and

SF<sub>6</sub> and <sup>3</sup>H/<sup>3</sup>He(0). The <sup>3</sup>He(0) tracer represents the initial <sup>3</sup>H concentration at the time of recharge and is the sum of the measured concentrations of <sup>3</sup>H and <sup>3</sup>He<sub>trit</sub>. The ratio of <sup>3</sup>H/<sup>3</sup>He(0) is a surrogate for the relative age of water, in that values near zero represent old water, and conversely, values near 1.0 represent young water (Böhlke 2002). The computer program TRACERMODEL1 (Böhlke 2006) was used in this study to calculate theoretical curves for the different lumped-parameter models using atmospheric input data for the various tracers.

## Results

### Ground Water Age Distributions

All water samples from the SAS and the PSW have relatively high SF<sub>6</sub> concentrations (greater than 3.0 pptv [parts per trillion by volume]) and most <sup>3</sup>H concentrations greater than 2 <sup>3</sup>H units (Figure 5). These sample concentrations plot close to modeled curves for exponential-piston flow for young water, and/or a binary mixing curve dominated by young water (less than 7 years in age). Young ages for PSW water were corroborated using CFC-113 and SF<sub>5</sub>CF<sub>3</sub> analyses in 2006, which both gave apparent ages of 5 years (L.N. Plummer, USGS, written communication, 2007). Consistently young ages for PSW water samples (less than 7 years) were found for water samples taken during pumped (P) and ambient conditions (NP) (Figure 5). Data for SF<sub>6</sub> and <sup>3</sup>H/<sup>3</sup>He(0) also show similar age relations with the lumped-parameter model curves. However, possible diffusion of <sup>3</sup>He into sampling material (Teflon tubing) contributed to a large uncertainty in <sup>3</sup>He<sub>trit</sub> values for water from the PSW and SAS; therefore, only SF<sub>6</sub> and <sup>3</sup>H data are shown (Figure 5).

Water samples from three deep wells in the UFA (THC-F197, GARC-F200, and 113RC-F190) have low

concentrations of <sup>3</sup>H and SF<sub>6</sub> (Figure 5). The SF<sub>6</sub> and <sup>3</sup>H/<sup>3</sup>He(0) data show similar results for samples from the deep wells. Minor excess SF<sub>6</sub> in deep UFA wells (GARC-F200, WP-F299, and THC-F297) could be related to some natural background or low-level anthropogenic SF<sub>6</sub> contamination. These samples plot on the lower left-hand side of the lumped-parameter modeled curves (Figure 5) and likely represent water that are older than 60 years. This water also contains high concentrations of sulfate, indicating a deep flowpath through the aquifer. These findings are consistent with a study by Swancar and Hutchinson (1995) that found low <sup>3</sup>H concentrations associated with high sulfate concentrations.

Water samples from shallow wells in the UFA (GARC-F75, RP-F77, THC-F75, and RP-F103) had slightly higher <sup>3</sup>H and SF<sub>6</sub> concentrations than water samples from deep wells, and these samples likely represent mixtures of about 75% to 80% old water (more than 60 years) with 20% to 25% young water (recharged within the past 7 years) based on the binary mixing model. Water samples from wells WP-F150 and 113RC-H50 plot near the midpoint of the binary mixing curve and likely represent 50/50 mixtures of old and young water. Water from the 43- to 46-m open zone, which WP-F150 taps, contains a higher proportion of young water than shallower wells in the UFA. To test the possibility of a preferential path from the SAS to this zone, in 2006, two other wells (62SRP-F160 and MAS-F160) were sampled in 2006 that tap the same high-flow zone as WP-F150, which was resampled. Water samples from MAS-F160 had a high proportion of young water, and WP-F150 and 62SRP-F160 had slightly lower proportions of young water. This 43- to 46-m zone is likely connected to the highly transmissive zone at nearly the same depth identified in the PSW borehole from geophysical measurements (Katz et al. 2007).

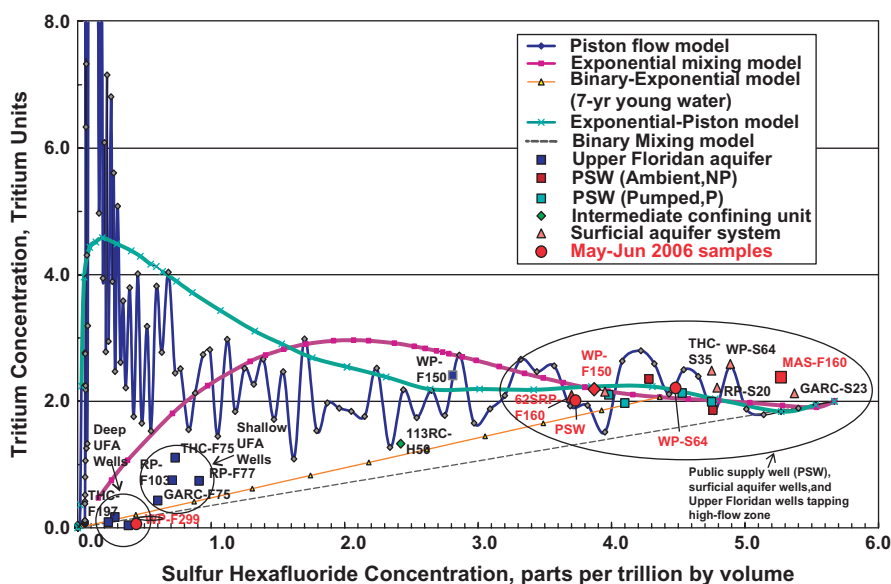


Figure 5. Plot showing measured concentrations of SF<sub>6</sub> and <sup>3</sup>H in water samples from wells, and lumped-parameter modeled curves for various ground water age distributions from the SAS, ICU, and UFA in the study area.

## Redox Conditions

The occurrence, concentration, and transformation of many anthropogenic contaminants (such as nitrate and VOCs) and naturally occurring contaminants (such as As) in ground water are controlled by oxidation-reduction (redox) conditions. Distinct differences in redox conditions exist among water from the SAS, ICU, and UFA. Water samples from 9 of 11 monitoring wells in the SAS consistently had dissolved oxygen concentrations greater than or equal to 1 mg/L (Table 1). The depth to the water table at those wells generally was greater than or equal to 4.5 m, and the top of the screened interval generally was less than 1.5 m below the water table. Water from LRP-S25 and THC-S46 had low dissolved oxygen concentrations (0.5 mg/L or less). The depth to the water table at those wells was 3 m or less and 7.6 m or more, respectively, but the screen tops at both of those wells were further below the water table (about 1.5 to 2.5 m) than many of the other wells.

Water samples from two of the four wells in the ICU (62SRP-H55 and LP-H40) had high dissolved oxygen concentrations (more than 2 mg/L) (Table 1). These two wells have screen tops that are less than or equal to 4 m below the water table. The other two wells (113RC-H50 and LRP-H105) had low dissolved oxygen concentrations (less than 0.5 mg/L) and screen tops that were greater than or equal to 6 m below the water table. These locally variable redox conditions are related to differences in sediment mineralogy and chemistry, depth below the water table, and other factors such as residence time of water in the ICU and preferential flowpaths from the SAS (Katz et al. 2007).

All but two monitoring wells in the UFA (MAS-F64 and MAS-F160) had dissolved oxygen concentrations consistently less than or equal 0.5 mg/L (Table 1). Water from most of these monitoring wells had detectable (more than 0.01 mg/L) sulfide concentrations (Katz et al. 2007).

## Nitrate-N Concentrations in Ground Water

Nitrate-N concentrations in water samples from the PSW ranged from 0.61 to 3.6 mg/L, which were similar to those found in oxic water from the SAS and ICU (Table 1; Figure 6). Nitrate-N concentrations in the SAS ranged from less than 0.06 to 6.1 mg/L, and did not exceed the U.S. EPA (1993) maximum contaminant level of 10 mg/L for drinking water. Nitrate-N concentrations in the ICU ranged from 0.27 to 3.5 mg/L (Table 1). Lower nitrate concentrations in water from LRP-H105 (0.27 mg/L) and 113RC-H50 (0.65 mg/L) compared with elevated concentrations of 2.4 and 3.5 mg/L from LP-H40 and 62SRP-H55, respectively, indicate possible denitrification. This is consistent with higher  $\delta^{15}\text{N}$  values and lower dissolved oxygen concentrations in wells LRP-H105 and 113RC-H50 than wells 62SRP-H55 and LP-H40 (Katz et al. 2007). Nitrate-N concentrations above the background levels of 0.1 mg/L (Maddox et al. 1992) in the SAS and ICU likely result from past agricultural practices (Katz et al. 2007).

Nitrate-N concentrations in water from the UFA generally were low (less than 0.06 mg/L). Water from

the UFA, which generally is anoxic in this area, had dissolved oxygen concentrations less than 0.5 mg/L (Figure 6) and contained measurable amounts of hydrogen sulfide. Denitrification likely occurs in parts of the UFA, as indicated by excess nitrogen gas values and elevated nitrogen isotope values for water from a depth interval of between 43 and 49 m below land surface (62SRP-F160, MAS-R-F160, LRP-F160, WP-F150) (Katz et al. 2007). However, water from other parts of the UFA contains measurable nitrate-N. Well MAS-F64 had a nitrate-N concentration of 1.2 mg/L. Likewise, elevated nitrate-N concentrations were found in water samples from 62SRP-F160 (2.0 mg/L) and MAS-F160 (0.94 mg/L) (Tables 1 and 2). These wells likely withdraw some water from the transmissive zone in the UFA that is tapped by the PSW and likely is hydraulically connected to the SAS.

## VOCs in Ground Water

A total of 17 of 85 VOCs were detected at measurable concentrations in one or more ground water samples (Figure 7). More VOCs were detected in water from the SAS (16) than in the underlying ICU (8) and UFA (10). Six VOCs were detected in water from the PSW: trichloromethane, *cis*-1,2-dichloroethene, trichloroethene, tetrachloroethene (PCE), MTBE (methyl ter-butyl ether), and carbon disulfide (Figure 7). Wellhead water samples from the PSW were collected and analyzed for VOCs on seven different dates between October 2002 and June 2005. PCE and carbon disulfide were detected in only two samples. MTBE and *cis*-1,2-dichloroethene were detected in very low concentrations in only one sample collected in October 2002. Trace concentrations of PCE were detected in all samples, and trichloromethane was detected in all but one sample. Median concentrations of MTBE, trichloroethene, and *cis*-1,2-dichloroethene in the PSW were similar to median concentrations in water from monitoring wells in the UFA (Table 3). Median concentrations of carbon disulfide, PCE, and trichloromethane were higher in PSW water than in water from UFA monitoring wells (Katz et al. 2007). In fact, similar median trichloromethane concentrations (0.17  $\mu\text{g/L}$ ) were found in water samples from the PSW and the SAS (Table 3). These similar concentrations of compounds indicate that water from the SAS likely is entering the PSW. Trichloromethane (commonly known as chloroform) was the most frequently detected compound in water from all three hydrogeologic units. All detected concentrations of VOCs in the PSW and in monitoring wells were below any levels for health advisories or maximum contaminant levels (Toccalino et al. 2004; U.S. EPA 1993). VOC concentrations typically were below 0.1  $\mu\text{g/L}$ , with the exception of trichloromethane, which ranged from 0.01 to 2.6  $\mu\text{g/L}$  in the SAS (Katz et al. 2007).

## As Concentrations and Speciation

As concentrations in water from the PSW ranged from 3.2 to 3.5  $\mu\text{g/L}$  when collected using the inline turbine pump. However, As concentrations ranged from 4.2 to 18.9  $\mu\text{g/L}$  for samples collected at various depths in



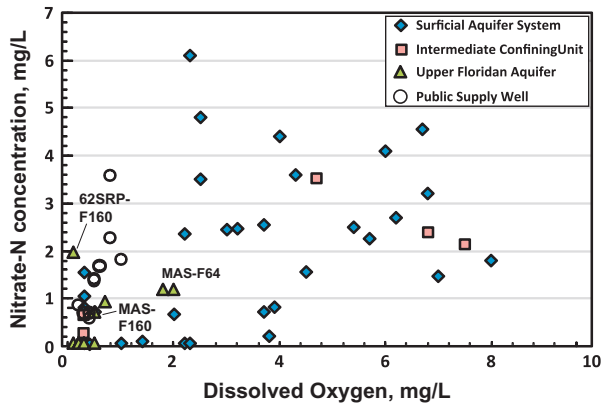
**Table 1**  
**Physical Properties and Chemistry of Water Samples from the SAS, ICU, and UFA in the Study Area**

Site Name	Well Depth, m	Casing Depth, m	Sample Date	Sample Time	Temperature, °C	SC	DO	pH	NO <sub>3</sub> -N	Cl	SO <sub>4</sub>	HS	As, µg/L	Fe, µg/L	Mn, µg/L	Sr, µg/L	As[III], µg/L	As[V], µg/L	
SAS																			
BBP-S45	12	9	August 11, 2001	1200	25.0	594	3.9	6.9	0.82	10.8	53.8								
BBP-S45	12	9	December 9, 2004	1300	25.5	475	3.8	7.1	0.21	7.54	31.4	0.002	1.4	<6	0.5	92.1			
BBP-S45	12	9	June 22, 2005	1130	25.9	526	3.7	7.1	0.72	9.91	30.9	0.004							
THC-S46	14	11	December 18, 2003	1300	24.5	693	0.3	6.9	1.1	36.5	44.4	<0.001	2.6	979	672	273	2	E0.9	
THC-S46	14	11	August 5, 2004	1200	25.0	697	0.3	6.9	0.81	34.9	45.1	0.02		984	460				
THC-S46	14	11	November 17, 2004	1600	25.7	705	0.3	6.7	0.59	42.7	43.9	0.008		654	345				
THC-S46	14	11	November 14, 2005	1700	27.0	707	0.3	6.8	1.6	42.5	44.6	0.013		662	261				
62SRP-S34	10	7	August 12, 2004	930	25.5	540	6.8	6.3	3.2	28.9	12.8		0.4	<6	4				
WP-S64	20	16	January 14, 2004	1500	26.0	474	5.4	7.5	2.5	21.3	87.2	<0.001	0.2	<6	0.4	254	<1	E0.7	
WP-S64	20	16	August 4, 2004	1600	26.5	482	6.7	7.5	4.6	30.6	73	0.005	0.2	<6	E0.1	245	<1	<1.2	
WP-S64	20	16	November 18, 2004	1200	27.3	455	6	7.5	4.1	26.2	59	0.002		E3	<0.6				
WP-S64	20	16	June 14, 2005	1130	26.5	457	5.7	7.5	2.3	20.8	86.3			E3	<0.6				1.3
RP-S20	6	3	December 4, 2003	1400	24.5	502	2.2	6.4	<0.06	18.8	30.5	0.007	2.4	3910	939	175	1.2		
RP-S20	6	3	August 11, 2004	1500	24.0	791	1.4	6.6	0.1	20.3	80.3	<0.001		330	155				
RP-S20	6	3	November 16, 2004	1500	24.2	435	0.3	6.8	<0.06	2.68	9.6	<0.001		657	194				
RP-S20	6	3	June 16, 2005	1500	25.0	613	1	6.6	<0.06	7.01	13.1			644	410				
LRP-S25	8	5	August 10, 2004	1100	26.0	447	0.5	7.5	0.72	10.9	75.8	<0.001		6	5.8				
LRP-S25	8	5	June 15, 2005	1500	25.0	442	0.4	7.3	E0.04	16.3	94.2	<0.001		11	14.8				
JARP-S40	11	8	June 27, 2005	1030	29.0	236	2.3	6.7	<0.06	11.3	23.5			E5	197				
113RC-S35	11	8	December 11, 2003	1300	26.0	379	2.5	6.8	3.5	9.92	47.2	<0.001	E0.2	<6	5.1	489	<1	<1.2	
113RC-S35	11	8	August 12, 2004	1300	27.5	370	4	6.6	4.4	2.03	26.6			<6	E0.5				
113RC-S35	11	8	November 16, 2004	1300	27.3	316	2.2	6.6	2.4	1.85	28.6	0.002		E4	2				
113RC-S35	11	8	June 15, 2005	1100	27.5	373	4.3	6.6	3.6	6.75	47.6			<6	<0.6				
LP-S30	9	6	August 10, 2004	1200	29.0	65	8	4.4	1.8	5.7	7.3	<0.001		6	2.3				
LP-S30	9	6	November 1, 2004	1600	28.2	92	6.2	5	2.7	11.7	5.6	0.004	<0.2	10	3.6	33.3			
LP-S30	9	6	June 21, 2005	1130	26.0	70	7	5.3	1.5	4.96	11.6	<0.001		E6	1.4				
QRP-S20	6	3	August 11, 2004	1345	28.0	185	3.7	5.9	2.6	9.05	17.5			349	8.7				
QRP-S20	6	3	November 15, 2004	1700	24.9	234	2.3	5.9	6.1	3.21	11	0.012	0.3	48	9.3	96.2			
QRP-S20	6	3	June 21, 2005	1630	24.5	166	2	6.2	0.67	15.6	5	0.001		332	23.1				
GARC-S23	7	4	December 17, 2003	1200	25.0	515	2.5	6.3	4.8	8.93	120	0.006	0.4	E6	92.4	662	<1	<1.2	
GARC-S23	7	4	August 5, 2004	1600	26.0	540	4.5	5.9	1.6	6.2	191	0.005		E4	32.8				
GARC-S23	7	4	November 17, 2004	1100	27.7	504	3	5.7	2.5	4.74	171	0.005		7	30.1				
GARC-S23	7	4	June 13, 2005	1115	27.1	450	3.2	5.8	2.5	6.64	138			7	57.7				
ICU																			
62SRP-H55	17	14	November 3, 2004	1700	26.6	456	4.7	7.1	3.5	12.7	18.3	0.008	0.3	E3	2.3	68.9	<1	<1.2	
LRP-H105	32	29	December 7, 2004	1600	25.1	288	0.3	7.4	0.27	8.49	25.1	<0.001	1.5	<6	5.8	507	E0.9	E1	
LRP-H105	32	29	June 15, 2005	1510	29.5	334	0.6	8.3				0.002							
113RC-H50	15	12	December 9, 2003	1300	25.5	0	0.3	7.3	0.65	13.2	151	0.15	7.9	156	54.1	1580	4	3.4	
LP-H40	12	9	August 10, 2004	1500	32.0	262	7.5	7.8	2.2	4.94	14.2			<6	<0.8				
LP-H40	12	9	December 8, 2004	1500	26.4	259	6.8	7.5	2.4	8.36	6.7	0.007	0.3	<6	0.3	90	<1	<1.2	

**Table 1**  
Continued

Site Name	Well Depth, m	Casing Depth, m	Sample Date	Sample Time	Temperature, °C	SC	DO	pH	NO <sub>3</sub> -N	Cl	SO <sub>4</sub>	HS	As, µg/L	Fe, µg/L	Mn, µg/L	Sr, µg/L	As[III], µg/L	As[V], µg/L	
UFA																			
THC-F75	23	20	January 12, 2004	1500	24.5	515	0.1	7.3	<0.06	7.11	137	0.6	1.1	111	85.7	1200	<1	<1.2	
THC-F75	23	20	June 14, 2005	1640	26.6	489	0.2	7.3				0.533							
THC-F197	60	57	January 15, 2004	1400	25.0	958	0.3	7.2	<0.06	9.38	371	1.5	1.9	90	15.3	3780	1.1	1.3	
62SRP-F160	49	46	November 2, 2004	1200	28.7	596	0.1	7.2	2.0	27.9	89.7	0.002	3.1	E4	2.8	666	<1	2.3	
MAS-F64	20	16	February 16, 2005	1300	25.5	262	1.8	7.7	1.2	15.4	12.8	<0.001	0.6	<6	1.5	64.1	<1	<1.2	
MAS-F64	20	16	June 16, 2005	1100	26.0	219	2	8	1.2	15.2	9.2			<6	E0.6				
MAS-F160	49	14	November 3, 2004	1200	26.7	546	0.7	7.4	0.94	18.5	63.4	0.004	2	<6	2.8	566	<1	1.6	
MAS-F160	49	14	June 16, 2005	1040	27.0	548	0.5	7.2	0.72	19.1	69.8	0.008		91	26.7				
WP-F150	46	43	January 28, 2004	1300	25.2	569	0.2	7.4	<0.06	19.1	139	0.018	16.5	12	6.8	1690	14.1	2.9	
WP-F150	46	43	August 4, 2004	1100	26.0	584	0.3	7.4	<0.06	20.9	133	0.11	5.6	24	5.3	1720	5.2	E1.1	
WP-F299	91	88	January 22, 2004	1600	26.0	1000	0.2	7.2	<0.06	9.41	355	1.88	12.6	79	7	3840	5.6	7.3	
WP-F299	91	88	August 3, 2004	1400	26.0	1000	0.3	7.1	<0.06	9.03	369	1.71	2.5	108	6.1	3980	1.1	E1.1	
RP-F77	23	20	December 3, 2003	1300	23.5	562	0.2	7.3	<0.06	7.6	93.6	0.29	14.6	127	9	1890	10	3.9	
RP-F77	23	20	June 16, 2005	1610	25.2	586	0.4	7				0.48							
RP-F103	31	28	December 2, 2003	1500	23.5	759	0.2	7.2	<0.06	8.59	227	0.51	4.9	75	8.8	2460	3.1	1.4	
LRP-F160	49	46	November 4, 2004	1300	27.8	458	0.5	7.8	<0.06	16.3	77.2	0.043	2.4	9	14.2	939	1.5	E0.8	
GARC-F75	23	20	December 15, 2003	1400	20.5	852	0.2	7.3	<0.06	8.72	296	1.02	0.7	9	23.2	2990	0.8	E0.8	
GARC-F75	23	20	June 13, 2005	1200	28.0	825	0.5	7.2				0.66							
GARC-F200	61	58	December 16, 2003	1300	25.0	1070	0.2	7.2	<0.06	9.74	413	1.65	1.7	57	70.1	4110	1.1	E1	
I13RC-F190	58	55	December 8, 2003	1300	25.0	1010	0.3	7.2	<0.06	9.29	383	1.1	6	172	38.4	4080	3.7	1.8	
I13RC-F190	58	55	June 15, 2005	1130	27.1	1040	0.3	7.1				0.66							
PSW	53	36	October 21, 2002	1600	26.5	608	0.4	7.2	0.72	17.8	129	<0.001	3.5	24	2.2	1230			
PSW	53	36	January 28, 2004	1600	24.0	603	0.2	7.3	0.89	22.8	122	0.048	3.2	25	2.5	1260	2	E1.2	
PSW	53	36	October 21, 2004	1500	26.0	606	0.5	7.3	1.4	25	116	0.03	3.2	6	1.8	1100	<1	2.6	
PSW	53	36	February 16, 2005	1600	25.0	584	0.4	7.3	0.61	26	112	0.005		44	6.5				
PSW	53	36	June 20, 2005	1600	26.4	618	0.3	7.4	0.72	24	121	0.038		31	3.4				

Note: Concentration units are in milligrams per liter unless otherwise noted; T, water temperature; SC, specific conductance in microsiemens per centimeter; E, estimated concentration, below reported laboratory reporting level; NO<sub>3</sub>-N, nitrate as nitrogen; well depth and casing depth are in meters below land surface; blank cell, no sample collected.



**Figure 6.** Plot showing nitrate-N and dissolved oxygen concentrations in water samples from the SAS, ICU, UFA, and PSW.

the PSW borehole. Water samples from wells in the SAS and ICU had As concentrations less than 8 µg/L (Table 1). Most water samples from monitoring wells in the UFA were less than the 10 µg/L maximum contaminant level for drinking water; however, water samples from WP-F299, WP-F150, and RP-F77 had As concentrations that ranged from 12.6 to 16.5 µg/L (Table 1). Higher median As concentrations were found in water samples from the UFA (4.6 µg/L) compared to samples from the ICU (0.9 µg/L) and the SAS (0.4 µg/L) (Figure 8). The higher As concentrations in water samples from the SAS and ICU generally were associated with higher concentrations of iron, which indicate the likely association of As with iron oxyhydroxide coatings on sands and clay material (Pichler et al. 1999). Under reducing conditions in the UFA and for water from 113-RC-H50 in the ICU, most water samples had higher As(III) concentrations than As(V) concentrations (Table 1). Concentrations of both As(III) and As(V) in water from the oxic SAS generally were near the laboratory method reporting level for both As species.

#### Chemical Variations with Depth in the PSW Borehole

Water samples were collected from three overlapping depth intervals in the PSW borehole (after removal of the turbine pump) during ambient (nonstressed) and pumping (stressed) conditions to assess effects of pumping on water quality (detailed methods in Katz et al. 2007). Substantial chemical differences were found in water samples from the three overlapping depth intervals (Table 2) in the PSW borehole. Water samples from the 49- to 53-m zone collected during ambient conditions contained higher concentrations of nitrate-N, and trichloromethane (chloroform) than water collected from the other depth zones during ambient conditions and for any interval during pumping conditions. Additionally, lower concentrations were found in the 49- to 53-m interval for strontium, iron, and manganese during ambient conditions compared to samples from any interval during pumping conditions (Katz et al. 2007).

During normal pumping conditions for the PSW (with the inline turbine pump), As concentrations were

**Table 2**  
**Chemical Properties of Water Samples Collected from Various Depth Intervals in the PSW**

Site Name	Depth Interval Sampled, m b/s	Sampling Date	Sampling Time	Temperature, °C	Specific Conductivity, µS/cm	Dissolved O <sub>2</sub>	pH	NO <sub>3</sub> -N µg/L	Fe, µg/L	Mn, µg/L	Sr, µg/L	As, µg/L	As(III), µg/L	As(V), µg/L	Trichloromethane, µg/L
PSW-wellhead-P	38-53	October 21, 2004	1500	26.0	606	0.5	7.3	1.4	6	1.8	1100	3.2	1.5	E1.0	0.29
PSW-140-NP	43-53	October 27, 2004	1600	26.4	577	0.8	7.3	2.3	<6	3	788	11.7	E0.8	8.7	0.52
PSW-160-NP	49-53	October 27, 2004	1800	26.2	537	0.8	7.3	3.6	<6	0.8	515	4.2	<1	2.6	0.80
PSW-160-P	49-53	October 28, 2004	1100	24.1	567	1.0	7.3	1.8	E3	2	912	18.9	E0.6	14.2	0.44
PSW-140-P	43-53	October 28, 2004	1400	25.8	586	0.6	7.3	1.7	E5	2.2	934	16.0	2.1	10.7	0.37
PSW-125-P	38-53	October 28, 2004	1600	25.9	583	0.6	7.3	1.7	9	1.7	937	53.3	3.3	9.3	0.35

Notes: Concentrations of constituents are in milligrams per liter unless otherwise noted. P denotes pumping conditions; NP, ambient (nonpumping conditions); wellhead-P, entire interval sampled using turbine pump; E, estimated concentration below laboratory reporting level; m b/s, meters below land surface.

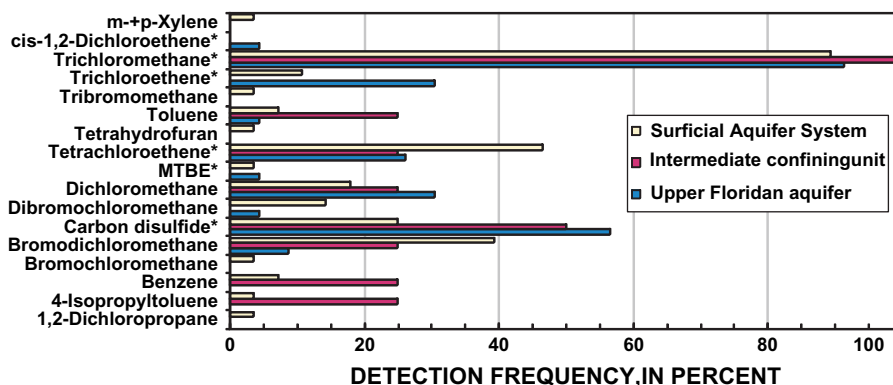


Figure 7. Plot showing detection frequency of VOCs in ground water from the SAS, ICU, and UFA in the Temple Terrace, Florida, study area. Compounds denoted with an asterisk were found in water from the studied PSW.

	Carbon Disulfide	MTBE	PCE	Trichloroethene	Trichloromethane (chloroform)	cis-1,2-Dichloroethene
SAS	0.059	0.130	0.030	0.020	0.17	ND
ICU	0.057	ND	0.010	ND	0.22	ND
UFA	0.107	0.034	0.02	0.040	0.08	0.022
PSW	0.027	0.034	0.061	0.040	0.17	0.022

Note: Concentrations are in micrograms per liter; ND, not detected.

3.2 to 3.5 µg/L in water samples collected on three previous dates (Table 1). The As concentration in water from the lowermost (49 to 53 m) depth interval was 4.2 µg/L during ambient conditions on October 27, 2004. On the following day, however, and under pumping conditions, the As concentration in water from this same interval was 19 µg/L. Similarly, higher As concentrations were measured in water from the 43- to 53-m interval during pumping conditions (16 µg/L) compared to ambient conditions (12 µg/L). This change in concentration indicates

that As movement to the PSW was enhanced during pumping from a high-flow zone in the UFA that was identified from geophysical logging of the PSW borehole.

As(V) concentrations were higher than As(III) concentrations in the 49- to 53-m depth interval (Table 2). This interval tended to have slightly higher concentrations of dissolved oxygen compared to the zones represented by monitoring wells in the UFA and lower concentrations of hydrogen sulfide (Table 1).

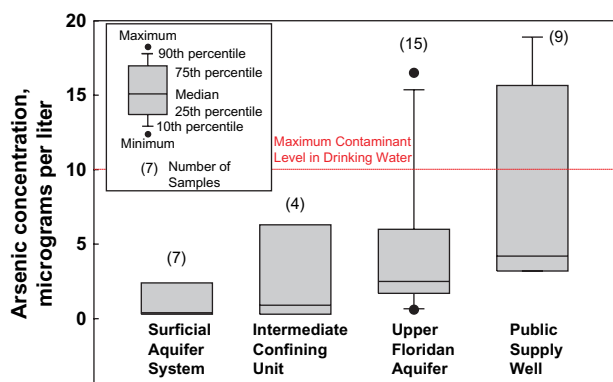


Figure 8. Boxplot showing the distribution of As concentrations in water samples from the SAS, ICU, UFA, and PSW.

## Discussion

### Contaminant Movement and Mixing of Water in the PSW

Differences in chemical signatures and age distributions of water from the PSW and monitoring wells in the three hydrogeologic units indicate that the PSW receives mixtures of water from both the SAS and the UFA. Based on mass-balance geochemical modeling scenarios involving major chemical constituents, the PSW withdraws a mixture of about 30% to 60% water from the SAS and about 40% to 70% water from the UFA (Katz et al. 2007). The movement of oxic water from the surficial aquifer into the PSW is consistent with elevated nitrate-N concentrations in the PSW, similar VOC detection frequencies in the PSW compared with monitoring wells in the SAS, and elevated As concentrations relative to samples from UFA monitoring wells.

The enhanced mobilization of As is consistent with a study of As release from pyrite in the Suwannee Limestone in west-central Florida, which tends to be most abundant in high-porosity zones (Price and Pichler 2006). They reported that As in excess of 2 ppm is associated with impurities in the Suwannee Limestone, such as trace minerals and organic matter. Furthermore, they found that framboidal pyrite in the Suwannee Limestone contains As concentrations between 100 and 11,200 ppm, with an average concentration of 2300 ppm for 25 samples. Slight increases in dissolved oxygen could enhance pyrite dissolution as was seen on a larger scale during cycle testing at an aquifer storage and recovery facility in Tampa, Florida. Oxygen-rich recharge water was injected into the Suwannee Limestone, and water recovered during various cycle tests contained up to 130 µg/L of As concentration, although no As speciation data were collected (Arthur et al. 2002).

Concentration differences for As species between the 49- to 53-m zone and the other sampled zones also are consistent with oxic water from the surficial material into the highly transmissive zone (49 to 53 m) in the UFA. Water samples from the PSW had As(V)/As(III) ratios that ranged from 0.6 to 24 (median 2.8), which were considerably higher than As(V)/As(III) ratios for water samples from UFA monitoring wells (range 0.20 to 1.3; median 0.90).

#### Vulnerability of the PSW to Contamination

The vulnerability of the studied PSW to contamination is indicated by age-dating tracer concentrations that show mixtures containing a large component of young water (generally less than 7 years). Natural short-circuiting features (sinkholes, conduits, and other solution features) facilitate the movement of very young water toward the PSW, which is enhanced during pumping. Age tracer concentrations in most water samples collected from the PSW are very similar to those for SAS water samples. Tracer concentrations in recently collected water samples (2005 through 2006) from UFA monitoring wells, which withdraw water from a similar depth interval as the PSW (a high transmissivity zone), are higher than concentrations for water samples from shallower zones in the UFA.

Nitrate-N and trichloromethane concentrations are related to the proportion of young water in water samples from wells. The median nitrate-N concentration was 1.0 mg/L in water samples that contain more than 50% young water compared to less than 0.06 mg/L for water samples that contain less than 50% young water. Similarly, the median trichloromethane concentration was 0.18 µg/L in water samples that contain more than 50% young water compared to the median concentration of 0.04 µg/L in water samples that contain 50% or less young water (less than 7 years). Also, maximum concentrations of nitrate-N (6.1 mg/L) and trichloromethane (2.6 µg/L) were considerably higher in water dominated by a young component than in older water (0.06 mg/L and 0.25 µg/L, respectively). This trend is influenced by young water in the oxic SAS where well depths are shallow and where

contaminant loading is high from certain urban land-use activities. Pumping of ground water by the PSW and other wells in the immediate area can enhance the downward movement of these and other contaminants. The studied PSW is located in a wellfield with other public water supply wells. However, this study could not directly evaluate the effects of pumping from other wells on water quality in the PSW. The presence of large solution features observed at depths of 43 to 53 m from televiwer images of the PSW borehole (Katz et al. 2007), along with the presence of a large component of young water in samples from UFA monitoring wells that also tap this zone (based on new data from 2006), indicates that this highly transmissive zone in the UFA may extend for several hundreds of meters in this area.

#### Summary and Conclusions

The vulnerability of the studied PSW to contamination in the karstic UFA near Tampa, Florida, was assessed by combining age tracer and geochemical data from an earlier stage of the study (2002 through 2005) (Katz et al. 2007) with new information on ground water age and anthropogenic contaminants collected during 2006. Concentrations of the age-dating tracers SF<sub>6</sub>, <sup>3</sup>H, and <sup>3</sup>He in samples from the PSW during both ambient and pumping conditions were consistent with binary mixtures dominated by young water (less than 7 years). Similarly, water samples from monitoring wells in the SAS had SF<sub>6</sub> and <sup>3</sup>H concentrations that indicated a substantial proportion of young water (less than 7 years). In contrast, most water samples from monitoring wells in the UFA system had lower SF<sub>6</sub> and <sup>3</sup>H concentrations than water from the PSW and indicated mixtures containing higher proportions of old water (older than 60 years).

Predominantly, young water in the PSW (less than 7 years) was consistent with elevated concentrations of anthropogenic and natural contaminants, and indicates that the PSW is withdrawing water and contaminants from the SAS. Nitrate-N concentrations in PSW water (0.72 to 3.6 mg/L) were more similar to the higher median concentration in the oxic SAS (1.6 mg/L) than that for the anoxic UFA (0.06 mg/L). The six volatile organic compounds detected in trace concentrations (below drinking water standards) in the PSW were found more often in water samples from the SAS than from the UFA. Likewise, elevated As concentrations (3 to 19 mg/L) and higher As(V)/As(III) ratios in the PSW indicate that oxic water from the SAS likely mobilizes As from pyrite in the UFA matrix.

Water from the SAS moves downward into the UFA under natural gradients and its movement is enhanced due to pumping stresses. Sands and clayey sands that compose the overlying SAS are highly permeable and also allow for rapid downward movement to the water table and eventually into the UFA. The combination of large solution features observed at depths of 43 to 53 m from televiwer images of the PSW borehole (Katz et al. 2007), along with the presence of a large component of

young water in samples from UFA monitoring wells that also tap this interval, indicates a highly transmissive zone that may extend for several hundreds of meters in this area. Monitoring and water quality protection efforts for PSWs in this area and in other parts of the karstic UFA should emphasize areas where breaches in the confining unit exist and where high pumping stresses induce rapid downward flow from overlying hydrogeologic units and surface features. Contaminants from various sources at the land surface can move rapidly into the UFA (source of water supply) due to the presence of sinkholes and other solution features that can provide a direct hydraulic connection between the aquifer and the surface.

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