

Chemical Characteristics, Water Sources and Pathways, and Age Distribution of Ground Water in the Contributing Recharge Area of a Public-Supply Well near Tampa, Florida, 2002-05

By Brian G. Katz, Christy A. Crandall, Patricia A. Metz,
William S. McBride, and Marian P. Berndt

National Water-Quality Assessment Program
Transport of Anthropogenic and Natural
Contaminants (TANC) to Public-Supply Wells

Scientific Investigations Report 2007-5139

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

U.S. Department of the Interior
DIRK KEMPTHORNE, Secretary

U.S. Geological Survey
Mark D. Myers, Director

U.S. Geological Survey, Reston, Virginia: 2007

For product and ordering information:

World Wide Web: <http://www.usgs.gov/pubprod>

Telephone: 1-888-ASK-USGS

For more information on the USGS--the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment:

World Wide Web: <http://www.usgs.gov>

Telephone: 1-888-ASK-USGS

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this report is in the public domain, permission must be secured from the individual copyright owners to reproduce any copyrighted materials contained within this report.

Suggested citation:

Katz, B.G., Crandall, C.A., Metz, P.A., McBride, S., and Berndt, M.P., 2007, Chemical characteristics, water sources and pathways, and age distribution of ground water in the contributing recharge area of a public-supply well near Tampa, Florida, 2002-05: U.S. Geological Survey Scientific Investigations Report 2007-5139, 83 p.

Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with credible scientific information that helps to enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (<http://www.usgs.gov/>). Information on the Nation's water resources is critical to ensuring long-term availability of water that is safe for drinking and recreation and is suitable for industry, irrigation, and fish and wildlife. Population growth and increasing demands for water make the availability of that water, now measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, State, and local information needs and decisions related to water-quality management and policy (<http://water.usgs.gov/nawqa>). The NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. From 1991-2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (<http://water.usgs.gov/nawqa/studyu.html>).

Multiple national and regional assessments are ongoing in the second decade (2001–2012) of the NAWQA Program as 42 of the 51 Study Units are reassessed. These assessments extend the findings in the Study Units by determining status and trends at sites that have been consistently monitored for more than a decade, and filling critical gaps in characterizing the quality of surface water and ground water. For example, increased emphasis has been placed on assessing the quality of source water and finished water associated with many of the Nation's largest community water systems. During the second decade, NAWQA is addressing five national priority topics that build an understanding of how natural features and human activities affect water quality, and establish links between sources of contaminants, the transport of those contaminants through the hydrologic system, and the potential effects of contaminants on humans and aquatic ecosystems. Included are topics on the fate of agricultural chemicals, effects of urbanization on stream ecosystems, bioaccumulation of mercury in stream ecosystems, effects of nutrient enrichment on aquatic ecosystems, and transport of contaminants to public-supply wells. These topical studies are conducted in those Study Units most affected by these issues; they comprise a set of multi-Study-Unit designs for systematic national assessment. In addition, national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, selected trace elements, and aquatic ecology are continuing.

The USGS aims to disseminate credible, timely, and relevant science information to address practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, regional, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Robert M. Hirsch
Associate Director for Water

Contents

Abstract.....	1
Introduction.....	2
Purpose and Scope	4
Description of Study Area	4
Previous Studies	5
Acknowledgments.....	6
Methods.....	6
Design of Monitoring Well Network	6
Drilling, Coring, and Well Installation	7
Collection and Analysis of Water Samples	12
Age Dating of Ground Water.....	13
Tritium and Tritiogenic Helium-3.....	13
Sulfur Hexafluoride.....	14
Quality Assurance.....	15
Lithology, Mineralogy, and Elemental Analysis of Core Material	15
Hydrogeologic Setting.....	16
Lithology and Mineralogy of the Hydrogeologic Units	19
Estimation of Aquifer Properties	22
Ground-Water Flow Patterns.....	24
Ground-Water Chemistry.....	24
Chemical Composition and Mineral Saturation Indexes.....	24
Dissolved Organic Carbon and Dissolved Solids Concentrations	25
Redox Conditions	30
Stable Isotopes of Water.....	31
Ground-Water Age and Age Distributions.....	35
Apparent Sulfur Hexafluoride and Tritium/Helium-3 Ground-Water Ages.....	35
Assessing Ground-Water Age Distributions Using Lumped Parameter Models	39
Occurrence of Anthropogenic and Naturally Occurring Contaminants in Ground-Water Samples.....	41
Nitrate-N Concentrations and Isotopes and Dissolved Gases	41
Volatile Organic Compounds.....	46
Pesticides.....	51
Sulfur Species and Hydrogen Sulfide	52
Radon-222 and Uranium.....	54
Arsenic Concentrations and Speciation	60
Temporal Variability in Water Chemistry from Surficial Aquifer System Wells and the Public-Supply Well	60
Sources and Mixing of Water in the Public-Supply Well.....	62
Chemical Variations with Depth during Ambient and Pumping Conditions	62
Estimating Mixing Proportions of Water Using Geochemical Mass-Balance Modeling	64
Movement of Contaminants to the Public-Supply Well.....	65
Summary.....	67
Selected References.....	69

Appendix A1. Summary of quality-assurance results for organic compounds in blanks and replicates	79
Appendix A2. Summary of quality-assurance results for selected chemical constituents in field blank and replicate samples	80
Appendix A3. Percent recovery values for surrogate compounds added to ground-water and surface-water samples at the U.S. Geological Survey National Water Quality Laboratory	82
Appendix A4. Oxidation-reduction (redox) classification scheme developed for the transport of anthropogenic and natural contaminants to public-supply wells	85

Figures

1. Map showing large- and small-scale areas for the study of the transport of anthropogenic and natural contaminants (TANC) to public-supply wells, photolineaments, degree of confinement of the Upper Floridan aquifer, and selected karst features in west-central Florida	3
2. Map showing location of potential sources of contaminants to ground water in the Temple Terrace, Florida, study area.....	5
3. Map showing lines of hydrogeologic sections, sampling site locations, and direction of ground-water flow in the Upper Floridan aquifer in the Temple Terrace, Florida, study area	7
4. Plot showing input of sulfur hexafluoride to atmosphere in the northern hemisphere and tritium concentrations in rainfall from Ocala, Florida, during 1950-2005.....	14
5A. Chart showing stratigraphic and hydrogeologic units of the Temple Terrace, Florida, study area	17
5B. Cross sections showing generalized hydrogeologic sections A-A' and B-B'	18
6. Plot showing geophysical logs of the public-supply well borehole at Temple Terrace, Florida	23
7. Trilinear (Piper) diagram of major-ion chemistry for ground-water and surface-water samples from the Temple Terrace, Florida, study area.....	25
8-25. Plots showing:	
8. Dissolved oxygen and hydrogen sulfide concentrations with well depth from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area.....	30
9. Oxygen and hydrogen isotopes in ground water and surface water from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area.....	31
10. Comparison of apparent ages based on the piston-flow assumption and measured concentrations of sulfur hexafluoride, tritium, and helium-3 in water samples from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area	35
11. Measured concentrations of sulfur hexafluoride and tritium in water samples from wells, and lumped-parameter modeled curves for various ground-water age distributions from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area	40

12. Measured concentrations of sulfur hexafluoride, tritium, the ratio of tritium to the sum of helium-3 and tritium in water samples from wells, and lumped-parameter modeled curves for ground-water age distributions from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area	41
13. Nitrate-N concentrations with well depth in the Temple Terrace, Florida, study area	42
14. Values for delta nitrogen-15 and delta oxygen-18 of nitrate in water from wells in the Temple Terrace, Florida, study area.....	42
15. Detection frequency of volatile organic compounds in ground water from the surficial aquifer system, intermediate confining unit, Upper Floridan aquifer, and stormwater retention ponds in the Temple Terrace, Florida, study area	46
16. Concentrations of selected volatile organic compounds detected in water samples from the surficial aquifer system, intermediate confining unit, Upper Floridan aquifer, and public-supply well in the Temple Terrace, Florida, study area	50
17. Comparison of trichloromethane (chloroform) and dichloromethane (methylene chloride) concentrations in water samples collected from the oxic surficial aquifer system and the anoxic Upper Floridan aquifer in the Temple Terrace, Florida, study area	50
18. Pesticides detected in ground-water samples and surface-water samples from the Temple Terrace, Florida, study area	51
19. Sulfate concentrations and delta sulfur-34 of sulfate in water samples from the surficial aquifer system, intermediate confining unit, Upper Floridan aquifer, and retention ponds in the Temple Terrace, Florida, study area.....	53
20. Relation between sulfate-to-chloride ratios and sulfate concentrations in water from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area	53
21. Radon-222 concentrations with well depth below land surface for the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area	54
22. Median concentrations of radon-222, arsenic, uranium, hydrogen sulfide, iron, and dissolved organic carbon in oxic and anoxic water from monitoring wells and the public-supply well in the Temple Terrace, Florida, study area	55
23. Arsenic concentrations with well depth and arsenic species (arsenic (III) and arsenic (V) concentrations) in water samples from wells in the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area, October 2004.....	60
24. Temporal variability of chloride, nitrate-N, dissolved organic carbon, and ground-water levels in water samples collected from wells RP-S20, WP-S64, GARC-S23, and TTP-4 in the Temple Terrace, Florida, study area	61
25. Relation between the sulfur hexafluoride apparent recharge year and concentrations of nitrate-N, and trichloromethane in water samples from the surficial aquifer system, intermediate confining unit, Upper Floridan aquifer, and public-supply well in the Temple Terrace, Florida, study area	66

Tables

1. Well construction and location information for monitoring wells tapping the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer	8
2. Description of lithology and results from grain-size analysis from sediments underlying the study area.....	9
3. Summary of water-quality and solid-phase analyses in the transport of anthropogenic and natural contaminants (TANC) small-scale study area.....	12
4. Mineralogy of surficial sediments or rock, elemental composition from acid extractions, and concentrations of iron and sulfide from extractions of selected samples of core material.....	20
5. Physical properties and chemistry of water samples from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the study area	26
6. Data for delta oxygen-18 and delta hydrogen-2, delta carbon-13 in dissolved inorganic carbon, nitrogen and oxygen isotopes of nitrate, delta sulfur-34 of sulfate, and radon-222 in water samples from the surficial aquifer system, intermediate confining unit, Upper Floridan aquifer, ponds, and river	32
7. Summary of sulfur hexafluoride results for water samples from wells in the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer	36
8. Summary of tritium/helium-3 age data using piston-flow model for water samples from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer	38
9. Dissolved gas data, calculated excess nitrogen gas concentration, estimated recharge temperature, and excess air concentration in water samples collected from the public-supply well and monitoring wells in the Temple Terrace, Florida, study area	43
10. Volatile organic compounds detected in water samples from the surficial aquifer system, intermediate confining unit, Upper Floridan aquifer, and stormwater retention ponds	47
11. Concentrations of pesticides detected in ground-water and surface-water samples	52
12. Concentrations of trace elements and arsenic species, arsenic (III), and arsenic (V) in ground-water samples.....	56
13. Chemical properties of water samples collected from various depth intervals in the public-supply well.....	63
14. Chemical mass transfer associated with mixing scenarios and comparison of observed and modeled isotopic composition	66

Conversion Factors, Datum, Abbreviated Units, and Acronyms

SI to Inch/Pound

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
centimeter per year (cm/yr)	0.3937	inch per year
gram (g)	0.03527	ounce, avoirdupois
square kilometer (km ²)	0.3861	square mile
liter (L)	0.2642	gallon
liter per minute (L/min)	4.403 x 10 ⁻³	gallon per second
meter (m)	3.281	foot
meter per day (m/d)	3.281	foot per day
meter squared per day (m ² /d)	10.76	foot squared per day
millimeter (mm)	0.03937	inch
picocurie per liter (pCi/L)	0.037	becquerel per liter

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

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

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

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

Chemical Abbreviations

$\delta^{13}\text{C}$	Delta carbon-13
$\delta^2\text{H}$	Delta hydrogen-2
$\delta^{18}\text{O}$	Delta oxygen-18
$\delta^{34}\text{S}$	Delta sulfur-34
$\delta^{15}\text{N}$	Delta nitrogen-15
^3H	Tritium
^3He	Helium-3
$^3\text{H}(0)$	Initial tritium concentration
^4He	Helium-4
$^3\text{He}_{\text{trit}}$	Tritogenic helium-3
MTBE	Methyl tert-butyl ether
Ne	Neon
SF_6	Sulfur hexafluoride

Other Abbreviations

cm^3/L	cubic centimeter per liter
μm	micron
$\mu\text{g}/\text{L}$	microgram per liter
mg/kg	milligram per kilogram
mg/L	milligram per liter
mL	milliliter
mmol/kg	millimole per kilogram
nM	nanomolar
ppm	parts per million
pptv	parts per trillion by volume

Acronyms

ICP-OES	Inductively coupled plasma optical emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
NAWQA	National Water-Quality Assessment Program
TANC	Transport of Anthropogenic and Natural Contaminants
USGS	U.S. Geological Survey
NOAA	National Oceanic and Atmospheric Administration
PVC	Polyvinyl chloride

Chemical Characteristics, Water Sources and Pathways, and Age Distribution of Ground Water in the Contributing Recharge Area of a Public-Supply Well near Tampa, Florida, 2002-05

By Brian G. Katz, Christy A. Crandall, Patricia A. Metz, William S. McBride, and Marian P. Berndt

Abstract

In 2001, the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey began a series of studies on the transport of anthropogenic and natural contaminants (TANC) to public-supply wells. The main goal of the TANC program was to better understand the source, transport, and receptor factors that control contaminant movement to public-supply wells in representative aquifers of the United States. Studies were first conducted at regional scales at four of the eight TANC study areas during 2002-03 and at small (local) scales during 2003-05 in California, Nebraska, Connecticut, and Florida.

In the Temple Terrace study area near Tampa, Florida, multiple chemical indicators and geochemical and ground-water flow modeling techniques were used to assess the vulnerability of a public-supply well in the karstic Upper Floridan aquifer to contamination from anthropogenic and naturally occurring contaminants. During 2003-05, water samples were collected from the public-supply well and 13 surrounding monitoring wells that all tap the Upper Floridan aquifer, and from 15 monitoring wells in the overlying surficial aquifer system and the intermediate confining unit that are located within the modeled ground-water contributing recharge area of the public-supply well.

Six volatile organic compounds and four pesticides were detected in trace concentrations (well below drinking-water standards) in water from the public-supply well, which had an open interval from 36 to 53 meters below land surface. These contaminants were detected more frequently in water samples from monitoring wells in the overlying clastic surficial aquifer system than in water from monitoring wells in the Upper Floridan aquifer in the study area. Likewise, nitrate-N concentrations in the public-supply well (0.72-1.4 milligrams

per liter) were more similar to median concentrations in the oxic surficial aquifer system (2.1 milligrams per liter) than to median nitrate-N concentrations in the anoxic Upper Floridan aquifer (0.06 milligram per liter) under sulfate-reducing conditions. High concentrations of radon-222 and uranium in the public-supply well compared to those in monitoring wells in the Upper Floridan aquifer appear to originate from water moving downward through sands and discontinuous clay lenses that overlie the aquifer.

Water samples also were collected from three overlapping depth intervals (38-53, 43-53, and 49-53 meters below land surface) in the public-supply well. The 49- to 53-meter interval was identified as a high-flow zone during geophysical logging of the wellbore. Water samples were collected from these depth intervals at a low pumping rate by placing a low-capacity submersible pump (less than 0.02 cubic meter per minute) at the top of each interval. To represent higher pumping conditions, a large-capacity portable submersible pump (1.6 cubic meters per minute) was placed near the top of the open interval; water-chemistry samples were collected using the low-capacity submersible pump. The 49- to 53-meter depth interval had distinctly different chemistry than the other two sampled intervals. Higher concentrations of nitrate-N, atrazine, radon, trichloromethane (chloroform), and arsenic (and high arsenic (V)/arsenic (III) ratios); lower concentrations of dissolved solids, strontium, iron, manganese, and lower nitrogen and sulfur isotope ratios were found in this highly transmissive zone in the limestone than in water from the two other depth intervals.

Movement of water likely occurs from the overlying sands and clays of the oxic surficial aquifer system and intermediate confining unit (that contains high radon-222 and nitrate-N concentrations) into the anoxic Upper Floridan aquifer (that contains low radon-222 and nitrate-N concentrations).

2 Chemical Characteristics, Water Sources and Pathways, and Age Distribution of Ground Water

Differences in arsenic concentrations in water from the various depth intervals in the public-supply well (3.2-19.0 micrograms per liter) were related to pumping conditions. The high arsenic concentrations found in the high flow zone during pumping conditions indicates that oxic water from the surficial aquifer system may travel into conduits in the Upper Floridan aquifer and mobilize arsenic from pyrite in the aquifer matrix.

Geochemical mass-balance mixing models for the public-supply well indicate that 50 to 70 percent of water withdrawn from the public-supply well is being contributed from the surficial aquifer system and 30 to 50 percent from the Upper Floridan aquifer. Geochemical models also indicate the dissolution of small amounts of calcite, gypsum, and dolomite as water moves toward the public-supply well.

Concentrations of age tracers sulfur hexafluoride (SF_6), tritium (^3H), and helium-3 (^3He) in samples from the public-supply well during low- and high-rate pumping conditions were consistent with binary mixtures dominated by young water (less than 7 years). Similarly, water samples from monitoring wells in the surficial aquifer system had SF_6 and ^3H concentrations that indicate a substantial proportion of young water (less than 7 years). In contrast, most water samples from monitoring wells in the Upper Floridan aquifer had lower SF_6 and ^3H concentrations than water from the public-supply well, indicating mixtures containing higher proportions of older waters (greater than 50 years). The presence of young water (less than 7 years) in the public-supply well and surficial aquifer system indicates the vulnerability of public-supply wells in this area to contamination associated with highly transmissive zones in the Upper Floridan aquifer that are directly connected to the overlying surficial aquifer system.

Selected monitoring wells in the surficial aquifer system were sampled several times during 2003-05 at different hydrologic conditions to evaluate temporal variability in water quality. These wells were sampled four times before and after three tropical cyclones that passed through the area in summer 2004. Additionally, water-quality variations were evaluated for the public-supply well based on five samples collected during 2002-05. Chloride concentrations decreased from the summer 2004 water samples to the winter 2004-05 samples from three wells following the recharge pulse from high rainfall and corresponding peak in water-level elevation in October 2004. Nitrate-N concentrations increased in water from one well from January 2004 to August 2004, but decreased in water from another well during the same period. Nitrate-N concentrations also increased in water samples from two other monitoring wells in the surficial aquifer system, from January 2004 to August 2004, but decreased in subsequent samples from these two wells. Nitrate-N concentrations in water from a well located near the Hillsborough River remained below the detection limit, as reducing conditions persisted during December 2003 to July 2005. Dissolved oxygen concentrations increased in water samples from two wells in the surficial aquifer system, and the public-supply well in August and September 2004 during and following the above normal rain-

fall in June through September 2004. The increase in dissolved oxygen concentrations likely results from recent recharge of water containing high levels of oxygen compared to low levels in ground water prior to the excess rainfall period. Dissolved oxygen concentrations decreased in water from a well near the Hillsborough River in fall 2004, which may indicate the influx of river water with high dissolved organic carbon and subsequent consumption of oxygen as water moves toward this well.

Introduction

The vulnerability of public-supply wells to contamination has raised health concerns throughout the United States. Anthropogenic contaminants, such as solvents, disinfection byproducts, and other volatile organic compounds (Ivahnenko and Zogorski, 2006; Schaap and Zogorski, 2006; Zogorski and others, 2006) and pesticides (Gillion and others, 2006) have been detected in low concentrations in water from drinking-water supply wells across the United States. Ground-water contamination from nutrients, such as nitrate, are widespread (Nolan and others, 1998) particularly in karstic aquifers (Katz, 2004). In addition, other studies have found high levels of naturally occurring contaminants, such as radon (Sowerby and others, 2000), uranium (B. Jurgens, U.S. Geological Survey, written commun., 2007; M.K. Landon, U.S. Geological Survey, written commun., 2007), and arsenic (Focazio and others, 1999; Welch and others, 2000) also are present in drinking water wells.

In response to these concerns, the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program began a series of studies in 2001 to assess the vulnerability of public-supply wells to contamination with regard to the transport of anthropogenic and naturally occurring contaminants (TANC) to public-supply wells at regional and small scales at several sites in the United States (Eberts and others, 2005). The TANC studies were built on previous NAWQA studies that found low levels of mixtures of contaminants in ground water beneath urban areas across the United States (Hamilton and others, 2004).

The overall objectives of the TANC studies are to: (1) identify the dominant contaminants and sources of those contaminants in public-supply wells in representative water-supply aquifers across the United States; (2) assess the effects of natural processes and human activities on the occurrence of contaminants in public-supply wells in representative aquifers; (3) identify the factors that are most important to incorporate into public-supply well vulnerability assessments in different settings and at different scales; (4) develop simple methods and models for screening public-supply wells for vulnerability to contamination in unstudied areas and from emerging contaminants; and (5) increase understanding of the potential effects of water-resources development and management decisions on the quality of water from public-supply wells (Eberts and others, 2005).

The Floridan aquifer system provides drinking water to millions of people throughout the southeastern United States. The Upper Floridan aquifer is particularly vulnerable to contamination from various land-use activities in areas where it is unconfined or poorly confined as in west-central Florida. This vulnerability is due in part to the presence of numerous karst features, such as sinkholes, which facilitate the

movement of water from surface features and overlying hydrogeologic units to the Upper Floridan aquifer (fig. 1). In addition, lineaments of sinkholes and other solution features that trend predominantly in a northeast-southwest direction have been mapped throughout the area and reveal the regionally extensive karst terrane (fig. 1).

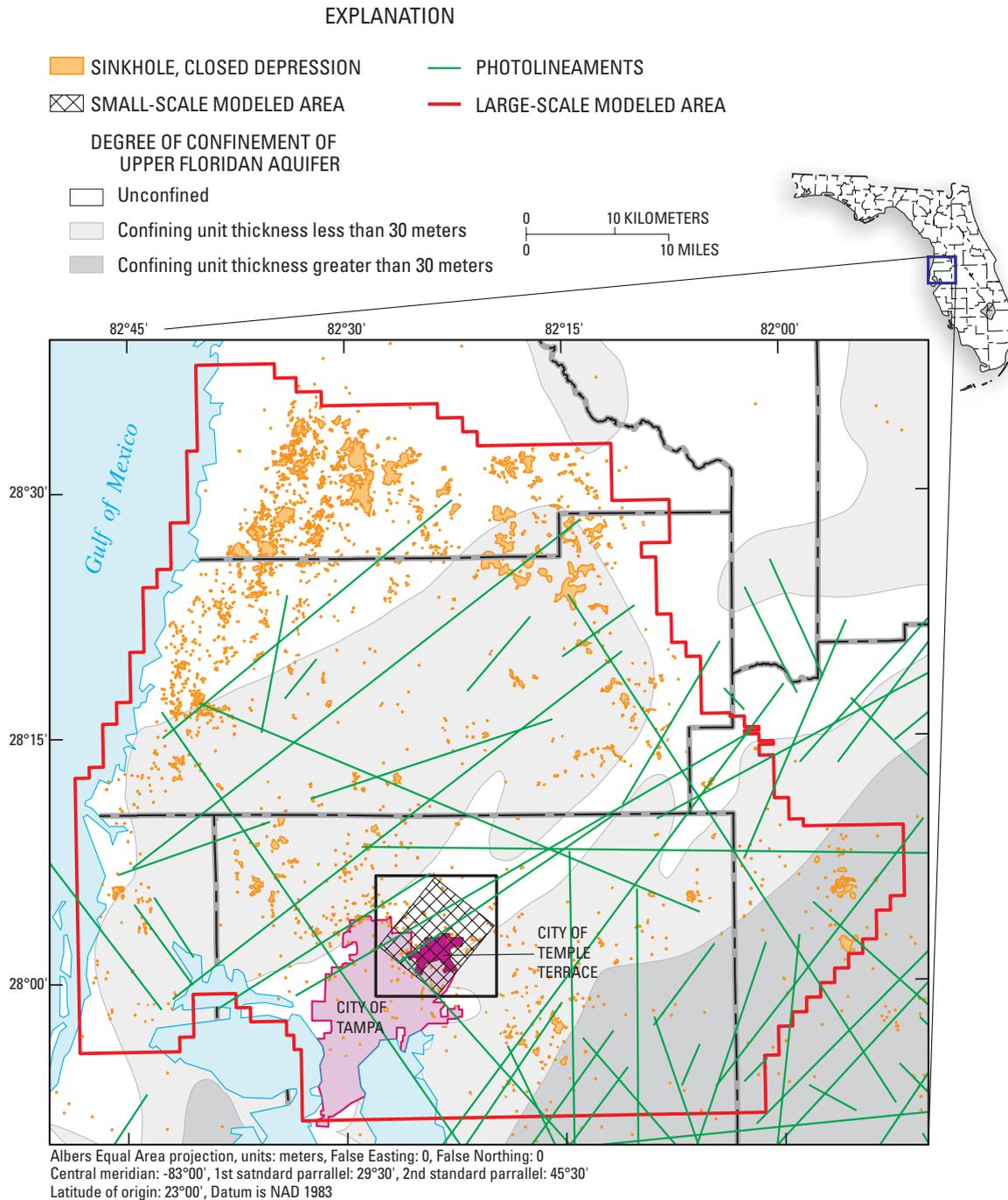


Figure 1. Large- and small-scale areas for the study of the transport of anthropogenic and natural contaminants (TANC) to public-supply wells, photolineaments (modified from Culbreath, 1988; Knochenmus and Robinson, 1996), degree of confinement of the Upper Floridan aquifer, and selected karst features in west-central Florida.

4 Chemical Characteristics, Water Sources and Pathways, and Age Distribution of Ground Water

This study focuses on a public-supply well located in an urban area where various anthropogenic activities at the land surface provide potential sources of contaminants, such as underground storage tanks, fertilizers applied to lawns and golf courses, stormwater retention ponds, and other commercial operations. Additionally, hydrogeologic and geochemical conditions in the subsurface may facilitate the ground-water transport of uranium, radon-222, and arsenic present in minerals that make up the limestone that composes the Upper Floridan aquifer and overlying material to public-supply wells.

The public-supply well (referred to as TTP-4) in the City of Temple Terrace was sampled for a variety of chemical and bacteriological constituents, as part of a source water-quality assessment study by the USGS NAWQA Program in 2002. Several contaminant groups, at concentrations below maximum contaminant levels, were found in water from TTP-4 including nitrate, volatile organic compounds, pesticides, methyl tert-butyl ether (MTBE), solvents, uranium, and arsenic. Several of these compounds have been detected in other community water system wells in the northern Tampa Bay area (Metz and others, 2007). Construction and operational practices of TTP-4 are similar to many other community water system wells that supply water in the Tampa Bay region at a pumping rate of 2,650 L/min (liters per minute).

The construction and operational practices of TTP-4 also are representative of community and public-supply wells throughout northern Florida and other karstic aquifers in the United States. Consequently, this study provides important information about the transport and fate of contaminants that can be introduced to the land surface or released from minerals that compose the aquifer matrix and material overlying the principal aquifer, as they move to deeper ground water that is eventually withdrawn for public-water supply. This study investigates the dominant factors affecting the vulnerability of public-supply wells to contamination, such as geochemical conditions in the aquifer, the amount and rate of pumping, and mixing of water from different hydrogeologic units.

Purpose and Scope

The purpose of this report is to assess factors affecting the vulnerability to contamination of a public-supply well in the Upper Floridan aquifer near Tampa, Florida. The report presents information on the hydrogeologic setting, occurrence and distribution of ground-water ages, and selected chemical characteristics of the ground water in the contributing recharge area of a public-supply well. The occurrence and distribution of selected inorganic and organic chemical constituents that are useful for developing basic interpretations of ground-water recharge and discharge patterns and pathways are described. Factors are assessed that influence transport of anthropogenic contaminants (for example, nitrate, volatile organic compounds, and pesticides) and naturally occurring compounds of concern (radon-222, arsenic, uranium, dissolved organic

carbon, and hydrogen sulfide) to supply wells for the TANC study area at Temple Terrace near Tampa, Florida. This report includes a description of the design of the monitoring well network, methods of data collection and analysis, estimates of apparent ground-water ages and ground-water age distributions using atmospheric tracers and lumped parameter models, and isotopic and other chemical information for ground- and surface-water samples. This report is intended to serve as a foundation for synthesis analyses comparing results between the Temple Terrace study area and other TANC study areas in Nebraska, California, and Connecticut.

Description of Study Area

The small-scale study area is 86 km² (square kilometers) and encompasses the city of Temple Terrace, which is located northeast of Tampa, Florida, in north-central Hillsborough County (fig. 1). Temple Terrace is in the Hillsborough River drainage basin, and is bounded on the west and southwest by the city of Tampa and on the east and south by the Hillsborough River (fig. 2). Public-supply wells in Temple Terrace tap the Upper Floridan aquifer, which underlies most of the Southeast 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 1,135 people per square kilometer. The growth in population occurred while land use transitioned from agricultural in 1950 to commercial and residential in the 1970s and later. Temple Terrace is located on a local topographic high, with land-surface elevations close to 27 m (meters) 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. During high-water conditions, excess water is pumped from these basins and discharged into the Hillsborough River.

Average annual rainfall in the Tampa area was 114 cm (centimeters) for the period 1971-2000, as recorded at the National Oceanic and Atmospheric Administration (NOAA) station at the Tampa International Airport (National Climatic Data Center, 2005). On average, about 60 percent of the rainfall occurs from June through September. August is typically the wettest month, with about 17 percent of the annual rainfall. November is typically the driest month, with slightly less than 4 percent of the annual rainfall.

Potential sources of contaminants to ground water in the Temple Terrace study area include underground storage tanks, septic tanks, stormwater runoff to retention ponds, dry cleaners and other commercial operations that use solvents, chemicals applied to golf courses and lawns, and hazardous waste sites (fig. 2).

Previous Studies

A detailed hydrogeologic and water-quality study was conducted by the USGS in the early 1970s, in cooperation with the City of Temple Terrace, to provide information to the City for the development of additional ground-water supplies and to minimize problems with poor quality water (Stewart and others, 1978). Data were collected on aquifer properties,

water-quality variations with depth in the Upper Floridan aquifer, geohydrologic characteristics of the Upper Floridan aquifer and surficial material, ground-water levels, and chemistry and microbiology of water samples from wells and surface-water sites. Degradation of water quality in Temple Terrace public-supply wells as early as 1968 was documented, including high concentrations of total coliform bacteria, fecal streptococci, and color (Stewart and others, 1978).

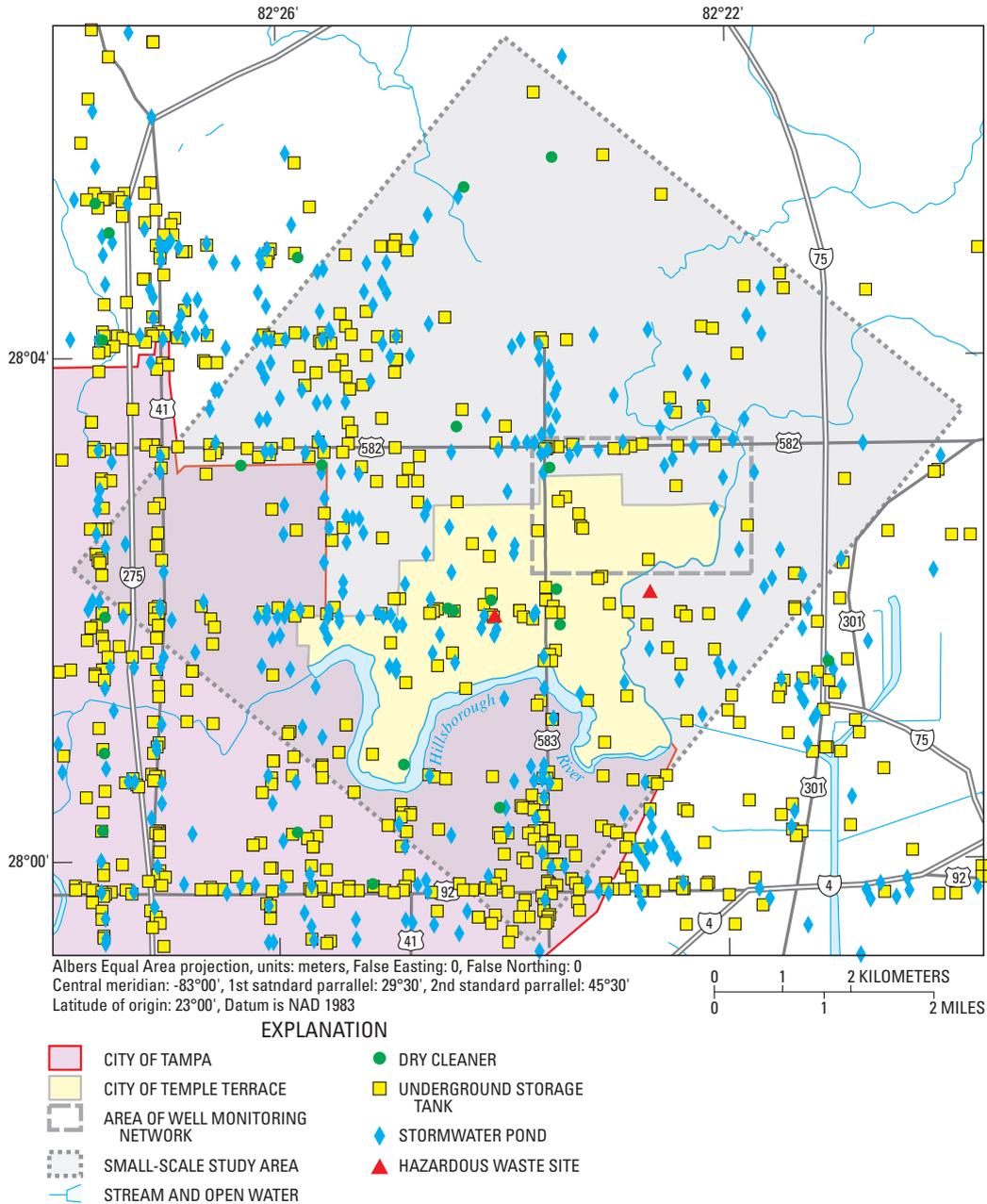


Figure 2. Location of potential sources of contaminants to ground water in the Temple Terrace, Florida, study area.

Geologic sections showing the thickness and configuration of shallow sedimentary layers that underlie the Hillsborough River were constructed from seismic-profile records along a river subreach near Temple Terrace as part of a study to evaluate connections between ground water and surface water in the Hillsborough River basin (Wolansky and Thompson, 1987). That study described leakage of river water to the Upper Floridan aquifer based on decreasing river flow along a section of the river that included Temple Terrace (Wolansky and Thompson, 1987). However, interactions between ground water and surface water are complex, as a study in the early 1970s found that the Hillsborough River receives inflow from both the water-table aquifer (within the surficial aquifer system) and the Upper Floridan aquifer south and east of Temple Terrace due to head relations between ground water and surface water that change seasonally (Stewart and others, 1978).

Other studies have characterized the hydrogeology and hydrochemistry of the Upper Floridan aquifer and surficial aquifer system in this area (Miller, 1986; Trommer, 1987; Aucott, 1988; Bush and Johnston, 1988; Sprinkle, 1989; Berndt and Katz, 1992; Katz, 1992; Knochenmus and Robinson, 1996; Yobbi, 2000). Swancar and Hutchinson (1995) related the stable isotope composition and tritium concentrations to the potential for contamination of ground water in the shallow Upper Floridan aquifer in west-central Florida.

A regional study of the transport of anthropogenic and natural contaminants in 2002-03 in the Tampa, Florida, area was designed to identify factors affecting contaminant transport based on existing data for public-supply wells, and to delineate contributing recharge areas of public-supply wells using an existing ground-water flow model (Paschke, 2006). During October 2002 to January 2003, a number of (30) community water system wells in the northern Tampa Bay area were sampled for 260 anthropogenic organic compounds as part of a NAWQA source water study for wells that provide drinking water (Metz and others, 2007). The 10 most frequently occurring anthropogenic organic compounds in the United States (Zogorski and others, 2006) were detected in more than 10 percent of the 30 source water samples, and included volatile organic compounds and pesticides. Samples generally averaged three compounds, and 70 percent of the samples had at least one volatile organic compound (Metz and others, 2007). This study also found a significant correlation between the number of anthropogenic organic compounds detected and population within a 500-m radius of a community water system well. Chloroform concentrations were highest beneath areas where residential land use was greater than 73 percent. Similar findings were noted for pesticides in source water for community water system wells (Metz and others, 2007).

Acknowledgments

Assistance with water-quality sampling was provided by the following individuals: Bruce Bernard, Darlene Blum,

Terry Petrosky, John Pittman, and Ann Tihansky. The authors thank Amy Swancar, Lynne Fahlquist, and J.K. Böhlke for their review comments and suggestions that improved earlier versions of this report. We gratefully acknowledge the logistical assistance from the City of Temple Terrace Department of Utilities.

Methods

This section contains information about the sampling network design, monitoring well installation, water-quality sampling and analysis, quality assurance, and data analysis. This section also describes the collection of aquifer material samples for characterizing lithology and mineralogy and elemental analysis of core material from hydrogeologic units, collection and analysis of chemical and isotopic constituents, and age dating of ground water.

Design of Monitoring Well Network

Wells were installed in the contributing recharge area of public-supply well TTP-4 based on a regional ground-water flow model (C.A. Crandall, U.S. Geological Survey, written commun., 2007) and in adjacent areas to better understand ground-water flow patterns and to determine the occurrence of various chemicals in the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer. Additionally, selected monitoring wells were sampled several times during the study to evaluate temporal variability in water quality. Monitoring wells were installed in two phases: (1) during late fall 2003 and winter 2004, and (2) during summer 2004 (fig. 3). Monitoring wells were located in the contributing recharge area of the public-supply well. Contributing recharge areas of the public-supply well were delineated using particle-tracking software and a stochastic model that incorporated fracture flow (C.A. Crandall, U.S. Geological Survey, written commun., 2007). During the first phase of well drilling, 15 wells were installed in 5 well nests, with each nest containing 3 wells. Most of these nests consisted of one shallow well screened in the surficial aquifer system, one well screened near the top of the Upper Floridan aquifer, and one deep well in the Upper Floridan aquifer. Because the intermediate confining unit was absent at most locations, only one well (113RC-H50) was installed in that unit during phase 1. During the second phase of well drilling, another 15 monitoring wells were installed. These well locations were based on updated estimates of the contributing recharge area of public-supply well TTP-4 based on Monte Carlo probabilistic methods to incorporate uncertainty and karst features into the model (C.A. Crandall, U.S. Geological Survey, written commun., 2007). A total of 12 monitoring wells were installed in the surficial aquifer system, 4 in the intermediate confining unit, and 14 in the Upper Floridan aquifer. Surface-water samples were collected from the Hillsborough River (denoted as station

HRiver in figures and tables) and stormwater retention ponds (fig. 3). Well depth and other well construction information are contained in table 1.

Drilling, Coring, and Well Installation

Hollow-stem augering techniques that conformed to USGS protocols (Lapham and others, 1995) were used to install monitoring wells in the surficial aquifer system, intermediate confining unit, and shallow Upper Floridan aquifer (wells less than 60-m deep). Mud-rotary methods were used for the installation of the deep monitoring wells in the Upper Floridan aquifer. Equipment was decontaminated between sites by steam cleaning. All monitoring wells consisted of threaded polyvinyl chloride (PVC) pipe (schedule 40, 10-cm diameter) and had 3-m-long screens with 1-mm (millimeter) slots. Clean silica sand was packed around the well screens. The wells were sealed by placing bentonite above the sand packing material to land surface, and cementing above the bentonite at the surface with a steel well protector and locking cap. Wells were developed using a surging pump until stabilization of field properties (pH, specific conductance, temperature, dissolved oxygen) and turbidity.

Split-spoon samples were collected in boreholes, and samples of rock (cores) were collected in one well (MAS-F160). A description of the lithology of the cores and cuttings obtained during well drilling and a summary of analyses performed on selected core samples are presented in table 2. Core samples were collected using a split-spoon sampler (with clear plastic liners) in unconsolidated sediment or a core barrel in rock. Subsamples were processed in a closed chamber that was purged with ultra-pure nitrogen gas. Some subsamples of core material were stored in capped plastic cylinders, and other samples were stored in glass jars and kept on ice. Core samples were analyzed for bulk and clay mineralogy, elemental composition, organic matter content, bulk density, and volumetric moisture content (table 3). Recharge estimates were based on unsaturated zone properties (R. Healy, U.S. Geological Survey, written commun., 2004). Pore water extracted from cores collected at various depths at the Lynnwood Park (LP) and Lightfoot Retention Pond (LRP) sites were analyzed for nitrate-N, chloride, sulfate, and bromide (P. McMahon, U.S. Geological Survey, written commun., 2004). Particle-size distribution of core subsamples was characterized using optical diffraction and a particle-size analyzer (Gee and Or, 2002). Sediments in the size range of

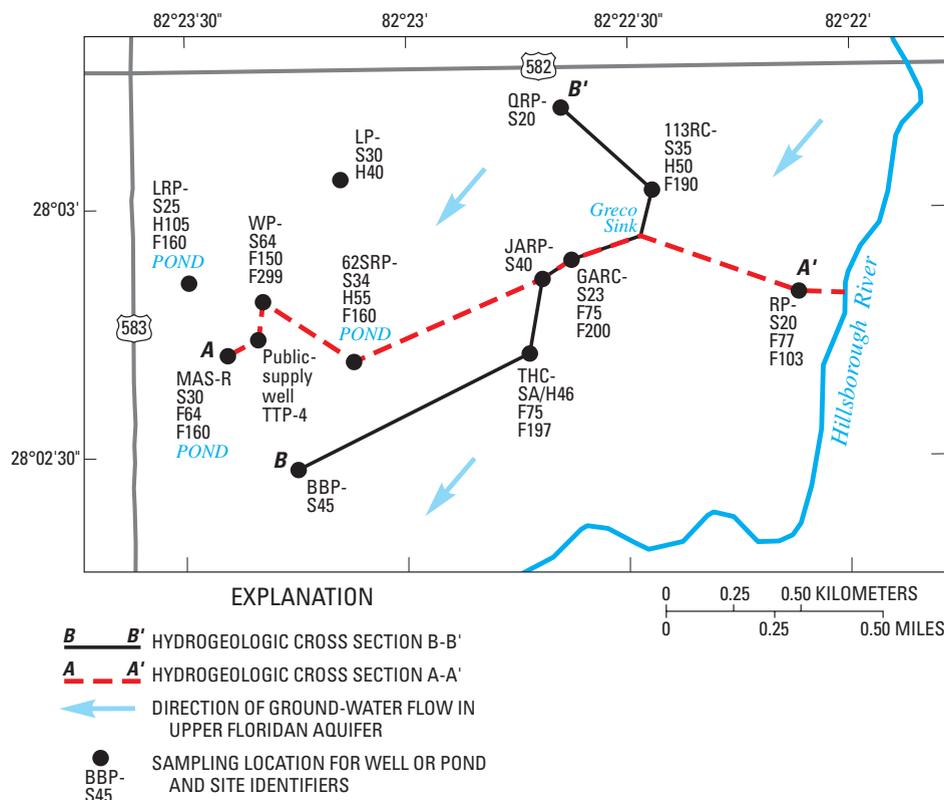


Figure 3. Lines of hydrogeologic sections, sampling site locations, and direction of ground-water flow in the Upper Floridan aquifer in the Temple Terrace, Florida, study area.

Table 1. Well construction and location information for monitoring wells tapping the surficial aquifer system (SAS), intermediate confining unit (ICU), and Upper Floridan aquifer (UFA).

[Index numbers are identified in table 1. Latitude and longitude (degrees, minutes, seconds) for each well are contained in first 13 digits of the station identifier. NAVD 88, North American Vertical Datum of 1988. Well depth and depth to top of screen are in meters below land surface]

Index no.	Site identifier	Well name	Site name	Land surface elevation, (meters above NAVD 88)	Well depth (meters)	Depth to top of screen (meters)	Casing diameter (centimeters)	Aquifer
1	280301082222703	Rec Ctr at 113th Ave	113RC-S35	12.90	11	8	10	SAS
2	280301082222702	Rec Ctr at 113th Ave	113RC-H50	12.83	15	12	10	ICU
3	280301082222701	Rec Ctr at 113th Ave	113RC-F190	12.91	58	55	10	UFA
4	280241082224403	Terrace Hill Circle	THC-SA/H46	15.98	14	11	10	SAS/ICU
5	280241082224402	Terrace Hill Circle	THC-F75	16.00	23	20	10	UFA
6	280241082224401	Terrace Hill Circle	THC-F197	16.05	60	57	10	UFA
7	280247082231903	Water Plant	WP-S64	24.54	20	16	10	SAS
8	280247082231902	Water Plant	WP-F150	24.58	46	43	10	UFA
9	280247082231901	Water Plant	WP-F299	24.59	91	88	10	UFA
10	280253082223803	Rec Ctr at Gillette Ave.	GARC-S23	12.39	7	7	10	SAS
11	280253082223802	Rec Ctr at Gillette	GARC-F75	12.58	23	20	10	UFA
12	280253082223801	Rec Ctr at Gillette	GARC-F200	12.50	61	58	10	UFA
13	28024908220703	Railway Park	RP-S20	11.24	6	3	10	SAS
14	28024908220702	Railway Park	RP-F77	11.24	23	20	10	UFA
15	28024908220701	Railway Park	RP-F103	11.25	31	28	10	UFA
16	280303082230902	Lynnwood Park	LP-S30	15.20	9	6	10	SAS
17	280303082230901	Lynnwood Park	LP-H40	15.23	12	9	10	ICU
18	280311082223901	Queensway Ret. Pond	QRP-S20	11.09	6	3	10	SAS
19	280241082230703	62nd Street Ret. Pond	62SRP-S34	21.76	10	7	10	SAS
20	280241082230702	62nd Street Ret. Pond	62SRP-H55	21.76	17	14	10	ICU
21	280241082230701	62nd Street Ret. Pond	62SRP-F160	21.64	49	46	10	UFA
22	280228082231501	Bonnie Brae Park	BBP-S45	16.31	12	9	10	SAS
23	280242082232403	Mas Residence	MAS-R-S30	20.40	9	6	10	SAS
24	280242082232403	Mas Residence	MAS-R-F64	20.34	20	16	10	UFA
25	280242082232401	Mas Residence	MAS-R-F160	20.43	49	14	25	UFA
26	280250082233003	Lightfoot Ret. Pond	LRP-S25	20.32	8	5	10	SAS
27	280250082233002	Lightfoot Ret. Pond	LRP-H105	20.38	32	29	10	UFA
28	280250082233001	Lightfoot Ret. Pond	LRP-F160	20.33	49	46	10	UFA
29	280251082224201	Jaqueline Arbor Ret. Pond	JARP-S40	13.22	11	8	10	SAS
30	Not available	Temple Terrace #4 (public-supply well)	TTP-4	24.65	53	36	30	UFA
31	280244082202000	Railway Park, Hillsborough River	HRIVER	7.17				
32	280242082232900	Mas Retention Pond	MAS-POND	15.99				
33	280242082230800	62nd St. Retention Pond	62SRP-POND	18.62				
34	280250082233200	Lightfoot Recreation Center Retention Pond	LRP-POND	18.64				

Table 2. Description of lithology and results from grain-size analysis from sediments underlying the study area.

[Index numbers are identified in table 1. Depth, in meters below land surface; zone: SZ, saturated zone; UZ, unsaturated zone; NA, no samples available]

Index no.	Site name	Depth, meters	UZ or SZ	Lithology	Lithologic description	Percent sand based on class size	Percent clay and silt based on class size
1	113RC-S35	0-1.2	UZ	Silty sand	Sand, top soil, and organics; tan to white	83	17
		1.2-1.8	UZ	Silty sand	Sand, fine white with iron staining; brownish-yellow top soil; silt		
		2.7-3.4	UZ	Silty sand	Sand, fine white sand with small amount of pale brown silt		
		4.3-4.9	UZ	Silty sand	Light gray sand; silt		
		7.3-7.9	SZ	Clayey sand	Olive-yellow clayey sand, iron staining		
		8.8-9.8	SZ	Clayey sand	Yellow clayey sand, pieces of weathered limestone		
		10.4-11.0	SZ	Clayey sand	Light gray clayey sand, pieces of weathered limestone		
2	113RC-H50	11.9-12.5	SZ	Clayey sand	Light gray clayey sand, pieces of weathered limestone		
		13.4-13.7	SZ	Clayey sand	Light brownish gray clayey sand, pieces of weathered limestone		
		13.7-14.0	SZ	Clayey sand	Dark gray clayey sand, very dark layer at 46 ft		
		13.7-15.2	SZ	Limemud	Drilled 100 ft into a paleo sink, backfilled to 50 ft		
3	113RC-F190	15.2-25.9	SZ	Limestone	75-85 ft void		
		25.9-31.7	SZ	Limestone	85-104 ft very soft		
		31.7-62.5	SZ	Limestone	Hard to soft limestone		
4	THC-SA/H46	0-0.61	UZ	Silty sand	Soil zone, dark grey sand, silt, and organics	93	7
		1.5-2.1	UZ	Silty sand	Pale yellow sand		
		3.0-3.7	UZ	Clayey sand	Pale yellow sand and clay with iron staining		
		4.6-5.2	UZ	Clayey sand	Brownish yellow clayey sand (iron staining) to dense plastic clay		
		6.1-6.7	UZ	Clayey sand	Yellow sand at top interlaced with clay/sandy clay		
		7.6-8.2	UZ	Sandy clay	Light-gray, sandy clay, light greenish gray dense clay		
		9.1-9.8	UZ	Clayey sand	Light yellow-brown sandy clay, small pieces of weathered limestone		
		10.7-11.3	SZ	Clayey sand	Light yellow-brown sandy clay to soft lime mud		
11.6-14.0	SZ	Clayey sand	Light yellow-brown sandy clay to soft lime mud				
5	THC-F75	14.0-23.8	SZ	Limestone	Pale yellow, soft to hard, void at 73 ft		
6	THC-F197	22.9-60.0	SZ	Limestone	Hard to soft, moderately sandy and clayey		
7	WP-S64	0-0.61	UZ	Silty sand	Pale yellow silty sand, some organics	95	5
		1.5-2.1	UZ	Silty sand	Pale yellow silty sand		
		3.0-3.7	UZ	Silty sand	Pale yellow sand and dark brown silt		
		4.6-5.2	UZ	Silty sand	Pale yellow sand and dark brown silt		
		6.1-6.7	UZ	Silty sand	Pale yellow sand and dark brown silt		
		7.6-8.2	UZ	Silty sand	Pale yellow sand and dark brown silt		
		9.1-9.8	UZ	Silty sand	Pale yellow sand and dark brown silt		
		10.7-11.3	UZ	Silty sand	Pale yellow sand and dark brown silt		
		12.2-12.8	UZ	Clayey sand	Pale yellow sand and light greenish gray clay		
		13.7-14.3	UZ	Limestone	Clayey, weathered		
		14.9-15.2	UZ	Limestone	Pale yellow soft, lime mud		
15.2-16.8	SZ	Limestone	Pale yellow soft, lime mud	53	47		
16.8-19.8	SZ	Limestone	Limestone, soft				
8	WP-F150	19.8-45.7	SZ	Limestone	Hard to soft, moderately sandy and clayey		
9	WP-F299	45.7-91.4	SZ	Limestone	White to tan, soft to hard, vuggy, granular, fossiliferous		
10	GARC-S23	0-0.61	UZ	Silty sand	Pale yellow top soil; pale brown sand and organics	93	7
		1.2-1.8	UZ	Silty sand	Pale yellow sand, organics, silt, iron staining		
		2.7-3.4	UZ	Clayey sand	Pale yellow sand, silt; clayey sand, iron staining		
		4.3-4.9	SZ	Clayey sand	Reddish yellow sand and clay, hit a hard pan layer, iron stained		
		5.8-6.4	SZ	Clay	Dense reddish yellow plastic clay with iron staining		
11	GARC-F75	6.4-7.0	SZ	Limestone	White		
		7.0-22.9	SZ	Limestone	Hard to soft		
12	GARC-F200	22.9-61.0	SZ	Limestone	Hard to soft		
13	RP-S20	0-1.5	UZ	Silty sand	Soil zone, dark grey silt and organics		

10 Chemical Characteristics, Water Sources and Pathways, and Age Distribution of Ground Water

Table 2. Description of the lithology and results from grain-size analysis from sediments underlying the study area.—Continued

[Index numbers are identified in table 1. Depth, in meters (m) below land surface; SZ, saturated zone; UZ, unsaturated zone; NA, no samples available]

Index no.	Site name	Depth, meters	UZ or SZ	Lithology	Lithologic description	Percent sand based on class size	Percent clay and silt based on class size
		1.5-2.1	UZ	Silty sand	Light brownish gray top soil, sand with silt and organics	83	17
		2.7-3.4	UZ	Silty sand	Light brownish gray sand, with silt and organics		
		4.3-4.9	SZ	Silty sand	Very dark gray sand, with silt and organics		
		5.8-6.1	SZ	Clayey sand	Light brownish gray sand and clay		
		6.1-6.4	SZ	Sandy clay	Light greenish gray clay and sand		
14	RP-F77	6.4-6.7	SZ	Sandy clay	Light greenish gray		
		6.7-7.0	SZ	Limemud	Limemud, white, some chert		
		7.0-8.2	SZ	Limestone	Chert in places, voids, soft to hard		
15	RP-F103	23.5-31.4	SZ	Limestone	Voids down section, soft to hard		
16	LP-S30	0-1.5	UZ	Sand	Orange-brown to orange		
		1.5-3.0	UZ	Sand	Pale yellow-orange		
		3.0-4.0	UZ	Sand	Pale yellow-white		
		4.3-4.6	UZ	Clayey sand	Pink-orange		
		4.6-8.2	SZ	Clayey sand	Red-orange		
		8.2-8.8	SZ	Sandy clay	Yellow, stiff		
17	LP-H40	8.8-10.7	SZ	Clayey sand	Yellow-orange, dark to pale		
		10.7-11.9	SZ	Sandy clay	Yellow-orange clay, stiff to gummy with sand		
		11.9-12.5	SZ	Limestone	White-Pale yellow, very soft, weathered residuum		
18	QRP-S20	0-2.4	UZ	Sand	Light gray to light yellow brown		
		2.4-2.7	SZ	Sand	Brown		
		2.7-5.5	SZ	Clayey sand	Light yellow brown		
		5.5-6.1	SZ	Clayey sand	Very pale brown to pink clay with sand		
19	62SRP-S34	0-3.0	UZ	Sand	Light yellow-orange		
		4.0-5.2	UZ	Sand	Light orange		
		5.5-7.9	UZ	Clayey sand	Light orange		
		7.9-9.1	UZ	Clayey sand	Light brown		
		9.1-10.4	SZ	Limemud	Light yellow clayey carbonate mud, weathered limestone		
20	62SRSP-H55	10.4-12.2	SZ	Limemud	Dense clay/carbonate mud, with light yellow limestone chips		
		12.2-13.7	SZ	Sandy clay	White with iron staining		
		13.7-16.8	SZ	Limestone	White, muddy fine-grained		
21	62SRP-F160	16.8-19.8	SZ	Limestone	White, friable,		
		19.8-22.9	SZ	Limestone	White, circulation loss		
		22.9-26.5	SZ	Limestone	Light brown, hard		
		26.5-27.1	SZ	Limestone	Hard, circulation loss		
		27.4-29.0	SZ	Limestone	Soft		
		29.0-33.5	SZ	Limestone	White		
		33.5-34.1	SZ	Limestone	Hard slow drilling possibly clay		
		34.7-36.6	SZ	Limestone	White		
		36.6-37.2	SZ	Chert	Chert		
		37.2-40.5	SZ	NA	Void		
		42.7-44.2	SZ	Limestone	Very hard		
		44.2-47.9	SZ	NA	Void		
		47.9-48.8	SZ	Limestone	Greenish-gray clay with light brown		
		48.8	SZ	Limestone	Light brown, fossiliferous		
22	BBP-S45	0-3.0	UZ	Sand	Yellow		

Table 2. Description of the lithology and results from grain-size analysis from sediments underlying the study area.—Continued

[Index numbers are identified in table 1. Depth, in meters (m) below land surface; SZ, saturated zone; UZ, unsaturated zone; NA, no samples available]

Index no.	Site name	Depth, meters	UZ or SZ	Lithology	Lithologic description	Percent sand based on class size	Percent clay and silt based on class size
		3.0-4.6	UZ	Clayey sand	Mottled orange		
		4.6-6.1	UZ	Clayey sand	Pale brown to yellow		
		6.1-8.8	UZ	Sandy clay	Stiff, some possibly oxidized chert		
		8.8-10.1	SZ	NA	Lost circulation, small amount of rock present		
		10.1-10.7	SZ	NA	Void		
		10.7-12.2	SZ	NA	No cuttings		
23	MAS-R-S30	0-4.6	UZ	Sand	Light brown to red-orange		
		4.6-6.1	UZ	Sand	Red-orange to red-brown		
		6.1-9.1	SZ	Sand	Light brown to gray-red		
		9.1-9.8	UZ	Clayey sand	Pinkish-white		
24	MAS-R-F64	10.1-10.7	UZ	Clay	Light greenish gray		
		12.2-13.7	SZ	NA	Lost circulation, bit dropped 4 ft		
		13.7-21.3	SZ	Limestone	Soft drilling carbonate mud		
25	MAS-R-F160	21.9-25.0	SZ	Limestone	Hard, chert, brown limestone		
		25.6-27.4	SZ	Limestone	Alternating hard and soft drilling		
		28.7-42.7	SZ	Limestone	Alternating hard and soft drilling		
		42.7-45.7	SZ	Limestone	White		
		45.7-46.3	SZ	Limestone	White, highly fossiliferous, friable fractured		
		46.3-46.9	SZ	Limestone	Poorly cemented, fossiliferous, mollusks, gastropods		
		46.9-48.8	SZ	Limestone	Cavernous, calcite, vugs and fossil derived moldic porosity		
		48.8	SZ	Limestone	Well cemented		
26	LRP-S25	0-2.1	UZ	Sand	Yellow-orange, brown		
		2.1-4.9	SZ	Sand	Yellow-orange, brown		
		4.9-8.5	UZ	Sand	Very pale brown		
27	LRP-H105	8.5-9.8	UZ	Sand	Very pale brown with small white nodules		
		9.8-12.2	UZ	Sand	Very pale brown with small white nodules		
		12.2-12.8	UZ	Sand	Very pale brown with small white nodules		
		12.8-14.0	SZ	Sand	Fine white		
		14.0-16.5	SZ	Clayey sand	Light brown, pinkish-gray sand, slight clay		
		16.5-17.7	SZ	Clayey sand	Red changing to yellowish-green brown sand with clay		
		17.7-23.2	SZ	Sand, clay, chert	Red-orange clayey sand, siliceous fossiliferous/agateized coral/chert		
		26.5-27.4	SZ	Limestone	Brown chert capping friable pale yellow limestone, iron stained		
		27.4-28.3	SZ	Clay	Pale blue-green, stiff		
		28.3-31.7	SZ	Limestone	Crumbly, fossiliferous, molluscs, at 105 ft sandy infill		
		31.7-32.0	SZ	Limestone	Sandy infill, light yellow-brown		
28	LRP-F160	32.0-33.5	SZ	Limestone	Pale yellow/white, hard, fine grained, difficult drilling		
		33.5-34.4	SZ	Clay	Blue, plastic		
		34.4-35.1	SZ	Limestone	Sandy infill light yellow-brown		
		37.2-39.6	SZ	Limestone	Light brown		
		45.7-47.9	SZ	Limestone	Pale yellow, fractured, vugs, molluscan moldic porosity		
		47.9-48.8	SZ	Limestone	Soft drilling, crumbly		
29	JARP-S40	0-6.1	UZ	Sand	Fine to very fine brown sand		
		6.1-8.8	SZ	Sand	Light brown sand with small amounts of red-orange clay		
		8.8	SZ	Chert	Chert and clay		
		9.1-12.2	SZ	Sand; clay	Alternating hard and soft sand clay; clayey sand; light greenish-gray		

Table 3. Summary of water-quality and solid-phase analyses in the transport of anthropogenic and natural contaminants (TANC) small-scale study area.

Samples and sampling locations		Chemical and physical analyses	
Public-Supply Well, TTP-4			
A total of 7 well head samples from entire open interval		Tritium/Helium-3 and sulfur hexafluoride (age dating), radon-222, radium, 85 volatile organic compounds (VOCs), trace elements, arsenic species (As(III) and As(V)), major ions, nutrients, dissolved gases, dissolved organic carbon, 128 pesticides and pesticide degradation products, stable isotopes (carbon, nitrogen, oxygen, hydrogen, and sulfur), 67 organic wastewater compounds	
A total of 5 samples from three targeted zones during depth-interval sampling with various pumping conditions			
Monitoring Wells (Installed in 2003-2004)			
A total of 64 samples collected from 29 wells tapping the surficial aquifer system, intermediate confining unit and Upper Floridan aquifer		Tritium/Helium-3 and sulfur hexafluoride (age dating), radon-222, radium, 85 volatile organic compounds (VOCs), trace elements, arsenic species (As(III) and As(V)), major ions, nutrients, dissolved gases, dissolved organic carbon, 128 pesticides and pesticide degradation products, stable isotopes (carbon, nitrogen, oxygen, hydrogen, and sulfur)	
Surface-Water Sites			
A total of 4 surface-water samples collected from three stormwater retention ponds and 1 streamwater site (Hillsborough River)		Major ions, nutrients, 85 volatile organic compounds (VOCs), stable isotopes (carbon, nitrogen, oxygen, hydrogen, sulfur), pesticides, and trace elements	
Core and Solid Phase Material Collected During Initial Well Installation			
A total of 13 samples of sediment or rock collected at 9 sites (details shown in table 4)		X-Ray diffraction, elemental analysis of acid extracts, organic matter, bulk density, moisture content, nitrate, chloride, particle size, bulk and clay mineralogy, denitrification measurements with pore water extracts	

0.04 μm (micron) to 2 mm were analyzed using a commercially built apparatus (K.S. Perkins, U.S. Geological Survey, written commun., 2005).

Collection and Analysis of Water Samples

Water samples were collected from monitoring wells, public-supply well TTP-4, stormwater retention ponds, and the Hillsborough River during 2003-05 according to NAWQA protocols (Koterba and others, 1995; Lapham and others, 1995). Use of these methods allows for the collection of consistent ground-water chemistry data among study units across the United States. Samples were collected using a submersible pump with PTFE (Teflon) tubing to minimize cross contamination from one well site to another. Each well was purged a minimum of three casing volumes, and water samples were collected after field properties (temperature, pH, specific conductance, and dissolved oxygen) had stabilized. Chambers were used to process and preserve samples. Alkalinity (as calcium carbonate) was measured in the field using fixed end-point titration methods. Sampling equipment was cleaned after the collection of samples at each site using dilute phosphate-free liquid detergent and a methanol rinse, followed by several rinses of deionized water.

Water samples were collected from each stormwater retention pond using slightly different techniques to coincide with different configurations of inflow pipes and pond characteristics. All samples were collected under static conditions, when no water was entering the ponds, using a stainless steel weighted bottle sampler with a Teflon bottle. There are two storm drains that empty into the Lightfoot Retention Pond (LRP). At this site, a 1-L (liter) water sample was collected at each of six locations around the circumference of the retention pond at a depth of about 16 cm about 1 m from the edge of water. At the MAS retention pond, 2 L of water were collected directly in front of each of three storm drains. A depression in front of each drain allowed the sampler to be completely submerged in these locations. The sample was collected at a depth of about 30 cm and located approximately 1 m from the edge of water. At the 62nd Street retention pond, water levels were low. However, there was a small depression (about 3-5 m in circumference), containing water directly in front of the storm drain that feeds this pond. A 2-L sample was collected at each of three points around this depression at a depth of about 8 cm and located about 1 m from the edge of water. The 6 L of water collected from each pond were composited using a 14-L Teflon churn splitter before being split into multiple sample containers. The composited samples were sent to the various laboratories for analyses as described below.

Field properties (temperature, specific conductance, dissolved oxygen, and pH) were measured at various locations in each pond and median values were recorded.

Samples of ground water and surface water were analyzed for major ions, nutrients, dissolved organic carbon, dissolved gases, 128 pesticides and pesticide degradates, 85 volatile organic compounds (Connor and others, 1998), stable isotopes (carbon, nitrogen, oxygen, hydrogen, and sulfur), trace elements, arsenic speciation, uranium, and radon-222 (table 3). Selected ground-water samples were collected for age dating and analyzed for sulfur hexafluoride (SF₆), tritium (³H), and helium-3 (³He).

Samples for major ions, trace elements, and nutrients were filtered through a 0.45- μ m capsule filter and analyzed using inductively coupled plasma atomic emission spectrometry, graphite furnace atomic absorption spectrometry, ion-exchange chromatography, and colorimetry procedures described in Fishman and Friedman (1989), Faires (1993), Fishman (1993), McLain (1993), Garbarino (1999), and Patton and Kryskalla (2003).

Dissolved gases (nitrogen gas, argon, carbon dioxide, and methane) were analyzed in ground-water samples at the USGS Chlorofluorocarbon Laboratory in Reston, Virginia. Dissolved gases were measured by gas chromatography after extraction in headspaces of glass samplers (Busenberg and others, 1998). Hydrogen sulfide was measured in the field using colorimetric methods (Hach, 2002).

Water samples for radon-222 were collected in a syringe prior to contact with the atmosphere and injected into a mineral-oil based scintillation solution in a 30-mL (milliliter) glass scintillation vial. The sample was shipped overnight to the laboratory and analyzed by liquid-scintillation counting methods (Prichard and Gesell, 1977).

Stable isotopes of oxygen, hydrogen, carbon, sulfur, and nitrogen are used in this study to help understand sources of water and reactions affecting the chemical composition of ground water. Their effectiveness in the identification and quantification of biogeochemical processes in numerous hydrogeologic studies has been well documented (including Clark and Fritz, 1997; Cook and Herczeg, 2000). Samples for stable isotopes of hydrogen, oxygen, sulfur, and nitrogen were analyzed by the USGS Stable Isotope Laboratory in Reston, Virginia. Isotope data are presented in delta (δ) notation as the ratio of the heavy to the light isotope, normalized to a standard (eq. 1).

$$\delta_{\text{sample}} = 1000[(R_{\text{sample}}/R_{\text{standard}})-1] \quad (1)$$

where R_{sample} and R_{standard} are the ratio of the heavy to the light isotope in the sample and in the standard, respectively. Delta hydrogen-2 ($\delta^2\text{H}$) and delta oxygen-18 ($\delta^{18}\text{O}$) are analyzed using an isotope ratio-mass spectrometer by hydrogen gas water equilibration and carbon dioxide water equilibration techniques, respectively, and reported relative to Vienna Standard Mean Ocean Water (Epstein and Mayeda, 1953; Coplen and others, 1991, 1994; K.M. Revesz, U.S. Geological Survey,

written commun., 2003). Dissolved sulfate is analyzed for delta sulfur-34 ($\delta^{34}\text{S}$) using methods of Carmody and others (1997) and reported relative to the Vienna Canyon Diablo Troilite. Isotopes of nitrogen and oxygen of nitrate are analyzed by bacterial conversion of nitrate to nitrous oxide and reported relative to nitrogen gas in air and Vienna Standard Mean Ocean Water, respectively (Sigman and others, 2001; Casciotti and others, 2002; Revesz and Casciotti, 2003). Water samples are analyzed for delta carbon-13 ($\delta^{13}\text{C}$) using mass-spectrometry techniques at the University of Waterloo Environmental Isotope Laboratory and reported relative to the Vienna Pee Dee Belemnite standard (Coplen, 1994).

Volatile organic compounds, pesticides, pesticide degradates, dissolved organic carbon, major ions, trace elements, nutrients, and radon-222 were analyzed by the USGS National Water Quality Laboratory in Lakewood, Colorado. Samples for volatile organic compounds were unfiltered and determined by gas chromatography and mass spectrometry using methods described in Connor and others (1998). Pesticides were sampled using a 0.7- μ m glass-fiber filter and analyzed by carbon-18 solid-phase extraction and capillary column gas chromatography and mass spectrometry (Zaugg and others, 1995; Lindley and others, 1996; Sandstrom and others, 2001; Madsen and others, 2003). Dissolved organic carbon samples were collected by forcing raw water samples through a 0.45- μ m glass-fiber filter using high purity nitrogen gas. Dissolved organic carbon samples were analyzed by methods described by Brenton and Arnett (1993).

Age Dating of Ground Water

Water samples were collected and analyzed from selected wells for the transient environmental tracer ³H, its radioactive decay product ³He, and SF₆. Anthropogenic activities, such as industrial processes and atmospheric testing of thermonuclear devices, have released SF₆ and ³H into the atmosphere in low but measurable concentrations (fig. 4). Precipitation that incorporates SF₆ and ³H 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. The tritium/tritiogenic helium-3 (³H/³He_{trit}) and SF₆ 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 and others, 1989; Plummer and Busenberg, 1999; Busenberg and Plummer, 2000).

Tritium and Tritiogenic Helium-3

The continued decrease and low concentrations of ³H in rainfall in the Southeast have resulted in limited use of the ³H method for age dating ground waters recharged during the past 20 to 30 years. However, by measuring ³He_{trit}, the stable daughter product of ³H decay that has accumulated in ground-water systems, the dating range and precision can be enhanced

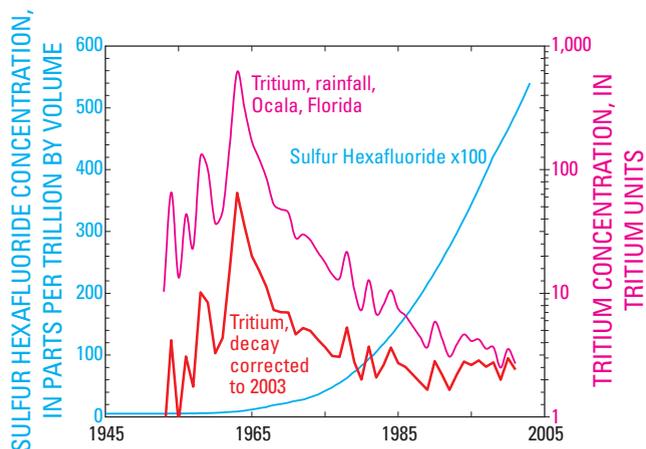


Figure 4. Input of sulfur hexafluoride to atmosphere in the northern hemisphere (from Busenberg and Plummer, 2000; E. Busenberg, U.S. Geological Survey, written commun., 2005) and tritium concentrations in rainfall from Ocala, Florida, (from Michel, 1989; R.L. Michel, U.S. Geological Survey, written commun., 2005), during 1950-2005.

(Plummer and others, 1998; Cook and Böhlke, 1999). Combined measurements of ^3H and its daughter product of radioactive decay, $^3\text{He}_{\text{trit}}$, define a relatively stable tracer of the initial ^3H input to ground water, which can be used to calculate the $^3\text{H}/^3\text{He}_{\text{trit}}$ age from a single water sample (Schlosser and others, 1988, 1989; Solomon and Sudicky, 1991). The $^3\text{H}/^3\text{He}_{\text{trit}}$ ratio yields the following equation for the piston-flow assumption in which the apparent age (T, years) can be expressed as (Torgersen and others, 1979):

$$T = 1/\lambda_T [\ln (1 + ^3\text{He}_{\text{trit}}/^3\text{H})], \quad (2)$$

where λ_T is the radioactive decay constant for ^3H (the concentration in tritium units), and $^3\text{He}_{\text{trit}}$ is the tritiogenic helium-3 content in tritium units. One tritium unit is equal to 1 ^3H atom in 10^{18} hydrogen atoms, and is equivalent to 3.2 pCi/L (picocuries per liter) of water. A He-isotope mass balance is used to calculate the amount of tritiogenic and non-tritiogenic ^3He in the sample. Non-tritiogenic ^3He (which generally is negligible in a shallow aquifer with local recharge) is corrected for by using measured concentrations of helium-4 (^4He) and neon (Ne) in the water sample and assuming solubility equilibrium with air at the water temperature measured during sampling (Schlosser and others, 1988, 1989). It is assumed that ^3H and $^3\text{He}_{\text{trit}}$ concentrations in ground water are not affected by contamination, sorption, and microbial degradation processes that can alter the concentrations of other transient tracers, such as chlorofluorocarbons (Plummer and others, 1998). The distribution of ^3H and $^3\text{He}_{\text{trit}}$ can be affected by hydrodynamic dispersion and mixing different age waters (Solomon and Sudicky, 1991; Reilly and others, 1994).

Information about ground-water transit times can be obtained by comparing measured ^3H concentrations in ground

water with the long-term ^3H input function of rainfall measured at the International Atomic Energy Agency precipitation monitoring station in Ocala, Florida (fig. 4), which is about 175 km (kilometers) northeast of the Temple Terrace study area. Atmospheric weapons testing beginning in the early 1950s increased ^3H concentrations in rainfall in this area to a maximum of several hundred tritium units during the mid-1960s, followed by a nearly logarithmic decrease in concentrations to the present. Analytical uncertainty (one sigma) for ^3H using the low-level counting procedure is about ± 0.15 to 0.30 tritium units (Ludin and others, 1998).

Water samples for the determination of $^3\text{H}/^3\text{He}_{\text{trit}}$, ^4He , and Ne were collected in pinched-off copper tubes (10-mm diameter, 80-cm length, about 40-mL volume) while applying back pressure to prevent formation of gas bubbles. These samples were analyzed at the Noble Gas Laboratory of Lamont-Doherty Earth Observatory in Palisades, New York, by using quantitative gas extraction followed by mass spectrometric techniques (Schlosser and others, 1989; Ludin and others, 1998). A similar procedure was used to collect water samples from the public-supply well (depth-interval sampling in October 2004) and other selected wells for analysis of $^3\text{H}/^3\text{He}_{\text{trit}}$, ^4He , and Ne by the USGS Noble Gas Laboratory in Denver, Colorado.

Sulfur Hexafluoride (SF_6)

The stability of SF_6 in the hydrosphere has led to its effective use for dating ground water recharged during the past 30 years (Busenberg and Plummer, 2000). This technique presumes that SF_6 concentrations in the aquifer have not been altered by biological, geochemical, or hydrologic processes.

Apparent ages for SF_6 are estimated based on the equilibrium partitioning between recharging ground water and the partial pressures of SF_6 in the troposphere or soil atmosphere (fig. 4). Concentrations of SF_6 in ground water are functions of the atmospheric partial pressures and the temperature at the base of the unsaturated zone during recharge. 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 and others, 1993). An apparent age of the sampled water is determined from a comparison of the partial pressure of SF_6 in the sample, calculated from measured concentrations using solubility data, with the record of atmospheric partial pressures over the northern hemisphere at different times (fig. 4). The input function for SF_6 was obtained from atmospheric input curves, and assuming a ratio of summer-to-winter infiltration coefficient of 1.0.

Ground-water samples for the SF_6 dating method were collected in 1-L safety-coated glass bottles by placing the sampling discharge line in the bottom of the bottle and displacing the air in the bottle with ground water. After about 2 L of overflow, the sampling line was removed. The bottles were capped with polyseal conical screw-caps without headspace and wrapped with electrical tape to prevent the caps from

coming loose during shipping. Samples were analyzed for SF₆ at the Chlorofluorocarbon Laboratory in Reston, Virginia, using procedures described by Busenberg and Plummer (2000).

Quality Assurance

Quality-assurance samples were collected to assess laboratory performance and to help identify potential contamination problems associated with field collection methods. Quality-assurance information for this study included the collection of 10 replicate samples, 24 blank samples, and laboratory surrogate spike samples. Surrogate compounds were added to each of the samples submitted for pesticide and volatile organic compound analyses including laboratory reagent blank samples, field blank samples, and regular ground-water and surface-water samples. These compounds, which are not normally found in the environment, are used to determine if there are interferences from other chemicals in the sample matrix and to evaluate the efficacy of the laboratory's analytical methods to detect compounds that are chemically similar. Replicate samples were collected and analyzed for volatile organic compounds, pesticides, major ions, nutrients, and trace elements which were the most frequently sampled constituents. Field blank samples were processed using nitrogen-purged universal blank water that was certified for use in the collection of blank samples for volatile organic compounds, pesticides, low-level nutrients, dissolved organic carbon, major ions, and trace elements.

Only two organic compounds were detected in blank samples (app. A1). Concentrations of methylene chloride (dichloromethane) ranged from 0.1 to 0.6 µg/L (microgram per liter) in five samples. Chloroform (trichloromethane) was detected in one sample at a concentration of 0.09 µg/L. Several inorganic constituents were detected in concentrations that were slightly greater than the method reporting level in three samples. These included cobalt, nickel, strontium, calcium, sodium, and silica. The low concentrations of strontium, calcium, sodium, and silica detected in blank water samples were well below concentrations measured in water samples from wells, ponds, and the river, and therefore, do not constitute a contamination problem.

Replicate analyses for organic compounds generally agreed within ±10 percent, with the exception of dichloromethane and carbon disulfide, which agreed within ±30 percent (app. A2). Replicate analyses for inorganic compounds were within ±10 percent for most constituents, with the exception of nickel and selenium (two constituents not detected in most environmental samples). One set of replicate water samples for dissolved organic carbon from WP-S64 (collected on June 14, 2005) showed considerable variability, 1.1 and 13.7 mg/L (milligrams per liter); however, the exact cause for this analytical discrepancy (or contamination of one replicate sample) is not known (app. A2). Three other water samples collected from this well on previous dates had

dissolved organic carbon concentrations that ranged from 0.6 to 1.5 mg/L.

Two surrogate organic compounds, alpha-HCH-d6 (chemical abstract service registry number 319-84-6) and diazinon-d10, were added to each of the 30 pesticide samples collected in this study. The median recoveries of alpha-HCH-d6 and diazinon-d10 were 85.0 percent (range from about 69-197 percent) and about 95.5 percent (range from about 69-211 percent), respectively (app. A3). Recovery values that range from 70 to 130 percent generally are considered to be within acceptable limits, although this range can vary considerably for specific compounds. Values that exceed this range may indicate possible problems with analytical methodology. Three surrogate compounds were added to the 69 samples of ground water and surface water analyzed for volatile organic compounds and laboratory reagent samples (app. A3). Median percent recoveries for 1,2-dichloroethane-d4, 1-bromo-4-fluorobenzene, and toluene-d8 were 115 percent (range from 99-147), about 93 percent (range from about 58.3-112 percent), and about 99 (range from about 93-113) percent, respectively.

Lithology, Mineralogy, and Elemental Analysis of Core Material

Geologic descriptions of the surficial sediments, intermediate confining unit, and limestone that composes the hydrogeologic units were based on characterization of well cuttings, split-spoon coring, and grain-size analysis. Mineralogical analysis of selected cores also was performed using x-ray diffraction and mass spectrometry. Physical analyses were made of selected core materials including bulk density, percent organic matter (loss on ignition), and volumetric moisture content (R. Healy, U.S. Geological Survey, oral commun., 2005).

The abundance of elements in grain coatings or other mineral phases from core samples were evaluated using different acids and reagents, including: (1) 10-percent nitric acid, (2) 6N hydrochloric acid, (3) 0.5 M hydroxylamine hydrochloride extractable iron, and (4) acid-volatile and chromium-reducible sulfides. All extractions were performed on an "as received" basis (that is, wet), but the moisture content was determined for a separate subsample and used to correct the analytical concentrations to dry weight. The extractions listed above were performed in the laboratory; however, for the latter two extractions, core samples were first subsampled in a nitrogen gas atmosphere glove bag and the bottles and flasks were flushed with nitrogen gas in the field before shipment to the laboratory for analysis.

The coatings extraction (hydrochloric acid and nitric acid) methods were primarily intended to target ferric oxyhydroxides and their associated trace elements, but they also can be used to extract other oxides and clay, carbonate, and sulfide phases to varying degrees. The sample/solution ratio for the 6N hydrochloric acid and 10-percent nitric acid extractions

were 5 ± 1 g (gram) of wet weight to 15 mL of acid solution, whereas that for 0.5 M hydroxylamine hydrochloride extraction was 4 to 10 g (gram) of wet sediment to 75 mL of reagent. The sediment-acid aliquots were set on a shaker table for 6 hours, then centrifuged, filtered with 0.45- μ m pore filters, and analyzed for several minor elements including arsenic and uranium. Leachate derived from the 10-percent nitric acid extractions was analyzed for aluminum, chromium, copper, iron, manganese, nickel, and vanadium by inductively coupled plasma optical emission spectroscopy (ICP-OES). Further dilution to 5 percent was required for analysis of arsenic, cadmium, lead, and uranium with inductively coupled plasma mass spectrometry (ICP-MS), which yielded lower detection limits. Analysis of the 6N hydrochloride acid extractants required dilution to 1.6 N hydrochloride acid prior to analysis by ICP-MS. Leachate derived from the 6N hydrochloric acid extractions was diluted to 10 percent and analyzed by ICP-MS for iron, manganese, aluminum calcium, cadmium, chromium, copper, potassium, magnesium, sodium, nickel, lead, vanadium, zinc, and uranium. The 0.5 M hydroxylamine hydrochloride and 6 N hydrochloric acid extractions were performed according to Lovley and Phillips (1987) and analyzed by ICP-MS. The 0.5 M hydroxylamine hydrochloride and 6 N hydrochloride acid extracts were analyzed using the ferrozine method with a Hach DR/2400 Spectrophotometer (Hach, 2002).

Sulfide phases in sediments or rock were extracted using the method described by Allen and others (1991, 1993) and summarized in U.S. Environmental Protection method 9030B (U.S. Environmental Protection Agency, 1996) for acid soluble and acid insoluble sulfides. The method was modified to avoid the oxidization of hydrogen sulfide by soluble ferric iron by the addition of stannous chloride (M.L. Tuttle and K.M. Conko, U.S. Geological Survey, oral commun., 2003) and further modified by the addition of chromium chloride (Canfield and others, 1986; Bowles and others, 2003) to include pyrite-bound sulfide. Sulfide phases that are extracted by this method include pyrite, elemental sulfur, and acid volatile monosulfides. Samples of 5 to 20 g of undried sediment were transferred to a 250-mL round-bottomed flask (under nitrogen gas stream) with 10 g of stannous chloride. The flask was attached to a nitrogen gas stream on a heating mantle, and 75 mL of deaerated 6 N hydrochloric acid and 50 mL of chromium chloride were added. The samples were heated and kept at a sub-boiling temperature for 1 hour. Hydrogen sulfide was collected in two sequential aliquots of 100 mL of 0.5M sodium hydroxide. Sulfide was analyzed colorimetrically by means of a DR/2400 Hach Spectrophotometer using the methylene blue method specified by the manufacturer (Hach, 2002).

Hydrogeologic Setting

The geology of the study area consists of sand, clay, and carbonate rocks that were deposited primarily in a marine

environment. The geologic 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 and others, 1978). Some of these sinkholes are open to the Upper Floridan aquifer and may receive water from the Hillsborough River or wetland areas near the sinks. These wetland areas and the Hillsborough River usually contain highly colored (tannic) water or have degraded water quality due to elevated bacteriological constituents. Continuous seismic-reflection profiling on the Hillsborough River near Temple Terrace indicated about a 3-m thickness of surficial material overlying the limestone that composes the Upper Floridan aquifer and filling large solution cavities in the limestone (Wolansky and Thompson, 1987). Interactions between ground water and the Hillsborough River have been documented in previous studies (Stewart and others, 1978; Wolansky and Thompson, 1987).

Principal hydrogeologic units that lie within this sedimentary sequence include the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer. The uppermost surficial aquifer system, is an unconfined sand and clayey sand aquifer and is separated from the Upper Floridan aquifer by the clay-rich intermediate confining unit, which controls the amount of recharge between the two aquifers. The underlying Upper Floridan aquifer is a highly productive carbonate aquifer and is the principal source of freshwater in west-central Florida (Miller, 1986). The generalized hydrogeologic columns and sections of the study area are shown in figures 5A and 5B. Lithologic information that was used to construct the hydrogeologic sections is included in table 2. Water-level data from wells completed at various depths are included in these sections to show the vertical and horizontal flow regime within the study area.

The surficial aquifer system is a permeable hydrogeologic unit contiguous with land surface that principally consists of unconsolidated to poorly indurated clastic deposits of the undifferentiated surficial deposits (Southeastern Geological Society, 1986). The surficial aquifer system contains a water table; the depth to this water surface is variable and ranges from about 3 to 15 m below land surface. The surficial aquifer system 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.

The intermediate confining unit is a nonwater-yielding layer that controls the downward leakage between the surficial aquifer system and Upper Floridan aquifer. The extent, thickness, and permeability of the clay unit is variable throughout

SERIES	STRATIGRAPHIC UNIT	GENERAL LITHOLOGY	HYDROGEOLOGIC UNIT
Holocene to Pliocene	Undifferentiated Sands and Clays	Quartz sand , silty sand, clayey sand, peat, shell	surficial aquifer system
	-----	----- Clay , minor quartz sand, phosphate, fine-grained dolomite, residual limestone	----- intermediate confining unit
Miocene	Hawthorn Group Tampa Member of the Arcadia Formation	Limestone , minor quartz sand, phosphate, chert, clay, fine-grained dolomite	Upper Floridan aquifer Tampa/Suwannee producing zone
Oligocene		Suwannee Limestone	
Eocene	Ocala Limestone	Limestone , micritic, chalky, very fine- to fine-grained, soft, poorly indurated, trace organics, clays and dolomite, abundant foraminifera	Ocala semiconfining unit
	Avon Park Formation	Limestone, dolomite, and evaporites Limestone and dolomite interbeds typical in upper part, deeper beds are continuous dolomite with increasing evaporites at base Limestone is fine-grained, tan, recrystallized packstone with variable amounts of organic-rich laminations near top Dolomite is hard, brown, sucrosic in texture and commonly fractured Evaporites occur in dolomite as interstitial gypsum and anhydrite with evaporite filling pore space and as interbeds in the lower part	Ocala/Avon Park producing zone Avon Park producing zone ----- Middle confining unit

Figure 5A. Columns showing stratigraphic and hydrogeologic units of the Temple Terrace, Florida, study area (from Tihansky, 2005).

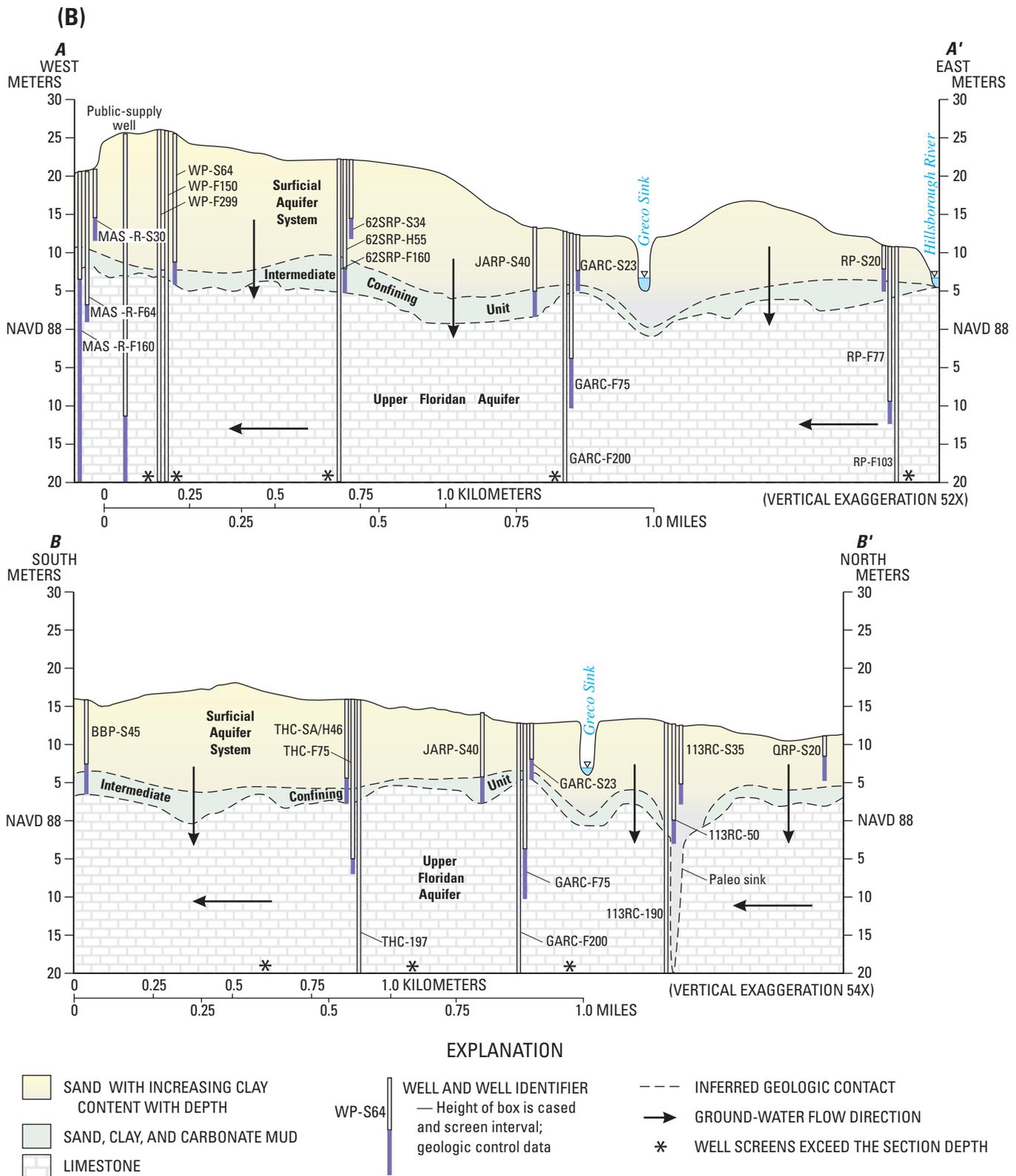


Figure 5B. Generalized hydrogeologic sections A-A' and B-B'. Lines of sections shown in figure 3.

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 surficial aquifer system and moves downward to the Upper Floridan aquifer through breaches in the intermediate confining unit, where present. Many of these breaches in the intermediate confining unit serve as preferential flow paths to the underlying Upper Floridan aquifer.

The Upper Floridan aquifer 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. Most production wells in the study area are developed in the Tampa Member of the Arcadia Formation; wells that are deeper than 99 to 107 m likely tap the upper part of the Ocala Limestone (Stewart and others, 1978).

Caliper logs of production and monitoring wells that were logged by Stewart and others (1978) show sections of relatively large borehole diameters. These large borehole diameters represent solution openings and cavities that may be intercepted by wells. The most productive water-yielding zone of the Upper Floridan aquifer in the Temple Terrace area is a cavernous zone ranging from 37 to 55 m below land surface (Stewart and others, 1978). Wells that tap this zone can yield as much as 5,700 L/min. Public-supply well TTP-4 (index no. 30; table 1) is open to this high-yielding cavernous zone.

Lithology and Mineralogy of the Hydrogeologic Units

The geologic description of the surficial sediments, clay unit, and limestone that compose the hydrogeologic units is based on well cuttings, split-spoon coring, and grain-size analysis. Mineralogical analysis of selected cores also was performed using x-ray diffraction and mass spectrometry. The lithology, lithologic description, and the results of the grain-size analysis for selected wells are presented in table 2.

Mineralogical results of the x-ray diffraction and ICP-MS analyses that were used to determine the chemical composition of major oxides and trace metals in acid extractions of solid-phase material are summarized in table 4. The x-ray diffraction methods used list the relative abundance of bulk minerals, with 1 being the highest and 5 being the least abundant mineral (table 4). Carr and Alverson (1959) performed a comprehensive investigation of the mineralogy and geology of the middle Tertiary rocks underlying west-central Florida, which may explain some of the geochemical constituents observed in this study. They suggest that extensive weathering has occurred in the Hawthorn Group in the study area and that leaching forms a weathering profile of downward increasing solubility. The typical weathering sequence from top to bottom includes quartz sand, iron-stained clayey sand with iron and phosphatic hardpans, blue-green or iron-stained clays, a thin

sequence of slightly calcareous clay, and chert that passes abruptly to a weathered limestone surface.

Some of the soluble byproducts found in this weathering profile in the Hawthorn Group include iron, phosphorous, aluminum, silica, and calcium. Where clays are dominant in the sequence, the abundance of aluminum oxide and iron oxide proportionally increases. Calcium concentrations increase with depth and are related to dissolution of weathered limestone residuum and from the underlying limestone.

The surficial deposits overlying the limestone surface and that were described from well cuttings collected in this study range from about 6 to 15 m thick. Surficial deposits were thinnest in the eastern boundary of the study area near the Hillsborough River, and thickest along the western edge of the study area, where a sand terrace is present. In general, the sediments are composed of an upper fine-grained sand unit, a sequence of clayey sand, and a lower sequence of sandy clay.

The uppermost surficial deposit is a well sorted, very fine to fine quartz sand that generally is less than 3 m thick. The sand is white to buff colored near the surface and contains a mixture of organic matter and silt. Below the organic layer, the sand was stained a pale yellow-orange color, which was probably due to the influence of iron leaching in the shallow ground-water system.

Grain-size analyses indicated that 95 percent of these upper sediments consist of sand, with the remaining sediments composed of silts and clays. The mineralogy of this unit indicates that quartz is the most abundant mineral with lesser amounts of plagioclase, potassium feldspar, calcite, and minimal amounts of total clays. Aluminum and iron were most abundant, with lesser amounts of calcium. Ferrous iron, which is produced during reducing conditions, was the dominant form of iron present.

Below the sand and organic layer, the clay content gradually increases, creating a sequence of clayey sand, which generally is less than 11 m thick. Grain-size analysis of the clayey sand sequence was variable, with the sand ranging from 52 to 95 percent and the remaining sediments composed of silt and clays. The clayey sand sequence also was the most variable in terms of mineralogy, which is probably due to the variability in the clay content.

Quartz, total clays, and potassium feldspar were the most abundant minerals in the clayey sand sequence (table 4). The clays that were encountered in decreasing order of abundance include kaolinite, illite, smectite, and goethite (table 4). The clay was calcareous in places, especially near the limestone contact as indicated by increased calcium ions. Other dominant elements include aluminum, iron, magnesium, and potassium. The highest levels of arsenic, 1.4 mg/kg (milligrams per kilogram), were found in the clayey sand unit but was far below the levels of the most abundant major ions. Aluminum oxide and iron oxide increased in relation to the proportion of the clay content; ferrous iron, similar to the overlying unit, was the dominant form of iron present (table 4).

Table 4. Mineralogy of surficial sediments or rock, elemental composition from acid extractions, and concentrations of iron and sulfide from extractions of selected samples of core material.—Continued

[Index numbers are identified in table 1. Relative abundance of bulk minerals determined by X-ray diffraction, with 1 being the highest and 5 being the lowest. Mineralogy of surficial sediments or rock and major oxides determined by 6 N hydrochloric acid extractions in which samples were extracted for 6 hours on a shaker table, centrifuged, filtered (0.45 micron) and diluted to 1.2 N hydrochloric acid for analysis by inductively coupled plasma-mass-spectrometry. Same procedure for iron, as described, except used 0.5 M hydrochloric acid hydroxylamine in the extraction process. Same procedure for sulfide as described for the acid volatile and chromium reducible sulfides extraction process. Values shown in milligrams per kilogram, except where noted; NR, not reported; --, not detected; <, less than]

Solid-phase sampling site	Index no.	Sample depth, meters	Lithology	Calcium	Iron	Aluminum	Magnesium	Potassium	Sodium	Manganese	Vanadium	Chromium	Copper	Lead	Uranium	Arsenic
Elemental Analysis of Surficial Sediments or Rock																
ROCK-- GAFLWP-55	7	18.3	Limestone	220,000	700	830	2,200	170	96	54	25	3	6	3	5	0.37
ROCK-- GAFL Phase 2 002b	27	26.8	Clay and limestone	220,000	920	460	1,500	210	100	16	6	3	5	3	0.96	0.07
GAFL pII 003 Lightfoot rec ctr,	27	27.4	Limestone; chert	320	1,600	940	83	11	10	<0.5	9	2	5	1	0.23	--
ROCK-- GAFLWP-200	9	62.5	Limestone	270,000	180	120	1,900	8	68	5	7	6	5	0.31	3.4	0.06
ROCK-- GAFLWP-300	9	91.4	Limestone	260,000	280	130	1,900	8	76	11	8	6	5	0.41	3.6	0.07
GAFL WP300	9	93.0	Lime sediment	--	170	240	2,100	58	93	6	8	6	4	--	--	0.18
Solid-phase sampling site	Index no.	Sample depth, meters	Lithology	Aluminum oxide	Iron oxide	Manganese oxide	Calcium oxide	Magnesium oxide	Potassium oxide	Sodium oxide	Ferrous iron	Ferric iron	Total iron	Sulfide		
Major Oxides																
GAFL THC-05 5	4	1.8	Sand	487	287	NR	26	NR	NR	NR	33	NR	25	0.22		
GAFL GII4	10	4.3	Clayey sand	7,892	10,111	NR	1,926	105	86	4	NR	NR	NR	NR		
GAFL pII -001a Lynwood Pk	16	8.8	Clayey sand	16,064	6,434	245	NR	NR	NR	NR	210	170	380	0.31		
GAFL pII 0016 Lightfoot rec ctr.	27	20.7	Clayey sand; chert	4,347	1,716	23	NR	NR	NR	NR	4200	1300	5500	0.34		
GAFL pII 0016 Lynwood Pk	17	11.6	Sandy clay	4,914	7,291	< 1	NR	NR	NR	NR	4400	400	4800	0.23		
GAFL RP-20	13	6.2	Sandy clay	4,522	3,780	6	9,024	1,019	88	47	490	NR	470	60		
ROCK-- GAFLWP-55	7	18.3	Limestone	1,569	1,001	70	NR	NR	NR	NR	NR	NR	NR	NR		
ROCK-- GAFL Phase 2 002b	27	26.8	Clay and limestone	869	1,315	21	NR	NR	NR	NR	NR	NR	NR	NR		
GAFL pII 003 Lightfoot rec ctr	27	27.4	Limestone; chert	1,777	2,288	< 1	NR	NR	NR	NR	130	20	150	3.8		
ROCK-- GAFLWP-200	9	62.5	Limestone	227	258	6	NR	NR	NR	NR	NR	NR	NR	NR		
ROCK-- GAFLWP-300	9	91.4	Limestone	454	400	14	NR	NR	NR	NR	NR	NR	NR	NR		
GAFL WP300	9	93.0	Lime sediment	246	243	8	NR	NR	NR	NR	61	6	67	115		

Below the clayey sand sequence where the clay content continues to increase, a sequence of sandy clay is present. This sequence corresponds to the intermediate confining unit, which is composed of deposits of the Hawthorn Group. This unit was the most difficult to interpret in the study area because of the varying amounts of sands and discontinuous clays and the absence of this unit due to subsidence, which disrupted the continuity of the unit. Generally, this unit was less than 1.5 m thick. Carr and Alverson (1959) and Sinclair (1974) describe the clay in the intermediate confining unit as a weathered residuum of the limestone in the underlying Tampa Member of the Arcadia Formation. Elevated concentrations of radium and radionuclides that are commonly associated with clay minerals also are present in the intermediate confining unit (Carr and Alverson, 1959).

The intermediate confining unit in the study area varied in color, composition, and permeability. This unit has a dense plastic consistency, a tan, greenish-gray or orange-red color, and varying amounts of sand, chert, and carbonate mud. The clay may be calcareous in places, particularly near the underlying limestone contact. Minerals in this sandy clay unit, in decreasing order of abundance, are quartz, calcite, potassium feldspar, and total clay. The most abundant clays were smectite, illite, and kaolinite; calcium, iron, and aluminum were the most abundant elements. The highest concentration of uranium (8.9 mg/kg) was detected in the sandy clay unit and is probably related to the high clay mineral content. Concentrations of aluminum oxide and iron oxide also were elevated due to high clay content. Concentrations also were elevated for calcium oxide, which reflects the calcareous nature of the clay. Ferrous iron, similar to the overlying units, was the dominant form of iron present.

The highly weathered limestone of the Tampa Member underlies the intermediate confining unit and is identified as the top of the Upper Floridan aquifer. The Tampa Member is tan to white, soft to hard, usually sandy and fossiliferous, and commonly contains clay lenses and cavities. The Tampa Member is generally less than 30 m thick in this region; the depth to the top of the Tampa Member ranges from 4.3 to 11.0 m above NAVD 88 at RP-F77 and WP-F150, respectively (based on well cuttings collected for 14 wells throughout the study area).

At two sites, sands and clays were present far below the typical depth to the top of limestone found at other sites, which indicates that infilling by overburden materials into solution cavities has occurred. At wells LRP-H105 (index no. 27; table 2) and 113RC-H50 (index no. 2; table 2), the depth to limestone was about 6 and 18 m below NAVD 88, respectively, which suggests the wells were drilled into paleo-sinkholes. The infilling and raveling of the overburden materials into limestone cavities increase the connection of overlying units to the Upper Floridan aquifer.

The mineralogy indicates the weathered limestone of the Tampa Member is relatively impure, and contains considerable amounts of sand and clay. The minerals identified in the upper sequence of the Tampa Member (index no. 7 and 27; table 4) were calcite with lesser amounts of quartz and total clays. The

clays that were associated with the limestone were smectite, illite, and kaolinite. Major elements that compose the rock were calcium, magnesium, iron, and aluminum. Concentrations of iron oxide and aluminum oxide in the upper sequence of the Tampa Member were elevated compared to lower units, which reflects the higher clay content associated with this unit. Ferrous iron was the dominant form of iron present, but at levels much lower than the overlying sand and clay layers. The mineralogy of the lower sequence of the Tampa Member (index no. 21 and 25; table 4) include calcite, halite, goethite, and total clays. The clay minerals associated with the lower limestone sequence were smectite and illite.

The Suwannee Limestone underlies the Tampa Member with a thickness of about 60 to 76 m in the study area. The limestone is white to light tan in color, soft and granular in appearance, and contains abundant fossil detritus and organic structures such as casts, molds, and borings of mollusks and tests of foraminifera and bryozoa (Carr and Alverson, 1959). Many fossil molds within this unit give it a high porosity.

The mineralogy of the Suwannee Limestone includes calcite as the most abundant mineral, with trace amounts of quartz and clays. The most abundant elements include calcium and magnesium, with lesser amounts of iron and aluminum. Amounts of iron oxide and aluminum oxide were considerably lower than in the overlying material, which indicates a reduced clay content. Ferrous iron was the dominant form of iron present, but at levels much lower than in the overlying material.

Estimation of Aquifer Properties

Hydraulic properties (for example, hydraulic conductivity, vertical conductance, and effective porosity) were obtained from previous hydrogeologic studies of the Upper Floridan aquifer in the Tampa Bay area (Knochenmus and Robinson, 1996; J. Arthur, Florida Geological Survey, written commun., 2003). Porosity and permeability of the limestone rock matrix can be enhanced by dissolution and/or fracturing. Previous studies have correlated fractures observed in limestone outcrops in west-central Florida with the occurrence of fracture traces and surface lineaments (Vernon, 1951). Using surface geophysical methods, Culbreath (1988) found that the surface lineaments with corresponding gravity anomalies had a preferred orientation between 45 and 55 degrees east and west of north (fig. 1). Geologic structures aligned in this preferred orientation are believed to occur at the surface as lineaments because they parallel the stress fields associated with earth tides (Culbreath, 1988). Fracture zones typically are enlarged by chemical dissolution in karstic aquifer systems. In a study of Floridan aquifer system properties in west-central Florida, Stewart and Wood (1984) found that the porosity can be 10 to 100 times that of the intergranular matrix in places where vertical to near-vertical fractures have been enlarged by dissolution.

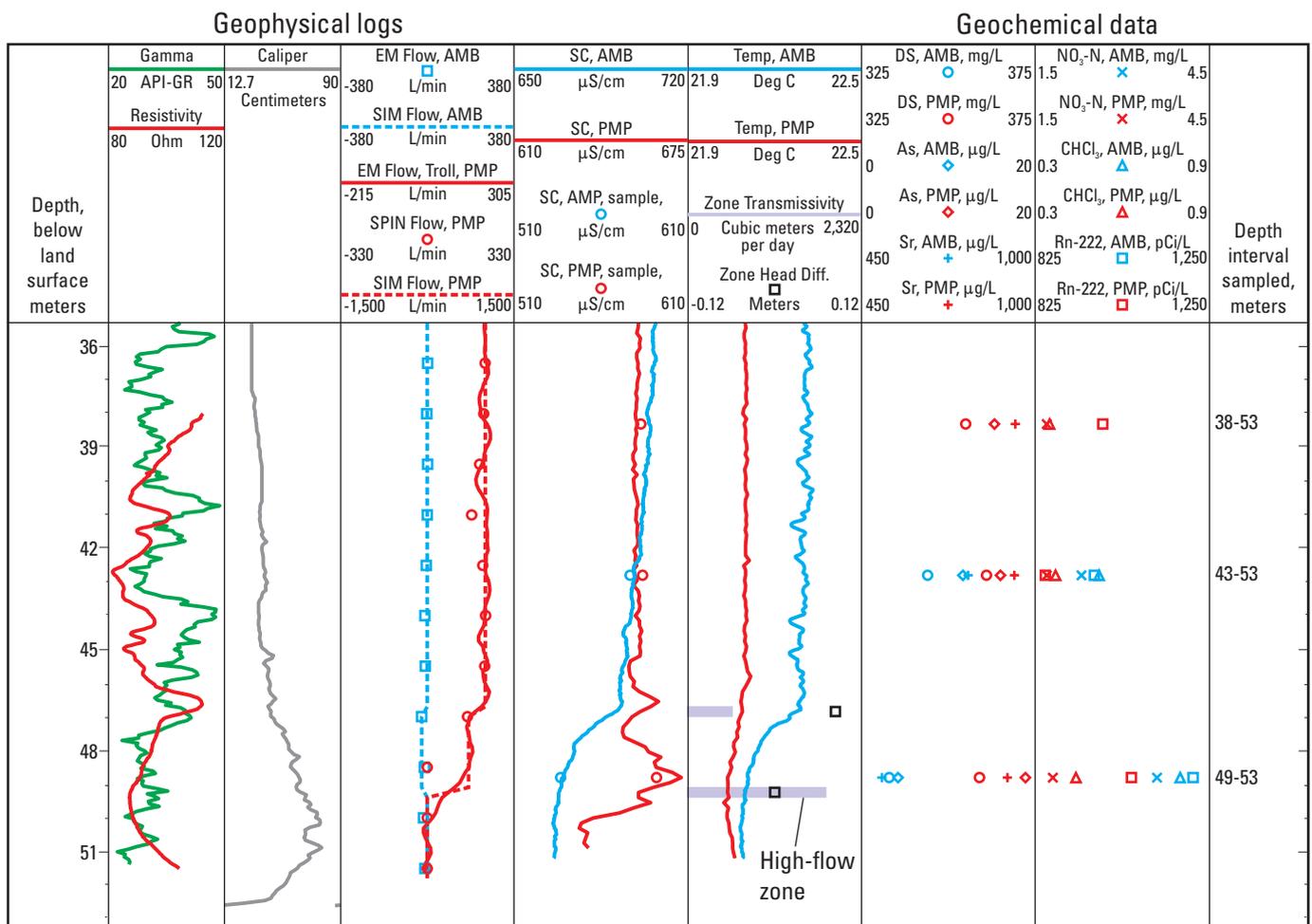
Information on particle-size distribution, bulk density, and moisture content of core material were used to estimate

annual recharge (R. Healy, U.S. Geological Survey, written commun., 2004). Recharge estimates were highly variable and ranged from 0.8 to 43 cm/yr (centimeters per year), with a median value of 13 cm/yr. Transmissivity values for the Upper Floridan aquifer ranged from 2,700 to 12,100 m²/d (meters squared per day) based on data from an aquifer test conducted in March 1975 for a public-supply well cased to 28 m with an open hole to 146 m, with an average storage coefficient of 3.4 x 10⁻⁴ (Stewart and others, 1978). Effective porosity ranged from 0.02 (Avon Park Formation) to 0.49 (Ocala Limestone).

Geophysical measurements were made in the open interval of the Upper Floridan aquifer of the public-supply well borehole (36-53 m below land surface) in October 2004 (J.H. Williams, U.S. Geological Survey, written commun., 2007)

to obtain detailed information on well construction, aquifer properties, rock lithology and solution features, dominant flow zones, permeability, and water quality. Logs include caliper, gamma, spontaneous potential, fluid resistivity, temperature, flow meter, and optical televiewer. Continuous data from the various probes are displayed graphically in figure 6.

Based on the analysis of the flowmeter, fluid, and specific conductance logs (fig. 6), the public-supply well penetrated high-flow zones at 46.8 and 49.2 m below land surface. Borehole flow was downward under ambient conditions from the upper to the lower zone. Under pumping conditions, the lower zone contributed 70 percent of the 1,020 L/min discharged from the well. Flowmeter model analysis suggested that the



API-GR=American Petroleum Institute-gamma ray units
 AMB=ambient conditions
 PMP= pumped conditions
 EM Flow=flow measurements made with an electromagnetic flowmeter placed at selected depths, in liters per minute (L/min)
 EM Flow, Troll=flow log made with an electromagnetic flowmeter as it is trolled up or down borehole, in liters per minute (L/min)
 SIM Flow=flow log simulated with Paillet's model (1998 and 2000), which has been matched to measure ambient and pumped flows by trial-and-error adjustment of flow zone transmissivity and head, in liters per minute (L/min)

SPIN Flow=flow measurements made with a spinner flowmeter placed at selected depths, in liters per minute (L/min)
 Temp=temperature, in degrees celsius (Deg C)
 SC=specific conductance, in microsiemens per centimeter (µS/cm)
 DS=dissolved solids, in milligrams per liter (mg/L)
 As=arsenic, in micrograms per liter (µg/L)
 Sr=strontium, in micrograms per liter (µg/L)
 NO₃-N=nitrate as nitrogen, in milligrams per liter (mg/L)
 CHCl₃=trichloromethane, in micrograms per liter (µg/L)
 Rn-222=radon-222, in picocuries per liter (pCi/L)

Figure 6. Geophysical logs of the public-supply well borehole at Temple Terrace, Florida.

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. The fluid logs and discrete-depth samples at 48.8 m under ambient and pumping conditions indicated that the specific conductance of water from the upper zone was about 10 percent less than that from the lower zone. Caliper and televiwer logs revealed large solution openings in the Upper Floridan aquifer limestone at depths greater than 47 m. Specific conductance decreased substantially in this interval indicating that lower conductance water is entering the 45- to 53-m zone, possibly water moving downward from the surficial aquifer system, which has lower conductance than water from the Upper Floridan aquifer. Temperature also showed a slight decrease (about 0.3 °C) through this interval. Chemical data for water samples collected from three overlapping depth intervals (38-53, 43-53, and 49-53 m) are presented later in this report.

Ground-Water Flow Patterns

The water table in the surficial aquifer system follows closely to the land surface and is affected by regional discharge features and rainfall and recharge events. Ground-water elevation is highest at well 62SRP-S34 with a median of 12.74 m above NAVD 88. Well 62SRP-S34 is one of the westernmost monitoring wells tapping the surficial aquifer system in the study area and where land-surface elevations are relatively high. The water table is also higher at well WP-S64 (median of 8.37 m median) than at other surficial aquifer system wells because of the higher elevation and location of the well on the remnant marine terrace. Water-table elevations generally are above the potentiometric surface of the Upper Floridan aquifer (C.A. Crandall, U.S. Geological Survey, written commun., 2007). The regional ground-water flow direction in the Upper Floridan aquifer is generally from the north-northeast to south-southwest in the study area (fig. 3). Pumping affects ground-water levels in the Upper Floridan aquifer, especially in those wells screened in the same zone as most of the public-supply wells. Water levels in storm retention ponds are generally above those of the surficial aquifer system and the Upper Floridan aquifer and reflect input from stormwater runoff during wet periods. As a result of likely hydraulic connections between some retention ponds and the subsurface, leakage of surface water can recharge the surficial aquifer system and Upper Floridan aquifer. Parts of the Upper Floridan aquifer are in direct hydraulic contact with the Hillsborough River, although exchange of water between the river and aquifer depends in part on operations at the downstream reservoir on the Hillsborough River and on rainfall/recharge events.

The size and orientation of the ground-water contributing recharge area of the public-supply well has evolved over time (C.A. Crandall, U.S. Geological Survey, written commun., 2007). The first contributing recharge area of the public-supply well was obtained using a regional

ground-water flow model, MODPATH (Harbaugh and others, 2000), and was used to guide the siting of the first set of monitoring wells installed in 2003. Next, probabilistic ground-water flow models were used to incorporate uncertainty in the delineation of the contributing recharge area, and to determine locations for new monitoring wells installed in 2004. The probabilistic flow models consisted of two separate methods, with the first being a stochastic parameter uncertainty method that was used by MODPATH to calculate time of travel for various particles in the Upper Floridan aquifer to the public-supply well. The second probabilistic method, referred to as the fracture continuum method, incorporated karst information such as sinkholes and fracture orientation into the contributing recharge area calculation. This information was used by MODPATH to calculate time of travel for various particles to the public-supply well (C.A. Crandall, U.S. Geological Survey, written commun., 2007).

Ground-Water Chemistry

This section describes the general chemical characteristics of waters from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace study area including water types, redox conditions, pH, saturation indices with respect to selected minerals, and stable isotope composition. Subsequent sections describe the distribution of selected anthropogenic and naturally occurring contaminants in the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer with special emphasis on the comparison between water chemistry in public-supply well TTP-4 and these three hydrogeologic units in the study area. Differences in chemical signatures among the various hydrogeologic units are used to better understand important ground-water flow patterns and pathways, and to generate hypotheses for processes controlling water quality in the public-supply well.

Chemical Composition and Mineral Saturation Indexes

Water from 8 of 11 wells tapping the surficial aquifer system had pH values below 7.0 (median values 5.0-6.9), and water from three wells had pH values ranging from 7.1 to 7.5. Two of the three wells (BBP-S45 and WP-S64) had depths to water greater than 10 m. Water samples from wells in the intermediate confining unit had median pH values that ranged from 7.3 to 7.9. Water from the Upper Floridan aquifer had median pH values that ranged from 7.2 to 7.9.

Water types for samples from the three hydrogeologic units and surface waters were somewhat variable, although dominated by calcium bicarbonate, calcium-bicarbonate-sulfate, and calcium-sulfate-bicarbonate (fig. 7). Calcium was the dominant cation in water from 10 of 11 wells in the surficial aquifer system, all four wells in the intermediate confining

unit, all wells in the Upper Floridan aquifer, the three retention ponds, and Hillsborough River. The dominant anion in these waters was more variable, and was either bicarbonate or sulfate. Deep wells in the Upper Floridan aquifer tended to have sulfate as the dominant anion. Water from 9 of 13 wells in the Upper Floridan aquifer had a calcium-sulfate-bicarbonate water type, and four wells had a calcium-bicarbonate-sulfate water type. Water from the remaining well had a calcium-bicarbonate water type.

Variability in saturation indices with respect to calcite, dolomite, and gypsum for water from the three hydrogeologic units (table 5) reflect differences in their mineralogy (table 4). Median saturation indices with respect to calcite are -0.40, -0.16, and 0.08 for water samples from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer, respectively. Variable amounts of minerals containing calcium magnesium carbonate in the surficial aquifer system and intermediate confining unit account for the large variability in saturation indices with respect to calcite and dolomite (table 5). As would be expected for water from the carbonate Upper Floridan aquifer, samples are saturated

with respect to calcite and slightly undersaturated with respect to dolomite. Samples from deep wells in the Upper Floridan aquifer (for example, GARC-F200) are saturated with respect to dolomite. Water samples from the Upper Floridan aquifer are slightly undersaturated with respect to gypsum, whereas water samples from the intermediate confining unit and surficial aquifer system are highly undersaturated with respect to gypsum.

Dissolved Organic Carbon and Dissolved Solids Concentrations

Dissolved organic carbon concentrations were highly variable (0.6 to 18.1 mg/L) in water samples from the surficial aquifer system (table 5). This large variation likely indicates that some wells are located near recharge areas that receive surface water with elevated concentrations of dissolved organic carbon, such as retention ponds and the Hillsborough River. Dissolved organic carbon concentrations in water samples from stormwater retention ponds ranged from 3.7 to

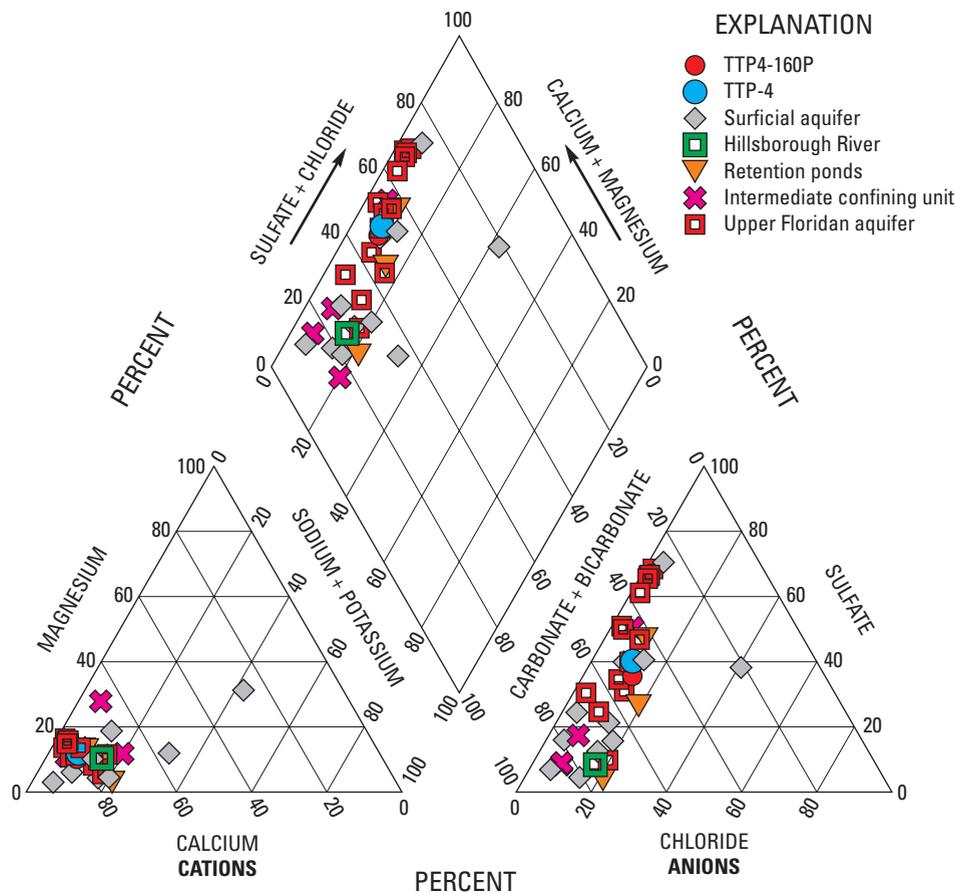


Figure 7. Major-ion chemistry for ground-water and surface-water samples from the Temple Terrace, Florida, study area.

26 Chemical Characteristics, Water Sources and Pathways, and Age Distribution of Ground Water

Table 5. Physical properties and chemistry of water samples from the surficial aquifer system (SAS), intermediate confining unit (ICU), and Upper

[Concentrations are in milligrams per liter (mg/L) unless otherwise noted; P, STORET parameter code; temperature, in degrees Celsius; specific conductance, in microsiemens per meters below measuring point; SI, saturation index; PCO₂, partial pressure of carbon dioxide in water sample]

Site name	Aquifer or hydro-geologic unit	Site identifier	Date	Time	P00010	P00095	P00300	P00400	P00453	P00608	P00613	P00631	P00671	P00681
					Temperature	Specific conductance	Dissolved oxygen	pH	Bicarbonate	Ammonium as nitrogen	Nitrite as nitrogen	Nitrate as nitrogen	Orthophosphate as phosphorus	Dissolved organic carbon
BBP-S45	SAS	280228082231501	8/11/2004	1200	25.0	594	3.9	6.9	294	<0.04	<0.008	0.82	0.159	0.9
BBP-S45	SAS	280228082231501	12/9/2004	1300	25.5	475	3.8	7.1	253	E0.02	<0.008	0.21	0.334	0.6
BBP-S45	SAS	280228082231501	6/22/2005	1130	25.9	526	3.7	7.1	263	<0.04	<0.008	0.72	0.171	0.7
THC-F197	UFA	280241082224401	1/15/2004	1400	25.0	958	0.3	7.2	214	0.17	<0.008	<0.06	0.026	2.6
THC-F197	UFA	280241082224401	1/28/2004	1210										
THC-F75	UFA	280241082224402	1/12/2004	1500	24.5	515	0.1	7.3	162	0.11	<0.008	<0.06	0.131	1.9
THC-F75	UFA	280241082224402	6/14/2005	1640	26.6	489	0.2	7.3	154					
THC-S46	SAS	280241082224403	12/18/2003	1300	24.5	693	0.3	6.9	315	0.07	0.011	1.05	0.089	1.1
THC-S46	SAS	280241082224403	1/15/2004	1120										
THC-S46	SAS	280241082224403	8/5/2004	1200	25.0	697	0.3	6.9	317	0.05	E0.004	0.81	0.092	0.8
THC-S46	SAS	280241082224403	11/17/2004	1600	25.7	705		6.7	343	E0.03	E0.004	0.59	0.048	0.7
THC-S46	SAS	280241082224403	6/14/2005	1700	27.0	707	0.3	6.8	316	E0.03	E0.007	1.55	0.15	0.7
62SRP-F160	UFA	280241082230701	11/2/2004	1200	28.7	596	0.1	7.2	200	<0.04	0.009	1.99	0.025	1
62SRP-F160	UFA	280241082230701	6/20/2005	1600	26.5	579	0.6	7.2	197					
62SRP-H55	ICU	280241082230702	11/3/2004	1700	26.6	456	4.7	7.1	232	E0.02	<0.008	3.54	0.044	1040
62SRP-S34	SAS	280241082230703	8/12/2004	930	25.5	540	6.8	6.3	274	<0.04	E0.005	3.21	0.014	13.8
62SRP-POND	POND	280242082230800	6/21/2005	1220	29.0	362	2.3	7.2	108	1.41	0.043	0.91	0.29	17.8
MAS-R-F160	UFA	280242082232401	11/3/2004	1200	26.7	546	0.7	7.4	224	E0.02	0.011	0.94	0.029	0.9
MAS-R-F160	UFA	280242082232401	6/16/2005	1040	27.0	548	0.5	7.2	211	<0.04	0.013	0.72	0.022	1.1
MAS-R-F64	UFA	280242082232403	2/16/2005	1300	25.5	262	1.8	7.7	105	<0.04	<0.008	1.2	0.017	0.5
MAS-R-F64	UFA	280242082232403	6/16/2005	1100	26.0	219	2	8	82	<0.04	<0.008	1.2	0.007	0.5
MAS-POND	POND	280242082232900	6/21/2005	1100	28.5	172	2.9	7.1	72	<0.04	<0.008	<0.06	0.12	9.3
TTP-4	UFA	No data	10/21/2002	1600	26.5	608	0.4	7.2	188	E0.04	0.02	0.72	0.03	0.9
TTP-4	UFA	No data	1/28/2004	1600	24.0	603	0.2	7.3	189	E0.02	0.033	0.89	0.021	1.9
TTP-4	UFA	No data	9/22/2004	1600	25.5	599	0.7	7.3						
TTP-4	UFA	No data	10/21/2004	1500	26.0	606	0.5	7.3	170	<0.04	0.008	1.4	0.018	0.9
TTP-4	UFA	No data	2/16/2005	1600	25.0	584	0.4	7.3	184	E0.02	0.042	0.61	0.014	0.9
TTP-4	UFA	No data	6/20/2005	1600	26.4	618	0.3	7.4	194	E0.02	0.048	0.72	0.016	1.2
WP-F299	UFA	280247082231901	1/22/2004	1600	26.0	1,000	0.2	7.2	225	0.17	<0.008	<0.06	0.036	2.4
WP-F299	UFA	280247082231901	8/3/2004	1400	26.0	1,000	0.3	7.1	215					2.2
WP-F150	UFA	280247082231902	1/28/2004	1300	25.2	569	0.2	7.4	158	0.17	<0.008	<0.06	0.034	1.2
WP-F150	UFA	280247082231902	8/4/2004	1100	26.0	584	0.3	7.4	156	0.18	<0.008	<0.06	0.028	1.2
WP-F150	UFA	280247082231902	6/14/2005	1110	26.9	576	0.6	7.4	157		<0.008			
WP-S64	SAS	280247082231903	1/14/2004	1500	26.0	474	5.4	7.5	124	<0.04	<0.008	2.5	0.049	0.8
WP-S64	SAS	280247082231903	8/4/2004	1600	26.5	482	6.7	7.5	112	<0.04	<0.008	4.6	0.051	0.6
WP-S64	SAS	280247082231903	11/18/2004	1200	27.3	455	6	7.5	132	<0.04	<0.008	4.1	0.054	1.5
WP-S64	SAS	280247082231903	6/14/2005	1130	26.5	457	5.7	7.5	120	<0.04	<0.008	2.3	0.048	13.7
RP-F103	UFA	280249082220701	12/2/2003	1500	23.5	759	0.2	7.2	256	0.14	<0.008	<0.06	0.037	2
RP-F103	UFA	280249082220701	1/14/2004	1135	22.5	792	0.1	7.2						
RP-F77	UFA	280249082220702	12/3/2003	1300	23.5	562	0.2	7.3	251	0.21	<0.008	<0.06	0.05	2.4
RP-F77	UFA	280249082220702	6/16/2005	1610	25.2	586	0.4	7	251					
RP-S20	SAS	280249082220703	12/4/2003	1400	24.5	502	2.2	6.4	303	0.04	<0.008	<0.06	0.125	3.3
RP-S20	SAS	280249082220703	8/11/2004	1500	24.0	791	1.4	6.6	392	<0.04	<0.008	0.1	0.084	2.5

Floridan aquifer (UFA) in the study area.

centimeter; E, estimated concentration, below reported laboratory reporting level; ROE-DS, residue on evaporation, dissolved solids, mg/L; DTW, depth to water in

P00915	P00925	P00930	P00935	P00940	P00945	P00950	P00955	P39086	P70300	P99118	P72019	Calcite SI	Dolomite SI	Gypsum SI	log PCO ₂
Calcium	Magne- sium	Sodium	Potassium	Chloride	Sodium	Fluoride	Silica	Alkalinity as CaCO ₃	ROE-DS	Hydrogen sulfide	DTW				
94.2	3.85	25.8	0.82	10.8	53.8	0.5	7.46	241	293		8.84	-0.15	-1.33	-1.75	-1.45
83.5	2.49	17.6	0.58	7.54	31.4	0.6	8.52	207	274	0.002	9.64	-0.03	-1.24	-2.00	-1.71
92.2	2.85	15.9	0.82	9.91	30.9	0.4	9.37	215	300	0.004	10.0	0.03	-1.09	-1.98	-1.69
195	23.3	8.17	1.05	9.38	371	0.6	15.1	176	759	1.5	9.77	0.2	-0.19	-0.81	-1.91
96.7	8.11	8.21	0.74	7.11	137	0.3	14.2	133	365	0.6	9.70	-0.02	-0.79	-1.36	-2.12
								126		0.533	9.52				
130	6	16.5	1.16	36.5	44.4	0.3	14.7	262	405	0	9.61	0	-1.00	-1.75	-1.43
125	5.36	13.7	1.14	34.9	45.1	0.2	15	260	329	0.02	8.65	-0.00	-1.02	-1.75	-1.42
133	6.3	17.3	1.26	42.7	43.9	0.2	16.4	281	426	0.008	8.94	-0.14	-1.25	-1.75	-1.18
131	5.86	14.6	1.15	42.5	44.6	0.2	16.5	259	452	0.013	9.50	-0.06	-1.10	-1.74	-1.31
95.5	10.8	12.3	1.35	27.9	89.7	0.2	13.6	164	353	0.002	14.5	0.03	-0.50	-1.55	-1.90
								162			15.3				
64.8	16.6	6.3	0.84	12.7	18.3	E0.1	31.9	190	281	0.008	13.6	-0.16	-0.54	-2.35	-1.74
81.7	14	17.3	2.14	28.9	12.8	0.2	9.18	224	272		8.31				
53.2	4.13	10.4	2.7	22.7	44.5	0.3	9.13	89	260			-0.42	-1.57	-1.99	-2.15
85.9	5.94	19	8.36	18.5	63.4	0.1	12.6	184	326	0.004	13.5	0.22	-0.35	-1.71	-2.06
94.6	6.52	11.2	2.79	19.1	69.8	0.2	12.1	173	337	0.008	14.0	0.04	-0.71	-1.64	-1.88
36.2	1.73	13.6	0.5	15.4	12.8	0.1	15.9	86	164	0	13.6	-0.11	-1.19	-2.62	-2.68
34.9	1.82	4.88	0.46	15.2	9.2	E0.1	17.7	67	150		13.4	0.08	-0.78	-2.76	-3.09
25.5	0.91	7.34	2.03	11.9	3.9	E0.1	2.4	59	112			-0.95	-2.96	3.24	-2.21
106	9.52	10.3	0.94	17.8	129	0.3	12.7	154	390	0					
110	11	10.9	1.16	22.8	122	0.3	13.5	155	390	0.048		0.09	-0.49	-1.37	-2.05
										0.025					
98.1	8.41	11.2	1.04	25	116	0.3	13.3	139	380	0.03		0.03	-0.65	-1.43	-2.08
103	8.51	11.3	1.08	26	112	0.3	12.4	151	369	0.005		0.07	-0.60	-1.42	-2.06
109	10.4	11.6	1.11	24	121	0.3	13.2	159	390	0.038		0.23	-0.20	-1.38	-2.13
195	23.6	9.01	1.4	9.41	355	0.6	15.3	185	760	1.88	18.4	0.23	-0.10	-0.83	-1.89
183	23.3	7.31	1.27	9.03	369	0.6	14.9	177	753	1.71	17.5	0.09	-0.36	-0.83	-1.80
102	11.5	10.7	1.09	19.1	139	0.5	13.9	130	386	0.018	18.4	0.09	-0.42	-1.35	-2.22
94.1	10.2	10.3	1.07	20.9	133	0.5	13.1	128	375	0.11	17.5	0.07	-0.47	-1.38	-2.22
								128		0.103	18.2				
77.6	6.39	12.2	1.79	21.3	87.2	0.2	8.43	102	294	0	16.2	0.02	-0.69	-1.60	-2.42
67.8	5.32	14.7	1.86	30.6	73	0.2	8.92	94	287	0.005	15.1	-0.05	-0.85	-1.71	-2.44
65.6	5.4	13.3	2.39	26.2	59	0.1	9.88	108	280	0.002	15.3	0.01	-0.69	-1.81	-2.38
70.4	5.76	10.6	1.58	20.8	86.3	0.4	8.13	98	283		16.3	-0.03	-0.78	-1.63	-2.43
151	15.8	6.24	0.74	8.59	227	0.4	15.8	210	578	0.51	4.90	0.2	-0.27	-1.05	-1.83
106	10.4	7.88	0.71	7.6	93.6	0.5	28.3	206	394	0.29	5.21	0.2	-0.29	-1.49	-1.93
								206		0.48	4.71				
114	2.8	9.32	0.29	18.8	30.5	0.2	16.2	248	355	0.007	4.85	-0.51	-2.25	-1.93	-0.92
147	2.72	16.5	0.21	20.3	80.3	0.4	12.5	322	343	0	2.63	-0.18	-1.76	-1.46	-1.04

28 Chemical Characteristics, Water Sources and Pathways, and Age Distribution of Ground Water

Table 5. Physical properties and chemistry of water samples from the surficial aquifer system (SAS), intermediate confining unit (ICU), and Upper

[Concentrations are in milligrams per liter (mg/L) unless otherwise noted; P, STORET parameter code; temperature, in degrees Celsius; specific conductance, in microsiemens per meters below measuring point; SI, saturation index; PCO₂, partial pressure of carbon dioxide in water sample]

Site name	Aquifer or hydro-geologic unit	Site identifier	Date	Time	P00010	P00095	P00300	P00400	P00453	P00608	P00613	P00631	P00671	P00681
					Temperature	Specific conductance	Dissolved oxygen	pH	Bicarbonate	Ammonium as nitrogen	Nitrite as nitrogen	Nitrate as nitrogen	Orthophosphate as phosphorus	Dissolved organic carbon
RP-S20	SAS	280249082220703	11/16/2004	1500	24.2	435	0.3	6.8	267	<0.04	<0.008	<0.06	0.124	2.6
RP-S20	SAS	280249082220703	6/16/2005	1500	25.0	613	1	6.6	373	<0.04	<0.008	<0.06	0.118	2.2
LRP-F160	UFA	2802500822233001	11/4/2004	1300	27.8	458	0.5	7.8	153	0.47	<0.008	<0.06	0.018	1.7
LRP-H105	ICU	2802500822233002	12/7/2004	1600	25.1	288	0.3	7.4	134	0.09	<0.008	0.27	0.051	1.7
LRP-H105	ICU	2802500822233002	6/15/2005	1510	29.5	334	0.6	8.3	139					
LRP-S25	SAS	2802500822233003	8/10/2004	1100	26.0	447	0.5	7.5	154	0.09	0.014	0.72	0.068	1.6
LRP-S25	SAS	2802500822233003	6/15/2005	1500	25.0	442	0.4	7.3	120	0.2	<0.008	E0.04	0.026	1.7
LRP-POND	POND	2802500822233200	6/21/2005	0915	27.5	400	8.4	8.8	100	<0.04	0.054	0.61	0.021	3.7
JARP-S40	SAS	280251082224201	6/27/2005	1030	29.0	236	2.3	6.7	89	<0.04	<0.008	<0.06	<0.006	1.5
GARC-F200	UFA	280253082223801	12/16/2003	1300	25.0	1,070	0.2	7.2	218	0.18	<0.008	<0.06	0.035	2.1
GARC-F75	UFA	280253082223802	12/15/2003	1400	20.5	852	0.2	7.3	215	0.22	<0.008	<0.06	0.048	0.5
GARC-F75	UFA	280253082223802	6/13/2005	1200	28.0	825	0.5	7.2	221					
GARC-S23	SAS	280253082223803	12/17/2003	1200	25.0	515	2.5	6.3	193	<0.04	E0.007	4.81	0.006	0.7
GARC-S23	SAS	280253082223803	8/5/2004	1600	26.0	540	4.5	5.9	70	<0.04	<0.008	1.56	E0.003	0.9
GARC-S23	SAS	280253082223803	11/17/2004	1100	27.7	504	3	5.7	70	<0.04	<0.008	2.45	<0.006	18.1
GARC-S23	SAS	280253082223803	6/13/2005	1115	27.1	450	3.2	5.8	69	<0.04	<0.008	2.47	E0.003	0.7
113RC-F190	UFA	280301082222701	12/8/2003	1300	25.0	1,010	0.3	7.2	222	0.17	<0.008	<0.06	0.023	2.8
113RC-F190	UFA	280301082222701	6/15/2005	1130	27.1	1,040	0.3	7.1	226					
113RC-H50	ICU	280301082222702	12/9/2003	1300	25.5	0	0.3	7.3	166	0.06	0.03	0.65	0.023	1.8
113RC-S35	SAS	280301082222703	12/11/2003	1300	26.0	379	2.5	6.8	157	<0.04	E0.007	3.51	0.019	0.6
113RC-S35	SAS	280301082222703	8/12/2004	1300	27.5	370	4	6.6	135	<0.04	E0.006	4.41	0.014	0.9
113RC-S35	SAS	280301082222703	11/16/2004	1300	27.3	316	2.2	6.6	141	<0.04	E0.004	2.36	0.019	2.3
113RC-S35	SAS	280301082222703	6/15/2005	1100	27.5	373	4.3	6.6	137	<0.04	<0.008	3.6	0.01	1.1
LP-H40	ICU	2803030822230901	8/10/2004	1500	32.0	262	7.5	7.8	120	<0.04	E0.006	2.15	0.029	2.3
LP-H40	ICU	2803030822230901	12/8/2004	1500	26.4	259	6.8	7.5	127	<0.04	<0.008	2.4	0.069	0.4
LP-S30	SAS	2803030822230902	8/10/2004	1200	29.0	65	8	4.4	5	<0.04	<0.008	1.8	<0.006	0.3
LP-S30	SAS	2803030822230902	11/1/2004	1600	28.2	92	6.2	5	5	<0.04	<0.008	2.7	<0.006	13.5
LP-S30	SAS	2803030822230902	6/21/2005	1130	26.0	70	7	5.3	5	<0.04	<0.008	1.47	<0.006	0.4
QRP-S20	SAS	280311082223901	8/11/2004	1345	28.0	185	3.7	5.9	54	0.04	<0.008	2.55	0.019	5
QRP-S20	SAS	280311082223901	11/15/2004	1700	24.9	234	2.3	5.9	94	<0.04	<0.008	6.11	0.008	3.7
QRP-S20	SAS	280311082223901	6/21/2005	1630	24.5	166	2	6.2	58	0.16	E0.006	0.67	0.012	4.6
HRIV-WA	River	280244082220100	1/30/2004	1410	14.0	281	6.6	7.2	116					
HRIV-RR	River	280248082220200	6/22/2005							0.027	0.004	0.102	0.323	19.8
			8/30/2005			253		7.38						
TTP-4-140-NP	UFA	No data	10/27/2004	1600	26.4	577	0.8	7.3	180	<0.04	0.039	2.29	0.022	1.1
TTP-4-160-NP	UFA	No data	10/27/2004	1800	26.2	537	0.8	7.3	170	<0.04	0.011	3.6	0.024	0.8
TTP-4-160-P	UFA	No data	10/28/2004	1100	24.1	567	1	7.3	182	<0.04	0.035	1.84	0.014	0.9
TTP-4-140-P	UFA	No data	10/28/2004	1400	25.8	586	0.6	7.3	183	<0.04	0.02	1.72	0.016	0.9
TTP-4-125-P	UFA	No data	10/28/2004	1600	25.9	583	0.6	7.3	182	<0.04	0.013	1.69	0.022	0.9
TTP-4-entire-P	UFA	No data	10/21/2004	1500	26.0	606	0.5	7.3	170	<0.04	0.008	1.44	0.018	0.9

Floridan aquifer (UFA) in the study area.—Continued

centimeter; E, estimated concentration, below reported laboratory reporting level; ROE-DS, residue on evaporation, dissolved solids, mg/L; DTW, depth to water in

P00915	P00925	P00930	P00935	P00940	P00945	P00950	P00955	P39086	P70300	P99118	P72019	Calcite SI	Dolomite SI	Gypsum SI	log PCO ₂
Calcium	Magne- sium	Sodium	Potassium	Chloride	Sodium	Fluoride	Silica	Alkalinity as CaCO ₃	ROE-DS	Hydrogen sulfide	DTW				
86.6	1.67	5.56	E0.12	2.68	9.6	0.4	10.9	219	260	0.01	4.01	-0.30	-1.96	-2.48	-1.39
124	2.5	7.46	0.2	7.01	13.1	0.4	11.5	306	363		4.22	-0.22	-1.79	-2.27	-1.05
69.6	7.16	14.1	5.93	16.3	77.2	0.3	8.46	125	278	0.043	13.3	0.39	0.16	-1.69	-2.62
48.4	5.01	4.63	1.03	8.49	25.1	0.6	10.3	110	177	0	2.72	-0.21	-1.05	-2.25	-2.28
								118		0.002	14.0				
70.2	6.79	8.67	1.17	10.9	75.8	0.6	9.75	126	278	0	2.16	0.08	-0.50	-1.69	-2.32
69.1	7.32	8.95	1.09	16.3	94.2	0.5	8.14	98	275	0	3.03	-0.26	-1.14	-1.60	-2.23
66.3	7.46	8.44	1.35	15.1	92.7	0.5	11.1	82	262			1.09	1.61	-1.64	-3.88
25.6	3.46	16.5	1.12	11.3	23.5	E0.1	3.6	73	131		6.56	-1.28	-3.03	-2.50	-1.72
225	26.5	11.3	1.24	9.74	413	0.5	14.8	179	832	1.65	5.93	0.25	-0.09	-0.73	-1.91
170	19.7	7.87	0.93	8.72	296	0.3	15.2	176		1.02	6.25	0.26	-0.08	-0.92	-2.01
								181		0.66	6.00				
98.7	10.2	12.1	0.63	8.93	120	<0.2	12.6	159	346	0.006	6.00	-0.93	-2.50	-1.41	-1.03
89.8	8.86	6.62	0.42	6.2	191	0.2	9.16	58	364	0.005	4.83	-1.80	-4.25	-1.25	-1.06
78.2	10	5.97	0.34	4.74	171	0.3	8.79	58	343	0.005	5.27	-2.02	-4.57	-1.34	-0.84
68.7	8.76	6.91	0.42	6.64	138	<0.2	12.1	57	309		5.73	-1.97	-4.48	-1.46	-0.95
211	26.9	6.13	0.97	9.29	383	0.5	15.6	182	776	1.1	6.43	0.24	-0.07	-0.78	-1.90
								185		0.66	6.25				
117	9.28	8.04	0.97	13.2	151	0.3	13.9	136	395	0.15	6.55	0.07	-0.61	-1.27	-2.10
64.7	5.9	5.89	0.68	9.92	47.2	<0.2	8.72	129	234	0	6.49	-0.63	-1.94	-1.90	-1.61
46	3.78	10.5	3.24	2.03	26.6	<0.2	4.68	111	189		5.09	-0.99	-2.68	-2.24	-1.45
43.5	4.35	11.4	2.55	1.85	28.6	E0.1	4.88	115	177	0.002	5.81	-1.00	-2.62	-2.23	-1.44
54.9	5.41	12.1	2.98	6.75	47.6	<0.1	4.97	112	223		6.38	-0.93	-2.49	-1.95	-1.45
31.3	3.41	14.6	4.55	4.94	14.2	0.3	2.34	98	155		5.67	0.07	-0.41	-2.64	-2.68
39.8	4.11	6.18	1.08	8.36	6.7	0.3	6.05	104	144	0.007	8.40	-0.18	-0.98	-2.88	-2.39
2.9	2.19	2.77	1.08	5.7	7.3	<0.2	2.8	4	46	0	6.52	-5.52	-10.77	-3.80	-0.48
3.36	3.32	4.89	1.26	11.7	5.6	E0.1	3.83	4	48	0.004	7.74	-5	-9.63	-3.87	-1.22
2.16	1.79	7.15	0.9	4.96	11.6	<0.1	2.46	4	41	0	8.20	-4.94	-9.61	-3.72	-1.56
26.5	0.767	6.45	2.75	9.05	17.5	<0.2	2.83	44	136		2.45	-2.27	-5.69	-2.58	-1.14
39.5	1.05	3.72	2.93	3.21	11	E0.1	2.03	77	150	0.012	3.03	-1.92	-5.07	-2.65	-0.92
22.9	1.06	7.65	2.5	15.6	5	E0.1	3.19	48	95	0.001	3.46	-2.04	-5.05	-3.16	-1.43
								95							
												-0.7	-2.10	-2.69	-1.92
39.9	3.34	8.9	0.08	14.8	10.2	0.215	8.7		186						
97.2	7.89	12.2	1.19	28.1	96.4	0.2	12.8	148	344	0	17.5	0.07	-0.60	-1.50	-2.05
90.1	7.71	12.9	1.18	31	78.7	0.1	12.8	140	333	0.001	17.5	0.02	-0.67	-1.60	-2.08
102	8.36	11.8	1.19	27.9	103	0.2	12.8	150	359	0.008	17.5	0.06	-0.64	-1.46	-2.06
101	8.23	11.6	1.15	26.9	106	0.2	12.8	150	361	0	17.5	0.07	-0.59	-1.45	-2.05
99.8	8.72	11.6	1.17	26.9	107	0.3	13.2	150	355	0.001	17.5	0.07	-0.56	-1.45	-2.05
98.1	8.41	11.2	1.04	25	116	0.3	13.3	139	380	0.03		0.03	-0.65	-1.42	-2.08

17.8 mg/L (table 5) with a median concentration of 9.3 mg/L. The range of dissolved organic carbon concentrations in water from the intermediate confining unit and Upper Floridan aquifer was substantially smaller than that from the surficial aquifer system and retention ponds, with median concentrations of 1.8 and 2.0, respectively. Dissolved solids concentrations in water were less than 500 mg/L from the surficial aquifer system, intermediate confining unit, and stormwater retention ponds. Dissolved solids concentrations were considerably higher in most water samples from the Upper Floridan aquifer with five wells that had concentrations in water ranging from 580 to 830 mg/L.

Redox Conditions

Redox conditions are important in controlling many chemical processes in ground water, such as the speciation of naturally occurring elements (for example, sulfur, arsenic, and iron) and the transformation/biodegradation of anthropogenic compounds (for example, nitrate, trichloromethane, and trichloroethene). A scheme was developed for the regional-scale TANC studies using various chemical indicator species to classify redox conditions in ground water (S.S. Paschke, U.S. Geological Survey, written commun., 2007). This redox classification scheme is presented in appendix A4. A redox category was assigned to each ground-water sample; however, the present study has modified this scheme based on data that are available for hydrogen sulfide and methane. In some instances, conflicting or overlapping indicators of redox conditions occur and are related to mixtures of water with different redox indicators. However, the detection of hydrogen sulfide in water from most wells in the Upper Floridan aquifer (table 5) allowed the classification of these waters as sulfate reducing.

Distinct differences in redox conditions exist among waters from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer. Water samples from 9 of 11 monitoring wells screened in the surficial aquifer system consistently had dissolved oxygen concentrations greater than or equal to 1 mg/L (fig. 8). 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 samples from wells RP-S20 and QRP-S20 are indicative of mixed redox conditions because dissolved oxygen concentrations were greater than or equal to 1 mg/L, but iron concentrations were greater than 300 $\mu\text{g/L}$ (micrograms per liter). Water from wells with mixed redox conditions or anoxic conditions likely are influenced by surface features like sinkholes, retention ponds, or the Hillsborough River. Water from LRP-S25 and THC-S46 had dissolved oxygen concentrations less than or equal to 0.5 mg/L. The depth to the water table at those wells was less than or equal to 3 m and greater than or equal to 7.6 m, respectively, but the screen tops at both of those wells were farther below the water table (about 1.5-2.5 m) than many of the other wells.

Water from well THC-S46 had low dissolved oxygen concentrations (less than 0.5 mg/L) and elevated iron and manganese concentrations indicating anoxic conditions (iron-manganese reducing conditions).

Water samples from two of the four wells in the intermediate confining unit (62SRP-H55 and LP-H40) had dissolved oxygen concentrations greater than 2 mg/L (dissolved oxygen-reducing conditions). These two wells have screen tops that are generally less than or equal to 4 m below the water table. The other two wells (113RC-H50 and LRP-H105) had concentrations of dissolved oxygen less than 0.5 mg/L. The suboxic water samples from these two wells also had nitrate-N concentrations of about 0.5 mg/L and methane concentrations greater than 0.1 mg/L, indicating nitrate-iron reducing conditions. Water from 113RC-H50 had manganese concentrations less than 50 $\mu\text{g/L}$ and iron concentrations greater than 100 $\mu\text{g/L}$. Wells 113RC-H50 and LRP-H105 had screen tops that were generally 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 intermediate confining unit.

All but two monitoring wells in the Upper Floridan aquifer (62SRP-F160 and MAS-R-F160) had dissolved oxygen concentrations less than or equal to 0.5 mg/L and only one well (MAS-R-F64) had a dissolved oxygen concentration greater than 1 mg/L. Most of these monitoring wells had detectable (greater than 0.01 mg/L) sulfide concentrations (fig. 8); water samples from only a few wells had manganese concentrations greater than 50 $\mu\text{g/L}$ or iron concentrations less than 100 $\mu\text{g/L}$ (sulfate-reducing conditions). Two of the wells

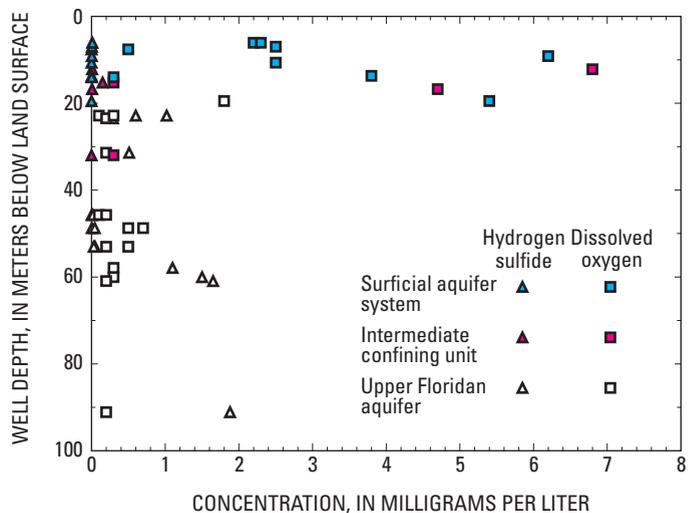


Figure 8. Dissolved oxygen and hydrogen sulfide concentrations with well depth from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area.

had methane concentrations greater than 0.1 mg/L. Concentrations of hydrogen gas ranged from 0.4 to 2.1 nM (nanomolar), which are characteristic of iron-reducing or sulfate-reducing conditions. Subtle differences in redox processes related to dissolved oxygen/nitrate/iron/sulfate reduction and methanogenesis could not be mapped spatially, but vary with depth and are related to organic carbon content, ground-water residence time, and hydraulic connections between the surficial aquifer system and Upper Floridan aquifer.

Stable Isotopes of Water

Variations in the delta hydrogen-2 ($\delta^2\text{H}$) and delta oxygen-18 ($\delta^{18}\text{O}$) composition of ground water, rainfall, retention pond water, and river water were used to examine sources of water, flow patterns, and mixing processes in the ground-water system (table 6). The isotopic composition of ground- and surface-water samples are plotted relative to the global meteoric water line (Craig, 1961) and a local meteoric water line determined from a previous study (Sacks, 2002) (fig. 9). Differences in the slope and intercept of these two meteoric water lines are related to several factors including storm-track origin, rainfall amount and intensity, atmospheric temperature, and the number of evaporation and condensation

cycles. The isotopic composition of water from wells in the surficial aquifer system, and from a shallow well in the Upper Floridan aquifer (RP-F77) plot between these two lines, indicating that these waters have not been affected by evaporation. In contrast, water from other shallow monitoring wells in the Upper Floridan aquifer and two retention ponds (MAS-POND and LRP-POND) are slightly enriched relative to the global meteoric water line. Further enrichment of the stable isotopic composition is noted for the four deep monitoring wells in the Upper Floridan aquifer and Hillsborough River. The higher $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for water from the Hillsborough River water indicate that evaporative enrichment of these isotopes has occurred. The isotopic composition of water from the public-supply well is consistent with possible mixing of water from the surficial aquifer system and Upper Floridan aquifer as the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values plot between those for water from both hydrogeologic units (fig. 9).

The enriched isotopic signature for the deep wells in the Upper Floridan aquifer (GARC-F200, THC-F197, 113RC-F190, and WP-F299) indicates that recharge water has undergone evaporation prior to recharging the aquifer. One possible source for isotopically enriched waters is recharge water that occurs in wetland areas located several kilometers upgradient from the study area. The presence of higher amounts of dissolved organic carbon in these waters also indicates a

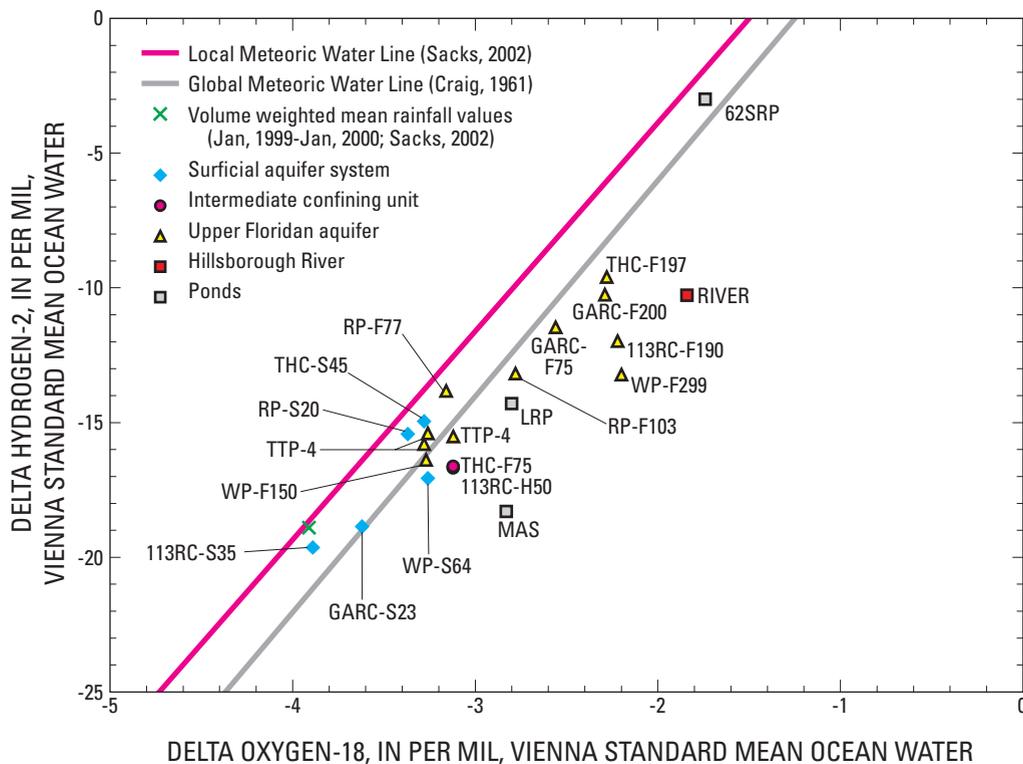


Figure 9. Oxygen and hydrogen isotopes in ground water and surface water from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area.

Table 6. Data for delta oxygen-18 ($\delta^{18}\text{O}$) and delta hydrogen-2 ($\delta^2\text{H}$), delta carbon-13 ($\delta^{13}\text{C}$) in dissolved inorganic carbon, nitrogen and oxygen isotopes of nitrate ($\delta^{15}\text{N}$ of NO_3), delta sulfur-34 of sulfate ($\delta^{34}\text{S}$), and radon-222 in water samples from the surficial aquifer system (SAS), intermediate confining unit (ICU), Upper Floridan aquifer (UFA), ponds, and river.

[Delta (δ) values are reported as per mil relative to standards listed in report]

Site name	Aquifer or hydrogeologic unit	Site identifier	Sample date	Sample time	$\delta^{13}\text{C}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{15}\text{N}$ of nitrate	$\delta^{18}\text{O}$ of nitrate	Radon-222	$\delta^{34}\text{S}$
BBP-S45	SAS	280228082231501	12/9/2004	1300				4.7	2.8		
THC-F197	UFA	280241082224401	1/15/2004	1400		-9.6	-2.3	8.2	18.9	140	24.0
THC-F75	UFA	280241082224402	1/12/2004	1500		-17.6	-3.2	11.7	15.6	840	25.2
THC-F75	UFA	280241082224402	1/28/2004	1300				9.3	22.6		
THC-S46	SAS	280241082224403	12/18/2003	1300		-15.0	-3.3	6.4	5.9	900	7.7
62SRP-F160	UFA	280241082230701	11/2/2004	1200				9.4	9.9	30	11.1
62SRP-H55	ICU	280241082230702	11/3/2004	1700				5.5	4.6	1,150	8.5
62SRP-POND	POND	280242082230800	6/21/2005	1220	-12.8	-3.0	-1.7	6.2	16.6		11.6
MAS-R-F160	UFA	280242082232401	11/3/2004	1200				9.2	8.1	460	7.6
MAS-R-F64	UFA	280242082232403	2/16/2005	1300				7.2	6.0	3,170	5.8
MAS-POND	POND	280242082232900	6/21/2005	1100	-6.5	-18.3	-2.8				
TTP-4	UFA	280244082232001	1/28/2004	1600	-12.6	-15.5	-3.1	10.0	9.6	780	16.8
TTP-4	UFA	280244082232001	10/21/2004	1500	-12.3	-15.4	-3.3	6.4	6.6		15.4
WP-F299	UFA	280247082231901	1/22/2004	1600	-10.6	-13.2	-2.2	17.1	16.0	980	24.0
WP-F150	UFA	280247082231902	1/28/2004	1000?				13.1	23.5		
WP-F150	UFA	280247082231902	1/28/2004	1300		-16.4	-3.3	13.1	23.5	1,080	15.3

Table 6. Data for delta oxygen-18 ($\delta^{18}\text{O}$) and delta hydrogen-2 ($\delta^2\text{H}$), delta carbon-13 ($\delta^{13}\text{C}$) in dissolved inorganic carbon, nitrogen and oxygen isotopes of nitrate ($\delta^{15}\text{N}$ of NO_3^- and $\delta^{18}\text{O}$ of NO_3^-), delta sulfur-34 of sulfate ($\delta^{34}\text{S}$), and radon-222 in water samples from the surficial aquifer system (SAS), intermediate confining unit (ICU), Upper Floridan aquifer (UFA), ponds, and river.—Continued

[Delta (δ) values are reported as per mil relative to standards listed in report]

Site name	Aquifer or hydrogeologic unit	Site identifier	Sample date	Sample time	$\delta^{13}\text{C}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{15}\text{N}$ of nitrate	$\delta^{18}\text{O}$ of nitrate	Radon-222	$\delta^{34}\text{S}$
WP-S64	SAS	280247082231903	1/14/2004	1500		-17.1	-3.3	4.4	3.5	2,660	16.7
RP-F103	UFA	280249082220701	12/2/2003	1500		-13.2	-2.8	5.9	14.7		24.1
RP-F103	UFA	280249082220701	1/14/2004	1135						660	
RP-F77	UFA	280249082220702	12/3/2003	1300		-13.8	-3.2	4.2	11.1	1,390	22.7
RP-S20	SAS	280249082220703	12/4/2003	1400		-15.4	-3.4	10.0	-0.4	400	5.7
LRP-F160	UFA	280250082233001	11/4/2004	1300				4.7		420	26.2
LRP-H105	ICU	280250082233002	12/7/2004	1600				8.1	6.2	130	18.4
LRP-POND	POND	280250082233200	6/21/2005	915	-14.1	-14.3	-2.8	7.4	6.9		17.8
GARC-F200	UFA	280253082223801	12/16/2003	1300		-10.3	-2.3	21.0	17.9	500	23.9
GARC-F75	UFA	280253082223802	12/15/2003	1400		-11.5	-2.6	11.0			24.0
GARC-S23	SAS	280253082223803	12/17/2003	1200		-18.9	-3.6	2.9	2.3	3,130	16.4
113RC-F190	UFA	280301082222701	12/8/2003	1300		-12.0	-2.2	5.9	7.1	510	24.6
113RC-H50	ICU	280301082222702	12/9/2003	1300		-16.7	-3.1	9.2	7.6	3,330	21.7
113RC-S35	SAS	280301082222703	12/11/2003	1300		-19.6	-3.9	2.8	4.4	2,440	16.8

Table 6. Data for delta oxygen-18 ($\delta^{18}\text{O}$) and delta hydrogen-2 ($\delta^2\text{H}$), delta carbon-13 ($\delta^{13}\text{C}$) in dissolved inorganic carbon, nitrogen and oxygen isotopes of nitrate ($\delta^{15}\text{N}$ of NO_3 and $\delta^{18}\text{O}$ of NO_3), delta sulfur-34 of sulfate ($\delta^{34}\text{S}$), and radon-222 in water samples from the surficial aquifer system (SAS), intermediate confining unit (ICU), Upper Floridan aquifer (UFA), ponds, and river.—Continued

[Delta (δ) values are reported as per mil relative to standards listed in report]

Site name	Aquifer or hydrogeologic unit	Site identifier	Sample date	Sample time	$\delta^{13}\text{C}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{15}\text{N}$ of nitrate	$\delta^{18}\text{O}$ of nitrate	Radon-222	$\delta^{34}\text{S}$
LP-H40	ICU	280303082230901	12/8/2004	1500				1.5	4.0	3,050	7.9
LP-H40	ICU	280303082230901	12/8/2004	1510				1.8	4.2		
LP-S30	SAS	280303082230902	11/1/2004	1600				1.7	2.4		
QRP-S20	SAS	280311082223901	11/15/2004	1700				1.7	1.5		
HRIV-WA	RIVER	280244082220100	1/30/2004	1410		-10.3	-1.8				
HRIV-RR	RIVER	280248082220200	6/22/2005		-14.4	-11.7	-2.3	5.7	4.3		
TTP-4-140-NP	UFA	280244082232001	10/27/2004	1600		-15.7	-3.3	8.0	8.2	970	12.9
TTP-4-160-NP	UFA	280244082232001	10/27/2004	1800		-15.9	-3.4	6.0	7.0	1,210	11.0
TTP-4-160-P	UFA	280244082232001	10/28/2004	1100		-16.0	-3.2	8.9	8.9	1,060	13.5
TTP-4-140-P	UFA	280244082232001	10/28/2004	1400		-15.4	-3.3	7.8	8.2	850	13.7
TTP-4-125-P	UFA	280244082232001	10/28/2004	1600		-15.8	-3.3	7.7	8.0	990	13.9
TTP-4-entire-P	UFA	280244082232001	10/21/2004	1500	-12.3	-15.4	-3.3	6.4	6.6		15.4

possible source of recharge from wetland areas to the north. Other sources for the high sulfate waters include upwelling of waters from deep flow paths in the Upper Floridan aquifer and/or recharge during different climatic conditions (Sacks, 1996).

Ground-Water Age and Age Distributions

Two age-dating methods were used to determine apparent ages of ground water and age distributions by incorporating various lumped parameter models. These two methods include measurements of the concentrations of tritium (^3H) and its radioactive decay product helium-3 (^3He) and measurements of the concentrations of sulfur hexafluoride (SF_6). Comparison of the two independent ages from these methods can be used as a verification for sampling and analytical methods and to evaluate mixing and other processes in the flow system.

Apparent Sulfur Hexafluoride and Tritium/ Helium-3 Ground-Water Ages

The SF_6 and $^3\text{H}/^3\text{He}$ apparent ages of ground water, assuming a piston-flow model, generally were concordant and ranged from young water (less than 1 year) to water more than 60 years old (fig. 10). Apparent ages for water from the surficial aquifer system were much younger than those from the intermediate confining unit and Upper Floridan aquifer (tables 7 and 8; fig. 10). The $^3\text{H}/^3\text{He}$ and SF_6 apparent ages for water from the public-supply well ranged from less than 1 year to 8 years, respectively (tables 7 and 8; fig. 10). Also of note is the relatively young apparent age of 12 years for water from

WP-F150, a 46-m-deep monitoring well in the Upper Floridan aquifer near the public-supply well that likely is withdrawing water from a highly transmissive zone similar to the 43- to 49-m zone identified using geophysical measurements of the borehole for the public-supply well.

Differences in SF_6 and $^3\text{H}/^3\text{He}$ apparent ages for water from the surficial aquifer system are related to the thickness of the unsaturated zone, depth below the water table, and the presence of clays within the surficial material. For example, water from LP-S30 had an apparent SF_6 age of 13 to 15 years, whereas water from the slightly deeper well, 113RC-S35, had an apparent age of 7 years. The unsaturated zone thickness was greater at LP-S30 (8.5 m) than that at 113RC-S35 (6.7 m), and clay material was noted throughout a larger interval for LP-S30 than for 113RC-S35, which may account for a longer time of travel to LP-S30 than 113RC-S35. Even though the unsaturated zone thickness for WP-S64 was 16 m, the SF_6 apparent age for water from this well was only 3 to 4 years. The unsaturated zone at WP-S64 contains a greater thickness of sand/silt material than at LP-S30 and 113RC-S35, and the presumed higher permeability may account for the younger water at WP-S64 than at LP-S30.

The $^3\text{H}/^3\text{He}$ apparent age calculations are sensitive to the amount of terrigenous helium-4 (^4He) from decay of uranium-series radionuclides and excess air. Terrigenous ^4He (relative to the total ^4He) generally was less than 5 percent, but water samples from two sites, 113RC-F190 and GARC-F200, had values of 10 to 12 percent (table 8). Other studies reported a highly variable distribution of uranium in sediments that compose the Upper Floridan aquifer (Kaufman, 1968). Uranium concentrations in water samples were highly variable, but median uranium concentrations were higher for water samples from the Upper Floridan aquifer than from the surficial aquifer system and intermediate confining unit (see below for more detailed information on uranium concentrations). With large fractions of terrigenous helium (greater than 10 percent), the $^3\text{He}/^4\text{He}$ ratio of the terrigenous helium (R_{terr}) needs to be known accurately. Non-tritogenic ^3He resulting from terrigenous sources are adjusted using an R_{terr} of $2\text{E}-08$ (Schlosser and others, 1988). If this ratio is allowed to vary over two orders of magnitude (somewhat unlikely, but useful for illustrating estimates of age uncertainty) for an R_{terr} of $2\text{E}-07$, apparent ages would be younger by 8 years for 113RC-F190 and 6 years for GARC-F200. Using an R_{terr} of $2\text{E}-09$, there would be no appreciable differences in apparent ages.

The apparent lack of agreement between SF_6 and $^3\text{H}/^3\text{He}$ apparent ages for the presumed older waters (greater than 60 years based on low tracer concentrations) from the Upper Floridan aquifer could result from complex mixtures of water from deep zones within the aquifer and the age dating limits of the SF_6 method. Another possibility for the minor excess SF_6 is that there is some natural background or low-level anthropogenic SF_6 contamination in these water samples (GARC-F200, WP-F299, and THC-F297) from deep parts of the Upper Floridan aquifer. To assess and quantify possible ground-water mixing scenarios, measured concentration data for SF_6 were

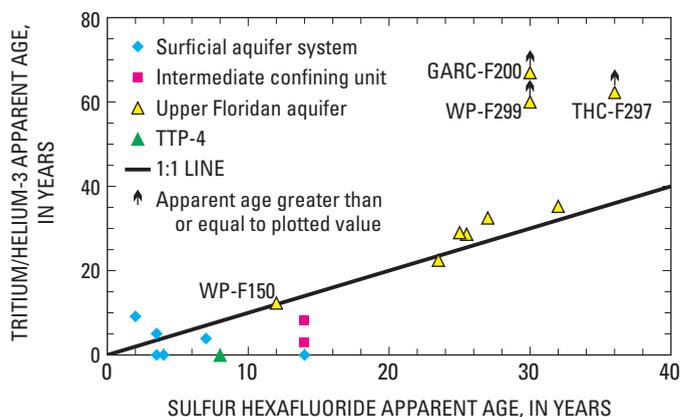


Figure 10. Comparison of apparent ages based on the piston-flow assumption and measured concentrations of sulfur hexafluoride, tritium, and helium-3 in water samples from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area.

Table 7. Summary of sulfur hexafluoride (SF₆) results for water samples from wells in surficial aquifer system (SAS), intermediate confining unit (ICU), and Upper Floridan aquifer (UFA).

[mL, milliliters; °C, degrees Celsius; femtomol/kg, 10⁻¹⁵ moles per kilogram; pptv, parts per trillion by volume; calculated for recharge elevation of 15 meters; PFM, piston-flow assumption]

Site name	Aquifer	Sampling date	Time	Excess air, mL	Recharge temperature, °C	SF ₆ concentration, femtomol/kg	SF ₆ partial pressure, pptv	PFM SF ₆ recharge year	PFM SF ₆ age, years
RP-S20	SAS	12/04/03	1400	0.4	22.8	1.247	4.788	2000.5	3
RP-S20	SAS	12/04/03	1400	0.4	21.8	1.285	4.781	2000.5	3
113RC-S35	SAS	12/11/03	1300	1.3	20.7	1.258	3.949	1997.0	7
113RC-S35	SAS	12/11/03	1300	1.3	20.7	1.299	4.077	1997.0	7
GARC-S23	SAS	12/17/03	1200	0.5	20.6	1.523	5.366	2002.5	1
GARC-S23	SAS	12/17/03	1200	0.5	20.6	1.470	5.178	2002.0	2
THC-S45	SAS	12/18/03	1300	2.3	21.0	1.734	4.809	2000.5	3
THC-S45	SAS	12/18/03	1300	2.3	21.0	1.702	4.720	2000.0	4
WP-S64	SAS	01/14/04	1500	0.2	22.0	1.262	4.888	2000.5	4
WP-S64	SAS	01/14/04	1500	0.2	22.0	1.294	5.013	2001.5	3
LP-S30	SAS	08/30/05	1700	2.0	23.0	0.832	2.518	1990.5	15
LP-S30	SAS	08/30/05	1700	2.0	23.0	1.015	3.074	1993.0	13
LP-H40	ICU	08/30/05	1400	2.0	23.0	0.881	2.669	1991.5	14
LP-H40	ICU	08/30/05	1400	2.0	23.0	0.933	2.826	1992.0	14
113RC-H50	ICU	12/09/03	1300	2.3	20.0	0.895	2.422	1990.0	14
113RC-H50	ICU	12/09/03	1300	2.3	20.0	0.906	2.452	1990.5	13
GARC-F75	UFA	12/15/03	1400	2.4	20.8	0.226	0.616	1977.5	26
GARC-F75	UFA	12/15/03	1400	2.4	20.8	0.214	0.585	1977.0	27
THC-F75	UFA	01/12/04	1500	1.8	21.0	0.246	0.727	1979.0	25
THC-F75	UFA	01/12/04	1500	1.9	21.0	0.246	0.717	1978.5	26
RP-F77	UFA	12/03/03	1300	2.6	19.1	0.356	0.908	1980.5	23
RP-F77	UFA	12/03/03	1300	2.6	19.1	0.361	0.920	1980.5	23
RP-F103	UFA	12/02/03	1500	2.2	21.0	0.252	0.707	1978.5	25
RP-F103	UFA	12/02/03	1500	2.2	21.0	0.252	0.708	1978.5	25
WP-F150	UFA	01/28/04	1300	1.4	23.2	0.878	2.907	1992.5	12
WP-F150	UFA	01/28/04	1300	1.4	23.2	0.821	2.719	1991.5	13
113RC-F190	UFA	12/08/03	1300	1.8	19.2	0.100	0.282	1972.0	32
113RC-F190	UFA	12/08/03	1300	1.8	19.2	0.117	0.329	1973.0	31

Table 7. Summary of sulfur hexafluoride (SF₆) results for water samples from wells in surficial aquifer system (SAS), intermediate confining unit (ICU), and Upper Floridan aquifer (UFA).—Continued

[mL, milliliters; °C, degrees Celsius; femtomol/kg, 10⁻¹⁵ moles per kilogram; pptv, parts per trillion by volume; calculated for recharge elevation of 15 meters; PFM, piston-flow assumption]

Site name	Aquifer	Sampling date	Time	Excess air, mL	Recharge temperature, °C	SF ₆ concentration, femtomol/kg	SF ₆ partial pressure, pptv	PFM SF ₆ recharge year	PFM SF ₆ age, years
THC-F197	UFA	01/15/04	1400	1.9	19.2	0.070	0.195	1968.0	36
THC-F197	UFA	01/15/04	1400	1.9	19.2	0.098	0.273	1971.5	33
GARC-F200	UFA	12/16/03	1300	1.8	19.9	0.718	2.063	1988.5	15
GARC-F200	UFA	12/16/03	1300	1.8	19.9	0.133	0.383	1974.0	30
WP-F299	UFA	01/22/04	1600	2.1	18.9	0.124	0.335	1973.0	31
WP-F299	UFA	01/22/04	1600	2.1	18.9	0.135	0.364	1974.0	30
WP-F299	UFA	08/29/05	1500	2.0	23.0	0.183	0.555	1977.0	29
WP-F299	UFA	08/29/05	1500	2.0	23.0	0.157	0.475	1975.5	30
TTP-4 125-PUMPING	UFA	10/28/04	1600	2.0	23.0	1.299	3.932	1996.5	8
TTP-4 125-PUMPING	UFA	10/28/04	1600	2.0	23.0	1.297	3.926	1996.5	8
TTP-4 140-NONPUMPING	UFA	10/27/04	1600	2.0	23.0	1.357	4.108	1997.5	7
TTP-4 140-NONPUMPING	UFA	10/27/04	1600	2.0	23.0	1.318	3.990	1997.0	8
TTP-4 140-PUMPING	UFA	10/28/04	1400	2.0	23.0	1.258	3.810	1996.0	9
TTP-4 140-PUMPING	UFA	10/28/04	1400	2.0	23.0	1.112	3.366	1994.5	10
TTP-4 160-NONPUMPING	UFA	10/27/04	1800	2.0	23.0	1.424	4.311	1998.0	7
TTP-4 160-NONPUMPING	UFA	10/27/04	1800	2.0	23.0	1.422	4.306	1998.0	7
TTP-4 160-PUMPING	UFA	10/28/04	1100	2.0	23.0	1.504	4.554	1999.5	5
TTP-4 160-PUMPING	UFA	10/28/04	1100	2.0	23.0	1.308	3.961	1997.0	8
TTP-4	UFA	08/31/05	1000	2.0	23.0	1.268	3.839	1996.5	9
TTP-4	UFA	08/31/05	1000	2.0	23.0	1.247	3.775	1996.0	10

Table 8. Summary of tritium/helium-3 (³H/³He) age data using piston-flow model for water samples from the surficial aquifer system (SAS), intermediate confining unit (ICU), and Upper Floridan aquifer (UFA).

[Estimated recharge temperature is 21 degrees Celsius. Recharge elevation is approximately 20 meters NAVD 88 (North American Vertical Datum of 1988); TU, tritium units; µcc STP/kg, micrometers cubed of gas at standard temperature and pressure per kilogram of water; 1 sigma, one standard deviation for analytical method; NA, laboratory analytical problem; LDEO, Lamont Doherty Earth Observatory, Palisades, New York; USGS, U.S. Geological Survey Noble Gas Laboratory, Denver, Colorado; NA, not applicable; >, greater than]

Site name	Aquifer	Sampling date	Tritium, tritium units	Tritium error, 1 sigma	Delta helium-3 measured, percent	Helium-4, µcc STP/kg	Neon, µcc STP/kg	Helium-4 terrigenic, percent	Tritium/helium-3 age, years	Tritium/helium-3 age error, years	Analytical laboratory
RP-F103	UFA	12/2/2003	0.753	0.05	2.94	57.48	218.00	5.1	29	1.5	LDEO
RP-F77	UFA	12/3/2003	0.74	0.07	3.07	58.06	227.38	1.4	22	2.0	LDEO
RP-S20	SAS	12/4/2003	2.216	0.06	-1.1	49.5	204.74	0.0	0	2.2	LDEO
113RC-F190	UFA	12/8/2003	0.17	0.05	-8.34	61.81	221.05	10.4	35	5.5	LDEO
113RC-H50	ICU	12/9/2003	1.329	0.05	2.31	62.55	248.64	0.0	8	2.1	LDEO
113RC-S35	SAS	12/11/2003	2.145	0.06	4.85	52.03	217.46	0.0	4	1.5	LDEO
GARC-F75	UFA	12/15/2003	0.428	0.04	-0.38	58.8	220.69	5.9	33	4.0	LDEO
GARC-F200	UFA	12/16/2003	0.04	0.04	-7.98	62.46	220.18	11.7	67	18.0	LDEO
GARC-S23	SAS	12/17/2003	2.125	0.06	-0.51	169.17	606.62	1.6	9	7.6	LDEO
THC-S46	SAS	12/18/2003	2.483	0.06	-1.18	60.55	245.60	0.0	0	7.5	LDEO
THC-S75	SAS	1/12/2004	1.108	0.07	12.33	54.06	214.04	1.2	29	1.9	LDEO
WP-S64	SAS	1/14/2004	2.591	0.06	-1.11	44.64	179.10	2.9	5	2.3	LDEO
THC-F197	UFA	1/15/2004	0.09	0.04	0.93	57.74	215.80	6.7	62	9.1	LDEO
WP-F150	UFA	1/28/2004	2.409	0.06	7.81	50.69	206.08	0.0	12	1.9	LDEO
TTP-4	UFA	1/28/2004	2.211	0.07	NA	NA	NA	NA	NA	NA	LDEO
TTP-4-140P	UFA	10/28/2004	1.97	0.02	-2.60	57.2	229.30	1.57	0	2	USGS
TTP-4-140NP	UFA	10/27/2004	2.35	0.02	-2.40	56.9	229.90	0.32	0	2	USGS
TTP-4-125P	UFA	1/28/2004	2.13	0.01	-2.40	55.4	227.20	-0.42	0	2	USGS
TTP-4-160P	UFA	1/28/2004	1.99	0.02	-2.50	56.3	227.80	-0.94	0	2	USGS
TTP-4	UFA	10/21/2004	2.1	0.05	-2.60	54.1	214.00	2.47	0	2	USGS
TTP-4-160NP	UFA	10/27/2004	1.86	0.04	-6.00	49.3	226.70	-11.80	0	2	USGS
LP-H40	ICU	8/30/2005	2.03	0.03	-0.30	54.6	229.50	-0.09	3	2	USGS
LP-S30	SAS	8/30/2005	2.58	0.01	-2.10	43.8	204.30	-0.34	0	2	USGS
WP-F299	UFA	8/29/2005	<0.05	0.01	-10.10	59	267.20	0.01	>45	NA	USGS
TTP-4	UFA	8/31/2005	2.17	0.03	-5.10	59.7	241.20	0.00	0	2	USGS

compared to theoretical age-distribution curves generated using lumped parameter models.

Assessing Ground-Water Age Distributions using Lumped Parameter Models

Analytical procedures are capable of determining extremely low concentrations of the tracers SF_6 , ^3H , and ^3He in ground water; however, the subsequent interpretation of age or mean residence time of ground water in complex karstic aquifer systems still is fraught with a high degree of uncertainty. In many previous studies where SF_6 and $^3\text{H}/^3\text{He}_{\text{trit}}$ (tritium/tritogenic helium-3) 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 surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer systems. These models treat 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 (Maloszewski and Zuber, 1982; Zuber, 1986). By fitting measured tracer concentrations to modeled output curves, the response function accounts for the distribution of ages at a sampled site (Zuber and others, 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 assume a steady-state flow system and assume that the selected tracers behave like a water molecule. Although this assumption typically is valid for tritium, which is part of the water molecule, the gas tracer SF_6 may or may not be transported in exactly the same way as the water. The mean residence time of ground water at a given well represents the time elapsed since recharge and isolation of the tracer from the modern atmosphere. Flow system characteristics are represented by two end-member lumped-parameter models: piston flow and exponential flow. 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. Dye tracer studies have indicated that flow through conduits can be fast, on the order of 3,000 to 23,000 m/d (meter per day) (Wilson and Skiles, 1988).

Other lumped parameter models that account for mixing include the combined exponential and piston-flow model. The exponential flow model and the combined flow model have one fitted parameter in common (total mean transit time or mean-tracer age). The combined flow model has an additional fitting parameter (x), the ratio of $\tau\text{PFM}/\tau\text{EM}$. This fitting parameter (x) is slightly different than the parameter (n), which represents the total volume to the volume with the exponential distribution of ages (Maloszewski and Zuber, 1996).

In addition to the above 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) with older water (decades), presumably from deeper parts of the Upper Floridan aquifer. In principle, both end members of a binary mixture can be of any age, but the calculation is greatly simplified if it is assumed that one or both end members is either "young" (assumed to represent recharge that occurred after 1995) or "old" (recharged before 1950 with undetectable SF_6 concentrations). Ground-water ages were determined using combinations of tracers including SF_6 and ^3H , and SF_6 and $^3\text{H}/^3\text{H}(0)$. The $^3\text{H}(0)$ tracer represents the initial tritium concentration at the time of recharge and is the sum of the measured concentrations of ^3H and $^3\text{He}_{\text{trit}}$. The ratio of $^3\text{H}/^3\text{H}(0)$ is a surrogate for the relative age of water, in that values near zero represent old waters, and conversely, values near 1.0 represent young waters (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.

All samples from the surficial aquifer system and the public-supply well TTP-4 have SF_6 concentrations greater than 3.0 pptv (parts per trillion by volume) and ^3H concentrations greater than 2 tritium units as shown in figure 11. These sample concentrations plot along the modeled curve for piston flow for young waters, and/or a binary mixing curve dominated by young water (less than 6 years in age). In contrast, water samples from three deep wells in the Upper Floridan aquifer (THC-F197, GARC-F200, and 113RC-F190) have low concentrations of ^3H and SF_6 . These samples plot on the lower left-hand side of the lumped-parameter modeled curves (fig. 11) and likely represent waters that are considerably older than 60 years. These waters also contain high concentrations of sulfate, indicating a deep flow path through the aquifer. These findings are consistent with a study by Swancar and Hutchinson (1995) that found higher ^3H concentrations in isotopically light waters compared to isotopically heavier

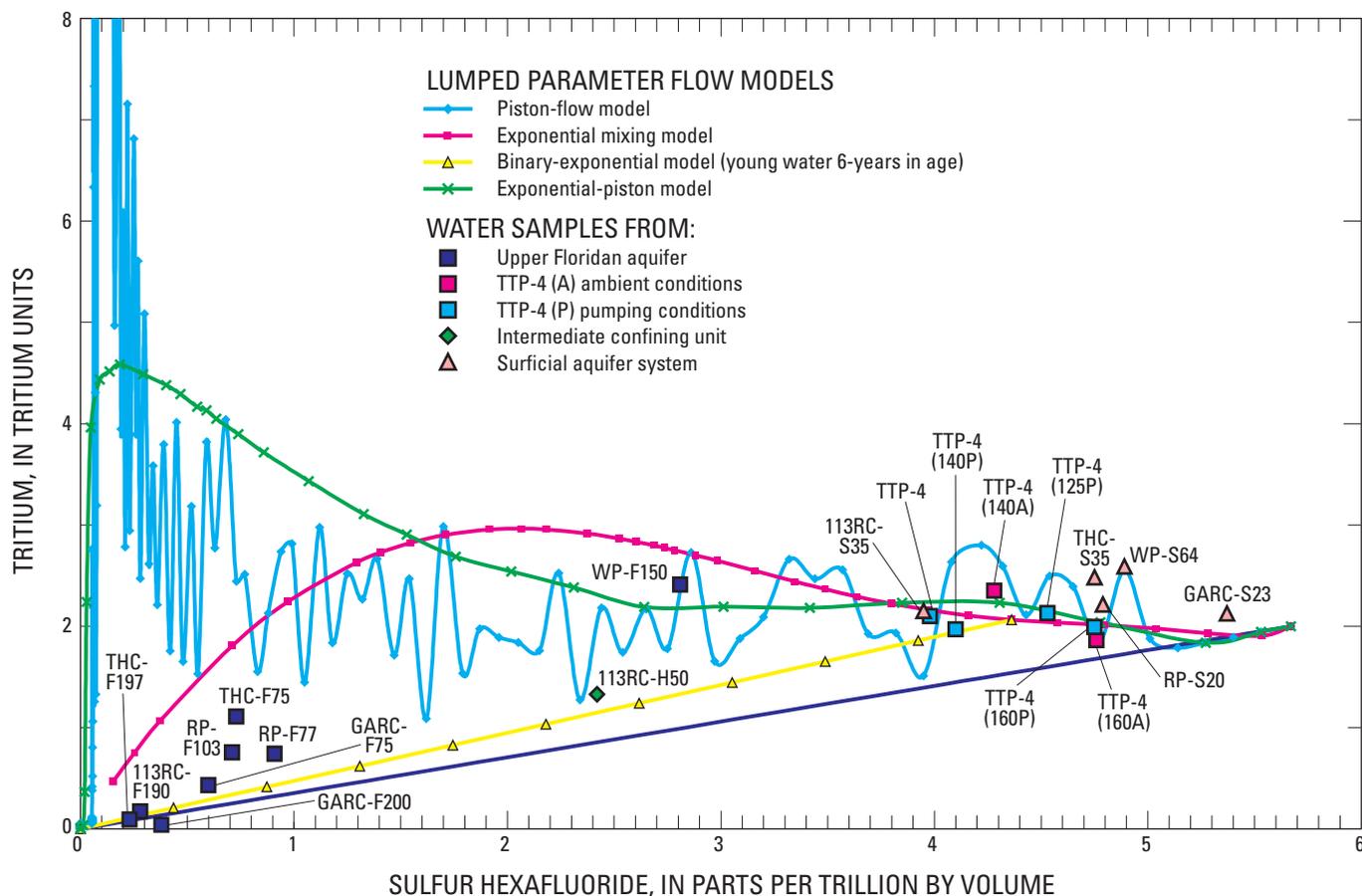


Figure 11. Measured concentrations of sulfur hexafluoride and tritium in water samples from wells, and lumped-parameter modeled curves for various ground-water age distributions from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area.

waters that had low ^3H concentrations (old waters), high sulfate concentrations, and were anoxic.

Water samples from shallow wells in the Upper Floridan aquifer (GARC-F75, RP-F77, THC-F75, and RP-F103) had slightly higher ^3H and SF_6 concentrations than water samples from deep wells, and these samples likely represent mixtures of about 75- to 80-percent old water (greater than 60 years) with 20- to 25-percent young water (recharged within the past 6 years). 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 waters. 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 Upper Floridan aquifer. This zone might be connected to the highly transmissive zone identified in the public-supply well borehole from geophysical measurements.

A plot of SF_6 and $^3\text{H}/^3\text{H}(0)$ shows similar results for samples from the deep wells, which represent old waters (fig. 12). Again, concentrations of SF_6 and $^3\text{H}/^3\text{H}(0)$ for the shallower Upper Floridan aquifer wells plot to the right of

the deep wells along the binary mixing-exponential mixing modeled curves showing mixtures of young and old waters. The SF_6 and $^3\text{H}/^3\text{H}(0)$ concentrations in water from WP-F150 plot close to those for 113RC-S35 and 113RC-H50, indicating the higher fraction of young water at this site. Although the tracer concentrations for most samples from the surficial aquifer system and the public-supply well TTP-4 plot in the upper right-hand side of figure 12 and represent young waters, they plot below all lumped-parameter mixing curves, which could result from several possible scenarios. First, ^3He and/or SF_6 may have been lost due to degassing during sampling. Loss of ^3He could result in an age that is biased younger than the true age. Degassing of SF_6 is less likely, but would result in an age that is biased older than the true age. However, based on the relatively higher ^3H and SF_6 concentrations for these waters, they likely contain mostly young recharge waters (within the past 6 years). Second, preferential loss of ^3He due to diffusion into the Teflon sampling line would result in a higher $^3\text{H}/^3\text{H}(0)$ value than expected without ^3He degassing, and a shift to the right of the modeled curves. Finally, confine-

ment of $^3\text{He}_{\text{trit}}$ can be one of the problems of $^3\text{H}/^3\text{He}$ dating of very shallow water-table environments (L.N. Plummer, U.S. Geological Survey, written commun., 2007). The $^3\text{H}/^3\text{He}$ clock starts at the seasonal low in the water table in wet climates (Cook and Solomon, 1997), and as the water table rises during wet-season recharge, the $^3\text{He}_{\text{trit}}$ becomes confined in the aquifer. The $^3\text{He}_{\text{trit}}$ subsequently could be lost from these samples during seasonal lows in the water table, as was reported for water-table springs in Shenandoah National Park (Plummer and others, 2001). Results from sampling for additional age-dating tracers may help to resolve some of these issues.

water retention ponds, and the Hillsborough River. Emphasis is placed on comparisons between the occurrence of contaminants in water from the public-supply well relative to water samples from the surficial aquifer system, intermediate confining unit and Upper Floridan aquifer. Important factors affecting contaminant occurrence, concentrations, and fate also are presented.

Occurrence of Anthropogenic and Naturally Occurring Contaminants in Ground-Water Samples

This section presents information on selected anthropogenic and naturally occurring contaminants in water from monitoring wells, public-supply well TTP-4, storm-

Nitrate-N Concentrations and Isotopes and Dissolved Gases

Nitrate-N concentrations generally were highest in water samples from the oxic surficial aquifer system compared to those from the intermediate confining unit, the Upper Floridan aquifer, stormwater retention ponds, and the Hillsborough River (table 5; fig. 13). Nitrate-N concentrations did not exceed the U.S. Environmental Protection Agency (1993) maximum contaminant level of 10 mg/L for drinking water in any water samples collected in this study. Nitrate-N concentrations in the surficial aquifer system ranged from less than 0.06 to 6.1 mg/L, with a median value of 1.6 mg/L. Nitrate-N

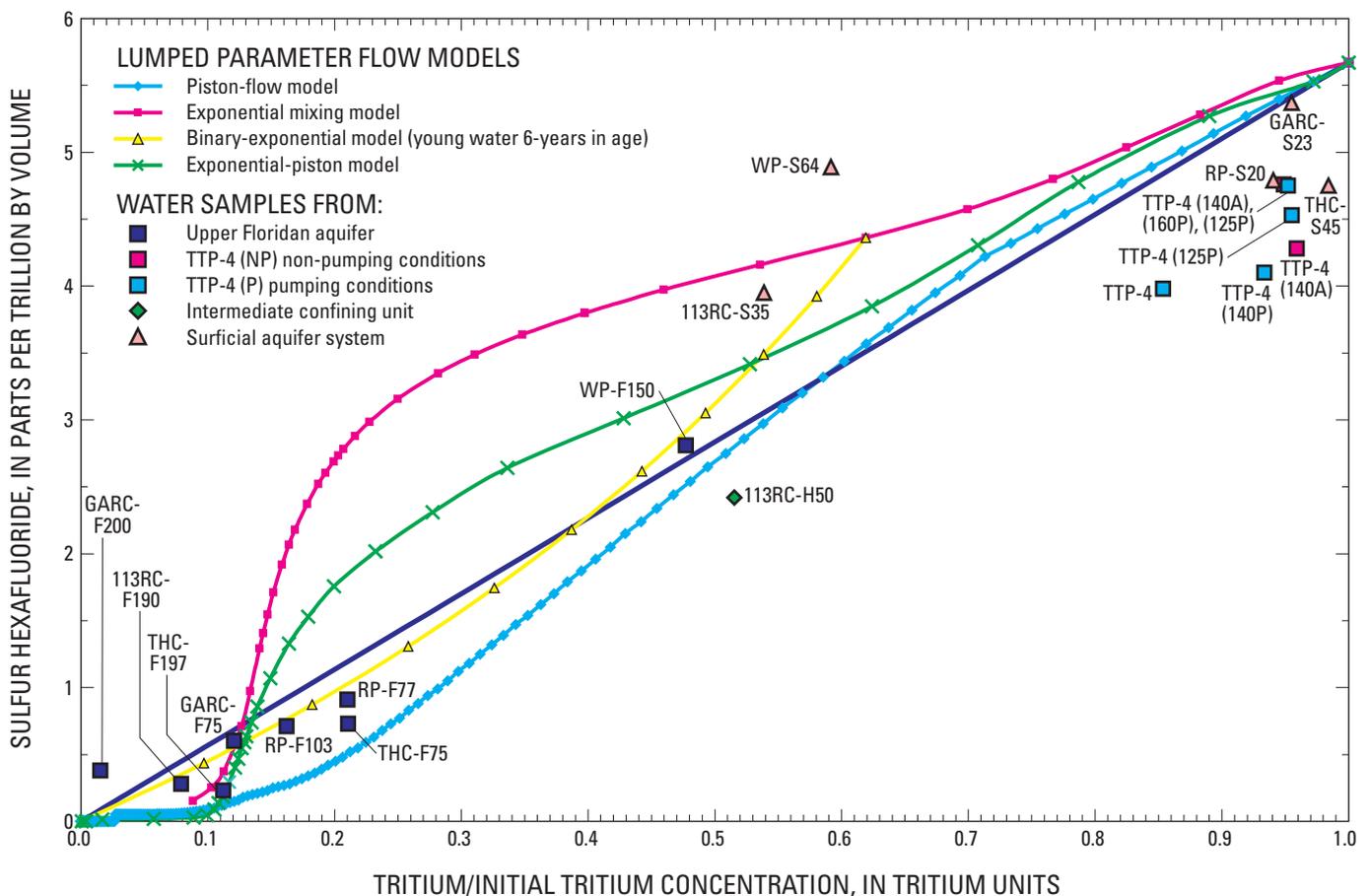


Figure 12. Measured concentrations of sulfur hexafluoride, tritium, the ratio of tritium to the sum of helium-3 and tritium in water samples from wells, and lumped-parameter modeled curves for ground-water age distributions from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area.

concentrations above the background levels of 0.1 mg/L (Maddox and others, 1992) in the surficial aquifer system likely result from past agricultural practices, fertilizer application to lawns, leakage from septic tanks prior to sewerage of the area, and possibly leaky sewer lines. Nitrogen isotope values for these waters generally were less than 5 per mil, indicating that nitrate likely originated from an inorganic fertilizer source. Water samples from three wells had delta nitrogen-15 ($\delta^{15}\text{N}$) values greater than 6 per mil at sites RP-S20 (10.0 per mil), LRP-H105 (8.1 per mil) and THC-S46 (6.4 per mil) as noted in table 6. The higher $\delta^{15}\text{N}$ values may represent denitrification in these waters because methane gas was measured in these water samples (0.3-0.9 mg/L), and excess nitrogen gas was estimated at 0.4 and 3 cm³/L (cubic centimeters per liter) for RP-S20 and LRP-S25, respectively. Excess nitrogen gas was estimated by comparing measured argon and nitrogen gas concentrations to those expected at equilibrium with a recharge temperature of 23 °C. Water from RP-S20 likely is a mixture of surface water from the Hillsborough River and reduced ground water, as indicated by the combined presence of dissolved oxygen (2.2 mg/L), methane (0.9 mg/L), and dissolved organic carbon (3.3 mg/L).

Nitrate-N concentrations were variable in water from the intermediate confining unit and ranged from 0.27 to 3.5 mg/L, with a median concentration of 2.2 mg/L (table 5). Nitrate-N concentrations in water were lower in LRP-H105 (0.27 mg/L) and 113RC-H50 (0.65 mg/L) compared with concentrations in 62SRP-H55 (3.5 mg/L) and LP-H40 (2.4 mg/L). Water from wells LRP-H105 and 113RC-H50 also had higher $\delta^{15}\text{N}$ values and lower dissolved oxygen concentrations than wells

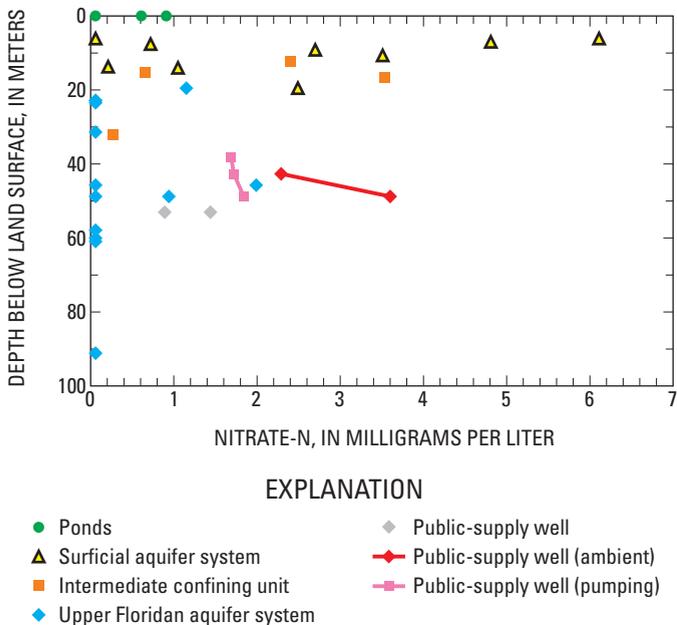


Figure 13. Nitrate-N concentrations with well depth in the Temple Terrace, Florida, study area.

62SRP-H55 and LP-H40, indicating that denitrification likely occurs in parts of the intermediate confining unit. The dissolved methane concentration in water from 113RC-H50 (0.2 mg/L) and an estimated excess nitrogen gas of 1.5 cm³/L also are consistent with denitrification.

Nitrate-N concentrations in water from the Upper Floridan aquifer generally were less than the method reporting level of 0.06 mg/L. Water from the Upper Floridan aquifer, which generally is anoxic in this area, had dissolved oxygen concentrations less than 0.5 mg/L and contained measurable amounts of hydrogen sulfide. Methane concentrations generally were less than 0.1 mg/L, with the exception of LRP-F160 (0.43 mg/L). In addition, there are several other notable exceptions. Water from the shallowest Upper Floridan aquifer well, MAS-F64, had an elevated 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), MAS-R-F160 (0.94 mg/L), and public-supply well TTP-4 (0.61-3.6 mg/L). These wells likely withdraw some water from a transmissive zone in the Upper Floridan aquifer that is hydraulically connected to the surficial aquifer system.

The $\delta^{15}\text{N}$ values for water samples from the Upper Floridan aquifer ranged from 4.2 to 21 per mil and were higher than those for the surficial aquifer system and intermediate confining unit (table 6). Denitrification likely occurs in parts of the Upper Floridan aquifer, as indicated by estimated excess nitrogen gas values (table 9) that ranged from 1.5 to 4 cm³/L for water from a depth interval of between 43 and 49 m below land surface (62SRP-F160, MAS-R-F160, LRP-F160, WP-F150). Also, the ratio of enrichment of $\delta^{18}\text{O}$ to $\delta^{15}\text{N}$ of the residual nitrate-N was close to 0.5 (points plot along dashed trend lines with slope of 0.5 in fig. 14) for samples from the anoxic Upper Floridan aquifer. Previous studies also have shown that the enrichment of oxygen to nitrogen was

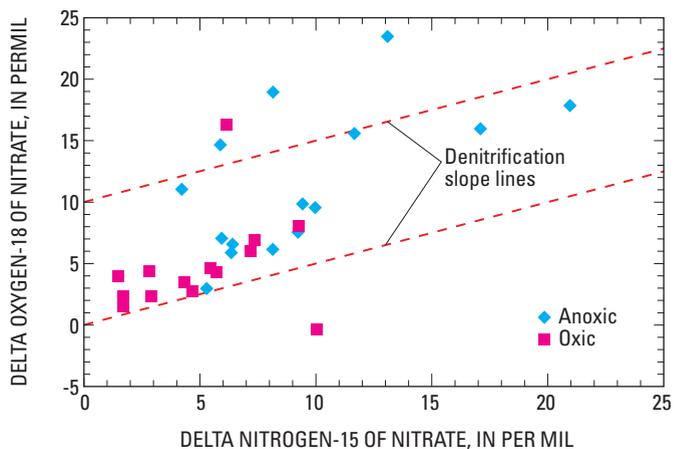


Figure 14. Plot showing values for delta nitrogen-15 and delta oxygen-18 of nitrate in water from wells in the Temple Terrace, Florida, study area.

Table 9. Dissolved gas data, calculated excess nitrogen gas concentration, estimated recharge temperature, and excess air concentration in water samples collected from the public-supply well and monitoring wells in the Temple Terrace, Florida, study area.

[SAS, surficial aquifer system; ICU, intermediate confining unit; UFA, Upper Floridan aquifer. Recharge elevation assumed to be 10 to 30 meters above the NAVD 88 (North American Vertical Datum of 1988). Values in milligrams per liter, except where noted. Excess air in cubic centimeters per liter (cm³/L) at standard temperature and pressure conditions. Sample lost at wells GARC-F75 and BBP-S45. Sample leak occurred at well WP-S64]

Site name	Aquifer	Date collected	Time collected	Field temperature, degrees Celsius	Methane	Carbon dioxide	Nitrogen	Oxygen	Argon	Calculated excess nitrogen gas, mg/L	Calculated recharge temperature, degrees Celsius	Excess air, cm ³ /L
RP-F103	UFA	12/2/2003	1500	23.50	0.1931	0.0000	16.8232	0.1794	0.5797		21.1	2.3
RP-F103	UFA	12/2/2003	1500	23.50	0.1902	0.0000	16.7976	0.1980	0.5800		21.0	2.2
RP-F77	UFA	12/3/2004	1300	23.50	0.0921	0.0000	17.6684	0.2067	0.6066		19.1	2.6
RP-F77	UFA	12/3/2004	1300	23.50	0.0937	0.0000	17.6868	0.2249	0.6075		19.1	2.6
RP-S20	SAS	12/4/2003	1400	24.50	0.8944	0.0000	14.5919	0.7843	0.5258		23.9	0.7
RP-S20	SAS	12/4/2003	1400	24.50	0.9337	0.0000	15.0378	1.0985	0.5362		23.4	1.1
113RC-F190	UFA	12/8/2003	1300	25.00	0.0384	0.0000	16.9316	0.2048	0.5939		19.2	1.9
113RC-F190	UFA	12/8/2003	1300	25.00	0.0385	0.0000	16.9462	0.2029	0.5944		19.2	1.9
113RC-H50	ICU	12/9/2003	1300	25.50	0.1785	0.0000	18.7037	0.2032	0.5934		24.1	4.9
113RC-H50	ICU	12/9/2003	1300	25.50	0.1711	0.0000	18.6604	0.1830	0.5931		24.0	4.8
113RC-S35	SAS	2/1/2003	1300	26.00	0.0162	0.0000	17.0169	2.4159	0.5696		23.3	3.0
113RC-S35	SAS	2/1/2003	1300	26.00	0.0160	0.0000	16.7438	2.4166	0.5622		23.8	2.9
GARC-F75	UFA	2/15/2003	1400	24.50	0.0000	0.0000	0.0000	0.0000	0.0000		99.9	-0.0
GARC-F75	UFA	2/15/2003	1400	24.50	0.0301	0.0000	17.0322	0.2119	0.5848		20.9	2.4
GARC-F200	UFA	2/16/2003	1300	25.00	0.0289	0.0000	16.3005	0.2278	0.5768		20.2	1.5
GARC-F200	UFA	2/16/2003	1300	25.00	0.0295	0.0000	17.0290	0.1917	0.5925		19.7	2.1
GARC-S23	SAS	2/17/2003	1200	25.00	0.0405	0.0000	16.2952	2.2366	0.5582		23.2	2.3
GARC-S23	SAS	2/17/2003	1200	25.00	0.0396	0.0000	16.0657	2.1664	0.5517		23.7	2.2
THC-S46	SAS	2/18/2003	1300	24.50	0.6965	0.0000	18.6746	0.2081	0.6141		20.5	4.0
THC-S46	SAS	2/18/2003	1300	24.50	0.6552	0.0000	18.3892	0.2079	0.6056		21.2	3.9
THC-F75	UFA	1/12/2004	1500	24.50	0.0139	0.0000	16.9417	0.2197	0.5742		22.3	2.7
THC-F75	UFA	1/12/2004	1500	24.50	0.0144	0.0000	16.9276	0.2064	0.5721		22.7	2.8
THC-F75	UFA	1/12/2004	1501	25.00	0.0141	0.0000	17.1795	0.1846	0.5805		21.9	2.8
THC-F75	UFA	1/12/2004	1501	25.00	0.0148	0.0000	16.7962	0.1892	0.5732		22.1	2.5
WP-S64	SAS	1/14/2004	1500	26.00	0.0000	0.0000	14.8676	5.4955	0.5320		23.6	0.9
WP-S64	SAS	1/14/2004	1500	26.00	0.0000	0.0000	32.6324	11.0498	0.8358		22.3	18.4

Table 9. Dissolved gas data, calculated excess nitrogen gas concentration, estimated recharge temperature, and excess air concentration in water samples collected from the public-supply well and monitoring wells in the Temple Terrace, Florida, study area.—Continued

[SAS, surficial aquifer system; ICU, intermediate confining unit; UFA, Upper Floridan aquifer. Recharge elevation assumed to be 10 to 30 meters above the NAVD 88 (North American Vertical Datum of 1988). Values in milligrams per liter, except where noted. Excess air in cubic centimeters per liter (cm³/L) at standard temperature and pressure conditions. Sample lost at wells GARC-F75 and BBP-S45. Sample leak occurred at well WP-S64]

Site name	Aquifer	Date collected	Time collected	Field temperature, degrees Celsius	Methane	Carbon dioxide	Nitrogen	Oxygen	Argon	Calculated excess nitrogen gas, mg/L	Calculated recharge temperature, degrees Celsius	Excess air, cm ³ /L
THC-F197	UFA	1/15/2004	1400	25.00	0.0366	0.0000	16.9290	0.2199	0.5934		19.3	1.9
THC-F197	UFA	1/15/2004	1400	25.00	0.0398	0.0000	16.9659	0.1633	0.5949		19.2	1.9
WP-F300	UFA	1/22/2004	1600	26.00	0.0309	0.0000	17.1766	0.2236	0.6004		18.9	2.0
WP-F300	UFA	1/22/2004	1600	26.00	0.0310	0.0000	17.2875	0.1996	0.6026		18.8	2.1
WP-F150	UFA	1/28/2004	1300	25.00	0.0026	0.0000	19.4985	0.1841	0.5441	3.0	26.4	3.2
WP-F150	UFA	1/28/2004	1300	25.00	0.0025	0.0000	19.5210	0.1797	0.5445	3.0	26.4	3.2
TTP-4	UFA	1/28/2004	1600	24.00	0.0006	0.0000	18.5728	0.1928	0.5670		28.7	5.8
TTP-4	UFA	1/28/2004	1600	24.00	0.0022	0.0000	18.5182	0.1989	0.5665		28.6	5.7
LP-S30	SAS	11/11/2004	1600	28.00	0.0000	0.0000	13.4637	6.4737	0.4848		28.1	0.5
LP-S30	SAS	11/12/2004	1600	28.00	0.0022	0.0000	13.3303	6.4560	0.4850		27.6	0.3
62SRP-F160	UFA	11/2/2004	1200	29.00	0.0000	0.0000	19.5383	0.5186	0.5465	3.0	26.0	3.2
62SRP-F160	UFA	11/2/2004	1200	29.00	0.0000	0.0000	19.7392	0.6296	0.5514	3.0	25.7	3.3
MAS-R-F160	UFA	11/3/2004	1200	27.00	0.0000	0.0000	18.6615	0.6803	0.5559	2.0	24.7	3.0
MAS-R-F160	UFA	11/3/2004	1200	27.00	0.0000	0.0000	18.4735	0.7533	0.5520	2.0	24.8	2.8
LRP-F160	UFA	11/4/2004	1300	28.00	0.4345	0.0000	15.8982	0.4557	0.5089	1.0	28.0	2.0
LRP-F160	UFA	11/4/2004	1300	28.00	0.4247	0.0000	15.9051	0.4086	0.5112	1.0	27.6	1.9
QRP-S20	SAS	11/15/2004	1700	25.00	0.0064	0.0000	15.5861	3.6182	0.5409		24.2	1.8
QRP-S20	SAS	11/15/2004	1700	25.00	0.0067	0.0000	15.6336	3.5005	0.5407		24.4	1.9
LRP-S25	SAS	12/7/2004	1600	25.00	0.3243	0.0000	17.3707	0.6284	0.5320	2.0	25.1	1.8
LRP-S25	SAS	12/7/2004	1600	25.00	0.3423	0.0000	17.8618	0.5468	0.5393	2.0	25.3	2.3
LP-H40	ICU	12/8/2004	1500	26.00	0.0000	0.0000	16.5669	7.4635	0.5662		22.6	2.4
LP-H40	ICU	12/8/2004	1500	26.00	0.0000	0.0000	16.4222	7.4664	0.5628		22.8	2.3
LP-H40	ICU	12/8/2004	1505	26.00	0.0000	0.0000	16.2370	7.4170	0.5622		22.4	2.0
LP-H40	ICU	12/8/2004	1505	26.00	0.0000	0.0000	16.5600	7.5012	0.5669		22.5	2.4
BBP-S45	SAS	12/9/2004	1300	26.00	0.0000	0.0000	15.6538	4.2695	0.5411		24.3	1.9

Table 9. Dissolved gas data, calculated excess nitrogen gas concentration, estimated recharge temperature, and excess air concentration in water samples collected from the public-supply well and monitoring wells in the Temple Terrace, Florida, study area.—Continued

[SAS, surficial aquifer system; ICU, intermediate confining unit; UFA, Upper Floridan aquifer. Recharge elevation assumed to be 10 to 30 meters above the NAVD 88 (North American Vertical Datum of 1988). Values in milligrams per liter, except where noted. Excess air in cubic centimeters per liter (cm³/L) at standard temperature and pressure conditions. Sample lost at wells GARC-F75 and BBP-S45. Sample leak occurred at well WP-S64]

Site name	Aquifer	Date collected	Time collected	Field temperature, degrees Celsius	Methane	Carbon dioxide	Nitrogen	Oxygen	Argon	Calculated excess nitrogen gas, mg/L	Calculated recharge temperature, degrees Celsius	Excess air, cm ³ /L
BBP-S45	SAS	12/9/2004	1300	26.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	99.9	0.0
TTP-4	UFA	10/21/2004	1500	26.00	0.0020	0.0000	18.5724	0.5137	0.5483	2.0	25.8	3.2
TTP-4	UFA	10/21/2004	1500	26.00	0.0022	0.0000	18.6044	0.5084	0.5480	2.0	26.0	3.2
TTP-4-140-NP	UFA	10/27/2004	1600	26.50	0.0008	0.0000	18.9228	0.4964	0.5627	2.0	24.3	3.1
TTP-4-140-NP	UFA	10/27/2004	1600	26.50	0.0008	0.0000	18.7089	0.5194	0.5608	2.0	24.0	2.9
TTP-4-160-NP	UFA	10/27/2004	1800	26.00	0.0008	0.0000	18.1529	0.8798	0.5631	1.0	24.9	3.5
TTP-4-160-NP	UFA	10/27/2004	1800	26.00	0.0000	0.0000	18.0219	0.8890	0.5598	1.0	25.1	3.4
TTP-4-160-P	UFA	10/28/2004	1100	24.00	0.0013	0.0000	19.0357	0.4847	0.5538	2.0	26.2	3.7
TTP-4-160-P	UFA	10/28/2004	1100	24.00	0.0012	0.0000	18.8632	0.5283	0.5530	2.0	25.8	3.4
TTP-4-140-P	UFA	10/28/2004	1400	26.00	0.0014	0.0000	18.9641	0.5390	0.5537	2.0	26.0	3.6
TTP-4-140-P	UFA	10/28/2004	1400	26.00	0.0014	0.0000	18.7383	0.5149	0.5493	2.0	26.1	3.4
TTP-4-125-P	UFA	10/28/2004	1600	26.00	0.0014	0.0000	18.7294	0.6156	0.5503	2.0	25.9	3.3
TTP-4-125-P	UFA	10/28/2004	1600	26.00	0.0014	0.0000	18.7534	0.5910	0.5494	2.0	26.2	3.4
MAS-R-F64	UFA	2/16/2005	1300	25.50	0.0017	0.0000	17.1506	1.9250	0.5542	0.0000	26.5	3.9
MAS-R-F64	UFA	2/16/2005	1300	25.50	0.0014	0.0000	17.0820	1.9498	0.5527	0.0000	26.5	3.8
WP-F300	UFA	8/29/2005	1500	26.00	0.0313	23.0771	16.4633	0.1226	0.5718	0.0000	21.4	2.0
WP-F300	UFA	8/29/2005	1500	26.00	0.0324	22.7853	17.0061	0.1146	0.5826	0.0000	21.1	2.5
LP-H40	ICU	8/30/2005	1400	33.01	0.0024	10.0379	14.9362	6.0556	0.5281	0.0000	24.5	1.2
LP-H40	ICU	8/30/2005	1400	33.01	0.0031	10.3694	14.8320	5.8721	0.5295	0.0000	24.0	1.0
LP-S30	SAS	8/30/2005	1700	32.05	0.0032	38.5133	13.3620	6.6908	0.4974	0.0000	25.4	-0.2
LP-S30	SAS	8/30/2005	1700	32.05	0.0034	38.4362	13.4288	6.7101	0.4980	0.0000	25.5	-0.1
TTP-4	UFA	8/31/2005	1000	25.00	0.0015	13.4187	18.9733	0.1166	0.5566	2.0	25.5	3.5
TTP-4	UFA	8/31/2005	1000	25.00	0.0018	13.1166	19.1016	0.1125	0.5601	2.0	25.3	3.6

close to 1:2; thus, denitrification produces a slope of about 0.5 on plots of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of residual nitrate (Kendall and Aravena, 1999). Some denitrification also could be occurring in parts of the surficial aquifer system and Upper Floridan aquifer as $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of residual nitrate plot along the trend lines with 0.5 slope. This may indicate that denitrification is likely occurring in parts of the ground-water system farther from the water table that contain lower amounts of oxygen than present near the water table.

In most water samples from the surficial aquifer system and intermediate confining unit and some parts of the Upper Floridan aquifer, concentrations of nitrogen gas and argon are consistent with atmospheric equilibration during ground-water recharge with minor amounts of excess air added either during recharge or as a result of sampling methods (table 9).

The apparent recharge temperatures are 24 ± 2 °C (assuming a 15-m elevation for recharge and 100-percent humidity at the water table) with about 0 to 5 cm³/L of excess air during recharge. This calculated recharge temperature agrees closely with a mean annual air temperature of 22.8 °C (Owenby and Ezell, 1992).

Volatile Organic Compounds

A total of 20 out of 85 volatile organic compounds were detected at measurable concentrations in one or more water samples (table 10; fig. 15). Concentrations generally were below 1 µg/L and well below U.S. Environmental Protection Agency (1993) maximum contaminant levels where available. More volatile organic compounds were detected in water from

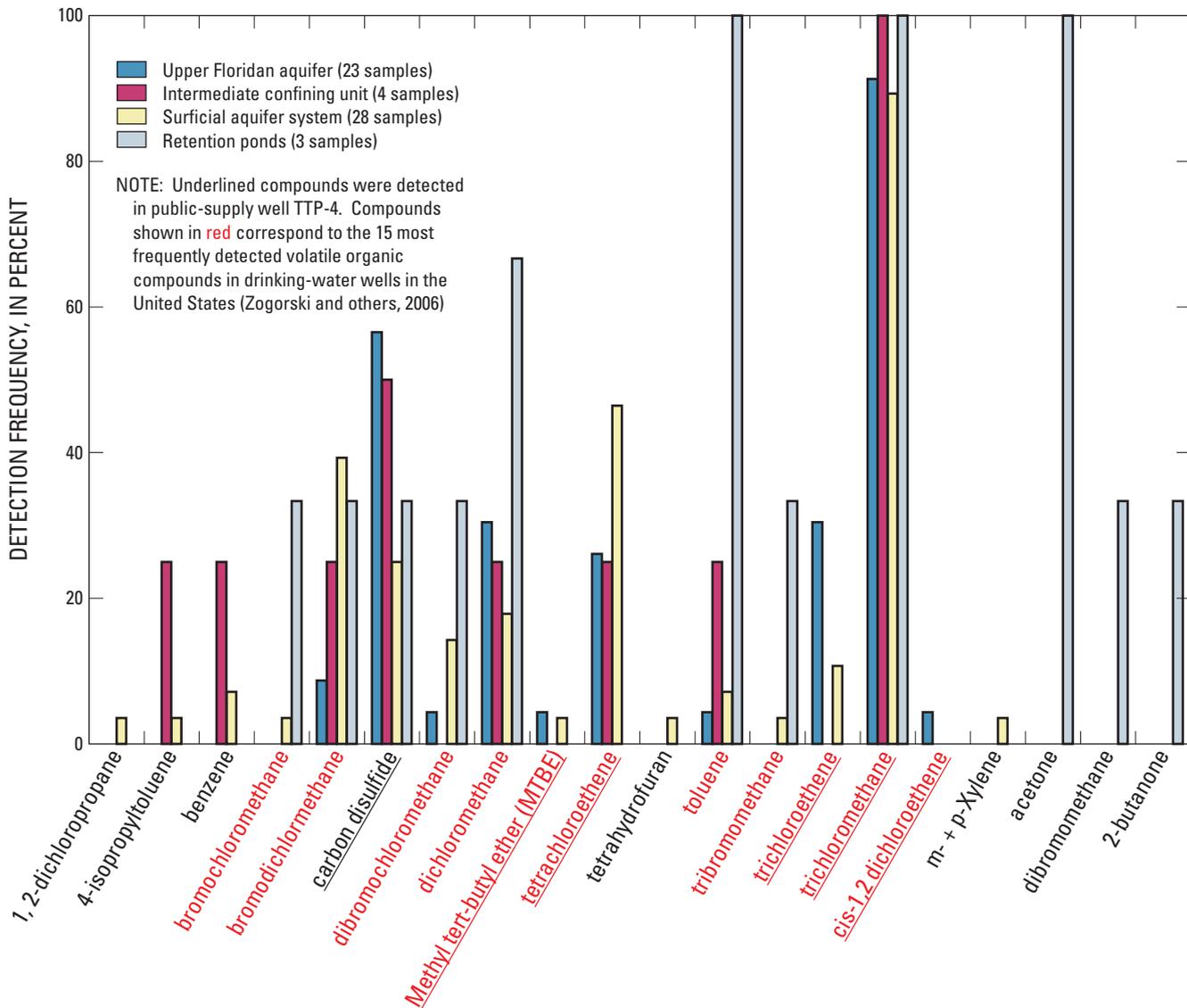


Figure 15. Detection frequency of volatile organic compounds in ground water from the surficial aquifer system, intermediate confining unit, Upper Floridan aquifer, and stormwater retention ponds in the Temple Terrace, Florida, study area.

the surficial aquifer system (16) than in the underlying intermediate confining unit (8) and Upper Floridan aquifer (10). A total of 11 volatile organic compounds were detected in water samples from retention ponds (table 10; fig. 15). Trichloromethane (commonly known as chloroform) was the most frequently detected compound in water from all three hydrogeologic units. Concentrations of volatile organic compounds generally were below 0.1 µg/L, with the exception of trichloromethane, which ranged from 0.01 to 2.6 µg/L in the surficial aquifer system (fig. 16). Trichloromethane was detected more frequently in oxic water samples (dissolved oxygen concentrations greater than 0.5 mg/L) than from anoxic water samples (fig. 17). In contrast, dichloromethane (commonly known as methylene chloride) was detected more frequently in anoxic waters. The higher detection frequency in anoxic waters likely is related to reductive dehalogenation under anaerobic conditions (Vogel and others, 1987; Suflita and others, 1988).

Of the 20 volatile organic compounds detected in ground-water samples, high median concentrations were found in the water from the surficial aquifer system for 12 of these compounds. High median concentrations of carbon disulfide, trichloroethene, and cis-1,2 dichloroethene were found in the anoxic water samples from the Upper Floridan aquifer. Slightly higher median concentrations of benzene and

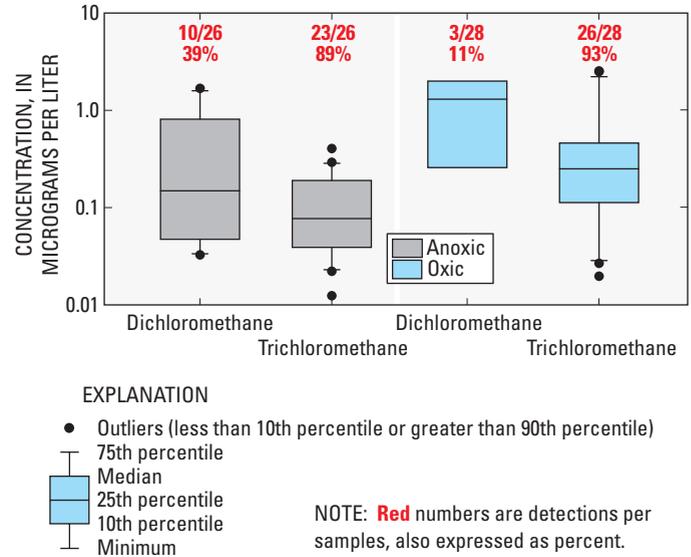


Figure 17. A comparison of trichloromethane (chloroform) and dichloromethane (methylene chloride) concentrations in water samples collected from the oxic surficial aquifer system and the anoxic Upper Floridan aquifer in the Temple Terrace, Florida, study area.

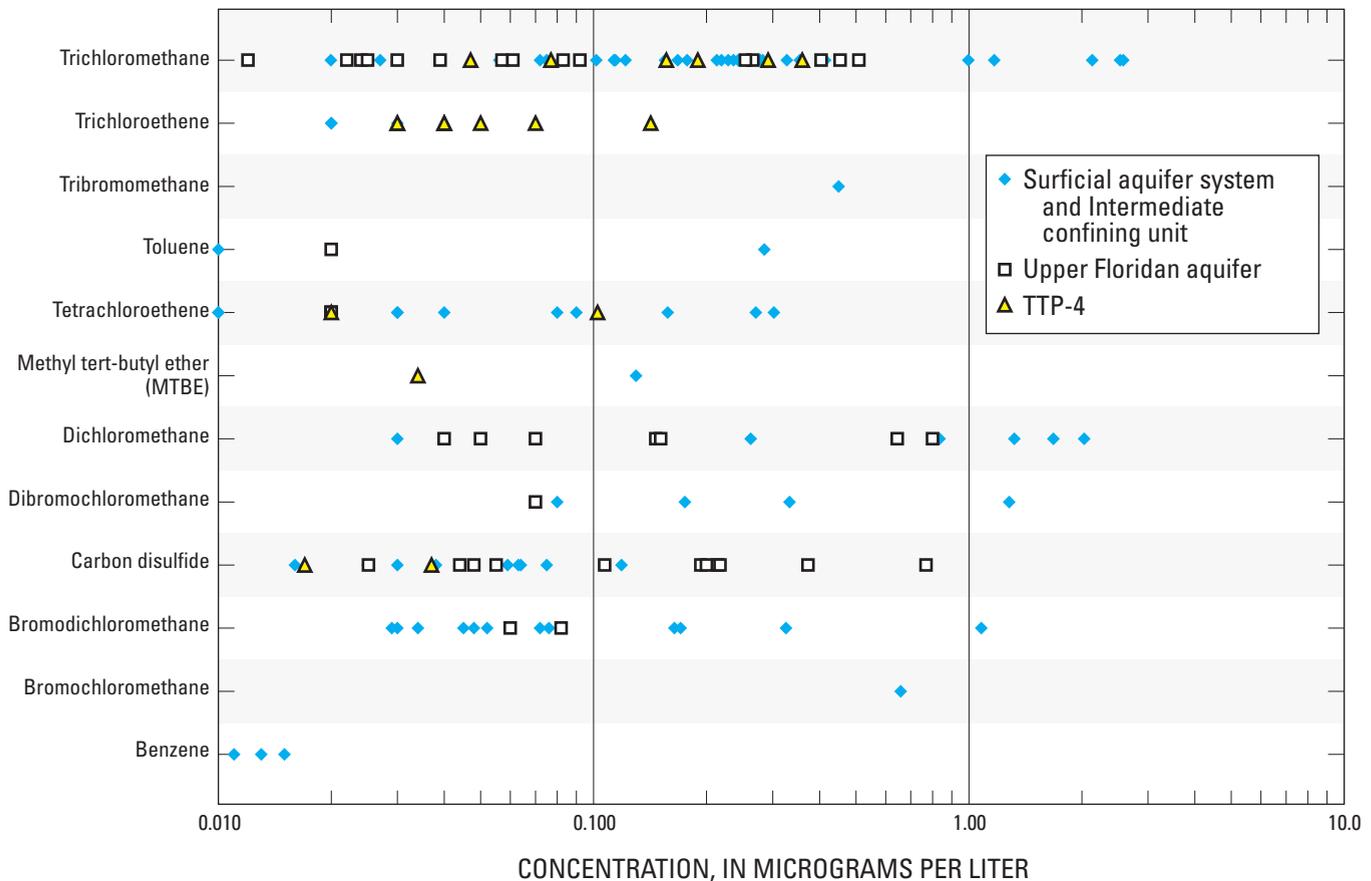


Figure 16. Concentrations of selected volatile organic compounds detected in water samples from the surficial aquifer system, intermediate confining unit, Upper Floridan aquifer, and public-supply well in the Temple Terrace, Florida, study area.

trichloromethane were found in water samples from the intermediate confining unit than the surficial aquifer system. All detected concentrations of volatile organic compounds in the public-supply well and in monitoring wells were below any levels for health advisories or maximum contaminant levels (Toccalino and others, 2004). Six volatile organic compounds were detected in water from the public-supply well: trichloromethane, cis-1,2-dichloroethene, trichloroethene, tetrachloroethene, methyl tert-butyl ether (MTBE), and carbon disulfide. Water samples were collected from TTP-4 on seven different dates (between October 2002 and June 2005) and analyzed for volatile organic compounds. Tetrachloroethene and carbon disulfide were detected in only two samples. MTBE and cis-1,2-dichloroethene were detected in low concentrations in only one sample collected in October 2002. Trace concentrations of tetrachloroethene 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 public-supply well were similar to median concentrations in water from the Upper Floridan aquifer. Median concentrations of carbon disulfide, tetrachloroethene, and trichloromethane were higher in water from the public-supply well than from water samples from Upper Floridan aquifer monitoring wells. Median concentrations of trichloromethane were similar in water (0.17 µg/L) from the public-supply well to monitoring wells in the surficial aquifer system (fig. 16). Similar concentrations of compounds detected in water samples from the public-supply well and from surficial aquifer system monitoring wells indicate that water from the surficial aquifer system likely is entering the public-supply well.

The high detection frequency of trichloromethane in this study is consistent with other ground-water quality studies in the Tampa Bay area (Metz and others, 2007), but higher than that found in the Nation’s drinking-water supply wells where the detection frequency was 11.4 percent using an assessment level of 0.2 µg/L (Zogorski and others, 2006; Schaap and Zogorski, 2006; Ivahnenko and Zogorski, 2006). Several potential sources of trichloromethane in ground water include recharge of chlorinated water, direct releases such as spills and leaking underground storage tanks, dehalogenation of tetrachloroethane, and some natural sources (Ivahnenko and Barbash, 2004). Trichloromethane also is a disinfection byproduct that is produced during the chlorination of drinking water and wastewater that contains naturally occurring organic material. In the Tampa Bay area study, the high occurrence of trichloromethane was attributed to disinfection byproducts produced during chlorination because other disinfection byproducts (bromodichloromethane and bromoform) also were detected (Metz and others, 2007). Furthermore, trichloromethane was found only in residential and commercial areas and not in undeveloped areas. Recharge of chlorinated waters is a likely source of trichloromethane in the Temple Terrace area, as other disinfection byproducts commonly were found in water samples from the surficial aquifer system such as dibromochloromethane and bromodichloromethane (fig. 16).

Carbon disulfide, a solvent, also was detected frequently in both the present study and in the community supply well study in the northern Tampa Bay area (Metz and others, 2007).

Pesticides

Five pesticides were detected in low concentrations in ground-water samples: atrazine, deethylatrazine (an atrazine breakdown product or degradate), prometon, simazine, and dieldrin (fig. 18; table 11). Concentrations of atrazine in ground water were less than 3 µg/L, which is the U.S. Environmental Protection Agency (1993) maximum contaminant level for drinking water. The highest atrazine concentration (0.12 µg/L) in ground water was found in a water sample from well THC-S46 in the surficial aquifer system. An atrazine concentration of 1.58 µg/L was found in water from a nearby retention pond (62SRP-POND) and

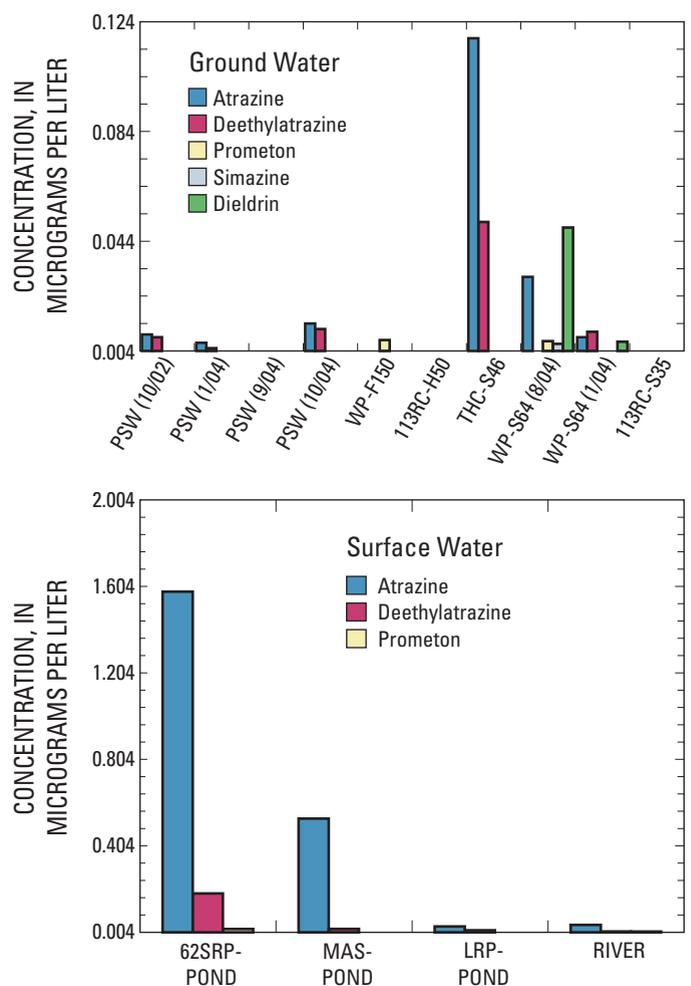


Figure 18. Pesticides detected in ground-water samples and surface-water samples from the Temple Terrace, Florida, study area.

Table 11. Concentrations of pesticides detected in ground-water and surface-water samples.

[Concentrations are in micrograms per liter (µg/L). Blank cell denotes compound not detected; E, estimated concentration, below laboratory reporting level]

Site name	Sample date	Atrazine	Deethylatrazine	Prometon	Simazine	Dieldrin
TTP-4	10/21/02	0.010	E0.009	E0.003		
TTP-4	01/28/04	0.007	E0.005	E0.004		
TTP-4	09/22/04	E0.004				
TTP-4	10/21/04	0.014	E0.012	E0.004		
THC-S46	12/18/03	0.120	E0.051			
WP-S64	01/14/04	0.009	E0.011	E0.003		E0.007
WP-S64	08/04/04	0.031	E0.033	0.0076	.00700	0.0500
WP-F150	08/04/04			0.008		
113RC-S35	12/11/03	0.004				
113RC-H50	12/9/03	E0.002				
62SRP-POND	06/21/05	1.580	E0.184	0.0190		
MAS-POND	06/21/05	0.530	E0.020			
LRP-POND	06/21/05	0.031	E0.013			
HRIV-RR	06/22/05	0.038	E0.008	E0.007		

could be a source for the elevated concentration in the shallow surficial aquifer system water sample (THC-S46). Focused recharge beneath stormwater retention ponds may contribute pesticides and other organic contaminants to water in the surficial aquifer system, which ultimately could move downward to the Upper Floridan aquifer under natural gradients or during pumping stresses. Low concentrations of atrazine, deethylatrazine, and prometon were found in water from public-supply well TTP-4. Atrazine was detected in four samples from TTP-4, whereas deethylatrazine and prometon were detected in three of four samples. Prometon was the only pesticide detected in any monitoring well in the Upper Floridan aquifer (WP-F150), which is open to a similar interval as TTP-4. Water from WP-F150 is younger than that from other Upper Floridan aquifer monitoring wells, indicating that there could be a connection between this zone in the aquifer and the overlying surficial material. This possibility is explored in more detail in the subsequent discussion of water chemistry from depth-interval sampling. Similar detections of pesticides in water from TTP-4 and from surficial aquifer system wells indicate the likely contribution of water in the surficial aquifer system to water withdrawn during pumping by TTP-4.

Dieldrin, a known carcinogen, has a risk specific dose (RSD4) level of 0.2 µg/L at the 10⁻⁴ (one in 10,000) cancer risk level (U.S. Environmental Protection Agency, 1993; Toccalino and others, 2004). Trace concentrations of dieldrin were detected in water from WP-S64 and 62SRP-S34 (0.007 and

0.049 µg/L), but were less than a factor of 4 lower than the RSD4 level.

Most pesticide detections in water from community supply wells in the northern Tampa Bay area included atrazine and deethylatrazine (Metz and others, 2007). Atrazine is highly mobile in sandy soils and widely used as an herbicide along road rights-of-way and lawns. Several studies have shown that atrazine can persist in ground water for long periods of time (Denver and Sandstrom, 1991; Barbash and others, 1999).

Sulfur Species and Hydrogen Sulfide

Differences in sulfate concentrations and delta sulfur-34 (δ³⁴S) of sulfate were useful in distinguishing sources of water and solutes in monitoring wells and the public-supply well. Concentrations of δ³⁴S values for ground-water samples were highly variable, ranging from +5.7 per mil in water from the surficial aquifer system to +26.2 per mil for the Upper Floridan aquifer (fig. 19; table 6). This large range likely reflects the sulfur isotopic composition of various possible sources of sulfate, including dissolution of terrestrial evaporite minerals (gypsum and anhydrite), oxidation of sulfide minerals or organic sulfides, atmospheric precipitation of ocean-derived aerosols, and atmospheric precipitation of windblown sulfate dust from soils. Localized anthropogenic sources (that is, industrial emissions and fertilizers) could result in isotopically

light sulfate (Sacks, 1996). The $\delta^{34}\text{S}$ content of oceanic sulfate (and hence evaporite minerals that precipitate from the ocean) at any given time in the geologic past is related to several processes including the composition of sulfate in rivers that enters the ocean, sulfate reduction, and removal from the ocean (Pearson and Rightmire, 1980). Sulfate in modern ocean water has a $\delta^{34}\text{S}$ value of +20 per mil. All waters in this study show increasing sulfate to chloride ratios with increasing sulfate concentration (fig. 20). Solution of evaporite minerals (gypsum and anhydrite) would produce this water composition.

A plot of $\delta^{34}\text{S}$ values of dissolved sulfate relative to sulfate concentrations indicates two distinct groups of waters from the Upper Floridan aquifer (fig. 19). Group 1 has $\delta^{34}\text{S}$ values that range from about +21 to +26 per mil with variable sulfate concentrations (less than 1 to 400 mg/L). Group 2 has much lower $\delta^{34}\text{S}$ values (+5 to 16.8 per mil) and sulfate concentrations (generally less than 120 mg/L), and are isotopically similar to water from the surficial aquifer system and intermediate confining unit. Differences in median chemical composition are consistent with the sulfur isotopic composition and sulfate concentrations between these two groups (tables 5 and 6). The higher median saturation index with respect to gypsum for Group 1 (-0.92) compared to Group 2 (-1.49) is consistent with the higher $\delta^{34}\text{S}$ values that reflect dissolution of sulfate evaporite minerals. The $\delta^{34}\text{S}$ values for

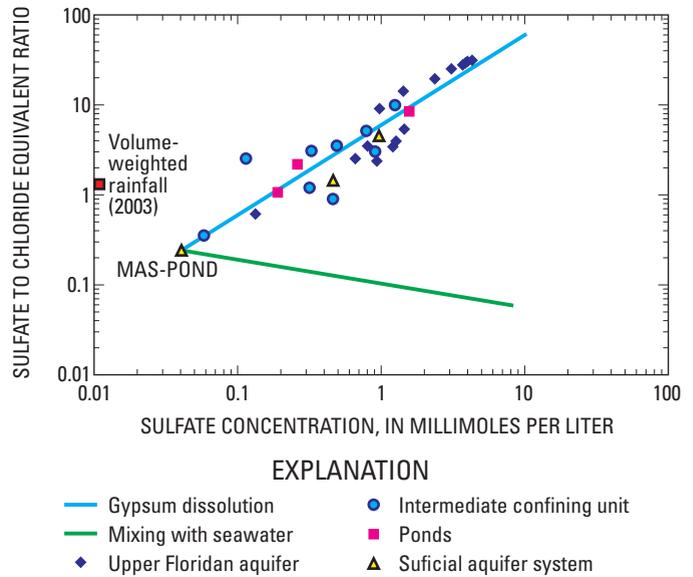


Figure 20. Relation between sulfate-to-chloride ratios and sulfate concentrations in water from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area.

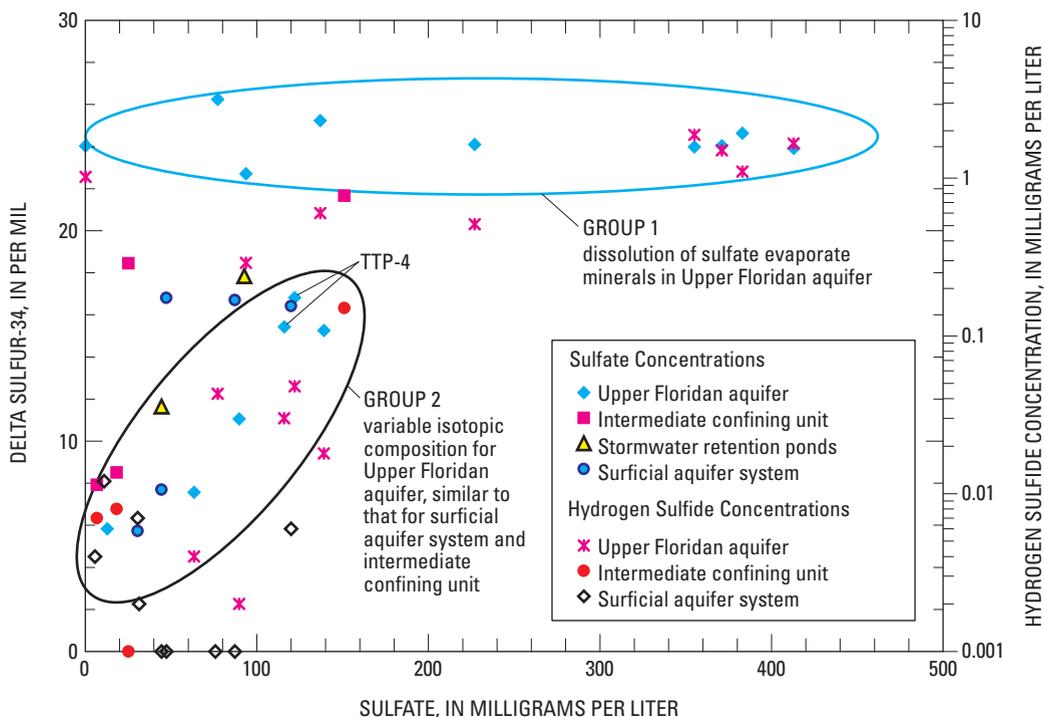


Figure 19. Sulfate concentrations and delta sulfur-34 of sulfate in water samples from the surficial aquifer system, intermediate confining unit, Upper Floridan aquifer, and retention ponds in the Temple Terrace, Florida, study area.

Group 1 waters are slightly higher than those of samples of sulfate evaporite minerals from the Upper Floridan aquifer that range from +19 to +22 per mil (Pearson and Rightmire, 1980). Group 1 waters also have higher median concentrations of hydrogen sulfide and dissolved organic carbon and lower dissolved oxygen, which indicate sulfate reduction reactions and isotope fractionation that could result in enrichment of the $\delta^{34}\text{S}$ in the aqueous phase. Waters from the surficial aquifer system, intermediate confining unit, and Floridan aquifer system with lower sulfate concentrations and lower $\delta^{34}\text{S}$ likely represent values typical of rainfall with some excess sulfate (Pearson and Rightmire, 1980). Water samples from public-supply well TTP-4 have $\delta^{34}\text{S}$ values and sulfate concentrations that are midway between the two end member values, and likely indicate a mixture of water from these two different groups (fig. 19).

High sulfate concentrations could be related to upwelling that likely is enhanced by preferential vertical flow through fractures and faults that connect deep and shallow parts of the Upper Floridan aquifer (Sacks, 1996). Fractures and faults are associated with the structural high of the Ocala Platform that is present throughout the northern and central parts of peninsular Florida (Faulkner, 1973). Diffusion also may account for the transport of sulfate-rich ground water within the more stagnant deeper part of the Upper Floridan aquifer in west-central Florida (Sacks, 1996).

Radon-222 and Uranium

Concentrations of radon-222 were highly variable in the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer, but were generally higher in water samples from the surficial aquifer system and intermediate confining unit than from the Upper Floridan aquifer (table 6; fig. 21). Median concentrations were 2,440, 2,100, and 645 pCi/L (picocuries per liter) for water samples from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer system, respectively. Water from public-supply well TTP-4 had a radon-222 concentration of 780 pCi/L, which is slightly higher than the median concentration in water from monitoring wells tapping the Upper Floridan aquifer. In response to human health concerns regarding ingestion of radon in drinking water, the U.S. Environmental Protection Agency has proposed new regulations to protect people from exposure to radon. The proposed maximum contaminant level for community water systems using ground water is 300 pCi/L, and the proposed alternative maximum contaminant level is 4,000 pCi/L. The U.S. Environmental Protection Agency (1999) expects that community water systems serving 10,000 persons or less would meet the alternative maximum contaminant level of 4,000 pCi/L; however, radon-222 concentrations in water from the public-supply well and most monitoring wells would exceed the lower 300 pCi/L maximum contaminant level. Sowerby and others (2000) estimated that 44 \pm 6 percent of the community water systems

in Florida using ground water would exceed the 300-pCi/L maximum contaminant level for radon.

Uranium concentrations also were variable in water samples from the three hydrogeologic units, and median uranium concentrations in water samples were 0.96, 0.85, and 2.4 $\mu\text{g/L}$ from the surficial aquifer system, intermediate confining unit, and Floridan aquifer, respectively (table 12; fig. 22). Uranium concentrations in water from the public-supply well and from monitoring wells in the three hydrogeologic units were below the U.S. Environmental Protection Agency maximum contaminant level of 30 $\mu\text{g/L}$ for drinking water. Higher median uranium concentrations were found in water samples from the Upper Floridan aquifer compared to samples from the surficial aquifer system or intermediate confining unit, which was unexpected given that redox conditions are anoxic in the Upper Floridan aquifer and the mobility of uranium is lower in reducing conditions. However, the formation of uranyl di- and tri-carbonate complexes in neutral and alkaline solutions (Langmuir, 1978) may account for the higher uranium concentrations found in the Upper Floridan aquifer compared to the surficial aquifer system and intermediate confining unit. Speciation calculations using the geochemical computer modeling program PHREEQC (Parkhurst and Appelo, 1999) indicate that uranium (IV) is present as the $\text{U}(\text{OH})_4$ complex and uranium (VI) is present as the tri-carbonate complex carbon anhydrase/uranium dioxide/carbon ion, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$, in water from the Upper Floridan aquifer. The microbially mediated reduction of uranium (VI) in anoxic waters has been shown to decrease substantially when $\text{Ca-UO}_2\text{-CO}_3$ complexes are present (Brooks and others, 2003).

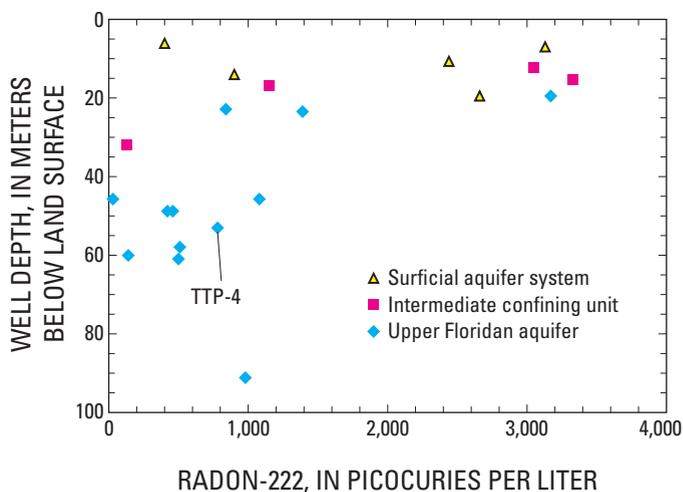


Figure 21. Radon-222 concentrations with well depth below land surface for the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area.

The dominant uranium species in all ground-water samples from the Upper Floridan aquifer is the neutral complex, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$. However, at two surficial aquifer system sites (LP-S30 and QRP-S20) where calcium concentrations and saturation indices with respect to calcite were relatively low, the dominant uranium species included uranyl mono- and di-carbonate complexes (UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{-2}$) and UO_2^{+2} . Uranium concentrations are higher in acid leachates of solid-phase material from the surficial aquifer system and intermediate confining unit compared to Floridan aquifer system material (table 4) based on acid extractions using 10-percent nitric acid and 6 N hydrochloric acid. Uranium concentrations in 6 N hydrochloric acid leachates of solid-phase material were

higher in samples of the Upper Floridan aquifer limestone (3.4-5.0 mg/kg) and from the LP site (7.7 mg/kg) compared to the milder acid extraction using 10-percent nitric acid (table 4).

No correlation was found between radon-222 and uranium concentrations, even though radon-222 is a daughter product of the decay series for uranium-238. Different mechanisms of radon-222 emanation from clastic sediments and solid limestone (Cecil and Green, 2000) and chemical factors affecting uranium solubility (Langmuir, 1978; Osmond and Cowart, 2000) may account for the lack of a correlation between these two radiochemicals.

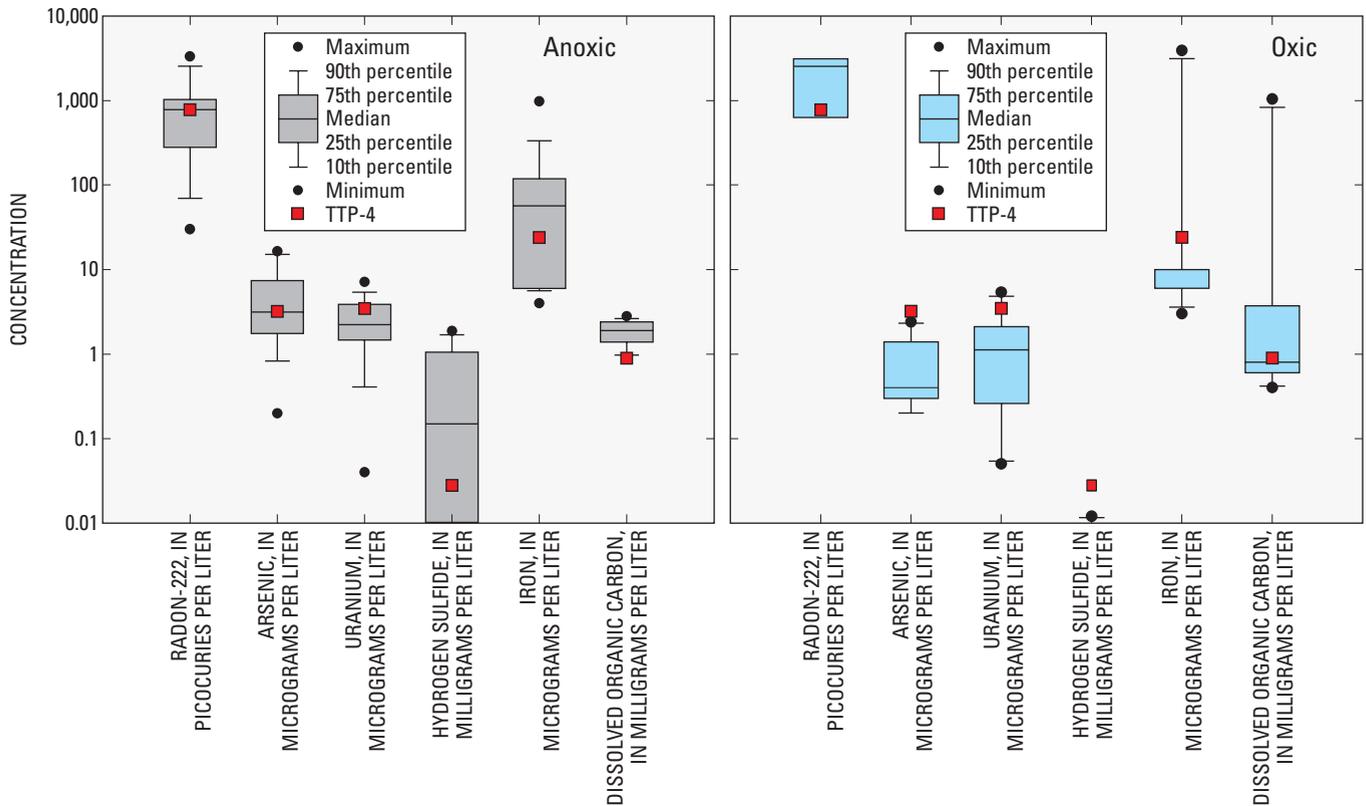


Figure 22. Median concentrations of radon-222, arsenic, uranium, hydrogen sulfide, iron, and dissolved organic carbon in oxic and anoxic water from monitoring wells and the public-supply well in the Temple Terrace, Florida, study area.

Table 12. Concentrations of trace elements and arsenic species As(III) and As(V) in ground-water samples.

[SAS, surficial aquifer system; ICU, intermediate confining unit; UFA, Upper Floridan aquifer. Concentrations are shown in micrograms per liter. E, concentration measured below analytical method reporting level; P code, U.S. Environmental Protection Agency STORET code; <, less than]

Site name	Aquifer or hydrogeologic unit	Site identifier	Sample date	Sample time	P01000 Arsenic	P01005 Barium	P01020 Boron	P01046 Iron	P01056 Manganese	P01080 Strontium	P01106 Aluminum	P22703 Uranium	P62452 Arsenic (III)	P62453 Arsenic (V)
BBP-S45	SAS	280228082231501	8/11/2004	1200				E5	2.9					
BBP-S45	SAS	280228082231501	12/9/2004	1300	1.4	10	12	<6	0.5	92.1	3	1.63		
THC-F197	UFA	280241082224401	1/15/2004	1400	1.9	19	23	90	15.3	3780	3	2.89	1.1	1.3
THC-F75	UFA	280241082224402	1/12/2004	1500	1.1	22	19	111	85.7	1200	10	1.46	<1	<1.2
THC-F75	UFA	280241082224402	1/28/2004	1300										
THC-S46	SAS	280241082224403	12/18/2003	1300	2.6	44	10	979	672	273	3	1.51	2	E0.9
THC-S46	SAS	280241082224403	8/5/2004	1200				984	460					
THC-S46	SAS	280241082224403	11/17/2004	1600				654	345					
THC-S46	SAS	280241082224403	6/14/2005	1700				662	261					
62SRP-F160	UFA	280241082230701	11/2/2004	1200	3.1	18	28	E4	2.8	666		7.13	<1	2.3
62SRP-F160	UFA	280241082230701	6/20/2005	1600										
62SRP-H55	ICU	280241082230702	11/3/2004	1700	0.3	17	15	E3	2.3	68.9	2	0.26	<1	<1.2
62SRP-S34	SAS	280241082230703	8/12/2004	930				<6	4					
62SRP-POND	POND	280242082230800	6/21/2005	1220				47	27.9					
MAS-R-F160	UFA	280242082232401	11/3/2004	1200	2	47	25	<6	2.8	566	2	5.39	<1	1.6
MAS-R-F160	UFA	280242082232401	6/16/2005	1040				91	26.7					
MAS-R-F64	UFA	280242082232403	2/16/2005	1300	0.6	13	11	<6	1.5	64.1	15	2.53	<1	<1.2
MAS-R-F64	UFA	280242082232403	6/16/2005	1100				<6	E0.6					

Table 12. Concentrations of trace elements and arsenic species As(III) and As(V) in ground-water samples.—Continued

[SAS, surficial aquifer system; ICU, intermediate confining unit; UFA, Upper Floridan aquifer. Concentrations are shown in micrograms per liter. E, concentration measured below analytical method reporting level; P code, U.S. Environmental Protection Agency STORET code; <, less than]

Site name	Aquifer or hydrogeologic unit	Site identifier	Sample date	Sample time	P01000 Arsenic	P01005 Barium	P01020 Boron	P01046 Iron	P01056 Manganese	P01080 Strontium	P01106 Aluminum	P22703 Uranium	P62452	P62453
													Arsenic (III)	Arsenic (V)
MAS-POND	POND	280242082232900	6/21/2005	1100			35		2.8					
TTP-4	UFA	280244082232001	10/21/2002	1600	3.5	12	26	24	2.2	1230	<2	2.97		
TTP-4	UFA	280244082232001	1/28/2004	1600	3.2	14	34	25	2.5	1260	E1	3.61	2	E1.2
TTP-4	UFA	280244082232001	10/21/2004	1500	3.2	13	28	6	1.8	1100	<2	3.47	<1	2.6
TTP-4	UFA	280244082232001	2/16/2005	1600				44	6.5					
TTP-4	UFA	280244082232001	6/20/2005	1600				31	3.4					
WP-F299	UFA	280247082231901	1/22/2004	1600	12.6	20	25	79	7	3840	3	3.97	5.6	7.3
WP-F299	UFA	280247082231901	8/3/2004	1400	2.5	20	30	108	6.1	3980	2	1.31	1.1	E1.1
WP-F150	UFA	280247082231902	1/28/2004	0										
WP-F150	UFA	280247082231902	1/28/2004	1300	16.5	14	36	12	6.8	1690	E2	1.09	14.1	2.9
WP-F150	UFA	280247082231902	8/4/2004	1100	5.6	13	35	24	5.3	1720	E1	0.62	5.2	E1.1
WP-S64	SAS	280247082231903	1/14/2004	1500	0.4	22	32	<6	0.4	254	15	2.11	<1	E0.7
WP-S64	SAS	280247082231903	8/4/2004	1600	0.2	20	35	<6	E0.1	245	9	1.61	<1	<1.2
WP-S64	SAS	280247082231903	11/18/2004	1200				E3	<0.6					
WP-S64	SAS	280247082231903	6/14/2005	1130				E3	<0.6					
RP-F103	UFA	280249082220701	12/2/2003	1500	4.9	14	21	75	8.8	2460	8	2.23	3.1	1.4
RP-F77	UFA	280249082220702	12/3/2003	1300	14.6	14	22	127	9	1890	3	4.32	10	3.9
RP-S20	SAS	280249082220703	12/4/2003	1400	2.4	63	39	3910	939	175	2	0.77	1.2	1.3
RP-S20	SAS	280249082220703	8/11/2004	1500				330	155					
RP-S20	SAS	280249082220703	11/16/2004	1500				657	194					
RP-S20	SAS	280249082220703	6/16/2005	1500				644	410					

Table 12. Concentrations of trace elements and arsenic species As(III) and As(V) in ground-water samples.—Continued

[SAS, surficial aquifer system; ICU, intermediate confining unit; UFA, Upper Floridan aquifer; Concentrations are shown in micrograms per liter. E, concentration measured below analytical method reporting level; P code, U.S. Environmental Protection Agency STORET code; <, less than]

Site name	Aquifer or hydrogeologic unit	Site identifier	Sample date	Sample time	P01000		P01005	P01020	P01046	P01056	P01080	P01106	P22703	P62452	P62453
					Arsenic	Barium									
LRP-F160	UFA	280250082233001	11/4/2004	1300	2.4	17	24	9	14.2	939	8	2	1.5	E0.8	
LRP-H105	UFA	280250082233002	12/7/2004	1600	1.5	11	20	<6	5.8	507	18	0.57	E0.9	E1	
LRP-S25	SAS	280250082233003	8/10/2004	1100				6	5.8						
LRP-S25	SAS	280250082233003	6/15/2005	1500				11	14.8						
LRP-POND	POND	280250082233200	6/21/2005	915				E5	E0.4						
JARP-S40	SAS	28025108224201	6/27/2005	1030				E5	197						
GARC-F200	UFA	280253082223801	12/16/2003	1300	1.7	24	22	57	70.1	4,110	E2	1.74	1.1	E1	
GARC-F75	UFA	280253082223802	12/15/2003	1400	0.7	18		9	23.2	2,990	11	0.23	0.8	E0.8	
GARC-S23	SAS	280253082223803	12/17/2003	1200	0.4	38	16	E6	92.4	662	20	1.14	<1	<1.2	
GARC-S23	SAS	280253082223803	8/5/2004	1600				E4	32.8						
GARC-S23	SAS	280253082223803	11/17/2004	1100				7	30.1						
GARC-S23	SAS	280253082223803	6/13/2005	1115				7	57.7						
113RC-F190	UFA	280301082222701	12/8/2003	1300	6	19	26	172	38.4	4,080	M	2.25	3.7	1.8	
113RC-H50	ICU	280301082222702	12/9/2003	1300	7.9	14	21	156	54.1	1,580	3	4.66	4	3.4	
113RC-S35	SAS	280301082222703	12/11/2003	1300	E0.2	14	15	<6	5.1	489	2	0.64	<1	<1.2	
113RC-S35	SAS	280301082222703	8/12/2004	1300				<6	E0.5						
113RC-S35	SAS	280301082222703	11/16/2004	1300				E4	2						
113RC-S35	SAS	280301082222703	6/15/2005	1100				<6	<0.6						

Table 12. Concentrations of trace elements and arsenic species As(III) and As(V) in ground-water samples.—Continued

[SAS, surficial aquifer system; ICU, intermediate confining unit; UFA, Upper Floridan aquifer. Concentrations are shown in micrograms per liter. E, concentration measured below analytical method reporting level; P code, U.S. Environmental Protection Agency STORET code; <, less than]

Site name	Aquifer or hydrogeologic unit	Site identifier	Sample date	Sample time	P01000		P01005	P01020	P01046	P01056	P01080	P01106	P22703	P62452	P62453
					Arsenic	Barium									
LP-H40	ICU	280303082230901	8/10/2004	1500					<6	<0.8					
LP-H40	ICU	280303082230901	12/8/2004	1500	0.3	17	22	22	<6	0.3	90	7	1.12	<1	<1.2
LP-S30	SAS	280303082230902	8/10/2004	1200					6	2.3					
LP-S30	SAS	280303082230902	11/1/2004	1600	<0.2	22	22	22	10	3.6	33.3	142	0.07		
LP-S30	SAS	280303082230902	6/21/2005	1130					E6	1.4					
QRP-S20	SAS	280311082223901	8/11/2004	1345					349	8.7					
QRP-S20	SAS	280311082223901	11/15/2004	1700	0.3	15	38	38	48	9.3	96.2	8	0.05		
QRP-S20	SAS	280311082223901	6/21/2005	1630					332	23.1					
HRIV-RR	RIVER	280248082220200	8/30/2005						0.16	0.014					
TTP-4-140-NP	UFA	280244082232001	10/27/2004	1600	11.7	14	26	26	<6	3	788	<2	4.87	E0.8	8.7
TTP-4-160-NP	UFA	280244082232001	10/27/2004	1800	4.2	16	27	27	<6	0.8	515	<2	5.34	<1	2.6
TTP-4-160-P	UFA	280244082232001	10/28/2004	1100	18.9	14	24	24	E3	2	912	<2	5.38	E0.6	14.2
TTP-4-140-P	UFA	280244082232001	10/28/2004	1400	16	14	24	24	E5	2.2	934	<2	5.24	2.1	10.7
TTP-4-125-P	UFA	280244082232001	10/28/2004	1600	15.3	14	26	26	9	1.7	937	<2	4.93	3.3	9.3
TTP-4-entire-P	UFA	280244082232001	10/21/2004	1500	3.2	13	28	28	6	1.8	1,100	<2	3.47	1.5	E1

Arsenic Concentrations and Speciation

Water samples from wells in the surficial aquifer system and intermediate confining unit had arsenic concentrations less than 8 µg/L (fig. 23A). Most water samples from monitoring wells in the Upper Floridan aquifer 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 arsenic concentrations that ranged from 12.6 to 16.5 µg/L. Higher median arsenic concentrations were found in water samples from the Upper Floridan aquifer (4.6 µg/L) compared to samples from the intermediate confining unit (0.9 µg/L) and the surficial aquifer system (0.4 µg/L). The slightly higher arsenic concentrations in the water samples from the surficial aquifer system and intermediate confining unit generally were associated with higher concentrations of iron, which indicate the likely association of arsenic with iron oxyhydroxide coatings on sands and clay material (Pichler and others, 1999).

Arsenic concentrations in water samples from the public-supply well ranged from 3.2 to 3.5 µg/L when collected using the in-line turbine pump; however, during depth-interval sampling of the public-supply well borehole, concentrations ranged from 4.2 to 18.9 µg/L. These variations in arsenic concentrations with depth in the public-supply wells were observed during different pumping conditions and are discussed in more detail in the following section on sources and mixing of water in the public-supply well.

Under reducing conditions in the Upper Floridan aquifer and for water from 113-RC-H50 in the intermediate confining unit, most water samples had higher arsenic (III) concentrations than arsenic (V) concentrations (fig. 23B). In contrast, water samples from the public-supply well had arsenic (V) concentrations that tended to be higher than arsenic (III) concentrations, which most likely indicates different redox conditions due to the downward movement of oxygenated water from the surficial aquifer system through a highly transmissive zone in the limestone of the Upper Floridan aquifer. Mobilization of arsenic may result from the formation of arseno-carbonate complexes under anaerobic conditions (Kim and others, 2000) and/or oxidation of finely disseminated pyrite in the limestone that composes the Upper Floridan aquifer (Price and Pichler, 2006). Concentrations of both arsenic (III) and arsenic (V) in water from the oxic surficial aquifer system generally were near the method reporting level for both arsenic species (table 12). Arsenic concentrations in water from monitoring wells in the three hydrogeologic units generally were less than the 10-µg/L maximum contaminant level for drinking water (table 12).

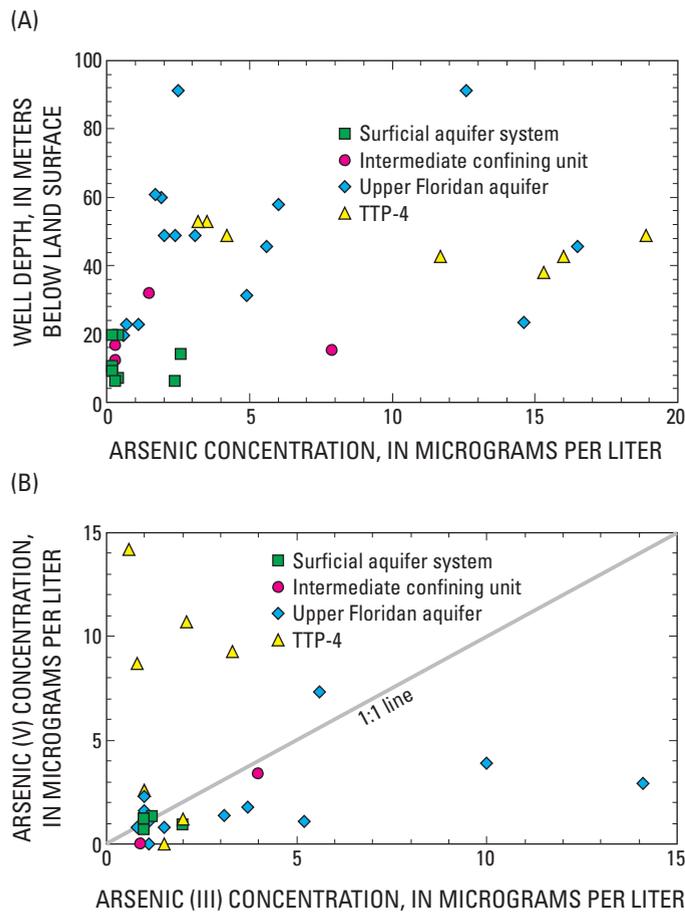


Figure 23. Arsenic concentrations with well depth and arsenic species (arsenic (III) and arsenic (V) concentrations) in water samples from wells in the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer in the Temple Terrace, Florida, study area, October 2004.

Temporal Variability in Water Chemistry from Surficial Aquifer Wells and the Public-Supply Well

Selected monitoring wells were sampled several times during 2003-05 during different hydrologic conditions to obtain information about temporal variability in water quality. Temporal variations in water quality are presented for three monitoring wells in the surficial aquifer system (RP-S20, WP-S64, and GARC-S23) that were sampled four times before and after three tropical cyclones that passed through the area in summer 2004 (fig. 24). Additionally, water-quality variations were evaluated for TTP-4 based on five samples collected during 2002-05. Near or slightly below normal amounts of monthly rainfall were recorded prior to the earliest samples collected from the surficial aquifer system wells in December 2003 and the public-supply well in October 2002. During June through September 2004, however, about 109 cm of rainfall were recorded at the NOAA station at the Tampa airport, which was about 43 cm above normal rainfall for these 4 months. Ground-water levels increased substantially during and after this period. Water levels increased more than

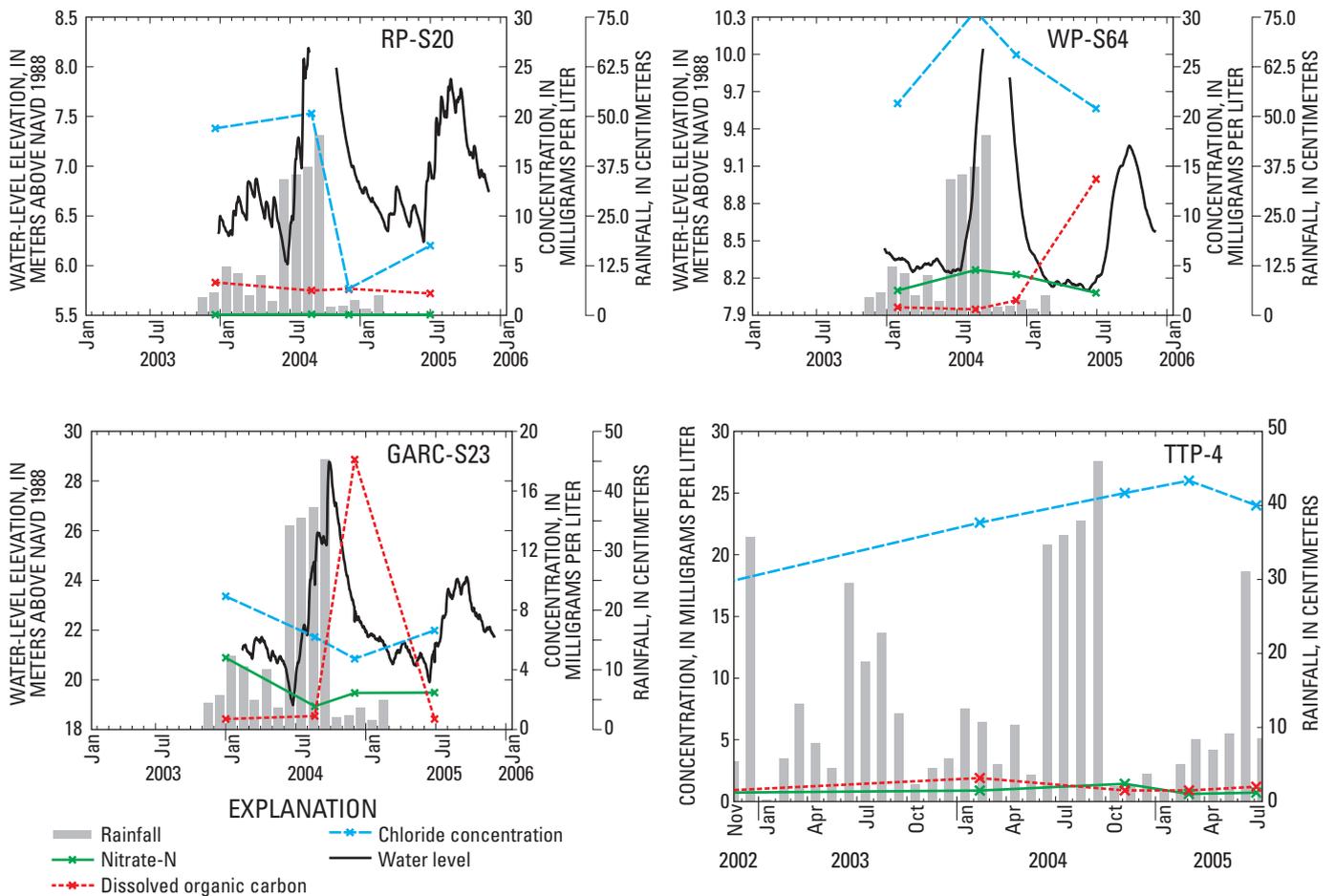


Figure 24. Temporal variability of chloride, nitrate-N, dissolved organic carbon, and ground-water levels in water samples collected from wells RP-S20, WP-S64, GARC-S23, and TTP-4 in the Temple Terrace, Florida, study area.

3 m in well GARC-S23 (fig. 24), and it is assumed that water levels increased about the same amount in wells RP-S20 and WP-S64, although data are missing where peak water levels would be expected to occur (fig. 24). No water-level data were available for TTP-4.

Substantial variations in some chemical constituents were observed in water from monitoring wells in the surficial aquifer system in response to this increased recharge. Chloride concentrations in water samples from three wells decreased from summer 2004 to winter 2004-05 following the recharge pulse from high rainfall and corresponding peak in water-level elevation in October 2004. Nitrate-N concentrations increased in WP-S64 from January to August 2004, but concentrations decreased at GARC-S23 during the same period. Nitrate-N concentrations in water samples from two other monitoring wells in the surficial aquifer system, 113RC-S35 and BBP-S45, also increased from January to August 2004, but decreased in subsequent samples from these two wells. Nitrate-N concentrations in RP-S20, located near the Hills-

borough River, remained below the detection limit, as reducing conditions persisted during December 2003 to July 2005. Dissolved organic carbon concentrations were constant in WP-S64 through December 2004 and increased substantially in the June 2005 sample. Nitrate-N concentrations decreased during this same period in water samples from WP-S64.

Dissolved oxygen concentrations increased in water samples from GARC-S23 (2.5 to 4.5 mg/L), WP-S64 (5.4 to 6.7 mg/L), and TTP-4 (0.2 to 0.7 mg/L) in August and September 2004 during and following the above-normal rainfall in June through September (table 5). The increase in dissolved oxygen concentrations likely resulted from recent recharge of water containing elevated levels of oxygen compared to lower levels in ground water prior to the excess rainfall period. Dissolved oxygen concentrations decreased in water from RP-S20 (2.2 to 0.3 mg/L) in fall 2004, which may indicate the influx of river water with elevated dissolved organic carbon and subsequent consumption of oxygen as water moves toward this well.

As seen from the temporal chemical variations described herein, hydrologic conditions greatly affect the occurrence and movement of anthropogenic and naturally occurring contaminants in ground water from the study area, particularly the surficial aquifer system. These variations in chemistry among monitoring wells in the surficial aquifer system are related in part to differences in unsaturated zone thickness, depth of well below the water table, possible interactions with surface water (such as the Hillsborough River or stormwater retention ponds), but also to source loading of anthropogenic contaminants from various land-use activities. Chemical constituents in water in surficial aquifer system wells show rapid responses to rainfall and recharge, but water from TTP-4 does not show similar fluctuations even though TTP-4 is withdrawing some water from the surficial aquifer system (see subsequent section). Additional studies would be helpful in separating out effects of pumping of TTP-4 and seasonal changes in recharge on water quality of the public-supply well in this dynamic system.

Sources and Mixing of Water in the Public-Supply Well

Based on the aforementioned differences in chemical and isotopic signatures in water from public-supply well TP-4 and monitoring wells in the three hydrogeologic units, the public-supply well receives mixtures of water from both the surficial aquifer system and Upper Floridan aquifer. For example, six volatile organic compounds and four pesticides were detected in trace concentrations in water from the public-supply well, and these contaminants were detected more frequently in water samples from monitoring wells in the overlying surficial aquifer system than in water from monitoring wells in the Upper Floridan aquifer in the study area. Likewise, nitrate-N concentrations in the public-supply well were more similar to median concentrations in the surficial aquifer system than very low nitrate-N concentrations in the anoxic Upper Floridan aquifer (sulfate-reducing conditions). This section presents information about differences in water chemistry with depth in the open-hole interval of the public-supply well, and quantification of mixing proportions of water from the surficial aquifer system and Upper Floridan aquifer.

Chemical Variations with Depth during Ambient and Pumping Conditions

Water samples were collected from three overlapping depth intervals in the public-supply well during ambient (non-stressed) and pumping (stressed) conditions to assess the effect of pumping on water quality. A low-flow submersible pump (Grundfos®) at a pumping rate of about 3.8 L/min was used to collect water-quality samples at three depth intervals under ambient and pumping conditions. A large-capacity submers-

ible pump, used to simulate pumping conditions in the well, was lowered to 38 m (same depth as turbine pump), and water was pumped at 1,320 L/min (compared to about 2,650 L/min for the turbine pump). For ambient conditions, only the low-capacity submersible pump was used to collect water samples (3.8 L/min). Samples were taken from the lowermost depth interval by placing the low-flow submersible pump at a depth of 48.8 m below land surface, which represents an interval (49.8-53.9 m) that includes the previously described high-flow zones in the borehole. A second depth interval (43-53 m) was sampled by placing the pump at a depth of 43 m. A third depth interval (38-53 m) was sampled by placing the low-flow submersible pump at a depth of 38 m. Samples from this depth interval presumably represent water quality for the entire 38- to 53-m open-hole interval, and should have similar chemistry as water samples collected from the public-supply well borehole under regular pumping conditions using the in-line turbine pump (on October 21, 2004). Differences in water quality among the three overlapping intervals provide an indication of the contribution of water entering the open interval above the two high-flow zones. Samples from discrete zones would have been preferable; however, packers were not used due to the large variations in the diameter of the borehole; therefore, discrete zones could not be isolated for sampling.

Water samples collected from the three depth intervals were analyzed for multiple chemical and isotopic constituents (table 13). Field measurements also were made for pH, dissolved oxygen, specific conductance, temperature, alkalinity, and depth to water. There were substantial differences in the concentrations of chemical constituents at the three sampled depth intervals (table 13). For example, water samples from the 49- to 53-m zone collected during ambient conditions contained higher concentrations of nitrate-N, orthophosphate, radon-222, atrazine, and trichloromethane (chloroform) than water collected from the other depth zones during ambient conditions, and for the entire 38- to 53-m interval during pumping conditions. Additionally, lower concentrations were found in the 49- to 53-m interval for strontium, iron, manganese, and dissolved solids as well as lower values of delta nitrogen-15 ($\delta^{15}\text{N}$) of nitrate and delta sulfur-34 ($\delta^{34}\text{S}$) of sulfate during ambient conditions compared to samples from the entire 35- to 53-m interval during pumping conditions (with a turbine pump on October 21, 2004).

During normal pumping conditions for the public-supply well (with the turbine pump), arsenic concentrations were 3.2 to 3.5 $\mu\text{g/L}$ in water samples collected in October 2002 and January 2004 and on October 21, 2004. The arsenic concentration in water from the lowermost (49-53 m) depth interval was 4.2 $\mu\text{g/L}$ during ambient conditions on October 27, 2004. On the following day, however, and under pumping conditions, the arsenic concentration in water from this same interval was 19 $\mu\text{g/L}$. Similarly, higher arsenic concentrations were measured in water from the 43- to 53-m interval during pumping conditions (16 $\mu\text{g/L}$) compared to ambient conditions (12 $\mu\text{g/L}$). This indicates that arsenic

Table 13. Chemical properties of water samples collected from various depth intervals in the public-supply well.

[Concentrations shown in milligrams per liter. Deethylatrazine is an atrazine degradate; $\delta^{15}\text{N}$, delta nitrogen-15; $\delta^{18}\text{O}$, delta oxygen-18; $\delta^{34}\text{S}$, delta sulfur-34; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; pCi/L , picocuries per liter; P, pumping conditions; NP, nonpumping conditions; E, estimated concentration below laboratory reporting level; <, less than]

Site name	Depth interval sampled, meters below land surface	Sampling date	Sampling time	Temperature, degrees Celsius	Specific conductance, $\mu\text{S}/\text{cm}$	Dissolved oxygen, mg/L	pH	Concentration, milligrams per liter										$\delta^3\text{H}$, per mil
								Bicarbonate	Ammonium-nitrogen	Nitrite-nitrogen	Nitrate-nitrogen	Orthophosphate as phosphorus	Dissolved organic carbon	Calcium	Magnesium	Sodium	Potassium	
TTP-4-entire-P	38-53	10/21/2004	1500	26	606	0.5	7.3	170	<0.04	0.008	1.4	0.018	0.9	98	8.4	11	1.0	
TTP-4-140-NP	43-53	10/27/2004	1600	26.4	577	0.8	7.3	180	<0.04	0.039	2.3	0.022	1.1	97	7.9	12	1.2	
TTP-4-160-NP	49-53	10/27/2004	1800	26.2	537	0.8	7.3	170	<0.04	0.011	3.6	0.024	0.8	90	7.7	13	1.2	
TTP-4-160-P	49-53	10/28/2004	1100	24.1	567	1.0	7.3	182	<0.04	0.035	1.8	0.014	0.9	102	8.4	12	1.2	
TTP-4-140-P	43-53	10/28/2004	1400	25.8	586	0.6	7.3	183	<0.04	0.02	1.7	0.016	0.9	101	8.2	12	1.2	
TTP-4-125-P	38-53	10/28/2004	1600	25.9	583	0.6	7.3	182	<0.04	0.013	1.7	0.022	0.9	100	8.7	12	1.2	

Site name or number	Depth interval sampled, meters below land surface	Concentration, micrograms per liter										Dissolved solids, mg/L					
		Chloride	Sulfate	Fluoride	Silica	Arsenic per mil	Hydrogen sulfide, mg/L	$\delta^{34}\text{S}$, per mil	Radon-222, pCi/L	$\delta^{18}\text{O}$ of nitrate	$\delta^{15}\text{N}$ of nitrate						
TTP-4-entire-P	38-53	25	116	0.3	13	3.2	13	28	6	1.8	1,100	<2	3.47	1.5	E1.0	380	-15.4
TTP-4-140-NP	43-53	28	96	0.2	13	11.7	14	26	<6	3	788	<2	4.87	E0.8	8.7	344	-15.7
TTP-4-160-NP	49-53	31	79	0.1	13	4.2	16	27	<6	0.8	515	<2	5.34	<1	2.6	333	-15.9
TTP-4-160-P	49-53	28	103	0.2	13	18.9	14	24	E3	2	912	<2	5.38	E0.6	14.2	359	-16.0
TTP-4-140-P	43-53	27	106	0.2	13	16.0	14	24	E5	2.2	934	<2	5.24	2.1	10.7	361	-15.4
TTP-4-125-P	38-53	27	107	0.3	13	15.3	14	26	9	1.7	937	<2	4.93	3.3	9.3	355	-15.8

Site name or number	Depth interval sampled, meters below land surface	Concentration, micrograms per liter												
		$\delta^{18}\text{O}$	$\delta^{15}\text{N}$ of nitrate	$\delta^{34}\text{S}$ per mil	Hydrogen sulfide, mg/L	Radon-222, pCi/L	Atrazine	Deethylatrazine	Prometon	Hexazinone	Dieldrin			
TTP-4-entire-P	38-53	-3.26	6.4	6.6	0.03	780	0.014	E0.012	E0.006	<0.009	<0.016	<0.024	0.29	E0.045
TTP-4-140-NP	43-53	-3.33	8.0	8.2	0	970	0.017	E0.020	<0.013	E0.003	E0.005	<0.024	0.52	E0.026
TTP-4-160-NP	49-53	-3.44	6.0	7.0	0.001	1,210	0.02	E0.026	<0.013	E0.002	E0.005	E0.008	0.80	<0.038
TTP-4-160-P	49-53	-3.24	8.9	8.9	0.008	1,060	0.016	E0.018	<0.013	<0.009	<0.016	<0.024	0.44	E0.025
TTP-4-140-P	43-53	-3.28	7.8	8.2	0	850	0.015	E0.017	<0.013	E0.003	<0.016	<0.024	0.37	E0.032
TTP-4-125-P	38-53	-3.28	7.7	8.0	0.001	990	0.014	E0.017	<0.013	E0.003	<0.016	<0.024	0.35	E0.033

movement to the public-supply wells was enhanced during pumping from a transmissive (high-flow) zone in the Upper Floridan aquifer that was identified from geophysical logging of the public-supply well borehole. This enhanced transport of arsenic is consistent with a study of arsenic release from pyrite in the Suwannee Limestone, which tends to be most abundant in high porosity zones (Price and Pichler, 2006). That study found an average of 3.5 ppm (parts per million) of arsenic in samples from the Suwannee Limestone, which was about one third higher than the reported global average of 2.5 ppm for arsenic in limestone (Baur and Onishi, 1969). Price and Pichler (2006) also conclude that arsenic 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 arsenic concentrations between 100 and 11,200 ppm, with an average concentration of 2,300 ppm from 25 samples. In the present study, low arsenic concentrations (0.06 to 0.37 ppm) were found in acid extractions (10-percent nitric acid) of limestone rock samples from cores collected during well drilling at the Water Plant (WP) site. Higher concentrations of arsenic (0.13-1.4 mg/kg) were found in acid extractions of clayey sand samples from cores collected during drilling in the surficial aquifer system and intermediate confining unit (table 4). Kim and others (2000) found that carbonation of arsenic sulfide minerals results in the formation of arseno-carbonate complexes under anaerobic conditions, which may account for elevated levels of arsenic in carbonate rock aquifers.

Further information about the behavior and mobility of arsenic in ground water can be ascertained from arsenic speciation data. Arsenic (V) concentrations tended to be higher than arsenic (III) concentrations in the 49- to 53-m depth interval (table 13). This interval tended to have slightly higher concentrations of dissolved oxygen compared to the zones in the Upper Floridan aquifer and lower concentrations of hydrogen sulfide (table 5). Water in this zone likely is a mixture of oxygenated water from the surficial aquifer system and/or intermediate confining unit with anoxic water in the Upper Floridan aquifer. Slight increases in dissolved oxygen could enhance pyrite dissolution as 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 $\mu\text{g/L}$ of arsenic, although no arsenic speciation data were collected (Arthur and others, 2002).

Concentration differences for arsenic and other chemical constituents between the 49- to 53-m zone and the other zones are consistent with water that moves downward from the surficial material into the highly transmissive zone in the Upper Floridan aquifer. Water from monitoring wells in the surficial aquifer system and intermediate confining unit in the contributing recharge area of the public-supply well contains higher concentrations of nitrate-N, trichloromethane, atrazine, and orthophosphate than water from monitoring wells in the Upper

Floridan aquifer. Conversely, water from the surficial aquifer system and intermediate confining unit contains lower concentrations of dissolved solids, strontium, iron, and manganese than water from the Upper Floridan aquifer. The lower values of $\delta^{15}\text{N}$ in water from the surficial aquifer system and from the 49- to 53-m zone likely are related to little or no denitrification in the oxic surficial aquifer system material compared to that in the anoxic Upper Floridan aquifer. The lower $\delta^{34}\text{S}$ in this zone also is more similar to lower median sulfur isotope values for water from the surficial aquifer system than from the Upper Floridan aquifer. Thus, it is likely that the transmissive zone at 49 to 53 m (high-flow rate) is hydraulically connected to the surficial aquifer system and receives a mixture of water from the surficial aquifer system and Upper Floridan aquifer. During pumping conditions, water from the 49- to 53-m zone is blended with water from other depth-interval zones, and concentrations are more similar to the other depth intervals (sampled during ambient and pumping conditions).

Estimating Mixing Proportions of Water Using Geochemical Mass-Balance Modeling

Chemical and isotopic tracer data consistently indicate that the public-supply well withdraws water containing mixtures of the surficial aquifer system and the Upper Floridan aquifer. Concentrations of anthropogenic compounds, such as nitrate, volatile organic compounds, and pesticides are closer to those found in water from monitoring wells in the surficial aquifer system than from wells in the Upper Floridan aquifer. Likewise, concentrations of naturally occurring compounds in water from the public-supply well, such as radon-222, uranium, arsenic, dissolved organic carbon, and hydrogen sulfide, generally fall between those concentrations for water from the surficial aquifer system and Upper Floridan aquifer. Geochemical mass-balance modeling techniques (NETPATH; Plummer and others, 1994) were used to quantify mixing proportions of water in the public-supply well with water from the different hydrogeologic units and to calculate mass transfer associated with sources and sinks of major dissolved constituents. Input data to NETPATH includes solute concentrations in possible end members; that is, water samples from wells in the surficial aquifer system, intermediate confining unit, and Floridan aquifer system and the mixture represented by the public-supply well. Information for the isotopic composition of soil gases and minerals also are included in the modeling (Plummer and others, 1994). The mass-transfer models are constrained by the concentration of the following dissolved constituents in end-member and mixed waters: carbon, sulfur, calcium, magnesium, and iron. In addition to these chemical constraints, an electron balance is included to account for conservation of electrons under redox conditions. The models contain the following phases: calcite, dolomite, gypsum, carbon dioxide, pyrite, amorphous iron oxide (represented by FeOOH), and organic matter (represented stoichiometrically by CH_2O). Plausible mixing reaction models are valid within

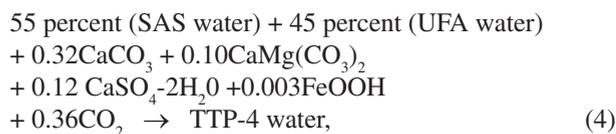
the constraints of available thermodynamic data and agreement between calculated and observed isotopic values.

For a two-component mixture containing end-member waters from the surficial aquifer system and Upper Floridan aquifer, the fraction of surficial aquifer system water (F_{SAS}) in the mixture is defined as:

$$F_{SAS} = (Y_m - Y_{UFA}) / (Y_{SAS} - Y_{UFA}), \quad (3)$$

where Y_m , Y_{SAS} , and Y_{UFA} denote the concentrations of a selected constituent in the mixture, surficial aquifer system water, and Upper Floridan aquifer water, respectively. The chemical and isotopic composition of the two end members are represented by WP-S64 (surficial aquifer system water) and WP-F150 (Upper Floridan aquifer water), which are located within 1 km of the public-supply well. The mixing calculations are based on two principal assumptions: (1) the concentrations of constituent Y in the end members mix to produce the concentration of Y in the mixed public-supply well water during pumping conditions; and (2) the concentration of constituent Y is not modified by reactions after mixing has occurred. Calculations of mixing proportions were constrained using concentrations of SF_6 , nitrate-N, and chloride.

The calculated mixing proportions of surficial aquifer system water that mix with Upper Floridan aquifer water ranged from 30 to 62 percent for four plausible models (table 14). Mixing proportions were similar for models constrained using SF_6 and chloride, both of which are considered to be nonreactive (conservative) tracers. These mass-balance model mixing proportions are consistent with mixtures dominated by young waters (less than 8 years) in the public-supply well. Water from the public-supply well contains elevated concentrations of SF_6 and 3H compared to monitoring wells in the Upper Floridan aquifer that contain mixtures dominated by older waters (greater than 60 years). These mass-transfer mixing models also indicated reactions involving dissolution of variable amounts of calcite, dolomite, and gypsum, degradation (oxidation) of organic carbon (CH_2O), and carbon dioxide (carbonic acid) produced from microbial reactions (respiration and fermentation). The following equation is an example of the geochemical mass-balance reaction obtained using SF_6 concentrations to determine the mixing proportions of waters from the surficial aquifer system (SAS) and Upper Floridan aquifer (UFA):



where the coefficients in front of the various phases represent chemical mass transfer in millimoles per kilogram of solution.

Dissolution of the limestone matrix of the Upper Floridan aquifer in the study area is consistent with water from WP-S64 and WP-F150, which is slightly under or at saturation with respect to calcite and undersaturated with respect to dolomite.

The sensitivity of the mass-transfer coefficients in table 14 is about 0.05 mmol/kg (millimoles per kilogram), based on consideration of laboratory analytical errors, variability in mineral stoichiometry, and temporal variability in the concentration of major ions in ground water. Results are reported to the nearest 0.01 mmol/kg. As a means of checking the sensitivity of the models to uncertainties in data, comparisons were made of the modeled $\delta^{13}C_{DIC}$ composition of dissolved inorganic carbon (DIC) and $\delta^{34}S$ of sulfate with the measured (observed) concentration data for these two isotopes. Model-calculated values of $\delta^{13}C_{DIC}$ and $\delta^{34}S$ typically agreed with observed values within ± 0.3 per mil. The following $\delta^{13}C$ values were used in the models for various carbon sources and sinks: calcite, 0 ± 1 per mil; dolomite, 0 per mil (Plummer and others, 1994); and carbon dioxide and CH_2O , -25 ± 5 per mil (Rightmire and Hanshaw, 1973; Burchardt and Fritz, 1980).

Mass-transfer coefficients calculated from the mixing models are consistent with all chemical and isotopic measurements in ground water from the study area. The results should be considered non-unique because it cannot be ruled out that other mineral phases could be present in trace amounts and may contribute substantial amounts of dissolved constituents to water withdrawn by the public-supply well. Other recharge or mixing scenarios could produce mass-balance models that are consistent with these data. The likelihood of this possibility is small, given that the chemical composition of other end-member wells representing the surficial aquifer system and Upper Floridan aquifer were tested in many other mixing models. There was less agreement, however, between measured and calculated isotopic compositions than in the four models presented in table 14.

Movement of Contaminants to the Public-Supply Well

Isotopic and other chemical signatures in multiple water samples collected from the public-supply well during 2002–05 consistently indicated a mixture of water from the surficial aquifer system and Upper Floridan aquifer. Concentrations of anthropogenic contaminants (nitrate-N and trichloromethane) and naturally occurring contaminants (arsenic and radon-222) are higher during pumping conditions. Public-supply well TTP-4 is located in a well field with other public-supply wells. This study could not evaluate the effects of pumpage from other wells on water quality in TTP-4. Based on extensive geochemical indicators measured in water samples and information obtained during geophysical logging of the borehole for TTP-4, a highly transmissive zone in the Upper Floridan aquifer likely is hydraulically connected to the surficial aquifer system and parts of the intermediate confining unit. Large solution features were observed in televiwer images of the borehole at depths greater than 43 m. The areal and vertical extent of this transmissive zone, however, is not known. It would be useful to collect additional water samples from monitoring wells in the Upper Floridan aquifer in the

Table 14. Chemical mass transfer associated with various mixing scenarios and comparison of observed and modeled isotopic composition.

[mmol/kg, millimoles per kilogram; CH₂O, dissolved organic matter; δ¹³C, delta carbon-13 of dissolved inorganic carbon; δ³⁴S-SO₄, delta sulfur-34 of sulfate; Cl, Chloride; N, nitrogen; SF₆, sulfur hexafluoride; DIC, dissolved inorganic carbon; SAS, surficial aquifer system; UFA, Upper Floridan aquifer]

Mixing scenario	End members, mixing percentage			Phases, mass transfer, mmol/kg						Isotopic composition, per mil				
	SAS WP-S64	UFA WP-F150	UFA 49-53 meter zone	CH ₂ O	Calcite	Dolomite	Gypsum	FeOOH	Pyrite	Carbon dioxide	Computed	Measured	Computed	Measured
				δ ¹³ C _{DIC}										
1	33	67		0.12	0.35	0.05	0	0	0.32	-13.1	-12.9	15.6	16.7	
2 (SF ₆)	55	45		0.17	0.32	0.1	0.12	0.003	0.36	-13.3	-12.9	16.5	16.7	
3 (N)	30	70		0.13	0.34	0.04	0	0.01	-0.01	-13.2	-12.9	16.1	16.7	
4 (Cl)	62		38	0.11	-0.004	0.06	0.33	0	0.33	-14.2	-12.5	17.3	15.4	

study area that are open to the 45- to 50-m interval to determine if similar mixtures dominated by young water are present throughout other parts of the study area.

Focused recharge beneath stormwater retention ponds may contribute contaminants to the surficial aquifer system. The highest atrazine concentration in ground water (0.12 µg/L) was found in a water sample from the surficial aquifer system, well THC-S46 (table 11). A higher atrazine concentration of 1.58 µg/L was found in water from the nearby retention pond (62SRP-POND) and likely is a source for the elevated concentration of atrazine and dissolved organic carbon in water from THC-S46. Water from the surficial aquifer system moves downward into the Upper Floridan aquifer under natural gradients that can be enhanced as a result of pumping stresses.

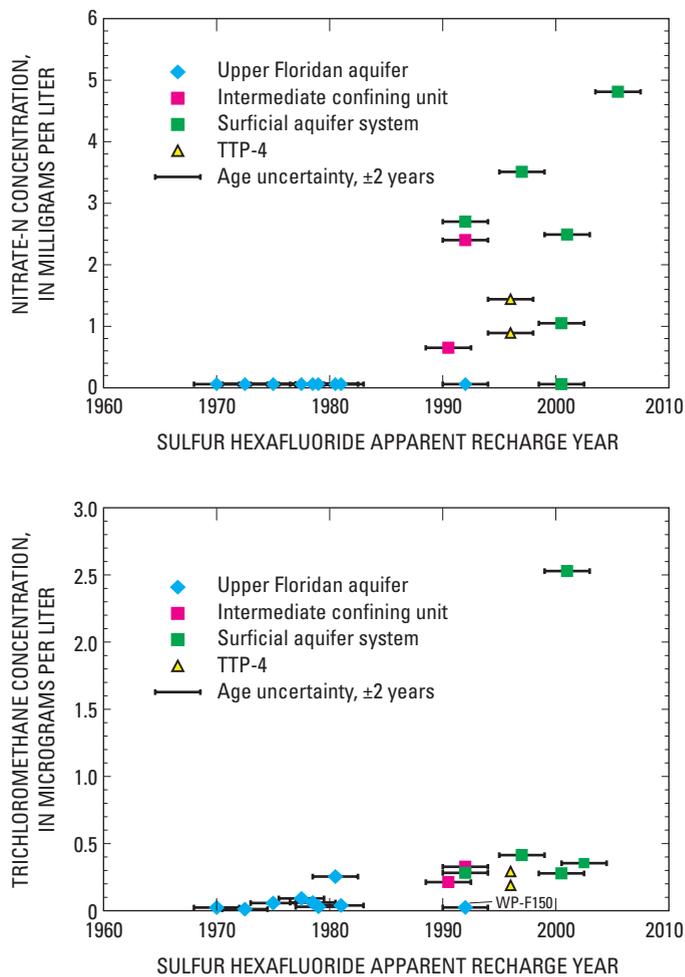


Figure 25. Relation between the sulfur hexafluoride apparent recharge year and concentrations of nitrate-N, and trichloromethane in water samples from the surficial aquifer system, intermediate confining unit, Upper Floridan aquifer, and public-supply well in the Temple Terrace, Florida, study area.

The vulnerability of the public-supply well to contamination is further indicated by age-dating tracer concentrations that show a young water component, generally less than 10 years. Nitrate-N and trichloromethane concentrations show a relation with age of water from monitoring wells in the study area, with higher concentrations of these two anthropogenic contaminants found in increasingly younger waters (fig. 25). This trend is influenced by young waters occurring in the oxic surficial aquifer system where well depths are shallow and where contaminant loading is high from certain urban land-use activities. Pumping of ground water by the public-supply well and other wells in the immediate area can enhance the downward movement of these and other contaminants.

Although the effect of the degree of confinement was not evaluated in this study, in another study more than three times as many detections of volatile organic compounds were found in unconfined parts of the Upper Floridan aquifer compared to areas where the aquifer is semiconfined (Metz and others, 2007). That study also found 16 detections of disinfection byproducts in unconfined areas, but only two detections in semiconfined areas of the Upper Floridan aquifer. Public-supply well TTP-4 is in an unconfined part of the aquifer, and unknown sinkholes also may further enhance downward transport of contaminants.

A three-dimensional calibrated ground-water flow model with particle tracking has been used to simulate the age distribution of water to the public-supply well and to monitoring wells in the surficial aquifer system and Upper Floridan aquifer (C.A. Crandall, U.S. Geological Survey, written commun., 2007). This calibrated flow model also is being used to simulate the arrival of contaminants to these wells from the release of potential contaminant sources at the land surface. Results of this flow model agree with the geochemical observations presented herein.

Summary

The vulnerability of a public-supply well to anthropogenic and naturally occurring contaminants was studied near Tampa, Florida, as part of the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program. Water samples were collected during 2003-05 from the public-supply well and from 29 monitoring wells that tap the unconfined or poorly confined Upper Floridan aquifer and the overlying surficial aquifer system and intermediate confining unit. The karstic Upper Floridan aquifer is particularly vulnerable to contamination from a variety of sources due to the presence of sinkholes and other solution features that can provide a direct hydraulic connection between the aquifer and the surface. Sands and clayey sands that compose the overlying surficial aquifer system are highly permeable and allow for rapid downward movement of water to the water table and eventually into the Upper Floridan aquifer.

Multiple isotopic and other chemical tracers were analyzed in water samples from the public-supply well, 12 monitoring wells that tap the Upper Floridan aquifer, and from 15 monitoring wells in the overlying surficial aquifer system and intermediate confining unit. All monitoring wells were located along ground-water flow paths within the modeled ground-water contributing recharge area of the public-supply well. Geophysical logging of the public-supply well borehole revealed large solution features near the bottom of the open interval of the well (46-53 m below land surface) and two zones of high ground-water flow in the limestone rock matrix.

Water samples were collected under different pumping (stressed) conditions from three overlapping depth intervals in the public-supply well following removal of the turbine pump. First, a low-capacity submersible pump (less than 3.8 L/min) was placed at the top of each interval and samples were collected during ambient (non-stressed) conditions. Second, a large-capacity portable submersible pump (1,320 L/min) was placed near the top of the open interval (38 m below land surface) while water-chemistry samples were collected using the low-capacity submersible pump to represent pumping conditions in the public-supply well.

The lowermost 49- to 53-m depth interval had distinctly different chemistry compared with the two other sampled intervals. Water samples collected from this depth interval during ambient conditions contained higher concentrations of nitrate-N, orthophosphate, radon-222, atrazine, and trichloromethane than water collected from the other depth zones during ambient conditions, and for the entire 38- to 53-m interval during pumping conditions. Additionally, low concentrations were found in the 49- to 53-m interval for strontium, iron, manganese, and dissolved solids as well as low values of delta nitrogen-15 ($\delta^{15}\text{N}$) of nitrate and delta sulfur-34 ($\delta^{34}\text{S}$) of sulfate. Arsenic concentrations were high in the 49- to 53-m zone during pumping conditions along with high ratios of arsenic (V)/arsenic (III). Mixing of waters with variable redox conditions occurs during pumping conditions and likely accounts for differences in the concentrations of arsenic species (arsenic (V) and arsenic (III)) between samples collected from the lowermost depth interval (49-53 m) and the entire open interval (38-53 m). Considerably higher concentrations of the more oxidized arsenic species (arsenic (V)) were measured in water samples from the lowermost depth interval than in water from the entire open interval. Movement of water likely occurs from the overlying sands and clays of the oxic surficial aquifer system and the discontinuous intermediate confining unit, which contains elevated radon-222 and nitrate-N concentrations, into the anoxic Upper Floridan aquifer (lower radon-222 and nitrate-N concentrations). Differences in arsenic concentrations in water from the various depth intervals in the public-supply well (3.2-19 $\mu\text{g/L}$) were related to pumping conditions. Arsenic concentrations exceeded the U.S. Environmental Protection Agency maximum contaminant

level of 10 µg/L in water samples from specific depth intervals in the public-supply well borehole, but arsenic concentrations did not exceed the maximum contaminant level in the well-head sample.

Concentrations of age-dating tracers sulfur hexafluoride (SF₆), tritium (³H), and helium-3 (³He) in samples from the public-supply well during low- and high-rate pumping conditions were consistent with binary mixtures dominated by young water (less than 7 years). Similarly, water samples from monitoring wells in the surficial aquifer system had SF₆ and ³H concentrations that indicate a substantial proportion of young water (less than 7 years). In contrast, most water samples from monitoring wells in the Upper Floridan aquifer system had lower SF₆ and ³H concentrations than water from the public-supply well and indicated mixtures containing higher proportions of old waters (greater than 60 years).

Six volatile organic compounds and four pesticides were detected in trace concentrations (well below drinking-water standards and other health-based screening levels) in water from the public-supply well. These contaminants were detected more frequently in water samples from monitoring wells in the overlying surficial aquifer system than in water from monitoring wells in the Upper Floridan aquifer in the study area. Likewise, nitrate-N concentrations in the public-supply well (0.72-3.6 mg/L) were more similar to median concentrations in the oxic surficial aquifer system (2.1 mg/L) than median nitrate-N concentrations (0.06 mg/L) in the anoxic Upper Floridan aquifer (sulfate-reducing conditions). Denitrification likely occurs in the deeper parts of surficial aquifer system and in the Upper Floridan aquifer based on excess nitrogen gas concentrations and highly enriched nitrogen- and oxygen-isotopic composition of nitrate.

Focused recharge beneath stormwater retention ponds and unknown sinkholes may contribute contaminants to the surficial aquifer system and the Upper Floridan aquifer. The highest atrazine concentration (0.12 µg/L) in ground water was found in a sample from the surficial aquifer system at well THC-S46. A high atrazine concentration of 1.58 µg/L was found in water from the nearby stormwater retention pond (62SRP-POND) and likely is a source for the elevated concentration of atrazine and dissolved organic carbon in water from THC-S46. Water from the surficial aquifer system moves downward into the Upper Floridan aquifer under natural gradients and can be enhanced due to pumping stresses.

Geochemical mass-balance mixing models for the public-supply well indicate that 50 to 70 percent of water withdrawn from the public-supply well is contributed from the surficial aquifer system, and 30 to 50 percent from the Upper Floridan aquifer. Geochemical models also indicate the dissolution of small amounts of calcite, gypsum, and dolomite as water moves toward the public-supply well. Even though mass-transfer coefficients calculated from the mixing models were consistent with all chemical and isotopic measurements in ground water from the study area, results should be considered non-unique because it cannot be ruled out that other

mineral phases could be present in trace amounts and may contribute substantial amounts of dissolved constituents to water withdrawn by the public-supply well. Other recharge or mixing scenarios could produce mass-balance models that are consistent with these data. The likelihood of this possibility is small, given that the chemical composition of other end-member wells representing the surficial aquifer system and Upper Floridan aquifer were tested in other mixing models. The presence of a large component of water from the surficial aquifer system that is withdrawn during pumping of the studied public-supply well demonstrates the vulnerability of public-supply wells in this area to contamination.

Selected monitoring wells in the surficial aquifer system were sampled several times during 2003-05 to evaluate temporal variability in water quality in response to changing hydrologic conditions. These wells were sampled four times before and after three tropical cyclones passed through the area in summer 2004. Water-quality variations also were evaluated for public-supply well TTP-4 based on five samples collected during 2002-05. The dynamic nature of the hydrologic response to recharge in this karst setting was observed by large fluctuations in chemistry. Chloride concentrations decreased from summer 2004 water samples to winter 2004-05 samples from all three monitoring wells following the recharge pulse from high rainfall and corresponding peak in water-level elevation in October 2004. Nitrate-N concentrations increased in water from one well from January to August 2004, but decreased in water from another monitoring well during the same period. Nitrate-N concentrations also increased in water samples from two other monitoring wells in the surficial aquifer system, from January to August 2004, but decreased in subsequent samples from these two wells. Nitrate-N concentrations in water from a well located near the Hillsborough River remained below the detection limit, as reducing conditions persisted during December 2003 to July 2005. Dissolved oxygen concentrations increased in water samples from two wells in the surficial aquifer system, and the public-supply well in August and September 2004 during and following the above-normal rainfall in June through September 2004. The increase in dissolved oxygen concentrations likely results from recent recharge of water containing elevated levels of oxygen compared to lower levels in ground water prior to the excess rainfall period. Dissolved oxygen concentrations decreased in water from a well near the Hillsborough River in fall 2004, which may indicate the influx of river water with elevated dissolved organic carbon and subsequent consumption of oxygen as water moves toward this well.

A hydrologic flow model of the contributing recharge area of the public-supply well is consistent with the observed geochemical conditions and can be used to evaluate changes in hydrologic conditions. Further information about flow pathways and the extent of high transmissive zones in the Upper Floridan aquifer that are directly connected to the surficial aquifer system would be helpful in better understanding the movement of contaminants to other public-supply wells that tap the Upper Floridan aquifer.

Selected References

- Aeschbach-Hertig, W., Schlosser P., Stute, M., Simpson, H.J., Ludin, A., and Clark, J.F., 1998, A $^3\text{H}/^3\text{He}$ study of ground-water flow in a fractured bedrock aquifer: *Ground Water*, v. 36, p. 661-670.
- Allen, H.E., Fu, G., Boothman, W., Di Toro, D.M., and Mahony, J.D., 1991, Determination of acid volatile sulfide and selected simultaneously extractable metals in sediment: U.S. Environmental Protection Agency Report 821-R-91-100, 18 p.
- Allen, H.E., Fu, G., and Deng, B., 1993, Analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments: *Environmental Toxicology and Chemistry*, v. 12, p. 1441-1453.
- Arthur, J.D., Dabous, A.A., and Cowart, J.B., 2002, Mobilization of arsenic and other trace elements during aquifer storage and recovery, southwest Florida, in Aiken, G.R., and Kuniansky, E.L., eds., U.S. Geological Survey Artificial Recharge Workshop Proceedings, Sacramento, California: p. 20-32.
- Aucott, W.R., 1988, Areal variation in recharge to and discharge from the Upper Floridan aquifer in Florida: U.S. Geological Survey Water-Resources Investigations Report 88-4057, 1 sheet.
- Barbash, J.S., Thelin, G.P., Kolpin, D.W., and Gillion, R.J., 1999, Distribution of major herbicides in ground water of the United States: U.S. Geological Survey Water-Resources Investigations Report 98-4245, 57 p.
- Baur, W.H., and Onishi, B.H., 1969, Arsenic, in Wedepohl, K.H., ed., *Handbook of Geochemistry*: Berlin, Germany, Springer Verlag, p. A1-A33.
- Berndt, M.P., and Katz, B.G., 1992, Hydrochemistry of the surficial and intermediate aquifer systems in Florida: U.S. Geological Survey Water-Resources Investigations Report 91-4186, 24 p.
- Böhlke J.K., 2002, Groundwater recharge and agricultural contamination: *Hydrogeology Journal*, v. 10, p. 153-179.
- Böhlke, J. K., 2006, Tracermodell1- Excel workbook for calculation and presentation of environmental tracer data for simple groundwater mixtures: Use of chlorofluorocarbons in hydrology—A guidebook, Section III.10.3: Vienna, International Atomic Energy Agency, STI/PUB/1238, p. 239-243.
- Bowles, K.C., Ernste, M.J., and Kramer, J.R., 2003, Trace sulfide determination in oxic fresh waters: *Analytica Chimica Acta*, v. 477, p. 113-124.
- Brenton, R.W., and Arnett, T.L., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of dissolved organic carbon by UV-promoted persulfate oxidation and infrared spectrometry: U.S. Geological Survey Open-File Report 92-480, 12 p.
- Brooks, S.C., Fredrickson, J.K., Carroll, S.L., Kennedy, D.W., Zachara, J.M., Plymale, A.E., Kelly, S.D., Kemner, K.M., and Pendorf, S., 2003, Inhibition of bacterial U(VI) reduction by calcium: *Environmental Science and Technology*, v. 37, p. 1850-1858.
- Burchardt, B., and Fritz, P., 1980, Environmental isotopes as environmental and climatological indicators, in Fritz, P., and Fontes, J.S., eds., *Handbook of Environmental Isotope Geochemistry*: Amsterdam, Elsevier Scientific Publishing Company, p. 473-504.
- Busenberg, E., Weeks, E., Plummer, L.N., and Bartholomay, R.C., 1993, Age dating groundwater by use of chlorofluorocarbons (CCl_3F and CCl_2F_2), and distribution of chlorofluorocarbons in the unsaturated zone, Snake River Plain aquifer, Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 93-4054, 47 p.
- Busenberg, E., and Plummer, L.N., 2000, Dating young ground water with sulfur hexafluoride—Natural and anthropogenic sources of SF_6 : *Water Resources Research*, v. 36, p. 3011-3030.
- Busenberg, E., Plummer, L.N., Bartholomay, R.C., and Wayland, J.E., 1998, Chlorofluorocarbons, sulfur hexafluoride, and dissolved permanent gases in ground water from selected sites in and near the Idaho National Engineering and Environmental Laboratory, Idaho, 1994-1997: U.S. Geological Survey Open-File Report 98-274, 72 p.
- Bush, P.W., and Johnston, R.H., 1988, Ground-water hydraulics, regional flow, and ground-water development of the Floridan aquifer system in Florida and in parts of Georgia, South Carolina, and Alabama—Regional Aquifer-System Analysis: U.S. Geological Survey Professional Paper 1403-C, 80 p.
- Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M., and Berner, R.A., 1986, The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales: *Chemical Geology*, v. 54, p. 149-155.
- Carmody, R.W., Plummer, L.N., Busenberg, E., and Coplen, T.B., 1997, Methods for collection of dissolved sulfate and sulfide and analysis of their sulfur isotopic composition: U.S. Geological Survey Open-File Report 97-234, p. 91.
- Carr, W.J., and Alverson, D.C., 1959, Stratigraphy of Middle Tertiary rocks in part of west-central Florida: U.S. Geological Survey Bulletin, Report: B 1092, 111 p.

- Casciotti, K.L., Sigman, D.M., Hastings, M.G., Böhlke, J.K., and Hilkert, A., 2002, Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method: *Analytical Chemistry*, v. 74, p. 4905-4912.
- Cecil, L.D., and Green, J.R., 2000, Radon-222, in Cook, P., and Herczeg, A.L., eds., *Environmental Tracers in Subsurface Hydrology*: Boston, Kluwer Academic Publishers, chap. 6, p. 175-194.
- Chapelle, F.H., Bradley, P.M., Lovley, D.R., O'Neill, K., Landmeyer, J.E., 2002, Rapid evolution of redox processes in a petroleum hydrocarbon-contaminated aquifer: *Ground Water*, v. 40, no. 4, p. 353-360.
- Chapelle, F.H., McMahon, P.B., Dubrovsky, N.M., Fujii, R.F., Oaksford, E.T., Vroblesky, D.A., 1995, Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems: *Water Resources Research*, v. 31, no. 2, p. 359-371.
- Clark, I.D., and Fritz, P., 1997, *Environmental isotopes in hydrogeology*: New York, Lewis Publishers, 328 p.
- Connor, B.F., Rose, D.L., Noriega, M.C., Murtagh, L., and Abney, S.R., 1998, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory -- Determination of 86 volatile organic compounds in water by gas chromatography/mass spectrometry, including detections less than reporting limits: U.S. Geological Survey Open-File Report 97-829, 86 p.
- Cook, P.G., and Böhlke, J.K., 1999, Determining timescales for groundwater flow and solute transport, in Cook, P.G., and Herczeg, A.L., eds., *Environmental Tracers in Subsurface Hydrology*: Boston, Kluwer Academic Publishers, p. 1-30.
- Cook, P., and Herczeg, A.L., eds., 2000, *Environmental tracers in subsurface hydrology*: Boston, Kluwer Academic Publishers, 529 p.
- Cook, P.G., and Solomon, D.K., 1997, Recent advances in dating young groundwater: Chlorofluorocarbons, $^3\text{H}/^3\text{He}$, and ^{85}Kr : *Journal of Hydrology*, v. 191, p. 245-265.
- Coplen, T.B., 1988, Normalization of oxygen and hydrogen isotope data: *Chemical Geology (Isotope Geoscience Section)*, v. 72, p. 293-297.
- Coplen, T.B., 1994, Reporting of stable hydrogen, carbon, and oxygen isotopic abundances: *Pure and Applied Chemistry*, v. 66, p. 273-276.
- Coplen, T.B., 2000, Laboratory Information Management System (LIMS) for light stable isotopes: U.S. Geological Survey Open-File Report 00-345, p. 121.
- Coplen, T.B., Böhlke, J.K., and Casciotti, K., 2004, Using dual-bacterial denitrification to improve ^{15}N determinations of nitrates containing mass-independent ^{17}O : *Rapid Communications in Mass Spectrometry*, v. 18, p. 245-250.
- Coplen, T.B., Brand, W.A., Gehre, M., Gröning, M., Meijer, H.A.J., Toman, B., and Verkouteren, R.M., 2006, New guidelines for ^{13}C measurements: *Analytical Chemistry*, v. 78, p. 2439-2441.
- Coplen, T.B., and Krouse, H.R., 1998, Sulphur isotope data consistency improved: *Nature*, v. 392, p. 32.
- Coplen, T.B., Wildman, J.D., and Chen, J., 1991, Improvements in the gaseous hydrogen-water equilibration technique for hydrogen isotope ratio analysis: *Analytical Chemistry*, v. 63, p. 910-912.
- Craig, H., 1961, Isotopic variations in meteoric waters: *Science*, v. 133, p. 1702-1703.
- Culbreath, M.A., 1988, Geophysical investigation of lineaments in south Florida: MS Thesis, Department of Geology, University of South Florida, Tampa, 97 p.
- Denver, J.M., and Sandstrom, M.W., 1991, Distribution of dissolved atrazine and two metabolites in the unconfined aquifer, southeastern Delaware, in Mallard G.E., and Aronson, D.A., eds., *U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Monterey, California, March 11-15, 1991*: U.S. Geological Survey Water-Resources Investigations Report 91-4034, p. 324-318.
- Eberts, S.M., Erwin, M.L., and Hamilton, P.A., 2005, Assessing the vulnerability of public-supply wells to contamination from urban, agricultural, and natural sources: U.S. Geological Survey Fact Sheet 2005-3022, 4 p.
- Epstein, S., and Mayeda, T., 1953, Variation of O-18 content of water from natural sources: *Geochimica et Cosmochimica Acta*, v. 4, p. 213-224.
- Faires, L.M., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of metals in water by inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 93-125, 217 p.
- Faulkner, G.L., 1973, Geohydrology of the Cross-Florida Barge Canal with special reference to the Ocala vicinity: U.S. Geological Survey Water-Resources Investigations 1-73, 117 p.
- Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125.

- Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.
- Focazio, M.J., Reilly, T.E., Rupert, M.G., and Helsel, D.R., 2002, Assessing ground-water vulnerability to contamination: Providing scientifically defensible information for decision makers: U.S. Geological Survey Circular 1224, 33 p.
- Focazio, M.J., Welch, A.H., Watkins, S.A., Helsel, D.R., and Horn, M.A., 1999, A retrospective analysis on the occurrence of arsenic in ground-water resources of the United States and limitations in drinking-water-supply characterizations: U.S. Geological Survey Water-Resources Investigation Report 99-4279, 21 p.
- Furlong, E.T., Anderson, B.D., Werner, S.L., Soliven, P.P., Coffey, L.J., and Burkhardt, M.R., 2001, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by graphitized carbon-based solid-phase extraction and high-performance liquid chromatography/mass spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01-4134, 73 p.
- Garbarino, J.R., 1999, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of dissolved arsenic, boron, lithium, selenium, strontium, thallium, and vanadium using inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 99-093, 31 p.
- Gee, G.W., and Or, D., 2002, Particle-size analysis, *in* Dane, J.H., and Topp, G.C., eds., *Methods of Soil Analysis, Part 4—Physical Methods*: Soil Science Society of America Book Series No. 5: Madison, Wisconsin, Soil Science Society of America, p. 255-293.
- Gillion, R.J., Barbash, J.E., Crawford, C.G., Hamilton, P.A., Martin, J.D., Nakagaki, N., Nowell, L.H., Scott, J.C., Stackelberg, P.E., Thelin, G.P., and Wolock, D.M., 2006, Pesticides in the Nation's streams and ground water, 1992-2001: U.S. Geological Survey Circular 1291, 150 p.
- Hach Company, 2002, DR/2400 Spectrophotometer Procedures Manual: Loveland, CO, USA, 450 p.
- Hamilton, P.A., Miller, T.L., and Myers, D.N., 2004, Water quality in the Nation's streams and aquifers—Overview of selected findings, 1991-2001: U.S. Geological Survey Circular 1265, 20 p.
- Harbaugh, A.W., Banta, E.R., Hill, M.C., and McDonald, M.G., 2000, MODFLOW-2000: The U.S. Geological Survey modular ground-water model—User guide to modularization concepts and the ground-water flow process: U.S. Geological Survey Open-File Report 00-92, 121 p.
- Heaton T.H.E., and Vogel, J.C., 1981, Excess air in ground-water: *Journal of Hydrology*, v. 50, p. 201-216.
- Ivahnenko, T., and Barbash, J.E., 2004, Chloroform in the hydrologic system—Sources, transport, fate, occurrence, and effects on human health and aquatic organisms: U.S. Geological Survey Scientific Investigations Report 2004-5137, 34 p.
- Ivahnenko, T., and Zogorski, J.S., 2006, Sources and occurrence of chloroform and other trihalomethanes in drinking-water supply wells in the United States, 1986-2001: U.S. Geological Survey Scientific Investigations Report 2006-5015, 13 p.
- Katz, B.G., 1992, Hydrochemistry of the Upper Floridan aquifer in Florida: U.S. Geological Survey Water-Resources Investigations Report 91-4196, 37 p.
- Katz, B.G., 2004, Nitrate contamination in karst ground water, *in* Culver, D., and White, W., eds., *Encyclopedia of Caves*: Amsterdam, The Netherlands, Elsevier Science, p. 415-418.
- Kaufman, M.I., 1968, Uranium isotope investigation of the Floridan aquifer and related natural waters of north Florida: M.S. Thesis, Florida State University, 65 p.
- Kendall, C., Aravena, R., 1999, Nitrogen isotopes in ground-water systems, *in* Cook, P., and Herczeg, A.A., eds., *Environmental Tracers in Subsurface Hydrology*: Boston, Kluwer Academic Publishers, chap. 9, p. 261-298.
- Kim, M.J., Nriagu, J., and Haack, S., 2000, Carbonate ions and arsenic dissolution by groundwater: *Environmental Science and Technology*, v. 34, p. 3094-3100.
- Knochenmus, L.A. and Robinson, J.L., 1996, Descriptions of anisotropy and heterogeneity and their effect on ground-water flow and areas of contribution to public-supply wells in a karst carbonate aquifer system: U.S. Geological Survey Water-Supply Paper 2475, 43 p.
- Koterba, M.T., Wilde, F.D., Lapham, W.W., 1995, Ground-water data collection protocols and procedures for the National Water Quality Assessment Program: Collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95-399.
- Kreitler, C.W., 1975, Determining the source of nitrate in groundwater by nitrogen isotope studies. University of Texas, Austin: Texas Bureau of Economic Geology Report of Investigation No. 83, 57 p.
- Langmuir, D., 1978, Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits: *Geochimica et Cosmochimica Acta*, v. 42, p. 547-549.

- Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1995, Ground-water data collection protocols and procedures for the National Water-Quality Assessment Program: Selection, installation, and documentation of wells and collection of related data: U.S. Geological Survey Open-File Report 95-398, 69 p.
- Lindley, C.E., Stewart, J.T., and Sandstrom, M.W., 1996, Determination of low concentrations of acetochlor in water by automated solid-phase extraction and gas chromatography with mass selective detection: *Journal of AOAC International*, v. 79, no. 4, p. 962-966.
- Lovley, D.R., and Phillips, E., J., P., 1987, Rapid assay for microbially reducible ferric iron in aquatic sediments: *Applied Environmental Microbiology*, v. 53, no. 7, p. 1536-1540.
- Ludin, A., Weppernig, R., Bonisch, G., and Schlosser, P., 1998, Mass spectrometric measurement of helium isotopes and tritium: Palisades, New York, Lamont-Doherty Earth Observatory, Technical Report 98-06.
- Maddox, G.L., Lloyd, J.M., Scott, T.M., Upchurch, S.B., and Copeland, R., eds., 1992, Florida's Ground-Water Quality Monitoring Network Program: Background hydrogeochemistry: Florida Geological Survey Special Publication no. 34, 364 p.
- Madsen, J.E., Sandstrom, M.W., and Zaugg, S.D., 2003, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—A method supplement for the determination of fipronil and degradates in water by gas chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 02-462, 11 p.
- Maloszewski, P., and Zuber, A., 1982, Determining the turnover time of groundwater systems with the aid of environmental tracers 1; Models and their applicability: *Journal of Hydrology*, no. 57, p. 207-231.
- Maloszewski, P., and Zuber, A., 1996, Lumped parameter models for the interpretation of environmental tracer data: *Manual on Mathematical Models in Isotope Hydrology*, IAEA-TECDOC 910, IAEA, Vienna, p. 9-50.
- Marella, R.L., and Berndt, M.P., 2005, Water withdrawals and trends from the Upper Floridan aquifer in the southeastern United States, 1950-2000: U.S. Geological Survey Circular 1278, 20 p.
- McLain, B., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of chromium in water by graphite furnace atomic absorption spectrophotometry: U.S. Geological Survey Open-File Report 93-449, 16 p.
- Metz, P.A., Delzer, G.C., Berndt, M.P., Crandall, C.A., and Toccalino, P.L., 2007, Anthropogenic organic compounds in ground water and finished water of community water systems in the northern Tampa Bay area, Florida, 2002-04: U.S. Geological Survey Scientific Investigations Report 2006-5267, 48 p.
- Michel, R.L., 1989, Tritium deposition in the continental United States 1953-1983: U.S. Geological Survey Water-Resources Investigations Report 89-4072, 46 p.
- Miller, J.A., 1986, Hydrogeologic framework of the Floridan aquifer system: U.S. Geological Survey Professional Paper 1403-B, 91 p.
- National Climatic Data Center, National Oceanic and Atmospheric Agency (NOAA), 2005, Climatography of the United States No. 20 Monthly Station Climate Summaries for the 1971-2000, <http://www.ncdc.noaa.gov/normals.html>.
- Nolan, B.T., Ruddy, B.C., Hitt, K.J., and Helsel, D.R., 1998, A national look at nitrate contamination of ground water: *Water Conditioning and Purification*, v. 39, p. 76-79.
- Osmond, J.K., and Cowart, J.B., 2000, U-series nuclides as tracers in groundwater hydrology, in Cook, P., and Herczeg, A.L., eds., *Environmental Tracers in Subsurface Hydrology*: Boston, Kluwer Academic Publishers, chap. 9, p. 146-173.
- Owenby, J.R., and Ezell, D.S., 1992, Monthly station normals of temperature, precipitation, and heating and cooling degree days 1961-1990, Florida: Asheville, N.C., U.S. Department of Commerce National Oceanic and Atmospheric Administration, National Climatic Data Center, 28 p.
- Paillet, F.L., 1998, Flow modeling and permeability estimation using borehole flow logs in heterogenous fractured formations: *Water Resources Research*, v. 32, p. 997-1010.
- Paillet, F.L., 2000, Field technique for estimating aquifer parameters using flow log data: *Ground Water*, v. 38, no. 4, p. 510-521.
- Parkhurst, D.L., and Appelo, C.A.J., 1999, User's guide to PHREEQC (Version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 310 p.
- Paschke, S.S., ed., 2006, Hydrogeologic settings and ground-water flow simulations for regional studies of the transport of anthropogenic and natural contaminants to public-supply wells – Studies begun in 2001: SECTION 5: Hydrogeologic Setting and Ground-Water Flow Simulations of the Northern Tampa Bay Regional Study Area, Florida, by C.A. Crandall: U.S. Geological Survey Professional Paper 1737-A.

- Patton, C.J., and Kryskalla, J.R., 2003, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Evaluation of alkaline persulfate digestion as an alternative to Kjeldahl digestion for determination of total and dissolved nitrogen and phosphorus in water: U.S. Geological Survey Water-Resources Investigations Report 03-4174, 33 p.
- Pearson, F.J., Jr., and Rightmire, C.T., 1980, Sulphur and oxygen isotopes in aqueous sulphur compounds, *in* Fritz, A.P., and Fontes, J.C., eds., *Handbook of Environmental Isotope Geochemistry*, Volume 1, The Terrestrial Environment: Elsevier, Amsterdam, p. 227-258
- Pichler, T., Veizer, J., and Hall, G.E.M., 1999, Natural input of arsenic into a coral-reef ecosystem by hydrothermal fluids and its removal by Fe(III) oxyhydroxides: *Environmental Science and Technology*, v. 33, p. 1273-1378.
- Plummer L.N., and Busenberg, E., 1999, Chlorofluorocarbons, *in* Cook, P.G., and Herczeg A.L., eds., *Environmental Tracers in Subsurface Hydrology*: Kluwer Academic Press, chap. 15, p. 441-478.
- Plummer, L.N., Busenberg, E., Böhlke, J.K., Nelms, D.L., Drenkard, S., Michel, R.L., and Schlosser, P., 2001, Groundwater residence times in Shenandoah National Park, Blue Ridge Mountains, Virginia, USA: A multitracer approach: *Chemical Geology*, v. 179, p. 93-111.
- Plummer, L.N., Busenberg, E., Drenkard, S., Schlosser, P., Ekwurzel, B., Weppernig, R., McConnell, J.B., and Michel, R.L., 1998, Flow of river water into a karstic limestone aquifer, 2; Dating the young fraction in groundwater mixtures in the Upper Floridan aquifer near Valdosta, Georgia: *Applied Geochemistry*, v. 13, p. 1017-1043.
- Plummer, L.N., Prestemon, E.C., and Parkhurst, D.L., 1994, An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH, version 2.0: U.S. Geological Survey Water-Resources Investigations Report 94-4169, 130 p.
- Price, R.E., and Pichler, T., 2006, Abundance and mineralogical association of arsenic in the Suwannee Limestone (Florida): Implications for arsenic release during water-rock interaction: *Chemical Geology*, v. 228, p. 44-56.
- Prichard, H.M., and Gesell, T.F., 1977, Rapid measurements of radon-222 concentrations in water with a commercial liquid scintillation counter: *Health Physics*, v. 33, p. 577-581.
- Qi, H., Coplen, T.B., Geilmann, H., Brand, W.A., and Böhlke, J.K., 2003, Two new organic reference materials for ^{13}C and ^{15}N measurements and a new value for the ^{13}C of NBS 22 oil: *Rapid Communications in Mass Spectrometry*, v. 17, p. 2483-2487.
- Reilly, T.E., Plummer, L.N., Phillips, P.J., and Busenberg, E., 1994, The use of simulation and multiple environmental tracers to quantify groundwater flow in a shallow aquifer: *Water Resources Research* no. 30, p. 421-433.
- Revesz, K.M., Landwehr, J.M., and Keybl, J., 2001, Measurement of delta C-13 and delta O-18 isotopic ratios of CaCO_3 using a Thermoquest Finnigan GasBench II Delta Plus XL continuous flow isotope ratio mass spectrometer with application to Devils Hole /core DH-11 calcite: U.S. Geological Survey Open-File Report 01-257, 17 p.
- Rightmire, C.T., and Hanshaw, B.B., 1973, Relationship between the carbon isotope composition of soil CO_2 and dissolved carbonate species in groundwater: *Water Resources Research*, v. 9, p. 958-967.
- Sacks, L.A., 1996, Geochemical and isotopic composition of ground water with emphasis on sources of sulfate in the Upper Floridan aquifer in parts of Marion, Sumter, and Citrus Counties, Florida: U.S. Geological Survey Water-Resources Investigations Report 95-4251, 47 p.
- Sacks, L.A., 2002, Estimating ground-water inflow to lakes in central Florida using the isotope mass-balance approach: U.S. Geological Survey Water-Resources Investigations Report 02-4192, 47 p.
- Sacks, L.A., Herman, J.S., and Kauffman, S.J., 1995, Controls on high sulfate concentrations in the Upper Floridan aquifer in southwest Florida: *Water Resources Research*, v. 31, p. 2541-2551.
- Sandino, A., and Bruno, J., 1992, The solubility of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{s})$ and the formation of U(VI) phosphate complexes: Their influence in uranium speciation in natural waters: *Geochimica et Cosmochimica Acta*, v. 56, p. 4135-4145.
- Sandstrom, M.W., Stoppel, M.E., Foreman, W.T., and Schroeder, M.P., 2001, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of moderate-use pesticides and selected degradates in water by C-18 solid-phase extraction and gas chromatography/mass spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01-4098, 70 p.
- Schaap, B.D., and Zogorski, J.S., 2006, Occurrence of trihalomethanes in the Nation's ground water and drinking-water supply wells, 1985-2002: U.S. Geological Survey Scientific Investigations Report 2006-5068, 64 p.
- Schlosser, P., Stute, M., Dorr, H., Sonntag, C., and Munnich, K.O., 1988, Tritium/ ^3He dating of shallow groundwater: *Earth Planetary Science Letters*, v. 89, p. 353-362.
- Schlosser P., Stute, M., Sonntag, C., and Munnich, K.O., 1989, Tritogenic ^3He in shallow ground water: *Earth Planetary Science Letters*, v. 94, p. 245-256.

- Scott, T.M., 1988, The lithostratigraphy of the Hawthorn Group (Miocene) of Florida: Florida Geological Survey Bulletin no. 59, 148 p.
- Sigman, D.M., Casciotti, K.L., Andreani, M., Barvord, C., Galanter, M., and Böhlke, J.K., 2001, A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater: *Analytical Chemistry*, v. 73, p. 4145-4153.
- Sinclair, W.C., 1974, Hydrogeologic characteristics of the surficial aquifer in northwest Hillsborough County, Florida: Florida Bureau of Geology Information Circular 86, 98 p.
- Sinclair, W.C., 1982, Sinkhole development resulting from ground-water withdrawal in the Tampa area, Florida: U.S. Geological Survey Water-Resources Investigations 81-50, 19 p.
- Smedley, P.L., and Kinniburgh, D.G., 2002, A review of the source, behaviour and distribution of arsenic in natural waters: *Applied Geochemistry*, v. 17, p. 517-568.
- Solomon, D.K., and Sudicky, E.A., 1991, Tritium and helium-3 isotope ratios for direct estimation of spatial variations in groundwater recharge: *Water Resources Research*, v. 27, p. 2309-2319.
- Southeastern Geological Society, 1986, Hydrogeological units of Florida: Compiled by Southeastern Geological Society Ad Hoc Committee on Florida Hydrostratigraphic Unit Definition: Florida Geological Survey Special Publication no. 28, 8 p.
- Sowerby, J.R., Carter, K.C., Dragovitsch, S.T., and Byer, J.C., 2000, Occurrence of radon in Florida's public water supplies: Florida Department of Environmental Protection, 31 p.
- Sprinkle, C.L., 1989, Geochemistry of the Floridan aquifer system in Florida and parts of Georgia, South Carolina, and Alabama: U.S. Geological Survey Professional Paper 1403-I, 105 p.
- Stackelberg, P.E., Kauffman, L.J., Ayers, M.A., and Baehr, A.L., 2001, Frequently co-occurring pesticides and volatile organic compounds in public supply and monitoring wells, southern New Jersey: *Environmental Toxicology and Chemistry*, v. 20, p. 853-865.
- Stewart, J.W., Goetz, C.L., and Mills, L.R., 1978, Hydrogeologic factors affecting the availability and quality of ground water in the Temple Terrace area, Hillsborough County, Florida: U.S. Geological Survey Water-Resources Investigations Report 78-4, 38 p.
- Stewart, M.T., and Wood, J., 1984, Geophysical characteristics of fracture zones in the carbonate Floridan aquifer, *in* Proceedings, Conference sponsored by the Florida Sinkhole Institute, University of Central Florida, College of Engineering, Orlando, p. 225-229.
- Suflita, J.M., Gibson, S.A., and Beeman, R.E., 1988, Anaerobic biotransformation of pollutant chemicals in aquifers: *Journal of Industrial Microbiology and Biotechnology*, v. 3, p. 179-194.
- Swancar, A., and Hutchinson, C.B., 1995, Chemical and isotopic composition and potential for contamination of water in the Upper Floridan aquifer, west-central Florida, 1986-1989: U.S. Geological Survey Water-Supply Paper 2409, 70 p.
- Tesoriero, A.J., Spruill, T.B., and Eimers, J.L., 2004, Geochemistry of shallow ground water in coastal plain environments in the southeastern United States: Implications for aquifer susceptibility: *Applied Geochemistry*, v. 19, p. 1471-1482.
- Thiros, S.A., 2000, Quality of shallow ground water in areas of recent residential and commercial development in Salt Lake Valley, Utah, 1999: U.S. Geological Survey Fact Sheet 106-00, 6 p.
- Tihansky, A.B., 2005, Effects of aquifer heterogeneity on ground-water flow and chloride concentrations in the Upper Floridan aquifer near and within an active pumping well field, west-central Florida: U.S. Geological Survey Scientific Investigations Report 2004-5268, 75 p.
- Toccalino, P.L., Norman, J.E., Phillips, R.H., Kauffman, L.J., Stackelberg, P.E., Nowell, L.H., Krietzman, S.J., and Post, G.B., 2004, Application of health-based screening levels to ground-water quality data in a state-scale pilot effort: U.S. Geological Survey Scientific Investigations Report 2004-5174, 64 p.
- Torgersen, T., Clarke, W.B., and Jenkins, W.J., 1979, The tritium/helium-3 method in hydrology: *Isotope Hydrology 1978*, IAEA, Vienna, p. 917-929.
- Trommer, J.T., 1987, Potential for pollution of the Upper Floridan aquifer from five sinkholes and an internally drained basin in west-central Florida: U.S. Geological Survey Water-Resources Investigations Report 87-4013, 103 p.
- U.S. Environmental Protection Agency, 1993, Health Advisories for drinking water contaminants, Office of Water Health Advisories: Ann Arbor, MI, Lewis Publishers.
- U.S. Environmental Protection Agency, 1996, Test methods for evaluating solid waste, Method 9030B: U.S. Environmental Protection Agency Publication SW-846.
- U.S. Environmental Protection Agency, 1999, Proposed radon in drinking water rule: U.S. Environmental Protection Agency Publication 815-F-99-006, 6 p.
- Vernon, R.O., 1951, Geology of Citrus and Levy Counties, Florida: Florida Geological Survey Bulletin no. 33, p. 47-52.

- Vogel, T.M., Criddle, C.S., and McCarty, P.L., 1987, Transformations of halogenated aliphatic compounds: *Environmental Science and Technology*, v. 21, p. 722-736.
- Welch, A.H., Westjohn, D.B., Helsel, D.R., and Wanty, R.B., 2000, Arsenic in ground water of the United States—Occurrence and geochemistry: *Ground Water*, v. 38, no. 4, p. 589-604.
- Wilson, W.L., and Skiles, W.C., 1988, Aquifer characterization by quantitative dye tracing at Ginnie Spring, northern Florida: *Proceedings of the Second Conference on Environmental Problems in Karst Terranes and Their Solutions: The Association of Ground Water Scientists and Engineers*, Dublin, Ohio, p. 121-141.
- Wolansky, R.M., and Thompson, T.H., 1987, Relation between ground water and surface water in the Hillsborough River Basin, west-central Florida: U.S. Geological Survey Water-Resources Investigations Report 87-4010, 58 p.
- Yobbi, D.K., 2000, Application of nonlinear least-squares regression to ground-water flow modeling, west-central Florida: U.S. Geological Survey Water-Resources Investigations Report 00-4094, 58 p.
- Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95-181, 60 p.
- Zogorski, J.S., Carter, J.M., Ivahnenko, T., Lapham, W.W., Moran, M.J., Rowe, B.L., Squillace, P.J., and Toccalino, P.L., 2006, Volatile organic compounds in the Nation's ground water and drinking-water supply wells: U.S. Geological Survey Circular 1292, 101 p.
- Zuber, A., 1986, Mathematical models for the interpretation of environmental radioisotopes in groundwater systems, *in* Fritz, P., and Fontes, J.C., eds., *Handbook of Environmental Geochemistry: The Terrestrial Environment*: Amsterdam, Elsevier, v. 2, p. 1-59.
- Zuber, A., Michalczyk, Z., and Maloszewski, P., 2001, Great tritium ages explain the occurrence of good-quality groundwater in a phreatic aquifer of an urban area, Lublin, Poland: *Hydrogeology Journal*, v. 9, p. 451-460.
- Zuber, A., and Motyka, J., 1998, Hydraulic parameters and solute velocities in triple-porosity karstic-fissured-porous carbonate aquifers: Case studies in southern Poland: *Environmental Geology*, v. 34, p. 243-250.

Appendixes

Appendix A1. Summary of quality-assurance results for organic compounds in blanks and replicates.

[Concentrations are in micrograms per liter ($\mu\text{g/L}$); NR, not reported; P code, U.S. Environmental Protection Agency STORET code; E, estimated concentration, below method reporting level; VOC, volatile organic compound; yyyyymmdd, year, month, day]

Station identifier	Site name	Sample date, yyyyymmdd	Sample start time	Diazinon-d10, surrogate, Schedule 2003, percent recovery	Carbon disulfide ($\mu\text{g/L}$)	Dichloromethane ($\mu\text{g/L}$)	Trichloromethane ($\mu\text{g/L}$)
				P99994	P77041	P34423	P32106
Blanks							
280247082231903	WP-S64	20040114	1200	NR	<.04	E0.1	
280247082231903	WP-S64	20040114	1205	NR	<.04	0.1	
280253082223802	GARC-F75	20031215	0915	NR	<.04	0.4	
280253082223802	GARC-F75	20031218	0940	NR	<.04	0.6	E0.09
Replicates							
280247082231901	WP-F299	20040122	1600	80.2	E0.77	0.8	
280247082231901	WP-F299	20040122	1601	69.5	E0.42	0.7	
280301082222703	113RC-S35	20031211	1300	88.8	<.04	2.0	
280301082222703	113RC-S35	20031211	1305	78.4	<.04	3.2	

Station identifier	Site name	Sample date, yyyyymmdd	Sample time	Isobutyl alcohol-d6, surrogate, water, unfiltered, percent recovery	1,2-Dichloroethane-d4, surrogate, Schedule 2090, percent recovery	1-Bromo-4-fluorobenzene, surrogate, VOC schedules, percent recovery
				P62835	P99832	P99834
Blanks						
280241082224403	THC-S46	20031218	0935	75.5	110	83.8
280241082224403	THC-S46	20050614	1415	NR	120	78.4
280241082224403	THC-S46	20050614	1430	NR	121	77.0
280247082231902	WP-F150	20040128	0915	91.4	127	91.9
280247082231902	WP-F150	20040128	0945	107	132	87.8
280249082220701	RP-F103	20031015	1515	109	120	97.5
280249082220701	RP-F103	20031015	1715	108	120	96.2
280253082223802	GARC-F75	20031215	1000	81	110	58.3
280253082223802	GARC-F75	20031218	0940	82.3	113	77.1
280303082230902	LP-S30	20050621	1000	NR	131	93.8
280303082230902	LP-S30	20050621	1001	NR	130	92.8

80 Chemical Characteristics, Water Sources and Pathways, and Age Distribution of Ground Water

Appendix A2. Summary of quality-assurance results for selected chemical constituents in field blank and replicate samples.

[E, estimated concentration, reported below method reporting level; P code, U.S. Environmental Protection Agency STORET code; cm, centimeter; mg/L, milligrams per liter;

Station identifier	Site name	Sample date, yyyymmdd	Sample time	Absorbance, UV, 254 nm, 1 cm pathlength, water, filtered, units per centimeter	Absorbance, UV, organic constituents, 280 nm, 1 cm pathlength, water, filtered	Calcium, mg/L	Sodium, mg/L	Silica, mg/L	Sulfide, water, filtered, field, mg/L	Organic carbon, mg/L	Chromium, µg/L	Cobalt, µg/L	Copper, µg/L	Manganese, µg/L
				P50624	P61726	P00915	P00930	P00955	P99118	P00681	P01030	P01035	P01040	P01056
Blanks														
280241082224403	THC-S46	20050614	1430	<0.004	<0.004	0.08	0.29	1.42		E0.2				<0.6
280247082231902	WP-F150	20040128	0945							1.9				
280247082231902	WP-F150	20040128	0955								<0.8	0.871	<0.4	E0.1
280247082231903	WP-S64	20040114	1210								<0.8	<0.014	<0.4	<0.2
280249082220701	RP-F103	20031015	1715								E0.4	0.788	E0.4	<0.2
280250082233001	LP-F160	20041104	1050	<0.004	<0.004	0.05	<0.20	0.04		1.3	<0.8	0.324	<0.4	<0.2
280303082230902	LP-S30	20050621	1000	0.005	0.004					0.4				

Station identifier	Site name	Sample date, yyyymmdd	Sample time	Absorbance, UV, 254 nm, 1 cm pathlength, water, filtered, units per centimeter	Absorbance, UV, organic constituents, 280 nm, 1 cm pathlength, water, filtered	Dissolved oxygen, water, unfiltered, mg/L	Potassium, mg/L	Bromide, mg/L	Total nitrogen (nitrate + nitrite + ammonia + organic-N), water, filtered	Organic carbon, mg/L	Arsenic, µg/L	Arsenite (H3AsO3), µg/L as arsenic	Boron, µg/L	Cadmium, µg/L
				P50624	P61726	P00300	P00935	P71870	P62854	P00681	P01000	P62452	P01020	P01025
Replicates														
280241082224402	THC-F75	20040112	1500			0.1	0.74	E.01	0.14	1.9	1.1	<1.0	19	<0.04
280241082224402	THC-F75	20040112	1501				0.72	0.02	0.14		1	<1.0	18	<0.04
280241082230701	RP-F103	20041102	1200	0.022	0.017	0.1	1.35	0.11	1.95	1	3.1	<1.0	28	0.21
280241082230701	RP-F103	20041102	1205	0.023	0.017	0.8				0.9				
280244082232001	TTP-4	20050620	1601	0.028	0.02					1.2				
280244082232001	TTP-4	20050620	1600	0.027	0.018	0.3	1.11		0.78	1.2				
280247082231901	WP-F299	20040122	1600			0.2	1.4	0.03	0.22	2.4	12.6	5.6	25	0.17
280247082231901	WP-F299	20040122	1601							2.4	12.3		31	0.17
280247082231903	WP-S64	20050614	1131	0.011	0.008		1.61		2.22	1.1				
280247082231903	WP-S64	20050614	1130	0.01	0.007	5.7	1.58		2.35	13.7				
280253082223801	GARC-F200	20031216	1300			0.2	1.24	0.03	0.24	2.1	1.7	1.1	22	<0.04
280253082223801	GARC-F200	20031216	1306									<1.0		
280301082222703	113RC-S35	20031211	1300			2.5	0.68	0.05	3.7	0.6	E.2	<1.0	15	0.11
280301082222703	113RC-S35	20031211	1305							0.5	0.2		16	0.11
280303082230901	LP-H40	20041208	1500	0.007	0.006	6.8	1.08	0.05	2.43	0.4	0.3	<1.0	22	0.16
280303082230901	LP-H40	20041208	1505	0.007	0.005	6.8	1.16	0.04	2.44	0.4	0.3		22	0.17

µg/L, micrograms per liter, UV, ultraviolet; nm, nanometers; yyyyymmdd, year, month, day; <, less than; Th-230, Thorium-230; Cs-137, Cesium-137]

Molybdenum, µg/L	Nickel, µg/L	Strontium, µg/L	Zinc, µg/L
P01060	P01065	P01080	P01090

E0.2	0.43	1.36	<0.6
<0.4	0.06	<0.40	1.1
<0.4	0.43	<0.40	<0.6
<0.4	0.16	0.4	E0.4

Chromium, µg/L	Copper, µg/L	Lead, µg/L	Lithium, µg/L	Manganese, µg/L	Molybdenum, µg/L	Nickel, µg/L	Selenium, µg/L	Vanadium, µg/L	Alpha/radioactivity 2-sigma combined uncertainty, water, filtered, Th-230	Alpha radioactivity, water, filtered, Th-230 curve, picocuries per liter	Deuterium/Protium ratio, water, unfiltered, per mil	Gross beta radioactivity, water, filtered, Cs-137 curve, picocuries per liter	Radium-226, water, filtered, radon method, picocuries per liter
P01030	P01040	P01049	P01130	P01056	P01060	P01065	P01145	P01085	P75987	P04126	P82082	P03515	P09511
<0.8	0.6	<0.08	1	85.7	3	1.76	1.4	2	2	1	-17.6	2.1	0.52
<0.8	0.5	<0.08	1	84.7	3	1.44	1.2	1.8	2.4	3.3	-15.7	2.2	0.59
<0.8	0.7	<0.08	1.9	2.8	16.4	2.44	7.8	12.6					
				3.4									
<0.8	2	<0.08	4.1	7	86.7	4.41	0.6	0.8					
<0.8	2	0.09	3.7	6.9	91.1	3.62	0.8	0.9					
				<0.6									
				<0.6									
<0.8	1.4	<0.08	3.8	70.1	6.4	2.95	1.3	1.5					
E.5	0.9	<0.08	E.4	5.1	0.9	1	0.8	3.7					
E.6	1.1	<0.08	E.4	5.5	0.9	0.9	0.8	3.9					
1.6	1.1	<0.08	E.5	0.3	4	0.65	0.7	5.1					
1.5	1	<0.08	E.5	0.3	3.9	0.59	0.6	5.2					

Appendix A3. Percent recovery values for surrogate compounds added to ground-water and surface-water samples at the U.S. Geological Survey National Water Quality Laboratory.—Continued

[P code, U.S. Environmental Protection Agency STORET parameter code]

Site identifier	Site name	Sample date	Sample time	Bisphenol a-d3 surrogate		Caffeine-c13 surrogate		Decafluorobiphenyl surrogate		Fluoranthene-d10 surrogate		Diazinon-d10, Alpha-HCH-d6, surrogate		1,2-dichloroethane-d4, surrogate		1-bromo-4-fluorobenzene, surrogate		Toluene-d8, surrogate		Barban, (positive ion surrogate)		"2,4,5-t (negative ion surrogate)"		c13 caffeine (positive ion surrogate)		Isobutyl alcohol-d6		
				P99583	P99584	P99585	P99586	P99994	P99995	P99832	P99834	P99833	P90640	P99958	P99959	P62835												
280244082232001	TTP-4	20050216	1600												117	90.9	95.7											
280244082232001	TTP-4	20050620	1600												105	96.7	101											
280244082232001	TTP-4	20040128	1602							105																		
280244082232001	TTP-4	20040128	1603							107																		
280244082232001	TTP-4	20040128	1604							104																		
280247082231901	WP-F299	20040122	1600							80.2					126	95.5	103											101
280247082231901	WP-F299	20040122	1601							69.5					130	92.5	99.5											113
280247082231901	WP-F299	20040803	1400							94.3					117	103	100											
280247082231902	WP-F150	20040128	0915												127	91.9	103											91.4
280247082231902	WP-F150	20040128	0945							103					132	87.8	99.6											107
280247082231902	WP-F150	20040128	1300							100					135	98.7	102											102
280247082231902	WP-F150	20040804	1100							72					121	103	101											
280247082231903	WP-S64	20040114	1200												105	81.4	92.8											126
280247082231903	WP-S64	20040114	1205												112	80.6	96.4											130
280247082231903	WP-S64	20040114	1500							117					115	74.4	92.6											107
280247082231903	WP-S64	20040804	1600							69.3					121	101	99											
280247082231903	WP-S64	20041118	1200												114	96.8	97.8											
280247082231903	WP-S64	20050614	1130												127	75.6	98.6											
280247082231903	WP-S64	20050614	1131												122	76.8	97.6											
280247082231903	WP-S64	20050614	1132												110	101	101											
280249082220701	RP-F103	20031015	1515												120	97.5	101											109
280249082220701	RP-F103	20031015	1715												120	96.2	99.9											108
280249082220701	RP-F103	20031202	1500							96.3					143	100	102											156
280249082220702	RP-F77	20031203	1300							89.4					147	89.3	102											158
280249082220703	RP-S20	20031204	1400							91.9					145	81.2	99.8											148
280249082220703	RP-S20	20040811	1500												105	93.6	105											
280249082220703	RP-S20	20041116	1500												113	93.8	97.4											
280249082220703	RP-S20	20050616	1500												118	95.8	98.5											
280250082233001	LRP-F160	20041104	1050												104	89.6	96.8											101
280250082233001	LRP-F160	20041104	1055												106	89.1	96.6											99
280250082233001	LRP-F160	20041104	1300												107	90.3	95.1											98.7
280250082233002	LRP-H105	20041207	1600												107	95.9	101											91.9

Appendix A4. Oxidation-reduction (redox) classification scheme developed for the transport of anthropogenic and natural contaminants to public-supply wells.

[For a given redox indicator species, presence above significance level is consistent with some redox environments, (“Redox environments consistent with redox indicator species”), and inconsistent with other redox environments (“Redox environments contraindicated by redox indicator species”). Redox classification is based upon a combination of this redox classification system, understanding of position within ground-water flow system, understanding of mineralogy of solid phases, and data quality and quantity. In general, multiple redox indicator species are required to precisely characterize a given redox environment; mg/L, milligrams per liter, µg/L, micrograms per liter; >, greater than; <, less than]

Redox indicator species	Significance level	Redox environments consistent with redox indicator species	Redox environments contraindicated by redox indicator species
Dissolved oxygen	10.5 mg/L	Oxygen reducing	Denitrifying Manganese reducing Iron reducing Sulfate reducing Methanic
Nitrate	10.5 mg/L	Oxygen reducing Denitrifying	Manganese reducing Iron reducing Sulfate reducing Methanic
Sulfate	14 mg/L	Oxygen reducing Denitrifying	Sulfate reducing Iron reducing Manganese reducing Methanic
Nitrogen	(Nitrogen from recharge)	Denitrifying	Oxygen reducing Methanic
Manganese	150 µg/L	Manganese reducing	Manganese reducing Methanic
Iron	1.2100 µg/L	Iron reducing	Oxygen reducing Methanic Manganese reducing
³ Hydrogen sulfide	Presence	Sulfate reducing	Denitrifying Manganese reducing Iron reducing
Methane	Presence		Oxygen reducing Methanic Iron reducing Sulfate reducing

¹Significance levels for dissolved oxygen and nitrate are from Chapelle and others (1995), for sulfate, Chapelle and others (2002), and for manganese and iron, from Geological Survey of Sweden (<http://www.intemat.envirom.se/index.php3?main=/documents/legal/assess/assedoc/gndwdoc/aqui.htm>). The significance of the 4 mg/L sulfate concentration is that sulfate > 4 mg/L may compete with reductive pathways for degradation of chlorinated solvents; in other words, the iron-reducing, low sulfate zone may be useful for the anthropogenic contaminant analysis.

²This iron significance level also used by Smedley and Kinniburgh (2002). Iron-poor sediments or precipitation of an iron-bearing secondary phase may require a lower significance level for iron; and so forth, but must be applied consistently. Iron-reducing water is divided into two categories, “iron-reducing, high sulfate” (sulfate > 4 mg/L), and “iron-reducing, low sulfate” (sulfate < or = 4 mg/L).

³Note that hydrogen sulfide data do not allow identification of high- or low-sulfate conditions because hydrogen sulfide is produced by reduction of sulfate regardless of whether sulfate concentrations are > or < 4 mg/L.