Sources of nitrate contamination and age of water in large karstic springs of Florida

B. G. Katz

Abstract In response to concerns about the steady increase in nitrate concentrations over the past several decades in many of Florida's first magnitude spring waters (discharge ≥2.8 m^3/s), multiple isotopic and other chemical tracers were analyzed in water samples from 12 large springs to assess sources and timescales of nitrate contamination. Nitrate-N concentrations in spring waters ranged from 0.50 to 4.2 mg/L, and $\delta^{15}N$ values of nitrate in spring waters ranged from 2.6 to 7.9 per mil. Most $\delta^{15}N$ values were below 6 per mil indicating that inorganic fertilizers were the dominant source of nitrogen in these waters. Apparent ages of groundwater discharging from springs ranged from 5 to about 35 years, based on multi-tracer analyses (CFC-12, CFC-113, SF_6, $^3H/^3He$) and a piston flow assumption; however, apparent tracer ages generally were not concordant. The most reliable spring-water ages appear to be based on tritium and ^3He data, because concentrations of CFCs and SF_6 in several spring waters were much higher than would be expected from equilibration with modern atmospheric concentrations. Data for all tracers were most consistent with output curves for exponential and binary mixing models that represent mixtures of water in the Upper Floridan aquifer recharged since the early 1960s. Given that groundwater transit times are on the order of decades and are related to the prolonged input of nitrogen from multiple sources to the aquifer, nitrate could persist in groundwater that flows toward springs for several decades due to slow transport of solutes through the aquifer matrix.

Received: 8 January 2004 / Accepted: 23 March 2004
Published online: 31 July 2004

B. G. Katz
U.S. Geological Survey, 2010 Levy Avenue,
Tallahassee, Florida, USA
E-mail: bkatz@usgs.gov
Tel.: +1-850-9429500 ext. 3018
Fax: +1-850-9429521

Keywords Springs · Karst · Nitrate contamination · Springwater age · USA · Florida

Introduction

Springs provide sources of potable water, sites of recreational and cultural value, and afford a way to assess regional ground-water quality because spring waters integrate groundwater vertically, spatially and temporally from large parts of an aquifer. In Florida, as in many parts of the world, agricultural activities and other land uses have impaired the quality of spring waters by contributing large quantities of nutrients to ground-water recharge (Dietrich and Hebert 1997; Focazio and others 1998; Burg and Heaton 1998; Buzek and others 1998; Böhlke 2002). Nitrate-N concentrations in northern Florida spring waters have increased substantially from background concentrations in the UFA (≤ 0.1 mg/L; Katz 1992) to more than 5 mg/L during the past 40–50 years (Hornsby and Ceryak 1999; Katz and others 1999). Large quantities of nitrate-N are being discharged from springs to surface waters (Pittman and others 1997) and nuisance levels of algae and macrophytes occur in many spring-fed rivers (Jones and others 1996; Hornsby and Mattson 1998).

In response to human health and ecological concerns, the Florida Legislature approved funding in 2001 for the Florida Springs Initiative, a program designed to determine the status of first magnitude springs (discharge ≥2.8 m^3/s) in the State and to develop strategies for protecting this valuable resource. As part of this initiative, the U.S. Geological Survey (USGS) and the Florida Department of Environmental Protection conducted a study of 12 first magnitude springs to better understand sources of nitrate contamination, age of groundwater discharging from these springs, and mixing of waters from various zones of the Upper Floridan aquifer (UFA).

Protecting spring waters from further degradation in quality requires information on contamination sources and transit times of groundwater discharging from springs. Recent studies have used ground-water transit times derived from environmental tracers along with historical records of nitrogen loading to groundwater, to better understand the timing of nitrate input to the

subsurface and its movement through the ground-water system (Cook and Böhlke 1999; Katz and others 2001; Böhlke 2002). Environmental tracer data have shown that transit times of groundwater discharging from springs in karst systems can be highly variable. Using tritium (^{3}H) data, Dincer and Payne (1971) estimated ground-water transit times between 20 and 100 years for karst aquifers discharging to springs in southwestern Turkey. Using chlorofluorocarbons (CFCs) in spring waters from carbonate rocks in the Piedmont and Valley and Ridge physiographic provinces in the Chesapeake Bay watershed, USA, average ground-water residence times ranged from modern to 32 years (Focazio and others 1998). CFCs, sulfur hexafluoride (SF_6), and tritium/tritogenic helium-3 (^{3}H/ ^{3}He$_{trit}$) data showed that high-elevation springs in Shenandoah National Park, USA, discharged groundwater that was mainly less than a few years old (Plummer and others 2001). CFCs and ^{3}H/^{3}He data indicated that the average residence times of groundwater discharging from springs in the Suwannee River Basin, Florida, were 10–20 years and were related to spring magnitude (Katz and others 2001).

This paper describes the use of a multi-tracer approach to better understand sources of nitrate contamination in selected first magnitude springs in Florida. Also, dating techniques were applied by using chemical and isotopic tracers (CFCs, SF_6, ^{3}H and ^{3}He) along with lumped parameter flow models to assess timescales of nitrate contamination in groundwater discharging from these large karstic springs. By evaluating different tracers simultaneously, important information can be gleaned about ground-water transit times and the age-frequency distribution for spring waters (Böhlke 2002) that can be used for important resource-management decisions.

Description of sampled spring systems

Karst springs or spring groups that have average discharge values of 2.8 m^3/s or more are classified as first magnitude springs (Rosenau and others 1977). Florida's 33 first magnitude springs occur in the northern two-thirds of the peninsula and in the central and eastern panhandle (Fig. 1) where carbonate rocks are at or near land surface. Water discharging from these springs originates from the UFA, which consists of sediments that range in age from the late Eocene to mid-Oligocene (Scott and others 2002).

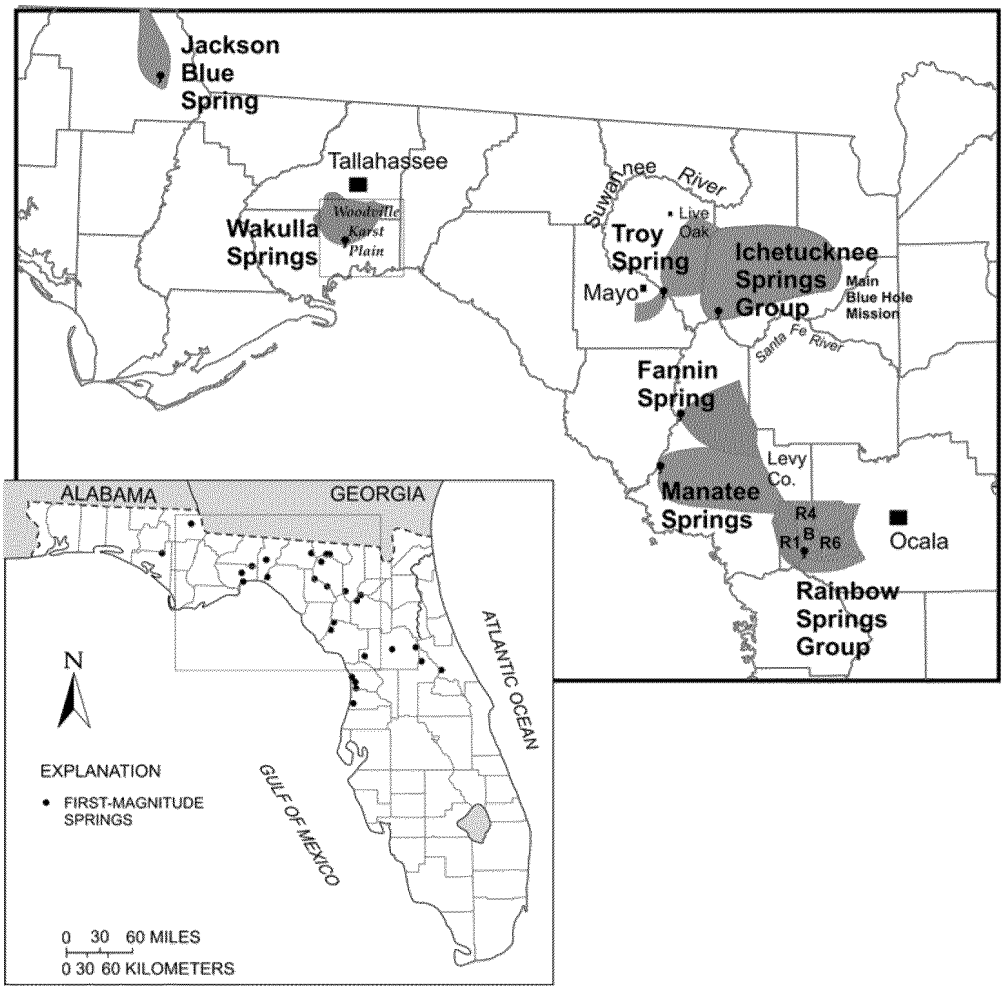

Fig. 1
Map showing locations of first-magnitude springs in Florida and approximate springshed boundaries for sampled springs. Springshed boundaries for Rainbow Spring #6 (R6), Rainbow Spring #4 (R4), Rainbow Spring #1 (R1), and Bubbling Spring (B) are based on groundwater domains as described by Jones and others (1996)

Several climatic, geologic, and hydrologic factors control the amount and variability of groundwater discharge from these springs. Dominant factors include the amount and frequency of rainfall and recharge, the porosity and permeability of the UFA, the size of the ground-water contributing area, and the hydraulic head distribution.
Northern Florida's climate is subtropical (long, warm summers and mild winters). Rainfall amounts vary considerably from year to year and typically increase with latitude as indicated by long-term annual mean rainfall amounts at the following National Oceanic and Atmospheric Administration (NOAA) stations in Florida: Ocala, 131 cm (1889–2000), approximately 30 km east of Rainbow Springs; Mayo, 142 cm (1948–2000), approximately 10 km west of Troy Springs; and Tallahasee, 167 cm (1883–2000), approximately 12 km north of Wakulla Springs. However, during mid-1998 to mid-2001, northern Florida experienced a severe drought with a rainfall deficit of more than 127 cm. The resulting decreased recharge to the UFA caused a lowering of the potentiometric surface, and consequently, discharge decreased significantly at many first magnitude springs, relative to historical values (Table 1).

Porosity and permeability of the UFA vary greatly near first magnitude springs, because openings in the water-bearing limestone range from small solution openings along joints or bedding planes to large cavernous openings and networks of conduits developed in modern karst or paleokarst areas. Differences in morphology and geometry of saturated caves and conduits associated with specific springs also can influence the discharge rate of spring waters (Kincaid 1999). Large conduit systems, mapped by cave divers for several springs, can extend for several km into the rocks of the UFA (Hornsby and Ceryak 1999). Variability in aquifer permeability near spring conduit networks is reflected by a large range in transmissivity, from 2,800 to greater than 1.1×10^6 m^2/day (Bush and Johnston 1988; Sepulveda 2002).
Recharge to the unconfined UFA ranges from 20 to 80 cm/yr (Faulkner 1973; Davis 1996; Grubbs 1998) and is highly variable spatially and seasonally. Ground-water drainage areas of first-magnitude springs can be categorized as intermediate flow systems (Toth 1963). Regional simulation of the ground-water flow system indicates that first-magnitude springs receive only a very small portion of water from upward movement from deep regional flow

Table 1
Physical properties and concentrations of major dissolved chemical species and stable isotopes, spring discharge, and saturation index with respect to calcite and dolomite in sampled spring waters

Spring name and (abbreviation)	Sample date	Time	Q	Median Q	Q record period	T	pH	SC	DO	Ca	Mg	Na	K	Cl	SO_4	HCO_3	F	NO_3-N	NH_3-N	PO_4-P
Wakulla (W)	10/22/2001	1000	3.65	9.9	1931-2001	20.8	7.59	324	2.48	44	10.0	5.5	0.6	8.4	9.7	179	0.2	1.1	<0.01	0.05
Fannin (F)	10/22/2001	1445	1.46	2.8	1930-2001	22.4	7.23	462	2.01	78	5.7	4.1	2.6	9.1	19	189	0.1	4.2	<0.01	0.07
Manatee (M)	10/22/2001	1700	4.36	5.1	1932-2001	22.3	7.28	478	1.65	82	6.2	3.8	1.2	8.0	34	168	0.1	1.8	<0.01	0.04
Rainbow Springs Group			18.0	18.0	1932-2001															
Rainbow #6 (R6)	10/23/2001	1110				23.4	7.65	347	5.71	55	6.5	3.9	0.3	6.9	45	145	0.1	1.0	<0.01	0.02
Rainbow #4 (R4)	10/23/2001	1330				23.4	7.95	161	6.61	43	5.0	2.7	0.1	5.2	4.9	149	0.1	1.4	<0.01	0.03
Rainbow #1 (R1)	10/23/2001	1230				23.5	7.68	251	5.33	23	3.5	2.4	0.1	4.3	4.6	79	<0.1	1.2	<0.01	0.02
Bubbling (B)	10/23/2001	1430				23.0	7.41	337	4.45	56	6.0	3.0	0.2	5.9	7.8	163	0.1	1.2	0.06	0.03
Ichetucknee Springs Group			5.27	5.4	1929-2001															
Ichetucknee Main (IMA)	10/24/2001	915				21.8	7.51	324	4.01	56	5.8	2.1	0.1	4.3	8.4	150	0.1	0.82	<0.01	0.02
Ichetucknee Blue Hole (IBH)	10/24/2001	1115				21.7	7.57	302	1.97	51	4.9	2.8	0.3	5.0	5.0	177	0.1	0.68	<0.01	0.04
Ichetucknee Mission (IMI)	10/24/2001	1400				21.6	7.51	320	0.37	51	6.6	3.9	0.5	6.2	9.5	182	0.2	0.50	<0.01	0.06
Troy (T)	10/25/2001	1045	3.00	4.2	1942-2001	21.5	7.35	359	0.48	61	7.0	2.8	1.0	5.9	11	202	<0.1	2.1	<0.01	0.04
Jackson-Blue (JB)	10/25/2001	1630	1.73	5.0	1929-2001	20.6	7.55	242	7.36	43	2.1	1.6	0.3	4.4	1.0	132	<0.1	3.1	<0.01	0.01
Jackson-Blue-(duplicate)	10/25/2001	1640	1.73			20.6	7.55	242	7.36	43	2.1	1.6	0.3	4.4	1.0	132	<0.1	3.1	0.01	0.01

Spring name	DOC	SiO_2	DS	Cal SI	Dol SI	δ^2H	$\delta^{18}O$	$\delta^{13}C$	$\delta^{15}N$
Wakulla (W)	0.9	11	270	0.00	-0.34	-15.9	-3.4	-13.5	7.9
Fannin (F)	0.8	6.1	320	-0.09	-0.99	-18.0	-3.6	-11.3	7.2
Manatee (M)	0.8	5.6	310	-0.07	-0.95	-18.6	-3.5	-11.3	6.0
Rainbow Springs Group									
Rainbow #6 (R6)	1.0	7.2	280	0.09	-0.43	-18.3	-3.8	-10.2	3.9
Rainbow #4 (R4)	0.8	6.0	230	0.32	0.04	-18.1	-3.7	-9.7	3.3
Rainbow #1 (R1)	0.8	6.5	130	-0.45	-1.39	-17.6	-3.7	-10.0	3.4
Bubbling (B)	1.0	6.6	260	-0.08	-0.80	-20.1	-3.8	-10.5	3.9
Ichetucknee Springs Group									
Ichetucknee Main (IMA)	0.6	6.9	240	-0.03	-0.73	-19.3	-3.9	-10.8	3.1
Ichetucknee Blue Hole (IBH)	0.4	9.2	260	0.06	-0.59	-17.5	-3.5	-11.8	3.8
Ichetucknee Mission (IMI)	0.9	12	270	0.00	-0.57	-17.5	-3.4	-12.3	6.2
Troy (T)	1.0	6.4	300	-0.04	-0.72	-18.1	-3.6	-11.8	6.7
Jackson-Blue (JB)	0.7	6.4	200	-0.15	-1.32	-20.4	-4.1	-12.0	2.6
Jackson-Blue-(duplicate)	0.8	6.4	200	-0.15	-1.32	-19.8	-4.2	-11.6	2.6

Concentrations of elements and species are in milligrams per liter unless otherwise noted; Q, 2001 spring discharge measurements in m^3/s (Scott and others 2002); T, temperature in degrees Celsius; SC, specific conductance in microsiemens per centimeter at 25 °C; DO, dissolved oxygen; DS, dissolved solids; DOC, dissolved organic carbon; NO_3-N represents the analysis of NO_2^- and NO_3^-, however NO_2^- concentrations in groundwater typically are below detection limits (Andrews 1994); Cal SI, calcite saturation index; Dol SI, dolomite saturation index; delta notation (δ) for the stable isotopes (^2H, ^{18}O, ^{13}C, and ^{15}N) are in per mil.

paths in the lower part of the UFA (Bush and Johnston 1988). The contribution of ground-water flow from local basins (Toth 1963) also is low given the subdued topographic relief and the relatively high aquifer permeability (Stringfield 1936; Faulkner 1973). However, contributions from local flow systems (sinking streams, sinkholes) increase substantially during high rainfall/recharge conditions, as indicated by elevated dissolved organic carbon concentrations in spring waters (Crandall and others 1999; Katz and others 2004). Although local variations in hydrogeology exist in each springshed, ground-water flow toward a typical first magnitude spring is shown conceptually in Fig. 2.

Detailed geographic and hydrogeologic descriptions of first magnitude springs and spring groups sampled in this study can be found in previous publications (Rosenau and others 1977; Jones and others 1996; Scott and others 2002). Based on an analysis of land-use data (1993), agriculture and forests generally were the dominant land-use types in designated springsheds (Table 2). Although different methods were used to characterize land use in 1977, the amount of forested land has decreased substantially from 1977 to 1993, but agricultural land use has remained relatively constant or increased slightly. Designated boundaries for springsheds are approximate and based on an analysis of regional potentiometric-surface data for the

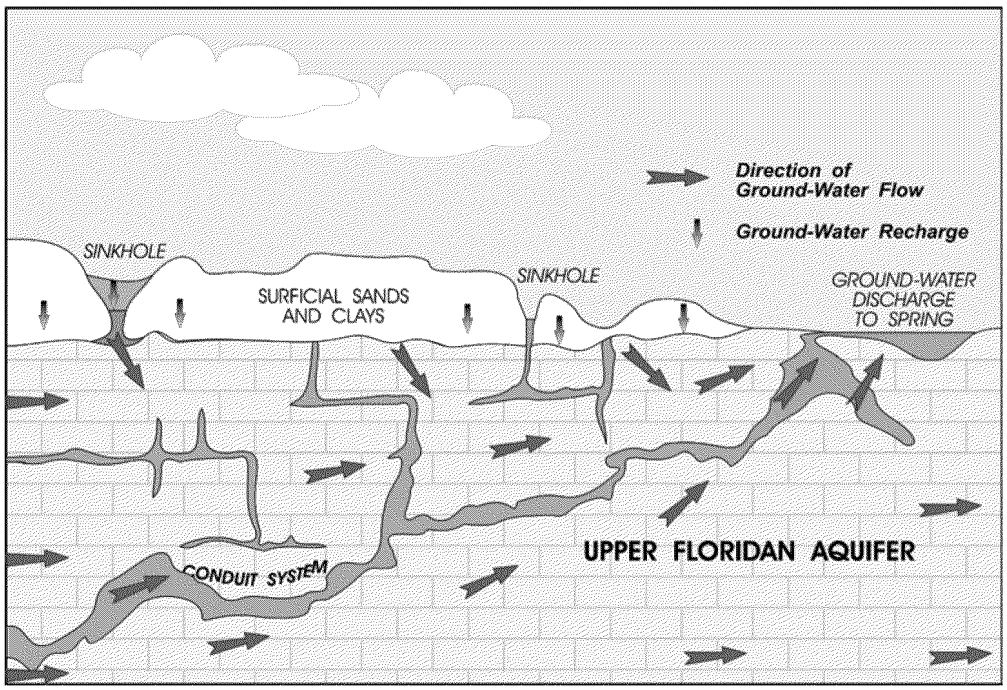

Fig. 2
Conceptualized groundwater flow patterns to large karstic springs in northern Florida

Table 2
Land-use percentages in designated springsheds based on 1993 and 1977 (in parentheses) land cover data. Percent of total agricultural land use that is cropland is shown for 1993 (1977 data could not be disaggregated)

Springshed	Land use type (%)						
	Approx. springshed area (km^2)	Total Agric.	Forests	Urban	Water and wetlands	Other	% Cropland relative to total agric. (1993)
Wakulla	380	14 (3)	45 (87)	31 (5)	9.7 (4.6)	0.3 (0.4)	24
Fannin	587	49 (43)	32 (48)	6.9 (1)	12 (7.1)	0.1 (0.9)	61
Manatee	975	22 (14)	43 (59)	6.6 (0.2)	28 (25)	0.4 (1.8)	42
Rainbow #6	126	58 (54)	15 (25)	21 (19)	1.4 (1.5)	4.6 (0.5)	56
Rainbow #4, and Bubbling	162	54 (40)	17 (44)	20 (14)	1.9 (1.5)	7.1 (0.5)	67
Rainbow #1	161	56 (36)	13 (33)	24 (27)	2.8 (3)	4.2 (1)	57
Itchetucknee	1.530	28 (26)	46 (60)	10 (3.4)	16 (10)	0 (0.6)	60
Troy	696	42 (45)	36 (51)	12 (0.8)	7.9 (1.9)	2.1 (1.3)	74
Jackson Blue	282	55 (60)	41 (38)	3.8 (0.5)	0.2 (1.3)	0 (0.2)	96

Agric., denotes agriculture. Land use statistics based on land classification 1993 land cover data, land-use classification based on Anderson and others (1976). Boundaries for springsheds as follows: Wakulla (Chelette and others 2002b); Fannin, Manatee, and Ichetucknee (W. Zwanka, 2003, written comm., Suwannee River Water Management District); Rainbow (Jones and others 1996); Troy (2000 potentiometric surface data, USGS, unpublished); Jackson Blue (Chelette and others 2002a)

UFA, for particular but not simultaneous time periods (Table 2). Springshed boundaries can expand or contract depending upon variations in groundwater levels, and recharge rates. Jones and others (1996) estimated that the groundwater basin for Rainbow Springs group ranged in size from approximately 1,670 km^2 at the end of a dry season (May 1995) to approximately 1,990 km^2 at the end of a wet season (September 1995).

Methods

Sample collection and analysis

Samples of water from the first magnitude springs were collected by lowering a positive displacement dual-piston pump head about 5–15 m into the spring vent. Water was pumped at approximately 0.06 L/s through 0.63-cm copper (refrigeration-grade) tubing. Sampling methodology varied somewhat depending on accessibility to the spring and site characteristics. Specific conductance, pH, dissolved oxygen, and temperature were measured in situ by using either a closed flow-through chamber or a multiprobe unit that was lowered directly into the spring vent. Field-sampling protocols, methods for chemical and isotopic analyses, are detailed by Katz and others (1999).

Dating spring waters

Anthropogenic activities, such as atmospheric testing of thermonuclear devices and various industrial processes, have released ^3H, CFCs, and SF_6, into the atmosphere in low but measurable concentrations over the past several decades (Fig. 3). Precipitation that incorporates ^3H, CFCs, and SF_6 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 the UFA. These dating methods presume that gas exchange between the unsaturated zone and air is fast, but that shallow groundwater remains closed to gas (CFCs, SF_6, ^3He) exchange after recharge (Schlosser and others 1989; Plummer and Busenberg 1999; Busenberg and Plummer 2000).

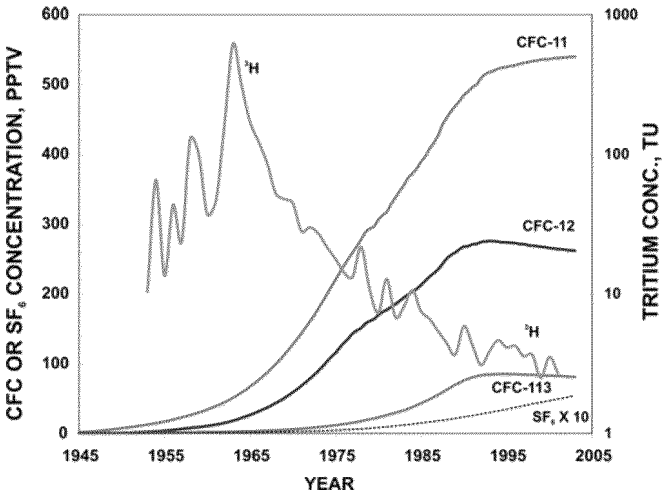

Fig. 3
Input history of atmospheric concentrations of CFCs and SF_6 (Plummer and Busenberg 1999: Busenberg and Plummer 2000), and tritium (^3H) concentrations in rainfall collected at the IAEA station in Ocala, Florida

^3H and $^3H/^3He$ age dating

Information about ground-water transit times can be obtained by comparing measured ^3H concentrations in groundwater with the long-term ^3H input function of rainfall measured at the International Atomic Energy Agency (IAEA) precipitation monitoring station in Ocala, Florida (Michel 1989; Fig. 3). Atmospheric weapons testing beginning in the early 1950s increased ^3H concentrations in rainfall in this area to a maximum of several hundred TU during the mid-1960s, followed by a nearly logarithmic decrease in concentrations to the present. ^3H concentration is reported in tritium units (TU), with 1 TU equal to 1 ^3H atom in 10^{18} hydrogen atoms. Combined measurements of ^3H and $^3He_{trit}$ (radioactive daughter product of tritium decay) define a relatively stable tracer of the initial ^3H input to groundwater, which can be used to calculate the $^3H/^3He_{trit}$ age from a single water sample (Schlosser and others 1988, 1989; Solomon and Sudicky 1991). $^3H/^3He_{trit}$ ages generally are not affected by contamination, sorption, and microbial degradation processes that can alter CFC or SF_6 concentrations (Plummer and others 1998; Busenberg and Plummer 2000). The distribution of ^3H and $^3He_{trit}$ can, however, be affected by hydrodynamic dispersion and mixing of different age waters (Solomon and Sudicky 1991; Reilly and others 1994). Non-tritiogenic ^3He, which generally is negligible in a shallow aquifer with predominantly young water, is determined from analyses of ^4He and Ne in the spring water sample (Schlosser and others 1988, 1989).
Water samples for the determination of $^3H/^3He_{trit}$, ^4He, and Ne were collected in pinch-off Cu tubes (10 mm diameter, 80 cm length, approximately 40 mL volume) while applying back pressure to the discharge from the sample tube to prevent formation of gas bubbles during sample collection. Samples were analyzed at the Noble Gas Laboratory of Lamont-Doherty Earth Observatory using quantitative gas extraction followed by mass spectrometric techniques (Schlosser and others 1989; Ludin and others 1998).

Chlorofluorocarbon and SF_6 age dating

The CFC and SF_6 dating techniques rely on the stability of these halogenated hydrocarbon and sulfur compounds (gases) in the hydrosphere, which has led to their effective use as tracers to age-date groundwater recharged during the past 50 years (Plummer and Busenberg 1999; Busenberg and Plummer 2000). If the CFC and SF_6 concentrations in the aquifer have not been altered by biological or geochemical processes, and are of atmospheric source, apparent ages can be evaluated.
Apparent ages for CFCs and SF_6 are estimated based on the equilibrium partitioning between recharging groundwater and the partial pressures of trichlorofluoromethane (CCl_3F, CFC-11), dichlorodifluoromethane (CCl_2F_2,

CFC-12), trichlorotrifluoroethane ($C_2Cl_3F_3$, CFC-113), and SF_6 in the troposphere or soil atmosphere (Fig. 3). Concentrations of CFCs and SF_6 in groundwater 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 N_2 and Ar 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 each CFC compound and SF_6 in the sample, calculated from their measured concentrations using solubility data for each compound, with the record of atmospheric partial pressures over North America at different times (Fig. 3). Input functions for CFCs and SF_6 were obtained from their atmospheric input curves, and assuming a ratio of summer-to-winter infiltration coefficient of 1.0. Concentrations of the three CFC compounds and SF_6 ideally provide four independent ages, which can be used as a crosscheck on the sampling and analytical methods, and used to evaluate mixing processes. Analytical procedures for CFCs and SF_6 are described by Busenberg and Plummer (1992 and 2000).

Estimating transit times of groundwater discharging from springs

Although analytical procedures are capable of determining very low concentrations of tracers in groundwater, the subsequent interpretation of ground-water age in complex aquifer systems is still fraught with a high degree of uncertainty. In many previous studies where CFCs, SF_6, and $^3H/^3He_{trit}$ have been used to date groundwater, flow systems were relatively well characterized and water samples typically were collected from narrow depth intervals. Extending tracer dating techniques to large springs in complex karst systems requires an analysis of several possible ground-water flow scenarios that might influence tracer concentrations in spring waters.

Apparent ages of groundwater that discharges from springs are based on the piston-flow assumption. The piston flow model (PFM) 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 groundwater. All flow lines are assumed to have similar velocities and hydrodynamic dispersion and molecular diffusion of the tracer are assumed to be negligible. For a PFM, the concentration of ^3H in a water parcel separated from the atmosphere since the time of recharge or entry into the ground-water system can be defined as (Zuber 1986):

$$C(t_i) = C_{in}(t_i - \tau) \exp(-\lambda\tau) \quad (1)$$

where $C(t_i)$ is the concentration at a given time, τ is the residence time of the water parcel in the aquifer, $C_{in}(t_i\text{-}\tau)$ is the input concentration at the time of recharge, and λ=0.05626 (the decay constant of ^3H). For nonradioactive tracers in the PFM, such as CFCs and SF_6, λ=0 and the concentration at any given time (t_i) is equal to the input concentration at time (t_i-τ).

Mean transit times of groundwater discharging from springs can be estimated for various mixing scenarios by using several lumped-parameter models (Maloszewski and Zuber 1982, 1996; Zuber 1986; Cook and Böhlke 1999). Lumped parameter models [the exponential model (EM), the combined exponential piston flow model (EPM), and the dispersion model (DM)] presume the following hydrologic conditions: (1) steady-state flow, (2) constant thickness of unsaturated zone, and (3) uniform recharge throughout the springshed. These three models have the same fitted parameter (mean transit time or mean-tracer age), and age distributions that are obtained from a response function, commonly presented as g(t) (Maloszewski and Zuber 1982). By fitting measured tracer concentrations to modeled output curves, the response function accounts for the distribution of ages at a sampling site (spring or well) and approximates observed data for an instantaneous injection of a conservative tracer into the entire recharge area (Zuber and others 2001). The EPM and DM each have an additional fitting parameter: the EPM contains (η), a ratio of the total volume to the volume with the exponential distribution of ages; the DM contains P_D, an apparent dispersivity of the aquifer system (Maloszewski and Zuber 1996). This term, which is unrelated to the actual dispersivity, represents the variance of the distribution of flow lines with different ages that converge at the sampled spring or well. FLOWPC (Maloszewski and Zuber 1996) is used to calculate mean transit times for the different lumped parameter models, and provides goodness of fit (Σ) estimates for each model (defined by the square root of differences between the observed data and the modeled curve, divided by the number of observations). In some cases where a reasonably good fit cannot be obtained, an additional fitting parameter (β) can be used that represents the ratio of a tracer-free flow component to the total spring flow.

In addition to the above models, binary mixing models (BM) are used to evaluate mixing scenarios involving relatively young water (recharged post-1995) or post-bomb recharge from the shallow part of the flow system with older water (decades or older) presumably from deeper parts of the UFA (Katz and others 2001). Mixtures with more than two end members could be present, but would require a large number of tracers to resolve the different components (Plummer and Busenberg 1999).

Results

Spring water chemistry

Spring waters are a Ca-HCO_3 type with generally low concentrations of dissolved solids (130–320 mg/L; Table 1). Spring waters tend to be oxic, with dissolved oxygen concentrations ranging from 0.4 (Ichetucknee Mission) to 7.4 mg/L (Jackson Blue) and low concentrations of organic carbon (0.4–1.0 mg/L). Saturation indices (SI) with respect to calcite and dolomite typically were slightly less than zero for most spring waters, indicating

that groundwater is slightly undersaturated or near saturation with respect to these two minerals that compose the limestone rock matrix of the UFA.

Nitrate-N concentrations in spring waters are elevated above background groundwater concentrations and range from 0.50 (Ichetucknee Mission) to 4.2 mg/L (Fannin Spring) (Table 1). Some of these variations may be attributed to differences in local land use (such as the amount of fertilized cropland in the springshed, input history of nitrogen, and proximity of N sources to the spring). Substantial increases in nitrate-N concentrations have occurred over the past several decades, based on historic nitrate concentration data for water samples collected from three springs in 1946 and from four springs in the early 1970s (Rosenau and others 1977). However, very limited nitrate data exist between these earliest samples and those from the early 1990s. Nitrate-N concentrations in 1946 water samples were 0.22, 0.38, and 0.45 mg/L for Ichetucknee, Manatee, and Fannin Springs, respectively. In 1972–1973, nitrate-N concentrations (mg/L) were already elevated in Troy (0.95) and Jackson Blue Springs (1.1), but much lower in Wakulla (0.25), and Rainbow Springs (0.16).

Dissolved nitrogen, argon, and neon

Concentrations of dissolved N_2, Ar, He, and Ne were used to estimate recharge temperatures and excess air (Heaton and Vogel 1981; Busenberg and others 1993; Stute and Schlosser 1999) and to evaluate potential for gas exchange in the spring systems. The slight increasing groundwater temperature gradient measured in spring waters from north to south is consistent with calculated N_2-Ar recharge temperatures (Fig. 4). Measured spring-water and N_2-Ar recharge temperatures agree reasonably well (±2°C) with long-term mean-annual air temperatures for Tallahassee (19.6°C), Mayo (19.8°C), and Ocala (21.6°C). Most waters that recharge the UFA, infiltrate through overlying sands and clayey sands, and have low excess air content (1.1 to 4.2 cm^3 STP/L in) based on N_2 and Ar concentrations (Fig. 4), which is typical for waters with relatively low amounts of excess air introduced during recharge (Busenberg and Plummer 2000). Quantities of excess air determined from the mass-spectrometric measurements of dissolved Ne are in close agreement, and within analytical uncertainties, and similar to quantities of excess air calculated from gas-chromatographic measurements of dissolved N_2 and Ar.

Nitrogen isotopes

$\delta^{15}N$ values of nitrate in spring waters ranged from 2.6‰ (Jackson Blue) to 7.9‰ (Wakulla Spring) and have no apparent relation to nitrate-N concentrations (Fig. 5). Most $\delta^{15}N$ values are below 6‰, which are similar to values observed elsewhere for ground-water nitrate recharged beneath cultivated land receiving artificial (inorganic) fertilizers (Gormly and Spalding 1979; Heaton 1986; Böhlke and Denver 1995; Fogg and others 1998; Kendall

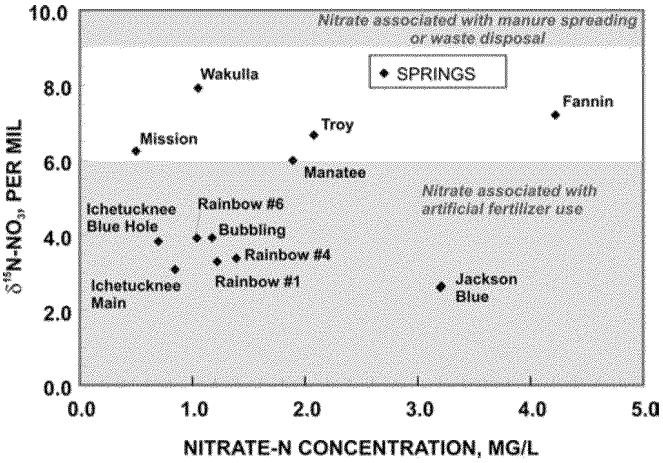

Fig. 5
Plot of $\delta^{15}N$-NO_3 and NO_3-N concentrations for groundwater and springs. Ranges of nitrogen isotope data for inorganic and organic nitrogen sources are derived from Böhlke (2002)

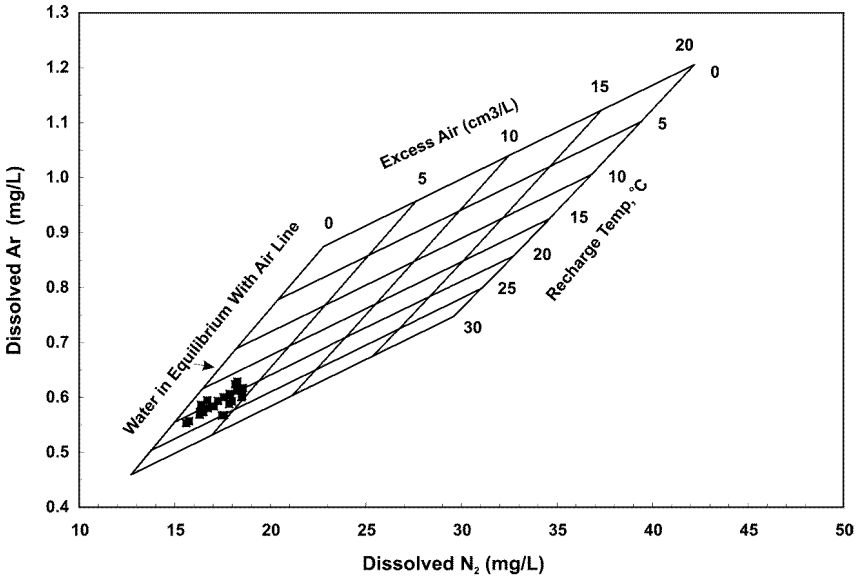

Fig. 4
Comparison of concentrations of dissolved N_2 and Ar in water from springs in relation to solubility equilibrium and excess air. The calculations assume an elevation of 10–30 m above mean sea level

Table 3
Concentrations of CFC-11, CFC-12, and CFC-113 in solution; and piston-flow model ages for sampled spring waters

Spring name	Amp. no.	Sampling date	Recharge temp (°C)	Recharge Elev. (m)	Calculated atmospheric mixing ratio (pptv)			Concentration in solution (pg/kg)			Piston-flow model age (yrs)		
					CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113	CFC-11 Age	CFC-12 Age	CFC-113 Age
Wakulla	1	10.22.01	17.7	10	4980	5720	1530	9565	2620	1190	Contam.	Contam.	Contam.
Wakulla	2	10.22.01	17.7	10	4960	5680	1530	9531	2604	1190	Contam.	Contam.	Contam.
Wakulla	5	10.22.01	17.7	10	5040	5640	1540	9694	2584	1200	Contam.	Contam.	Contam.
Fanning	2	10.22.01	25.0	10	718	733	144	996	251	77.9	Contam.	Contam.	Contam.
Fanning	4	10.22.01	25.0	10	717	717	123	994	245	66.6	Contam.	Contam.	Contam.
Fanning	6	10.22.01	25.1	10	731	650	174	1009	221	93.7	Contam.	Contam.	Contam.
Manatee	2	10.22.01	22.3	10	108	952	92.0	167	361	56.6	27.8	Contam.	Modern
Manatee	4	10.22.01	22.3	10	106	986	64.8	165	374	39.9	27.8	Contam.	13.8
Manatee	5	10.22.01	22.3	10	108	903	54.4	168	343	33.5	27.8	Contam.	15.3
Rainbow #6	2	10.23.01	21.8	10	349	542	132	556	210	83.3	Contam.	Contam.	Contam.
Rainbow #6	4	10.23.01	21.8	10	349	600	106	556	232	66.6	Contam.	Contam.	Contam.
Rainbow #6	5	10.23.01	21.8	10	350	541	100	557	209	62.8	Contam.	0.3	Contam.
Rainbow #4	2	10.23.01	21.2	10	227	522	113	370	207	73.4	15.8	7.8	Contam.
Rainbow #4	4	10.23.01	21.2	10	228	531	90.7	373	210	58.9	15.8	5.8	Modern
Rainbow #4	5	10.23.01	21.2	10	228	492	93.9	373	195	61.0	15.8	11.3	Contam.
Rainbow #1	2	10.23.01	20.6	10	163	420	84.5	273	170	56.6	22.8	15.3	8.3
Rainbow #1	3	10.23.01	20.6	10	164	369	89.4	276	150	59.8	22.3	18.3	Modern
Rainbow #1	4	10.23.01	20.6	10	160	404	76.5	269	164	51.2	23.3	16.3	11.8
Rainbow #1	5	10.23.01	20.6	10	157	387	53.7	264	157	36.0	23.8	17.3	15.3
Bubbling	2	10.23.01	20.9	10	236	581	90.1	391	233	59.4	14.8	Contam.	Modern
Bubbling	4	10.23.01	20.9	10	230	534	76.8	380	214	50.6	15.8	4.8	11.8
Bubbling	5	10.23.01	20.9	10	236	531	74.5	391	213	49.1	14.8	5.3	12.3
Itchetucknee Main	2	10.24.01	19.9	10	108	230	80.7	187	96.0	56.0	27.8	26.8	10.8
Itchetucknee Main	4	10.24.01	19.9	10	108	237	61.7	186	98.9	42.8	27.8	26.3	14.3
Itchetucknee Main	5	10.24.01	19.9	10	105	218	48.4	183	91.1	33.6	27.8	27.3	16.3
Itchetucknee Blue Hole	2	10.24.01	19.8	10	61.4	202	51.6	107	84.5	36.0	31.8	27.8	15.8
Itchetucknee Blue Hole	4	10.24.01	19.8	10	59.5	170	36.6	104	71.4	25.5	31.8	29.3	18.3
Itchetucknee Blue Hole	5	10.24.01	19.8	10	60.1	374	38.9	105	157	27.1	31.8	17.8	17.8
Ichetucknee Mission	2	10.24.01	20.0	10	43.7	180	46.7	75.4	75.0	32.2	33.8	28.8	16.3
Ichetucknee Mission	4	10.24.01	20.0	10	43.8	183	39.3	75.6	76.0	27.1	33.8	28.8	17.8
Ichetucknee Mission	5	10.24.01	19.9	10	41.9	190	41.5	72.7	79.4	28.8	34.3	28.3	17.3
Troy	2	10.25.01	22.0	10	50.5	256	102	79.6	98.1	63.9	33.3	25.3	Contam.
Troy	4	10.25.01	22.0	10	51.7	259	51.8	81.6	99.2	32.4	32.8	25.3	15.8
Troy	5	10.25.01	22.1	10	49.8	260	43.1	78.2	99.4	26.8	33.3	24.8	17.3

Jackson Blue	2	10.25.01	18.5	30	326	1,200.0	97.1	602	530	72.3	Contam.	Contam.	Contam.
Jackson Blue	4	10.25.01	18.5	30	316	1,140.0	83.8	583	506	62.4	Contam.	Contam.	9.8
Jackson Blue	5	10.25.01	18.5	30	316	1,180.0	70.4	584	520	52.4	Contam.	Contam.	12.8

Amp. denotes ampule number; pg/kg, picograms per kilogram; Contam., CFC concentrations in water samples are higher than values in equilibrium with 2001 atmospheric concentrations; NP, age calculation not possible due to likely contamination; yrs, years before sample date; Modern, age is close to zero

and Aravena 1999). δ^{15}N values above 6 and below 9‰ typically indicate a mixture of inorganic (fertilizers) and organic (human/animal wastes) sources of nitrogen. The higher δ^{15}N value for Wakulla Springs (7.9‰) is consistent with a mixture of inorganic and organic sources of N, as identified from detailed water-budget and nitrogen mass-balance calculations (Chelette and others 2002b). These calculations indicate that nitrate in groundwater discharging from Wakulla Springs originated from five main sources (in order of decreasing contribution): treated wastewater effluent; atmospheric deposition; wastewater residuals; fertilizers; and on-site waste disposal systems (based on a designated 388 km^2 contributing area in the Woodville Karst Plain). Limited historic data exist for nitrogen isotopes in spring waters; however, δ^{15}N values for samples collected from the Rainbow Springs group in 1995 are considerably lower than values reported herein for the 2001 samples, although both sets of data clearly indicate an inorganic source (fertilizers) of nitrogen. Nitrogen mass balance calculations for the Rainbow Springs group, indicated that pasture fertilization contributed the highest amount of nitrogen (3.6 million kg/yr) relative to animal wastes and other sources of nitrogen (Jones and others 1996). Water samples from Rainbow Springs 1, 4, and 6 in 1995 had δ^{15}N values of 0.7, 2.1, and 2.3‰, whereas in 2001, δ^{15}N values for these springs were 3.4, 3.3, and 3.9‰, respectively. Higher δ^{15}N values in 2001 (Rainbow Springs #1) may reflect a greater contribution from organic sources of nitrogen in groundwater discharging from these springs, or may be related to differences in analytical methods.

Denitrification can decrease nitrate concentrations and increase the δ^{15}N values of nitrate in an aquifer (Hübner 1986; Marrioti and others 1988). However, in these karstic spring systems, denitrification is assumed to be negligible given that spring waters are aerobic and contain very low dissolved organic carbon concentrations. Also, measured concentrations of N_2 and Ar in spring waters generally are consistent with atmospheric equilibration during groundwater recharge, with minor amounts of excess air added either during recharge or as a result of sampling methods. Thus, no direct evidence exists for excess N_2 (non-atmospheric) produced by denitrification (detection limit is around 0.5 mg/L) in spring water samples. However, denitrification at some time during the past within the aquifer system cannot be ruled out.

Apparent ages of spring waters

Apparent ages of spring waters ranged from about 5 to 34 years (Table 3) using CFC data. However, concentrations of CFC-11, CFC-12, and CFC-113 in spring-water samples generally did not yield concordant apparent ages, based on atmospheric equilibration data and the piston flow assumption. Most springs have concentrations of CFC-11, CFC-12, and CFC-113 within the range expected for air-saturated waters that are less than 40 years old; however, the apparent equilibration years are quite different for these compounds. Many of the spring waters have CFC-11, CFC-12 or CFC-113 concentrations that are higher than those possible for equilibrium with modern air

and are termed "contaminated" (Table 3). Two springs, Wakulla and Rainbow Springs #6, had concentrations of all three CFC compounds that exceeded atmospheric equilibration values and hence could not be dated using the CFCs. For most springs, apparent ages estimated using CFC-11 concentrations are substantially older than those obtained from CFC-12 and/or CFC-113 concentrations (Table 3). This likely indicates that CFC-11 was preferentially degraded (Plummer and Busenberg 1999), but if all three CFC compounds are presumed to be stable in the aquifer system, then the lack of concordance could result from complex mixtures of groundwater from shallow and deep flow paths that converge near the spring (discussed below).

SF_6 apparent ages ranged from 2.8 to about 15 years (Table 4) and generally were consistent with apparent ages derived from CFC-113 concentrations. SF_6 was highly contaminated in Troy Spring and Ichetucknee Blue Hole Spring, both areas where hydrologic studies introduced SF_6 as a tracer to measure groundwater velocities in nearby conduit systems in the early 1990s. Lower SF_6 apparent ages may result from a slight excess of SF_6 that could originate from low levels of contamination (Busenberg and Plummer 2000; Zoellmann and others 2001).

Tritium (^3H) concentrations measured in spring waters, 3.3 to 4.5 TU (Table 5), reflect the passing of the ^3H transient through the hydrologic system (Fig. 3). Prior to the advent of the atmospheric thermonuclear bomb testing in 1953, ^3H concentrations were on the order of 2 TU or less in this region (Thatcher 1962). As pre-bomb water would have a maximum concentration of 0.2 TU at the time of the study (2001), it is evident that the largest fraction of spring-water discharge is of relatively recent origin, and most likely from the period of the falling limb of the ^3H transient (Fig. 3). The ^3H data alone indicate that the spring waters could have apparent ages between 0 and about 25 years.

Apparent $^3H/^3He$ ages for spring waters ranged from 5 years (Manatee) to 34 years (Wakulla) (Table 5). $^3H/^3He$ apparent ages generally are much greater than those based on CFC-12, CFC-113, or SF_6 concentrations (Fig. 6). In contrast, CFC-11 apparent ages generally were greater than those derived from $^3H/^3He$, but as described above they likely reflect degradation of CFC-11. The greater $^3H/^3He$ apparent ages compared to those from CFC-12, CFC-113, or SF_6 may result from higher than expected concentrations of CFCs or SF_6 due to sources other than atmospheric equilibration at the time of recharge.

If $^3H/^3He_{trit}$ apparent ages have been significantly influenced by mixing, one would expect that measured $^3H+^3He_{trit}$ concentrations in spring waters would deviate greatly from the reconstructed original ^3H content (historical record of ^3H in rainfall is assumed to represent the ^3H concentration at the time of recharge). The ^3H record from the IAEA network station in Ocala, Florida, was used for this comparison and it was assumed that the local ^3H input history for each spring basin was closely approximated by this record (Fig. 7). Data are plotted for each spring water relative to the input history by assuming that the time of infiltration for each spring water is calculated

Table 4
Summary of SF_6 results for sampled spring waters using piston-flow model

Spring name	Sampling date	Time	T, °C	Excess Air (mL)	P(SF_6) (pptv)	Model SF_6 recharge date	Model SF_6 age years	Comments
Wakulla	10.22.01	1000	17.7	2.6	3.49	1995,0	6.8	
Wakulla	10.22.01	1000	17.7	2.6	2.89	1992,5	9.3	
Fannin	10.22.01	1430	25.1	3.9	2.36	1990,0	11.8	
Fannin	10.22.01	1430	25.1	3.9	2.38	1990,0	11.8	
Manatee	10.22.01	1700	19.7	1.9	4.55	1999,0	2.8	
Manatee	10.22.01	1700	19.7	1.9	2.54	1990,5	11.3	SS
Rainbow #6	10.23.01	1110	21.9	1.2	3.56	1995,0	6.8	BB
Rainbow #6	10.23.01	1110	21.9	1.2	3.19	1993,5	8.3	BB
Rainbow #4	10.23.01	1330	21.3	1.8	1.87	1987,0	14.8	
Rainbow #4	10.23.01	1330	21.3	1.8	2.04	1988,0	13.8	
Rainbow #1	10.23.01	1230	20.7	1.7	3.88	1996,5	5.3	
Rainbow #1	10.23.01	1230	20.7	1.7	1.55	1985,5	16.3	SS
Bubbling	10.23.01	1430	21.0	2.3	1.91	1987,5	14.3	
Bubbling	10.23.01	1430	21.0	2.3	1.83	1987,0	14.8	
Ichetucknee Main	10.24.01	930	20.1	2.5	2.86	1992,0	9.8	
Ichetucknee Main	10.24.01	930	20.1	2.5	2.84	1992,0	9.8	
Ichetucknee Blue Hole	10.24.01	1115	19.8	3.4	999	Contam.	Contam.	
Ichetucknee Blue Hole	10.24.01	1115	19.8	3.4	994	Contam.	Contam.	
Troy	10.23.01	1045	19.4	2.4	69.9	Contam.	Contam.	
Troy	10.23.01	1045	19.4	2.4	70.2	Contam.	Contam.	
Jackson Blue	10.25.01	1630	18.7	1.3	2.89	1992,5	9.3	
Jackson Blue	10.25.01	1630	18.7	1.3	2.91	1992,5	9.3	

P denotes partial pressure; pptv, parts per trillion by volume; Contam., sample contaminated by excess amounts of SF_6; SS, suspect sample due to possible loss of SF_6; BB, bottle broken during shipment or storage

Table 5
Summary of $^3H/^3He$ age data using piston-flow model for spring-water samples

Spring name	Sampling		Tritium					$^3H/^3He$	$^3H/^3He$
	date	Tritium TU	Error 1 sigma	δ^3He (%)	^4He (ccSTP/g)	Ne (ccSTP/g)	% ^4He terrigenic	age (yrs)	age error (yrs)
Wakulla	10.22.01	3.34	0.10	−52.44	2.027E−07	2.447E−07	69.3	33.5	0.72
Fannin	10.22.01	3.62	0.07	8.55	5.217E−08	2.135E−07	0.0	8.4	0.78
Manatee	10.22.01	3.57	0.07	−80.69	3.038E−07	2.137E−07	82.4	5.3	6.70
Rainbow #6	10.23.01	3.46	0.13	15.25	5.190E−08	2.080E−07	0.0	15.3	0.64
Rainbow #4	10.23.01	4.17	0.16	38.72	5.549E−08	2.255E−07	0.0	23.6	0.61
Rainbow #1	10.23.01	4.27	0.09	36.45	7.372E−08	2.943E−07	0.0	25.6	0.49
Bubbling	10.23.01	4.46	0.09	31.89	5.971E−08	2.392E−07	0.0	21.3	0.46
Ichetucknee Main	10.24.01	3.78	0.09	39.78	5.726E−08	2.313E−07	0.0	26.0	0.45
Ichetucknee Blue Hole	10.24.01	4.12	0.08	23.15	6.621E−08	2.404E−07	7.6	24.1	0.45
Ichetucknee Mission	10.24.01	3.76	0.09	1.17	7.570E−08	2.321E−07	22.4	23.4	0.51
Troy	10.25.01	3.40	0.14	25.44	5.657E−08	2.296E−07	0.0	21.0	0.68
Jackson Blue	10.25.01	4.11	0.15	−36.2	1.005E−07	2.095E−07	48.2	17.3	0.66

TU, tritium units; cc/STP/g, cubic centimeters of gas at standard temperature and pressure per gram of water; sigma, one standard deviation for analytical method

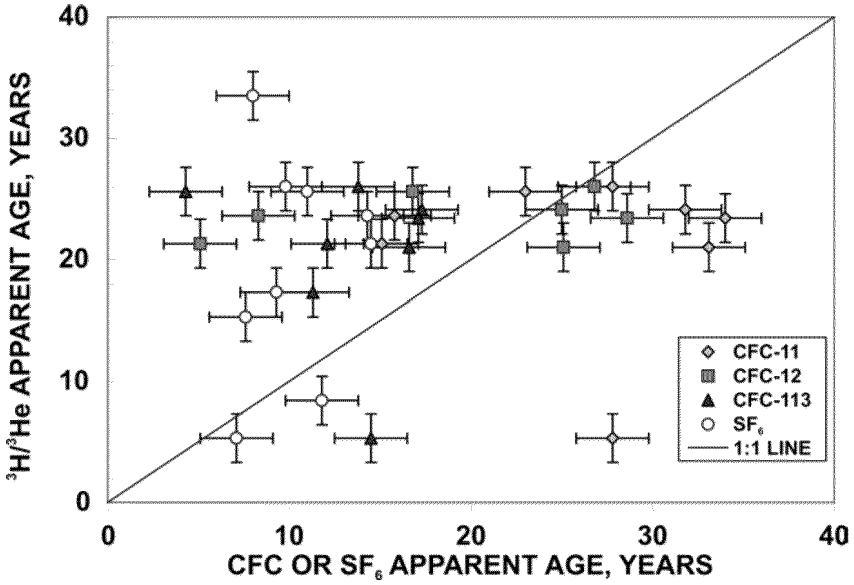

Fig. 6
Comparison of apparent ages of spring waters derived from concentrations of $^3H/^3He_{trit}$, CFC-11, CFC-12, CFC-113, and SF_6 and a piston-flow model

as the sampling date minus the $^3H/^3He_{trit}$ apparent age. Corresponding to these points on the time (x) axis, the "initial tritium," represents the sum of the measured ^3H and $^3He_{trit}$ concentrations (y-axis). If the water recharged the UFA with the initial ^3H contents as indicated by the input curve for Ocala rainfall, and subsequently was not affected by mixing or diffusive losses of ^3He, all initial ^3H points should fall on this ^3H input curve. With the exception of Wakulla Springs, the other 11 spring waters plot close to the input curve, even with the wide range of apparent ages (5–33 years) and similar ^3H contents. The overall agreement between the reconstructed initial ^3H with the rainfall input curve indicates that the $^3H/^3He_{trit}$ method generally is providing consistent age information, which could not be obtained from CFC, SF_6, or tritium data alone.

Mean transit times from historical ^3H records

Several possible ground-water mixing scenarios are investigated by comparing measured historical ^3H concentrations to theoretical output curves from various lumped parameter flow models. Historical ^3H data only exist for three springs sampled in this study: Troy (5 samples 1997–2001); Manatee (3 samples 1998–2001); and Wakulla (4 samples 1968, 1999–2001). Model parameters and results are listed (Table 6) for output curves from several plausible flow models that provided reasonably good fits to measured ^3H data (FLOWPC; Maloszewski and Zuber 1996). Relatively small ranges of mean transit times were found for Wakulla Springs (Fig. 8) and Manatee Springs for the various models; however, a larger range (20–70 years) is estimated for Troy Springs. Incorporating additional fitted parameters generally results in more

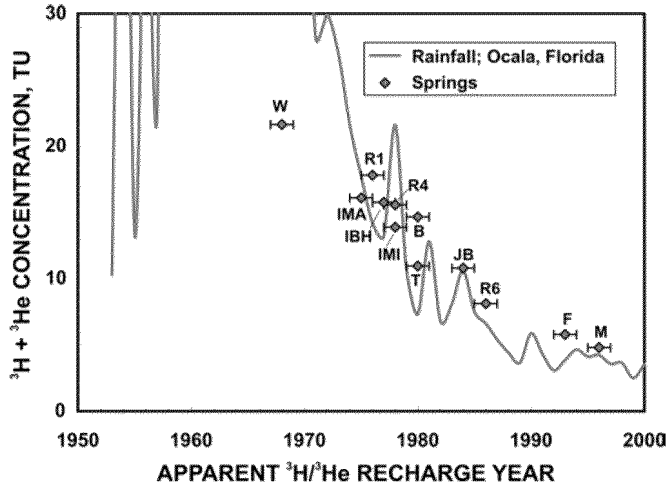

Fig. 7
Comparison of the measured tritium (^{3}H) and tritiogenic helium (^{3}He$_{trit}$) concentrations of spring samples and the ^{3}H input history recorded at the IAEA station in Ocala, Florida

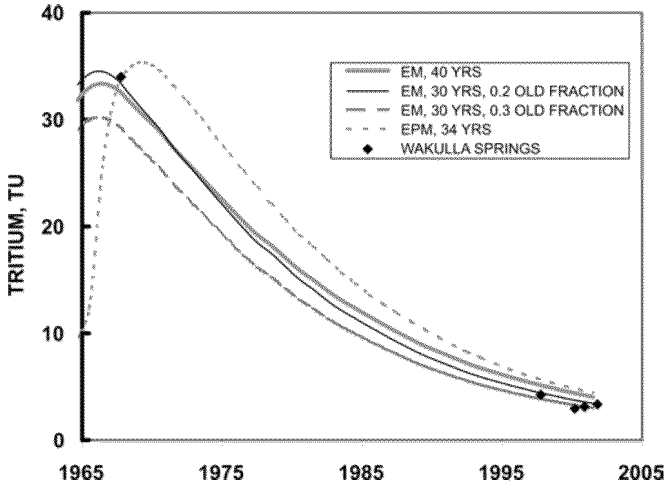

Fig. 8
Comparison of measured ^{3}H concentrations in water samples from Wakulla Springs during 1967 and 1998–2001 with theoretical curves determined from lumped-parameter models (EM, exponential model; EPM, exponential piston-flow model). Mean transit times are listed in legend after the model abbreviation followed by the ratio of a tracer-free flow component to the total springflow

ambiguous solutions; however, reasonably good fits were found between EM and EPM curves and measured ^{3}H data for a flow scenario that included a ^{3}H-free component (β=0.3), and estimated mean transit times were 20–30 years (Table 6). Several other output curves for other models provided reasonably good fits to measured ^{3}H data; however, they yielded transit times that were unrealistic, i.e. less than PFM apparent ages, which should represent the youngest possible age value (Zuber and others 2001).

Mean transit times using CFCs, SF_6, and $^3H/^{33}He_{trit}$

Ideally, multiple tracer data can provide a simultaneous evaluation of ground-water transit times and an age-frequency distribution for mixed waters (Böhlke 2002). However, 8 of the 12 sampled springs contain at least one CFC compound or SF_6 that likely originates from a non-atmospheric source of these compounds. In an attempt to include as much tracer data as possible and to reduce ambiguity of fitting tracer data with theoretical model curves, spring waters for which CFC and SF_6 data appeared to be unaffected by contamination are included and plotted against ^{3}H and ^{3}He$_{trit}$ data. The quantity ^{3}H/(^{3}H+^{3}He$_{trit}$), shown on the y-axis on Figs. 9 and 10, represents a surrogate water age. Values of ^{3}H/(^{3}H+^{3}He$_{trit}$) near zero correspond to apparently old waters (>50 years), whereas values approaching 1.0 correspond to young (recently recharged) waters (Böhlke 2002). Theoretical model curves in Figs. 9 and 10 were constructed for ground-water mean transit times that range from 1 year (upper right-hand side of plots) to 250 years (lower left-hand side of diagram).

Plots of CFCs or SF_6 data and ^{3}H/^{3}He data generally do not fit theoretical output curves for any one particular flow model. CFC-12 and ^{3}H/(^{3}H+^{3}He$_{trit}$) in spring waters generally plot above the theoretical model curves with the exception of one point that falls on the EM curve (Fig. 9a). Likewise, CFC-113 and ^{3}H/(^{3}H+^{3}He$_{trit}$) data show a similar

Table 6
Lumped parameter model results for 3H data

Spring name	Model	β	P_D	η	Σ	Mean transit time (years)
Troy	EM	0.3			0.134	30
	EM	0.0			0.117	70
	EPM	0.3		1.5	0.131	20
Manatee	EM	0.0			0.605	10
	EM	0.3			0.583	20
	EPM	0.3		1.5	0.565	20
	DM	0.0	0.5		0.589	10
Wakulla	EM	0.0			0.523	40
	EM	0.2			0.232	30
	EM	0.3			0.980	30
	EPM	0.0		1.1	0.605	34

β denotes ratio of tracer-free flow component to the total flow at the sampled spring; P_D, dispersion parameter; η, ratio of total volume to the volume with exponential distribution of ages; Σ, goodness of fit (see text for explanation)

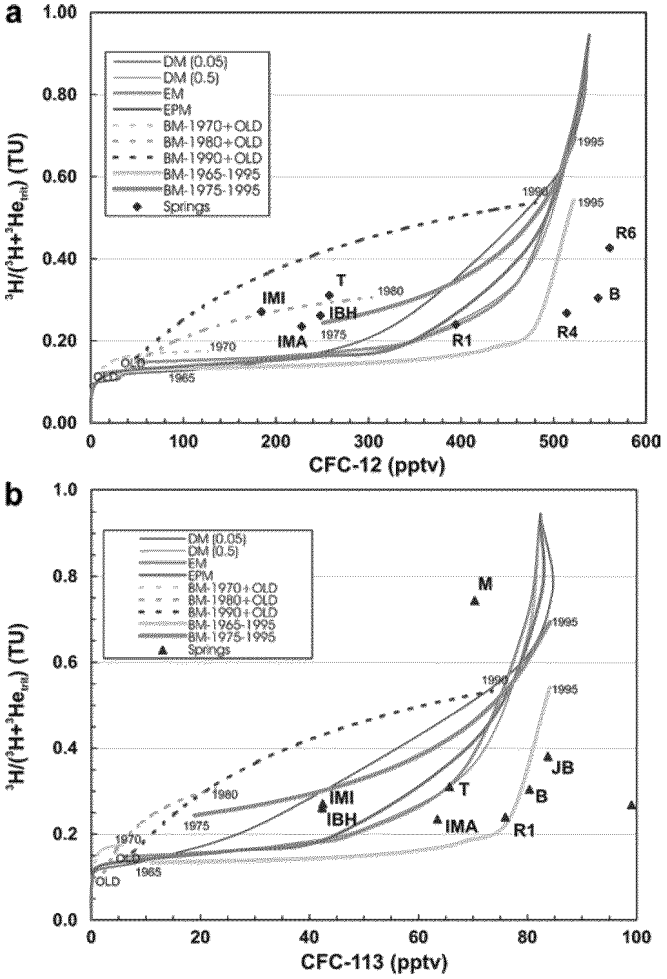

Fig. 9a,b
(**a**) Comparison of CFC-12 and $^3H/(^3H+^3He_{trit})$ concentrations to theoretical output curves for different flow scenarios using lumped parameter models [exponential piston flow (EPM), dispersion (DM), exponential (EM), and exponential model with 0.3 fraction of old water (<1940) with zero tritium, binary (BM)] for sampled spring waters. (**b**) Comparison of CFC-113 and $^3H/(^3H+^3He_{trit})$ concentrations to theoretical output curves for different flow scenarios using lumped parameter models for sampled spring waters. Abbreviations for spring names are listed in Table 1

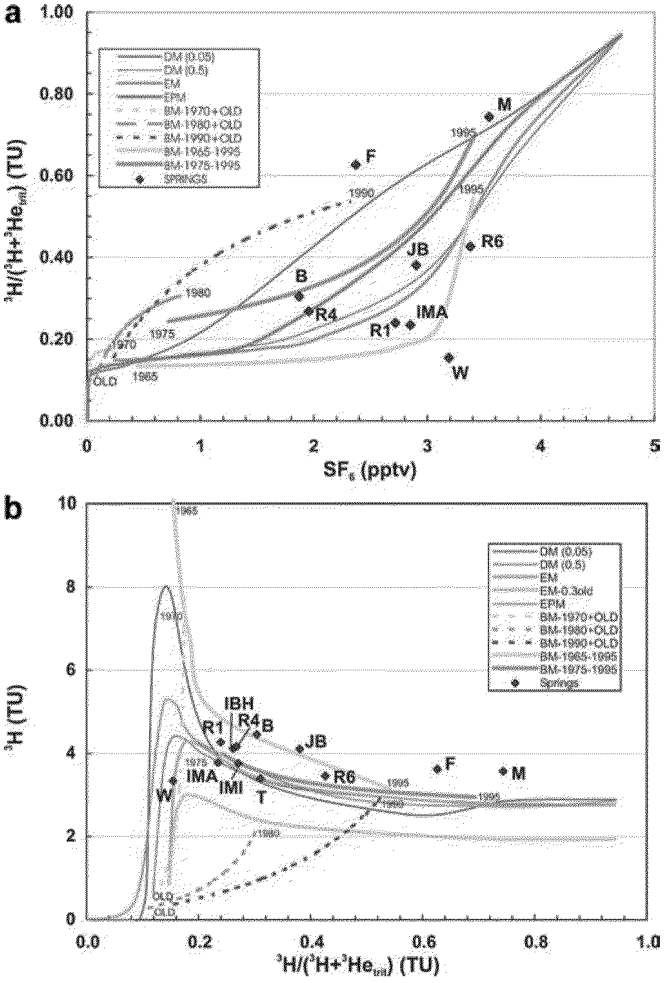

Fig. 10a,b
(**a**) Comparison of SF_6 and $^3H/(^3H+^3He_{trit})$ concentrations to theoretical output curves for different flow scenarios using lumped parameter models [exponential piston flow (EPM), dispersion (DM), exponential (EM), and exponential model with 0.3 fraction of old water (<1940) with zero tritium, binary (BM)] for sampled spring waters. (**b**) Comparison of ^3H and $^3H/(^3H+^3He_{trit})$ concentrations to theoretical output curves for different flow scenarios using lumped parameter models for sampled spring waters. Abbreviations for spring names are listed in Table 1

pattern with only one point that falls on the EM curve (Fig. 9b). SF_6 and $^3H/(^3H+^3He_{trit})$ data show a considerable amount of scatter and several points plot above the EM, DM, and EPM curves, and below the EM curve (Fig. 10a).

Presuming that ^3H and $^3He_{trit}$ concentrations are not affected by local contamination sources (as CFCs and SF_6 could be), measured ^3H and $^3H/(^3H+^3He_{trit})$ concentrations are reasonably consistent with an EM curve (Fig. 10b). However, flow scenarios represented by theoretical curves for DM and EPM overlap with measured ^3H and ^3He concentrations for mean transit times less than about 30 years (Figs. 9 and 10). With the somewhat limited dataset, it appears that the tracer data are not unique for any one particular flow scenario. However, since the EM curve provides a reasonably good fit to ^3H and $^3He_{trit}$ data for most springs, mean transit times (EM) can be estimated and range from 4 (Manatee Springs) to 40 years (Wakulla Springs).

Simple binary mixing scenarios also are considered for various end-member combinations of waters with different recharge dates. It is worth noting that none of the measured tracer concentration data plot close to BM curves that represent mixtures of young waters (recharged in 1970, 1980, or 1990) with an old end member containing pre-bomb (1950) contents of ^3H (0–2 TU) and zero concentrations of CFC-12, CFC-113, or SF_6 (Figs. 9 and 10). However, tracer concentration data are bounded by BM curves that represent mixtures of water recharged during the mid-1990s with water recharged either during the mid-1960s or 1970s (Figs. 9 and 10). Even though these simple mixing scenarios are non-unique, they indicate that spring waters likely contain mixtures of post-bomb waters, a scenario consistent with ^3H concentrations in spring

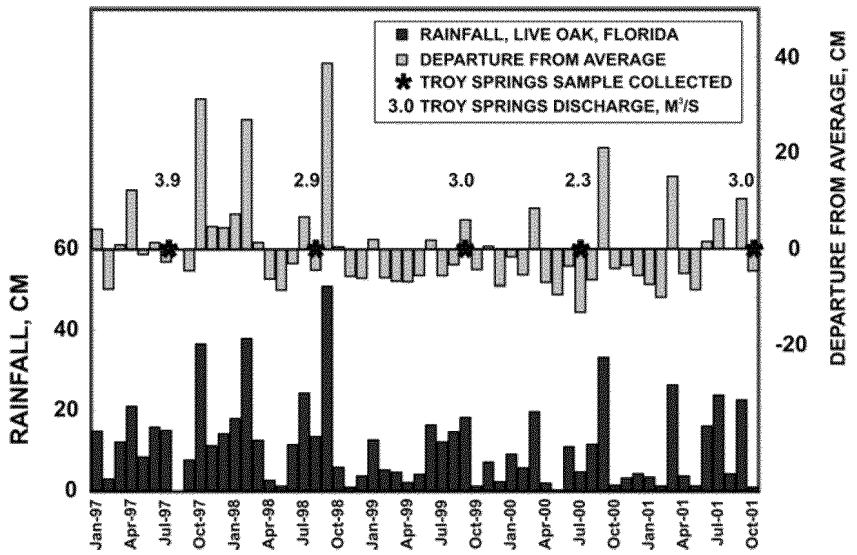

Fig. 11
Monthly rainfall and departures from normal rainfall for NOAA station in Live Oak, Florida. Also shown are dates of sample collection at Troy Springs and spring discharge at the time of sampling

waters that are higher than those of modern rainfall. In spring water samples where CFC contamination appears to be minimal (Manatee, Rainbow #1, Bubbling, Troy; and Ichetucknee Main, Blue, and Mission Springs), CFC data also are consistent with binary mixtures that contain varying fractions of young water (represented by recharge in 1995) and older water (represented by recharge in the early 1960s or the 1970s). For example, young water mixing fractions ranged from 20–45% for the three Ichetucknee springs, 50–70% for Rainbow #1, 80–84% for Bubbling, 47% for Troy, and 40–65% for Manatee Springs.

Age and variable springflow conditions

Water samples collected annually at Troy Spring during 1997–2001 provide additional insight about ground-water flow patterns to first magnitude springs over varying flow conditions. During 1997–2001, monthly rainfall amounts deviated substantially from long-term monthly averages (Fig. 11). Spring flow also varied during this period, although measurements are limited. Spring water samples collected in 1997–1998 were analyzed only for CFCs and ^{3}H (Katz and others 1999); but samples collected in 1999, 2000, and 2001 were analyzed for CFCs, SF_6, and $^{3}H/^{3}He$. During an extended drought period, October 1998–August 2000 (Fig. 11), apparent CFC ages (assuming no contamination from non-atmospheric sources) were higher in samples collected in 1999 and 2000 compared to those in 1997 and 1998 (Table 7). The slight decrease in CFC apparent ages for samples collected in 1998 relative to 1997 is within the range of age uncertainty (±1 year), given the variation in calculated recharge temperatures. However, CFC-12 apparent ages increased in spring water samples from 1999 and 2000. As mentioned previously, SF_6 concentrations are well above those expected for atmospheric equilibration and precluded age dating. $^{3}H/^{3}He_{trit}$ apparent ages also increased in samples collected in 2000 (23 years) compared to 1999 (19 years). It is likely that the greater apparent ages in samples from 2000 during the extended drought period (and associated lower springflow) result from mixtures that contained a higher contribution of older water (presumably from deep flow paths with longer mean transit times). A decrease in nitrate-N and dissolved oxygen concentrations during 1999 and 2000 compared to 1997–1998, also is consistent with a greater contribution of older groundwater to Troy Springs (Table 7). Similar trends (with only two to three samples) were observed for Manatee Springs and Little River Springs (spring flow 0.28–2.8 m^3/s) near Troy Springs. Denitrification is considered unlikely in these spring systems given that no excess N_2 was measured, that dissolved O_2 was present, and organic carbon is present in the aquifer in low amounts.

Discussion

Spring water age and chemistry

Spring water ages from a single "snapshot" in time may provide an opportunity to identify trends in groundwater chemistry over larger timescales (Aeschbach-Hertig and others 1998). Mean transit times and apparent ages ($^{3}H/^{3}He_{trit}$) of spring waters were tested for their degree of correlation (Spearman's Rho nonparametric statistic) with the concentrations of several chemical and physical variables (dissolved oxygen, pH, nitrate, major ions, silica, saturation indices with respect to calcite and dolomite, delta ^{13}C, and specific conductance). A statistically significant ($p<0.05$) inverse correlation was found between mean transit time (and apparent age) of groundwater and nitrate-N concentrations. A similar trend was observed for 24 springs with a range of flows in the Suwannee River basin (Katz and others 1999). Although the apparent age or transit time of groundwater discharging from springs does not necessarily represent the age of the nitrate contamination, it is of interest that the springs discharging younger waters tend to have higher nitrate concentrations, which suggests that the contribution of elevated nitrate concentrations is from more recent recharge. However, it is important to note that there are many other factors that

Table 7
Changes in tracer apparent ages and chemical constituents for Troy Spring, 1997–2001

Sample date	Discharge (m^3/s)	Apparent age (years)					NO_3-N (mg/L)	δ^{15}N-NO_3 (permil)	Diss. O_2 (mg/L)	Calcite SI	Dolomite SI	N_2 (mg/L)	Ar (mg/L)
		CFC-11	CFC-12	CFC-113	SF_6	$^3H/^3He$							
07.15.97	3.91	27	17	20	NS	NS	2.7	5.4	0.38	−0.20	−1.04	17.83	0.604
08.19.98	2.89	25	14	16	NS	NS	2.8	5.4	1.89	0.14	−0.38	19.06	0.605
09.16.99	3.00	27	22	Contam.	Contam.	19.4	2.0	5.5	0.83	−0.18	−1.02	18.91	0.614
07.28.00	2.32	34	26	28	Contam.	23.4	1.4	6.6	0.51	0.06	−0.52	18.26	0.604
10.25.01	3.00	33	25	16.6	Contam.	21.2	2.1	6.7	0.48	−0.04	−0.72	18.47	0.601

m^3/s, cubic meters per second; NS, not sampled; Contam., sample contaminated with non-atmospheric sources of chlorofluorocarbons or SF_6; SI, saturation index with respect to calcite or dolomite

affect nitrate concentrations in groundwater discharging from springs, such as the time distribution of nitrogen loading to the land surface, the proximity of nitrogen sources to a spring, and local climatic variations. A significant positive correlation was found between mean transit time (and apparent age) and silica concentrations. Although not statistically significant, there was a positive correlation between age and saturation indices with respect to calcite and dolomite. Higher silica concentrations and saturation indices with respect to calcite and dolomite with increasing age are consistent with chemical characteristics of older waters, as dissolution of calcite in limestone increases and approaches equilibrium SI values of zero or slightly above zero. No correlation between dissolved O_2 and age was found in this study, but was found for springs in the Suwannee River basin (Katz and others 1999).

Groundwater flow patterns: mixing of shallow and deep waters

The consistency of tracer data with exponential and simple binary mixing model curves indicate that ground-water discharge from sampled first magnitude springs is dominated by mixtures of groundwater recharged within the last four decades. Also, these mixtures may account for the similarity between tracer apparent ages and mean transit times for most spring waters. Despite the fact that dye-tracer studies indicate very rapid movement of solutes through conduit systems to springs (on the order of days to weeks; Wilson and Skiles 1988), ground-water mean transit times of 5 to 40 years reflect the slower movement of solutes through small openings in the aquifer matrix throughout the spring contributing area. Evidence from other tracer studies indicates that recent recharge (less than 1 year old) is likely a component of ground-water discharge from some springs, particularly under higher flow conditions. For example, based on ^{222}Rn and ^{18}O data, intrusion of river water into the unconfined UFA occurred in less than two days and accounted for more than 60% of spring flow during flood events on the Santa Fe River (Kincaid 1998). Also during high-flow conditions, elevated DOC concentrations were found in Little River Spring (near Troy Spring) and in the UFA adjacent to the Suwannee River (Crandall and others 1999) and in two springs in the Woodville Karst Plain (Katz and others 2004).

Springs discharge ground-water flow mainly from the shallow part of the aquifer, based on several chemical characteristics (low concentrations of dissolved solids, saturation indices with respect to calcite and dolomite that are less than 0, and well-oxygenated conditions). Groundwater flow toward Rainbow Springs and Silver Springs (another first magnitude spring in central Florida), was estimated to be a mixture of about 92% shallow water and 8% deep water, based on average sulfate concentrations near the top and bottom of the aquifer (Faulkner 1973). With the exception of Manatee Springs and Rainbow Springs #6, generally low sulfate concentrations (less than 20 mg/L) in spring waters (Table 1) indicate that spring flow is contributed mostly by groundwater from the

shallow part of the flow system. However, during baseflow, Wakulla Springs likely represents a mixture of water from shallow (35%) and deeper (65%) parts of the aquifer, based on ^{3}H and U isotope data (Osmond and others 1971).

It is important to note that apparent ages, mean transit times, and mixing fractions for groundwater discharging from springs are applicable for hydrologic conditions at the time of sampling. Spring-water samples generally were collected during base flow conditions and likely do not contain components of recent recharge that could be more significant during high-flow conditions. Recharge of recent origin from shorter ground-water flow paths and/or from sinkholes that are hydraulically connected to the UFA could contribute a much larger fraction of the total spring discharge at high flow (Katz and others 2004). Relative ages of representative spring waters in the Chesapeake Bay region appeared to be slightly younger on average during high-flow conditions than during low-flow conditions (Focazio and others 1998).

Tracers for dating springwaters in karstic systems

The relatively high degree of CFCs and SF_6 contamination from sources other than atmospheric equilibration was not entirely unexpected given that some CFC and SF_6 contamination was observed in previous studies (Katz and others 1999, 2001). One possible explanation is that low but above atmospheric concentrations of CFCs and SF_6 were introduced into the UFA with recent recharge that incorporated local sources of contamination (such as improper waste disposal of CFC refrigerants, electronic components and other materials containing SF_6). After the prolonged drought in northern Florida during 1998–2000, large amounts of rainfall were recorded one to two months prior to sampling in October 2001. For example, in August and September 2001, 44.7 cm of rain was recorded at Tallahassee, which is 11.4 cm more than the long-term average rainfall for those two months. CFC contamination in Wakulla Springs was noted in 2000 (unpublished data) during base-flow conditions; however, the large amount of rainfall in August and September 2000 may have introduced additional CFCs and SF_6 in recharge to the UFA. Likewise, in September 2001, 29.7 cm of rain was recorded at Ocala, Florida, near Rainbow Springs, and this amount was 15.8 cm above the long-term average rainfall for September. Similar increases were noted in September 2001 (9.29 cm, 2.43 cm above the long-term average) at a NOAA station near Fannin and Manatee Springs.

Groundwater residence times and nitrate contamination issues

It has been well documented that groundwater in karst systems is particularly vulnerable to nitrate contamination from agricultural activities (Coxon 1999). The two spring waters with the highest nitrate-N concentrations, Jackson Blue Spring (3.1 mg/L) and Fannin Spring (4.2 mg/L), have a very high percentage of agricultural land use in their designated springsheds (Table 2). In the Jackson Blue springshed, where cropland constitutes almost 97% of agricultural land use, the low δ^{15}N value (2.6‰) is consistent with nitrate originating from the application of inorganic nitrogen fertilizers. The higher δ^{15}N for Fannin Springs (7.2‰) likely is related to the lower percentage of cropland (about 60%) in the springshed and a higher contribution from organic sources of nitrogen (such as manure or septic tank effluent). Several factors likely control the highly complex relation between nitrate concentrations in groundwater discharging from large springs and various nitrogen sources, and include past and present land-use and waste-management practices, and hydrologic and climatic variability.

The apparent age (or the transit time) of spring waters may not necessarily represent the age of the nitrate contamination. To adequately describe the time scales of nitrate transport in the aquifer, a tracer should be transported into the aquifer in the same manner as the contaminant. Tritium enters the groundwater as a part of the water molecule, but nitrate is transported as a solute in recharge to the aquifer. However, because groundwater discharging from first magnitude springs is aerobic and low in dissolved organic carbon, denitrification is presumed to be negligible. Therefore, nitrate transport is assumed to be conservative and similar to ^{3}H and $^3He_{trit}$ transport at least in the saturated zone (Zoellmann and others 2001). Using countywide estimates of N inputs from various sources, nitrate trends in spring waters were consistent with fertilizer use during the past several decades (Katz and others 2001). It is possible that mean transit times for groundwater discharging from springs could be on the order of several decades, whereas the time period of nitrate contamination could be more recent depending upon the time distribution of nitrogen inputs to the surface, unsaturated zone processes, the proximity of nitrogen sources to the spring, and climatic variability. Given that ground water mean transit times can be as much as several decades, nitrate could persist in spring waters for tens of years due to the slow transport through the aquifer matrix and the prolonged input of nitrogen from multiple sources.

Elevated nitrate concentrations in sampled spring waters are directly affected by the application of inorganic fertilizers to their springsheds. Therefore, information on types, amount, and timing of fertilizer applied; and the quantity of nitrogen that leaches downward to the saturated zone following application would be beneficial in developing strategies for protecting groundwater from further degradation. Also, as land use in springsheds inevitably changes toward increased urbanization (such as in the Wakulla Springs basin), the siting of disposal sites for treated sewage effluent and to the density of septic tanks in spring contributing areas will require careful evaluation.

Acknowledgments This study was funded jointly by the Florida Department of Environmental Protection and the USGS. The authors thank J. Hannon and J.K. Böhlke for nitrogen isotope analyses; E. Busenberg, L.N. Plummer, J. Wayland, and G. Casile for CFCs and SF_6 analyses; P. Schlosser for H, Ne and He isotope analyses; and G. Casile, D. Munroe, K. Champion, and C. Tomlinson for water sampling assistance; W. Zwanka, G. Jones, A.

Chelette, A. Sepulveda and T.R. Pratt for preliminary delineation of springsheds; and L.N. Plummer, G. Phelps, and P.E. LaMoreaux for their comments that were helpful in revising this manuscript.

References

Aeschbach-Hertig W, Schlosser P, Stute M, Simpson HJ, Ludin A, Clark JF (1998) A $^3H/^3He$ study of groundwater flow in a fractured bedrock aquifer. Groundwater 36:661–670

Anderson JR, Hardy EE, Roach JT, Witmer RE (1976) A land use and land cover classification system for use with remote sensor data. U.S. Geological Survey Professional Paper 964, 28 pp

Andrews WJ (1994) Nitrate in groundwater and spring water near four dairy farms in north Florida 1990–93. U.S. Geological Survey Water-Resources Investigations Report 94–4162, 63 pp

Böhlke JK (2002) Groundwater recharge and agricultural contamination. Hydrogeology J 10:153–179

Böhlke JK, Denver JM (1995) Combined use of groundwater dating, chemical and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plain, Maryland. Water Resources Research 31:2319–2339

Burg A, Heaton THE (1998) The relationship between the nitrate concentration and hydrology of a small chalk spring, Israel. J Hydrology 204:68–82

Busenberg E, Plummer LN (1992) Use of chlorofluoromethanes (CCl_3F and CCl_2F_2) as hydrologic tracers and age-dating tools: example- the alluvium and terrace system of central Oklahoma. Water Resources Research 28:2257–2283

Busenberg E, Plummer LN (2000) Dating young groundwater with sulfur hexafluoride– Natural and anthropogenic sources of SF_6. Water Resources Research 36:3011–3030

Busenberg E, Weeks E, Plummer LN, Bartholemay RC (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 pp

Bush PW, Johnston RH (1988) Groundwater hydraulics, regional flow, and groundwater development of the Floridan aquifer system in Florida and parts of Georgia, South Carolina, and Alabama. U.S. Geological Survey Professional Paper 1403-C, 80 pp

Buzek F, Kadlecova R, Zak K (1998) Nitrate pollution of a karstic groundwater system. In: Isotope Techniques in the Study of Environmental Change, International Atomic Energy Agency Report 1024, Vienna, Austria, pp 453–464

Chelette AR, Pratt TR, Godin J (2002a) Florida Springs Initiative FY2001–2002 Final Report. Northwest Florida Water Management District Technical File Report 02–01, 6 pp

Chelette AR, Pratt, TR, Katz BG (2002b) Nitrate loading as an indicator of nonpoint source pollution in the lower St. Marks-Wakulla Rivers watershed. Northwest Florida Water Management District Water Resources Special Report 02–1, 138 pp

Cook PG, Böhlke JK (1999) Determining timescales for groundwater flow and solute transport. In: Cook PG, Herczeg AL (eds) Environmental Tracers in Subsurface Hydrology. Kluwer Academic Publishers, Boston, pp 1–30

Coxon C (1999) Agricuturally induced impacts. In: Drew D, Hotzl H (eds) Karst hydrogeology and human activities. Balkema, Rotterdam, pp 37–80

Crandall CA, Katz BG, Hirten JJ (1999) Hydrochemical evidence for mixing of river water and groundwater during high-flow conditions, lower Suwannee River Basin, Florida. Hydrogeology J 7:454–467

Davis JH (1996) Hydrogeologic investigation and simulation of ground-water flow in the Upper Floridan aquifer of north-central Florida and southwestern Georgia and delineation of contributing areas for selected city of Tallahassee, Florida, water-supply wells. U.S. Geological Survey Water-Resources Investigations Report 95–4296, 55 pp

Dietrich PG, Hebert D (1997) Regional discharge of a Triassic artesian karst aquifer: Mixing and age of spring waters in the Thuringian basin, Germany, estimated by isotope methods: In: Gunay G, Johnson AI (eds) Karst Waters and Environmental Impacts. Balkemia, Rotterdam, pp 221–229

Dincer T, Payne BR (1971) An environmental isotope study of the southwestern karst region of Turkey. J Hydrology 14:233–258

Faulkner GL (1973) Geohydrology of the Cross-Florida Barge Canal area with special reference to the Ocala vicinity. U.S. Geological Survey Water-Resources Investigations, 73–1, 117 pp

Focazio MJ, Plummer LN, Böhlke JK, Busenberg E, Bachman LJ, Powars DS (1998) Preliminary estimates of residence times and apparent ages of groundwater in the Chesapeake Bay Watershed, and water-quality data from a survey of springs. U.S. Geological Survey Water-Resources Investigations Report 97–4225, 75 pp

Fogg GE, Rolston DE, Decker DL, Louie DT, Grismer ME (1998) Spatial variation in nitrogen isotope values beneath nitrate contamination sources. Groundwater 36:418–426

Gormly JR, Spalding RF (1979) Sources and concentrations of nitrate-nitrogen in groundwater of the central Platte region, Nebraska. Groundwater 17:291–301

Grubbs JW (1998) Recharge rates to the Upper Floridan aquifer in the Suwannee River Water Management District, Florida. U.S. Geological Survey Water Resources Investigations Report 97–4283, 30 pp

Heaton THE, Vogel JC (1981) Excess air in groundwater. J Hydrology 50:201–216

Heaton THE (1986) Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: A review. Chemical Geology 59:87–102

Hornsby D, Ceryak R (1999) Springs of the Suwannee River Basin in Florida. Suwannee River Water Management District Report WR99–02, 178 pp

Hornsby D, Mattson R (1998) Surface water quality and biological monitoring network. Suwannee River Water Management District Annual Report WR-98–02

Hübner H (1986) Isotope effects of nitrogen in the soil and biosphere. In: Fritz P, Fontes JC (eds) Handbook of Environmental Geochemistry, vol. 2, The Terrestrial Environment B. Elsevier, New York, pp 361–425

Jones GW, Upchurch SB, Champion KM (1996) Origin of nitrate in groundwater discharging from Rainbow Springs, Marion County, Florida. Southwest Florida Water Management District, Ambient Ground-Water Quality Monitoring Program, 155 pp

Katz BG (1992) Hydrochemistry of the Upper Floridan aquifer in Florida. U.S. Geological Survey Water Resources Investigations Report 91–4196, 37 pp

Katz BG, Hornsby HD, Böhlke JK, Mokray MF (1999) Sources and chronology of nitrate contamination in spring waters, Suwannee River Basin, Florida. U.S. Geological Survey Water-Resources Investigations Report 99–4252, 54 pp

Katz BG, Hornsby HD, Böhlke JK (2001) Timescales for nitrate contamination of spring waters, northern Florida, USA. Chemical Geology 179:167–186

Katz BG, Chelette AR, Pratt TR (2004) Use of chemical and isotopic tracers to assess nitrate contamination and groundwater age, Woodville Karst Plain, USA. J Hydrology 289:36–61

Kendall C, Aravena R (1999) Nitrogen isotopes in groundwater systems. In: Cook P, Herczeg AL (eds) Environmental Tracers in Subsurface Hydrology. Kluwer, Boston, Ch. 9, pp 261–298

Kincaid TR (1998) River water intrusion to the unconfined Floridan aquifer. Environmental and Engineering Geoscience 4:361–374
Kincaid TR (1999) Morphologic and fractal characterization of saturated karstic caves. Ph.D dissertation, University of Wyoming, 174 pp
Kreitler CW (1975) Determining the source of nitrate in groundwater by nitrogen isotope studies. Univ. Of Texas, Austin, Texas Bur Econ Geol Rep Invest No 83, 57 pp
Ludin A, Weppernig R. Bonisch G, Schlosser P (1998) Mass spectrometric measurement of helium isotopes and tritium. Lamont-Doherty Earth Observatory, Palisades, NY, Technical Report 98–06
Maloszewski P, Zuber A (1982) Determining the turnover time of groundwater systems with the aid of environmental tracers 1. Models and their applicability. J Hydrology 57:207–231
Maloszewski P, Zuber A (1996) Lumped parameter models for the interpretation of environmental tracer data. In: Manual on Mathematical Models in Isotope Hydrology. IAEA-TECDOC 910, IAEA, Vienna, pp 9–50
Mariotti A, Landreau A, Simon B (1988) N isotope biogeochemistry and natural denitrification processed in groundwater: application to the chalk aquifer of northern France. Geochimica et Cosmochimica Acta 52:1869–1878
Michel RM (1989) Tritium deposition in the continental United States 1953–1983. U.S. Geological Survey Water Resources Investigations Report 89–4072, 46 pp
Osmond JK, Buie BF, Rydell HS, Kaufman MI, Wallick EI (1971) Uranium and tritium as natural tracers in the Floridan aquifer. Florida Water Resources Research Center Publication No. 14, University of Florida, Gainesville, 66 pp
Pittman JR, Hatzell HH, Oaksford ET (1997) Spring contributions to water quantity and nitrate loads in the Suwannee River during base flow in July 1995. U.S. Geological Survey Water-Resources Investigations Report 97–4152, 12 pp
Plummer LN, Busenberg E, Drenkard S, Schlosser P, Ekwurzel B, Weppernig R, McConnell JB, Michel RL (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 13:1017–1043
Plummer LN, Busenberg E (1999) Chlorofluorocarbons. In: Cook PG, Herczeg A (eds) Environmental Tracers in Subsurface Hydrology, Ch. 15, Kluwer Academic Press, Boston, pp 441–478
Plummer LN, Busenberg E, Böhlke JK, Nelms DL, Drenkard S, Michel RL, Schlosser P (2001) Groundwater residence times in Shenandoah National Park, Blue Ridge Mountains, Virginia, USA: a multitracer approach. Chemical Geology 179:93–111
Reilly TE, Plummer LN, Phillips PJ, Busenberg E (1994) The use of simulation and multiple environmental tracers to quantify groundwater flow in a shallow aquifer. Water Resources Research 30:421–433
Rosenau JC, Faulkner GL, Hendry CW Jr, Hull RW (1977) Springs of Florida. Florida Bureau of Geology Bulletin No. 31, 461 pp
Schlosser P, Stute M, Dorr H, Sonntag C, Munnich KO (1988) Tritium/^{3}He dating of shallow groundwater. Earth Planetary Science Letters 89:353–362
Schlosser P, Stute M, Sonntag C, Munnich KO (1989) Tritiogenic ^{3}He in shallow groundwater. Earth Planetary Science Letters 94:245–256
Scott TM, Means GH, Means RC, Meegan RP (2002) First magnitude springs of Florida. Florida Geological Survey Open File Report No. 85, 138 pp
Sepulveda N (2002) Simulation of ground-water flow in the intermediate and Floridan aquifer systems in peninsular Florida. U.S. Geological Survey Water-Resources Investigations Report 02–4009, 130 pp
Solomon DK, Sudicky EA (1991) Tritium and helium-3 isotope ratios for direct estimation of spatial variations in groundwater recharge. Water Resources Research 27:2309–2319
Stringfield VT (1936) Artesian water in the Florida peninsula. U.S. Geological Survey Water-Supply Paper 773-C, pp 115-195
Stute M, Schlosser P (1999) Atmospheric noble gases. In: Cook PG, Herczeg AL (eds) Environmental Tracers in Subsurface Hydrology. Kluwer, Boston, pp 349–377
Thatcher LL (1962) The distribution of tritium fallout in precipitation over North America. Bulletin International Association of Hydrological Sciences 7:48–58
Toth J (1963) A theoretical analysis of groundwater flow in small drainage basins. J Geophysical Research 68:4795–4812
Wilson WL, Skiles WC (1988) Aquifer characterization by quantitative dye tracing at Ginnie Spring, northern Florida. In: Proceedings of the Second Conference on Environmental Problems in Karst Terranes and Their Solutions. The Association of Groundwater Scientists and Engineers, Dublin, OH, pp 121-141
Zoellmann K, Kinzelbach W, Fulda C (2001) Environmental tracer transport (^{3}H and SF_6) in the saturated and unsaturated zones and its use in nitrate pollution management. J Hydrology 240:187–205
Zuber A (1986) Mathematical models for the interpretation of environmental radioisotopes in groundwater systems. In: Fritz P, Fontes JC (eds) Handbook of Environmental Geochemistry, Vol. 2: The terrestrial environment. Elsevier, Amsterdam, pp 1–59
Zuber A, Michalczyk Z Maloszewski P (2001) Great tritium ages explain the occurrence of good-quality groundwater in a phreatic aquifer of an urban area, Lublin, Poland. Hydrogeology J 9:451–460