

A Multitracer Approach for Assessing the Susceptibility of Ground-Water Contamination in the Woodville Karst Plain, Northern Florida

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INTRODUCTION

The unconfined Upper Floridan aquifer (UFA) is highly susceptible to contamination in the Woodville Karst Plain (WKP). Sinkholes, solution conduits, and other karst features provide direct pathways for the flow of surface water into the UFA, the source of potable water in southern Leon and Wakulla Counties (fig. 1). Water also can infiltrate rapidly through a relatively thin layer of highly permeable sands that mantle the underlying limestone that makes up the UFA.

Stream waters typically contain high concentrations of dissolved organic carbon (DOC) with considerable amounts of colloidal organic compounds, such as tannins and lignins. When surface water recharges the aquifer near sinkholes, tannins and lignins are transported into the ground water system. Tannins and lignins in ground water used for public drinking water can react with chlorine during the disinfection process resulting in the production of trihalomethanes and other disinfection byproducts (Rostad and others, 2000). Some of these byproducts are suspected to be mutagenic (Kronberg and Christman, 1989) and are difficult to remove from the water. Also, elevated levels of bacteria from surface water enter the aquifer predominantly during wet periods. Generally, these problems have not affected the water quality in large parts of the UFA mainly due to the high dilution factor (Katz and others, 1997) and sorption of reactive colloidal organic (DBP-precursor) compounds on the limestone matrix (Rostad and others, 2000).

Nonpoint sources of contamination, however, have the potential to degrade ground-water quality over large parts of the WKP. Fertilizers, septic-tank effluent, and atmospheric deposition can contribute large amounts of nitrate to ground water, as documented by previous studies in northern Florida (Fu and Winchester, 1994; Katz and others, 1999).

This study uses a multitracer approach to examine the susceptibility of the UFA to contamination, with particular emphasis on nitrate and its sources in ground and surface water in the WKP. Naturally occurring isotopes and other chemical tracers are used to assess sources of water and solutes, and age (residence time) of water in the aquifer. Information provided by naturally occurring tracers on the age and sources of contamination of ground water has been shown to be very useful in assessing the susceptibility of karst aquifers

to contamination from anthropogenic sources (Plummer and others, 1998; Cook and Bohlke, 1999).

DESCRIPTION OF STUDY AREA

The Woodville Karst Plain is characterized as a flat or gently rolling surface of highly porous quartz sand overlying Oligocene and Miocene age limestones (St. Marks Formation) that make up the UFA (Rupert, 1988). Limestone is generally within 8 meters of the surface in most of the karst plain. The top of the limestone has undergone extensive dissolution by chemically aggressive waters, and as a result, the karst plain contains numerous wet and dry sinkholes, natural bridges, and disappearing streams (Rupert and Spencer, 1988). Sinkholes in the area typically have formed as a result of dissolution, subsidence, and collapse of the limestone bedrock.

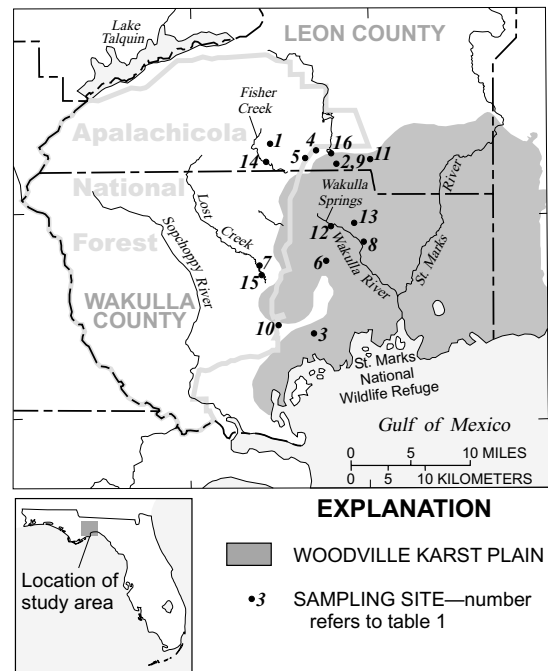


Figure 1. Study area showing location of sampled wells and streams in the Woodville Karst Plain.

Disappearing streams, such as Lost and Fisher Creeks, originate in the Apalachicola National Forest (Coastal Lowlands Physiographic Province), a flat, sandy part of western Leon and Wakulla Counties that

is underlain by thick clastic (clays and sands) deposits. The lowlands area, which reaches elevations of nearly 46 meters in northwestern Wakulla County, is characterized by shallow “bays” (densely wooded, swamplike areas) and numerous creeks with poorly defined channels that drain the bays (Rupert and Spencer, 1988). Fisher and Lost Creeks receive water from smaller creeks flowing out of bays and swamps, and both creeks flow in a southeasterly direction through narrow, meandering valleys and into sinkholes that are connected to the UFA.

Lost and Fisher Creeks are referred to as blackwater streams due to the high concentrations of tannins and lignins dissolved in the water. Tannins and lignin in river water originate from a spectrum of compounds that possess carboxyl and phenolic groups on their aromatic structures (Tissot and Welte, 1984). Tannins are typically concentrated in the bark and leaves of higher plants, such as cypress trees and bottomland hardwoods, which are present in the wetlands where Lost and Fisher Creeks originate. Lignin, a high-molecular weight polyphenol consisting of units constructed from phenylpropane, is located between the cellulose micelles of supporting tissues of plants (Tissot and Welte, 1984).

Land use (1995) in the WKP is predominantly forested (42%). Other land-use types in order of decreasing percentages of the total are as follows: water and wetland (35), agriculture and rangeland (11), transportation (9), and urban (3). Land-cover classification was based on remote-sensing techniques (Vogelmann and others, 1998). Most of the population in Wakulla County is concentrated in the WKP because most of the western half of Wakulla County and southwestern Leon County lies in the Apalachicola National Forest and is not open to development.

The climate of the study area is humid subtropical, with a mean annual temperature of 19.6 °C and a mean annual rainfall of 167 centimeters, for 1961-90, measured at the National Oceanic and Atmospheric Administration weather station at Tallahassee Regional Airport located in the northern part of the study area (Owenby and Ezell, 1992). The highest amount of monthly rainfall typically occurs during July and August, whereas the lowest typically occurs in April, October, and November.

Rainfall is the source of recharge to the UFA in the study area. Based on data from a recent study in which a calibrated ground-water flow model was developed for the UFA in Leon and Wakulla Counties and the surrounding area, recharge to the aquifer ranges from about 20 to 46 centimeters per year in the northern and southern parts of the study area, respectively (Davis, 1996). More recharge occurs in the southern part because there is very little direct surface runoff compared to the northern part. Recharge to the UFA probably occurs throughout the year, based on the close agreement between the mean

annual air temperature and ground-water temperatures measured during sampling.

METHODS

Several criteria were used to select ground- and surface-water sites (table 1). Wells were selected mainly from the western part of the WKP due to their proximity to sinking streams. Wells with a range of depths were selected to assess the vertical distribution and movement of contaminants in ground water. Water from Wakulla Springs was selected to represent ground-water discharge that is integrated both vertically and laterally from large parts of the UFA. McBride Slough is a discharge seep from the UFA. Lost and Fisher Creeks and Munson Slough are the largest streams that originate in wetland or highland areas outside of the WKP and flow directly into the UFA through sinkholes.

Table 1. Location of ground- and surface-water sites sampled in Woodville Karst Plain, well-construction information, and surface-water discharge

[Map No. is shown in fig. 1. Latitude and longitude are in degrees, minutes, seconds; well and casing depths measured in meters below land surface]

Map No.	Site name	Latitude	Longitude	Well depth	Casing depth	Casing diameter, centimeters
<i>Ground water sites</i>						
1	TPW-1	302008.47	842317.96	103.6	93.6	15
2	DSW-1	301840.88	841738.27	24.4	17.1	10
3	SCW-1	300618.00	841938.00	62.5	39.9	15
4	FPW-1	301939.00	841924.00	61.0	34.1	15
5	SPW-1	301905.00	842019.00	87.5	87.2	15
6	SHADE-1	301135.00	841834.00	98.1	54.9	15
7	AWC-1	301114.08	842412.23	39.3	22.9	15
8	GDW-1	301258.45	841524.41	14.6	6.4	10
9	DDW-1	301839.49	841738.07	47.9	34.4	10
10	WPR-1	300654.83	842236.93	36.6	10.7	15
11	WOOD-1	301859.59	841450.20	60.7	35.7	36
Map No.	Site Name	Latitude	Longitude	Discharge measurement date	Discharge, meters cubed per second	
<i>Springs or surface water sites</i>						
12	Wakulla Springs	301407.00	841810.00	10/16/97	8.779	
13	McBride Slough	301421.00	841612.00	9/11/97	0.484	
14	Fisher Creek	301848.00	842336.00	9/4/97	0.131	
15	Lost Creek	301033.00	842401.00	9/4/97	0.680	
16	Munson Slough below 8_mile Pond	301926.00	841808.00	9/11/97	0.002	

Water samples from streams, springs, and wells were collected in September and October 1997 using standard techniques (Koterba and others, 1995). Water samples from 10 wells were collected after a minimum of three well-bore volumes of water had been purged and readings of specific conductance, pH, dissolved oxygen (DO), and temperature had stabilized. A closed flow-through chamber was used to measure these properties to prevent contact of the ground water with the

atmosphere. At wells TPW-1, DSW-1, SCW-1, FPW-1, SPW-1, SHADE-1, and WOOD-1, water samples were collected from the existing pump and water-supply system upgradient of the pressure tank. Samples of water from Wakulla Springs were collected by lowering a positive-displacement, dual-piston pump about 15 meters into the spring vent. Water was pumped at about 0.06 liter per second through 0.63-centimeter copper (refrigeration grade) tubing. Samples of stream water were collected using a peristaltic pump, and sampling methodology varied somewhat depending on accessibility to the stream and site characteristics. Specific conductance, pH, DO, and temperature were measured at the time of sampling using either a mutiprobe unit that was lowered directly into the spring vent or streamwater column or a closed flow-through chamber.

Samples of ground water were collected for major element chemistry, DOC, environmental isotopes, and tritium/helium-3 ($^3\text{H}/^3\text{He}$). Samples of surface water were collected for the previously listed constituents with the exception of $^3\text{H}/^3\text{He}$. Samples for major ions were preserved in the field and analyzed in the U.S. Geological Survey laboratory in Ocala, Fla., using standardized procedures (Fishman, 1993). Concentrations of tannin and lignin in river water and ground water were measured in the field using a colorimetric procedure (tyrosine method) with a portable spectrophotometer (Hach Company, 1989). This method detects all hydroxylated aromatic compounds, including tannin, lignin, phenol and cresol (Kloster, 1974). Results are expressed as milligrams per liter tannic acid, with a method detection limit of about 0.1 mg/L and a 1 standard deviation (σ) precision of 0.1 mg/L.

The stable isotopes of oxygen ($^{18}\text{O}/^{16}\text{O}$), hydrogen ($^2\text{H}/\text{H}$), carbon ($^{13}\text{C}/^{12}\text{C}$), and nitrogen ($^{15}\text{N}/^{14}\text{N}$) were used to determine the origin of water and solutes, and to identify biogeochemical processes that control the chemical composition of ground water. Standard delta (δ) notation (Gonfiantini, 1981) was used for the stable isotopes, $^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/\text{H}$, $^{13}\text{C}/^{12}\text{C}$, and $^{15}\text{N}/^{14}\text{N}$. Oxygen- and hydrogen-isotope results are reported in per mil relative to Vienna Standard Mean Ocean Water and are normalized on scales such that the oxygen and hydrogen isotopic values of Standard Light Antarctic Precipitation are -55.5 and -428 per mil, respectively (Coplen, 1994). The 2σ precision of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ results is 0.2 and 1.5 per mil, respectively. The analysis of $\delta^{13}\text{C}_{\text{DIC}}$ of dissolved inorganic carbon (DIC) in ground and surface water involved the precipitation of the DIC using $\text{NH}_4\text{OH-SrCl}_2$, followed by filtering, drying, and acidifying the SrCO_3 precipitate to produce CO_2 , which was analyzed by mass spectrometric methods (Gleason and others, 1969). The 2σ precision for the analytical procedure is 0.2 per mil (Coplen, 1994). Values of $\delta^{13}\text{C}$ of

DIC are reported relative to Vienna Pee Dee Belemnite (Coplen, 1994).

Tritium (^3H) and its daughter product of radioactive decay, tritiogenic ^3He , were used to estimate the age of ground water 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, Fla., (Michel, 1989). The term "age" used in this paper is actually an apparent age because it could be affected by mixing or other physical processes. This age represents the time elapsed since recharge and isolation of the recharge water from the modern atmosphere. Combined measurements of ^3H and ^3He , define a relatively stable tracer of the initial ^3H input to ground water, which can be used to calculate the $^3\text{H}/^3\text{He}$ age from a single water sample (Schlosser and others, 1988, 1989). The $^3\text{H}/^3\text{He}$ age is based on a He-isotope mass balance used to calculate the amount of tritiogenic and nontritiogenic ^3He in the sample. Nontritiogenic ^3He , which generally is negligible in a shallow aquifer with predominantly young water, is corrected for by measuring the concentrations of ^4He and neon in the water sample and assuming solubility equilibrium with air at the water temperature measured during sampling (Schlosser and others, 1988, 1989). $^3\text{H}/^3\text{He}$ ages generally 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 ^3He can, however, be affected by hydrodynamic dispersion and mixing of different age waters (Solomon and Sudicky, 1991, Reilly and others, 1994).

Ground-water samples for $^3\text{H}/^3\text{He}$ analyses were collected in pinch-off copper tubes (10 millimeter diameter, 80 centimeter length, about 40-milliliter volume) for the determination of $^3\text{H}/^3\text{He}$, ^4He , and Ne (neon) while applying back pressure to the discharge from the sample tube to prevent formation of gas bubbles during sample collection. These samples were analyzed at the Noble Gas Laboratory of Lamont-Doherty Earth Observatory, Palisades, N.Y., using quantitative gas extraction followed by mass spectrometric techniques (Schlosser and others, 1989). Surface-water samples were collected and analyzed for ^3H according to methods presented by Michel (1989). Tritium activity is reported in tritium units (TU) (1 TU is equal to 1 ^3H atom in 10^{18} hydrogen atoms and 7.1 disintegrations per minute per gram of water) with a 1σ precision of <10% for waters containing >2 TU.

CHEMICAL AND ISOTOPIC COMPOSITION OF GROUND AND SURFACE WATER

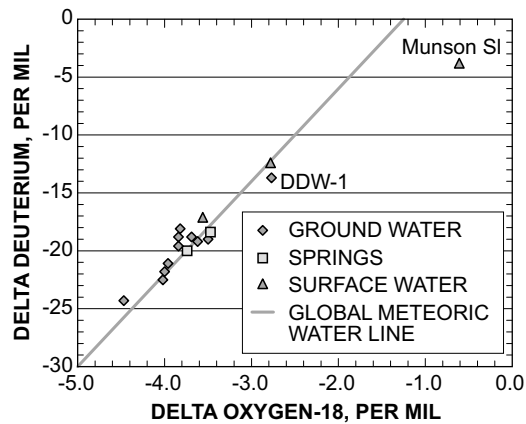
Water from the UFA in the WKP is a calcium-bicarbonate type with generally low dissolved-solids (DS) concentrations ranging from 130 to 274 mg/L (table 2). Water from WOOD-1 had a higher DS concentration of 432 mg/L; this public-supply well draws ground water from beneath residential land that could contribute elevated concentrations of solutes. DO concentrations were highly variable in shallow and deep parts of the aquifer; water from three of six deep wells (depths >60 meters) contained low DO concentrations, typically >0.5 mg/L. Saturation indices of water with respect to calcite (calcite SI) and dolomite (dolomite SI) (table 2) from the shallow part of the flow system and Wakulla Springs typically were <0, indicating that the waters generally are slightly undersaturated with these two minerals, which make up the limestone matrix of the UFA. Water from deeper parts of the aquifer tend to have higher saturation indices with respect to calcite and dolomite, possibly indicating the longer residence time of water in the ground-water flow system.

DOC concentrations in surface water ranged from 11 to 31 mg/L (table 2); however, DOC concentrations in ground water typically were much lower than in surface water. Water samples from six wells, Wakulla Springs, and McBride Slough were equal to or <0.6 mg/L (analytical method reporting limit is 0.1 mg/L) (table 2). Water samples from DSW-1, SCW-1, SHADE-1, AWC-1, and DDW-1, however, contained DOC concentrations above 1 mg/L, indicating that surface water containing elevated DOC concentrations probably is locally recharging the aquifer system and mixing with ground water. The fraction of colloidal organic carbon of the DOC was high in Fisher Creek (23%) and Lost Creek (30%), but was considerably lower in ground-water samples from DSW-1 (1.6%) and TPW-1 (3.6%) (Rostad and others, 2000). The large reduction in DOC and its colloidal fraction from surface water to ground water likely indicates significant biogeochemical attenuation of organic compounds by biodegradation, sorption, precipitation, and/or dilution processes (Rostad and others, 2000).

Delta $^{13}\text{C}_{\text{DIC}}$ values of ground water, which ranged from -16.8 to -12.8 per mil (table 2), are higher (enriched) relative to water from Fisher and Lost Creeks (-24.7 per mil). The $\delta^{13}\text{C}_{\text{DIC}}$ values of water from the UFA likely represent a mixture of DIC from two sources: CO_2 respired by microorganisms from the oxidation of organic carbon in the unsaturated zone (Deines, 1980), and dissolution of calcite in the aquifer matrix. Calcite dissolution in the aquifer is indicated by the: (1) substantial increase in $\delta^{13}\text{C}_{\text{DIC}}$ in water from the UFA compared to water from Fisher and Lost Creeks

and the surficial aquifer (Katz and others, 1997), (2) large increase in the saturation index of ground water with respect to calcite compared to that of water from Lost and Fisher Creeks (table 2), and (3) large increase in pH and calcium and bicarbonate concentrations (table 2).

Differences in values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in ground water and stream water provide information about the source(s) of water and possible mixing of ground water with surface water. Stable H and O isotopic values for most ground-water samples plot along the global meteoric water line (Craig, 1961), as do samples of rainfall from northwest of the study area (Katz and others, 1997), indicating that they are not affected by evaporation (fig. 2). $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for water from DDW-1 were slightly enriched relative to other ground-water samples and indicate that mixing with surface water affected by evaporation is likely. Values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were similar for water from Fisher and Lost Creeks and most ground-water samples, indicating that shallow ground-water discharge is a major contributor to streamflow. In contrast, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of water from Munson Slough (table 2) were highly enriched relative to most ground-water samples and were displaced to the right of the global meteoric water line, indicating that Munson Slough receives water that has been affected by evaporation. Similarly enriched values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were found for other ground- and surface-water sites in the northern part of the WKP, which were attributed to evaporation or mixing with surface water with an enriched isotopic signature (Katz and others, 1997).



from 0.22 to 0.71 mg/L, whereas water from other deep wells and wells open to shallow zones in the UFA had nitrate-N concentrations <0.02 mg/L (table 2). Background nitrate-N concentrations in ground water from northern Florida were <0.05 mg/L (Katz, 1992; Maddox and others, 1992). Water from Wakulla Springs and McBride Slough had elevated nitrate-N concentrations of 0.89 and 0.47 mg/L, respectively.

Nitrate concentrations in ground water were related to concentrations of DO and DOC. There was a statistically significant ($p < 0.05$) correlation (Spearman's Rho nonparametric statistic) between nitrate-N and DO concentrations, and a significant ($p < 0.001$) inverse correlation between nitrate and DOC concentrations.

Nitrate-N concentrations were at or below 0.02 mg/L in water samples from Lost Creek, Fisher Creek, and Munson Slough (table 2). Ammonium-N concentrations were higher in surface-water samples compared to ground-water samples and ranged from 0.03 to 0.28 mg/L. Two ground-water samples had elevated ammonium-N concentrations, TPW-1 and DDW-1. Both sites likely have direct connections to surface water, based on elevated DOC concentrations. Low concentrations of nitrate-N in surface water indicate that sinking streams are unlikely to contribute to the elevated concentrations of nitrate in ground water in the WKP.

$\delta^{15}\text{N-NO}_3$ values in ground water were variable, ranging from 1.7 to 13.8 per mil (table 2). Some of these variations can be attributed to local differences in land use and nitrate sources. For example, well WPR-1 is located in a county park adjacent to a turf-grass field, which receives artificial fertilizer. Water from this well had a $\delta^{15}\text{N-NO}_3$ value of 1.7 per mil, which was similar to values observed elsewhere where nitrate in ground water is recharged beneath cultivated land receiving artificial fertilizers (Heaton, 1986; Kendall and Aravena, 1999). In contrast, water from well GDW-1 had a $\delta^{15}\text{N-NO}_3$ value of 13.8 per mil, which is indicative of human or animal waste sources that commonly yield ground-water nitrate with $\delta^{15}\text{N}$ values about 8 per mil or more (Heaton, 1986; Kendall and Aravena, 1999). GDW-1 is a shallow residential well that is located near a septic-tank system. Water from other wells and Wakulla Springs had $\delta^{15}\text{N-NO}_3$ values of 6.8 to 8.9 per mil (table 2), which indicate that nitrate likely originates from a mixture of inorganic and organic sources of nitrogen. Delta $^{15}\text{N-NO}_3$ values could not be determined in ground-water samples from six sites because nitrate-N concentrations were near or below analytical detection limit.

Denitrification can decrease the concentrations and increase the $\delta^{15}\text{N}$ values of nitrate in ground water (Korom, 1992). Denitrification, however, is unlikely in shallow ground water from the WKP due to DO concentrations >1 mg/L in most ground-water samples.

Conversely, water from deeper wells had lower DO concentrations (generally <0.5 mg/L) and denitrification could not be ruled out given the low DO concentrations and elevated concentrations of DOC (table 2).

AGES AND RESIDENCE TIMES OF WATER FROM THE UPPER FLORIDAN AQUIFER

Tritium/ ^3He measurements, error estimates, and $^3\text{H}/^3\text{He}$ ages for water samples from the UFA are summarized in table 3. Ground-water ages ranged from 5.2 years (DSW-1) to 25.5 years (AWC-1). For Wakulla Springs, the apparent age (38.7 years) more realistically represents the average residence time of ground water that discharges from the UFA because springs integrate water from converging flow paths of varying age. The relatively small 1σ variations in age represent analytical uncertainty (table 3).

Other factors could result in additional uncertainty in age estimates. For instance, $^3\text{H}/^3\text{He}$ ages were calculated using water temperatures measured at the time of sampling (table 2) to calculate concentrations of He and Ne in water in solubility equilibrium with air. Variations in recharge temperature (21 °C) of about ± 2 °C (mean annual air temperature is 19.6 °C) would not significantly affect the calculated ground-water age (Plummer and others, 1998). The calculated age, however, is more sensitive to the fraction of terrigenous He (from excess air and decay of U-series radionuclides). Some ground-water samples contained elevated values of terrigenous ^4He (table 3); for instance, the percent of terrigenous ^4He of the total ^4He was 83.6% for water from Wakulla Springs, 26% from SCW-1, and 47% from SHADE-1. With large fractions of terrigenous helium, the $^3\text{He}/^4\text{He}$ ratio of the terrigenous He, R_{terr} , must be accurately known. Nonterrigenous ^3He resulting from terrigenous sources were adjusted using an R_{terr} of 2×10^{-8} (Schlosser and others, 1988). If this ratio were allowed to vary over 2 orders of magnitude (somewhat unlikely, but useful for illustrating estimates of age uncertainty), ground-water ages would be younger by <5 years for SHADE-1, SCW-1, SPW-1, and FP-1 using $R_{\text{terr}} = 2 \times 10^{-7}$ and there would be no appreciable age difference for $R_{\text{terr}} = 2 \times 10^{-9}$. For ground water discharging from Wakulla Springs, the minimum age would be 21 years ($R_{\text{terr}} = 2 \times 10^{-7}$), compared to 38.7 years using ($R_{\text{terr}} = 2 \times 10^{-8}$ and 2×10^{-9}). The large amount of terrigenous He at Wakulla Springs may result from the use of He-mixtures of gas used by scuba divers for cave exploration.

Since the $^3\text{H}/^3\text{He}$ dating method is independent of the mixing fractions of young surface water with ground water (Plummer and others, 1998) or younger ground water that mixes in the well bore during pumping, the $^3\text{H}/^3\text{He}$ age represents the age of the youngest fraction in the mixture. Consequently, this apparent age

(or average residence time in the case of spring waters) provides a realistic assessment of the susceptibility of the UFA to contamination by approximating the travel time for contaminants to reach a particular zone in the aquifer. If water in the UFA were vertically stratified by age, relatively young water (0-5 years) from the top of the open interval is assumed to mix with older water (>10 years) from greater depths in the borehole during sampling of the well. However, this assumption is complicated by ground-water flow paths of varying ages.

Relation Between Age of Ground Water and Other Variables

There was no discernable relation between the $^3\text{H}/^3\text{He}$ age of ground water and the depth of wells or depth to the top of the open interval. Although there was a positive correlation (Spearman's Rho nonparametric statistic) between ground-water ages and depth of well ($r=0.10$) and depth to top of casing ($r=0.13$), these correlations were not statistically significant ($p<0.05$). Likewise, there were correlations between ground-water age and DS ($r=0.25$), calcite SI ($r=0.15$), and dolomite SI ($r=0.23$), but none were statistically significant. Inverse correlations were found between ground-water age and DOC ($r= -0.30$; $p=0.39$) and DO (-0.15 , $p=0.66$).

Important implications can be drawn about ground-water age and water chemistry even though most correlations were not statistically significant, which could be due in part to the relatively small sample size ($n=11$). For instance, younger ground water (<10 years) tends to have higher DOC concentrations, lower DS, and lower saturation indices with respect to calcite and dolomite, and probably represents a mixture of ground and surface water. Older waters (>20 years) tend to have higher DS, lower DOC concentrations, and higher mineral saturation indices, all characteristics of ground water with longer residence times in the aquifer. Also, the inverse trend between ground-water age and DO concentrations indicates that oxygen has been consumed in water with longer aquifer residence times. Similar inverse trends (but statistically significant) were found between the age of spring waters and DO concentrations in the Suwannee River Basin of northern Florida (Katz and others, 1999).

Tritium in Surface Water and Ground Water

Tritium concentrations in water from Lost Creek, Fisher Creek, and Munson Slough, 5.4, 4.4, and 4.9 TU, respectively, were very similar to those measured in most ground-water samples (table 2). This finding supports the contention that ground water is a major contributor to base flow for Fisher and Lost Creeks based on the similarity between the stable isotopic composition of ground and surface water. Water from Munson Slough below 8-Mile Pond has undergone extensive evaporation based on its stable isotopic composition and has

similar tritium concentrations to the other two sampled surface waters. Water samples were collected during base-flow conditions and could represent a mixture of ground and surface water draining from wetlands or ponds.

The close similarity among ^3H concentrations for ground water, surface water, and rainfall (Katz and others, 1997) indicates that rainfall recharges the shallow ground-water system and moves through the UFA very rapidly, <10 years for parts of the shallow flow system and <30 years for deeper parts of the aquifer. ^3H concentrations in ground and surface water in the WKP reflect the passing of the ^3H transient through the hydrologic system.

Prior to the advent of the atmospheric testing of fusion weapons in 1953, ^3H concentrations were on the order of 2 TU or less in this region (Thatcher, 1962). Atmospheric weapons testing increased ^3H concentrations in this area to a maximum of several hundred TU during the mid-1960s, followed by a sharp decline in concentrations after the nuclear testing moratorium (fig. 3). Estimates of ^3H concentrations in precipitation during the post-nuclear testing period were derived for the study area using data from the long-term station in Ocala, Fla., and the Ottawa correlation (Michel, 1989). ^3H concentrations in rainfall have declined rapidly and have been <10 TU for over a decade. ^3H concentrations in pre-bomb (1953) recharge would have decayed to 0.2 to 0.8 TU by 1997, assuming estimates of 2 TU (Thatcher, 1962) to 8 TU (Plummer and others, 1993) in pre-bomb rainfall and a ^3H half-life of 12.43 years. Therefore, based on elevated tritium concentrations (table 2), waters sampled from the WKP is of relatively recent origin, and almost certainly from the period of the falling limb of the tritium transient (post-1963). To further resolve and constrain the average residence time of ground water that discharges to stream waters, additional ^3H data would need to be collected over a range of hydrologic conditions.

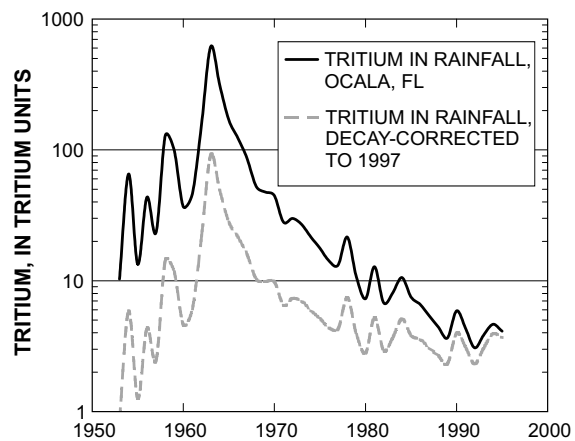


Figure 3. Concentrations of tritium in rainfall collected at Ocala, Fla. (Decay corrected to 1997.)

Table 2. Chemical characteristics, concentrations of selected chemical constituents, calcite, and dolomite saturation index for ground and surface water in Woodville Karst Plain

[°C, degrees Celsius; DOC, dissolved organic carbon, SI, saturation index; TU, tritium units; ND, not determined. Concentrations of elements and chemical species are in milligrams per liter unless otherwise noted; specific conductance is in microsiemens per centimeter]

Site name	Sample date	Temperature, °C	pH	Specific conductance	Dissolved oxygen	Calcium	Magnesium	Bicarbonate	Nitrate-nitrogen	Ammonia-DOC	Calcite SI	Dolomite SI	Dissolved solids	Delta C-13, per mil	Delta N-15, per mil	Delta O-18, per mil	Delta Deuterium, ² H, per mil	Tritium, TU	
TPW-1	9/3/97	22.0	7.61	265	0.30	47.4	1.8	124	<0.02	0.45	0.6	-0.08	-1.27	222	-13.0	ND	-3.8	-18.8	1.8
DSW-1	9/3/97	21.1	7.15	251	4.90	45.6	1.9	149	<0.02	<0.01	2.2	-0.47	-2.03	219	-16.8	ND	-3.5	-19.0	4.0
SCW-1	9/10/97	21.9	7.86	355	0.20	48.7	3.5	151	<0.02	0.04	1.0	0.26	-0.32	267	-12.8	ND	-4.0	-22.5	4.0
FPW-1	9/10/97	22.7	8.11	147	4.90	24.0	2.3	85	0.48	0.01	0.4	0.02	-0.67	130	-12.9	6.8	-4.0	-21.8	4.4
SPW-1	9/10/97	21.3	7.65	202	1.50	27.4	6.2	112	0.22	0.01	ND	-0.30	-0.95	162	-13.1	8.9	-3.6	-19.2	5.2
SHADE-1	9/10/97	21.7	7.93	300	0.20	47.2	7.1	173	<0.02	0.02	1.7	0.37	0.22	257	-14.6	ND	-3.7	-18.8	4.6
AWC-1	10/6/97	23.3	7.36	274	0.40	52.9	0.7	167	<0.02	0.04	1.2	-0.12	-1.79	239	-14.3	ND	-3.8	-19.6	7.6
GDW-1	9/24/97	21.6	7.53	306	0.50	52.1	5.4	178	0.18	0.01	0.4	0.03	-0.62	263	-15.0	13.8	-3.8	-18.1	4.5
DDW-1	9/24/97	22.5	7.49	155	0.30	23.8	3.2	88	<0.02	0.09	6.1	-0.59	-1.74	134	-14.3	ND	-2.8	-13.7	4.8
WPR-1	10/15/97	22.3	7.63	194	7.20	34.4	0.7	85	3.10	<0.01	<0.1	-0.32	-2.04	151	-14.9	1.7	-4.5	-24.3	ND
WOOD-1	10/8/97	22.8	7.31	497	2.20	62.2	24.6	310	0.71	0.01	<0.1	0.10	0.12	432	-14.9	7.8	-4.0	-21.1	4.2
Wakulla Springs	10/8/97	21.1	7.20	312	2.20	42.1	9.8	168	0.89	0.01	<0.1	-0.42	-1.18	259	-13.7	6.8	-3.5	-18.4	4.3
McBride Slough	9/11/97	20.0	7.54	203	3.37	50.5	7.1	180	0.47	0.02	0.6	0.01	-0.56	274	-14.3	7.1	-3.7	-20.0	4.9
Fisher Creek	9/4/97	23.9	3.91	52	6.90	0.3	0.3	ND	<0.02	0.08	21.0	-10.40	-20.50	42	-24.7	ND	-3.6	-17.1	4.4
Lost Creek	9/4/97	24.8	4.66	38	7.00	3.6	0.3	ND	<0.02	0.03	31.0	-7.76	-16.20	54	-24.7	ND	-2.8	-12.4	5.4
Munson Slough below 8-Mile Pond	9/11/97	23/6	6.66	71	2.60	12.5	2.5	51	<0.02	0.28	11.0	-7.89	-4.15	94	-17.8	ND	-0.6	-3.8	4.9

Table 3. Summary of ³H/³He results for ground-water samples, Woodville Karst Plain

[TU, tritium units, cm³ STP/g, cubic centimeters at standard temperature and pressure per gram of water; σ, standard deviation]

Site name	Sampling date	³ H ± 1σ, TU		³ He trit ± 1σ, TU		δ ³ He ± 1σ, percent		⁴ He 10 ⁻⁸	Ne, cm ³ STP/g	⁴ He-terrigenic, percent of ⁴ He	Apparent ³ H/ ³ He age ± 1σ, years
TPW-1	09/10/97	1.78	±0.27	2.15	±0.11	4.84	±0.31	6.38	25.85	-4.2	5.8 ±1.55
DSW-1	09/10/97	3.96	±0.26	2.16	±0.09	6.04	±0.31	5.14	21.24	-3.0	5.2 ±0.49
SCW-1	09/10/97	4.10	±0.08								
SCW-1	09/10/97	3.95	±0.08	-2.29	±0.15	-6.7	±0.36	7.30	21.63	25.7	19.8 ±2.29
SCW-1	09/10/97	4.03	±0.16								
FPW-1	09/10/97	4.15	±0.20	7.25	±0.09	23.1	±0.31	5.31	21.83	-4.0	16.2 ±0.56
FPW-1	09/10/97	4.62	±0.09								
SPW-1	09/10/97	5.14	±0.14	13.50	±0.09	39.48	±0.27	5.97	22.70	23.1	24.4 ±0.36
SPW-1	09/10/97	5.22	±0.10								
SHADE-1	09/10/97	4.62	±0.16	-18.78	±0.11	-28.82		11.98	24.80	47.1	23.1 ±0.82
SHADE-1	09/10/97	4.62	±0.16			-25.52		10.88	22.65	47.5	22.4 ±0.86
AWC-1	10/06/97	7.53	±0.15	25.60	±0.11	93.31	±0.23	4.84	20.47	-5.9	25.5 ±0.33
AWC-1	10/06/97	7.63	±0.18								
GDW-1	09/24/97	4.42	±0.09	5.92	±0.11	11.85	±0.24	8.33	31.07	2.2	16.8 ±0.40
GDW-1	09/24/97	4.47	±0.15								
DDW-1	09/24/97	4.64	±0.09	2.90	±0.11	8.8	±0.24	5.05	19.93	1.9	9.5 ±0.26
DDW-1	09/24/97	4.92	±0.15								
WOOD-1	10/08/97	4.18	±0.08	4.17	±0.11	11.97		5.62	22.93	-3.7	9.8 ±0.17
WOOD-1	10/08/97	4.18	±0.08								
Wakulla Springs	10/08/97	4.08	±0.08			-67.46	±1.00	37.09	23.95	83.6	38.7 ±1.07
Wakulla Springs	10/08/97	4.40	±0.15								

MIXING OF SURFACE WATER AND GROUND WATER

A two-component mixing model was used to estimate the fraction of surface water in the ground- and surface-water mixture in water from wells with elevated DOC concentrations. DOC concentrations were effective tracers of mixtures of river water with water from the UFA (Katz and others, 1998; Plummer and others, 1998). The fraction of surface water (F_{sw}) in the mixture is defined as: $F_{sw} = (Y_m - Y_{gw}) / (Y_{sw} - Y_{gw})$, where Y_m , Y_{gw} , and Y_{sw} denote the DOC concentrations in the mixture, ground water, and surface water, respectively.

DOC concentrations of the two end members were 20 mg/L for surface water (average of DOC concentrations for Fisher and Lost Creeks, and Munson Slough) and 0.10 mg/L for ground water. The mixing calculations assumed that DOC concentrations were not modified by reactions after mixing had occurred. For ground-water samples with DOC concentrations >0.1 mg/L, F_{sw} values ranged from 0.015 at GDW-1 and FPW-1 to 0.30 at DDW-1. The higher F_{sw} value at DDW-1 indicates the likelihood of a direct connection to a nearby sinkhole containing tannic water that contributes to the relatively young ground-water age at this site. The very young (5.8 years) water at TPW-1 (104 meters deep) is surprising; however, the F_{sw} value of 0.025 at TPW-1 indicates that there likely is a direct connection to a surface-water feature at this site.

SUSCEPTIBILITY OF THE AQUIFER TO CONTAMINATION

The use of naturally occurring isotopic and other chemical tracers in water from wells provides information about the susceptibility of the UFA to contamination on a local or site-specific scale that cannot be determined from other methods, such as mapping of surface karst features (Maddox, 1998). Even if solution features (sinkholes) were identified on a map, the susceptibility of a zone of interest in the aquifer near that feature could only be established by chemical data from a sampled well. Tracer data for Wakulla Springs, a first-magnitude spring, provide an assessment of regional impacts on water quality. Even though sinkholes provide direct pathways for water to enter the UFA from disappearing streams, such as Fisher and Lost Creeks, nitrate concentrations in stream water are at or below detection limits. Where direct connections exist between sinkholes and zones of the UFA, elevated concentrations of DOC from the tannic-rich surface waters result in elevated DOC concentrations in the ground water. Reactions between these naturally occurring organic compounds and chlorine during disinfection of the water for

public use can result in the formation of harmful products such as trihalomethanes (Rostad and others, 2000).

Nitrogen-isotope data for ground-water samples indicate that nitrate in water that recharges the aquifer originates from nonpoint sources, such as leachate from fertilizers and septic tanks, and not from sinking streams. Nitrate-N concentrations in Wakulla Springs increased from 0.25 mg/L in 1972 (Rosenau and others, 1977) to 0.86 mg/L in 1997. This large increase in nitrate over 25 years, coupled with a $\delta^{15}\text{N-NO}_3$ of 6.8 per mil, indicates that ground water draining the large regional area likely is contaminated with nitrate from several nonpoint sources.

Direct connections between ground water and surface water are indicated by elevated DOC concentrations. The high susceptibility of ground water to contamination and the presence of a dynamic flow system in the WKP are further indicated by young ages ($^3\text{H}/^3\text{He}$) for ground water of <10 years from both shallow and deep parts of the aquifer. $^3\text{H}/^3\text{He}$ ages define the age of the young fraction(s) in the mixture, which can result from mixing of surface water and/or recently recharged ground water near the water table. Ongoing studies in the WKP are assessing the spatial and vertical distribution of nitrate in ground water. Also, chemical tracer data for ground water along flow paths are being used to assess residence time of ground water and biogeochemical processes during various hydrologic conditions.

REFERENCES

- Cook, P.G., and Bohlke, J.K., 1999, Determining time-scales 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.
- Coplen, T.B., 1994, Reporting of stable hydrogen, carbon, and oxygen isotopic abundances: *Pure and Applied Chemistry*, v. 66, p. 273-276.
- Craig, H., 1961, Isotopic variations in meteoric waters: *Science*, v. 133, p. 1702-1703.
- Davis, J.H., 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 p.
- Deines, P., 1980, The carbon isotope composition of reduced organic carbon, *in* Fritz, P., and Fontes, J.C., eds., *Handbook of Environmental Isotope Geochemistry*: Amsterdam, Elsevier, v. 1A, p. 329-406.

- 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, 217 p.
- Fu, Ji-Meng, and Winchester, J.W., 1994, Sources of nitrogen in three watersheds of northern Florida, USA: Mainly atmospheric deposition: *Geochimica et Cosmochimica Acta*, v. 58, p. 1581-1590.
- Gleason, J.D., Friedman, I., and Hanshaw, B.B., 1969, Extraction of dissolved carbonate species from natural water for carbon isotope analysis: U.S. Geological Survey Professional Paper 650-D, p. 248-250.
- Gonfiantini, R., 1981, The δ -notation and the mass-spectrometric measurement techniques, *in* Gat, J.R., and Gonfiantini, R., eds., Stable isotope hydrology: Deuterium and oxygen-18 in the water cycle: Vienna, Austria, International Atomic Energy Agency, chap. 4, p. 35-84.
- Hassan, A.A., 1982, Methodologies for extraction of dissolved inorganic carbon for stable carbon isotopes studies: evaluation and alternatives: U.S. Geological Survey Water-Resources Investigations Report 82-6, 51 p.
- Hach Company, 1989, Water Analysis Handbook: Loveland, Colo., p. 584-586.
- Heaton, T.H.E., 1986, Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: A review: *Chemical Geology*, v. 59, p. 87-102.
- Hendry, C.W., and Sproul, C.R., 1966, Geology and ground-water resources of Leon County, Florida: Florida Geological Survey Bulletin no. 47, 178 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., Coplen, T.B., Bullen, T.D., and Davis, J.H., 1997, Use of chemical and isotopic tracers and geochemical modeling to characterize the interactions between ground water and surface water in mantled karst: *Ground Water*, v. 35, no. 6, p. 1014-1028.
- Katz, B.G., Catches, J.S., Bullen, T.D., and Michel, R.L., 1998, Changes in the isotopic and chemical composition of ground water resulting from a recharge pulse from a sinking stream: *Journal of Hydrology*, v. 211, p. 178-207.
- Katz, B.G., Hornsby, H.D., Bohlke, J.K., and Mokrav, M.F., 1999, Sources and chronology of nitrate contamination of spring waters, Suwannee River Basin, Florida: U.S. Geological Survey Water-Resources Investigations Report 99-4252, 54 p.
- Kendall, C., and Aravena, R., 1999, Nitrogen isotopes in groundwater systems, *in* Cook, P., and Herczeg, A.L., eds., Environmental Tracers in Subsurface Hydrology: Boston, Kluwer Academic Publishers, chap. 9, p. 261-298.
- Kloster, M.B. 1974, Determination of tannin and lignin: *Journal American Water Works Association*, v. 66, p. 44-51.
- Korom, S.F., 1992, Natural denitrification in the saturated zone: A review. *Water Resources Research*, v. 28, p. 657-668.
- Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, Ground-water-data-collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95-399, 113 p.
- Kronberg, L., and Christman, R.F., 1989, Chemistry of mutagenic by-products of water chlorination: *Science of the Total Environment*, v. 81-82, p. 219-230.
- Maddox, G., 1998, The big picture: Aquifer vulnerability mapping efforts in the Woodville Karst Plain of northern Florida: Proceedings of the Wakulla Springs Woodville Karst Plain Symposium, Florida Geological Survey Special Publication 46, p. 62.
- 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 34, 364 p.
- Michel, R.M. 1989, Tritium deposition in the continental United States 1953-1983: U.S. Geological Survey Water-Resources Investigations Report 89-4072, 46 p.
- Owenby, J.R., and Ezell, D.S., 1992, Monthly station normals of temperature, precipitation, and heating and cooling degree days 1961-90: U.S. Department of Commerce, Climatography of the United States No. 81, 26 p.
- 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. Part 2. Dating the young fraction in groundwater mixtures in the Upper Floridan aquifer near Valdosta, Georgia: *Applied Geochemistry*, v. 13, no. 8, p. 1017-1043.
- Plummer, L.N., Michel, R.L., Thurman, E.M., and Glynn, P.D., 1993, Environmental tracers for age-dating young ground water, *in* Alley, W.A., ed., Regional Ground-Water Quality, New York, Van Nostrand Reinhold, p. 255-294.
- Reilly, T.R., 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*, v. 30, p. 421-433.

- Rosenau, J.C., Faulkner, G.L., Hendry, C.W., Jr., and Hull, R.W., 1977, Springs of Florida: Florida Bureau of Geology, Bulletin No. 31, 461 p.
- Rostad, C.E., Leenheer, J.A., Katz, B.G., Martin, B.S., and Noyes, T.I., 2000, Characterization and disinfection byproduct formation potential of natural organic matter in surface and ground waters from northern Florida: *in* Barrett, S., Krasner, S., and Amy, G., eds., Natural organic matter and disinfection byproducts: Washington, American Chemical Society Symposium Series No. 761, p. 154-172.
- Rupert, F.R., 1988, The geology of Wakulla Springs: Florida Geological Survey Open-File Report 22, 18 p.
- Rupert, F.R., and Spencer, S., 1988, Geology of Wakulla County, Florida: Florida Geological Survey Bulletin No. 60, 46 p.
- Schlösser, 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.
- Schlösser 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
- 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.
- Thatcher, L.L. 1962, The distribution of tritium fallout in precipitation over North America: *Bulletin of International Association of Hydrological Sciences*, v. 7, p. 48-58.
- Tissot, B.P., and Welte, D.H., 1984, Petroleum formation and occurrence. Part I. Production and accumulation of organic matter: A geologic perspective: New York, Springer-Verlag, p. 1-66.
- Vogelmann, J.E., Sohl, T., Campbell, P.V., and Shaw, D.M., 1998, Regional land cover classification using LANDSAT thematic mapper and ancillary data sources: *Environmental Monitoring and Assessment*, v. 51, p. 415-428.