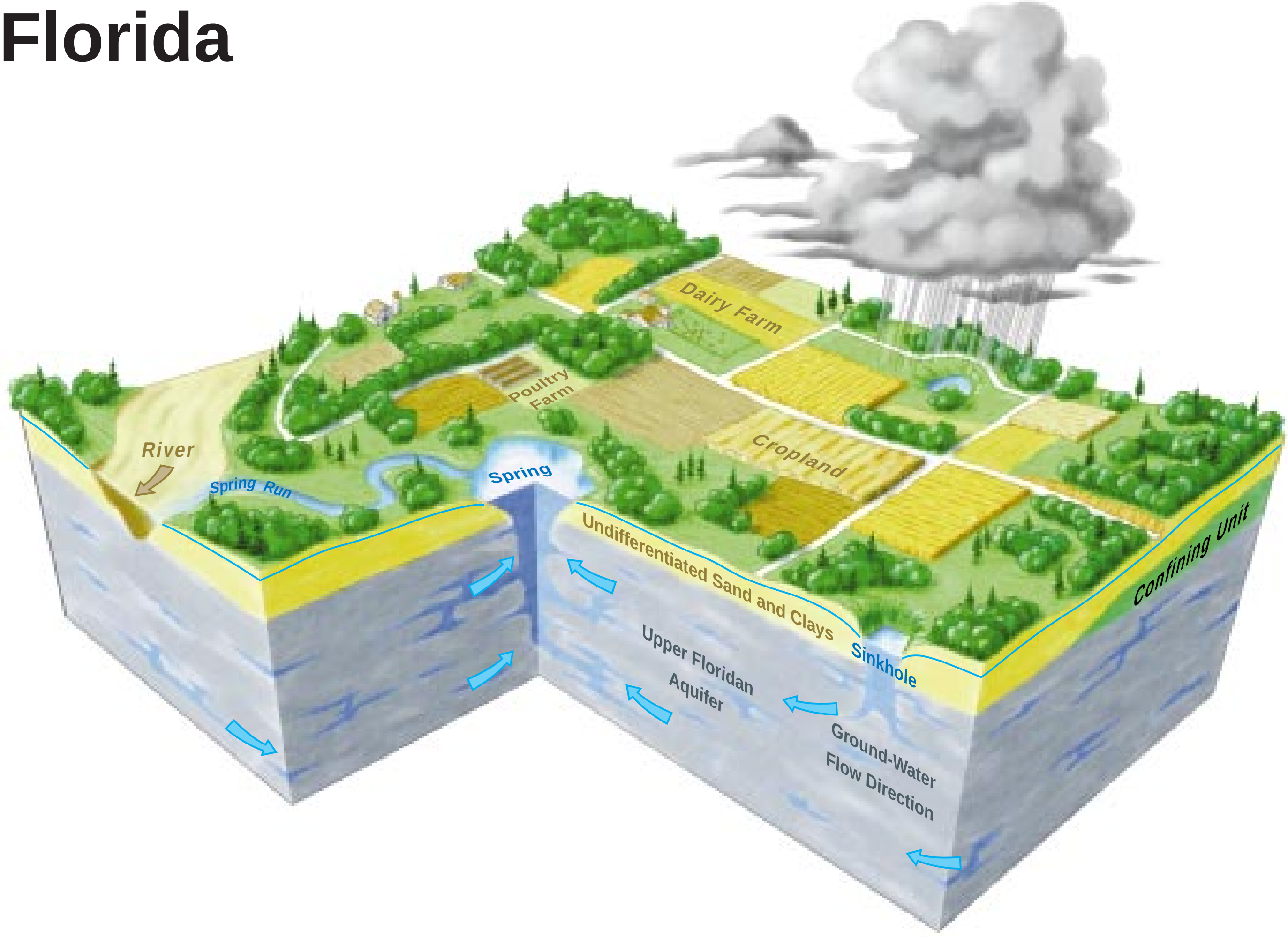
Sources and Chronology of Nitrate Contamination in Spring Waters, Suwannee River Basin, Florida



U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 99-4252

Prepared in cooperation with the
SUWANNEE RIVER WATER MANAGEMENT DISTRICT

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Tallahassee, Florida
1999

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Abstract

A multi-tracer approach, which consisted of analyzing water samples for naturally occurring chemical and isotopic indicators, was used to better understand sources and chronology of nitrate contamination in spring waters discharging to the Suwannee and Santa Fe Rivers in northern Florida. During 1997 and 1998, as part of a cooperative study between the Suwannee River Water Management District and the U.S. Geological Survey, water samples were collected and analyzed from 24 springs and two wells for major ions, nutrients, dissolved organic carbon, and selected environmental isotopes [$^{18}O/^{16}O$, D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$]. To better understand when nitrate entered the ground-water system, water samples were analyzed for chlorofluorocarbons (CFCs; CCl_3F, CCl_2F_2, and $C_2Cl_3F_3$) and tritium (^3H); in this way, the apparent ages and residence times of spring waters and water from shallow zones in the Upper Floridan aquifer were determined. In addition to information obtained from the use of isotopic and other chemical tracers, information on changes in land-use activities in the basin during 1954-97 were used to estimate nitrogen inputs from nonpoint sources for five counties in the basin. Changes in nitrate concentrations in spring waters with time were compared with estimated nitrogen inputs for Lafayette and Suwannee Counties.

Agricultural activities [cropland farming, animal farming operations (beef and dairy cows, poultry, and swine)] along with atmospheric deposition have contributed large quantities of nitrogen to ground water in the Suwannee River Basin in northern Florida. Changes in agricultural land use during the past 40 years in Alachua, Columbia, Gilchrist, Lafayette, and Suwannee Counties have contributed variable amounts of nitrogen to the ground-water system. During 1955-97, total estimated nitrogen from all nonpoint sources (fertilizers, animal wastes, atmospheric deposition, and septic tanks) increased continuously in Gilchrist and Lafayette Counties. In Suwannee, Alachua, and Columbia Counties, estimated nitrogen inputs from all nonpoint sources peaked in the late 1970’s, corresponding to the peak use in fertilizer during this time. Fertilizer use in Columbia, Gilchrist, Lafayette, and Suwannee Counties increased substantially during 1993-97.

The heavy use of fertilizers in the basin is corroborated by nitrogen isotope data. Values of $\delta^{15}N$ of nitrate ($\delta^{15}N-NO_3$) in spring waters range from 2.7 per mil (SUW718971) to 10.6 per mil (Poe Spring) with a median of 5.4 per mil. The range of values indicates that nitrate in the sampled spring waters most likely originates from a mixture of inorganic (fertilizers) and organic (animal wastes) sources; however, higher $\delta^{15}N$ values for Poe and Lafayette Blue Springs indicate that an organic source of nitrogen probably is contributing nitrate to these spring waters. Water samples from two wells sampled in Lafayette County have high $\delta^{15}N-NO_3$ values of 11.0 and 12.1 per mil, indicating the predominance of an organic source of nitrate. These two wells are located near dairy and poultry farms, where leachate from animal wastes may contribute nitrate to ground water. Dissolved-gas data (nitrogen, argon, and oxygen) indicate

that denitrification has not removed large amounts of nitrate from the ground-water system. Thus, variations in $\delta^{15}N\text{-}NO_3$ values of spring waters can be attributed to variations in $\delta^{15}N\text{-}NO_3$ values of ground-water recharge, and can be used to obtain information about source(s) of nitrate.

Extending the use of age-dating techniques (CFCs and ^3H) to spring waters in complex karst systems required the use of several different approaches for estimating age and residence time of ground water discharging to springs. These approaches included the use of a simple reservoir model, a piston-flow model, an exponential model, and a binary-mixing model. When age data (CFC-11, CFC-113, and ^3H) are combined for all springs, models that incorporate exponential mixtures seem to provide reliable estimates of average residence times of ground water discharging to springs. Whereas, data for some individual springs fit a binary-mixing model with more than 50 percent young water (recharged within the past 5 years), data from other individual springs fit a piston-flow model with a water age of about 25 years. The young ages of several spring waters (such as SUW718971, SUW725971, and Ginnie Spring) indicate the high vulnerability of the springs to contamination. For most springs, CFCs suggest that a large fraction of the water is more than 20 years old. Springs with lower flows tend to have young ages (shallow ground-water flow systems), whereas springs with higher flows tend to have older ages (deep ground-water flow systems).

The chemical composition of spring waters can be used as a qualitative indicator of age and ground-water residence time. Nitrate-nitrogen concentrations and dissolved oxygen in spring waters are inversely related to the apparent ages of spring waters and ground-water residence time in the basin. Silica concentrations increase as the age of spring waters increase.

Long-term trends in nitrate concentrations in selected spring waters were compared with estimated inputs of nitrogen from various sources in Suwannee and Lafayette Counties. In both counties, trends in nitrate concentrations in spring waters closely followed the estimated contribution of nitrogen from fertilizers. Decreasing nitrate concentrations in spring waters from Suwannee County followed the decrease in estimated fertilizer use from the mid-1970's to the early 1990's. Increasing nitrate concentrations in spring waters from Lafayette County followed the steady increase in fertilizer use from the early 1960's to the mid-1990's.

The relation between the concentration of nitrate in ground water and the amount of nitrogen that is added to a ground-water contributing area for a spring is controlled by complex interactions among hydrogeologic, land-use, and climatic factors, as well as several other land-management factors. Spring waters represent mixtures of converging flow paths that contain ground water with a range of ages. Even if nitrogen inputs were reduced substantially, it may take decades for nitrate concentrations in the ground-water system to return to near background levels.

INTRODUCTION

Springs provide not only sources of potable water, as well as recreational and cultural value, but they afford a way to assess ground-water quality because their discharge spatially and temporally integrates ground water from large parts of an aquifer. Agricultural activities and other land uses have impacted the quality of spring waters by contributing large quantities of nutrients to ground-water recharge in many parts of the world (Dietrich and Hebert, 1997; Focazio and others, 1998; Kendall, 1998). During the past 40 years, nitrate-nitrogen (N) concentrations in water from several springs have increased substantially from near background concentrations of nitrate-N (less than 0.1 milligram per liter (mg/L)) (Katz, 1992; Maddox and others, 1992) to more than 5 mg/L (Hornsby and Ceryak, 1999) in the Suwannee River Basin in northern Florida (fig. 1).

Discharge of water from springs into the Suwannee and Santa Fe Rivers has contributed substantial loads of nitrate-N to both rivers (Hornsby and Mattson, 1998). For example, along a 53-kilometer (km) reach of the Suwannee River, nitrate-N loads increased downstream from 2,300 kilograms per day (kg/d) just downstream of Dowling Park to 6,000 kg/d at Branford during base-flow conditions (Pittman and others, 1997). Nearly 90 percent of the increase in nitrate load occurred in the lower two-thirds of the studied reach, and was attributed mainly to discharge from spring flow and upward diffuse leakage of ground water through the riverbed (Pittman and others, 1997).

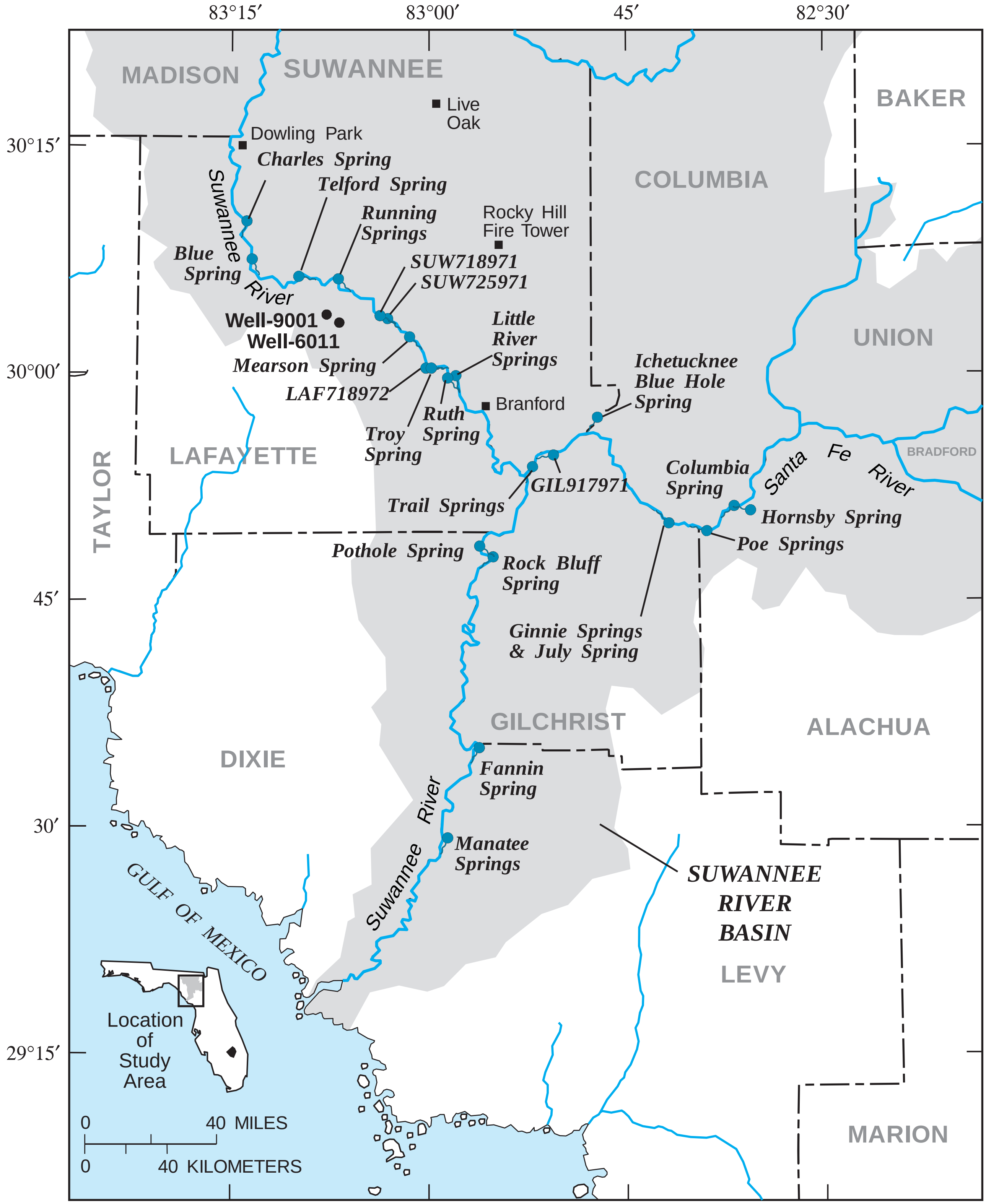

Figure 1. Map of study area showing location of sampled springs and wells.

Along this middle reach of the Suwannee River in north Florida, mean nitrate-N concentrations increase nearly four-fold from 0.15 mg/L at Suwannee Springs, (242 km from mouth of river) (Katz and others, 1997) to 1.38 mg/L at Branford, (123 km from river mouth) (Hornsby and Mattson, 1999). This increase in nitrate in river water at Branford is attributed to ground-water discharge because there are no major stream inputs to the middle Suwannee River in this region. Also, the concentration of nitrate in river water is inversely related to discharge; that is, concentrations are higher during base-flow conditions when the contribution from ground water is greatest (Hornsby and Mattson, 1996). Elevated concentrations of nitrate in rivers can cause eutrophication, which can result in algal blooms and depletion of oxygen that can lead to fish kills. Increases in nitrate concentrations from human activities may be causing adverse ecological effects, which are indicated by an increase in periphyton biomass along the middle and lower reaches of the Suwannee River (Hornsby and Mattson, 1996). Also of concern are the effects of high nitrate concentrations on the Suwannee River system's estuary which, in addition to the Suwannee River, has been designated as an outstanding Florida waterbody and a State Aquatic Preserve and National Wildlife Refuge.

Another important concern is elevated nitrate-N concentrations that have been measured in water from wells open to shallow parts of the Upper Floridan aquifer (less than 40 meters (m) below land surface) in parts of Suwannee and Lafayette Counties. Water from the Upper Floridan aquifer is the source of water supply in the study area. Numerous domestic and monitoring wells have yielded water with nitrate-N concentrations that exceed 10 mg/L, which is the maximum contaminant level set by the United States Environmental Protection Agency. This limit was set because of the health risk of high-nitrate water to infants, who can contract methemoglobinemia (Mueller and Helsel, 1996).

Identifying the sources of nitrate and understanding the chronology and processes affecting nitrate contamination of ground water are needed to develop effective management practices to prevent further degradation of water quality. At present, little information exists to determine the source(s) and fate of nitrate in the Upper Floridan aquifer in the Suwannee River Basin of northern Florida. The occurrence of many possible sources of nitrate in the basin makes it difficult to determine the relation between nitrate concentrations in ground water and the timing of nitrate introduced from a particular source or from multiple sources. Previous studies have identified animal wastes associated with dairy (Andrews, 1994) and poultry farming operations (Hatzell, 1995) and fertilizers applied to cropland (Hornsby, 1994) as important sources of nitrate to ground water in the Suwannee River Basin.

Purpose and Scope

This report describes the results of a cooperative study between the Suwannee River Water Management District (SRWMD) and the U.S. Geological Survey (USGS). The study was designed to evaluate sources and chronology of nitrate contamination in water from 24 selected springs and from two wells open to shallow zones of the Upper Floridan aquifer in the Suwannee River Basin. The study used a multi-tracer approach, which consisted of collecting and analyzing water samples for naturally occurring chemical and isotopic indicators, to better understand the sources and chronology of nitrate contamination of ground water in parts of the Suwannee River Basin in Florida.

Naturally occurring chemical and isotopic tracers provide important information on geochemical and hydrologic processes. For example, the concentrations of major ions, nutrients, and dissolved organic carbon give information on sources and processes that affect the concentration of solutes in the Upper Floridan aquifer. The stable isotopes of water, oxygen ($^{18}O/^{16}O$) and hydrogen (D/H) provide information on the origin of the water and mixing of different sources of water in springs and in zones of the aquifer. Measurements of carbon isotopes ($^{13}C/^{12}C$) provide information to assess rock-water interactions, evaluate the mixing of water from different sources, and quantify mass transfer associated with microbially mediated processes (for example, degradation of organic matter with associated terminal electron-accepting processes such as ferric iron reduction, sulfate reduction, and methanogenesis), Nitrogen isotopes ($^{15}N/^{14}N$) are used to evaluate sources of nitrate in ground water.

To better understand when nitrate entered the ground-water system, water samples were analyzed for chlorofluorocarbons (CFCs; CCl_3F (CFC-11), CCl_2F_2 (CFC-12), and $C_2Cl_3F_3$ (CFC-113)) and tritium (^3H) to assess the apparent ages (residence time) of spring waters and water from the Upper Floridan aquifer. Anthropogenic activities, such as industrial processes and atmospheric testing of thermonuclear devices, have released CFCs and ^3H, respectively, into the atmosphere in very low but measurable concentrations. Precipitation, which incorporates CFCs and ^3H from the atmosphere, infiltrates into the ground and carries a particular chemical or isotopic signature related to atmospheric conditions at the time of recharge. The concentration of CFCs and ^3H in ground water along a flow path or water from a spring provides information on ground-water age and residence time of water in the aquifer.

In addition to information on sources of nitrate obtained from the chemical and isotopic tracers, information on the hydrology of the Upper Floridan aquifer and present and historical land uses are presented to obtain a more complete understanding of the factors affecting the concentration of nitrate in springs and in parts of the aquifer. Substantial changes in land use have occurred along with associated inputs of nitrogen to the study area over the past 40 years. Estimates of nitrogen loading from nonpoint sources are provided for five counties in the study area (Suwannee, Lafayette, Gilchrist, Columbia, and Alachua) during 1950-97. Important nonpoint sources of nitrogen in the study area include fertilizers applied to cropland, atmospheric deposition, animal wastes, and discharges from septic tank systems.

Description of Study Area

The springs sampled in this study discharge ground water to the Suwannee and Santa Fe Rivers, which are located in the Suwannee River Basin in the north and north-central parts of peninsular Florida (fig. 1). The basin is characterized by karstic wetland and lowland topography, a small number of tributary streams, and an abundance of Upper Floridan aquifer springs. In a recent survey during low-flow conditions, Hornsby and Ceryak (1999) identified 197 springs in the Suwannee River Basin, of which, only 65 were previously reported (Rosenau and others, 1977). In addition to springs, other common karst features in the basin include numerous sinkholes, other solution cavities (caves, conduits), siphons, and disappearing streams. As a result of these features, interactions between ground water and surface water constitute a single dynamic system in most parts of the basin (Katz and others, 1997).

Spring-water flow commonly is classified by Meinzer's magnitude of discharge system (Rosenau and others, 1977). A first-magnitude spring has average flow greater than 2.8 cubic meters per second (m^3/s) (100 cubic feet per second (ft^3/s)); a second-magnitude spring has average flow ranging between 0.28 and 2.8 m^3/s (10 and 100 ft^3/s); and a third-magnitude spring discharges from 0.028 to 0.28 m^3/s (1 to 10 ft^3/s) (Rosenau and others, 1977). Seven of the 18 first-magnitude springs in the basin were sampled in this study: Troy, Fannin, Manatee, Ichetucknee Blue Hole, Hornsby, Columbia, and July (fig.1, table 1). Second-magnitude springs sampled included Ginnie, LAF718972, Poe, Pothole, Rock Bluff, Mearson, Ruth, Running, Little River, Charles, Lafayette Blue, and Telford (fig. 1, table 1). Water samples also were collected from the following third-magnitude springs: GIL917971, SUW718971, SUW725971, and Trail (fig. 1). Measured discharge values for sampled springs are presented in table 1.

Springs in the study area generally are categorized as water-table springs because the Upper Floridan aquifer is predominantly unconfined (Crane, 1986). Many of central Florida's large springs are categorized as artesian because water is confined in permeable sediments beneath impervious confining beds and is under sufficient hydrostatic pressure to rise to the surface through natural breaches in the overlying confining units (Rosenau and others, 1977). Ground-water discharge to springs results from the difference between the hydrostatic head at the spring vent and the recharge area, and from a system of solution cavities and conduits that are present in the limestone that forms the Upper Floridan aquifer.

Several climatic, geologic, and hydrologic factors control the amount of spring flow such as the amount and frequency of rainfall (recharge), the porosity and permeability of the aquifer, the size of the ground-water contributing area, the hydrostatic head within the aquifer, and the hydraulic gradient. The permeability of the Upper Floridan aquifer in the study area varies greatly due to differences in the size and type of openings in the water-bearing limestone that range from networks of small solution openings along joints or bedding planes to large cavernous openings 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 that have been mapped for many springs in the basin can extend for many kilometers into the rocks of the Upper Floridan aquifer (Hornsby and Ceryak, 1999). The variability in permeability is reflected by transmissivities that range from 2,800 to greater than 93,000 square meters per day (m^2/d) (30,000 to greater than 1,000,000 square feet per day (ft^2/d) (Bush and Johnston, 1988).

Table 1. Location of springs and wells sampled in study, springflow discharge, and estimated spring catchment area
[ft^3/s, cubic feet per second; m^3/s, cubic meters per second; km^2, square kilometers; NA, not applicable, R, recharge rate, in m/yr]

Spring/well site name	Date of sampling	Latitude	Longitude	County	Dis-charge ft^3/s	Dis-charge m^3/s	Date of dis-charge measure-ment	Estimated spring catch-ment area, km^2		
								R=0.5	R=0.2	R=0.8
Charles Spring	07/15/97	301002.0	831350.0	Suwannee	16.4	0.46	7/15/97	29	73	18
Lafayette Blue Spring	07/15/97	300733.0	831334.0	Lafayette	84.6	2.40	7/15/97	151	378	95
Little River Springs	07/15/97	295947.0	825759.0	Suwannee	76.1	2.16	7/15/97	136	340	85
Telford Spring	07/16/97	300624.0	830957.0	Suwannee	41.6	1.18	7/16/97	74	186	46
Troy Spring-97	07/15/97	300021.0	825951.0	Lafayette	138	3.91	7/15/97	247	617	154
Ichetucknee Blue Hole Spring	08/14/97	295709.0	824710.0	Columbia	117	3.31	8/14/97	209	523	131
Fannin Spring	08/18/98	293514.3	825607.7	Levy	109	3.09	7/16/98	195	487	122
GIL917971	08/20/98	295441.1	825032.5	Gilchrist	2	0.06	7/10/98	3.6	8.9	2.2
Ginnie Springs	08/21/98	295008.9	824200.0	Gilchrist	51	1.44	6/15/98	91	228	57
Hornsby Spring	08/21/98	295100.4	823536.0	Alachua	200	5.66	7/28/98	357	894	223
July Spring	08/21/98	295009.8	824150.0	Columbia	117	3.31	11/4/97	209	523	131
LAF718972	08/19/98	300021.2	830016.1	Lafayette	11	0.31	7/18/97	20	49	12
Manatee Springs	08/18/98	292921.3	825837.4	Levy	202	5.72	7/16/98	361	903	226
Poe Springs	08/21/98	294933.1	823859.9	Alachua	54	1.53	7/22/98	97	241	60
Pothole Spring	08/20/98	294837.8	825609.8	Dixie	32	0.91	9/23/97	57	143	36
Rock Bluff Spring	08/20/98	294755.8	825507.3	Gilchrist	45	1.27	8/17/98	80	201	50
Ruth Spring	08/19/98	295944.1	825837.2	Lafayette	13	0.37	8/24/98	23	58	15
Running Springs	08/18/98	300614.9	830657.0	Suwannee	22	0.62	6/24/97	39	98	25
SUW718971	08/19/98	300350.4	830343.7	Suwannee	9	0.25	7/10/98	16	40	10
SUW725971	08/19/98	300337.8	830312.0	Suwannee	8	0.23	7/10/98	14	36	9
Trail Springs	08/20/98	295353.4	825200.9	Gilchrist	9	0.25	9/16/97	16	40	10
Troy Spring-98	08/19/98	300021.1	825951.4	Lafayette	102	2.89	8/24/98	182	456	114
Mearson Spring	08/19/98	300228.0	830132.0	Lafayette	62	1.76	8/24/98	111	277	69
Columbia Spring	08/20/98	295113.0	823643.0	Columbia	210	5.95	8/20/98	375	938	235
Well-9001	07/16/97	300351.0	830748.0	Lafayette	NA	NA	NA	NA	NA	NA
Well-9001	03/09/98	300351.0	830748.0	Lafayette	NA	NA	NA	NA	NA	NA
Well-6011	07/16/97	300319.0	830650.0	Lafayette	NA	NA	NA	NA	NA	NA
Well-6011	03/09/98	300319.0	830650.0	Lafayette	NA	NA	NA	NA	NA	NA

The hydrogeology of the Suwannee River Basin is directly related to the physiography. In the northeastern part of the basin in the Northern Highlands, surface-water features are common, and the area is characterized by land-surface altitudes ranging from greater than 30 m to 70 m. Clayey sediments of the intermediate confining unit, which overlie the Upper Floridan aquifer, retard the infiltration of rainwater. Recharge rates to the Upper Floridan aquifer are less than 30 centimeters per year (cm/yr) in areas where the aquifer is confined (Grubbs, 1998). In contrast, the southern and southwestern parts of the basin lie within the Gulf Coastal Lowlands physiographic division, which is characterized by land altitudes that are less than 30 m and carbonate rock exposed at land surface or underlying the shallow subsurface. Where the Upper Floridan aquifer is unconfined in this area, recharge rates range from 40 to 80 cm/yr (Grubbs, 1998).

Ground-water flow toward most springs in the Suwannee River Basin typically follows intermediate to long flow paths-- localized flow systems generally do not exist except for small springs with low flow rates (fig. 2). Regional simulation of the ground-water-flow system demonstrated that major springs receive a small percentage of water from upward leakage from the lower part of the Upper Floridan aquifer (Bush and Johnston, 1988). The regional ground-water flow-model corroborated the importance of flow systems characterized as intermediate flow systems (Toth,

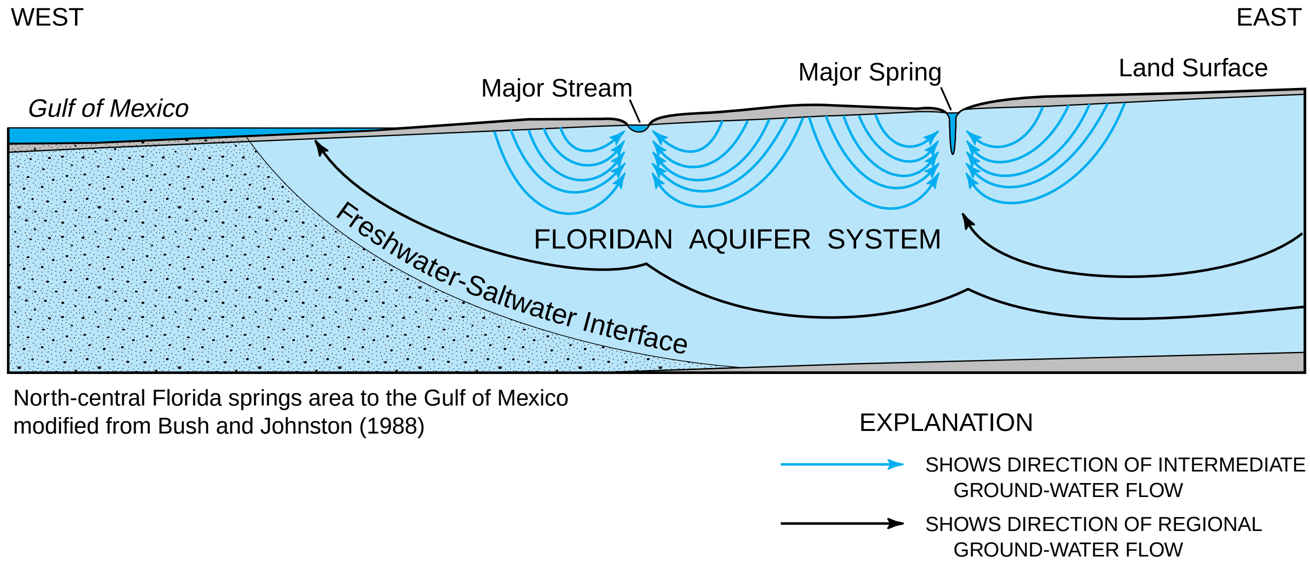

Figure 2. Schematic of idealized flow system in Suwannee River Basin.

1963) and the lack of local flow systems (which the regional model was not able to simulate). Bush and Johnston (1988) estimated that ground-water discharge in the lower Suwannee River Basin was a mixture of the following components, in percent: spring flow and discharge to surface-water bodies, 87; diffuse upward leakage, 9; and pumpage, 4. It is likely that ground-water flow toward springs represents a mixture of water from shallow and deeper flow systems. Faulkner (1973) estimated that ground-water flow toward Rainbow Springs and Silver Springs, which are first-magnitude springs in central Florida, was a mixture of about 92 percent shallow water and 8 percent deep water, resulting in an intermediate flow system in Toth's (1963) classification scheme. Using tritium, carbon-14, and carbon-13 data from Toth (1999), it was estimated that ground-water flow toward Ponce de Leon, Rock, and Wekiva Springs (in east-central Florida) was a mixture of about 70 to 100 percent shallow water (from intermediate flow paths) and 0 to 30 percent deep water (from regional flow paths).

In most parts of the basin, channels of the Suwannee and Santa Fe Rivers have cut into the aquifer rocks, thus springs discharge water to these two rivers because the river level is lower than that of the water table. During high river stage, however, many springs become flooded with river water and reversals in flow can occur if the hydraulic head of the spring (Upper Floridan aquifer) is lower than the hydrostatic pressure of the river (Rosenau and others, 1977; Kincaid, 1998; Hornsby and Ceryak, 1999).

The climate in the basin is subtropical and is characterized by long, warm summers and mild winters. Rainfall averages 132 cm/yr in the study area (Crane, 1986); however, there are large variations between locations and from year to year (Owenby and Ezell, 1992). Approximately 50 percent of the average annual rainfall occurs from June through September, but the shorter rainy season from late February through late April typically produces some of the highest stages of the Suwannee and Santa Fe Rivers and their tributaries.

Major land uses in the Suwannee River Basin include forest, agriculture (row crops; dairy, poultry, and swine farming operations, pasture), and wetlands. Percentages of each land-use type in the basin vary considerably by county. For example, in 1997, for the five counties that are contiguous with the middle reach of the Suwannee River and the Santa Fe River (Alachua, Columbia, Gilchrist, Lafayette, and Suwannee), the percentage of agricultural land ranged from 11 in Lafayette County to 35 in Suwannee County (table 2). Agricultural land use includes cropland, pasture lands, confined feeding operations (poultry, dairy, livestock, and swine). The percentage of agricultural land use has decreased in all five counties based on a comparison of recent data (1997) and that from the mid-1970's, which was based on a land-use and land-cover classification system for remote sensor data (Anderson and others, 1976; Mitchell and others, 1977). Based on 1997 data, forested land ranged from about 39 percent in Alachua County to 56 percent in Columbia County. Much of the forested land is planted by the paper industry for silviculture. Wetlands covered between 2 and 36 percent in Suwannee and Lafayette Counties, respectively.

Table 2. Percentage of land-use types in Alachua, Columbia, Gilchrist, Lafayette, and Suwannee Counties

[Upper number in each cell is for 1977 data, lower number is for 1995; km^2, square kilometers]

County (area in km^2)	Land use, in percent				
	Agricul-ture	Forest	Urban	Wetlands	Other
Alachua	35	43	5	11	6
(2,335)	24	39	14	17	6
Columbia	22	60	2	15	0
(2,063)	17	56	6	19	1
Gilchrist	34	55	1	9	1
(916)	29	47	9	13	1
Lafayette	15	51	0	33	0
(1,412)	11	49	2	36	1
Suwannee	47	49	1	1	0
(1,786)	35	52	9	2	1

Acknowledgments

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STUDY METHODS

Study methods are described below for sample collection and analysis, estimation of age of spring waters and average residence times of ground water, and estimation of nitrogen inputs from various non-point sources. More detailed information about these topics can be found in the references listed in each section.

Sample Collection and Analysis

Samples of water from 24 springs were collected during low-flow conditions along the Suwannee and Santa Fe Rivers in July and August 1997 and in August 1998 (fig. 1). Troy Spring was sampled in 1997 and in 1998. These springs were selected for sampling because previous data indicated that high loads of nitrate were being discharged to the Suwannee and Santa Fe Rivers in this area (Hornsby and Mattson, 1996; Hornsby and Ceryak, 1999). Water samples also were collected during low-flow conditions (August 1997) and during high-flow conditions (March 1998) from two wells open to shallow zones within the Upper Floridan aquifer. The wells were located in an agricultural area near the Suwannee River in Lafayette County (fig. 1). Well-9001 is screened in the interval from 7 to 13 m below land surface (bls), and well-6011 is screened in the interval from 26 to 32 m bls. Both wells were part of a statewide network designed to study the effects of different land uses on ground-water quality. These two wells were chosen for this study because of differences in depth and both previously yielded water samples having consistently high nitrate-N concentrations (10 to 20 mg/L in water samples collected in 1994 and 1996).

Samples of spring water were collected by lowering a positive displacement dual-piston (Bennett) pump head about 5 to 17 m into the spring vent. Water was pumped at approximately 0.06 liter per second (L/s) through 0.63-cm diameter copper (refrigeration-grade) tubing. Sampling methodology varied somewhat depending on accessibility to the spring and site characteristics. Water samples were collected from a boat at 14 springs, whereas samples were collected from the adjacent shoreline at the other nine springs. During the 1997 sampling, specific conductance, pH, dissolved oxygen, and temperature were measured by using a closed flow-through chamber to prevent contact of the spring water at depth with the atmosphere. During the 1998 spring-water sampling, a YSI multi-probe unit was lowered down into the spring vent to measure these four water properties *in-situ*. After field readings of these properties had stabilized, samples of spring water were collected for major element chemistry, dissolved organic carbon (DOC), ^{3}H, D, ^{18}O, ^{15}N, ^{13}C dissolved inorganic carbon (DIC), and CFCs (CFC-11, CFC-12, and CFC-113).

Water samples from wells -9001 and -6011 were collected after a minimum of three well-bore volumes of water had been purged and readings of specific conductance, pH, dissolved oxygen, 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 well-9001, the Bennett pump intake was positioned approximately 1 to 2 m above the open interval in the well after three casing volumes were purged using a submersible pump. At well-6011, water samples were collected from the existing water-supply system upgradient of the pressure tank by using an in-line submersible pump. Samples of ground water were collected for major element chemistry, DOC, ^{3}H, ^{2}H, ^{18}O, ^{15}N, ^{13}C (DIC), dissolved gases (N_2, Ar, CH_4), and CFCs (CFC-11, CFC-12, and CFC-113).

Water samples were collected for major element chemistry and DOC by using standard techniques (Brown and others, 1970; Wood, 1976; Koterba and others, 1995) that included field filtration using a 0.45-µm membrane filter for major ions, nutrients, silica, and using a 0.45-µm silver filter for dissolved organic carbon. These samples were preserved in the field and analyzed at the U.S. Geological Survey laboratory in Ocala, Fla., following standardized procedures (U.S. Geological Survey, 1999).

Isotopic Tracers

Isotopic values are reported using standard delta (δ) notation (Gonfiantini, 1981), as defined by the following expression:

$$\delta \text{ (per mil)} = [(R_{sample}/R_{standard}) - 1] \text{ X } 1{,}000.$$

For $\delta^{18}O$, R = $^{18}O/^{16}O$; for δD, R = D/H; for $\delta^{13}C$, R = $^{13}C/^{12}C$, and for $\delta^{15}N$, R = $^{15}N/^{14}N$. Results for oxygen and hydrogen isotopes are reported in per mil relative to Vienna Standard Mean Ocean Water (VSMOW), and are normalized on scales such that the oxygen and hydrogen isotopic values of Standard Light Antarctic Precipitation (SLAP) are -55.5 and -428 per mil, respectively (Coplen, 1994). The 2σ precision of delta oxygen-18 ($\delta^{18}O$) and delta deuterium (δD) results is 0.2 and 2 per mil, respectively. The 2σ precision for the analytical procedure is 0.2 per mil (Coplen, 1994). Samples for analysis of $\delta^{13}C$ in DIC were collected by direct precipitation in the field using ammoniacal-$SrCl_2$ solution followed by filtering, drying, and acidifying the $SrCO_3$ precipitate to produce CO_2, which was analyzed by mass spectrometric methods (Hassan, 1982). Values of $\delta^{13}C$ are reported relative to VPDB, Vienna Pee Dee Belemnite (Coplen, 1994). Stable isotope analyses of water samples were performed by the USGS Isotope Fractionation Laboratory in Reston, Virginia. Values of $\delta^{13}C$ were determined by mass spectrometry, and are reported as the per mil deviation from the VPDB standard (Coplen, 1994).

Water samples for nitrogen isotope analysis were filtered (0.45 µm membrane) into 1-liter (L) plastic bottles and kept chilled at 4 ^{o}C. Analytical techniques are described by Bohlke and Denver (1995) and Bohlke and Coplen (1995). Values of $\delta^{15}N$ for nitrate-N concentrations above 0.5 mg/L are normalized to values of +0.4 per mil for IAEA-N1 and +180.0 per mil for USGS-32 (Bohlke and Coplen, 1995) with analytical uncertainties of approximately +/- 0.1 per mil.

Age Dating Waters

The transient tracers, tritium and chlorofluorocarbons (CFCs), were used to estimate the age of ground water. Tritium (^{3}H) analyses provide estimates of the time of ground-water recharge, by comparing measured ^{3}H concentrations in ground water with the long-term ^{3}H input function of rainfall measured at the International Atomic Energy Agency (IAEA) precipitation monitoring station in Ocala, Florida (Michel, 1989) (fig. 3). ^{3}H activity is reported in tritium units (TU), with 1 TU equal to 1 ^{3}H atom in 10^{18} hydrogen atoms and 7.1 disintegrations per minute per gram of water. Water samples for ^{3}H analyses were enriched electrolytically and analyzed by liquid scintillation counting in the low-level ^{3}H laboratory of the U.S. Geological Survey in Menlo Park, Calif., using a modification of procedures described by Thatcher and others (1977). Analytical uncertainties for ^{3}H using the low-level counting procedure is approximately +/- 0.15 to 0.30 (R.L. Michel, USGS, 1998, written commun.).

The CFC age-dating technique was used in this study for assessing the apparent age of spring waters and water from two zones in the Upper Floridan aquifer. This technique, which has been used to age-date ground water (Upper Floridan aquifer) in karst areas of northern Florida (Katz and others, 1995a) and southern Georgia (Plummer and others, 1998a), is based on four main assumptions: (1) the partial pressures of CFCs are the same in both the soil (unsaturated zone) and the tropospheric atmospheres, which is valid for unsaturated zones less than 10 m in thickness (Busenberg and Plummer, 1992); (2) the aquifer has not been contaminated by local, near-surface sources of CFCs commonly found near or in urban areas; (3) the CFC concentration in recharge water is in equilibrium with the CFC partial pressure in the soil atmosphere; and (4) the CFC concentrations in the aquifer have not been altered by biological, geochemical, or hydrologic processes. The stability of CFC compounds in the hydrosphere has led to their effective use as tracers to age date ground water that has been recharged during the past 50 years (Plummer and others, 1993).

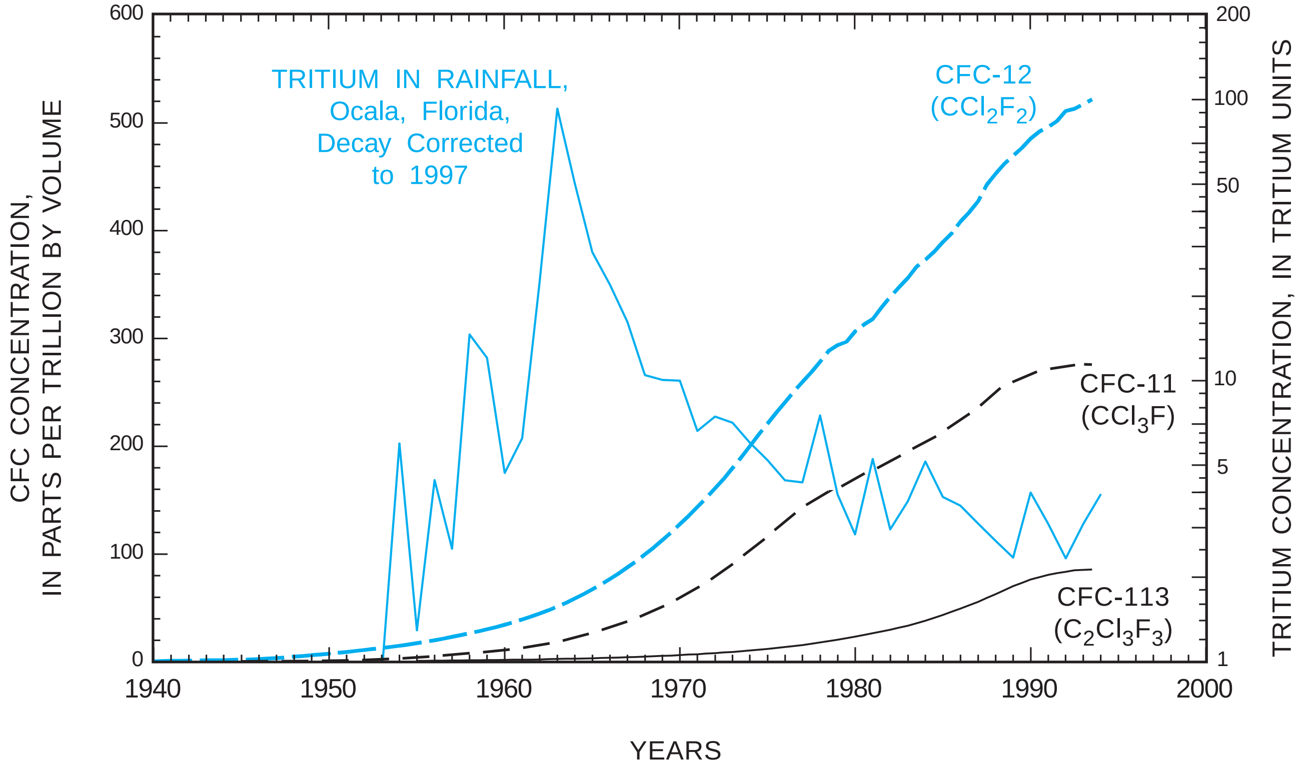


Figure 3. Concentrations of CFC-11, CFC-12, and CFC-113 in the atmosphere, 1940-1997 and tritium concentrations in rainfall collected at Ocala, Florida, decay corrected to 1997.

The apparent age of spring waters and water from zones in the aquifer is determined from a CFC-modeled recharge date (as defined by Busenberg and Plummer, 1992). A CFC-modeled recharge date is determined on the basis of the equilibrium partitioning between rainwater and the partial pressures of trichlorofluoromethane (CCl_3F, CFC-11), dichlorodifluoromethane (CCl_2F_2, CFC-12), and trichlorotrifluoroethane ($C_2Cl_3F_3$, CFC-113) in the troposphere or soil atmosphere (fig. 3). The CFC dating method actually provides three independent ages, which are based on measured concentrations of each of the three CFC compounds. Ideally, the three independent ages that are derived can be used as a cross-check on the sampling and analytical methods. An apparent age of the sampled water is modeled based on the comparison of the measured concentration of each CFC compound with calculated equilibrium partial pressures using solubility data for each compound with their respective atmospheric growth curve (fig. 3). The concentration of CFCs in ground water is a function of the atmospheric partial pressures and the temperature at the base of the unsaturated zone during recharge. Recharge temperature and quantity of dissolved excess air (Heaton and Vogel, 1981) were determined from gas-chromatography analyses of nitrogen (N_2) and argon (Ar) gases in the headspace of water samples collected in the field (Busenberg and others, 1993).

Estimation of Age of Spring Waters and Average Residence Time of Ground Water

In previous studies where CFCs have been used to age-date ground water, hydrologic systems have been relatively well characterized and water samples typically were collected from short depth intervals. Extending the CFC age-dating technique to complex karst systems, where both conduit and diffuse flow exist, requires an integration and comparison of several approaches that are based on different conceptualizations of how water moves through the aquifer. In this report, the age and residence times of ground water discharging to springs were estimated by using the following conceptual models of ground-water flow to springs: a simple reservoir, piston flow, exponential flow, and the binary mixing of waters from two reservoirs. A simple reservoir model uses aquifer properties and rates of recharge to the ground-water system to estimate the residence time of ground water discharging to springs. Steady-state flow conditions are assumed for the aquifer; that is, recharge rates and other aquifer properties remain constant at least on an inter-annual basis. The model also assumes that annual recharge is equal to annual discharge, and that the areal extent of the aquifer is equivalent to the watershed or contributing area to the spring. Average ground-water residence times can be approximated by using the following equation (after Focazio and others, 1998):

$$T = bn/R \,, \qquad (1)$$

where T is the average residence time of ground water in years, b is the aquifer thickness in length units, n is the porosity (unitless), and R is the annual recharge (or discharge) rate, expressed in length per time units. T also is equivalent to the turnover time, which can be defined as the volume of mobile water in the ground-water system divided by the volumetric flow rate of water through the system (Zuber, 1986). Using this relation, the mean age of water leaving the ground-water system is equivalent to the turnover time. The residence time of ground water is proportional to the amount of void space in the aquifer. From expression (1), longer residence times would be independently associated with a higher porosity, a larger thickness of aquifer, and a lower recharge rate.

Following from the physical definition of the ground-water flow system, input and output concentrations of naturally introduced tracers (CFCs and ^3H) can be used to provide information about the age of ground water and springs issuing from the flow system. Input concentrations are obtained from relatively well-known atmospheric input curves (fig. 3) and output concentrations are those measured at a particular time (t) in samples of spring water and ground water. Lumped-parameter models typically are used to interpret radioisotope and other age-related tracer data in ground-water hydrology studies (Richter and others, 1993). In these models, the aquifer is assumed to be homogeneous and spatial variations are ignored. They have an advantage over numeric simulation approaches in that few hydrologic parameters are needed, consequently, results from these models tend to represent idealized conditions. The two lumped-parameter models used to interpret age information in this report are the piston-flow and exponential-flow models. A brief explanation of each model follows along with some assumptions and limitations; a more detailed description of these models can be found in previous studies, such as Maloszewski and Zuber (1982), Zuber (1986), and Richter and others (1993).

For ground-water-flow systems that are assumed to be at steady state conditions, the relation between time-variable tracer input and output concentrations can be expressed mathematically for a lumped-parameter model (Zuber, 1986) as:

$$C_{\mathrm{out}}(t) = \int_{-\infty}^{\infty} C_{in}(t')^{-\lambda(t-t')} g(t-t')dt' \,, \qquad (2)$$

where $C_{out}(t)$ and $C_{in}(t)$ are the output and input concentrations, respectively; t' is the transit time of the tracer, and $g(t')$ is a weighting function or system response function for a given injection-detection mode, and t is the calendar time.

The most simplified lumped-parameter approach used is the piston-flow model, which assumes that a particular tracer moves like a slug through the aquifer, thus corresponding to plug flow in a single flow tube. That is, after a tracer is isolated from the atmosphere (at the time the ground-water system is recharged), it becomes incorporated in a parcel of water that moves from the recharge area with the mean velocity of ground water (Zuber, 1986). All flow lines are assumed to have similar velocities, and hydrodynamic dispersion and molecular diffusion of the tracer are assumed to be negligible. One of the limitations to using this method is the assumption that dispersion and mixing do not occur as water moves through the aquifer. In the case of springs that spatially and temporally integrate water from large parts of an aquifer, the ages of ground water determined by using a piston-flow model may in some cases, underestimate the actual age or residence time of spring water. The weighting function, $g(t')$, for a piston-flow model is $\delta(t'-\tau)$, where τ is the residence time. For a piston-flow model, the concentration of ^3H in a water parcel separated since the time of recharge or entry into the ground-water system can be defined as:

$$C(t) = C(o) \exp(-\lambda t) \,, \qquad (3)$$

where C(t) is the concentration at a given time (t), C(o) is the input concentration, and $\lambda = 0.05626$. For nonradioactive tracers in the piston-flow model, such as CFCs, the concentration at any given time (t) is equal to the input concentration at time, t=0.

A second approach for estimating average residence time (turnover time) of water in an aquifer involves the use of an exponential model (EM), which assumes that transit times in the aquifer are exponentially distributed and are related to the distribution of flow velocities. The model assumes steady-state flow conditions, areally distributed recharge to the aquifer, and constant recharge rates and other aquifer properties. The EM is mathematically similar to the well-known model of a well-mixed reservoir (that is, complete mixing within the aquifer). However, the exponential model also has been applied to aquifers where mixing of stratified ground-water flow occurs as discharge to springs (Vogel, 1967; Maloszewski and Zuber, 1982; Focazio and others, 1998; Richter and others, 1993). The weighting function, $g(t')$, for the exponential model is $(1/\tau_m)\exp(-t'/\tau_m)$, where τ_m is the average residence time.

A third approach used in this study to assess the ages of spring waters involves a binary-mixing model, which assumes that the age of water issuing from a spring can be represented by a simple mixture of relatively young water (recently recharged) from a relatively shallow flow system with older water originating from a deeper flow system. Two-component mixtures of spring waters would contain CFC compounds that yield different estimates of age resulting from the various fractions of young and old waters in the mixture. Mixing models typically are restricted to two end-member waters. With more than two waters mixing, the problem becomes essentially unsolvable because 2X-1 tracers would be needed for X separate and distinct waters mixing in springs. There are not enough well-established tracers that could be used for age dating (Plummer and Busenberg, 1999).

Estimation of Nitrogen Inputs from Nonpoint Sources

As a way of assessing how changes in land use in the basin during the past 50 years have affected nitrate concentrations in ground water discharging to springs, nitrogen inputs from various nonpoint sources were estimated. Methods for compiling and estimating nitrogen inputs for each of five selected counties (Suwannee, Lafayette, Gilchrist, Columbia, and Alachua) in the study area are discussed below. For each county, estimated N input loads were computed for fertilizers, atmospheric deposition, animal wastes (dairy and beef cows, layer and broiler chickens, and swine), effluent from septic tank systems, and atmospheric deposition.

Fertilizers

Estimates of N from fertilizers applied to cropland were computed by using two sources of information: (1) fertilizer sales records compiled annually by the Florida Department of Agriculture and Consumer Services (DACS), and (2) recommended rates of fertilizer application for various crop types by the Florida Institute of Food and Agricultural Sciences (Jones and others, 1974; Kidder and others, 1998). To obtain estimates of N inputs from fertilizer sales information, the amount of N was estimated for various materials sold as fertilizers. These dominant materials [with percentage by weight of N in parentheses (Farm Chemicals Handbook, 1998)] included anhydrous ammonia (82), ammonium nitrate (34), ammonium sulfate (21), cyanamid (21), potassium nitrate (16), nitrogen solutions (33), and urea (46). The relative amounts of these materials varied annually; however, the largest inputs of N were from the fertilizer materials anhydrous ammonia, ammonium nitrate, and nitrogen solutions. The amount of each material sold was multiplied by the percentage of N and summed to obtain the annual estimates of N from fertilizers sold in each county. Fertilizer sales data tended to overestimate the amount of N applied because not all fertilizer sold in a particular county was used in that county. There was no reliable way to track the amount of fertilizer sold in a particular county that was transported in or out of a county or that which was stockpiled in any given year. Therefore, estimated inputs of N from fertilizer sales information may represent maximum values of N inputs.

Another estimate of N inputs from fertilizers was obtained from recommended application rates for various crop types and published information on crop acreage in each county. N inputs from fertilizer applications for years 1954, 1959, 1964, and 1969 were calculated by multiplying the total amount of fertilizer applied per unit area by the area on which fertilizer was applied (from Florida Agricultural Census data) by the average percentage of N by weight for fertilizers sold in each county. The average percentage of N by weight was calculated from historical sales data for each county for these 4 years. The percent N in each fertilizer mixture was weighted by amount sold for quantities greater than 22,700 kilograms (kg) or 25 tons. This represented approximately 94 percent of the total weight of mixed fertilizers sold annually. The remaining 6 percent was assumed to have the same percentage of N as the known amount. Estimates of N loading from fertilizer application in 1974 and for the 5 individual years following 1974 were based on crop acreage information from the Florida Agricultural Census. Starting in 1974, data for major crop acreage were compiled for each county. The number of acres of harvested crops was multiplied by the recommended rates of fertilizer application for each crop type (Kidder and others, 1998) and summed to obtain the total N for each county for a given year. Since the sum of the harvested cropland acreage was less than the reported total acres on which fertilizers were applied (DACS Census data), the total N loading from fertilizers was adjusted by multiplying the N-loading amounts for the harvested cropland acreage by the ratio of total acres of fertilizer applied to the sum of the harvested cropland acreage.

Animal Wastes

Estimates of N inputs from animal manure were calculated for 1955-95 from the numbers of beef cattle, dairy cattle, swine, broiler chickens, and egg-laying chickens in each county (U.S. Department of Commerce, 5-year intervals from 1946-97), and from estimates of the nutrient content of manure for each of these animals, as described below. Estimates of losses due to volatilization and other processes resulting from various waste management practices are discussed in a later section.

Nutrient contributions, in kilograms per day (kg/day) of nitrogen, from animal wastes were as follows, based on 454 kg (1,000 pounds) of animal: dairy cows, 0.18; beef cows, broiler chickens, 0.50; egg-laying chickens, 0.38; and swine, 0.24. Average weights, in kg, of animals used in the calculations were: broiler chickens, 0.9; egg-laying chickens, 1.4; beef cows, 364; dairy cows, 635; and swine, 61 (American Society of Agricultural Engineers, 1996).

Nitrogen loading to ground water from poultry manure and poultry litter (combination of manure and bedding materials) during 1954-97 was estimated by using information on the annual estimates of the number of broilers (also called fryers or frying chickens) from Florida agricultural census data (DACS, 1954-97) and from estimates of the amount of annual manure production and its average total N content. An annual N-loading estimate of 0.022 kg per broiler is based on a manure production rate of 1.1 kg with an average total N content of 2 percent (Sloan and others, 1992; Vest and Merka, 1994).

Septic Tank Effluent

Annual N inputs from domestic septic tank systems were estimated by multiplying the average mass loading of N, 4.09 kg N per capita per year (Otis and others, 1993), by the number of people that are contributing wastes to septic tank systems in each of the five counties (U.S. Bureau of the Census, 1990). The percentage of the population contributing wastes to septic tanks or cesspools in each county was calculated from sewage disposal data from the 1990 Census of Housing: Alachua (27), Columbia (72), Gilchrist (88), Lafayette (83), and Suwannee (76). Sewage disposal data were available only from the 1990 Census of Housing (U.S. Bureau of the Census, 1993). To estimate N inputs from septic tanks prior to 1990, it was assumed that the percentage of the population on septic systems remained constant back to 1955. The average mass N loading assumes a water use of 170 liters per capita per day (Otis and others, 1993). Nitrogen loading from other human waste sources, such as commercial septic tank effluent and recreational vehicle wastewater, were assumed to be negligible in this study.

Atmospheric Deposition

Estimates of N loading from atmospheric deposition were obtained from measurements of nitrate (NO_3) and ammonium (NH_4) in rainfall collected at the long-term NADP/NTN station in Bradford Forest, in Bradford County, which is located in the eastern part of the Suwannee River Basin (fig. 1). Annual wet deposition rates of total inorganic nitrogen (NO_3-N and NH_4-N) for the the Bradford Forest station for 1979 to 1997 ranged from 2.01 to 3.99 kilograms per hectare (kg/ha). The nitrogen load from atmospheric deposition (wetfall plus dryfall) for each county was obtained by multiplying the annual wet deposition rates of inorganic N by the county area and by the dry-deposition enrichment factor. Using a mean total dry-deposition flux of nitrogen (0.96 times the wet-deposition flux, +/- 0.14) for northern Florida (Baker, 1991) results in atmospheric deposition rates for 1979-97 that range from 3.94 to 7.82 kg/ha. Dry-deposition fluxes of N were based on particulate and gas fluxes of nitric oxide (NO_2) and nitric acid (HNO_3) (Baker, 1991). The average of N loading estimates from atmospheric deposition during 1979-97 was assumed to represent N loading from atmospheric deposition during 1954-78.

CHEMISTRY OF SPRING WATERS AND WATER FROM WELLS

In this section, the concentrations of major ions, nutrients, and dissolved organic carbon are used to provide information on the sources and processes that affect solute concentrations in water from the Upper Floridan aquifer. Also, dissolved gas data, in particular Ar and N_2, are used to describe recharge processes in the ground-water system.

Major Ions and Nutrients

Water from springs and shallow zones in the Upper Floridan aquifer is classified as a calcium-bicarbonate (Ca-HCO_3) type having low dissolved solids concentrations in spring waters ranging from 150 to 250 mg/L (table 3). Dissolved organic carbon concentrations in spring water and ground water are low, typically less than or equal to 1 mg/L (analytical method reporting limit of 0.1 mg/L) with one exception; the DOC concentrations in water from Columbia Spring was 13 mg/L. Saturation indices of the spring waters with respect to calcite and dolomite were typically less than 0.0 (calcite SI ranged from -0.35 to 0.14, and dolomite SI ranged from -2.46 to -0.20) indicating that the waters are slightly undersaturated with respect to these two minerals which form the limestone rock matrix (table 3). Saturation indices with respect to calcite and dolomite were calculated by using the computer-based thermodynamic model WATEQFP (Plummer and others, 1994), which assumes that all dissolved species are at equilibrium with one another. When ground water is undersaturated with respect to calcite and dolomite, there is the potential for continued dissolution of the aquifer rock.

Nitrate-N concentrations in spring waters were quite variable. In some waters from springs such as Columbia, Ichetucknee Blue Hole, Poe, and Hornsby (table 3), nitrate-N concentrations were less than 1.0 mg/L, but still elevated above background nitrate concentrations of about 0.05 mg/L for the area (Katz, 1992; Maddox and others, 1992). Nitrate-N concentrations in other spring waters clearly show the impact of agricultural activities in the basin; in particular springs SUW718971 (29 mg/L) and SUW725971B (38 mg/L) likely receive recharge water from an area dominated by cropland (approximately 2,000 hectares (ha)) that is extensively fertilized and irrigated. Likewise, the nitrate-N concentration in water from spring GIL917971, which receives water from an area with cropland and animal farming operations was 26 mg/L. In most cases, nitrate-N concentrations in water samples collected from springs during this study were slightly higher than nitrate concentrations found in water samples previously collected from these same springs (Hornsby and Mattson, 1996).

During low-flow conditions in July 1997, nitrate-N concentrations in water from wells -9001 and -6011, tapping shallow zones of the Upper Floridan aquifer in Lafayette County, were 18 and 20 mg/L, respectively (table 3). In contrast, following a period of prolonged rainfall during the winter and early spring of 1998, nitrate-N concentrations decreased substantially in water samples from well-6011 (13 mg/L) and well-9001 (10 mg/L). A similar trend between high-flow and low-flow conditions was reported by Katz and others (1997) for ground-water samples collected in 1990 and 1991 from wells tapping the Upper Floridan aquifer in this area. The decrease in nitrate concentrations can be attributed in part to denitrification reactions (Katz and others, 1997); however, dilution with recharge water low in nitrate is another important factor.

The concentrations of other dissolved species, such as sulfate, potassium, and magnesium, also are higher in spring water and water from the two zones in the Upper Floridan aquifer than background concentrations of these species found in the Upper Floridan aquifer in this area (Katz, 1992; Maddox and others, 1992). Sulfate concentrations in spring waters and ground water are elevated by a factor of 3, with the exception of water from Ichetucknee Blue Hole Spring, which has sulfate concentrations below the median background concentration of 5.3 mg/L (Katz, 1992). Concentrations of potassium in water from the two wells in the agricultural area are more than an order of magnitude higher than background concentrations (0.49 mg/L; Katz, 1992). Magnesium concentrations are slightly higher than background (6.1 mg/L; Katz, 1992) in spring waters, but are 3 to 4 times higher in ground water collected from the two zones of the Upper Floridan aquifer. There is a significant ($p<0.05$) correlation between nitrate and potassium concentrations, as well as between chloride and potassium, and between sulfate and chloride in spring waters. The elevated concentrations of sulfate, chloride, potassium, and magnesium in spring water and ground water indicates the likely contribution from anthropogenic sources, such as fertilizers and leachate from animal wastes. Even though large amounts of phosphorus are applied to cropland in the basin, phosphate concentrations in

Table 3. Chemical characteristics, concentrations of major ions and other dissolved species, calcite and dolomite saturation indices for spring waters and ground water

[Concentrations of elements and species are in milligrams per liter, unless otherwise noted; °C, degrees Celsius; SC denotes specific conductance in microsiemens per centimeter; NA, not applicable; COC, dissolved organic carbon; SiO^2, dissolved silica; DS, dissolved solids; SI, saturation index]

SPRING OR WELL NAME	Sample date	Temperature, oC	pH	Specific conductance	Dissolved oxygen	Ca	Mg	Na	K	NO3-N	NH3-N	Organic N	HCO_3	Cl	SO_4	F	SiO_2	DS	DOC	PO_4	Calcite SI	Dolomite SI
SANTA FE RIVER SPRINGS																						
GIL917971	8/20/98	22.0	7.32	462	3.28	78.5	5.2	6.6	2.03	26.00	0.030	<0.2	197	9.8	15.6	0.10	5.5	210	0.1	0.04	0.01	-0.84
Ginnie Springs	8/21/98	22.3	7.51	305	4.64	54.0	4.7	2.4	0.23	1.20	0.030	<0.2	175	5.1	7.8	0.10	6.4	160	0.1	0.03	0.03	-0.69
July Spring	8/21/98	22.3	7.39	368	4.53	64.1	6.1	3.4	0.39	1.70	0.030	<0.2	208	6.3	11.5	0.12	6.6	190	0.1	0.03	0.04	-0.63
Poe Spring	8/21/98	22.3	7.45	387	1.56	67.3	5.2	5.2	0.56	0.82	0.030	<0.2	220	8.9	10.2	0.13	7.2	210	0.1	0.18	0.14	-0.51
Hornsby Spring	8/21/98	22.2	7.36	404	1.10	64.3	6.8	8.2	0.87	0.80	0.030	<0.2	193	11.9	32.2	0.18	10.0	220	1.1	0.20	-0.03	-0.73
Columbia Spring	8/20/98	24.6	7.29	332	2.71	48.8	7.9	7.7	1.05	0.42	0.050	0.4	132	11.4	41.0	0.19	11.0	180	13.0	0.24	-0.34	-1.13
Trail Spring	8/20/98	21.6	7.40	345	2.14	60.4	4.3	3.6	2.13	3.80	0.030	<0.2	177	6.2	13.7	0.10	4.9	180	0.1	0.03	-0.05	-0.94
Ichetucknee Blue Hole Spring	8/14/97	21.7	7.39	262	2.42	51.0	4.7	2.8	0.37	0.72	0.010	<0.2	176	4.7	4.3	0.13	9.3	150	0.1	0.04	-0.12	-0.97
median value		22.25	7.39	357	2.57	62.3	5.2	4.4	0.7	1.01	0.03	<0.2	185	7.63	12.55	0.13	6.90	185	0.10	0.04	-0.01	-0.79
LAFAYETTE CO. SPRINGS																						
Troy Spring	7/15/97	22.4	7.20	362	0.38	59.8	6.5	3.0	0.99	2.70	0.013	<0.2	196	6.1	11.0	0.1	6.4	184	0.7	0.02	-0.20	-1.04
Troy Spring	8/19/98	21.2	7.53	367	1.74	62.6	6.7	3.5	1.11	2.80	0.060	<0.2	203	6.2	10.8	0.10	6.4	190	0.1	0.03	0.14	-0.38
Mearson Spring	8/19/98	21.2	7.43	362	1.90	59.8	8.8	3.2	0.59	1.70	<0.01	<0.2	209	5.4	10.8	0.12	6.8	190	0.1	0.02	0.04	-0.46
Lafayette Blue Spring	7/15/97	21.8	7.11	423	0.87	64.9	10.5	5.5	0.70	2.00	0.012	<0.2	237	8.7	11.0	0.1	5.6	218	0.9	0.03	-0.19	-0.87
Ruth Spring	8/19/98	20.9	7.25	405	1.96	68.5	6.0	5.0	2.67	5.50	<0.01	<0.2	205	8.7	13.2	0.10	5.0	210	0.2	0.02	-0.10	-0.96
LAF718972	8/19/98	21.0	7.28	383	0.45	66.4	6.2	3.8	1.76	3.00	0.020	<0.2	214	7.6	8.4	0.10	4.7	200	1.3	0.03	-0.06	-0.85
median value		21.2	7.27	375	1.3	63.8	6.6	3.7	1.1	2.75	0.0	<0.2	206.9	6.9	10.9	0.1	6.0	195	0.5	0.0	-0.1	-0.9
LOWER SUWANNEE SPRINGS																						
Pothole Spring	8/20/98	21.6	7.25	451	2.32	78.6	0.1	3.5	0.71	1.50	0.040	<0.2	242	7.0	32.5	0.13	6.0	250	0.1	0.03	0.03	-2.46
Fannin Springs	8/18/98	22.3	7.28	452	3.03	79.3	5.2	4.3	2.38	4.50	0.010	<0.2	231	9.7	18.0	0.11	6.1	230	0.1	0.03	0.05	-0.76
Manatee Springs	8/18/98	22.1	7.20	460	2.00	83.1	5.8	3.7	0.99	1.70	0.010	<0.2	239	8.0	31.0	0.10	5.6	250	0.1	0.02	0.00	-0.86
Rock Bluff Spring	8/20/98	21.8	7.43	300	2.85	56.1	3.0	2.6	0.39	1.10	0.030	<0.2	167	4.5	10.8	0.10	5.0	160	0.1	0.03	-0.06	-1.09
median value		22.0	7.27	451.5	2.6	79.0	4.1	3.6	0.9	1.60	0.0	<0.2	234.8	7.5	24.5	0.1	5.8	240	0.1	0.0	0.0	-1.0
SUWANNEE CO. SPRINGS																						
Running Springs	8/18/98	21.2	7.50	344	2.20	54.3	13.0	2.3	0.39	2.10	0.020	<0.2	209	5.2	14.0	0.16	6.5	190	0.1	0.03	0.06	-0.20
Little River Springs	7/15/97	21.9	7.27	373	1.95	61.8	6.9	2.6	0.63	1.50	0.014	<0.2	201	5.9	18.3	0.1	6.5	195	0.4	0.01	-0.12	-0.88
SUW718971	8/19/98	21.0	7.41	455	5.52	58.5	16.2	5.4	3.49	29.00	0.070	<0.2	167	14.1	23.2	0.18	6.4	200	0.3	0.04	-0.11	-0.49
SUW725971A	8/19/98	21.1	7.42	481	5.90	61.8	14.9	6.0	4.20	37.00	<0.01	<0.2	149	16.1	27.0	0.17	5.5	200	0.1	0.02	-0.13	-0.58
Charles Spring-1	7/15/97	21.6	7.08	370	1.50	57.0	10.0	2.8	0.54	2.20	0.013	<0.2	200	5.1	17.0	0.1	6.3	190	0.8	0.04	-0.35	-1.14
Telford Spring	7/16/97	21.3	7.22	461	3.38	63.8	17.4	3.1	0.41	2.50	0.015	<0.2	226	5.9	43.6	0.2	7.0	246	0.5	0.03	-0.14	-0.54
SUW725971B	8/19/98	21.1	7.42	481	5.90	61.8	14.9	5.6	4.20	38.00	0.040	<0.2	149	16.1	27.0	0.17	5.5	200	0.1	0.02	-0.13	-0.58
Charles Spring-2	7/15/97	21.6	7.08	370	1.50	56.0	10.0	2.8	0.54	2.30	0.013	<0.2	200	5.1	17.0	0.1	6.2	189	1.0	0.04	-0.35	-1.14
median value		21.25	7.34	414	2.79	60.15	13.95	2.96	0.59	2.35	0.02	<0.2	200.5	5.89	20.73	0.17	6.45	197.5	0.35	0.03	-0.12	-0.56
LAFAYETTE CO. WELLS																						
Well-6011	7/16/97	22.6	7.21	560	4.38	70.5	16.6	8.3	6.19	20.00	0.018	<0.2	203	15.2	19.6	<.1	6.5	389	0.5	0.02	-0.57	-0.57
Well-9001	7/16/97	23.2	7.12	570	4.10	58.1	23.2	11.6	6.40	18.00	0.014	<0.2	225	14.1	15.8	0.1	7.4	402	0.8	0.41	-0.58	-0.58
Well-6011	3/9/98	22.3	7.00	501	2.14	65.0	14.2	6.4	4.89	13.00	0.094	<0.2	200	11.5	17.9	0.11	6.3	220	<0.1	0.03	-0.38	-1.10
Well-9001	3/9/98	23.0	7.27	319	1.52	62.3	18.4	7.6	4.89	10.00	0.024	<0.2	224	16.4	14.6	0.13	4.9	230	0.2	0.03	-0.07	-0.35

spring waters and ground water from the Upper Floridan aquifer are low, typically less than 0.05 mg/L, except water from Poe, Hornsby, and Columbia Springs, which range from 0.18 to 0.24 mg/L. Low phosphate concentrations in water from the Upper Floridan aquifer are related to the low solubility of phosphate, which is controlled by coprecipitation and adsorption reactions with metal oxides, particularly ferric and manganese oxyhydroxides (Hem, 1985).

Dissolved Gases

Dissolved gas data, particularly Ar and N_2, can provide valuable information on recharge processes in ground-water systems. The solubilities of Ar and N_2 vary substantially as a function of temperature (Weiss, 1970); consequently, concentrations of these gases in ground water can indicate the temperature of the unsaturated zone during recharge. The recharge-water temperature and amounts of excess air (Heaton and Vogel, 1981) can be evaluated from a plot of dissolved Ar versus N_2 concentrations (Busenberg and others, 1993). In figure 4, the solubilities of Ar and N_2 are shown for temperatures ranging between 0 and 30 ^oC at sea level along the zero-excess-air line, which is labeled water in equilibrium with air. The lines labeled 5, 10, 15, and 20 represent the equilibrium concentrations of Ar and N_2 with 5, 10, 15, and 20 cubic centimeters per liter (cm^3/L) of air added in excess of the equilibrium concentrations. Other information on the evolution of dissolved gases can be obtained from this plot. For example, adding radiogenic Ar will shift the sample composition vertically as shown in the lower right hand corner of the plot (fig. 4). Denitrification reactions involving the microbially mediated reduction of nitrate to N_2 will shift the dissolved-gas composition horizontally. Excess air added during recharge processes will shift the composition diagonally. The recharge-water temperature of a sample plotted on fig. 4 is obtained by extending a diagonal line parallel to the excess air lines from the sample to the recharge-water temperature axis on the right-hand side of the diagram (Busenberg and others, 1993). The excess-air content of the sample is obtained by following a diagonal line (parallel to the excess-air lines) from the sample to the excess-air axis on the top of the diagram.

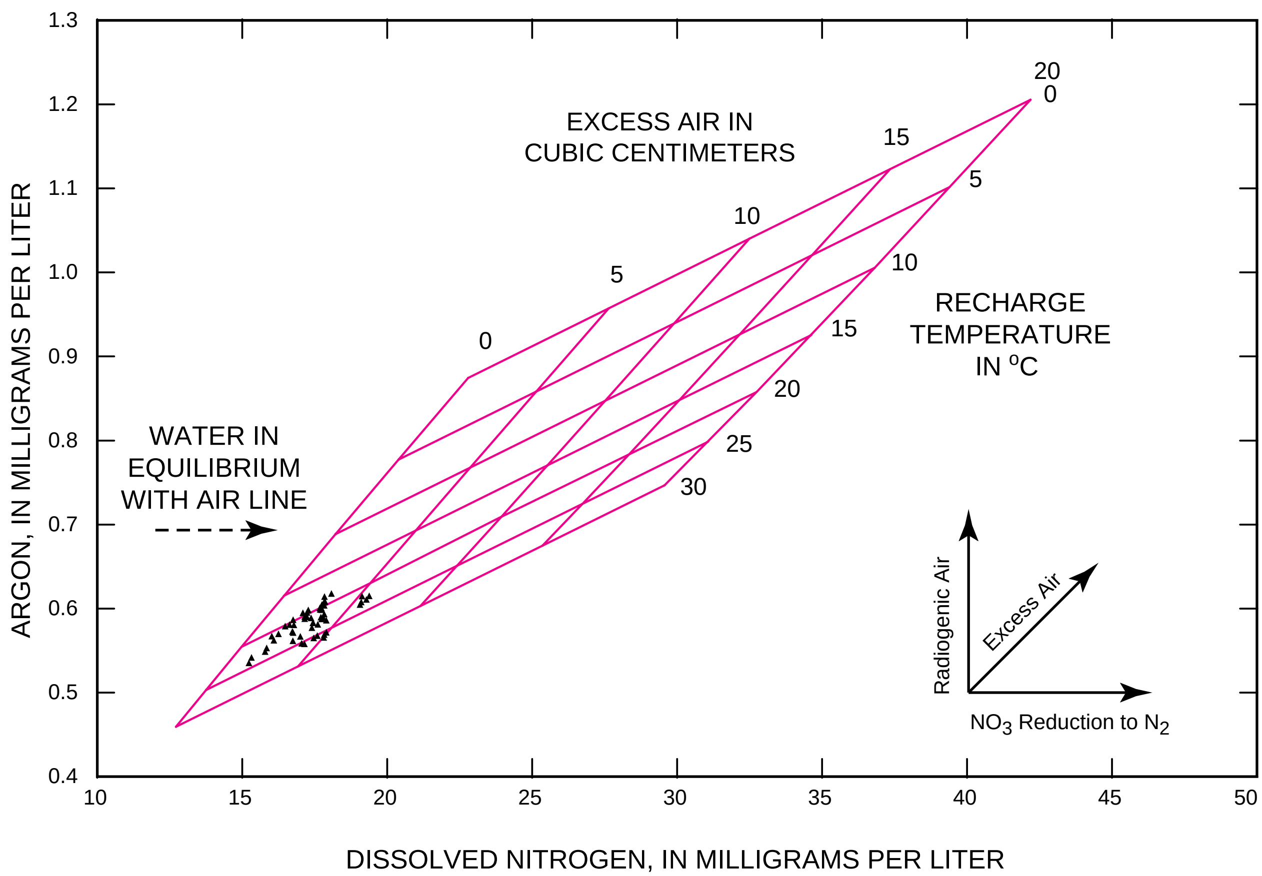


Figure 4. Dissolved nitrogen and argon concentrations in spring waters and water from wells.

The concentrations of N_2 and Ar in spring-water samples are consistent with atmospheric equilibration during ground-water recharge with minor amounts of excess air added either during recharge or as a result of sampling methods. The apparent recharge temperatures are 22 ± 3 °C (assuming an 8-m elevation for recharge and 100 percent humidity at the water table) with about 0 to 7 cm^3/L of excess air during recharge. This calculated temperature agrees closely with a mean annual air temperature of 20.4 °C at Live Oak, Fla., for the period 1961-90 (Owenby and Ezell, 1992). Also, $\delta^{15}N$ values of dissolved N_2 generally are consistent with air equilibration during recharge and with minor amounts of excess air (0.6 to 0.8 per mil). Water samples from well-6011 and from Troy and GIL917971 springs have slightly lower $\delta^{15}N$ (N_2) values (0.3 to 0.4 per mil), which could indicate small amounts of non-atmospheric N_2; however, some of those samples may have leaked slightly. Of the three sites, water from well-6011 seems most likely to have excess N_2, based on the isotope and N_2 concentration data (possibly as much as 2 to 3 mg/L). With the exception of water from well-6011, denitrification reactions likely have not reduced nitrate concentrations in the ground-water system.

Table 4. Dissolved gas data, calculated recharge temperature, and excess air for samples of spring water and water from wells

[mgL, milligrams per liter; mmol/L, millimoles per liter; °C, degrees Celsius; cm^3, cubic centimeters]

Spring/Well Name	Concentration in mg/L			Concentration in mmol/L			Recharge Temp. °C	Excess air cm^3
	CH_4	N_2	Ar	CH_4	N_2	Ar		
Santa Fe River Springs:								
GIL917791	0.000	17.832	0.569	0.000	0.637	0.014	25.7	4.2
GIL917791	0.000	17.897	0.572	0.000	0.639	0.014	25.4	4.2
Ginnie	0.000	16.016	0.567	0.000	0.572	0.014	20.8	1.2
Ginnie	0.000	16.095	0.562	0.000	0.575	0.014	21.7	1.6
Hornsby	0.001	19.130	0.615	0.000	0.683	0.015	21.6	4.6
Hornsby	0.001	17.441	0.583	0.000	0.623	0.015	22.1	3.0
July	0.000	15.786	0.549	0.000	0.564	0.014	23.1	1.6
July	0.000	15.843	0.553	0.000	0.566	0.014	22.6	1.5
Poe	0.001	16.752	0.572	0.000	0.598	0.014	22.1	2.3
Poe	0.001	16.727	0.573	0.000	0.597	0.014	21.8	2.2
Trail	0.000	17.450	0.583	0.000	0.623	0.015	22.1	3.0
Trail	0.000	17.400	0.577	0.000	0.621	0.014	22.9	3.2
Columbia	0.005	15.319	0.542	0.000	0.547	0.014	22.9	1.1
Columbia	0.006	15.226	0.535	0.000	0.544	0.013	23.8	1.2
Ichetucknee Blue Hole	0.000	17.729	0.601	0.000	0.633	0.015	20.1	2.8
Ichetucknee Blue Hole	0.000	17.738	0.599	0.000	0.633	0.015	20.4	2.9
Lafayette County Springs:								
Troy 1998	0.000	19.062	0.605	0.000	0.680	0.015	23.1	4.9
Troy 1998	0.000	19.103	0.608	0.000	0.682	0.015	22.7	4.8
Troy 1997	0.001	17.825	0.604	0.000	0.636	0.015	19.9	2.8
Troy 1997	0.001	17.689	0.599	0.000	0.631	0.015	20.3	2.8
Mearson	0.001	17.736	0.588	0.000	0.633	0.015	22.2	3.3
Mearson	0.001	17.710	0.590	0.000	0.632	0.015	21.8	3.2
Lafayette Blue	0.002	17.675	0.601	0.000	0.631	0.015	20.0	2.7
Lafayette Blue	0.002	17.751	0.605	0.000	0.634	0.015	19.6	2.7
Ruth	0.000	17.792	0.590	0.000	0.635	0.015	22.0	3.3
Ruth	0.000	17.829	0.593	0.000	0.636	0.015	21.5	3.3
LAF718972	0.004	19.278	0.611	0.000	0.688	0.015	22.7	5.0
LAF718972	0.004	19.380	0.615	0.000	0.692	0.015	22.3	5.0
Lower Suwannee Springs:								
Fannin	0.000	17.466	0.565	0.000	0.623	0.014	25.3	3.8
Fannin	0.000	17.587	0.568	0.000	0.628	0.014	25.1	3.9
Pothole	0.008	17.831	0.608	0.000	0.637	0.015	19.3	2.7
Pothole	0.008	17.858	0.608	0.000	0.637	0.015	19.3	2.7

Table 4. Dissolved gas data, calculated recharge temperature, and excess air for samples of spring water and water from wells (Continued)

[mgL, milligrams per liter; mmol/L, millimoles per liter; °C, degrees Celsius; cm^3, cubic centimeters]

Spring/Well Name	Concentration in mg/L			Concentration in mmol/L			Recharge Temp. °C	Excess air cm^3
	CH_4	N_2	Ar	CH_4	N_2	Ar		
Lower Suwannee Springs: (Continued)								
Manatee	0.001	17.603	0.581	0.000	0.628	0.015	22.9	3.4
Manatee	0.001	17.899	0.586	0.000	0.639	0.015	22.9	3.7
Rock Bluff	0.001	17.238	0.590	0.000	0.615	0.015	20.5	2.4
Rock Bluff	0.002	17.377	0.589	0.000	0.620	0.015	21.0	2.7
Suwannee County Springs:								
Running Spring	0.000	17.235	0.595	0.000	0.615	0.015	19.7	2.2
Little River	0.000	17.836	0.614	0.000	0.637	0.015	18.4	2.4
Little River	0.000	18.079	0.618	0.000	0.645	0.015	18.5	2.7
SUW 725971	0.000	16.253	0.570	0.000	0.580	0.014	21.0	1.5
SUW 725971-B	0.000	17.274	0.598	0.000	0.617	0.015	19.3	2.1
SUW 725971-B	0.000	16.478	0.579	0.000	0.588	0.014	20.1	1.5
SUW 718971	0.000	16.749	0.562	0.000	0.598	0.014	23.7	2.7
SUW 718971	0.001	17.006	0.567	0.000	0.607	0.014	23.6	2.9
Charles	0.001	17.157	0.591	0.000	0.612	0.015	20.2	2.2
Charles	0.001	17.152	0.588	0.000	0.612	0.015	20.6	2.3
Telford	0.000	16.757	0.587	0.000	0.598	0.015	19.7	1.7
Telford	0.000	17.096	0.595	0.000	0.610	0.015	19.3	2.0
Lafayette County wells:								
Well-6011 (7/16/97)	0.008	17.045	0.559	0.001	0.608	0.014	25.2	3.3
Well-6011 (7/16/97)	0.019	17.143	0.558	0.001	0.612	0.014	25.5	3.5
Well-9001 (7/16/97) Leak	0.000	17.812	0.566	0.000	0.636	0.014	26.2	4.3
Well-9001 (7/16/97)	0.000	16.628	0.581	0.000	0.594	0.015	20.3	2.8
Well-6011 (03/09/98)	0.001	18.056	0.548	0.000	0.645	0.014	30.5	5.4
Well-6011 (03/09/98)	0.001	17.890	0.545	0.000	0.639	0.014	30.6	5.3
Well-9001 (03/09/98)	0.000	17.380	0.564	0.000	0.620	0.014	25.2	3.7
Well-9001 (03/09/98) Leak	0.000	25.923	0.710	0.000	0.925	0.018	25.1	12.2

SOURCES OF SPRING WATER AND WATER FROM THE UPPER FLORIDAN AQUIFER

Stable isotopes of oxygen ($\delta^{18}O$) and hydrogen (δD) were used in this study to determine the origin of water and to characterize possible mixing of different sources of water in springs and in zones of the aquifer. Values of $\delta^{18}O$ and δD in spring waters cluster along the global meteoric water line (Craig, 1961), $\delta D = 8\delta^{18}O + 10$, (fig. 5), which indicates that springs receive ground water that is recharged from rainfall that undergoes little or no evaporation. The more or less random deviations from the meteoric water line indicate that the spring waters are affected little by evaporation or mixing with surface waters that would have enriched isotopic signatures due to evaporation. Since spring water is representative of ground water that is integrated both temporally and spatially with rainfall (meteoric water) that recharges the Upper Floridan aquifer, one would expect the stable isotopic composition of the spring waters to plot near the global meteoric water line. The observed small differences in isotopic composition likely are related to storm track origin, the number of evaporation and condensation cycles (Dansgaard, 1964), and temperatures of infiltrating rain in recharge areas for the springs. Similar values of $\delta^{18}O$ and δD were observed for monthly samples of rainfall (fig. 5) collected from June 1995 through June 1996 at the Rocky Hill Fire Tower in Suwannee County (fig. 1) (Katz and others, 1998). Monthly samples were composited from weekly samples collected by a wet/dry atmospheric deposition collector. Values of δD and $\delta^{18}O$ are slightly enriched (higher) in water from well-6011 (table 5) compared to the isotopic composition of other ground-water samples, indicating either that water recharging the aquifer at this site may have undergone some evaporation or that mixing has occurred with surface water that contains an enriched isotopic signature.

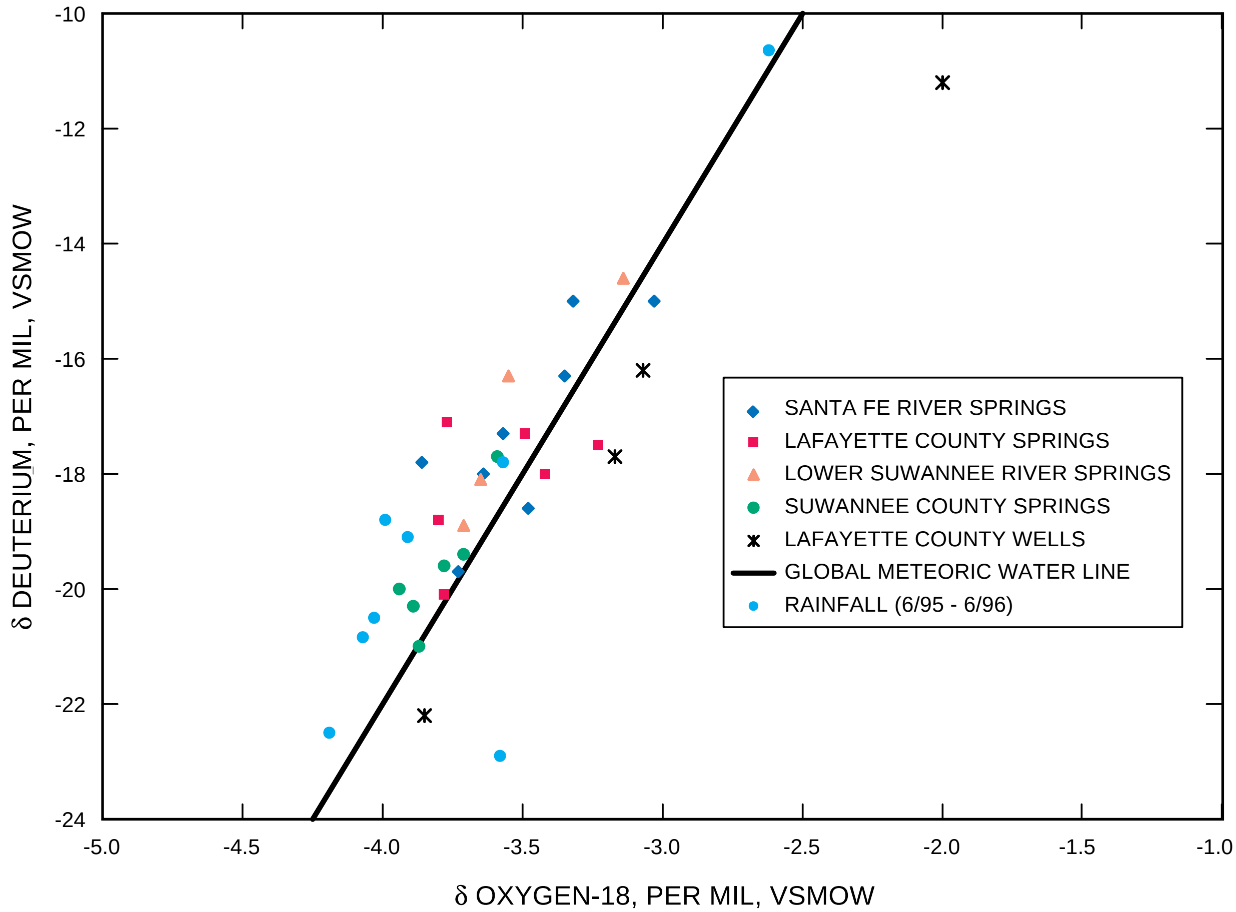


Figure 5. Deuterium and oxygen-18 content of spring water, ground water, and rainfall compared to the global meteoric water line.

Spring water in the unconfined Upper Floridan aquifer evolves mostly under open-carbon-dioxide (CO2) conditions, as indicated by calculated values (WATEQF; Plummer and others, 1994) of the partial pressure of CO_2 (expressed as log PCO_2, in atmospheres) that exceed the atmospheric value of –3.5 and range from -2.29 to -1.77. Values of $\delta^{13}C$ (DIC) are enriched (higher) in spring waters (-10.8 to -13.2 per mil) (table 5) compared to water from the surficial aquifer system (-18 to -25 per mil) in northern Florida (Katz and others, 1998). Rapid recharge rates in the study area, which result from the highly permeable sands, facilitate the downward transport of oxygen and DOC from the unsaturated zone. Heterotrophic bacteria present in the unsaturated zone aerobically degrade DOC in interstitial waters ($\delta^{13}C$ ~ -24 per mil) to produce CO_2 that is slightly enriched in its $\delta^{13}C$ content (Deines, 1980). DOC concentrations in the Upper Floridan aquifer can range from 0.03 to 0.80 millimoles per liter (mmol/L), indicating that organic carbon is present for microbial degradation reactions (Katz and others, 1998). The PCO_2, which has accumulated in the unsaturated zone to levels that exceed atmospheric, can persist in ground water because of the low rate of consumption of CO_2 by the dissolution of silicate minerals present in the sediments overlying the Upper Floridan aquifer (Katz and others, 1995b).

Most springs in the Suwannee River Basin in Florida intercept water from large parts of the aquifer, thus their ^{13}C composition is derived from nearly equimolar amounts of carbon from CO_2 ($\delta^{13}C$= -24 per mil from degradation of organic material) and from dissolution of calcite ($\delta^{13}C$= 0 per mil), according to the following reaction:

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^- . \qquad (4)$$

The conversion of CO_2 to HCO_3^- during the dissolution of calcite (under conditions that remain open to CO_2) was indicated by a decrease in PCO_2 levels in water from the Upper Floridan aquifer compared to

Table 5. Isotopic composition of spring waters and ground water

[δ, delta; CO., county; ND, not determined. Values are in per mil. Tritium concentrations are in tritium units]

Spring or well name	Sample Date	$\delta^{18}O$	δD	$\delta^{13}C$	$\delta^{15}N$-NO_3	Tritium
SANTA FE RIVER SPRINGS						
GIL917971	8/20/98	-3.73	-19.7	-11.8	6.4	3.3
Ginnie Springs	8/21/98	-3.57	-17.3	-10.8	3.7	5.2
July Spring	8/21/98	-3.64	-18.0	-11.2	4.1	5.4
Poe Spring	8/21/98	-3.35	-16.3	-11.9	10.6	5.1
Hornsby Spring	8/21/98	-3.03	-15.0	-11.5	8.7	5.8
Columbia Spring	8/20/98	-3.32	-15.0	-12.1	ND	4.3
Trail Spring	8/20/98	-3.86	-17.8	-11.2	8.7	4.5
Ichetucknee Blue Hole Spring	8/14/97	-3.48	-18.6	-12.0	4.4	5.8
LAFAYETTE CO. SPRINGS						
Troy Spring-97	7/15/97	-3.78	-20.1	-12.3	5.4	4.0
Troy Spring-98	8/19/98	-3.80	-18.8	-12.0	5.4	4.0
Mearson Spring	8/19/98	-3.77	-17.1	-11.7	4.5	4.2
Lafayette Blue Spring	7/15/97	-3.42	-18.0	-12.6	8.4	4.0
Ruth Spring	8/19/98	-3.49	-17.3	-11.9	6.9	3.0
LAF718972	8/19/98	-3.23	-17.5	-11.8	9.1	5.1
LOWER SUWANNEE SPRINGS						
Pothole Spring	8/20/98	-3.14	-14.6	-11.7	4.8	5.2
Fannin Springs	8/18/98	-3.65	-18.1	-11.5	7.1	3.7
Manatee Springs	8/18/98	-3.55	-16.3	-11.4	5.8	4.5
Rock Bluff Spring	8/20/98	-3.71	-18.9	-11.5	3.2	4.8
SUWANNEE CO. SPRINGS						
Running Springs	8/18/98	-3.94	-20.0	-11.5	6.2	5.3
Little River Springs	7/15/97	-3.87	-21.0	-12.0	3.9	4.2
SUW718971	8/19/98	-3.71	-19.4	-12.2	2.7	4.7
SUW725971A	8/19/98	-3.59	-17.7	-12.2	2.9	3.3
SUW725971B	8/19/98	-3.59	-17.7	-12.2	2.9	3.3
Charles Spring-1	7/15/97	-3.75	-19.3	-12.9	4.4	4.4
Charles Spring-2	7/15/97	-3.80	-19.9	-13.2	4.4	4.8
Telford Spring	7/16/97	-3.89	-20.3	-12.4	5.8	4.9
LAFAYETTE CO. WELLS						
Well-6011	7/16/97	-3.07	-16.2	-9.7	12.1	4.4
Well-9001	7/16/97	-3.85	-22.2	-8.3	11.0	4.0
Well-6011	3/9/98	-2.00	-11.2	-8.5	12.8	3.1
Well-9001	3/9/98	-3.17	-17.7	-8.9	10.2	6.6

PCO_2 levels in water from wells tapping the overlying surficial aquifer system in northern Florida (Katz and others, 1995b). Dissolution of calcite is indicated by other lines of evidence including: (1) water from springs and wells tapping shallow zones of the Upper Floridan aquifer was slightly undersaturated to equilibrium with respect to calcite (table 3); (2) the concentration of Ca^{2+} and HCO_3^- (DIC) increased substantially compared to rain (recharge) water; (3) $\delta^{13}C$ values (enrichment in ^{13}C) increased; and (4) molar concentrations of Ca^{2+} and HCO_3^- plotted along a line with slope of 2:1 indicating reaction (2). Several spring waters (SUW781971, SUW725971, GIL917971) have HCO_3^- /Ca^{2+} ratios that are substantially less than 2.0 (1.58-1.88), thus indicating that another source of Ca, such as gypsum ($CaSO_4$-$2H_2O$), is likely. When Ca concentrations in spring waters are adjusted by subtracting excess Ca resulting from dissolution of gypsum (containing equimolar amounts of Ca^{2+} and SO_4^{2}), above that of background sulfate concentrations in ground water (8 mg/L) (Katz, 1992; Maddox and others, 1992), the HCO_3^- /Ca^{2+} molar ratio approaches 2.0. These springs drain areas where high quantities of fertilizers and other soil treatments including gypsum have been applied. The low HCO_3^- /Ca^{2+} molar ratio of 1.77 for water from Columbia Spring may indicate mixing of ground water with water from the Santa Fe River, which contains substantially lower concentrations of HCO_3. Other evidence for surface-water mixing in this spring system is the high DOC concentration (13 mg/L) as compared to that in other spring waters.

SOURCES OF NITRATE IN SPRING WATER AND WATER FROM THE UPPER FLORIDAN AQUIFER

Values of $\delta^{15}N$ of nitrate ($\delta^{15}N$-NO_3) have been used to identify sources of nitrate contamination in ground water since the mid-1970's (Heaton, 1986). The method has been used successfully in areas with thin, permeable unsaturated zones and shallow water tables (Heaton, 1986), and in mantled karst aquifers (Wells and Krothe, 1989; Andrews, 1994; Hornsby, 1994). Low $\delta^{15}N$-NO_3 values (0 to 3 per mil) generally indicate an inorganic nitrate source (artificial or synthetic fertilizer); whereas higher $\delta^{15}N$-NO_3 values (10 to 20 per mil) typically indicate an organic (animal waste--manure spreading or waste disposal) source of nitrate. Values of $\delta^{15}N$-NO_3 that fall between 3 and 10 per mil likely are indicative of mixed inorganic and organic sources of nitrate or a soil organic nitrogen source.

An important assumption in using the nitrogen-isotope method is that nitrate has not been removed from ground water due to denitrification reactions that may occur in the aquifer between recharge and discharge to springs. Denitrification can result in an enrichment of ^{15}N of NO_3 and an increase in N_2, thus a corresponding increase in $\delta^{15}N$-NO_3 values could lead to conclusions about N sources that are not consistent with actual values during recharge. Generally, concentrations of N_2 and Ar are consistent with atmospheric equilibration during ground-water recharge with minor amounts of excess air added either during recharge or as a result of sampling methods. Consequently, denitrification reactions do not seem to be affecting nitrate concentrations in spring waters.

Values of δ^{15} N-NO_3 in water from the 24 sampled springs (table 5) range from 2.7 per mil (SUW718971) to 10.6 per mil (Poe Spring). The median $\delta^{15}N$-NO_3 value for all sampled spring waters is 5.4 per mil. The range of $\delta^{15}N$-NO_3 values indicates a variation in sources of nitrate. Spring waters with lower $\delta^{15}N$-NO_3 values (+2 to +6 per mil) and high NO_3 concentrations (greater than 20 mg/L), such as SUW718971 and SUW725971, likely are discharging nitrate from fields receiving artificial fertilizers. These two springs probably receive recharge water from an area dominated by cropland in Suwannee County (approximately 2,000 ha) that is extensively fertilized and irrigated. Springs such as Mearson, Little River, and Rock Bluff, are discharging waters with low NO_3 concentrations (less than 2 mg/L) and low $\delta^{15}N$-NO_3 values that may represent nitrate derived from fertilized fields (diluted) and or natural soil organic matter sources. Spring waters with higher $\delta^{15}N$-NO_3 values (> +9 per mil) generally indicate nitrate associated with manure spreading or waste disposal. The relatively high $\delta^{15}N$-NO_3 values for Poe Spring (10.6 per mil) and Lafayette Blue Spring (8.4 per mil) indicate the likelihood that nitrate originates from an organic source. These two springs are located in county parks where waste-disposal systems operated near the springs may contribute nitrate to ground water.

Water from wells-9001 and -6011 in Lafayette County sampled in 1997 have higher $\delta^{15}N$-NO_3 values than spring waters, 11.0 and 12.1 per mil, respectively, indicating the likelihood of an organic (animal waste) source of nitrate. Even though nitrate concentrations decreased substantially in water from these two wells following a period of sustained rainfall, the $\delta^{15}N$-NO_3 value in water samples from March 1998 decreased only slightly to 10.2 per mil in water from well-9001 and increased slightly to 12.8 per mil in well-6011. These two wells are located near and downgradient from dairy and poultry farms, where leachate from animal wastes may contribute nitrate to ground water.

No trend was observed between the concentration of nitrate and $\delta^{15}N$-NO_3 values in spring waters (fig. 6), indicating that concentrations of nitrate in spring waters and in zones of the Upper Floridan aquifer are not likely altered after recharge. A trend of higher $\delta^{15}N$-NO_3 values corresponding to lower nitrate concentrations would indicate denitrification reactions might be occurring. The presence of dissolved oxygen in all spring-water samples, low DOC concentrations (table 3), and little or no excess N_2 (based on dissolved gas data for Ar and N_2) (table 4) also indicate that denitrification reactions probably are not occurring.

Nitrogen isotope values obtained in this study correspond to the range in values obtained from previous studies in the basin. As part of a study of nitrate in ground water near four dairy farms in Lafayette and Suwannee Counties, Andrews (1994) reported the following values of $\delta^{15}N$-NO_3 (per mil) for water samples collected in May 1993: Lafayette County Blue Spring, 9.65; Telford Spring, 7.70; and Convict Springs, 8.90. Organic sources of nitrogen from leachate of livestock wastes and septic tanks were inferred to be the predominant source of nitrate to spring water (Andrews, 1994). The $\delta^{15}N$-NO_3 values reported by Andrews (1994) are about 1 to 2 per mil higher for Lafayette Blue and Telford Springs than nitrogen isotope data collected during the present study, and may be indicative of differences in analytical procedures between laboratories.

In a study of nitrate in ground water near dairy farms, Andrews (1994) concluded that the source of nitrate in shallow ground water tended to be leachate from livestock waste, whereas the source of nitrate in deeper ground water was attributed to leachate from synthetic fertilizers. Based on nitrogen-isotope analyses of water from 66 monitoring and drinking-water wells from the middle Suwannee River Basin, Hornsby (1994) found that water from four wells produced $\delta^{15}N$-NO_3 values that were equal to or greater than 10 per mil and indicated an organic N source. Hornsby (1994) found that three of the four wells were located downgradient from dairy or poultry operations, indicating the likelihood of localized sources of animal wastes. The majority of wells (44 of 66) yielded water with $\delta^{15}N$- NO_3 values that were less than or equal to 2 per mil, indicating that inorganic N (synthetic fertil-

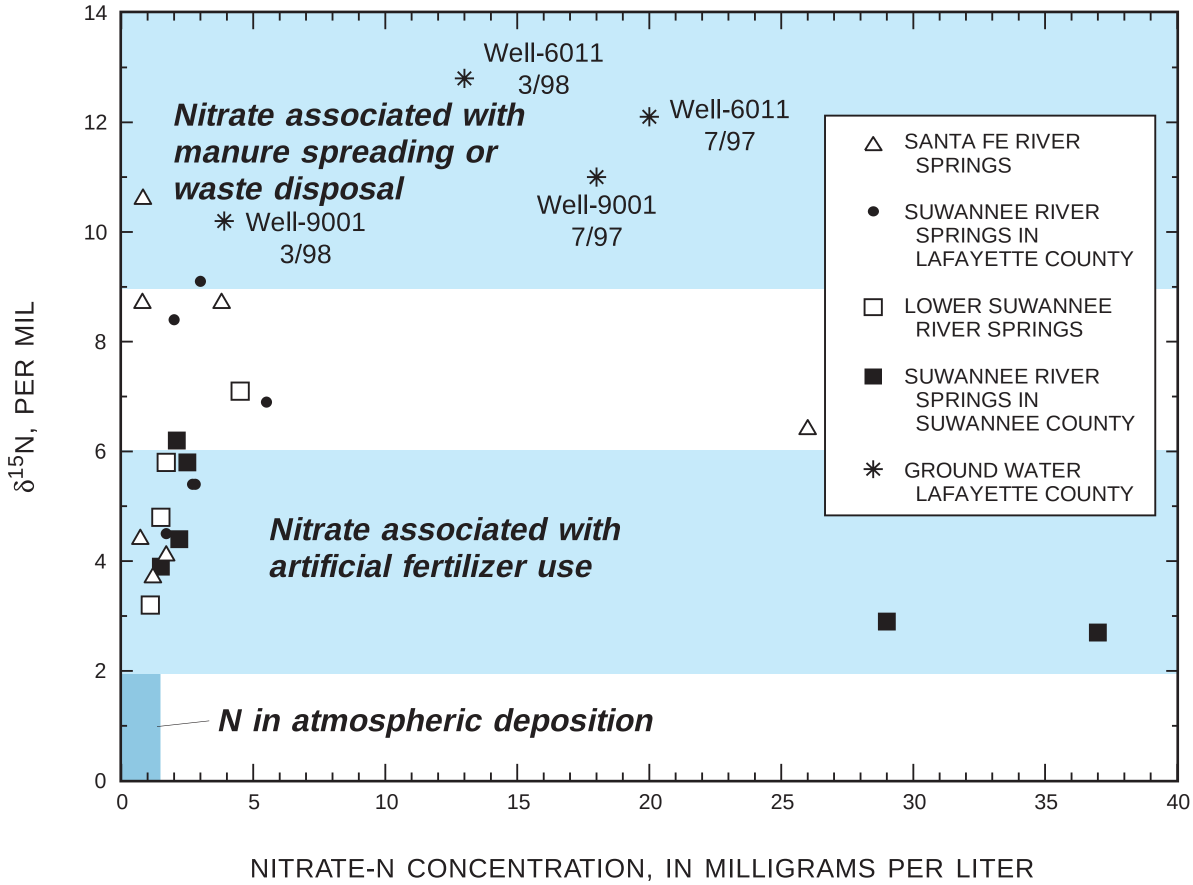


Figure 6. Graph of $\delta^{15}N$ versus NO_3^--N concentrations for spring water and water from zones in the Upper Floridan aquifer.

izers) and/or soil nitrogen was the dominant source of N in the middle Suwannee River Basin. It is important to note that the depth of the 66 wells ranged from 14 to 44 m (median depth 27 m) below land surface, and water samples from these wells were withdrawn from zones about 5 to 40 m deeper than the top of the aquifer, and therefore may not represent most recent nitrate contamination (Hornsby, 1994).

AGES AND RESIDENCE TIMES OF SPRING WATER AND WATER FROM THE UPPER FLORIDAN AQUIFER

A reservoir model (eq. 1; p. 11) was used to provide approximate ranges of residence times of ground water discharging to springs, and to provide a hydrogeologic framework for comparing estimated residence times and apparent ages obtained using data for CFCs and tritium. Even though the reservoir model cannot provide residence times for ground water discharging to a specific spring, one can obtain reasonable ranges of ground-water residence times for springs where some site-specific information is available (Focazio and others, 1998). Values of aquifer thickness, porosity, and recharge rates vary over the Suwannee River Basin, but reasonable ranges of these aquifer characteristics can be used to estimate their associated residence times (fig. 7). Residence times vary from about 5 to 80 years for a range of values for aquifer thickness (30 to 100 m), and porosity (0.05 to 0.4). For a range of recharge rates determined for the study area, 0.2 to 0.8 meter per year (m/yr) (Grubbs, 1998), along with aquifer thickness values of 30 and 100 m, calculated residence times range from about 5 to 50 years (fig. 7).

Chlorofluorocarbons

Assignment of age using concentrations of transient tracers, such as CFCs and ^3H, is based on an interpretation of ground-water flow conditions, and the assumption that CFC concentrations have not been altered by any biogeochemical processes other than

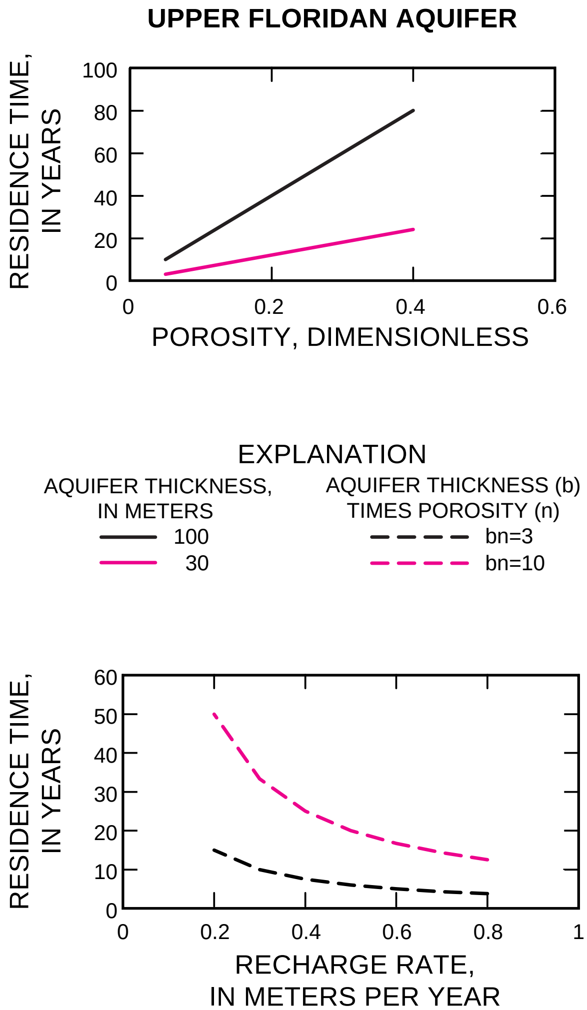


Figure 7. Graphs showing estimated average residence times for ground water calculated from ranges of hydrologic properties of the Upper Floridan aquifer using a reservoir model.

those established by air-water equilibrium during recharge. The term "apparent age" is used because it is not possible to know unequivocably if CFC concentrations have been affected by these processes. The presence of measurable CFCs in ground water and spring water is indicative that some fraction of the spring water or water from shallow zones in the aquifer was recharged after 1940 because CFCs are not detectable in older water (Plummer and Busenberg, 1999).

The apparent age of ground water collected from a well or a spring can have different connotations. For example, the age of water sampled from a well with a short screen interval is more indicative of a point along a ground-water flow path. In contrast, the age of spring water can be interpreted in different ways depending on how ground-water-flow conditions are conceptualized. Under simplified flow conditions, it can be assumed that ground water moves through the aquifer in a piston-like manner. The piston-flow assumption has been used to interpret the apparent age of water samples collected from wells and piezometers open to relatively narrow depth intervals of an aquifer in karst areas (for example, Katz and others, 1995a; Plummer and others, 1998b). Ground-water discharge from springs more likely integrates water from various converging flow paths, and therefore, the age of spring water represents a mean residence time of water from a part of the aquifer that contributes to spring flow (Focazio and others, 1998).

Concentrations of CFC-11, CFC-12, and CFC-113 in water samples reported in table 6 generally do not yield concordant piston-flow ages based on atmospheric equilibration data. Most springs have concentrations of CFC-11 and CFC-113 that are within the range expected for air-saturated waters that are less than 40 years old; however, the apparent equilibration years are different for these two compounds. Most spring waters have CFC-12 concentrations that are too high for air-saturated waters of any age, which likely represents contamination with a non-atmospheric source of CFC-12. The combined data from the three CFC compounds can be interpreted in several different ways, and different interpretations among springs are probable. In this report, apparent ages or residence times of spring waters have been estimated by using measured CFC-11 and CFC-113 concentrations (table 6) and three approaches for conceptualizing ground-water flow in the Upper Floridan aquifer: (1) simplified piston flow, (2) exponential flow, and (3) binary mixing. These three approaches assume that CFC-11 and CFC-113 concentrations were not degraded in the aquifer because ground waters are oxic and contain low concentrations of organic carbon. Recent studies of the stability of CFCs in water from the Upper Floridan aquifer near Valdosta, Ga., found that CFCs were stable in ground water, which was attributed to the low content of particulate organic carbon (Plummer and others, 1998b). CFC-12 data were not used to estimate the apparent age of spring waters due to the large number of samples that were contaminated (CFC-12 concentrations were above the value for water in equilibrium with the CFC-12 concentration in modern (1998) air).

Table 6. Concentration of CFC-11, CFC-12, and CFC-113 in water from springs and wells, calculated atmospheric partial pressure, and model CFC recharge dates

[°C, degrees Celsius; pg/kg, picograms per kilogram; Elev., elevation of land surface; pptv, parts per trillon by volume; Contam., CFC concentrations in water samples that are higher than values in equilibrium with 1998 atmospheric concentrations; ERR, denotes analytical problems]

Sample Name	Sample number	Sampling date	Sampling time	Recharge		Concentration in solution			Calculated atmospheric partial pressure in pptv			Model CFC recharge dates in years		
				Temp. (°C)	Elev. (meters)	pg/kg CFC-11	pg/kg CFC-12	pg/kg CFC-113	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113
Charles Spring	2	07/16/97	1404	20.4	6	201.0	157.5	19.5	115.7	375.4	28.9	1975.0	1984.0	1981.5
Charles Spring	4	07/16/97	1412	20.4	6	199.8	155.2	20.7	115.0	370.0	30.5	1974.5	1983.5	1982.0
Charles Spring	5	07/15/97	1414	20.4	6	201.9	157.9	19.3	116.2	376.4	28.6	1975.0	1984.0	1981.5
Lafayette Blue Spring	2	07/15/97	1616	19.8	6	213.9	315.7	19.0	119.9	735.0	27.2	1975.0	Contam.	1981.0
Lafayette Blue Spring	4	07/15/97	1624	19.8	6	215.7	319.7	17.3	121.0	744.3	24.8	1975.0	Contam.	1980.5
Lafayette Blue Spring	5	07/15/97	1628	19.8	6	222.9	318.0	11.5	125.0	740.5	16.4	1975.5	Contam.	1977.5
Little River Springs	2	07/15/97	904	18.5	6	2518.3	302.4	103.0	1331.1	668.0	138.0	Contam.	Contam.	Contam.
Little River Springs	4	07/15/97	912	18.5	6	152.5	181.9	14.9	80.6	401.9	20.0	1972.0	1985.5	1978.5
Little River Springs	6	07/15/97	920	18.5	6	150.2	178.9	16.9	79.4	395.3	22.7	1972.0	1985.0	1979.5
Telford Spring	2	07/16/97	759	19.5	6	186.9	136.9	17.5	103.4	315.1	24.7	1974.0	1980.5	1980.5
Telford Spring	4	07/16/97	807	19.5	6	185.4	135.7	16.2	102.5	312.1	22.8	1973.5	1980.0	1979.5
Telford Spring	5	07/16/97	811	19.5	6	193.6	140.1	17.7	107.1	322.3	25.0	1974.0	1981.0	1980.5
Troy Springs	1	07/15/97	1005	20.1	6	109.3	141.7	9.7	62.1	333.8	14.2	1970.0	1981.5	1976.0
Troy Springs	3	07/15/97	1013	20.1	6	99.5	121.5	13.5	56.5	286.2	19.6	1969.5	1978.0	1978.5
Troy Springs	5	07/15/97	1021	20.1	6	100.1	126.5	9.9	56.9	298.1	14.5	1969.5	1979.5	1976.5
Ichetucknee Blue Hole Spring	1	08/14/97	1130	20.0	6	119.6	64.7	76.6	67.7	151.8	111.0	1970.5	1971.5	Contam.
Ichetucknee Blue Hole Spring	3	08/14/97	1146	20.0	6	112.2	65.8	28.3	63.4	154.3	41.0	1970.5	1971.5	1984.5
Ichetucknee Blue Hole Spring	6	08/14/97	1216	20.0	6	111.9	65.7	18.5	63.3	154.1	26.7	1970.0	1971.5	1980.5
Well -9001	2	07/16/97	1019	20.3	6	277.3	178.8	35.4	158.9	424.6	52.0	1978.5	1986.5	1986.0
Well -9001	4	07/16/97	1027	20.3	6	282.4	176.0	34.2	161.8	417.9	50.2	1979.0	1986.5	1986.0
Well -9001	5	07/16/97	1031	20.3	6	295.9	184.4	30.2	169.6	437.9	44.4	1979.5	1987.0	1985.0
Well -6011	2	07/16/97	1154	25.3	6	695.2	45620.3	36.0	491.1	130517.6	67.5	Contam.	Contam.	1988.5
Well -6011	4	07/16/97	1204	25.3	6	690.6	44254.9	37.2	487.8	126611.2	69.8	Contam.	Contam.	1988.5
Well -6011	5	07/16/97	1208	25.3	6	670.5	48078.5	37.4	473.7	137550.4	70.1	Contam.	Contam.	1989.0
Well -9001	2	03/09/98	1210	22.0	6	93.2	66.5	9.2	59.0	173.0	14.8	1970.0	1972.5	1976.5
Well -9001	5	03/09/98	1235	22.0	6	99.5	64.6	9.4	63.0	168.1	15.1	1970.0	1972.0	1976.5
Well -9001	3	03/09/98	1220	22.0	6	94.3	69.5	ERR	59.7	180.7	ERR	1970.0	1973.0	ERR
Well -6011	2	03/09/98	1500	22.0	6	357.5	48926.8	17.7	226.3	127312.8	28.4	1986.0	Contam.	1981.5
Well -6011	4	03/09/98	1510	22.0	6	350.6	47363.3	19.4	221.9	123244.3	31.1	1985.5	Contam.	1982.0
Well -6011	5	03/09/98	1515	22.0	6	343.9	50769.3	20.4	217.7	132107.2	32.6	1985.0	Contam.	1982.5

Table 6. Concentration of CFC-11, CFC-12, and CFC-113 in water from springs and wells, calculated atmospheric partial pressure, and model CFC recharge dates (Continued)

[°C, degrees Celsius; pg/kg, picograms per kilogram; Elev., elevation of land surface; pptv, parts per trillon by volume; Contam., CFC concentrations in water samples that are higher than values in equilibrium with 1998 atmospheric concentrations; ERR, denotes analytical problems]

Sample Name	Sample number	Sampling date	Sampling time	Recharge		Concentration in solution			Calculated atmospheric partial pressure in pptv			Model CFC recharge dates in years		
				Temp. (°C)	Elev. (meters)	pg/kg CFC-11	pg/kg CFC-12	pg/kg CFC-113	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113
Columbia Spring	2	08/20/98	1655	23.4	7	221.1	293.2	23.4	149.0	806.8	40.2	1977.5	Contam.	1984.0
Columbia Spring	4	08/20/98	1705	23.4	7	217.1	294.0	24.0	146.2	808.8	41.1	1977.0	Contam.	1984.5
Columbia Spring	5	08/20/98	1710	23.4	7	221.5	281.5	22.1	149.2	774.6	38.0	1977.5	Contam.	1984.0
Fannin Spring	2	08/18/98	1225	25.2	7	2270.9	300.8	26.9	1650.7	885.8	50.2	Contam.	Contam.	1986.0
Fannin Spring	3	08/18/98	1230	25.2	7	2288.0	301.3	29.3	1663.1	887.4	54.6	Contam.	Contam.	1986.5
Fannin Spring	5	08/18/98	1240	25.2	7	1949.3	321.1	34.9	1416.9	945.6	65.2	Contam.	Contam.	1988.0
GIL 917971 spring	2	08/20/98	1310	25.5	7	271.9	208.3	39.7	200.1	620.4	75.2	1983.5	Contam.	1989.5
GIL 917971 spring	4	08/20/98	1320	25.5	7	255.9	177.4	33.5	188.3	528.4	63.5	1982.0	1994.0	1988.0
GIL 917971 spring	5	08/20/98	1325	25.5	7	255.5	169.9	33.7	188.0	505.9	63.7	1982.0	1991.5	1988.0
Ginnie Spring	2	08/21/98	915	21.2	7	302.0	210.5	24.4	184.7	531.2	37.5	1981.5	1994.5	1983.5
Ginnie Spring	4	08/21/98	925	21.2	7	303.2	213.4	26.3	185.4	538.5	40.5	1982.0	1996.0	1984.5
Ginnie Spring	5	08/21/98	930	21.2	7	308.8	209.2	27.5	188.9	527.9	42.4	1982.0	1994.0	1984.5
Hornsby Spring	2	08/21/98	1435	21.0	7	167.6	845.3	7.1	101.6	2115.8	10.8	1973.5	Contam.	1974.0
Hornsby spring	4	08/21/98	1445	21.0	7	164.6	839.2	6.8	99.7	2100.5	10.3	1973.5	Contam.	1974.0
Hornsby spring	5	08/21/98	1450	21.0	7	165.5	862.6	7.1	100.3	2159.1	10.7	1973.5	Contam.	1974.0
July Spring	2	08/21/98	950	22.8	7	495.7	318.1	31.9	325.4	855.0	53.1	Contam.	Contam.	1986.5
July Spring	4	08/21/98	1000	22.8	7	501.4	326.6	33.1	329.1	878.0	55.2	Contam.	Contam.	1986.5
July Spring	5	08/21/98	1005	22.8	7	495.1	313.8	32.1	325.0	843.4	53.4	Contam.	Contam.	1986.5
LAF 718972 spring	2	08/19/98	1235	22.5	7	688.5	820.4	212.8	446.1	2179.8	349.3	Contam.	Contam.	Contam.
LAF 718972 spring	4	08/19/98	1245	22.5	7	105.3	134.2	14.2	68.2	356.7	23.3	1971.0	1983.0	1980.0
LAF 718972 spring	5	08/19/98	1250	22.5	7	103.4	129.5	12.9	67.0	344.1	21.2	1970.5	1982.0	1979.0
Manatee Spring	2	08/18/98	1005	23.0	7	185.1	402.9	21.2	122.5	1091.6	35.7	1975.0	Contam.	1983.5
Manatee Spring	4	08/18/98	1015	23.0	7	188.8	415.6	21.8	125.0	1125.9	36.6	1975.5	Contam.	1983.5
Manatee Spring	5	08/18/98	1020	22.9	7	188.2	409.9	22.6	124.1	1106.2	37.9	1975.5	Contam.	1984.0
Mearson Spring	2	08/19/98	1125	22.0	7	157.3	242.9	20.9	99.7	632.9	33.5	1973.5	Contam.	1983.0
Mearson Spring	4	08/19/98	1135	22.0	7	158.2	243.8	20.5	100.2	635.1	32.7	1973.5	Contam.	1982.5
Mearson Spring	5	08/19/98	1140	22.0	7	157.7	234.0	20.4	99.9	609.5	32.6	1973.5	Contam.	1982.5
Poe Springs	2	08/21/98	1245	22.0	7	117.8	195.8	9.1	74.6	510.0	14.6	1971.5	1991.5	1976.5
Poe Springs	4	08/21/98	1255	22.0	7	118.7	197.1	9.5	75.2	513.4	15.3	1971.5	1992.5	1977.0
Poe Springs	5	08/21/98	1300	22.0	7	118.1	187.6	8.4	74.9	488.6	13.5	1971.5	1990.0	1976.0
Pot Hole Spring	2	08/20/98	905	19.3	7	152.8	137.0	24.4	85.7	319.8	34.1	1972.5	1981.0	1983.0
Pot Hole Spring	4	08/20/98	915	19.3	7	147.9	128.6	22.6	83.0	300.3	31.5	1972.0	1979.5	1982.5
Pot Hole Spring	5	08/20/98	920	19.3	7	147.7	126.4	22.9	82.8	295.0	32.1	1972.0	1979.0	1982.5

Table 6. Concentration of CFC-11, CFC-12, and CFC-113 in water from springs and wells, calculated atmospheric partial pressure, and model CFC recharge dates (Continued)

[°C, degrees Celsius; pg/kg, picograms per kilogram; Elev., elevation of land surface; pptv, parts per trillon by volume; Contam., CFC concentrations in water samples that are higher than values in equilibrium with 1998 atmospheric concentrations; ERR, denotes analytical problems]

Sample Name	Sample number	Sampling date	Sampling time	Recharge		Concentration in solution			Calculated atmospheric partial pressure in pptv			Model CFC recharge dates in years		
				Temp. (°C)	Elev. (meters)	pg/kg CFC-11	pg/kg CFC-12	pg/kg CFC-113	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113
Rock Bluff Spring	2	08/20/98	815	20.7	7	232.2	190.1	28.9	138.8	470.0	43.3	1976.5	1989.0	1985.0
Rock Bluff Spring	4	08/20/98	825	20.7	7	229.7	186.4	28.4	137.3	460.9	42.6	1976.5	1988.0	1984.5
Rock Bluff Spring	5	08/20/98	835	20.7	7	227.0	179.0	27.7	135.8	442.5	41.5	1976.0	1987.5	1984.5
Running Springs	2	08/18/98	1750	20.2	7	232.5	197.8	14.8	135.9	479.2	21.7	1976.0	1989.5	1979.5
Running Springs	4	08/18/98	1800	20.2	7	268.1	240.4	32.8	156.7	582.5	48.0	1978.0	Modern	1985.5
Running Springs	5	08/18/98	1805	20.2	7	235.0	197.1	14.8	137.4	477.7	21.7	1976.5	1989.5	1979.5
Ruth Spring	2	08/19/98	1515	21.8	7	231.8	148.8	27.3	145.6	384.5	43.3	1977.0	1984.5	1985.0
Ruth Spring	4	08/19/98	1525	21.8	7	220.6	131.0	24.0	138.6	338.6	38.0	1976.5	1982.0	1984.0
Ruth Spring	5	08/19/98	1530	21.8	7	232.0	148.5	27.7	145.8	383.9	43.9	1977.0	1984.5	1985.0
SUW 718971 spring	2	08/19/98	915	23.6	7	375.1	1106.9	35.3	254.9	3068.9	61.1	1988.0	Contam.	1987.5
SUW 718971 spring	4	08/19/98	925	23.6	7	373.3	1079.7	35.4	253.6	2993.6	61.2	1988.0	Contam.	1987.5
SUW 718971 spring	5	08/19/98	930	23.6	7	381.6	1104.4	35.6	259.3	3061.9	61.7	1989.0	Contam.	1987.5
SUW 725971 spring	2	08/19/98	1005	19.8	7	401.6	513.3	48.1	230.5	1223.6	68.9	1986.5	Contam.	1988.5
SUW 725971 spring	4	08/19/98	1015	19.8	7	398.7	509.2	48.2	228.8	1213.7	69.0	1986.0	Contam.	1988.5
SUW 725971 spring	5	08/19/98	1020	19.8	7	401.1	510.8	46.0	230.2	1217.4	66.0	1986.5	Contam.	1988.0
Trail Springs	2	08/20/98	1110	22.5	7	206.3	174.7	27.4	133.6	464.2	45.0	1976.0	1988.5	1985.0
Trail Springs	4	08/20/98	1120	22.5	7	205.8	174.7	27.2	133.4	464.1	44.6	1976.0	1988.5	1985.0
Trail Springs	5	08/20/98	1125	22.5	7	213.2	181.3	29.7	138.2	481.7	48.7	1976.5	1989.5	1985.5
Troy Spring	3	08/19/98	1330	22.9	7	137.9	137.6	17.6	90.9	371.3	29.4	1973.0	1983.5	1981.5
Troy Spring	4	08/19/98	1335	22.9	7	137.3	140.9	18.5	90.5	380.4	31.0	1973.0	1984.5	1982.0
Troy Spring	5	08/19/98	1340	22.9	7	136.4	133.6	18.9	89.9	360.4	31.6	1972.5	1983.0	1982.5

Table 7. Comparison of apparent ages of spring waters from piston-flow model (PFM), average residence times calculated using exponential-flow model (EM), and fraction of post-1993 water calculated using binary-mixing model (BMM)

[yrs, years; Contam., water sample was contaminated (CFC-11 concentrations were above those for water in equilibrium with CFC-11 in modern air)]

SPRING NAME	Tritium concen-tration, TU	CFC-11 Apparent age (PFM), yrs	CFC-113 Apparent age (PFM), yrs	CFC-11 Turnover time (EM), yrs	CFC-113 Turnover time (EM), yrs	Fraction of post-1993 water (BMM), CFC-11	Fraction of post-1993 water- (BMM), CFC-113
SANTA FE RIVER SPRINGS							
GIL917971	3.3	16	10	22	13	0.69	0.70
Ginnie	5.2	16	14	16	21	0.68	0.45
Hornsby	5.8	25	24	43	110	0.32	0.13
July	5.4	Contam.	12	Contam.	15	Contam.	0.56
Poe	5.1	27	22	64	81	0.27	0.17
Trail	4.5	22	13	32	19	0.48	0.50
Columbia	4.3	21	14	29	25	0.52	0.45
Ichetucknee Blue Hole	5.8	27	15	69	27	0.22	0.35
LAFAYETTE CO. SPRINGS							
Troy98	4.0	25	16	55	35	0.33	0.35
Troy97	4.0	28	18	77	66	0.21	0.18
Mearson	.	25	15	45	30	0.36	0.38
Lafayette Blue	4.0	22	17	29	44	0.42	0.27
Ruth	3.0	21	13	27	21	0.52	0.50
LAF718972	5.1	27	19	77	51	0.25	0.25
LOWER SUWANNEE SPRINGS							
Fannin	3.7	Contam.	11	Contam.	17	Contam.	0.63
Pothole	5.2	26	15	50	26	0.28	0.37
Manatee	4.5	23	14	36	28	0.43	0.44
Rock Bluff	4.8	22	13	27	19	0.50	0.50
SUWANNEE CO. SPRINGS							
Running	5.3	21	17	24	36	0.49	0.33
Little River	4.2	25	18	48	43	0.28	0.24
SUW725971A	4.7	12	10	7	6	0.82	0.76
SUW718971	3.3	10	11	9	13	0.92	0.68
Charles	4.6	22	15	33	31	0.42	0.33
Telford	4.9	23	17	34	38	0.37	0.27

Using the piston-flow approach, apparent ages of spring waters range from 10 (GIL917971) to 24 years (Hornsby Spring) using measured CFC-113 concentrations (table 7). For most spring waters, apparent ages estimated using CFC-11 concentration data are 1 to 12 years older than those obtained using CFC-113 data with ages, ranging from 16 (GIL917971 and Ginnie Springs) to 28 years (Troy Spring sampled in 1997). If the assumption is valid that CFC-11 and CFC-113 are stable in this system, then the lack of concordancy in apparent ages for spring waters obtained from CFC-11 and CFC-113 concentrations may result from mixtures of ground water of different ages converging from various flow paths. In relatively simple hydrogeologic settings, such as aquifers comprised of unconsolidated sediments, CFC-11 and CFC-113 concentration data typically would yield concordant ages (Plummer and Busenberg, 1999).

One way to represent spring waters as a mixture of water from various flow paths with different associated ages is to assume an exponential age distribution for ground-water discharge to springs. Average residence times (or turnover times; Zuber, 1986) can be estimated by using a exponential model. The exponential model provides a simplified way of accounting for mixing of stratified ground waters (of different ages) at discharge (Zuber, 1986), which gives this model an advantage over other simple reservoir models, which assume all discharge to be the same age or piston-flow models that assume plug flow. Average residence times calculated from the exponential model using CFC-11 and CFC-113 concentration data have a much larger range than apparent ages for ground water from springs calculated using these compounds with the piston-flow model. For example, average residence times range from 7 (SUW725971A) to 77 years (LAF718972 and Troy-97, sampled in 1997) using measured CFC-11 concentration data, and from 6 (SUW725971A) to 110 years (Hornsby Spring) using measured CFC-113 concentration data (table 7) (fig. 8). Differences in estimated average residence times for springs result from differences in measured CFC-11 and CFC-113 concentrations relative to their air-water equilibration values over time. The relation between apparent ages calculated by using a piston-flow model compared to average residence times of ground water estimated by using an exponential model is shown in figure 8 (modified from Focazio and others, 1998). For apparent ages less than or about 10 years, the average residence time is slightly less than the apparent age for CFC-11 and CFC-113. For apparent ages more than about 15 years, the exponential model residence times are significantly greater than the apparent ages for both CFC-11 and CFC-113 (fig. 8). The exponential model is particularly sensitive to small changes in CFC-113 concentration data due to the smaller range of CFC-113 concentrations in water that are in equilibrium with atmospheric concentrations compared to CFC-11.

Another approach that accounts for differences in apparent ages and residence times obtained by using CFC-11 and CFC-113 assumes that spring water is a simple binary mixture of ground water from two sources (Plummer and Busenberg, 1999): a shallow reservoir that contains young, recently recharged water and a deeper reservoir containing older ground water, recharged more than 50 years ago. Binary-mixing models were developed to test three scenarios that involve the mixing of a young water (recharged post-1993) with waters recharged in 1980, 1965, and 1940 and before. Since the atmospheric input concentrations for CFC-11 and CFC-113 have essentially flattened out after 1993, the model would not be able to distinguish recharge occurring in 1993 from more recent recharge, so recent recharge is considered as post-1993. Similarly, since the concentrations of CFC-11 and CFC 113 in the atmosphere were near zero in 1940, the model cannot distinguish between waters recharged in 1940 with those recharged prior to 1940. Hence, the term older ground water refers to that recharged prior to 1940. Curves shown in figure 9 were constructed based on methods in Plummer and Busenberg (1999) and recalculated for 22 ^{o}C recharge temperature.

When the apparent recharge dates (based on piston-flow assumption) for CFC-11 and CFC-113 (determined from measured concentrations of CFC-11 and CFC-113) are plotted on the various mixing curves (fig. 9), the closest agreement between mixing fractions determined by using measured concentration data for both CFC-11 and CFC-113 is for mixtures of young (post-1993)

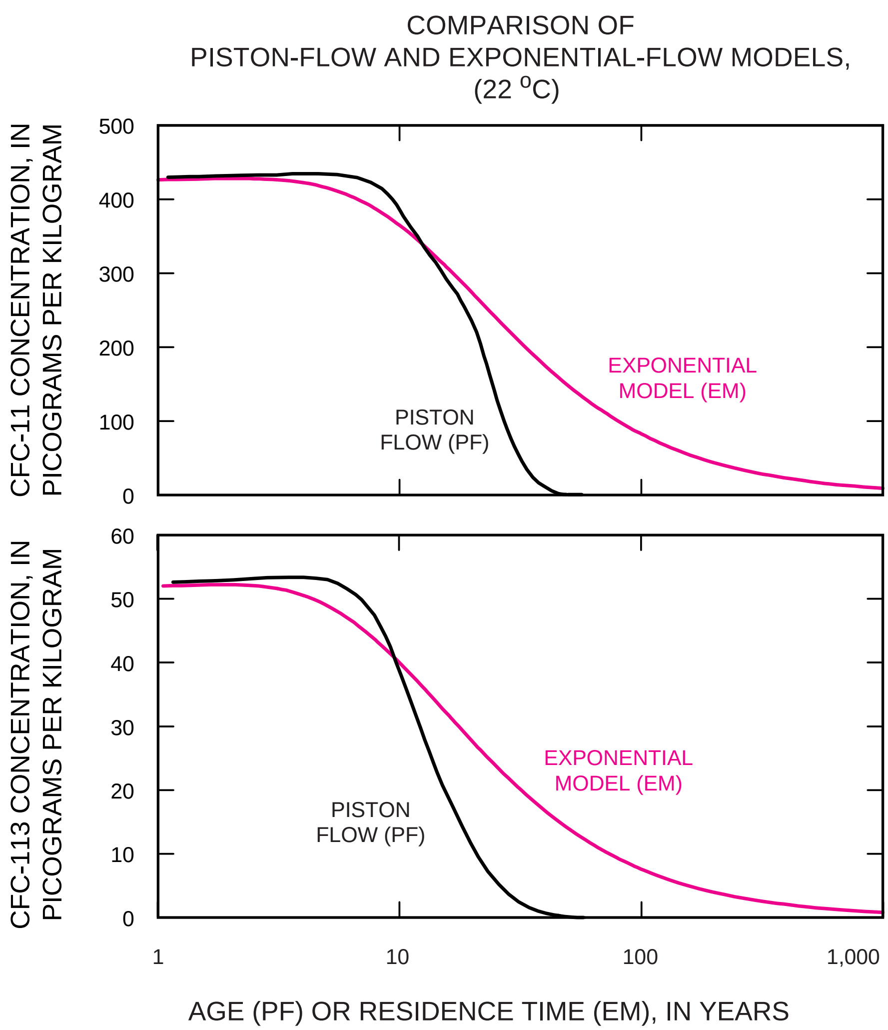


Figure 8. Graphs showing comparison of residence times calculated using an exponential model with apparent ages calculated using a piston-flow model using CFC-11 and CFC-113 concentrations at a recharge temperature of 22 °C.

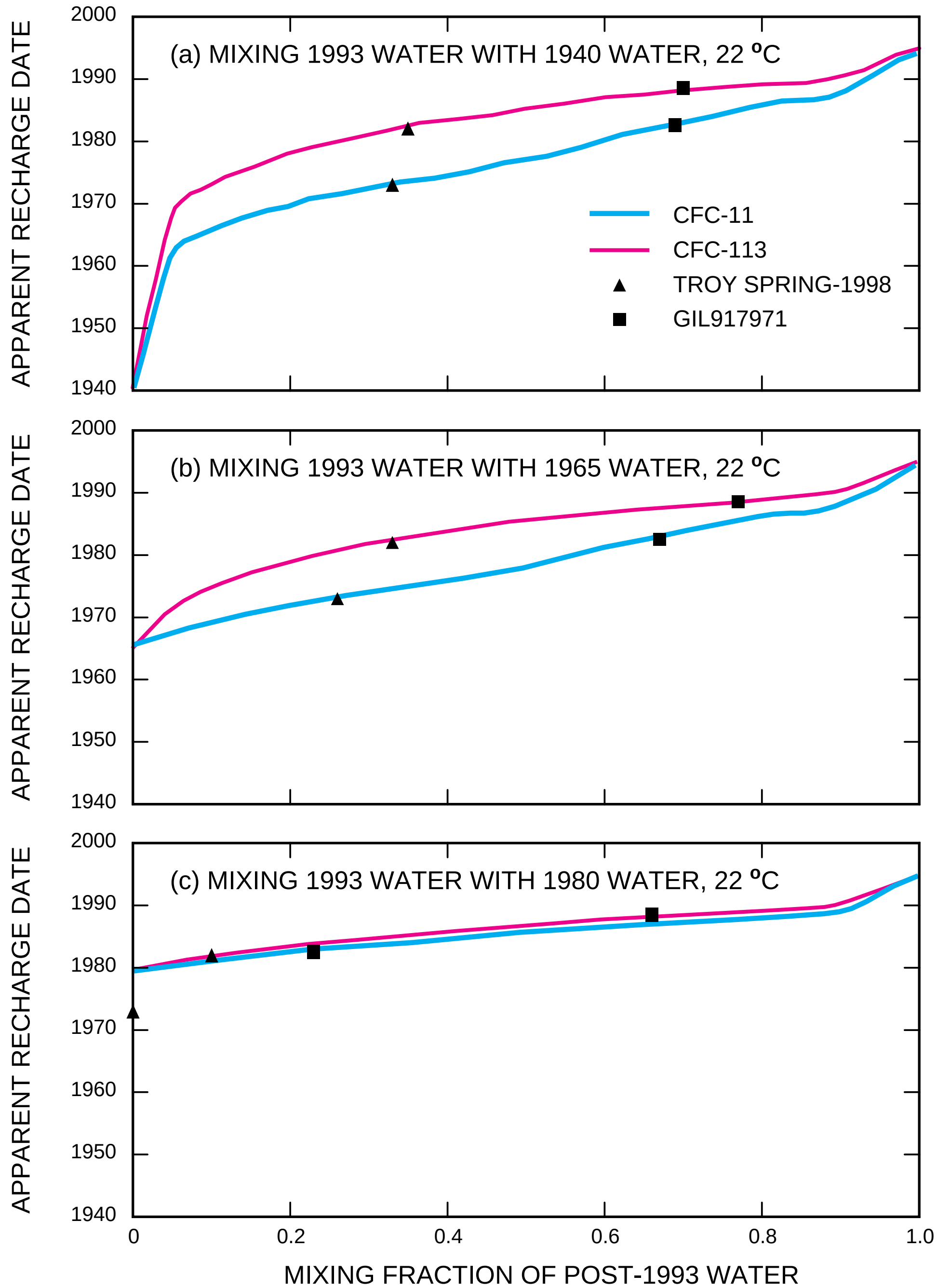


Figure 9. Binary-mixing model scenarios for ground water recharged post-1993 with waters recharged in (a) 1940 and before, (b) 1965, and (c) 1980.

water with old (pre-1940) water. Using apparent recharge dates determined from CFC-11, the mixing fraction of recent water (f_{1993}) ranged from 0.21 (Troy Spring 1997 sample) (fig. 9) to 0.92 (SUW718971); whereas f_{1993} ranged from 0.13 (Hornsby Spring) to 0.76 (SUW725971A) using CFC-113 data (table 7). Generally, f_{1993} values calculated by using CFC-11 and CFC-113 data agreed within +/- 0.05; however, the largest discrepancies between calculated f_{1993} values using CFC-11 and CFC-113 concentration data were for spring waters with extreme (very young or old) apparent ages or residence times, such as SUW718971 and Hornsby (table 7). For these two springs, the apparent ages calculated from CFC-11 and CFC-113 data are concordant (agree within one year); therefore, the concept of binary mixtures may not be appropriate as there may be only one water (SUW718971) or possibly more than two waters (Hornsby) in a mixture. The range of recent (post-1993) recharge in the presumed binary mixtures, which presumably originates from shallow flow systems, is similar to the estimate of 92 percent shallow water for the Rainbow Springs-Silver Springs drainage areas (Faulkner, 1973). This estimate was based on differences in sulfate concentrations in water from the top of the Upper Floridan aquifer, near the bottom of the aquifer (the middle of the Lower Floridan), and from Silver Springs.

The apparent age of water from wells (-6011 and -9001) open to the two shallow zones in the Upper Floridan aquifer ranges from 8 to 18 years using the piston-flow model approach. Higher than present-day concentrations of CFC-11 and CFC-12 in water from well-6011 may indicate a local source of contamination of CFCs, possibly from human wastes (Busenberg and Plummer, 1992). Elevated concentrations of N_2 in water from well-6011 (above what would be expected from water in equilibrium with N_2 and Ar in air) (table 4) indicate that nitrogen species, such as nitrate from septic tanks or animal wastes, are being transformed to nitrogen gases, possibly due to denitrification reactions in the aquifer (Katz and others, 1997).

It is important to note that the estimated apparent ages, mean residence times, and fraction of post-1993 recharge water mixtures for spring waters or water from zones in the aquifer are specific for the hydrologic conditions at the time of sampling. Samples were collected during low-flow conditions for the Suwannee and Santa Fe Rivers (fig. 10); however, flows in these two rivers can vary considerably depending upon the amount of rainfall (fig. 10). Spring water collected during low-flow or base-flow conditions in the Suwannee River (periods of low rainfall) probably yield older ages than spring water collected during high-flow conditions in the river (extended periods of high rainfall). The effect of hydrologic conditions on ages of spring waters probably results from the greater contribution of waters from longer ground-water-flow paths during low-flow conditions than during high-flow conditions when the contribution of younger waters from shorter ground-water-flow paths probably would be greater. Studies of the relative ages of spring waters in the Chesapeake Bay region determined that spring waters are younger during high-flow conditions than during low-flow conditions (Focazio and others, 1998).

Some of the hydrologic and hydraulic factors that affect the relative ages of spring water and water from shallow zones in the Upper Floridan aquifer are (1) the relative contribution of recharge from different parts of the basin; for example, nearby points of focused recharge such as sinkholes (relatively recent

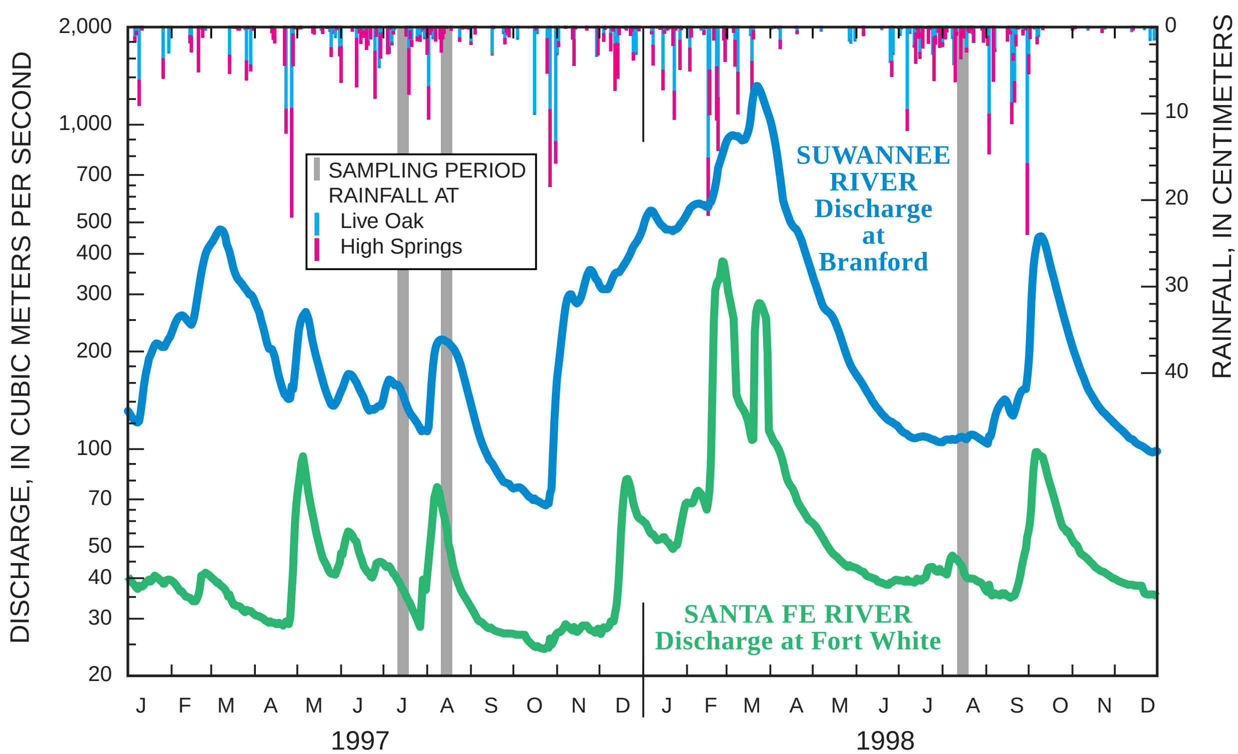


Figure 10. Graph showing discharge of Suwannee and Santa Fe Rivers, rainfall during 1997-98, and dates of collection of spring-water samples.

recharge) versus water moving along long ground-water-flow paths (relatively old recharge), (2) conduit size, extent, and distribution pattern, (3) the relation between the heads in the aquifer, the hydraulic gradient, and water levels in the Suwannee River, and (4) the size of the contributing area to a spring. Keeping these factors in mind, the relative ages of spring waters may provide useful information about the size of the contributing area to a spring system. For example, ground water discharging to springs with longer residence times probably indicates that older water from a deeper flow system is mixing with more recently recharged water that results in a mixture of ages.

The size of the catchment area for the springs sampled in this study was calculated from flow information (table 1), assuming that the measured discharge represents a long-term average flow for each spring and the recharge rate. This calculation also assumes that there are no other discharges from the catchment area besides that from the spring. The catchment area for sampled springs varies from 3.6 km^2 (GIL917971) to 375 km^2 (Columbia) based on an average recharge rate of 0.5 m/yr (table 1). For the range of recharge rates determined for the study area, 0.2 to 0.8 m/yr (Grubbs, 1998), the size of catchment areas for springs varies from 2.2 (GIL917971) to 938 km^2 (Columbia) (table 1). These estimated catchment areas are considerably lower than a value of 1,890 km^2 estimated for Silver Springs, which has a long-term average flow of 23 m^3/s and an average recharge rate of 39 cm/yr (Faulkner, 1973).

Tritium

Tritium (^3H) concentrations measured in spring water and water from two wells (in shallow zones of the Upper Floridan aquifer) were very similar and ranged from about 4.0 to 5.8 TU (table 5). Concentrations of ^3H in ground water in the study area reflect the passing of the ^3H transient through the hydrologic system (fig. 3). 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 during the late 1950’s through the mid-1960’s increased ^3H concentrations in rainfall in this area to a maximum of several hundred TU during the mid-1960's, followed by a sharp decline in concentrations after the moritorium in atmospheric nuclear testing. As pre-nuclear testing water would have a maximum concentration of 0.2 TU at this time (1998), it is evident that spring-water discharge (tritium values in table 5) is of relatively recent origin, and almost certainly from the period of the falling limb of the ^3H transient (fig. 3). Accurate dating of the water is not possible due to the lack of a long-term record of the ^3H transient in this area, as well as the slow change in ^3H concentrations over the past decade. Also, measured ^3H concentrations can be affected by hydrodynamic dispersion and mixing of different age waters (Solomon and Sudicky, 1991; Reilly and others, 1994). However, ^3H concentrations found in spring and ground waters are compatible with the estimates of high recharge rates (20 to 80 cm/yr; Grubbs, 1998) and the high transmissivity of the Upper Floridan aquifer in the study area (Crane, 1986; Bush and Johnston, 1988).

A comparison of measured ^3H concentrations in spring water with the ^3H record for rainfall collected at Ocala, Fla., was used to further constrain ground-water ages obtained by using the aforementioned models and data for CFC-11 and CFC-113. The majority of springs can be represented by exponential mixtures with average residence times of around 10 to 80 years (fig. 11). Tritium and CFC-113 data also are consistent with a binary-mixing model that includes a modern component (post-1993 recharge water) and an older component (mid-1970’s recharge water) (fig. 11). However, if the assumption is not valid that CFC-11 and CFC-113 are stable in this aquifer system, then the ^3H data alone would indicate that spring-water ages would range between 0 and about 25 years, but many spring waters would not be reliably distinguishable from modern rainfall that recharges the ground-water system.

Comparative Estimates of Spring-water Ages

When most springs are combined into a single data cluster and data on CFC-11, CFC-113, and ^3H are integrated (figs. 11 and 12), exponential-model mixtures seem to provide reliable estimates of average residence times of ground water discharging to springs. CFC and tritium data for the majority of spring waters cluster along a curve generated for the exponential model (figs. 11 and 12). However, for some springs, different conclusions can be drawn. For example, CFC-11 and CFC-113 data for the springs GIL917971, Rock Bluff, Manatee, Pothole, Trail, LAF718972, Troy-98, and Ruth (also tritium data) fit better with a two-component mixing model with more than 50 percent young water (post-1993) indicated by all three tracers (fig. 11). Tritium and CFC-113 data for Hornsby, SUW718971, GIL917971, and Columbia

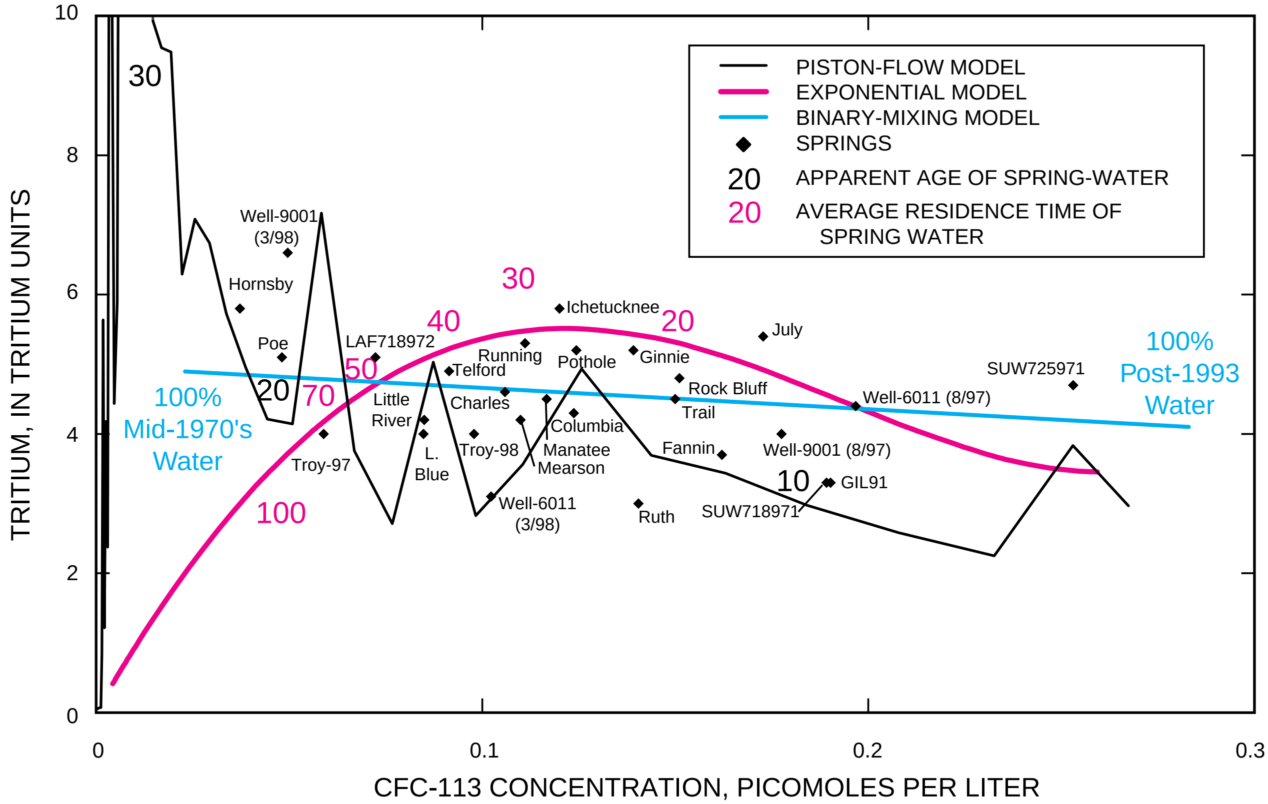


Figure 11. Graph showing concentrations of 3H and CFC-113 in water from springs and wells relative to estimated apparent age (piston-flow model), average residence time (exponential model), and fraction of post-1993 water mixed with water recharged in 1940 and before (binary-mixing model).

spring waters fit better with a piston-flow model; however, the data also are close to fitting an exponential model (fig. 11). One important conclusion that seems to fit most springs is that the CFCs indicate that spring waters likely have large fractions of water that are more than 20 years old.

Several hydrochemical processes could alter the concentrations of CFCs in the ground-water system, thereby affecting the interpretation of age and average residence times of spring waters. The age interpretations are predicated on the assumption that CFC-11 and CFC-113 are stable in this ground-water system, which may not be entirely valid. For the few spring waters that seem not to have been contaminated with non-atmospheric CFC-12, some degradation of CFC-11 was possible. Also, the low dissolved oxygen concentrations in some spring waters (table 3) could signify mixing components that have been subjected to sufficiently reducing conditions that could cause some degradation of CFC-11 and possibly CFC-113. If this is the case, the apparent ages and average residence times presented in table 7 are an overestimation of the actual ages and residence times of ground water in this system. If degradation of only CFC-11 has occurred, the older apparent recharge dates obtained by using CFC-11 data compared to those obtained by using CFC-113 data would not be realistic, and would preclude the use of CFC-11 data in binary-mixing models to estimate young and old fractions of mixing components for spring waters. Another possibility, albeit remote, is that CFC-113 concentrations are elevated due to contamination, as was the case for CFC-12 in many spring waters. If CFC-113 contamination has occurred, the apparent ages and average residence times presented in table 7 would be an underestimation of the actual ages or residence times. To resolve some of these issues, it would be worthwhile to conduct a comparative study of CFCs and trituim/helium-3 ($^3H/^3He$) age-dating techniques at selected springs to more effectively quantify mixing of waters of different ages. The $^3H/^3He$ and CFC age-dating techniques were used to date the young fraction in ground-water mixtures from the Upper Floridan aquifer near Valdosta, Ga., where old regional water receives recharge of young water from sinkholes and overlying confining beds (Plummer and others, 1998b).

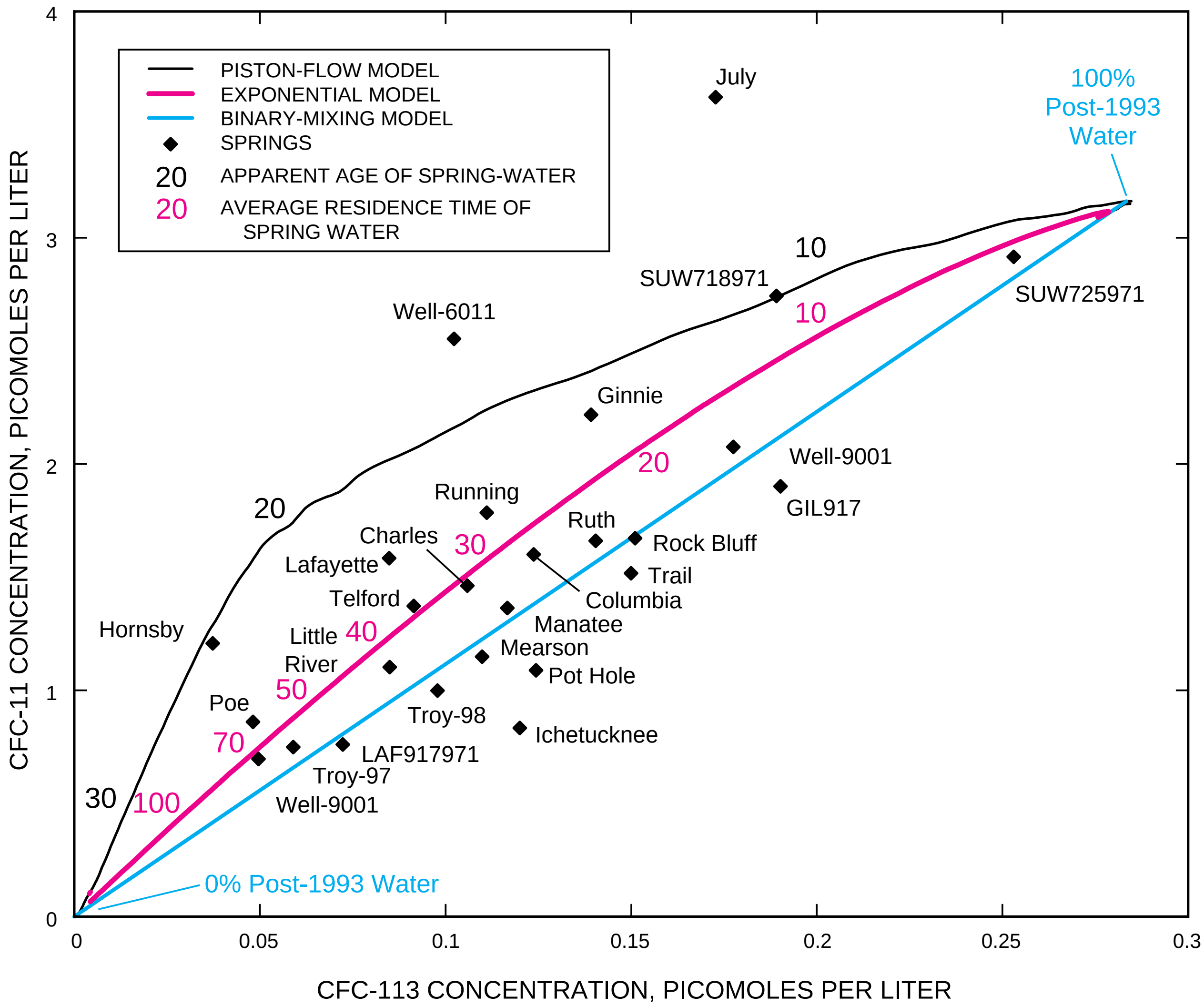
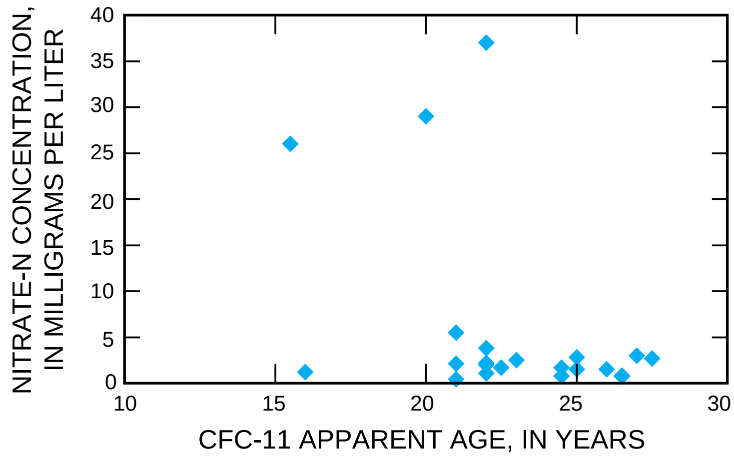


Figure 12. Graph showing concentration of CFC-11 and CFC-113 in water from springs and wells relative to estimated apparent age (piston-flow model), average residence time (exponential model), and fraction of post-1993 water mixed with water recharged in 1940 and before (binary-mixing model).

RELATION BETWEEN NITRATE, DISSOLVED OXYGEN CONCENTRATIONS, AND AGE OF SPRING WATER

Nitrate-N concentrations in water from springs and wells are inversely related to the apparent ages obtained from the piston-flow model and average residence times of spring waters obtained from the exponential model. Spearman's Rho statistic was used to determine if the concentration of nitrate and other chemical constituents were correlated with spring-water ages determined from the various models. This nonparametric statistic measures the strength of a monotonic increasing or decreasing correlation between two variables (Helsel and Hirsch, 1992). A correlation is considered to be statistically significant if the probability level (p) is less than 0.05. A significant inverse correlation was found between nitrate concentrations and apparent ages determined by using CFC-113 data and the piston-flow model. A correlation coefficient of -0.39 ($p<0.058$) indicated a marginally significant inverse relation between nitrate-N concentrations and average residence times estimated by using CFC-113 and the exponential model (table 8). Given the relatively small sample size (24), the result is of interest even though it is above the commonly used p value of <0.05. A significant positive correlation was found between nitrate concentrations and the fraction of post-1993 water obtained by using CFC-113 and the binary-mixing model (table 8). Several different patterns can produce the same correlation coefficients (Helsel and Hirsch, 1992); however, nitrate concentrations



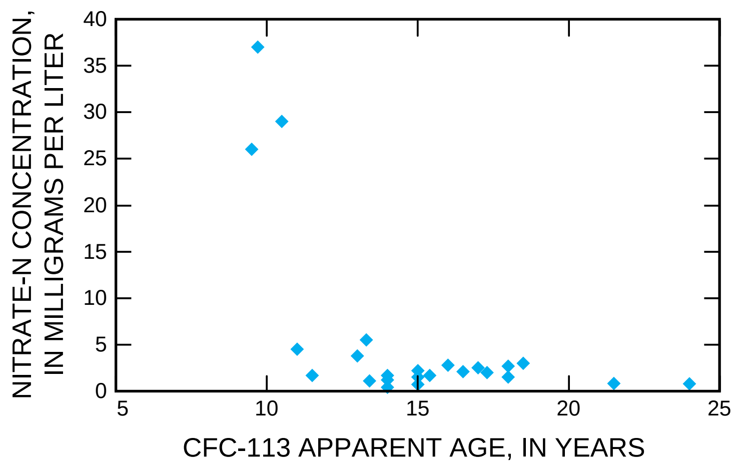


Figure 13. Graph showing nitrate-N concentration against apparent age of spring waters from piston-flow model.

and the age of spring waters (apparent age, average residence time, and fraction of post-1993 water) show a strong linear monotonic relation (figs. 13-15). This trend may indicate that recent recharge water contributes relatively higher concentrations of nitrate to ground water discharging from springs. Nitrate concentrations also are inversely related ($p < 0.001$) to the amount of spring discharge (table 8), indicating that the contributing area and hydraulic properties of the aquifer (conduit and diffuse flow) near the spring also are important factors.

Nitrate-N concentrations are significantly inversely correlated with spring-water discharge (table 8). While it may seem that this significant trend is controlled by the three spring waters with high nitrate concentrations (SUW718971, SUW725971, and GIL917971), when nitrate and discharge data for an additional 36 springs (Hornsby and Ceryak, 1999) are combined with data for springs presented in this report, there is a substantial increase in nitrate concentrations below a discharge value of 0.3 m^3/s (fig. 16). Ten of the combined 60 spring waters contain nitrate concentrations above 2.5 mg/L. This combined data set included only water samples collected during July 1997 and August 1998 for the 36 additional springs located throughout the Suwannee River Basin (Ceryak and Hornsby, 1999) to correspond with samples presented herein. Spring-water discharge is significantly correlated to the apparent ages of spring waters; that is, springs with lower flows tend to have young ages, whereas springs with higher flows tend to have increased ages. Springs, such as SUW718971,

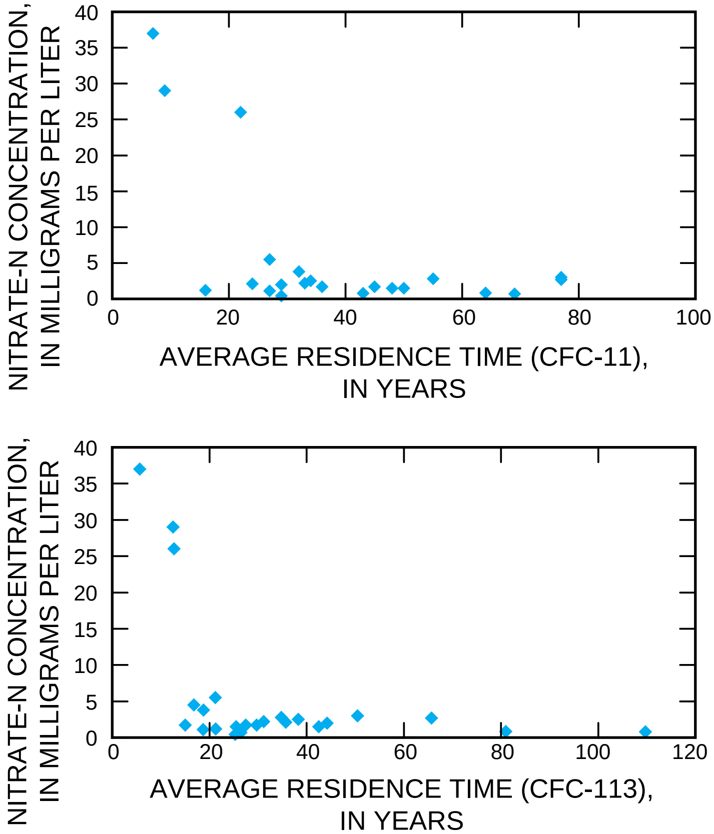


Figure 14. Graph showing nitrate-N concentration against average residence time of spring waters from exponential model.

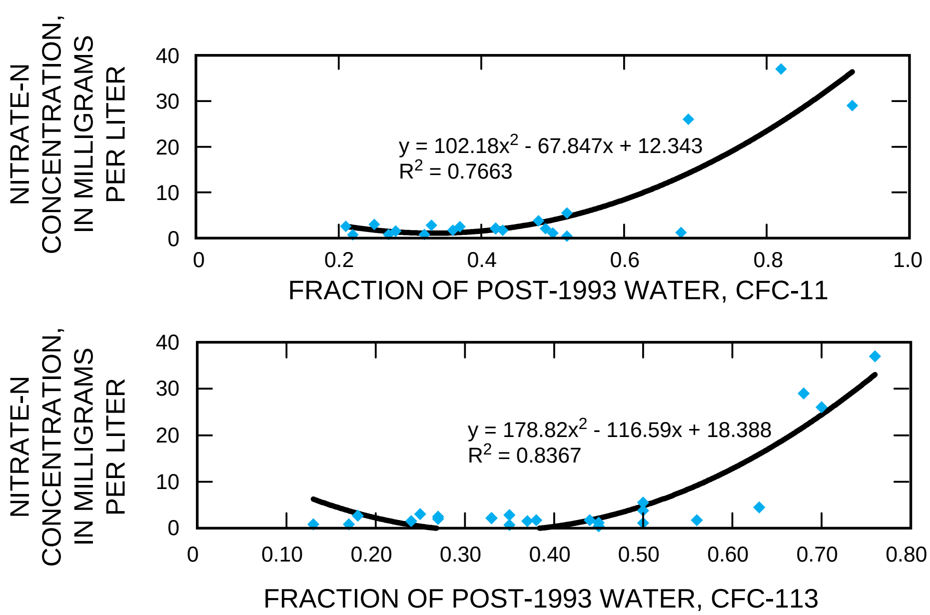


Figure 15. Nitrate-N concentration against fraction of post-1993 recharge waters from binary-mixing model.

SUW725971, and GIL917971, with smaller amounts of flow ranging from 0.06 to 0.25 m^3/s (2 to 9 ft^3/s), are receiving water from relatively shallow ground-water-flow systems that contain a relatively high proportion of recent recharge. In contrast, first-magnitude springs, such as Hornsby, Little River, and Troy, with flows ranging from 2.1 to 5.6 m^3/s (76 to 200 ft^3/s), receive water from large contributing areas with deep flow systems that contain a relatively higher proportion of older water with low concentrations of nitrate. Similar trends between nitrate concentrations and age were noted in spring waters discharging from a Triassic karst aquifer in Germany (Dietrich and Hebert, 1997); nitrate concentrations decreased with increasing age and proportion of old water.

Dissolved oxygen concentrations were inversely correlated (significant at $p<0.003$) with all estimates of spring-water age (table 8). This strong inverse correlation between dissolved oxygen indicates that dissolved oxygen could be used as a qualitative tracer of ground-water age. Recently recharged waters have relatively high dissolved oxygen concentrations, and as the residence time of water in the system increases, the dissolved oxygen concentrations decrease. Similar trends for dissolved oxygen in spring waters discharging from a Triassic karst aquifer in Germany were noted by Dietrich and Hebert (1997).

Marginally significant positive correlations were observed between silica and spring-water ages, but only for apparent ages estimated by using CFC-113 ($p<0.054$) and with older fractions of water estimated by using CFC-113 in binary-mixing models ($p<0.052$) (table 8). This increase in silica with spring-water age is consistent with older waters having more opportunity to incorporate silica from mineral dissolution, and may represent waters recharging from areas where the aquifer is semiconfined with overlying clays and clayey sands. Dietrich and Hebert (1997) also noted that silica was a usable qualitative marker for residence time of spring waters in a karst system. They also found that fluoride, dissolved solids, and $\delta^{13}C_{DIC}$ were effective markers of ground-water residence times for springs; however, similar concentrations of these constituents in water samples from most springs precluded their effectiveness as qualitative indicators of spring-water age in this study.

Correlations between spring-water age and spring-water flow were not as strong as one might expect. Half of these were statistically significant at $p <0.05$, while the other half were significant at p levels ranging between 0.05 and 0.11 (table 8). Variability in spring-water flow may provide enough scatter that results in a weaker correlation between spring-water ages than that observed between certain chemical indicators (dissolved oxygen and nitrate) and the age of spring waters.

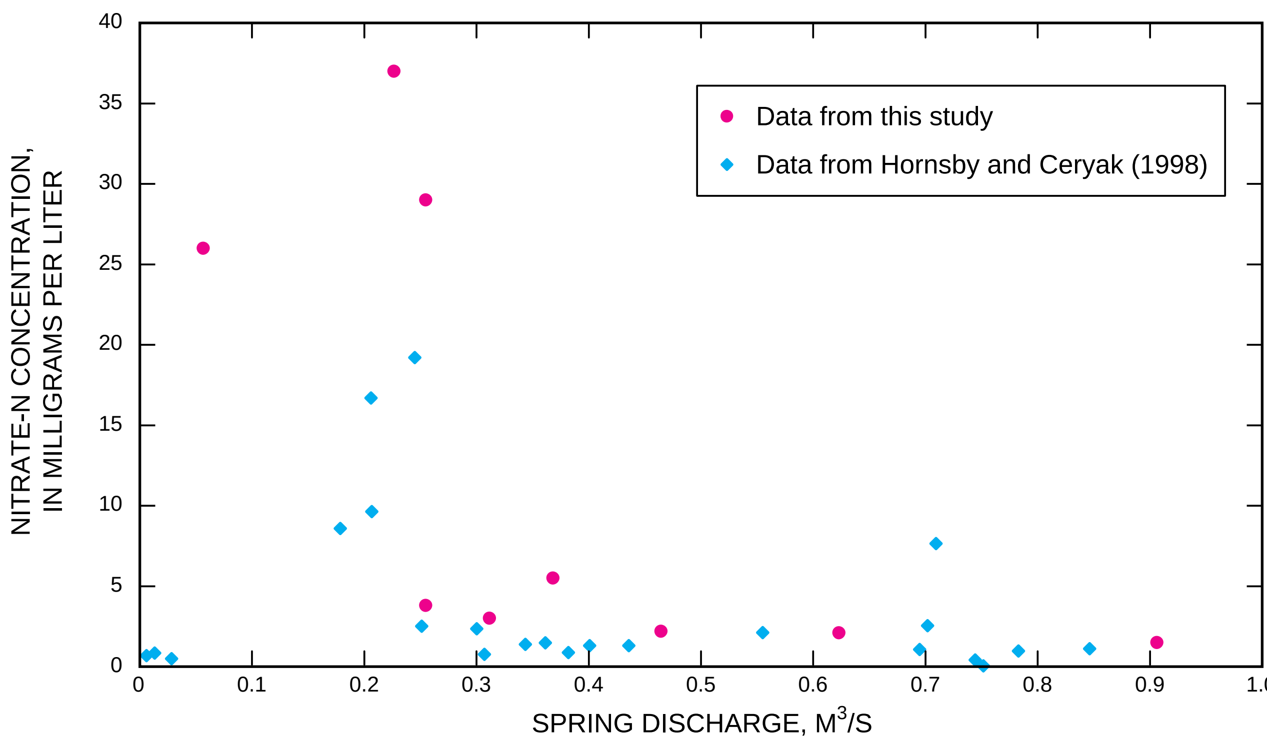


Figure 16. Nitrate-N concentrations versus spring-water discharge.

Table 8. Spearman's Rho correlation coefficients (top number in each cell), probability level of exceeding Rho (for the null hypothesis that Ho: Rho=0; intermediate number in each), and number of observations (bottom number in each cell)

[Statistically significant and marginally significant correlations (p <0.054)are shown in boldface. Spring-water apparent ages estimated using piston-flow model for CFC-11 (PFMC11) and for CFC-113 (PFMC113), residence times estimated using exponential model for CFC-11 (EMC11) and CFC-113 (EMC113), and fractions of post-1993 waters calculated using binary mixing models with CFC-11 (F93C11) and CFC-113 (F93C113). Chemical constituents are denoted as follows and are expressed in mg/L unless otherwise noted: tritium in TU (TRIT), nitrate-N (NO_3N), dissolved oxygen (O2DISS), delta carbon-13 in per mil (^{13}C), specific conductance in microsiemens per centimeter (SPECOND), fluoride (F), silica (SiO_2), dissolved solids (DS), sulfate (SO_4), phosphate (PO_4), calcite saturation index (CALSI), dolomite saturation index (DOLSI). Spring discharge is denoted by FLOW]

	TRIT	NO_3N	O2DISS	^{13}C	SPECOND	F	SiO_2	DS	SO_4	PO_4	CALSI	DOLSI	FLOW
PFMC11	0.33356	-0.28810	-0.59456	-0.11118	-0.08427	-0.01062	0.22392	0.09997	-0.22363	-0.14536	0.05632	-0.11480	0.41876
	0.1395	0.1935	0.0035	0.6223	0.7093	0.9626	0.3165	0.6580	0.3171	0.5186	0.8034	0.6110	0.0524
	21	22	22	22	22	22	22	22	22	22	22	22	22
PFMC113	0.37164	-0.44562	-0.75542	-0.21510	-0.20551	0.03135	0.39926	0.09045	-0.16171	0.05418	-0.03063	0.04241	0.33939
	0.0808	0.0291	0.0001	0.3128	0.3354	0.8844	0.0533	0.6743	0.4503	0.8015	0.8870	0.8440	0.1047
	23	24	24	24	24	24	24	24	24	24	24	24	24
EMC11	0.24544	-0.33201	-0.68155	-0.07825	-0.19700	-0.13631	0.25419	0.03809	-0.26995	-0.04785	0.08317	-0.17519	0.48615
	0.2836	0.1312	0.0005	0.7292	0.3795	0.5453	0.2537	0.8664	0.2244	0.8325	0.7129	0.4355	0.0218
	21	22	22	22	22	22	22	22	22	22	22	22	22
EMC113	0.26759	-0.39338	-0.81836	-0.25273	-0.14273	-0.03446	0.35763	0.15221	-0.14155	0.02488	-0.06402	0.02567	0.38172
	0.2170	0.0572	0.0001	0.2335	0.5058	0.8730	0.0862	0.4777	0.5094	0.9081	0.7663	0.9052	0.0657
	23	24	24	24	24	24	24	24	24	24	24	24	24
F93C11	-0.35496	0.37839	0.69285	0.10887	0.20803	0.09397	-0.29929	-0.04804	0.27816	0.05582	-0.04243	0.16671	-0.46806
	0.1144	0.0825	0.0004	0.6296	0.3529	0.6775	0.1760	0.8319	0.2101	0.8051	0.8513	0.4584	0.0280
	21	22	22	22	22	22	22	22	22	22	22	22	22
F93C113	-0.33739	0.45312	0.76873	0.26525	0.18732	0.00233	-0.40149	-0.09735	0.13233	-0.06735	0.10879	0.03963	-0.36536
	0.1154	0.0262	0.0001	0.2103	0.3808	0.9914	0.0518	0.6509	0.5376	0.7545	0.6129	0.8541	0.0792
	23	24	24	24	24	24	24	24	24	24	24	24	24
FLOW	0.20089	-0.63632	-0.27012	0.08801	-0.30890	0.09427	0.58573	-0.06372	0.00784	0.04561	0.01960	-0.12353	1.00000
	0.3580	0.0008	0.2018	0.6826	0.1419	0.6613	0.0026	0.7674	0.9710	0.8324	0.9276	0.5652	0.0
	23	24	24	24	24	24	24	24	24	24	24	24	24

CHRONOLOGY OF NITRATE CONTAMINATION OF GROUND WATER

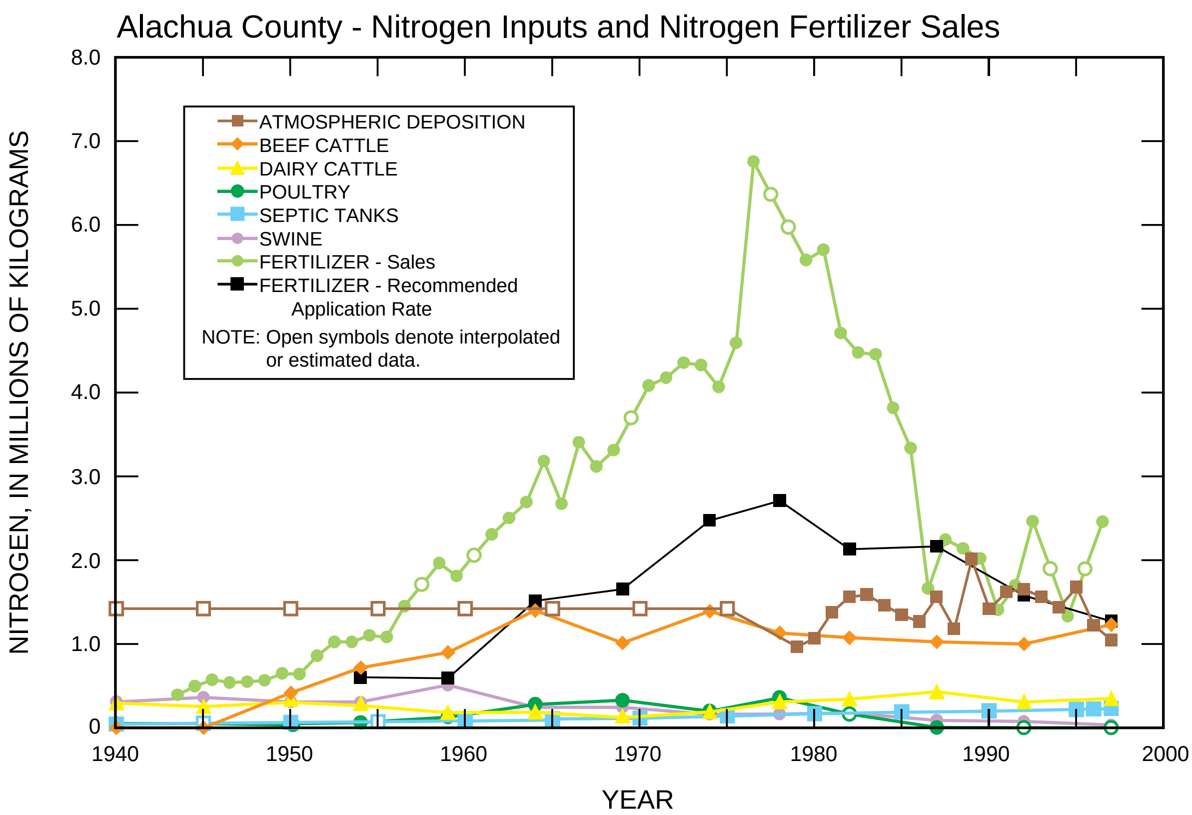
The information obtained from the chemical and isotopic tracers provides an important step in better understanding the sources of nitrate in springs and in shallow zones of the Upper Floridan aquifer. However, this information alone does not provide a complete understanding of the sources of nitrate and chronology of nitrate inputs to the ground-water system. Knowledge of other factors, such as changes in land uses with time, need to be integrated with the chemical and isotopic data to obtain a more complete understanding of the factors affecting the concentration of nitrate in springs and in parts of the Upper Floridan aquifer. There are four main sources of nitrogen to ground water: fertilizers applied to cropland, animal wastes from dairy and poultry operations, atmospheric deposition, and septic tank effluent. Changes in loading from these sources during the years 1955 to 1997 are presented below.

Nitrogen Inputs Associated with Land-use Changes, 1950-97

Estimated nitrogen inputs from various nonpoint sources in each county have varied considerably during the past 40 years as a result of changes in agricultural activities in the Suwannee River Basin. Variable fertilizer N inputs in each county are related to changes in the amount of cropland fertilized and crop type. During the past 40-year period, the amount of cropland fertilized varied considerably by county with Alachua and Suwannee Counties having the greatest (more than 100,000 ha) and Lafayette County the least (40,000-50,000 ha). The temporal distribution of fertilized cropland has varied annually for Alachua, Columbia, Gilchrist, and Suwannee Counties with the peak amount of fertilizer use occurring in the late 1970's. Peak fertilizer use in Lafayette County occurred in the late 1980's, but recent use during the past 5 years has increased substantially. Crop types also have varied during the past 50 years with corn being the dominant harvested crop until the early to mid 1980's when soybeans and hay became the dominant harvested crop types (DACS Census data).

During 1954-1997, ranges in total estimated nitrogen inputs, in million kilograms per year, for each county were: Alachua, 3.88 to 10.3; Columbia, 2.19 to 5.77; Suwannee, 2.75 to 10.9; Lafayette, 1.36 to 5.36; Gilchrist, 1.01 to 6.09; and (figs. 17-21). In the five counties, atmospheric deposition accounted for about 25 to 60 percent of the total N input during the 1950's and early 1960's. In Alachua, Columbia, Gilchrist, and Suwannee Counties, the relative contribution of nitrogen from fertilizers (based on fertilizer sales data) increased continuously from the 1950's, peaked around 1980, and decreased slightly after the early 1980's. In Lafayette County (fig. 20), the relative contribution of nitrogen from fertilizer use has increased continuously from the mid-1940's to the around 1990, decreased for a short time, then increased back to levels in the late 1980's. In Suwannee, Gilchrist, Lafayette, and Columbia Counties, fertilizer use has increased substantially from 1993 to 1997. In all five counties, the shape and pattern of the curve for estimated total N inputs from all nonpoint sources closely matches that for fertilizer use (figs. 17-21). The relative contribution of estimated N inputs from animal wastes (dairy and beef cows, poultry, and swine) to total estimated N inputs varied from about 15 to 30 percent for Columbia and Gilchrist Counties to about 27 to 49 percent for Lafayette County.

The relative contributions of nitrogen inputs from the various nonpoint sources in Suwannee and Lafayette Counties are given special emphasis in this report because of the high concentrations of nitrate in springs in these counties. Also, estimated N inputs from these two counties represent two extremes with regards to the relative amounts of fertilizer used and animal wastes. Prior to 1960, atmospheric deposition contributed the majority of the estimated total N inputs. In Suwannee County, the relative contribution of N from fertilizers increased from about 23 percent in 1955 to more than 60 percent in 1980 (fig. 19). Beginning in the early 1980's, the relative contribution of N from animal wastes (poultry, dairy and beef cows, and swine) began to increase, and by the late 1980's, estimated N inputs from animal wastes (poultry and dairy) contributed about 30 percent of the total estimated N inputs. During 1955-95, the contribution of estimated N inputs from animal wastes ranged from about 21 to 42 percent of the total estimated N inputs.



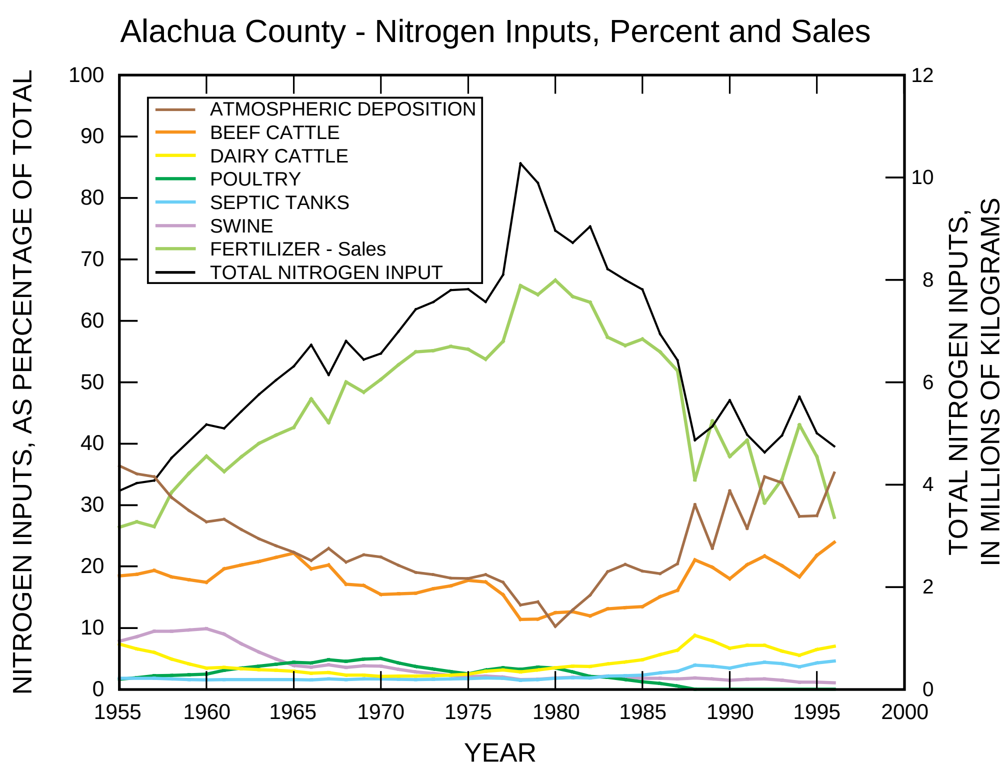
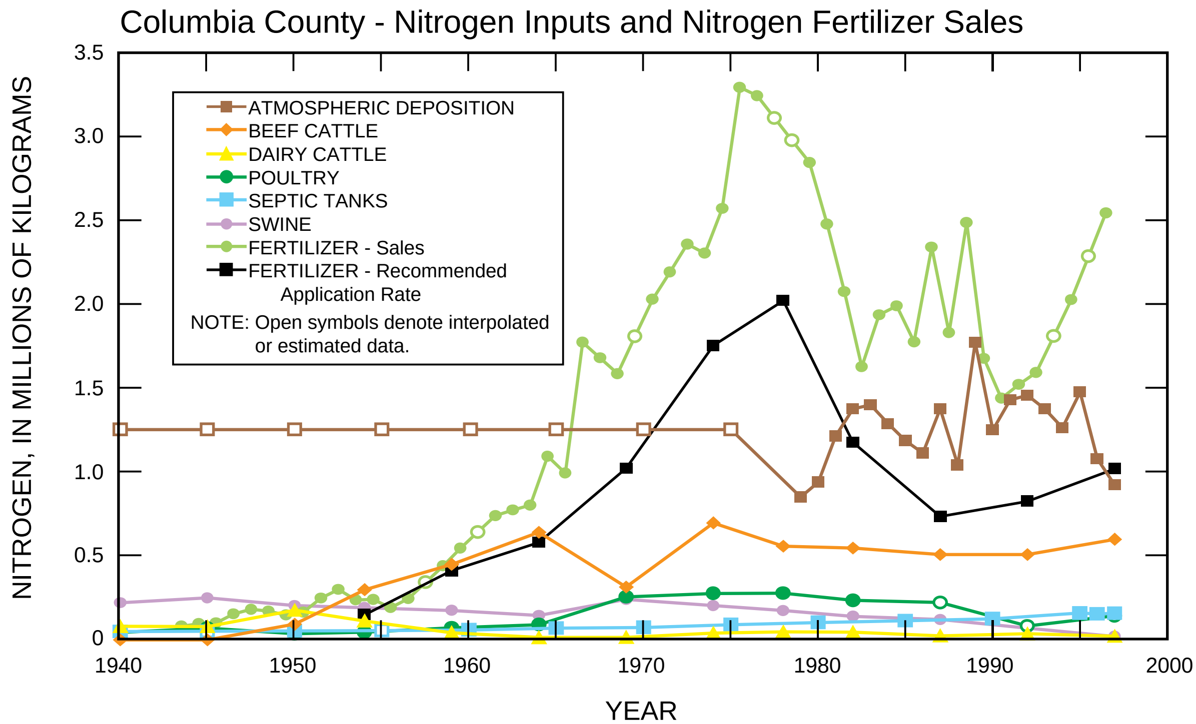


Figure 17. Estimated annual N inputs and relative percentage of total inputs of nitrogen from fertilizers, animal wastes, atmospheric deposition, and septic tanks for the years 1955-97 in Alachua County (interpolated data for missing years are denoted by open symbols).



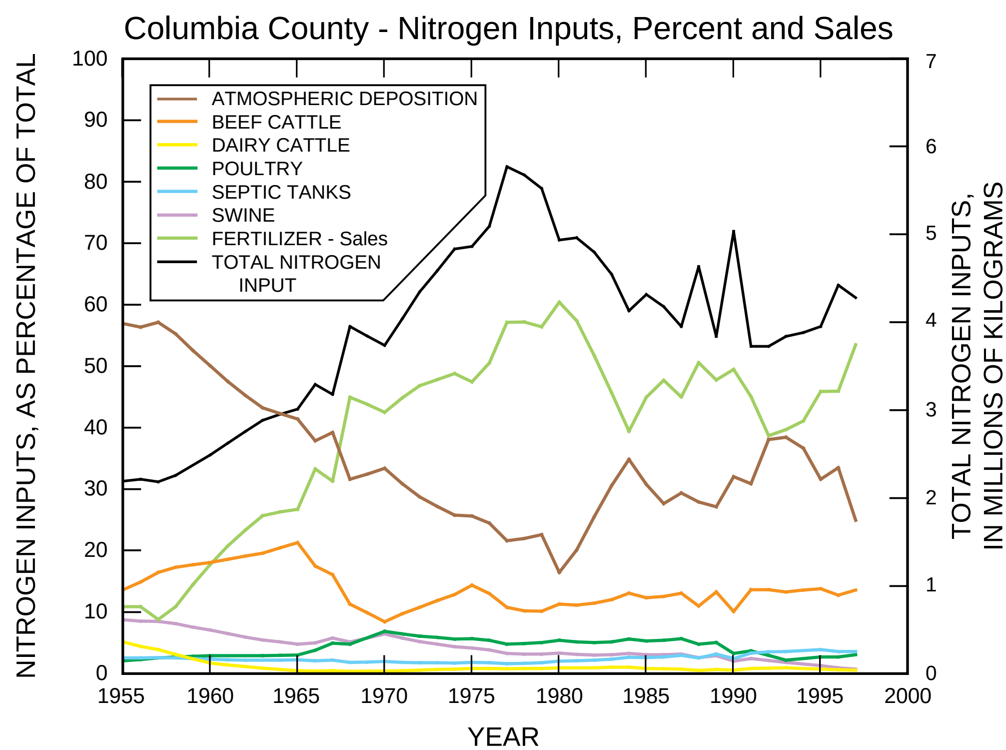
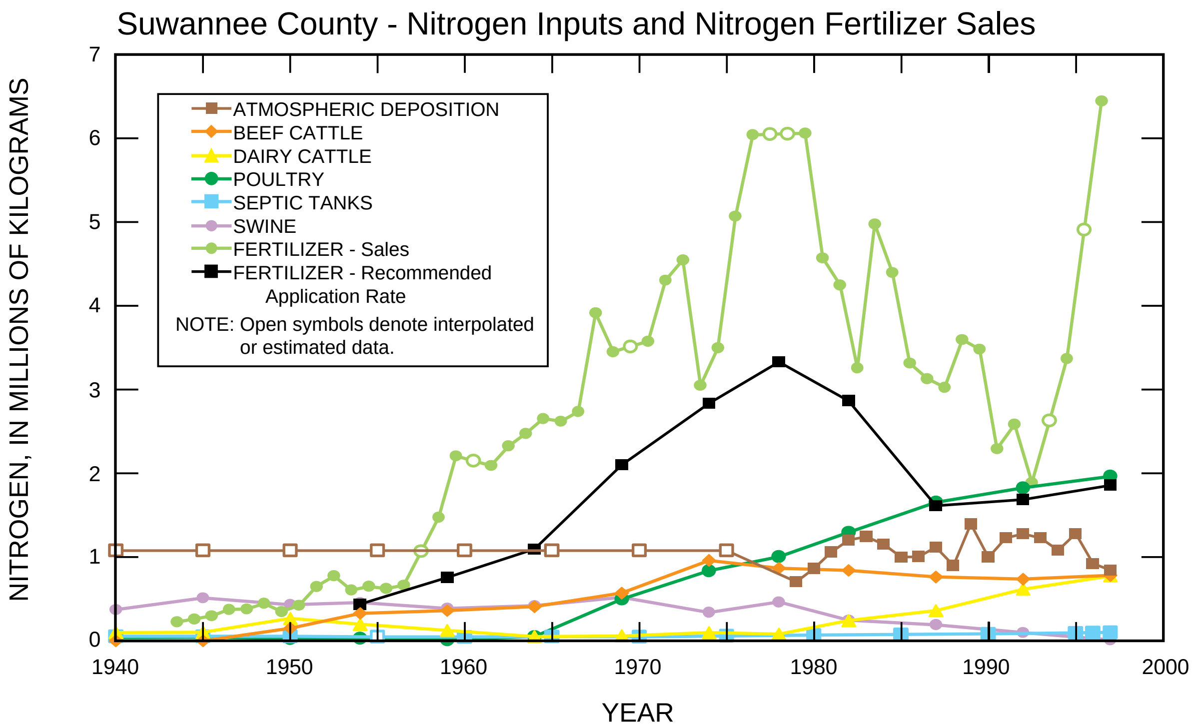


Figure 18. Estimated annual N inputs and relative percentage of total inputs of nitrogen from fertilizers, animal wastes, atmospheric deposition, and septic tanks for the years 1955-97 in Columbia County (interpolated data for missing years are denoted by open symbols).



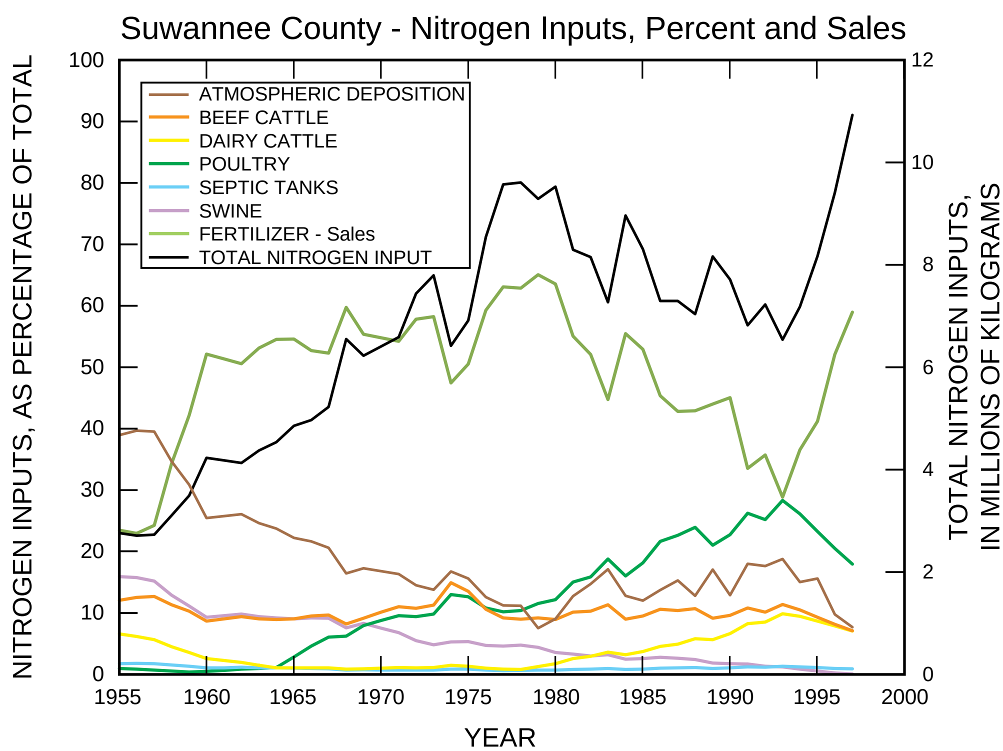
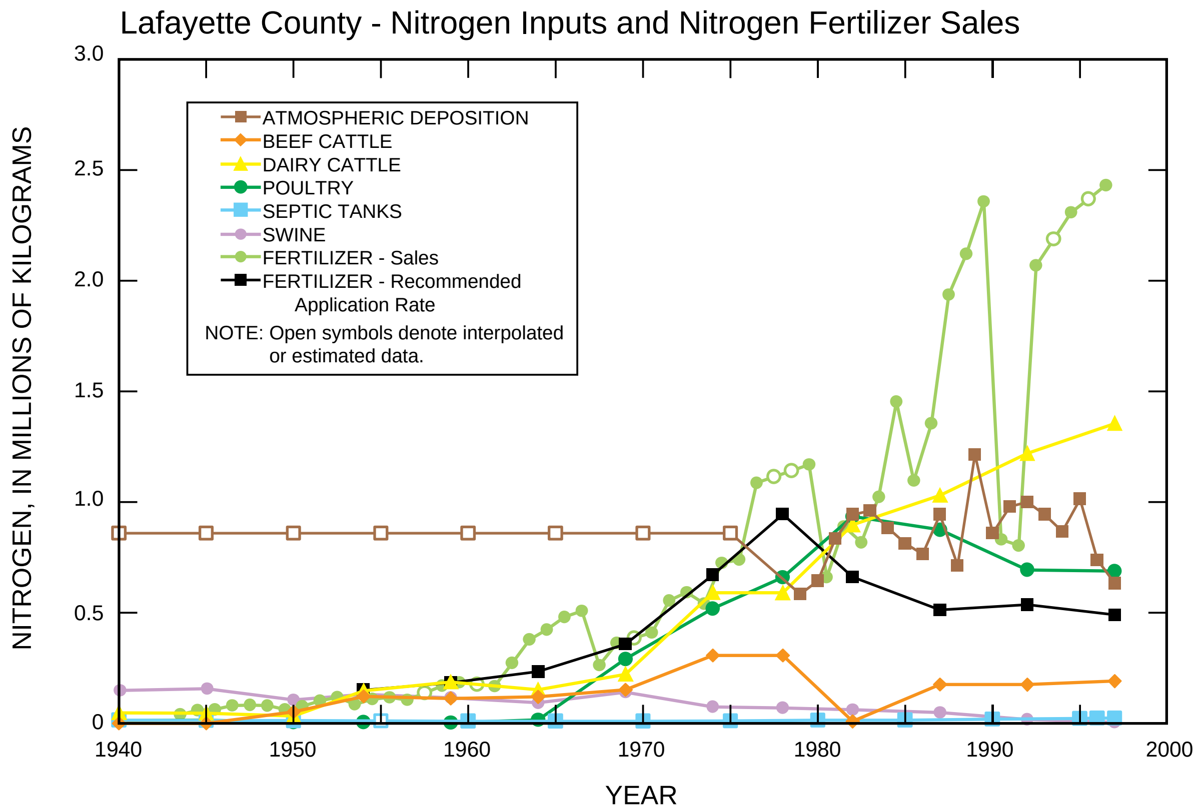


Figure 19. Estimated annual N inputs and relative percentage of total inputs of nitrogen from fertilizers, animal wastes, atmospheric deposition, and septic tanks for the years 1955-97 in Suwannee County (interpolated data for missing years are denoted by open symbols).



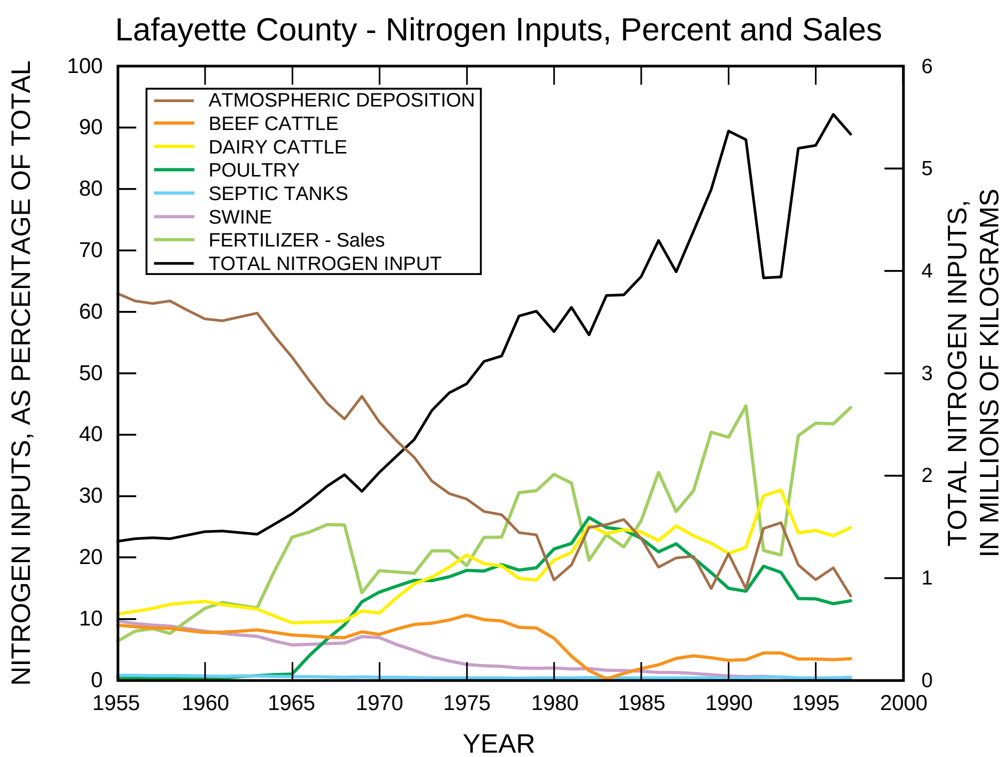
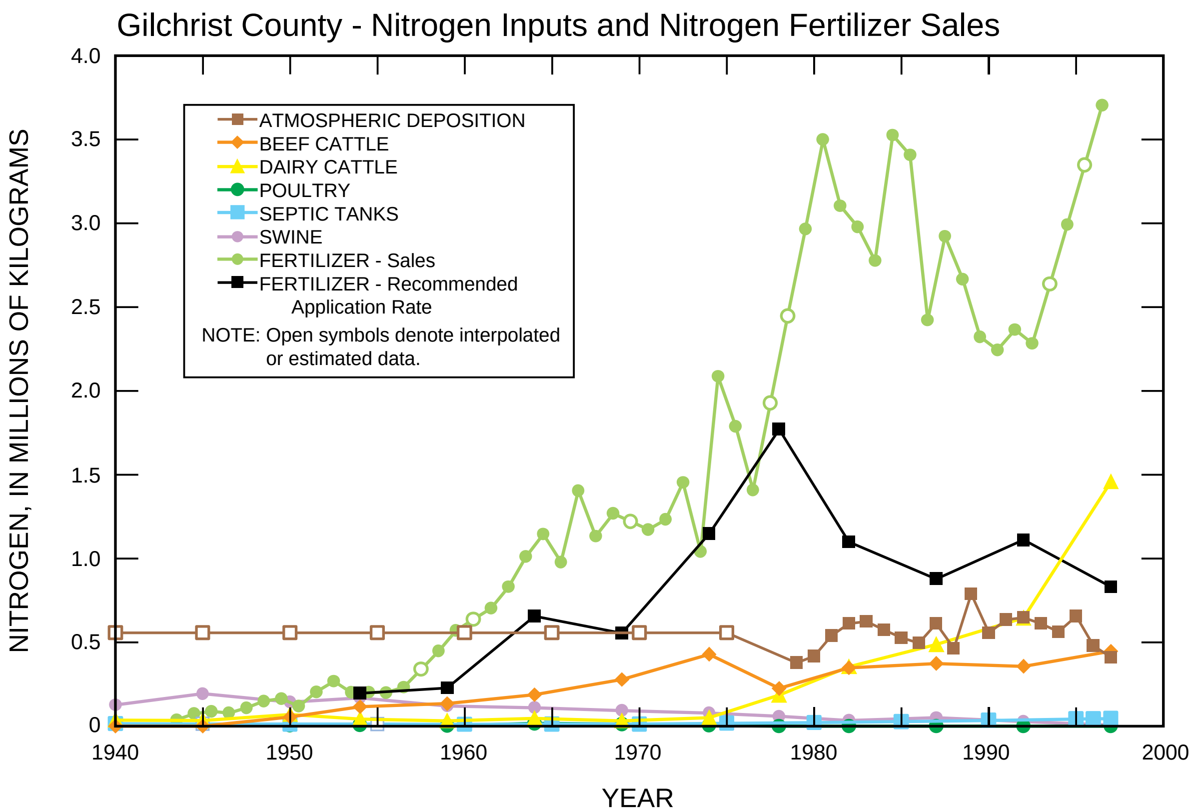


Figure 20. Estimated annual N inputs and relative percentage of total inputs of nitrogen from fertilizers, animal wastes, atmospheric deposition, and septic tanks for the years 1955-97 in Lafayette County (interpolated data for missing years are denoted by open symbols).



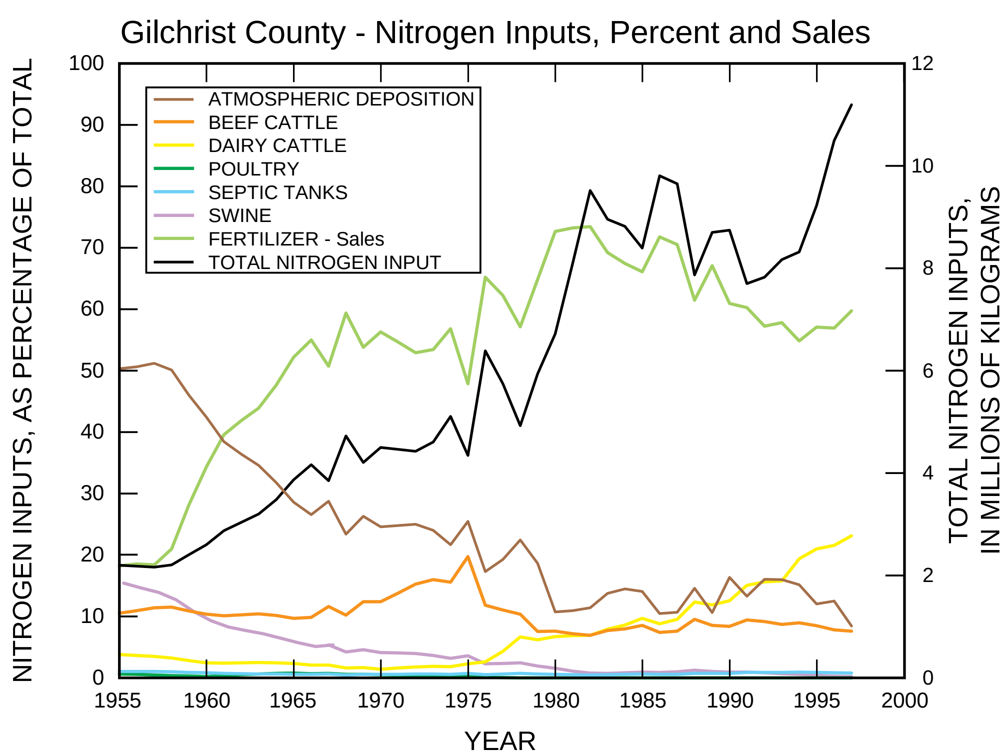


Figure 21. Estimated annual N inputs and relative percentage of total inputs of nitrogen from fertilizers, animal wastes, atmospheric deposition, and septic tanks for the years 1955-97 in Gilchrist County (interpolated data for missing years are denoted by open symbols).

In Lafayette County, the relative contribution of N from atmospheric deposition decreased from about 62 to 27 percent from 1955 to 1975, respectively, but remained the major source of N (fig. 20). N inputs from atmospheric deposition were calculated for the entire county area. The western part of the county consists of low-lying, poorly drained swamps referred to as San Pedro Bay, and ground water from this area typically does not flow toward springs that discharge into the Suwannee River. Therefore, the contribution from atmospheric deposition is somewhat overestimated relative to the other sources that mainly occur in the eastern part of the county. Based on ground-water-flow patterns inferred from potentiometric surface maps of the Upper Floridan aquifer, the eastern part of the county contributes most ground water to springs that discharge into the Suwannee River. From 1955 to 1985, the relative contributions of N from fertilizers and animal wastes (dairy cows, poultry) steadily increased. The estimated contribution of N from fertilizer continued to increase until 1990, while the relative contribution of N from animal wastes (dairy and poultry) decreased slightly during this period. From 1990-97, the contribution of N from animal wastes represented about 40 percent of the total N inputs.

Estimated inputs of nitrogen presented in figures 17-21 do not account for losses of nitrogen that may occur from several processes. For example, losses of N through volatilization of ammonia can vary considerably depending upon specific fertilizer and waste-handling management practices at a given farm. In an intensively farmed area in the mid-Atlantic coastal plain, Bohlke and Denver (1995) estimated that approximately 20 to 35 percent of the N applied as fertilizer could account for the observed nitrate concentrations in the ground-water reservoir and variations in nitrate concentrations with time. Manure from dairy and beef cows may be stored wet or dry, flushed with water into a holding pond or lagoon, spread fresh on land, or spread at some later time (Van Horn and others, 1991). As a result of different storage and land application methods, a range of N loading values to ground water was estimated. Minimum estimates of N loading to ground water (6.6 percent of the total N excreted) were obtained by assuming a tightly managed manure system that includes a cropping system and a land application system that are in nutrient balance (Van Horn and others, 1991). Maximum estimates of N leaching to ground water (60 percent of the total N excreted) were obtained from estimates of N volatilization losses in handling and assuming that the manure was stored in an open lot (Van Horn and others, 1991). Other estimates of nitrogen loss under certain conditions can decrease the content of nitrogen in manure by 25 to 80 percent (Kay and Hammond, 1985). These estimates of nitrogen losses do not consider recycling of nitrogen that may occur when animals consume grains grown within the basin (Asbury and Oaksford, 1997).

The composition and amount of poultry litter and manure can vary widely in both physical and chemical composition. Several factors affect the N composition such as type of birds raised, number of birds per unit area, nutrient composition of the feed, type and amount of bedding material, time in use, moisture content, and other management practices (Vest and Merka, 1994; Jacobs and others, 1996). Losses of N from poultry wastes can result from volatilization of ammonia during stockpiling, composting, or disposal in a lagoon. Approximately 30 to 60 percent of the total nitrogen in manure or litter that is incorporated into soil after spreading is available for crop utilization (Vest and Merka, 1994). However, the release of N from soil is dependent on the nitrogen content of manure, the form of N present, and the ratio of carbon to nitrogen. Depending upon methods of handling after production, the amount of nitrogen leached to ground water from poultry manure or litter could vary substantially from almost none to possibly as much as 30 percent. Some loss of N also may result from the transport of manure or litter away from the farm to other locations for application as fertilizer or as a food source for cattle (Jacob and Mather, 1997).

Under optimal site and operating conditions, conventional septic tank systems can remove nearly all biodegradable organic compounds, suspended solids, and fecal coliforms (Otis and others, 1993). However, septic tanks remove only about 30 percent of the nitrogen in raw domestic wastewater (University of Wisconsin, 1978). Further losses of N from septic tank effluent can result from adsorption, volatilization, mineralization, nitrification, denitrification, and biological uptake. For example, approximately 20 percent of nitrogen was lost from wastewater percolating through soil as a result of denitrification reactions (Jenssen and Siegrist, 1988). However, most of the ammonium, which comprises about 75 percent of the N in the effluent, and organic nitrogen are converted to nitrate by microorganisms under aerobic conditions. Based on soil lysimeter studies in southwest Florida, reductions in total Kjeldahl nitrogen (organic N plus ammonia N; TKN) concentrations were in excess of 97 percent in samples collected 0.6 and 1.2 m (2 and 4 ft) below the infiltrative surface, but nitrate-N concentrations increased to about 50 percent of the original TKN concentrations in septic tank effluent due to nitrification reactions (Otis and others, 1993). Nitrate can move freely in ground water with little or no attenuation.

Relations Between Nitrate Concentrations in Spring Waters and Sources of Nitrogen

In an effort to assess the influence of the various N sources on nitrate contamination of spring waters with time in Suwannee and Lafayette Counties, a comparison was made between long-term trends in nitrate concentration in water from selected springs and the estimated inputs of nitrogen contributed by the various sources. For this comparison, springs in Lafayette and Suwannee Counties were selected that had water samples analyzed for nitrate over a period of 15 years or more. The amount of nitrate-N load contributed to ground-water recharge from the different sources of nitrogen was estimated as follows: first, N inputs for each source were converted to a N flux expressed as grams per meter squared per year ($g/m^2/yr$). This was done by dividing the N input data by the county area in square kilometers-- for Suwannee County, the area was 1,786 km^2; and for Lafayette County, the area was 854 km^2 for the agriculture corridor along the Suwannee River (which was about 60 percent of the total land area of 1412 km^2). Second, N flux values ($g/m^2/yr$) were converted to nitrate-N concentrations, in mg/L, in recharge water by dividing the flux values by the average annual recharge rate of 500 liters per meter squared per year ($L/m^2/yr$) for areas where the Upper Floridan aquifer is unconfined in the Suwannee River Basin in Florida (Grubbs, 1998).

Suwannee County Springs

In Suwannee County, N inputs from fertilizers have contributed more than 50 percent of the nitrogen load to ground water from 1960-97. This estimate is consistent with $\delta^{15}N\text{-}NO_3$ values that indicate fertilizers are the dominant source of nitrate in spring waters and in ground water (Hornsby, 1994) from Suwannee County. The amount of N applied to fields per unit area increased by a factor of 6 to 8 between 1945 and the late 1970's. If all the fertilizer N were converted to nitrate and dissolved in the average annual recharge water (500 $L/m^2/yr$), the resulting ground-water concentrations would be approximately 2 to 3 times the observed nitrate concentrations in spring waters. This indicates that about 33 to 50 percent of the N applied as fertilizers (using county-wide estimates) accounts for nitrate concentrations in the ground-water reservoir and their variations with time. If N from all sources were converted to nitrate and dissolved in recharge water, the resulting ground-water concentration would be approximately 3 to 4 times the observed nitrate concentrations in spring waters.

Four springs have historical records of nitrate concentrations (Hornsby and Ceryak, 1999): Charles (1973-97), Little River (1980-97), Running (1980-98), and Telford (1980-97). Nitrate concentrations in these spring waters generally have remained constant or have decreased slightly with time. The trends in nitrate concentrations with time from these spring waters have similar shapes and for the most part are proportional to the fertilizer-use curve (fig. 19). However, the increasing trend in fertilizer use from 1993-97 is not matched by an increase in nitrate concentrations in spring waters during this same period. A lack of response to increased N inputs may result from a delay or lag of several years between N fertilizer applications and resulting nitrate contamination of ground water. This delay may result from temporary storage in the unsaturated zone, dilution due to increased rainfall during this time period, or other recharge processes.

Curves of nitrate concentrations in ground water were generated by using historical N input data for all sources and the three previously-cited models (piston flow, exponential flow, and binary mixing) to estimate apparent ages or residence times of spring waters (fig. 22). Simulated curves of ground-water nitrate concentrations obtained from these models were compared to the observed nitrate concentrations in the four spring waters to determine the consistency of age information obtained by using CFCs and nitrate and to further characterize the cycling of nitrate in the ground-water system. For these simulations, it was assumed that no nitrate is removed from the ground-water system (for example, by denitrification reactions).

The importance of N inputs contributed by fertilizers to ground water is demonstrated by both binary-mixing and exponential models. For example, observed temporal trends in nitrate concentrations observed in spring waters can be accounted for by a binary-mixing model that contains mixtures of about

40 percent young water, a recharge lag-time of 3 years between fertilizer application and subsequent ground-water contamination, and 60 percent old water (recharged prior to 1940) (fig. 22). Also, nitrate trends with time can be accounted for with the exponential model. Two possible scenarios were investigated using this model to simulate changes in nitrate concentrations in spring waters with time: (1) 50 percent N loading from fertilizer applications, and (2) 50 percent of N loading from all sources as the input function. The first scenario resulted in average ground-water residence times ranging from 10 years for Telford and Running Springs to about 40 years for Little River Spring, whereas the second scenario resulted in average residence times that ranged from 40 to 60 years. Average residence times estimated using exponential models with CFC-11 and CFC-113 data ranged from 24 to 38 years for Running, Charles, and Telford Springs and from 43 to 48 years for Little River Spring. Compared to residence times estimated using CFCs, the fertilizer-N input data alone tends to slightly underestimate average residence times whereas N input data from all sources tend to overestimate average residence times.

The position of the residence-time curves (generated from exponential model) relative to the temporal trend lines for nitrate concentrations in spring waters is very sensitive to the N loading percentage used in the exponential models. For example, if values below 50 percent N loading are modeled, the curves of the average residence time shift downward relative to the temporal spring-water nitrate trends. This results in an apparent decrease in the average residence time for

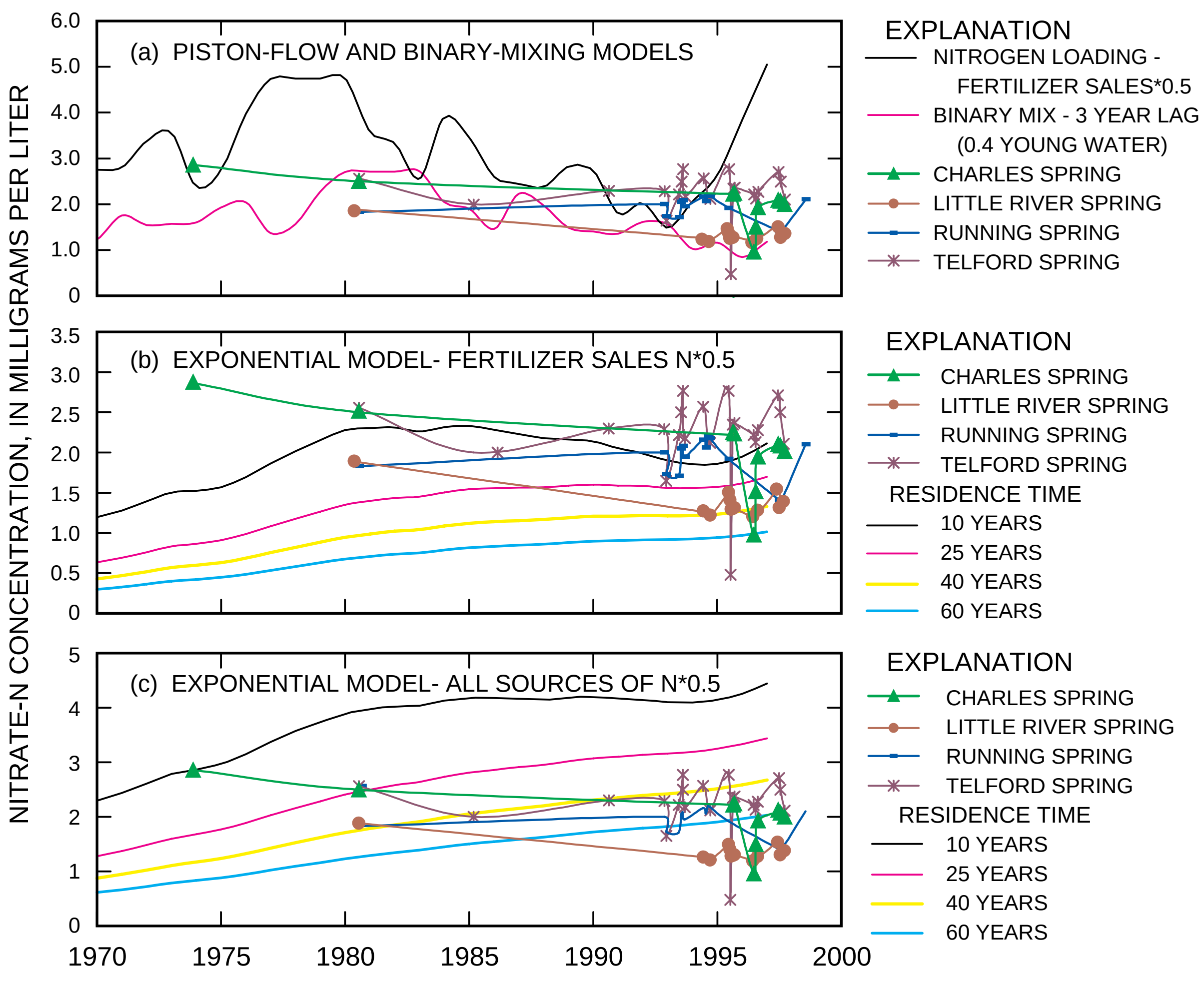


Figure 22. Long-term records of nitrate-N concentrations in spring waters, Suwannee County, relative to inputs of nitrogen from fertilizers and major nonpoint sources to ground-water recharge modeled using (a) piston-flow and binary-mixing models with a mixing fraction of 0.4 post-1993 water and a 3-year lag of recent and old (1940 and older) water, (b) exponential model with 50 percent of fertilizer nitrogen contribution to ground-water recharge and average residence time (RT) of 10 to 60 years, and (c) exponential model with 50 percent of nitrogen from all sources contributed to ground-water recharge and average residence time (RT) of 10 to 60 years.

ground water discharging to springs. Conversely, when N loading values greater than 50 percent are modeled, the curves of average residence time shift upward relative to the temporal nitrate trends for spring waters, which results in an apparent increase in the average residence time for ground water discharging to springs. The actual N loading percentage cannot be determined accurately, given the resolution of the temporal nitrate data for spring waters. Results from both the binary-mixing and exponential models indicate that substantial nitrate concentrations probably are being added to the ground-water system in water that is being recharged on a time-scale of about 1 to 5 years, even though the overall ground-water residence time for spring waters is on the order of 20 to 40 years.

Lafayette County Springs

In Lafayette County, even though estimated N inputs from fertilizers did not contribute more than 50 percent of the total estimated load of N to ground water, fertilizers still were the dominant contributor of N to ground water since the mid-1970's (fig. 20). The amount of N applied to fields increased by a factor of 8 to 10 during the period from 1950 to 1997 (fig. 20). As was the case in Suwannee County, if all the fertilizer N were converted to nitrate and dissolved in recharge water, the resulting ground-water concentrations would be approximately 2 to 3 times the observed nitrate concentrations in spring waters. Therefore, nitrate concentrations in the ground-water reservoir and variations in nitrate levels with time can be accounted for by about 33 to 50 percent of the N applied as fertilizers. If N from all sources were converted to nitrate and dissolved in recharge water, the resulting ground-water concentration would be approximately 4 to 5 times the observed nitrate concentrations in spring waters.

Three springs receiving ground water from Lafayette County have long-term records of nitrate concentrations (Hornsby and Ceryak, 1999): Troy (1960-98), Lafayette Blue (1980-97), and Mearson (1980-98). Nitrate-N concentrations have increased monotonically in water from Troy Spring from 0.06 mg/L in 1960 to 2.8 mg/L in 1998. The increase in nitrate concentrations in Troy Spring track the trend in fertilizer N inputs, which contribute substantially to the overall trend in total N inputs (fig. 23). Fertilizer sales in Lafayette County increased substantially during 1992-97 similar to the observed trend in Suwannee County. During this period, the increasing trend in fertilizer use during 1993-97 is seen by a relatively large increase in nitrate concentrations in Troy Spring, but only small increases in nitrate concentrations in water from Lafayette Blue and Mearson Springs (fig. 23). As was the case with springs in Suwannee County, a small response to increased N inputs may result from a delay or lag of several years between N fertilizer applications and resulting NO_3 contamination of ground water. This delay for springs from Lafayette County also may result from temporary storage in the unsaturated zone, dilution due to increased rainfall during this time period, aquifer characteristics (such as porosity), or other recharge processes.

Nitrate-N concentrations in ground water in Lafayette County were simulated by using historical N input data and the piston-flow, exponential-flow, and binary-mixing models (fig. 23). For Troy Spring, results from the exponential model simulated changes in nitrate concentration that generally matched observed changes in nitrate concentrations with time. However, the estimated average residence time of 10 years using 50 percent of N loading from fertilizers alone tended to underestimate the ground-water average residence time compared to estimates from CFC-11 and CFC-113 (35 to 77 years). When 50 percent of N loading from all sources is included in the exponential model, the N data for the three springs plot between the lines representing the 40- and 60-year average residence times (fig. 23), which more closely match average residence times obtained by using CFC-11 and CFC-113 data. Curves of nitrate concentrations simulated by a binary-mixing model tended to underestimate the observed changes in nitrate concentrations in water from Troy Spring. A piston-flow model using 50 percent of the N inputs from fertilizers also produces a curve that has a shape and a range of nitrate concentrations that are similar to the observed nitrate concentrations. Even though it is difficult to resolve the exact temporal relation between N inputs and resulting nitrate contamination of ground water contributing to spring flow due to limited data on nitrate in spring waters with time, all three models indicate the relative importance of the fertilizer inputs of N to the ground-water-flow system. Also, results from the models indicate that water containing high nitrate concentrations (dominated by fertilizer N) is recharging the ground-water system on a time-scale of less than 10 years. These findings are corroborated by the relatively low $\delta^{15}N\text{-}NO_3$ values for Troy and Mearson Springs, 5.4 and 4.5 per mil, respectively. The higher $\delta^{15}N\text{-}NO_3$ value for Lafayette Blue Spring (8.4 per mil) may indicate a mixed source of inorganic and organic nitrogen, possibly from septic tank effluent.

The complex relation between the concentration of nitrate in spring waters and the amount of nitrogen that is added to a ground-water-contributing area to a spring is controlled by several factors: hydrogeology, land-use, land-management practices, and climate. The amount and timing of rainfall relative to fertilizer applications can strongly influence the amount of N loading to ground water in any given year. Variations in nitrate concentrations in spring waters from Suwannee and Lafayette Counties during the past 5 to 10 years likely are related to large fluctuations in annual and monthly rainfall (and hence recharge) during this period. The amount of annual rainfall can vary by more than 100 percent. For instance, the amount of rainfall measured at Live Oak, Fla. (fig. 1) in Suwannee County, was about 84 cm in 1995 compared to 189 cm in 1991. Rainfall for any given month also varies considerably from one year to the next. For example, during 1991 and 1995, measured rainfall in June was 27.1 and 7.57 cm, respectively. Variations in the nitrogen concentrations of recharge waters that enter the subsurface with time also are related to natural processes that might lower the concentration of nitrate (dilution) or remove nitrate from the system (denitrification), and the distance, direction, and time between areas of recharge to and discharge from the ground-water system.

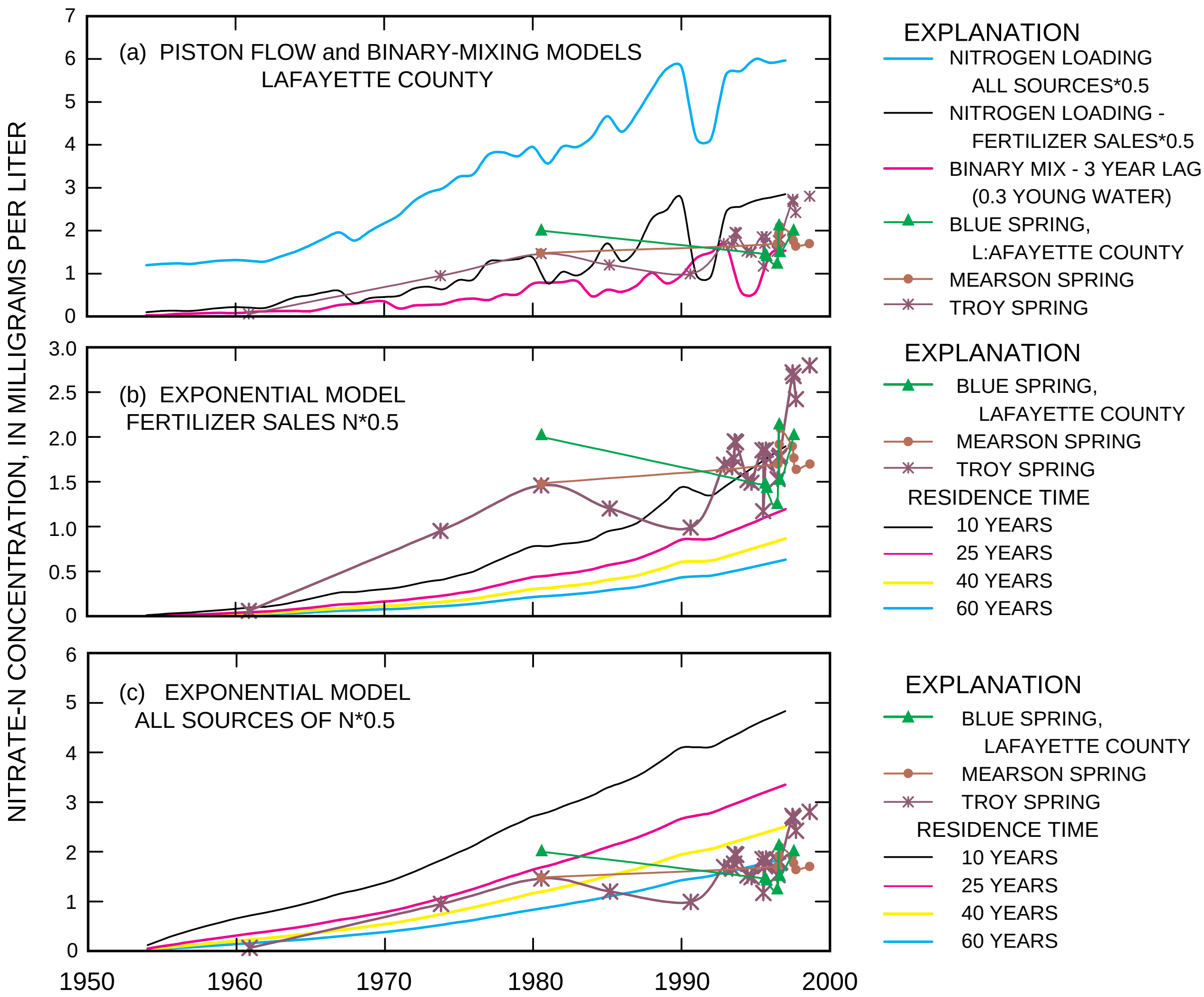


Figure 23. Long-term records of nitrate-N concentrations in spring waters, Lafayette County, relative to inputs of nitrogen from fertilizers and major nonpoint sources to ground-water recharge modeled using (a) piston-flow and binary-mixing models with a mixing fraction of 0.4 post-1993 water and a 3-year lag of recent and old (1940 and older) water, (b) exponential model with 50 percent of fertilizer nitrogen contribution to ground-water recharge and average residence time (RT) of 10 to 60 years, and (c) exponential model with 50 percent of nitrogen from all sources contributed to ground-water recharge and average residence time (RT) of 10 to 60 years.

SUMMARY AND CONCLUSIONS

A cooperative study between the Suwannee River Water Management District (SRWMD) and the U.S. Geological Survey (USGS) has evaluated sources of nitrate in spring waters and water from shallow zones in the Upper Floridan aquifer in the Suwannee River Basin. A multi-tracer approach, which consisted of analyzing water samples for naturally occurring chemical and isotopic indicators, was used to better understand the sources and chronology of nitrate contamination in spring waters discharging to the Suwannee and Santa Fe Rivers. During 1997 and 1998, water samples from 23 springs and two wells were collected and analyzed for major ions, nutrients, dissolved organic carbon (DOC), and selected environmental isotopes [$^{18}O/^{16}O$, D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$]. Water samples were analyzed for chlorofluorocarbons (CFCs; CCl_3F, CCl_2F_2, and $C_2Cl_3F_3$) and tritium (^3H) to assess the apparent ages and residence times of spring waters and water from shallow zones in the Upper Floridan aquifer. In addition to information obtained from the use of isotopic and other chemical tracers, information on changes in agricultural activities in the basin from 1954-97 were used to estimate N inputs from nonpoint sources for five counties in the basin.

Agricultural activities (cropland farming, animal farming operations (beef and dairy cattle, poultry, and swine) along with atmospheric deposition have contributed large quantities of nitrogen to ground water in the Suwannee River Basin in northern Florida. Changes in agricultural land use during the past 40 years in Alachua, Columbia, Gilchrist, Lafayette, and Suwannee Counties have contributed variable amounts of nitrogen to the ground-water system. From 1955-97, the total estimated N from all nonpoint sources (fertilizers, animal wastes, atmospheric deposition, and septic tanks) increased continuously in Gilchrist and Lafayette Counties. In Suwannee, Alachua, and Columbia Counties, estimated N inputs from all nonpoint sources peaked in the late 1970's corresponding to the peak in fertilizer use during this time. Fertilizer use in Columbia, Gilchrist, Lafayette, and Suwannee Counties has increased substantially during the past 5 years, based on records obtained from the Florida Department of Agriculture and Consumer Services. Even though estimated N inputs from animal wastes have increased in Suwannee and Lafayette Counties during the past 40 years, the relative contribution from fertilizers remains high.

Nitrate-N concentrations in spring waters were variable. Nitrate-N concentrations were less than 1.0 mg/L, but elevated above background nitrate concentrations of about 0.05 mg/L, in waters from Columbia, Ichetucknee Blue Hole, Poe, and Hornsby springs. In other spring waters, elevated nitrate-N concentrations clearly show the impact of agricultural activities in the basin, in particular, SUW718971 (29 mg/L) and SUW725971 (38 mg/L). These two springs likely receive recharge water from an area dominated by cropland that is extensively fertilized and irrigated.

The heavy use of fertilizers in the basin is corroborated by nitrogen isotope data, with values of $\delta^{15}N$ values of NO_3 in spring waters ranging from 2.7 per mil (SUW725791) to 10.6 per mil (Poe Spring) with a median of 5.4 per mil for all sampled spring waters. The range of values indicates that nitrate in the sampled spring waters most likely originates from a mixture of inorganic (fertilizers) and organic (animal wastes) sources; although higher $\delta^{15}N$ values for Poe and Lafayette Blue Springs indicate that an organic source of nitrogen probably is contributing nitrate to these spring waters. Water samples from the two wells sampled in Lafayette County have higher $\delta^{15}N$-NO_3 values of 11.0 and 12.1 per mil than values for spring waters, indicating the likelihood of an organic source of nitrate. These two wells are located near dairy and poultry farms, where leachate from animal wastes may contribute nitrate to ground water. Dissolved oxygen concentrations generally were in the range of 1 to 6 mg/L, indicating that ground water contributing to springs is not depleted in oxygen. Concentrations of dissolved gases, N_2 and Ar, are consistent with atmospheric equilibration during ground-water recharge with an apparent recharge temperature of 22 +/- 3^{o}C. The gas data indicate that denitrification has not removed large amounts of nitrate from the ground-water system. Variations in $\delta^{15}N$-NO_3 values of spring waters were not affected by denitrification, and can be attributed to variations in the $\delta^{15}N$-NO_3 values of ground-water recharge, thus provide reliable information about source(s) of nitrate.

Several models, including a well-mixed reservoir model, piston-flow model, exponential model, and a binary-mixing model were used to estimate ages and residence times of ground water discharging to springs. When most springs are combined into a single data cluster, and data on CFC-11, CFC-113, and tritium are simultaneously integrated, exponential mixtures seem to provide reliable estimates of average residence times of ground water discharging to springs from converging flow paths. However, some data for individual springs fit better with a binary-mixing model with more than 50 percent young water for all three tracers, whereas data from other individual springs fit with a piston-flow model with an age of about 25 years. The young ages of several spring waters, such as SUW718971, SUW725971, and Ginnie Spring indicate their high vulnerability to contamination. One important conclusion that seems to fit most springs is that the CFCs indicate that spring waters have large fractions of water that likely are more than 20 years old. To further quantify fractions of young and old water in spring waters, it would be useful to conduct a comparative study using CFCs and the tritium/helium age-dating technique for selected springs.

Spring-water discharge is related to the apparent ages of spring waters, that is springs with lower flows tend to have young ages whereas springs with higher flows tend to have increased ages. Springs, such as SUW718971, SUW725971, and GIL917971, with smaller amounts of flow, 0.06-0.25 m^3/s (2 to 9 ft^3/s), receive water from relatively shallow ground-water-flow systems and smaller contributing areas that likely contain a relatively high proportion of recent recharge. In contrast, first- and second-magnitude springs, such as Hornsby, Little River, and Troy, with flows of 2.1 to 5.6 m^3/s (76 to 200 ft^3/s), receive water from large contributing areas with deep flow systems that contain a relatively higher proportion of older water with low concentrations of nitrate.

The chemical composition of spring waters can be used as a qualitative indicator of age and ground-water residence time. Nitrate-N concentrations and dissolved oxygen in spring waters are inversely related to apparent ages of spring waters and ground-water residence time in the basin. Both nitrate and dissolved oxygen concentrations decrease with increasing residence time of ground water in the aquifer. Silica concentrations increase with age of spring waters. Similar concentrations of other chemical constituents, such as dissolved solids, delta $\delta^{13}C$, and fluoride, that correspond to a wide range of spring-water ages preclude their use as effective markers of relative age of spring waters in this study area, even though they have been used as qualitative indicators of age and mixing proportions of young and old waters of spring waters in other karst areas.

A comparison was made of long-term trends in nitrate concentrations in selected spring waters with estimated inputs of nitrogen from various sources in Suwannee and Lafayette Counties. In both counties, nitrate concentrations in spring waters closely followed the estimated contribution of nitrogen from fertilizers to ground water; nitrate concentrations decreased with time in four spring waters from Suwannee County, and increased with time in three spring waters from Lafayette County. Results from binary-mixing and exponential models indicate that water containing high nitrate concentrations (dominated by fertilizer N inputs) is recharging the ground-water system on a time-scale of less than 10 years, even though the overall average residence time of ground water discharging to springs can be on the order of 20 to 40 years.

The complex relation between the concentration of nitrate in ground water and the amount of nitrogen that is added to a ground-water contributing area to a spring is controlled by hydrogeologic, land-use, climatic, and several other land-management factors. Variations in the nitrogen concentration of water that enters the subsurface with time are related to changes in land-use practices, natural processes that might remove nitrate (denitrification) or lower (dilution) its concentration, and the distance, direction, and time between recharge to and discharge from ground water. Large quantities of nitrogen from fertilizers and other nonpoint sources currently are added to the ground water system. Spring waters represent mixtures of converging flow paths that contain ground water with a range of ages. Even if nitrogen inputs were reduced substantially, it may take decades for nitrate concentrations in the ground-water system to return to concentrations near background levels.

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