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TRACERS

Demystifying Ground-water Flow and Contaminant Movement in Karst Systems Using Chemical and Isotopic Tracers

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INTRODUCTION

In many karst systems throughout the world, ground water and surface water typically constitute a single dynamic system as a result of numerous solution features that facilitate the exchange of water between the surface and subsurface. The combined use of various geochemical and hydrologic tools has considerably enhanced our understanding of complex ground-water flow patterns and the mixing of ground water and surface water in diverse mantled karst systems. Naturally occurring isotopic and other chemical tracers (such as ^{18}O and ^2H , ^{222}Rn , $^{87}\text{Sr}/^{86}\text{Sr}$, ^{13}C , ^{15}N , and major dissolved species) along with geochemical modeling were very effective in quantifying interactions between surface water and ground water in several diverse karst systems in northern Florida. This paper briefly describes results from selected studies of hydrochemical interactions between water from the Upper Floridan aquifer and surface water, including leakage from a sinkhole lake, and a recharge pulse from a sinking stream. Also presented are geochemical techniques that were used to determine sources of nitrate contamination and average residence times of ground water discharging from 24 large springs in the Suwannee River Basin. More detailed information regarding these studies is provided in the references listed at the end of this paper.

INTERACTIONS BETWEEN A SINKHOLE LAKE AND GROUND WATER

In northern Florida, downward leakage of water from sinkhole lakes can be an important source of recharge to the upper Floridan aquifer in areas where the aquifer is poorly confined. Environmental isotopes (oxygen-18, deuterium, $^{87}\text{Sr}/^{86}\text{Sr}$, and tritium), chlorofluorocarbons (CFCs: CFC-11, CCl_3F ; CFC-12, CCl_2F_2 ; and CFC-113, $\text{C}_2\text{Cl}_3\text{F}_3$), and solute tracers (methane,

major ions, silica) were used to investigate ground-water flow patterns near Lake Barco, a seepage lake in a mantled karst setting in north-central Florida (fig. 1) (Katz and others, 1995a,b; Katz and Bullen, 1996). Stable isotope data indicated that the ground water down-gradient from the lake contained 11 to 67 percent lake water leakage, with a lower limit of detection of lake water in ground water of 4.3 percent. The mixing fractions of lake water leakage, which passed through organic-rich sediments in the lake bottom, were directly proportional to observed methane concentrations and increased with depth in the ground-water flow system. In aerobic ground water upgradient from Lake Barco, CFC-modeled ages ranged from 5 years near the water table to the 17 years for water collected at a depth of 30 m below the water table. CFC-modeled recharge ages (based on CFC-12) for anaerobic ground water downgradient from the lake ranged from 17 to 34 years and were consistent with tritium data. CFC-modeled recharge dates based on CFC-11 indicated preferential microbial degradation in anoxic waters. Vertical hydraulic conductivities, calculated using CFC-12 modeled recharge dates and Darcy's law were 0.17, 0.033, and 0.019 m/d for the surficial aquifer, intermediate confining unit, and lake sediments, respectively. These conductivities agreed closely with those used in the calibration of a three-dimensional ground-water flow model for transient and steady-state flow conditions (Lee, 1996).

Chemical patterns along evolutionary ground-water flow paths in silicate and carbonate units were interpreted using solute tracers, carbon and sulfur isotopes, and mass-balance reaction modeling for the complex hydrologic system involving ground-water inflow to and outflow from Lake Barco.

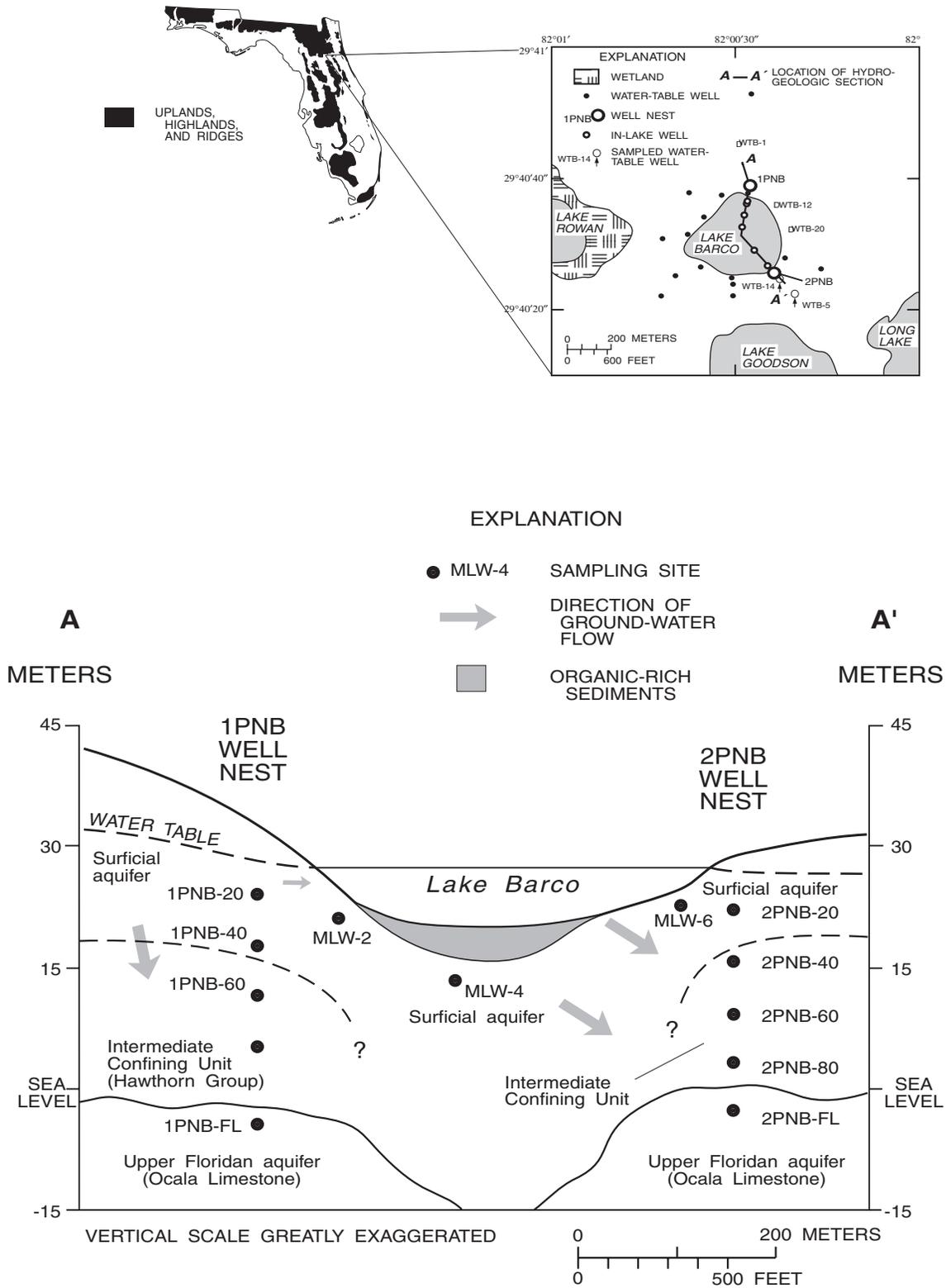


Figure 1. Location map of Lake Barco study area and cross section showing hydrogeologic framework and location of sampling sites.

Rates of dominant reactions along defined flow paths were estimated from modeled mass-transfer and ages obtained from CFC-modeled recharge dates. Ground water upgradient from Lake Barco remains oxic as it moves downward, reacting with silicate minerals in a system open to carbon dioxide (CO₂), producing only small increases in dissolved species. Beneath and downgradient of Lake Barco, the oxic ground water mixes with lakewater leakage in a highly reducing (methanogenic, low-sulfide), silicate-carbonate mineral environment. A mixing model, developed for anoxic ground water downgradient from the lake, accounted for the observed chemical and isotopic composition by combining different proportions of lake water leakage and infiltrating meteoric water. The evolution of major-ion chemistry and the ¹³C isotopic composition of dissolved carbon species in ground water downgradient from the lake can be explained by the aerobic oxidation of organic matter in the lake, anaerobic microbial oxidation of organic carbon, and incongruent dissolution of smectite minerals to kaolinite. The dominant process for the generation of methane was by the CO₂-reduction pathway based on the isotopic composition of hydrogen ($\delta^2\text{H}(\text{CH}_4) = -186$ to -234 per mil) and carbon ($\delta^{13}\text{C}(\text{CH}_4) = -65.7$ to -72.3 per mil). Rates of microbial metabolism of organic matter, estimated from the mass-transfer reaction models, ranged from 0.0047 to 0.039 millimoles per liter per year for ground water downgradient from the lake.

Results from this study provide a framework for a better understanding of the hydrochemical interaction between ground water and lake water in a karst setting, and were used to develop similar studies in other parts of Florida (Katz and others, 1997). The patterns and rates of chemical evolution of ground water near Lake Barco have important hydrochemical implications. First, the potential for mobilization of trace metals in anoxic ground water is high given its low sulfide content. Additional research on the hydrochemical interaction between lake water leakage and ground water is needed, particularly on a regional scale, because of the possibility for degradation of the quality of water in the Upper Floridan aquifer. Second,

higher amounts of CO₂ from microbially mediated reactions downgradient from lakes could result in greater amounts of calcite dissolution, thereby enhancing the development of secondary porosity and solution features.

RECHARGE PULSE FROM A SINKING STREAM

The Little River, an ephemeral stream that drains a watershed of approximately 88 km² in northern Florida (fig. 2), disappears into a series of sinkholes along the Cody Scarp and flows directly into and locally recharges the karstic Upper Floridan aquifer, the source of water supply in northern Florida. Changes in groundwater geochemistry caused by a major recharge pulse from the sinking stream were investigated using geochemical tracers and mass-balance modeling techniques (Katz and others, 1998). Nine monitoring wells, open to the uppermost part of the aquifer, were installed in areas near the sinks where numerous subterranean karst solution features had been identified using ground penetrating radar. During high-flow conditions in the Little River, the chemistry of water in some of the monitoring wells changed, reflecting the mixing of ground water with river water. Rapid recharge of river water into some parts of the aquifer during high-flow conditions was indicated by (1) enriched values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (-1.67 to -3.17 per mil and -9.2 to -15.6 per mil, respectively), (2) elevated concentrations of tannic acid, higher (more radiogenic) ⁸⁷Sr/⁸⁶Sr ratios, and (3) lower concentrations of ²²²Rn, silica, and alkalinity compared to low-flow conditions. Tannic acid concentrations, measured in the field using a portable spectrophotometer, provided real-time quantitative information about mixing of surface water with ground water. This technique also was used in a study of interactions between Suwannee River water and the Upper Floridan aquifer (Crandall and others, 1999). Based on mass-balance modeling, the dominant processes controlling carbon cycling in ground water are the dissolution of calcite and dolomite in aquifer material, and aerobic degradation of organic matter.

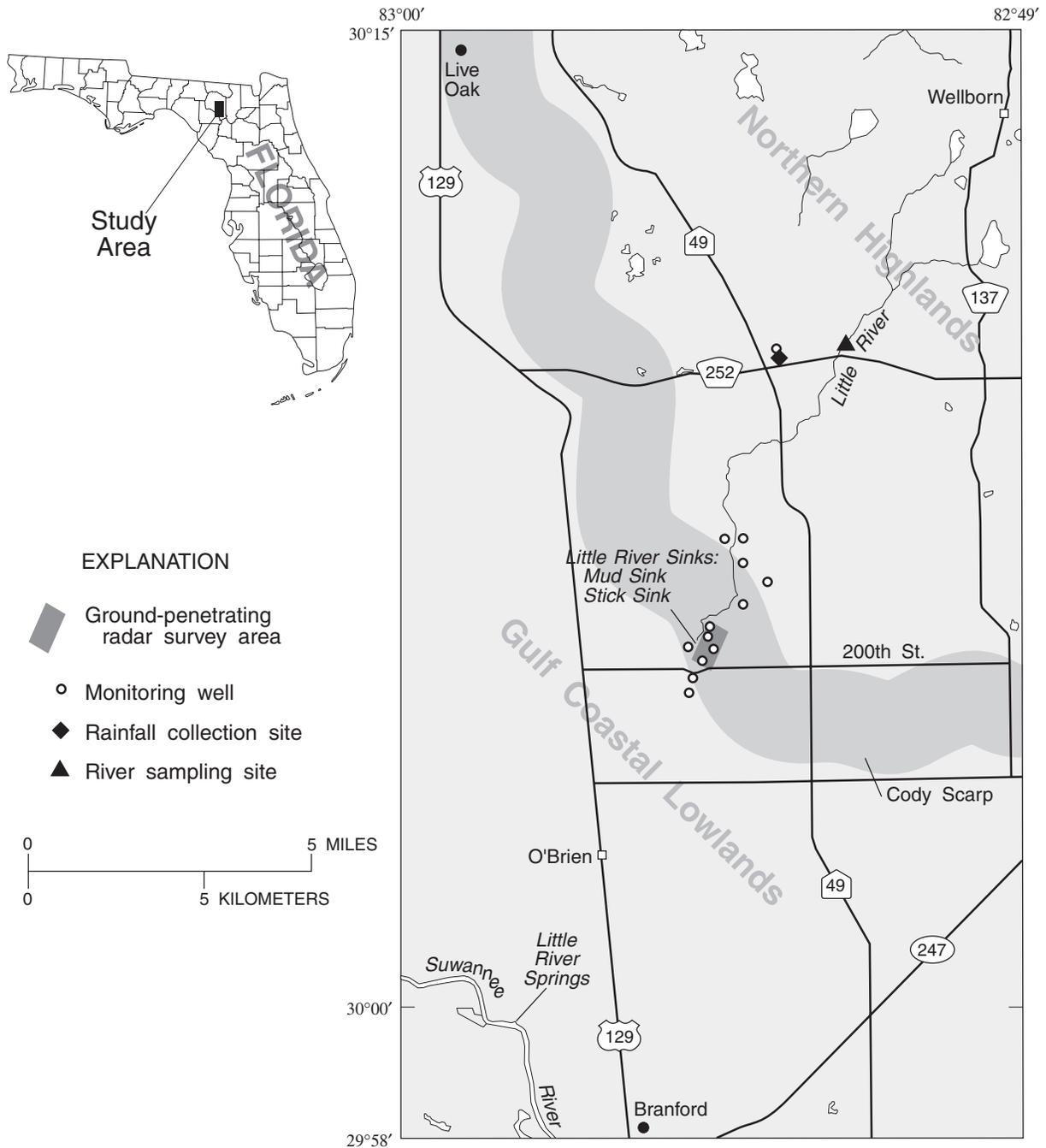


Figure 2. Location map of Little River study area showing sampling sites for ground water, river water, and rainfall.

The proportion of river water that mixed with ground water ranged from 0.13 to 0.84, based on binary mixing models using the tracers $\delta^{18}\text{O}$, $\delta^2\text{H}$, tannic acid, silica, tritium, ^{222}Rn , and $^{87}\text{Sr}/^{86}\text{Sr}$ (Katz and others, 1998). The effectiveness of these

tracers in quantifying the mixing between river water and ground water is related to the difference in the chemical and isotopic composition of the end members and to reactions with aquifer minerals that may occur after mixing.

The corrosiveness of the river water (low saturation index with respect to calcite, <-5.0) leads to rapid dissolution and subsequent enlargement of solution openings, resulting in an increase in the permeability of the aquifer near the Little River sinkholes. During high-flow conditions, the saturation index of ground water with respect to calcite decreased at all sites sampled, with the exception of one site, which did not show any evidence of river water mixing with ground water.

The increase in water levels in wells near the sinkholes, following the recharge pulse from the Little River, indicates the rapid response of the aquifer and can be used to evaluate the susceptibility of the unconfined aquifer to contamination. The hydrochemical response of the aquifer to this recharge pulse from the river is dependent on several factors, such as the degree of interconnectivity of the conduit system and the distance from the recharge input to the zones in the aquifer where the water is withdrawn. Chemical fluctuations often operate on several time scales that can range from days to weeks in response to individual rainfall or recharge events to seasonal cycles related to wet and dry periods. To gain a more complete understanding of the complex interactions among hydrochemical reactions, mixing phenomena, and rates of flow in the aquifer system, more detailed monitoring of stream and ground-water chemistry, ground-water levels, and analysis of stream hydrographs during storms is needed to determine the degree of connectivity between various zones in the aquifer and the location where the Little River disappears underground. This information, coupled with introduced tracers, such as fluorescent dyes, would provide critical data on ground-water flow rates and interconnectivity between various zones of the aquifer.

Although more chemical and hydrologic data are necessary to determine other locations in the aquifer where river water and ground water mix during high-flow conditions, this study demonstrated the effectiveness of combining geophysical techniques (such as ground-penetrating radar for placement of wells) with hydrochemical information (such as

naturally occurring chemical and isotopic tracers in river water and ground water). The investigation also showed that the unconfined Upper Floridan aquifer is highly susceptible to contamination from activities at the land surface in areas where karst features are prevalent. Where direct connections exist between sinkholes and zones in the UFA, recharge of tannic-rich surface waters mix with ground water resulting in elevated organic carbon concentrations. Reactions between these naturally occurring organic compounds and chlorine during disinfection of ground water for public consumption could result in the formation of harmful byproducts such as trihalomethanes (Rostad and others, 2000).

SPRINGS

A multitracer approach consisting of naturally occurring chemical and isotopic indicators, was used to assess sources and timescales of nitrate contamination in spring waters discharging to the Suwannee and Santa Fe Rivers in northern Florida (fig. 3). During 1997-2000, water samples were collected from

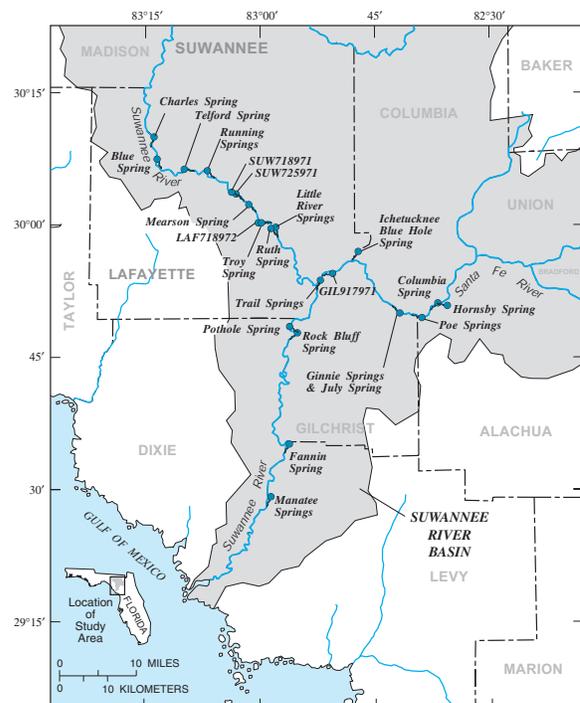


Figure 3. Location of springs sampled in the Suwannee River Basin.

24 springs and analyzed for major ions, nutrients, dissolved organic carbon (DOC), and selected environmental isotopes [$^{18}\text{O}/^{16}\text{O}$, D/H, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$] (Katz and others, 1999, 2001). Additional water samples were analyzed for chlorofluorocarbons (CFCs; CCl_3F , CCl_2F_2 , and $\text{C}_2\text{Cl}_3\text{F}_3$) and tritium (^3H) to assess the residence times and apparent ages 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 land-use activities in the Suwannee River basin during 1954-97 were used to estimate N inputs from non-point sources for five counties in the basin. Changes in nitrate concentrations in spring waters with time were compared with estimated N inputs for Lafayette and Suwannee Counties.

Agricultural activities including cropland farming, animal farming operations (beef and dairy cows, poultry, and swine), as well as atmospheric deposition have contributed large quantities of nitrogen to ground water in the Suwannee River basin. Changes in agricultural activities during the past 40 years in Alachua, Columbia, Gilchrist, Lafayette, and Suwannee Counties have resulted in variable inputs of nitrogen to the ground-water system. During 1955-97, 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 1970s corresponding to the peak in fertilizer use during this time. Fertilizer use in Columbia, Gilchrist, Lafayette, and Suwannee Counties has increased substantially during 1993-97.

This heavy usage of fertilizers in the basin is corroborated by nitrogen isotope data, with $\delta^{15}\text{N}$ values of NO_3 in spring waters that range from 2.7 per mil (SUW725791) to 10.6 per mil (Poe Spring), and 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, although higher $\delta^{15}\text{N}$ values for Poe and Lafayette Blue Springs

indicate that an organic source of nitrogen probably is contributing nitrate to these spring waters. 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 $\delta^{15}\text{N}-\text{NO}_3$ values of spring waters can be attributed to variations in $\delta^{15}\text{N}-\text{NO}_3$ 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 (Katz and others, 1999). These approaches included the use of piston-flow, exponential, and binary-mixing models. 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. However, data for some individual springs are consistent with a binary mixing model with more than 50 percent young water (recharged within the past 5 years) for all three tracers, whereas data from other individual springs fit 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 for most springs is that the CFCs indicate that spring waters have large fractions of water that is most likely more than 20 years old. Apparent ages of spring waters is significantly related to the springwater discharge rate, that is springs with lower flows tend to have young ages (shallow ground-water flow systems), whereas springs with higher flows tend to have increased ages (flow from deep systems is dominant). 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.

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 tracked the estimated contribution of nitrogen from fertilizers to ground water, that is nitrate concentrations decreased with time in four springs from Suwannee County as fertilizer use decreased, and increased with time in three springs from Lafayette County as fertilizer use increased.

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 a complex interaction among hydrogeologic, land-use, climatic, and 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.

Results from these studies in northern Florida have demonstrated that the analysis of naturally occurring tracers in ground water along with geochemical modeling lead to a better understanding of hydrochemical interactions between surface water and ground water, and of the processes controlling the chemical composition of water in the Upper Floridan aquifer. This information can assist regulators in making more informed environmental decisions for protecting the valuable water resources of this important aquifer system.

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