INTERACTIONS BETWEEN GROUND WATER AND SURFACE WATER IN THE SUWANNEE RIVER BASIN, FLORIDA[1]

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ABSTRACT: Ground water and surface water constitute a single dynamic system in most parts of the Suwannee River basin due to the presence of karst features that facilitate the interaction between the surface and subsurface. Low radon-222 concentrations (below background levels) and enriched amounts of oxygen-18 and deuterium in ground water indicate mixing with surface water in parts of the basin. Comparison of surface water and regional ground water flow patterns indicate that boundaries for ground water basins typically do not coincide with surface water drainage subbasins. There are several areas in the basin where ground water flow that originates outside of the Suwannee River basin crosses surface water basin boundaries during both low-flow and high-flow conditions. In a study area adjacent to the Suwannee River that consists predominantly of agricultural land use, 18 wells tapping the Upper Floridan aquifer and 7 springs were sampled three times during 1990 through 1994 for major dissolved inorganic constituents, trace elements, and nutrients. During a period of above normal rainfall that resulted in high river stage and high ground water levels in 1991, the combination of increased amounts of dissolved organic carbon and decreased levels of dissolved oxygen in ground water created conditions favorable for the natural reduction of nitrate by denitrification reactions in the aquifer. As a result, less nitrate was discharged by ground water to the Suwannee River.
(KEY TERMS: geochemistry; water quality; ground water hydrology; ground water/surface water interactions; hydrologic tracers; isotopes; watershed management.)

INTRODUCTION

Interactions between ground water and surface water typically result in a single dynamic flow system in many watersheds in Florida. Ground water and surface water are hydraulically connected through numerous karst features (such as sinkholes, conduit systems in the underlying limestone, and springs) that facilitate the exchange of water between the surface and subsurface, particularly where the Upper Floridan aquifer is unconfined (Figure 1). Unique problems can arise in protecting both ground water and surface water quality in karst areas because of the direct and rapid transport of recharge through conduits to the subsurface and through resurgence by springs. In some areas, recharge from unknown drainage pathways to areas of discharge may contribute to chemical and biological contamination of water supplies. Such contamination in karst areas has been documented in many studies (White, 1993).

Legislation enacted in 1993 mandated that the Florida Department of Environmental Protection (FDEP) develop and implement measures to protect the functions of ecosystems in the State. Watershed management is one of the main components of a program designed to protect and manage ecosystems. The FDEP has identified several key objectives to effectively address comprehensive watershed management issues (Barnett *et al.*, 1995): (1) more coordinated management of ground water and surface water resources; (2) more effective partnerships with local, regional, State, and Federal government agencies; (3) coordination of ground water and surface water monitoring efforts to assess the quality and quantity of the water resources and delineate the boundaries of three-dimensional watersheds; and (4) the development and maintenance of comprehensive statewide data bases for water resource information and monitoring networks oriented toward targeted watersheds.

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STUDY AREA

The Suwannee River basin in Florida consists of an area of 11,000 km^2 (Figure 2). The basin is characterized by karstic wetland and lowland topography, a small number of tributary streams, and an abundance of Upper Floridan aquifer springs. Land uses in the basin are predominantly forest, agriculture, and wetland (Ham and Hatzell, 1996). The basin can be subdivided into five subbasins (Figure 2) based on surface drainage patterns: the Suwannee River basin above the Withlacoochee River (Upper Suwannee River subbasin), the Withlacoochee River subbasin, the Alapaha River subbasin, the Santa Fe River subbasin, and the lower Suwannee River subbasin. The climate in the basin is subtropical and is characterized by long, warm summers and mild winters. Rainfall averages 132 cm per year (Crane, 1986); however, there are large variations between locations and from year to year. 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

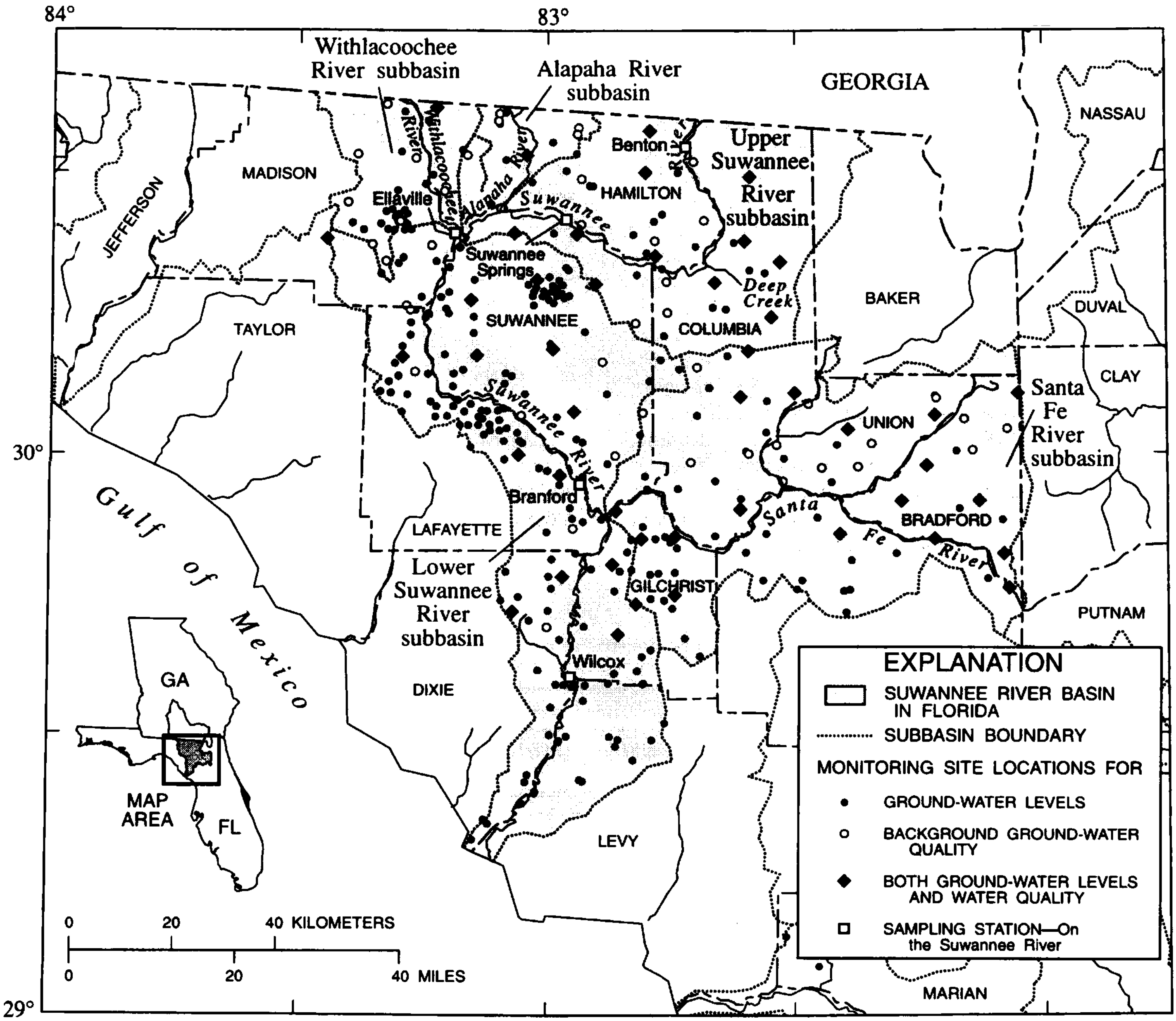

Figure 2. Study Area, Suwannee River Basin in Florida, Location of Monitoring Sites for Ground Water Levels and Background Ground Water Quality, and Surface Water Subbasins.

(limestone and dolostone) of the Upper Floridan aquifer. Surface runoff draining swamps, flatwoods, and lakes provides the flow for this portion of the river. In contrast, near the intersection of Hamilton, Columbia, and Suwannee Counties (Figure 2), the river channel deepens and the river is incised into carbonate rocks. Limestone outcrops and shoals are common along this part of the river. South of the confluence with the Santa Fe River, the basin is largely internally drained. Approximately nine first magnitude (average discharge of 2.8 m^3/s or more) and 63 second magnitude (average discharge of 0.28 to 2.8 m^3/s) springs discharge into the Suwannee River in the lower part of the basin (Rosenau *et al.*, 1977). Together, these springs contribute about 100 m^3/s to the Suwannee River, which represents about 30 to 50 percent of the average annual flow in the river, and strongly influence the water quality of the river (Hull *et al.*, 1981; Crane, 1986). The contribution of ground water sources to the water quality of the Suwannee River is discussed in greater detail in a later section.

Water-quality conditions in most sections of the Suwannee River are generally very good (Hand *et al.*, 1990). Nutrient concentrations of the Suwannee River and its tributaries for the period 1970 to 1991 were low, with median nitrate concentrations generally less than 0.4 mg/L as N. Median total phosphorus concentrations were generally less than 0.5 mg/L as P (Ham and Hatzell, 1996), except in reaches of the upper Suwannee River, above the confluence with the Withlacoochee River (Figure 2), where the river and its tributaries are affected by discharges from wastewater treatment plants, livestock feedlots, paper mills, and phosphate mines (Hand *et al.*, 1990). Naturally occurring phosphate deposits result in relatively high background phosphorus concentrations (greater than 1 mg/L as P) in the upper Suwannee River (Ham and Hatzell, 1996). Increasing development along the Suwannee River corridor accompanied by an increase in septic tank fields can have an adverse impact on river water quality due to increased nitrogen loading.

Monitoring Programs in the Suwannee River Basin

Historically, ground water and surface water systems in the Suwannee River basin have been monitored separately under specific programs, with the exception of a small number of studies of localized areas. During the past 30 years, a considerable amount of hydrologic data (such as river stage and ground water level) have been collected as part of extensive surface water and ground water networks.

The Suwannee River Water Management District (SRWMD) in cooperation with the FDEP and U.S. Geological Survey (USGS), maintains rainfall, water level, and water-quality monitoring networks in the Suwannee River basin. These networks were established to evaluate present surface water and ground water conditions and to determine short and long-term trends and conditions. As part of a surface water network, lake water levels are being measured regularly at 17 sites, river stage and discharge are monitored at 18 sites, and daily rainfall is recorded at 34 sites. Surface water quality samples are collected monthly, bimonthly, or quarterly at 52 sites by the SRWMD as part of the Surface Water Improvement and Management (SWIM) program, which was established in 1989. Currently, ground water levels are being measured at 328 sites in the basin, which includes monthly measurements at 43 wells and continuous measurements (using water-level recorders) at 32 wells.

Since 1987, information on ground water quality has been collected as part of the Florida Ground Water Quality Monitoring Network Program (FGWQMNP), which was established to delineate the baseline or background water quality of the major aquifer systems within Florida and to determine the effects of various land use activities on ground water quality. The 107 wells designed to monitor background water quality of the principal aquifers in the Suwannee River watershed were selected to avoid known areas of ground water contamination. Water from these wells is sampled every three years for major ions, nutrients, trace elements, and selected organic compounds (Maddox *et al.*, 1992). Also as part of the FGWQMNP, the effects of land-use practices on ground water quality are being studied at a mixed urban-industrial site and at an agricultural study area in the Suwannee River basin.

As part of the National Water Quality Assessment Program (NAWQA) study of the Georgia-Florida Coastal Plain, the USGS has sampled water from six wells in its regional background network for the surficial aquifer system (Crandall and Berndt, 1996). Seven sites on the Suwannee River in Florida and one site on the Santa Fe River are being sampled by NAWQA for bed material, water quality, and biological species (Ham and Hatzell, 1996).

METHODS AND APPROACH

Methods of collection and analysis of ground water samples, along with data screening procedures and quality assurance information for ground water quality data have been previously described (Katz, 1992; Maddox *et al.*, 1992). Chemical analyses of water from 107 wells tapping the poorly confined parts of the Upper Floridan aquifer (Figure 2) include data

TABLE 2. Mean Concentration, Number of Samples, and Range of Concentrations (in parentheses) of Selected Water-Quality Constituents Determined at Four Successive Downstream Locations (see Figure 2) on the Suwannee River.

[Concentrations are expressed as milligrams per liter unless otherwise noted. SC denotes specific conductance; μS/cm denotes microsiemens per centimeter; Alk denotes alkalinity, expressed as $CaCO_3$; TOC denotes total organic carbon; TON denotes total organic nitrogen as nitrogen (N); P denotes phosphorus; μg/L denotes micrograms per liter. Data are summarized from 1989-1995 (Hornsby and Mattson, 1996) and represent total concentrations of chemical constituents with the exception of TON and dissolved Fe, which are from 1968-1977 (Hull *et al.*, 1981).]

	Station Name and Distance in Kilometers From Mouth of River			
Constituent	Benton 315	Suwannee Springs 242	Branford 123	Wilcox 55.5
pH	4.20 74; (3.06-7.43)	5.88 74; (3.85-7.92)	7.15 74; (5.56-8.15)	7.31 73; (6.28-8.16)
SC, μS/cm	68 74: (43-160)	122 74; (42-355)	209 73; (29-447)	234 74; (48-500)
TOC	51 74; (21-76)	41 74; (6.3-81)	16 74; (2.3-37)	15 74; (2.0-36)
Alk	6.4 74; (0.4-23)	30 74; (0.4-150)	83 74; (3.9-150)	93 74; (14-160)
Ca	1.7 66; (0.1-10.6)	12 66; (2.4-44)	28 66; (3.4-54)	33 66; (5.9-57)
Mg	0.96 66; (0.1-4.4)	3.2 66; (1.0-13)	5.7 66; (1.1-21)	5.2 66; (1.2-9.6)
Na	3.6 66; (0.1-6.1)	5.0 66; (2.9-12)	5.3 66; (2.6-9.9)	4.9 66; (3.3-11)
K	0.65 66; (0.2-1.7)	0.73 66; (0.1-3.5)	1.1 66; (0.5-3.0)	1.3 66; (0.5-10)
Cl	7.6 66; (0.4-12)	7.5 66; (1.2-12)	7.1 66; (3.0-11)	7.5 66; (1.3-13)
SO_4	5.2 66; (1-17)	13 66; (1.0-43)	14 66; (1.0-32)	15 66; (1.0-27)
NO_3 as N	0.05 74; (0.01-0.22)	0.15 74; (0.01-0.72)	0.57 74; (0.05-1.1)	0.54 74; (0.05-1.0)
TON	0.678 16; (0.37-0.94)	0.73 46; (0.11-1.5)	0.44 83; (<0.02-1.4)	0.35 44; (0.01-0.93)
PO4-ortho as P	0.057 74; (0.004-0.19)	0.75 74; (0.05-3.9)	0.12 74; (0.04-0.33)	0.10 73; (0.05-0.27)
Fe, μg/L	460 5; (280-630)	410 12; (110-660)	210 32; (<3-570)	170 11; (<3-350)

particularly near Branford, Florida, where the water is dominated by Ca and HCO_3 ions resulting a Ca-HCO_3 water type. Accompanying this change in water type is a substantial decrease in TOC and an increase in pH. The chemistry of the river water near Branford, Florida, is controlled largely by spring water discharge to the river, and the similarity in water chemistry of the river water and spring water near Branford, Florida, is shown by the closeness of the points representing these waters in Figure 3.

A substantial increase in the concentration of NO_3 in the Suwannee River near Branford, Fla., (Table 2) probably is the result of the contribution of spring water with elevated NO_3 concentrations. This

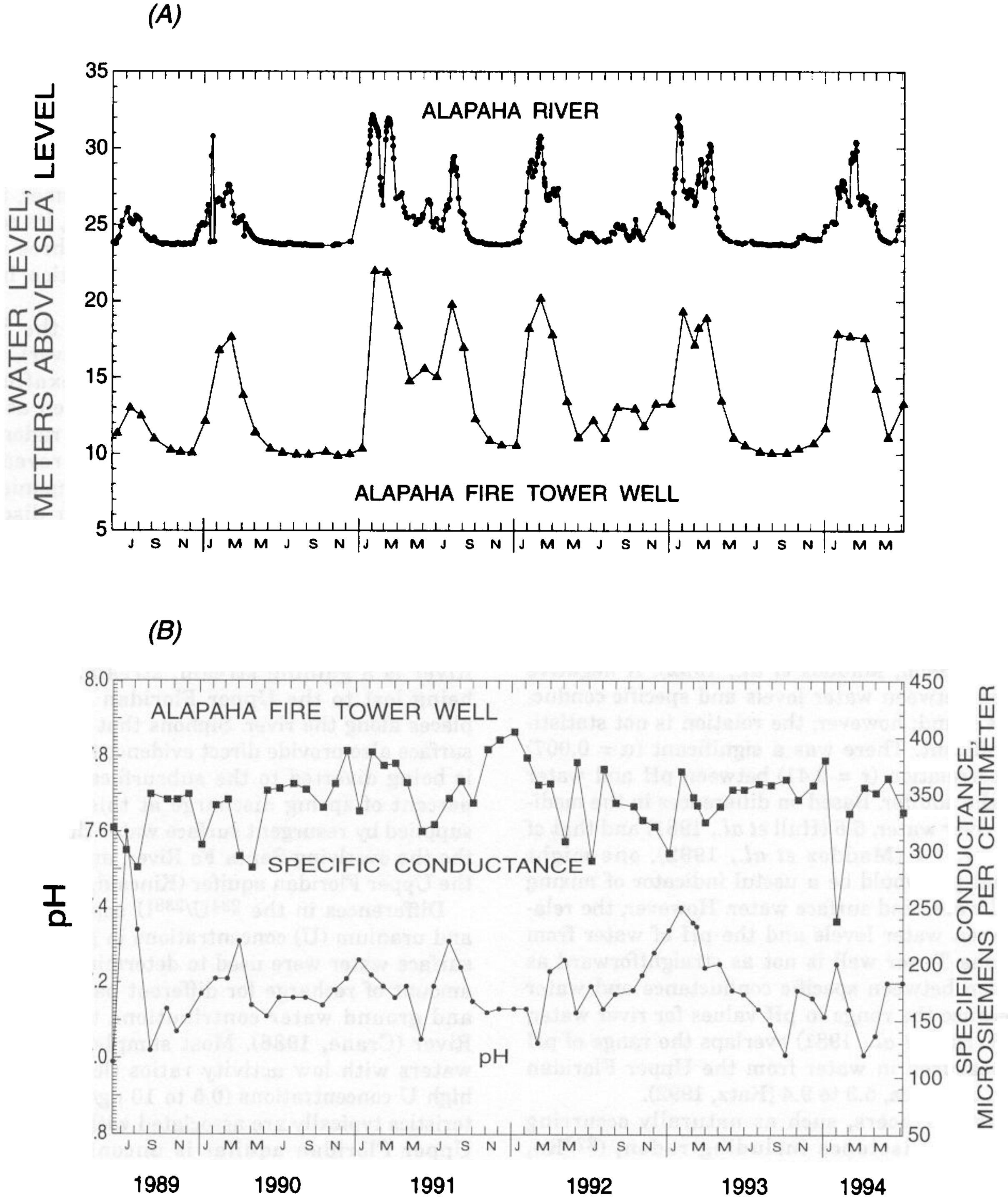

Figure 4. (a) Relation of Alapaha River Stage and Water Level in Alapaha Fire Tower Well, 1989-1994, and (b) Variation in pH and Specific Conductance in Water from Alapaha Fire Tower Well, 1989-1994.

connection is supported by the inverse relation between NO_3 concentrations and stage in the Suwannee River (Hornsby and Mattson, 1996). Large seasonal fluctuations in NO_3 concentrations, pH, and specific conductance of river water have been observed at several locations (Hornsby and Mattson, 1996). Low concentrations of these constituents during high-flow conditions from February through April and U concentrations that are anomalous when compared to those of other river systems of the world (Crane, 1986). The anomalous values result from mixing of some surface runoff (high UAR, low U concentration) with large amounts of ground water flow from springs and seeps (generally low UAR and high U concentrations).

The input of water to the Suwannee River from large springs south of Branford was traced using ^{226}Ra (Burnett *et al.*, 1990). Stream stations north of Branford tended to have a lower mean concentration of ^{226}Ra (0.189 disintegrations per minute per liter, dpm/L) compared to the mean concentration for stations south of Branford (0.270 dpm/L). Even though ^{226}Ra has a strong affinity for adsorption on aquifer minerals, the concentration of ^{226}Ra in ground water is generally several times to several orders of magnitude higher than in surface waters. Several first-order magnitude springs have relatively high ^{226}Ra concentrations (0.155 to 0.917 dpm/L) and the concentration of ^{226}Ra in these springs progressively increased in a downstream direction. This trend was attributed to the increasing contribution of water from deeper parts of the Upper Floridan aquifer that supply spring water to the lower reaches of the river (Burnett *et al.*, 1990).

A study of the hydraulic connections between the Suwannee River and the unconfined Upper Floridan aquifer along a 75-km reach from Ellaville to Branford, revealed that the direction of the hydraulic gradient in the aquifer is toward the river during low-flow conditions and away from the river during high-flow conditions (Hirten, 1996). The effect of elevated river stage on the potentiometric surface of the Upper Floridan aquifer can extend outward from the river to at least 3 km in this area during high-flow conditions based on a high correlation ($r^2 = 0.90$) between river stage and water levels measured in wells located less than 3 km from the river (Hirten, 1996). Water levels measured in wells located more than 3 km from the river also fluctuated in concert with river stage; however, Hirten (1996) noted that there was a lag time of approximately 25-45 days between a rise in river stage and a rise in ground water levels. Geochemical data for ground water near the river are very limited, but do indicate the possibility that river water mixes with ground water over distances of much less than 3 km (Hirten, 1996). Impacts on water quality from river water mixing with water in the Upper Floridan aquifer are probably restricted to smaller, localized areas compared to those areas where ground water levels are affected by high river stage. Dilution effects may account for the localized impact of river water on aquifer water quality.

Comparison of Ground Water and Surface Water Basin Boundaries

The accurate delineation of karst drainage basins represents a considerable challenge because of complex patterns of surface water and ground water flow. Studies have shown that in karst systems, surface water basins typically do not coincide with corresponding ground water basins (Gunay, 1988). Sinking streams can reappear in different basins because ground water divides are controlled by aquifer properties as well as by topographic conditions. Carbonate outcrop areas and joint and fracture patterns must be accurately mapped in great detail to determine the contribution from autogenic recharge, which consists of diffuse infiltration into fractured limestone and internal runoff into sinkholes (White *et al.*, 1995).

Two-dimensional (areal) boundaries for surface water and ground water subbasins in the Suwannee River basin were compared for two different hydrologic conditions: a relatively dry period with low-flow conditions during December 1990 to January 1991 and a wet period with high-flow conditions during April to May 1984. Patterns of ground water flow were determined from potentiometric-surface maps of the Upper Floridan aquifer constructed for low flow and high flow conditions. It was assumed that the aquifer regionally was isotropic and that flow lines were perpendicular to equipotential lines. These ground water flow patterns were superimposed on surface water basin boundaries (delineated based on topography) for the major subbasins within the Suwannee River basin. Generally, the comparison of ground water flow patterns with surface water basin boundaries indicate that ground water basins do not coincide with surface water drainage subbasins, except in some parts of the lower Suwannee River basin and the Santa Fe River subbasin (Figure 5) where ground water and surface water are well connected. The patterns of ground water flow were very similar during low-flow and high-flow conditions; therefore, only the potentiometric surface map constructed for high flow conditions is shown (Figure 5). There are several areas in the basin where ground water that originates outside of the Suwannee River basin crosses surface water basin boundaries during both low flow and high flow conditions. For example, in Hamilton County, during high-flow conditions water levels increased by nearly 6 m compared to levels measured during low-flow conditions; however, during both low- and high-flow conditions, ground water flow lines cross surface water drainage boundaries, particularly where a potentiometric surface high exists in eastern Hamilton and western separate shallow and deep ground water flow systems based on the depth or open interval of a well.

To define ground water and surface water drainage areas more accurately on a local scale, the hydraulic connections between discharge areas (such as springs) for the Upper Floridan aquifer and for surface water need to be determined for different flow conditions using tracer techniques involving dyes, naturally occurring isotopes and, in some cases, human exploration (cave diving). In one such study in the Santa Fe River basin, the degree of interconnection among springs that discharge from Ginnie Springs Park to the Santa Fe River was studied using rhodamine dye tracing experiments. Based on the dispersion of dye to more than one spring, Wilson and Skiles (1988) concluded that there is an extensive network of three-dimensional braided conduits in the aquifer system and unique ground water drainage divides do not exist within a few hundred meters of the spring discharge points.

Natural Remediation of Nitrate in Ground Water

High nitrogen loading from wastes generated by poultry and dairy farms, and fertilizers applied to cropland along the Suwannee River in Lafayette and Suwannee Counties has resulted in elevated NO_3 concentrations in the Upper Floridan aquifer (Andrews, 1994; Ceryak and Hornsby, 1996). Water of the Upper Floridan aquifer flows toward and discharges to the Suwannee River in this area and the discharges from many springs and seeps in the riverbed affect the concentration of NO_3 in the river (Hornsby and Mattson, 1996).

Ground water flow and its effect on water quality are being evaluated in a 73-km^2 study area adjacent to the Suwannee River in Lafayette County (Figure 6) as part of the FGWQMNP. The study area consists mainly of agricultural land use, such as dairy and poultry farms, cropland, and silvaculture. In April-

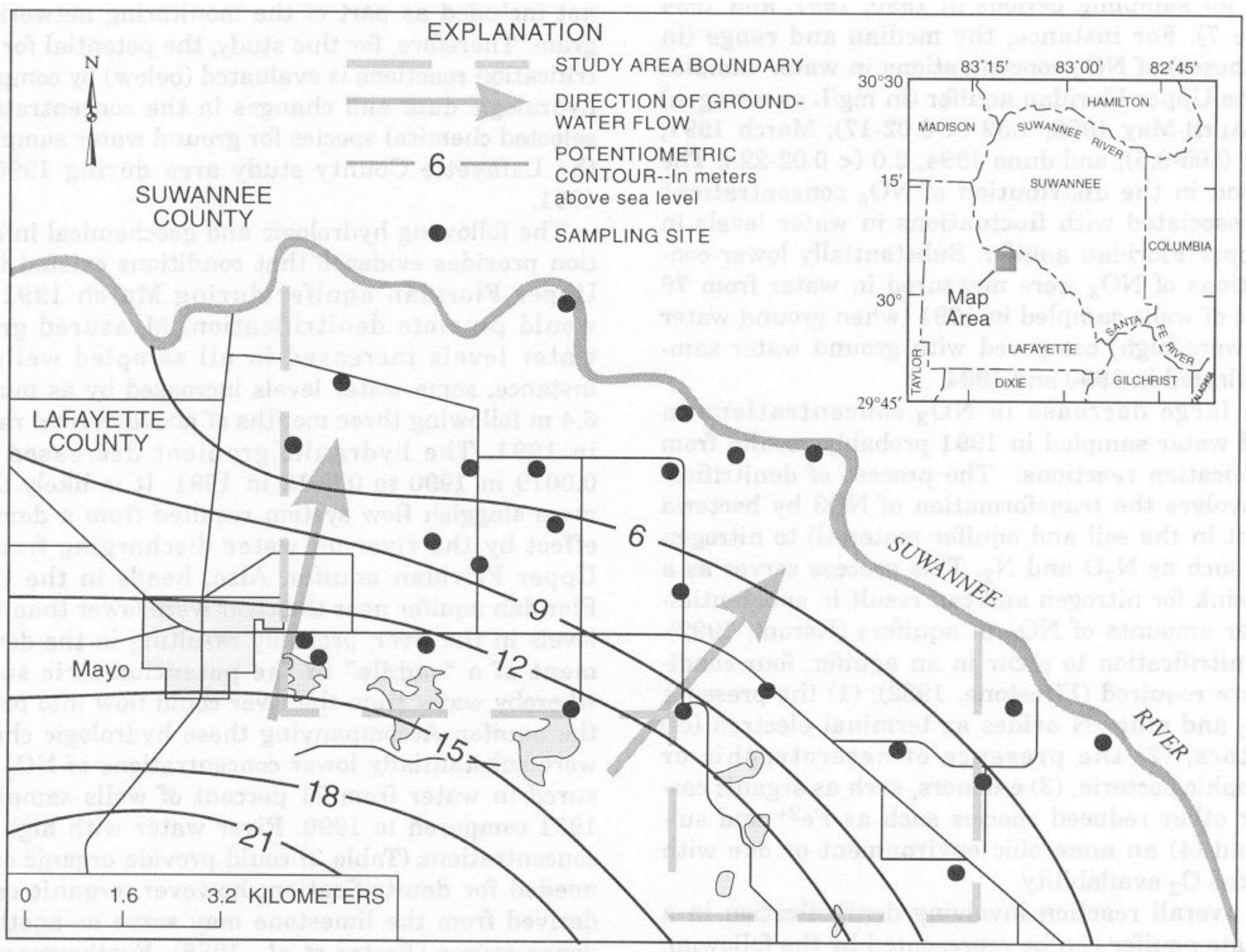

Figure 6. Lafayette County Agricultural Study Area With Potentiometric Surface of Upper Floridan Aquifer and Location of Sampling Sites.

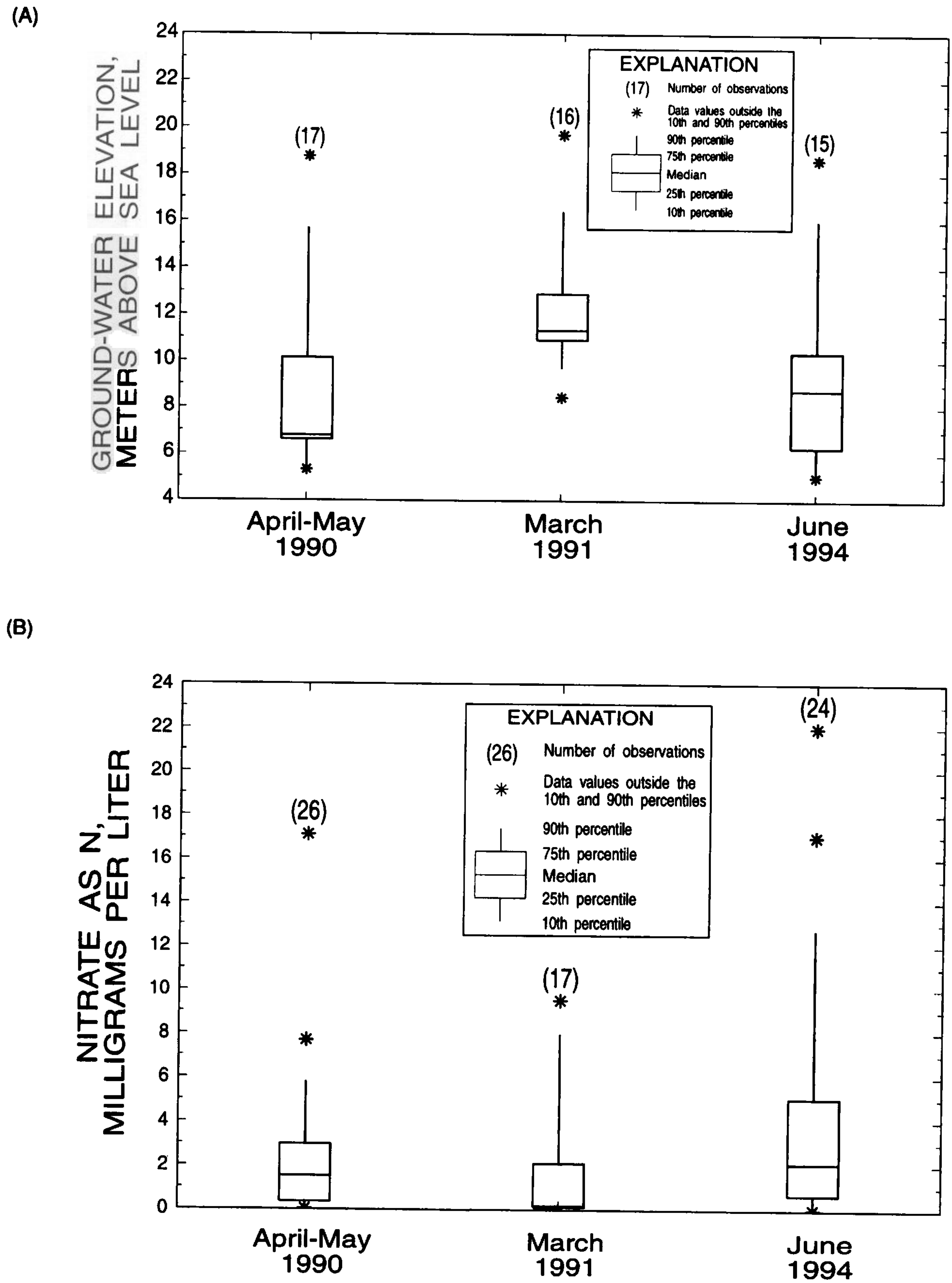

Figure 7. Differences in (A) Ground Water Levels and (B) Nitrate-N Concentrations in Ground Water, Lafayette County Study Area, During April-May 1990, March 1991, and June 1994.

conditions except in very localized areas. Sampling of ground water and surface water needs to be coordinated and conducted during changing hydrologic conditions, especially during periods of high and low flow.

Existing information on ground water levels collected during low- and high-flow conditions indicates that ground water basin boundaries (delineated from potentiometric-surface maps) generally do not coincide with boundaries for surface water subbasins and that there is flow of ground water across surface water subbasin divides. To define areal and vertical ground water basin boundaries more precisely, additional wells would be needed to refine the map of the potentiometric surface for the Upper Floridan aquifer and to obtain more detailed flow patterns. The use of ground water level data to evaluate the coincidence of ground water and surface water basin boundaries was compromised somewhat because these data were collected by different agencies for programs with different monitoring objectives.

Reduction in nitrate concentrations in ground water by denitrification processes is likely to occur naturally during periods of high flow conditions (high water levels in the Upper Floridan aquifer and high stages in the river and its tributaries). A period of above normal rainfall in 1991 resulted in high river stage and high ground water levels. The combination of a more sluggish ground water flow system during this period along with increased amounts of dissolved organic carbon (from river water) and less dissolved oxygen in ground water created conditions favorable for the natural reduction of nitrate in the Upper Floridan aquifer. Increases in pH and the concentrations of calcium, and bicarbonate in ground water were consistent with the denitrification process. More specialized sampling of ground water along flow paths for nitrogen isotopes and nitrous oxide compounds would provide much needed information to confirm and document the importance of naturally occurring denitrification reactions in parts of the watershed

The results of this study add to our understanding of hydrochemical interactions between ground water and surface water across spatial and temporal scales. The study findings also improve our knowledge of the importance of natural and anthropogenic factors on observed changes in environmental conditions that are related to the linkage of ground water and surface water systems in a watershed. In order to protect, sustain or manage watershed ecosystems, it is critical to establish an integrated monitoring program where various resources that comprise an ecosystem are evaluated both spatially and temporally (such as soil, ground water, surface water, sediments, the geologic framework, and atmospheric deposition).

It is unlikely that adequate State and Federal funding will be available in the foreseeable future to conduct delineation and mapping of zones of interaction between ground water and surface water in watersheds throughout Florida and other states. One solution to this problem might be the establishment of watershed coalitions, involving the private sector stakeholders, that could be responsible for generating the necessary resources for proper watershed assessments. The watershed coalitions will benefit their communities by not only identifying the threats to the health and function of watersheds, but also by being a part of the solution to existing problems.

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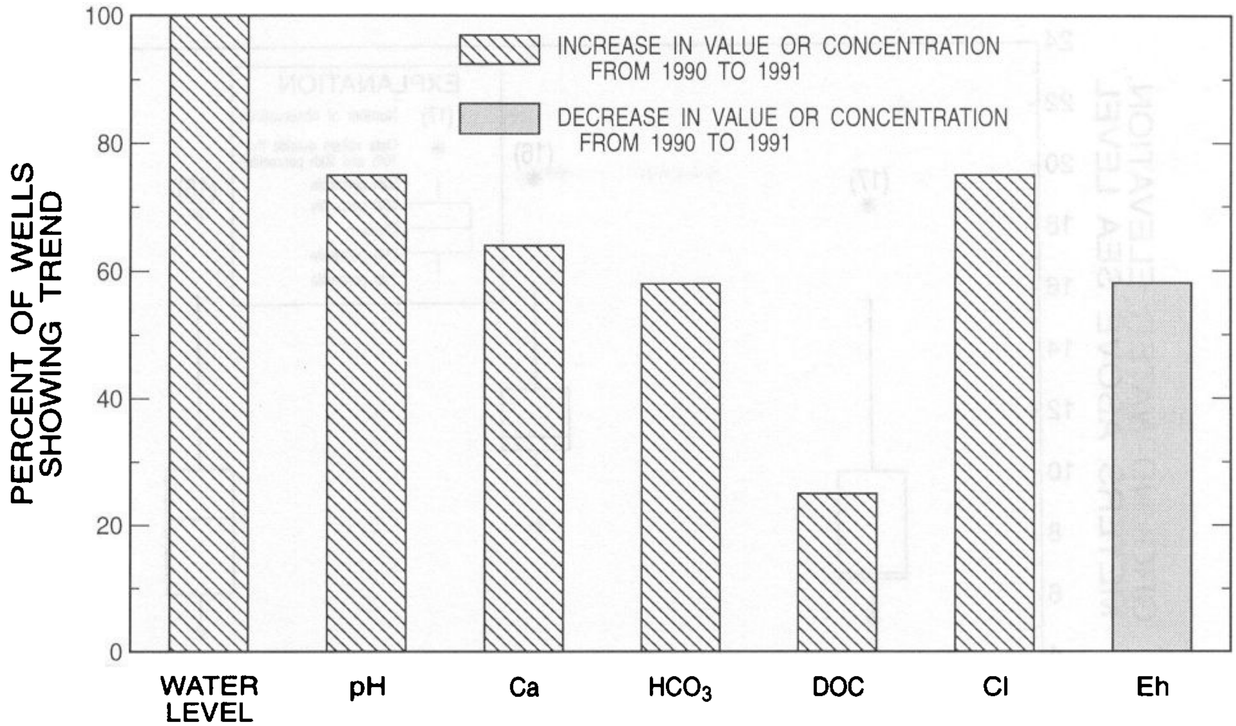

Figure 8. Changes in Water Level, Eh, pH, and Concentration of Selected Constituents in Ground Water From 1990 to 1991 in Lafayette County Study Area.

chloride and other major ions did not show a corresponding decrease from 1990 to 1991. For instance, chloride concentrations increased in water samples from 75 percent of the wells in which NO_3 concentrations decreased from 1990 to 1991. Water from 71 percent of wells sampled also showed a decrease in redox potential based on measured Eh, and an increase in measured pH, Ca^{2+}, HCO_3^-, and DOC (Figure 8).

The increase in pH, Ca^{2+}, and HCO_3^- is consistent with the overall denitrification reaction presented earlier. Additional evidence for more reducing conditions in ground water in 1991 compared to 1990 is the increase in dissolved iron in water from 61 percent of the wells that yielded water with decreased NO_3 concentrations. Also, an increase in sulfate concentrations in water from approximately 60 percent of the wells sampled indicates the possibility that sulfide is also an e-donor for the denitrification. In a study of the fate of NO_3 in ground water beneath several dairy farms in Suwannee and Lafayette Counties, Andrews (1994) noted that denitrification was more likely to occur in deeper rather than in very shallow ground water because deeper ground water had considerably lower dissolved oxygen concentrations than shallow ground water.

To reiterate, it is likely that a sluggish ground water flow system in March 1991, the significantly reduced amounts of dissolved oxygen in the aquifer, combined with increased amounts of organic carbon and other reduced species that could serve as e-donors, created conditions favorable for the natural reduction of NO_3 in ground water by denitrification. As a result, less NO_3 would be discharged by ground water to the Suwannee River during high-flow periods than would be discharged during low-flow periods.

SUMMARY AND CONCLUSIONS

The direct linkage between ground water and surface water in parts of the Suwannee River basin has been demonstrated by analysis of hydrologic and water-chemistry data collected during regional assessments and localized studies. Naturally occurring tracers (isotopes, major and minor chemical species), artificially introduced tracers (dyes and other synthetic compounds such as sulfur hexafluoride), and detailed data on ground water levels and river stage provide important information on the hydrochemical interactions between ground water and surface water. Complex ground water flow and mixing patterns can be revealed only through consistent monitoring with time and during varying hydrologic conditions. Insufficient chemical and hydrologic information exists at present to determine the lateral extent of mixing of river water with water in the Upper Floridan aquifer during periods of high flow

May 1990, March 1991, and June 1994, water samples from 18 wells tapping the Upper Floridan aquifer and seven springs that discharge into the Suwannee River were analyzed for NO_3 and other chemical constituents. The principal source of NO_3 in water discharged by springs to the Suwannee River was attributed to a combination of leachate from livestock wastes and septic tanks, based on measured nitrogen-isotope ($^{15}N/^{14}N$) ratios of NO_3 in water samples collected in May 1993 (Andrews, 1994).

In the study area, the dominant regional ground water flow direction is north to northeast toward the Suwannee River (Figure 6). However, during the 1991 sampling period, heads in the Upper Floridan aquifer near the Suwannee River were lower than water levels in the river creating the potential for water to flow from the Suwannee River into the Upper Floridan aquifer. Ground water levels in 1991 increased by as much as 6 m at some wells following three months of above normal rainfall, compared to water levels in 1990 and 1994 (near normal rainfall).

Nitrate concentrations in ground water varied widely for sampling periods in 1990, 1991, and 1994 (Figure 7). For instance, the median and range (in parentheses) of NO_3 concentrations in water samples from the Upper Floridan aquifer (in mg/L as nitrogen) were: April-May 1990, 1.52 (< 0.02-17); March 1991, 0.20 (< 0.05-9.5); and June 1994, 2.0 (< 0.02-22.). The variation in the distribution of NO_3 concentrations were associated with fluctuations in water levels in the Upper Floridan aquifer. Substantially lower concentrations of NO_3 were measured in water from 76 percent of wells sampled in 1991 (when ground water levels were high) compared with ground water samples collected in 1990 and 1994.

The large decrease in NO_3 concentrations in ground water sampled in 1991 probably results from denitrification reactions. The process of denitrification involves the transformation of NO3 by bacteria (present in the soil and aquifer material) to nitrogen gases, such as N_2O and N_2. This process serves as a major sink for nitrogen and can result in substantially lower amounts of NO_3 in aquifers (Korom, 1992). For denitrification to occur in an aquifer, four conditions are required (Firestone, 1982): (1) the presence of NO_3 and other N oxides as terminal electron (e-) acceptors, (2) the presence of heterotrophic or autotrophic bacteria, (3) e-donors, such as organic carbon, or other reduced species such as Fe^{2+} and sulfide, and (4) an anaerobic environment or one with restricted O_2 availability.

The overall reaction involving denitrification in a carbonate aquifer can be represented by the following expression:

$$4NO_3^- + 5CH_2O + 5CaCO_3 + 4H^+ \longrightarrow 2N_2 + 10HCO_3^- + 5Ca^{2+} + 2H_2O$$

In the above expression, an organic substrate represented by CH_2O serves as an electron donor. Intermediate products, such as nitrite (NO_2^-) and nitrogen gases (NO and N_2O) are produced but are not shown in the above reaction. In this overall denitrification reaction, hydrogen ions are consumed, resulting in an increase in pH. Assuming that dissolution of calcite (in limestone matrix comprising the Upper Floridan aquifer) occurs, bicarbonate and calcium ions are produced by the reaction. Other indicators of reduced or anoxic conditions would include an increase in dissolved iron and manganese concentrations.

To positively confirm that denitrification reactions have occurred it would be desirable to measure changes in specific indicator constituents, such as nitrous oxides and the isotopic composition of nitrogen species along flow paths. However, analyses for dissolved nitrogen gases and nitrogen isotopes were not included as part of the monitoring network program. Therefore, for this study, the potential for denitrification reactions is evaluated (below) by comparing hydrologic data and changes in the concentration of selected chemical species for ground water sampled in the Lafayette County study area during 1990 and 1991.

The following hydrologic and geochemical information provides evidence that conditions existed in the Upper Floridan aquifer during March 1991 that would promote denitrification. Measured ground water levels increased in all sampled wells; for instance, some water levels increased by as much as 6.4 m following three months of above normal rainfall in 1991. The hydraulic gradient decreased from 0.0019 in 1990 to 0.0012 in 1991. It is likely that a more sluggish flow system resulted from a damming effect by the river on water discharging from the Upper Floridan aquifer. Also, heads in the Upper Floridan aquifer near the river were lower than water levels in the river, probably resulting in the development of a "saddle" in the potentiometric surface whereby water from the river could flow into parts of the aquifer. Accompanying these hydrologic changes were substantially lower concentrations of NO_3 measured in water from 71 percent of wells sampled in 1991 compared to 1990. River water with high TOC concentrations (Table 2) could provide organic carbon needed for denitrification; however, organic carbon derived from the limestone may serve as another e-donor source (Foster *et al.*, 1985). Furthermore, the lower NO_3 concentrations likely were due to denitrification rather than dilution because concentrations of

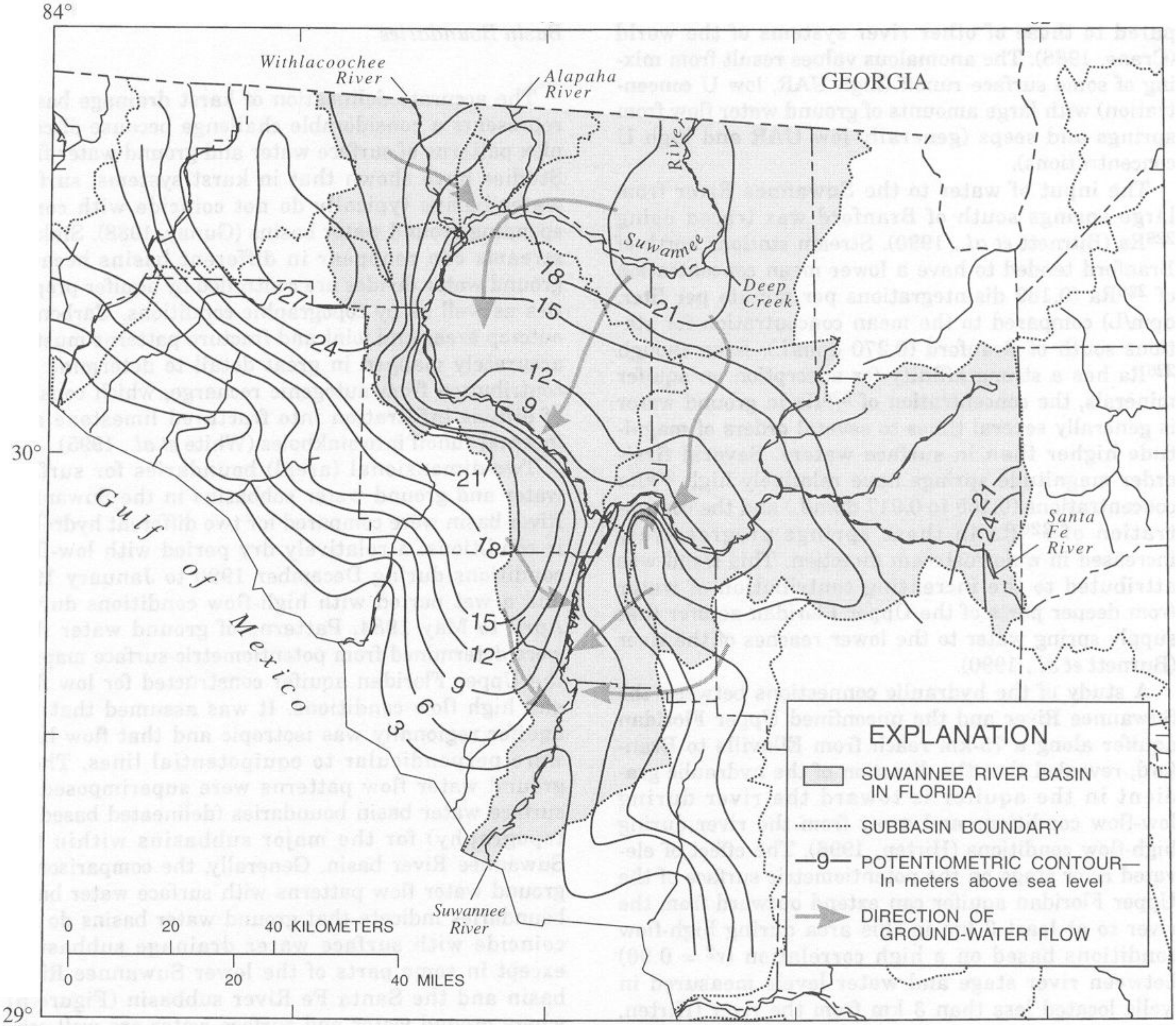

Figure 5. Potentiometric Surface of the Upper Floridan Aquifer and Ground Water Flow Patterns During High Flow Conditions Relative to Surface Water Subbasins.

Columbia County (Figure 5). Also, the area of a potentiometric surface high (represented by the 27-m contour) enlarges during high-flow conditions from a small area in northeast Taylor County to a much larger area that includes central Madison County (Figure 5). Ground water basin boundaries do not coincide with surface water basin boundaries in Madison, Taylor, and Jefferson Counties.

It is important to note that the ground water level data used for constructing potentiometric surface maps were collected as part of a program that was designed to delineate the regional potentiometric surface of the Upper Floridan aquifer rather than to delineate ground water basins. The wells in this network are open to different depths in the aquifer and the open intervals of these wells probably intercept both localized and regional ground water flow systems; therefore, the wells in the present network (approximately 250 wells in the basin) are not ideally suited to define two-dimensional boundaries for ground water basins accurately in most areas of the Suwannee River basin. No attempt was made to in 1994 and again in 1995 is due to dilution from a large contribution of surface runoff generated during spring rainfall.

In some locations in the basin, the hydraulic linkage between ground water and surface water is evidenced by the correlation of ground water and surface water levels. For example, variations in the stage of the Alapaha River are highly correlated ($r = 0.87$) with water levels in the Upper Floridan aquifer (Figure 4). Ground water levels in nearby Alapaha Fire Tower well increased significantly ($\alpha = 0.001$) with increasing stage in the Alapaha River during 1989-94.

Further evidence for the connection between ground water and surface water is indicated by water sampled from the Alapaha Fire Tower well, which represents a mixture of river water and ground water. The relative proportions of ground water and surface water in the mixture can be evaluated qualitatively based on changes in specific conductance of water samples from the well (Figure 4). During high flow conditions, surface water enters the aquifer, and the conductance of water in the aquifer decreases. This is due to the mixing of river water having lower median specific conductance (39 µS/cm, Hull *et al.*, 1981), with aquifer water having a higher median specific conductance (310 µS/cm, Maddox *et al.*, 1992). A negative correlation between water levels and specific conductance was found; however, the relation is not statistically significant. There was a significant ($\alpha = 0.007$) positive correlation ($r = 0.41$) between pH and water levels in the aquifer. Based on differences in the median pH of river water, 5.6 (Hull *et al.*, 1981) and that of the aquifer, 7.1 (Maddox *et al.*, 1992), one might expect that pH would be a useful indicator of mixing of ground water and surface water. However, the relation between water levels and the pH of water from the Alapaha Tower well is not as straightforward as the relation between specific conductance and water levels because the range in pH values for river water, 4.7 to 7.2 (Hull *et al.*, 1981) overlaps the range of pH values measured in water from the Upper Floridan aquifer in this area, 5.3 to 9.4 (Katz, 1992).

Hydrologic tracers, such as naturally occurring environmental isotopes including radon, (^{222}Rn, Ellins *et al.*, 1991; Kincaid, 1994); and oxygen (^{18}O/^{16}O), hydrogen (D/H), and carbon (^{13}C/^{12}C) (Katz *et al.*, 1995a, 1995b), can be used to quantify more precisely the mixing proportions of river water and water from the Upper Floridan aquifer for various flow conditions. Environmental isotopes and synthetic organic compounds have been used in a number of previous studies to establish and quantify the linkage between the river and aquifer where the interactions between ground water and surface water are much more complex. For example, naturally occurring radionuclides, such as uranium (^{238}U and ^{234}U), radium (^{226}Ra), and ^{222}Rn, were used to trace ground water influx to rivers and streamflow losses to ground water. These studies rely on the mobility of U, Ra, and Rn, which is controlled by different geochemical and physical processes leading to their separation or fractionation in ground water and surface water systems (Cowart and Burnett, 1994; Kraemer, in press). For example, ^{222}Rn is a gas and, hence, its concentration in ground water can be two to three orders of magnitude higher than the concentration in surface water.

In a study along a 2-km reach of the Santa Fe River (a tributary to the Suwannee River), measurements of ^{222}Rn and SF_6 (sulfur hexafluoride, a volatile synthetic gas that was injected as a tracer and used to estimate and correct for radon loss) in ground water and in surface water revealed that increases in river discharge were accompanied by corresponding increases in ground water discharge to springs, loss of streamflow to ground water, and input to springs from resurgent streamflow (Kincaid, 1994). One particularly noteworthy finding was that even though the regional potentiometric-surface map of the Upper Floridan aquifer shows that the Santa Fe River is a gaining stream, streamflow is actually being lost to the Upper Floridan aquifer in many places along the river. Siphons that are visible at the surface also provide direct evidence that stream water is being diverted to the subsurface. As much as 55 percent of spring discharge at this study area was supplied by resurgent surface water that originated in the the overlying Santa Fe River, and not water from the Upper Floridan aquifer (Kincaid, 1994).

Differences in the ^{234}U/^{238}U activity ratio (UAR) and uranium (U) concentrations in ground water and surface water were used to determine the source and amount of recharge for different parts of the aquifer and ground water contributions to the Suwannee River (Crane, 1986). Most sampled sites produced waters with low activity ratios (less than 1.0) and high U concentrations (0.5 to 10 µg/L). These characteristics typically are associated with areas where the Upper Floridan aquifer is unconfined and where recent and intense dissolution of aquifer minerals is occurring, such as in places where material overlying the Upper Floridan aquifer has been breached by sinkholes. For example, three water samples from a Suwannee River tributary basin (including the springs near Branford, Florida, and wells upgradient of the springs), had very low activity ratios (0.57) and high U concentrations (1.76 µg/L). Many springs had activity ratios greater than 0.75, which Crane attributed to a mixture of ground water from areas of high recharge with ground water from areas of little or no recharge. The Suwannee River has UAR values

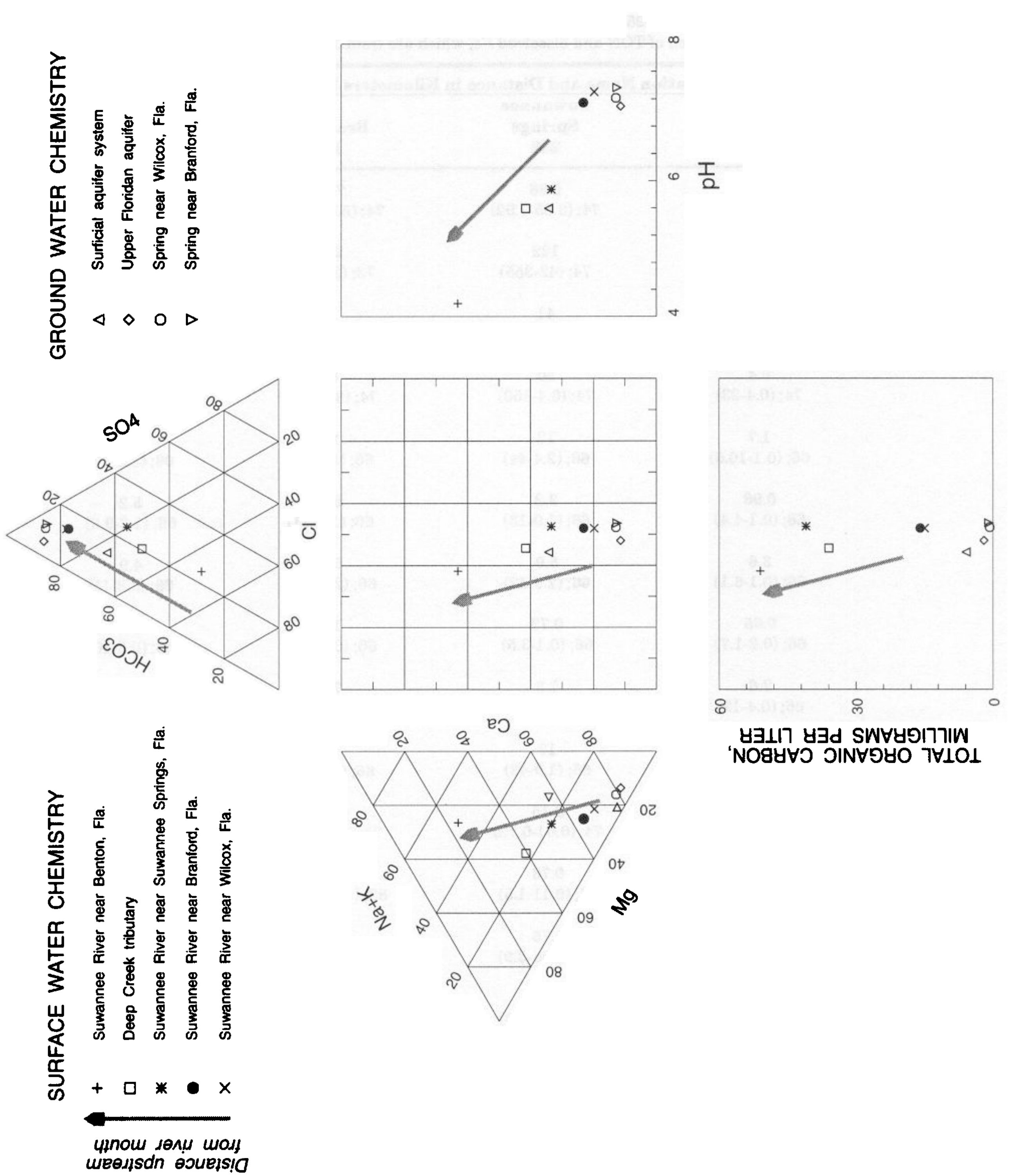

Figure 3. Durov Plot Showing Differences in the Major-Ion Composition, pH, and Total Organic Carbon Concentrations of River Water and Ground Water.

collected and compiled for the FGWQMNP (Katz, 1992; Maddox *et al.*, 1992). Methods of collection and analysis of water samples from the Suwannee River are described by Hull *et al.* (1981) and Environmental Services and Permitting, Inc. (1995).

Maps of the potentiometric surface of the Upper Floridan aquifer were constructed using water-level data for 226 wells that were measured during high-flow conditions in April and May 1984 and using water-level data for 325 wells measured during low-flow conditions in December 1990 and January 1991. The potentiometric contours that were constructed from water-level data were generalized to represent synoptically the altitude to which water would rise in tightly cased wells. No attempts were made to account for differing depths of wells, nonsimultaneous measurements of water levels, variable effects of pumping, and changing climatic influence.

Descriptive and nonparametric statistics were used to summarize the concentrations of selected chemical constituents. Boxplots were used to present the median, the 10th, 25th, 75th, and 90th percentiles, and probable outliers of nitrate concentrations in ground water from an agricultural study area in Lafayette County. Nonparametric statistical techniques were used for analysis of water-quality data, because these data generally were not normally distributed, and these techniques do not require equal variances. Hypothesis tests were used to determine if observed differences in concentrations or water levels are due to random variability or statistically significant populations. Spearman's Rho statistic was used to determine the degree of correlation between Alapaha River stage and water levels in a nearby well and the degree of correlation of pH and specific conductance with ground water levels. This nonparametric statistic measures the strength of an increasing or decreasing relation between two variables (Iman and Conover, 1983). All observations were given equal weight so that any extreme values will not have a disproportionate effect on the correlation. A positive or negative relation between two variables was considered significant at an alpha (α) value, or level of significance, of 0.05 or less.

RESULTS AND DISCUSSION

Water-Quality and Water-Level Evidence for Ground Water/Surface Water Interactions in the Basin

The water quality of the Suwannee River at any given location is affected by discharge of water from swamps and wetlands, the surficial aquifer system and the Upper Floridan aquifer, point sources, and nonpoint sources. During periods of low flow, much of the water in the Suwannee River in the upper part of the basin originates from tributary streams and discharge of water from the surficial aquifer system. In the lower Suwannee River subbasin, river flow originates from springs. Springs that normally discharge into the Suwannee River and its tributaries may temporarily become sinks when high-flow conditions cause flow to reverse (Giese and Franklin, 1996). Flood peaks of some streams in the Suwannee River basin were significantly attenuated as a result of substantial subsurface storage provided by the karstic nature of the Upper Floridan aquifer (Giese and Franklin, 1996).

The relative influence on water quality from various sources that contribute water to the Suwannee River are indicated by downstream changes in river water chemistry. Based on an analysis of water-quality data collected during 1968-1977 (Hull *et al.*, 1981) and 1989-1995 (Hornsby and Mattson, 1996), pH, specific conductance, and concentrations of calcium (Ca), magnesium (Mg), bicarbonate (HCO_3), and sulfate (SO_4) clearly show an increase with distance downstream (Table 2). For example, the mean pH increased from 4.20 at Benton, Florida, to 5.88 at Suwannee Springs, Florida, and to 7.31 at Wilcox, Florida (Hornsby and Mattson, 1981). Accompanying these increases, the concentrations of sodium (Na), potassium (K), and nitrate (NO_3) increased slightly, while the concentrations of total organic carbon (TOC), total organic nitrogen, and dissolved iron decreased in a downstream direction (Table 2). Trends in water chemistry are consistent with the relative contribution of water from surface water and ground water sources.

The effect of increasing ground-water discharge in a downstream direction on the chemistry of water in the Suwannee River in a downstream direction is shown in a Durov diagram (Figure 3). This diagram is similar to a quadrilinear Piper diagram with the exception that the intersection points from the two Piper triangles (showing the relative contribution of a particular cation or anion to the sum of cations or anions, in milliequivalents per liter) are plotted against two additional variables (pH and TOC, in this case) in adjacent scaled rectangles. For instance, near the headwaters of the river (near Benton, Florida), there is no dominant cation or anion in river water, which results in a mixed water type. The low pH, low dissolved solids (Table 2), and relatively high concentrations of TOC (Figure 3) in the river water near Benton, Florida, indicate the relatively large contribution of water from tributary streams and runoff originating in swamps and wetlands. Further downstream, the contribution from ground water increases, highest stages for the Suwannee River and its tributaries.

Hydrogeologic Framework of the Suwannee River Basin

The major hydrogeologic units in the Suwannee River basin include the surficial aquifer system, the intermediate confining unit, and the Upper Floridan aquifer (Table 1). The surficial aquifer system, which consists of undifferentiated sands and clays that are post Miocene in age, ranges in thickness from 3 to 10 m but may reach 15 to 18 m in the easternmost portion of the basin (Scott, 1991). The intermediate confining unit is composed of siliclastic sediments of Miocene age and is present only under the Northern Highlands in the northeastern part of the Suwannee River basin in Florida. The thickness of the intermediate confining unit in this geographic region may exceed 100 m (Scott, 1988). The Upper Floridan aquifer, the uppermost part of the Floridan aquifer system, consists of limestone and dolomite of Eocene age. The Upper Floridan aquifer is the primary source for industrial, agricultural, and municipal use in the Suwannee River basin in Florida. The base of potable water in the Upper Floridan aquifer ranges from approximately 300 m below land surface in the southern part of the study area to more than 380 m below land surface in the northern part of the study area (Ceryak *et al.*, 1983). Solution features (sinkholes, solution conduits, springs) characteristic of karst areas provide the opportunity for direct hydraulic and geochemical interactions between surface water and ground water in the Suwannee River basin.

The hydrogeology within the Suwannee River basin is directly related to the physiography. The northern part of the basin is located in the Northern Highlands, an area characterized by land surface altitudes greater than 30 m, reaching elevations up to 70 m. Surface water features are common in the Northern Highlands because clayey sediments of the intermediate confining unit underlie the surficial aquifer system and retard the infiltration of rainwater. The water levels of surface water features reflect the water table in the surficial aquifer system. The southern part of the Suwannee River basin lies in the Gulf Coastal Lowlands physiographic division, which is characterized by land altitudes that are less than 30 m and the presence of carbonate rock at or near land surface. The Highlands and Lowlands are separated by a topographic break referred to as the Cody Scarp (Puri and Vernon, 1964). With the exception of the Suwannee River, every river or stream that originates in the Northern Highlands disappears underground as it crosses this transition zone. The Suwannee River remains above ground in the Gulf Coastal Lowlands because it has incised the limestone of the Upper Floridan aquifer. The base flow for the Suwannee and Santa Fe rivers (Figure 2) is supplied by artesian spring flow.

Hydrology of the Suwannee River

The Suwannee River originates in the Okefenokee Swamp area of south Georgia and flows southward for approximately 390 km to the Gulf of Mexico. Near the river's headwaters, the channel is incised in sandy clays and clayey sands that overlie the carbonate rock

TABLE 1. Generalized Stratigraphic Column for Suwannee River Basin (modified from Scott, 1991).

System	Series	Formation	Hydrostratigraphic Unit	
Quaternary	Pleistocene and Holocene	Undifferentiated Siliclastic Sediments	Surficial Aquifer System	
Tertiary	Pliocene	Cypresshead Formation		
	Miocene	Hawthorn Group	Intermediate Confining Unit	
	Oligocene	Suwannee Limestone	Floridan Aquifer System	Upper Floridan Aquifer
	Eocene	Ocala Limestone Avon Park Formation Oldsmar Formation		

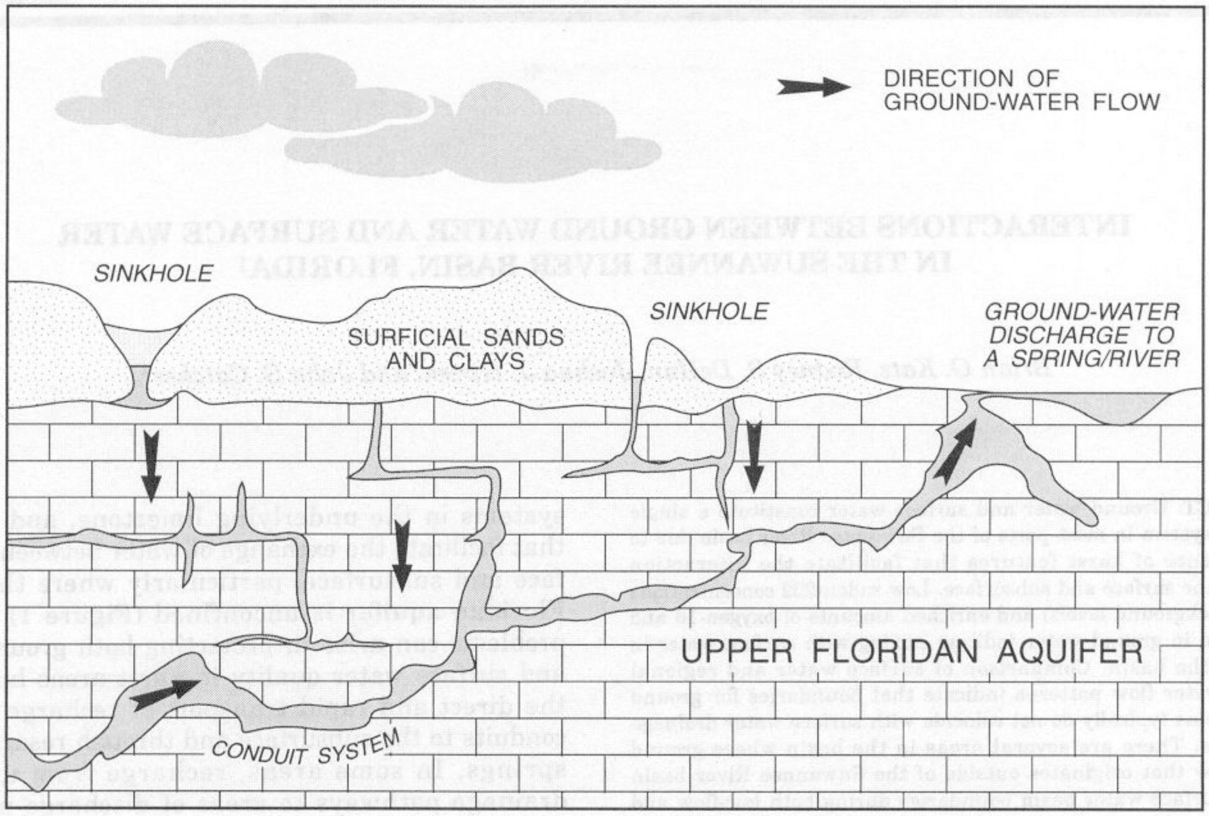

Figure 1. Generalized Hydrogeologic Section in the Suwannee River Basin Showing Karst Features That Facilitate the Exchange of Water Between the Surface and Subsurface.

The Suwannee River basin in Florida was one of several watersheds nationwide selected for a pilot study by the Intergovernmental Task Force on Monitoring Water Quality (ITFM). The study was designed to evaluate the effectiveness of current monitoring programs, coordinated among Federal, State, and local agencies, in addressing key issues related to monitoring water resources. Information gaps were found to exist in State and Federal monitoring programs and it was recommended by the ITFM that these gaps be addressed by developing an integrated, voluntary, nationwide strategy for water-quality monitoring (ITFM, 1995). The watershed approach has been recommended as a highly effective way to manage water resources because this approach integrates ground water and surface water systems (ITFM, 1995). Several other independent studies by national and international groups have recognized the need for integrated monitoring of the various hydrologic components of a watershed for evaluating ecosystem health (United Nations Economic Commission for Europe, 1993; Interagency Ecosystem Management Task Force, 1995; Council of State Governments, 1995).

This paper evaluates hydrologic and water-quality data for the Suwannee River basin in Florida to better understand the interactions between ground water and surface water within the context of watershed management concerns. Three critical watershed management issues are addressed in the paper: (1) the degree of hydrochemical interaction between ground water and surface water in the basin, (2) the coincidence of ground water subbasins and surface water subbasins under different hydrologic conditions, and (3) the ability of natural processes to reduce elevated concentrations of nitrate in the Upper Floridan aquifer. The approaches presented in this paper provide a framework for evaluating the importance of the interactions between ground water and surface water in a watershed context that can be extrapolated to other watersheds within Florida and nationwide where ground water and surface water systems are intimately linked.