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Hydrochemical Evidence for Mixing of River Water and Groundwater During High-Flow Conditions, Lower Suwannee River Basin, Florida, USA

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Abstract

Karstic aquifers are highly susceptible to rapid infiltration of river water, particularly during periods of high flow. Following a period of sustained rainfall in the Suwannee River basin, Florida, USA, the stage of the Suwannee River rose from 3.0–5.88 meters above mean sea level in April 1996 and discharge peaked at 360 cubic meters per second. During these high-flow conditions, water from the Suwannee River migrated directly into the karstic Upper Floridan aquifer, the main source of water supply for the area. Changes in the chemical composition of groundwater were quantified using naturally occurring geochemical tracers and mass-balance modeling techniques. Mixing of river water with groundwater was indicated by a decrease in the concentrations of calcium, silica, ^{222}Rn; and by an increase of dissolved organic carbon (DOC), tannic acid, and chloride, compared to low-flow conditions in water from a nearby monitoring well, Wingate Sink, and Little River Springs. The proportion of river water that mixed with groundwater ranged from 0.13–0.65 at Wingate Sink and 0.5–0.99 at well W-17258, based on binary mixing models using various tracers. The effectiveness of a natural tracer in quantifying mixing of river water and groundwater was related to differences in tracer concentration of the two end members and how conservatively the tracer reacted in the mixed water. Solutes with similar concentrations in the two end-member waters (Na, Mg, K, Cl, So_4, SiO_2) were not as effective tracers for quantifying mixing of river water and groundwater as those with larger differences in end-member concentrations (Ca, tannic acid, DOC, ^{222}Rn, HCO_3).

Introduction

Understanding the extent and magnitude of river/aquifer interactions is essential in addressing issues of water quality and supply and in ensuring the health of ecosystems (Winter et al., 1998). Karstic aquifers are more susceptible to the rapid introduction of contaminants from surface waters through sinkholes, conduits, and other solution features than other types of aquifers (White, 1993). Groundwater-flow patterns in karst regions are difficult to characterize because of heterogeneities in the aquifer matrix that result from spatially varying amounts of conduit and diffuse flow. In areas where an aquifer is hydraulically connected to a stream, both groundwater and surface-water systems are especially susceptible to contamination. For example, groundwater can discharge contaminants to a stream, resulting in degradation of surface-water quality (Hornsby and Mattson, 1996). Conversely, sinking streams in karst areas can be a major source of contamination to an aquifer (McConnell and Hacke, 1993; Plummer et al., 1998).

The Suwannee River and the Upper Floridan aquifer in Georgia and Florida, USA, have typically been studied as separate resources, even though they are hydraulically connected. In the Suwannee River basin, only a few studies have described interactions between groundwater and surface water, and these interactions have been shown to impact both systems (Ceryak, 1977; Crane, 1986; Katz et al., 1997). During low-flow conditions, groundwater contributes a major part of the nitrate load along the middle reach of the Suwannee River (Pittman et al., 1997; Hornsby and Mattson, 1996). During high-flow conditions, river water can flow into the aquifer and affect the chemical composition of groundwater (Crane, 1986; Hirten, 1996).

This paper presents the results of a study designed to characterize the extent and mechanisms of hydrochemical interactions between the Suwannee River and the Upper Floridan aquifer near Little River Springs, Florida, during high-flow conditions. This area was chosen for study because water from the Suwannee River reportedly backflows into Little River Springs during high flow and tea-colored (presumably river water) water has been reported in wells and sinkholes as great as 5 km from Little River Springs (W. Skiles Karst Environmental Services, Inc., personal communication, 1995). Changes in groundwater chemistry are compared for low- and high-flow conditions and the interactions between river water and the Upper Floridan aquifer are evaluated using chemical tracers (majors ions, tannic acid, dissolved organic carbon (DOC), silica, and radon (^{222}Rn). Geochemical mass-balance models were used to estimate mixing ratios of river and groundwater. Results of this study provide a greater understanding of river/aquifer interactions in karst systems.

Study Area

The Little River Springs study area is located in southwestern Suwannee County, Florida, in the Gulf Coastal Lowlands physiographic subdivision encompassing approximately 50 km^2 of karst terrain in the lower Suwannee River basin; locations are shown in *Figure 1*. The lower Suwannee River basin has been defined as that part of the basin below the confluence of the Withlacoochee River *(Figure 1)* (Crane, 1986). The area consists of gently sloping plains that extend toward the coast ranging in elevation from about 3–18.5 m (above mean sea level). The study area is covered by a thin veneer of sand 3–12 m thick underlain by limestone. Mature karst features are evident; for example, numerous sinkholes and closed basin depressions exist, and springs commonly discharge to the river *(Figure 1)*. Surface drainage is virtually nonexistent in the karst plain due to the permeable sands at land surface and the highly transmissive karst limestone below (Crane, 1986). The climate is characterized by long, warm summers and short, mild winters. For 1961–90, average annual temperature was 20.3^{o}C and average rainfall was 140 cm at Branford, Florida (Owenby and Ezell, 1992). Rainfall has a bimodal distribution that

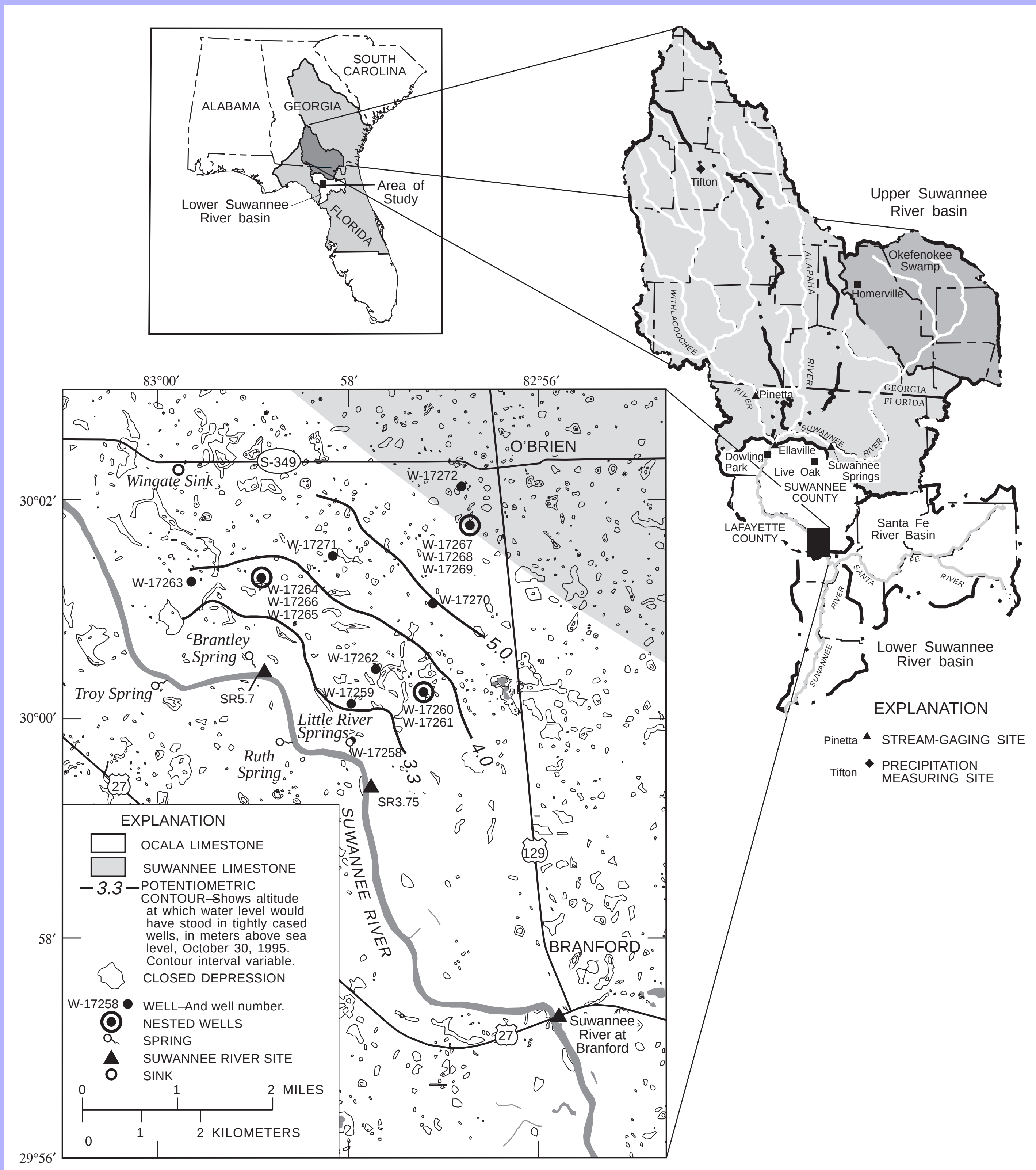

Figure 1. Study area, showing sampling sites for groundwater, river water, and spring water.

typically peaks in March due to frontal storm systems, and in September due to subtropical depressions and convective storms (Owenby and Ezell, 1992). Evapotranspiration ranges from approximately 77–99 cm/yr (Berndt et al., 1996).

The Ocala Limestone (late Eocene age) and the Suwannee Limestone (Oligocene age), outcrop at or near the surface in the study area and are marked by numerous karst features *(Figure 1)* (Burnson, 1982; Crane, 1986). The Avon Park and Oldsmar Formations of middle and early Eocene age, respectively, underlie the Suwannee and Ocala Limestones (Miller, 1986). These formations contain numerous fractures and lineaments that provide preferential flow paths where solution channels often form (Beatty, 1977; Crane, 1986). Collectively, these formations make up the Upper Floridan aquifer. The Ocala Limestone is one of the most permeable units of the Floridan aquifer system, due to the presence of large solution channels, and these channels carry most of the flow (Crane, 1986; Miller, 1986). The Ocala Limestone is composed of a white, fossiliferous, marine limestone that ranges from 30–60 m in thickness.

The Upper Floridan aquifer is composed of these permeable carbonate units interspersed with units of lower permeability and is approximately 400 m thick in the study area. The Floridan aquifer system consists only of the Upper Floridan aquifer in the study area, because the middle confining unit of the aquifer is absent (Miller, 1986). Transmissivity of the aquifer ranges from 23,000–100,000 m^2/d (Miller, 1986; Bush and Johnson, 1988). Annual recharge to the aquifer can exceed 35 cm in the study area, where infiltration is rapid due to the thin mantle of sand covering karst limestone (Crane, 1986; Grubbs, 1998). The Upper Floridan aquifer is the primary source of irrigation and drinking water for north-central Florida (Marella and Fanning, 1996).

The Upper Floridan aquifer is unconfined and in direct hydraulic contact with the Suwannee River in southwestern Suwannee County. Water is exchanged between the river and aquifer primarily through springs and diffuse flow (Pittman et al., 1997). During low-flow periods, usually in the summer and fall, water from the aquifer discharges to the river and sustains base flow (Crane, 1986; Pittman et al., 1997). The potentiometric surface of the Upper Floridan aquifer has a gradient of 0.5–1.5 m/km toward the river during periods of low river stage *(Figure 1)*. During periods of heavy rainfall, typically in March and April, river stage rises abruptly and exceeds groundwater levels; then, river water flows directly into the aquifer through conduits, small cavities, and fractures (Hull et al., 1981; Hirten, 1996; Katz et al., 1997). However, the extent of mixing in the aquifer and spring conduit systems is not known.

Two large karst features are present in the study area, Little River Springs and Wingate Sink. The vent for Little River Springs is connected to the river by a run that is approximately 100 m long. The spring conduit system, mapped by cave divers, ranges in depth from 24–37 m below land surface and extends along two main conduits into the aquifer (Skiles, 1976). The larger conduit leads approximately 1.6 km northeast from the spring vent away from the river. The smaller conduit leads southeast along the northeastern side of the river (Skiles, 1976). Average discharge of Little River Springs into the river ranges from 1.9–2.4 m^3/s during low flow (Pittman et al., 1997; Rosenau et al., 1977). During high-flow conditions on the river, river water flows into the spring vent.

Wingate Sink, in the northwestern part of the study area *(Figure 1)*, is a vertical shaft that extends approximately 49 m before opening up into a large room approximately 90 m long (W. Skiles, Karst Environmental Services, Inc., personal communication, 1998). The general flow direction in Wingate Sink trends northeast to southwest during low-flow periods, following regional groundwater flow. Wingate Sink reportedly becomes tannic during high-flow periods (W. Wingate, personal communication, 1998; W. Skiles, Karst Environmental Services, Inc., personal communication, 1994).

The Suwannee River, designated an “outstanding Florida water” because of its recreational and scenic value to the State (Fernald and Patton, 1984), originates in the western side of the Okefenokee Swamp in Georgia. The average annual discharge of the Suwannee River at Branford is 197 m^3/s (Meadows et al., 1991). Peak mean daily discharge in the Suwannee River usually occurs in March or April, due to precipitation from continental frontal systems (Crane, 1986). A secondary peak may occur in the fall (usually September) from tropical or subtropical depressions. During 1931–93, the average mean daily discharge of the Suwannee River at Branford was 338 m^3/s for April, compared to 175 m^3/s for September (Franklin et al., 1995).

Methods

Fifteen monitoring wells, ranging in depth from 10.2–22.0 m, were installed in the Upper Floridan aquifer from May through August 1995 using standard protocols (Lapham et al., 1995). Wells were constructed of threaded 10-cm diameter PVC casing with 1.5 m open intervals. At three sites *(Figure 1)*, nested wells were installed, and the depth of the top of the open interval ranges from 1.5–3.0 m. Wells were drilled approximately 2 m below the bottom of the casing. The annular space of the well was sealed with bentonite and cemented above the bentonite to the surface. At least one cavity or “soft rock zone” of 0.2 m or more was noted in 7 of the 15 wells (K. Campbell, Florida Geological Survey, written communication, 1996). Numerous subterranean karst features were identified in this area using ground-penetrating radar (Collins et al., 1994). Surface-water sampling sites were established on the Suwannee River at stations SR5.7 and SR3.75, above and below Little River Springs, respectively *(Figure 1)*. Sampling sites were also established at Little River Springs and Wingate Sink *(Figure 1)*.

Water levels in the wells were measured monthly during low flow (July through early March 1996), and weekly during the high flow (late March through April 1996). For this discussion, July 1995 through early March 1996 is referred to as the low-flow period, and April 1996 as the high-flow period. Water levels were also measured at Wingate Sink from February through April 1996 and at Little River Springs during high flow (April 1996). Discharge for the Suwannee River was computed from stage data recorded at Branford, Florida.

Water samples were collected quarterly from monitoring wells and Wingate Sink during July 1995 through January 1996. Water samples were also collected from Little River Springs and the Suwannee River (SR3.75 and SR5.7) in October 1995 and April 1996. A subset of sites was sampled during high flow: Wingate Sink, W-17258, W-17259, W-17260, W-17263, and W-17269. Water from wells that did not have elevated tannic-acid concentrations were not sampled for other chemical constituents during high flow. Groundwater samples were collected using a submersible pump constructed of stainless steel and Teflon. Prior to collection of water samples, at least three casing volumes were purged from the well (Koterba et al., 1995). The pump head was positioned approximately 0.5 m below the top of the open interval. During and after purging the well, specific conductance, pH, dissolved oxygen, and temperature were monitored in a closed flow-through chamber. When those properties stabilized, samples of groundwater were collected. River samples were collected using the equal-width-increment method collected into 3-L Teflon bottles (Shelton, 1994).

Water samples were collected and analyzed for major ions, nutrients, and DOC using standard protocols (Koterba et al., 1995). Samples for analysis of ^{222}Rn were collected using a glass syringe with a stainless steel needle, which was inserted into a small chamber with a Teflon membrane where backflow pressure could be created to eliminate air bubbles in the sample. A 10-mL water sample was withdrawn and injected into a scintillation cocktail. Tannins and lignins (reported as tannic acid) were measured colorimetrically in the field using a portable spectrophotometer, with a detection limit of 0.1 mg/L and an error of ± 0.08 mg/L (Hach Company, Inc., 1992). Data from quality-assurance samples (15% of total) indicate that no contamination resulted from sampling procedures and equipment and that good analytical reproducibility occurred in the laboratory.

Geochemical data were analyzed using statistical and graphical methods, and geochemical modeling techniques. Saturation indices of waters with respect to selected minerals were computed using WATEQFP (Plummer et al., 1994). Models that described mixing of river water and groundwater were derived using mass balance equations in NETPATH (Plummer et al., 1994).

Results and Discussion

Changes in River Stage and Discharge

Stage and discharge of the Suwannee River at Branford were relatively low from July 1995 through December 1995, compared to long-term values (1932–94) (Giese and Franklin, 1996b). Both river stage and water levels in the aquifer declined approximately 3–6 mm/d during July through mid-December 1995 in response to below-normal rainfall in July through September, compared to average monthly rainfall at Mayo (in Florida) and Quitman, Tifton, and Homerville (in Georgia) during 1961–90 (Owenby and Ezell, 1992). The lowest instantaneous river discharge at Branford occurred on December 19, 1995, and was 54.1 m^3/s (stage of 2.49 m) (Franklin and Meadows, 1996). A flow of this low magnitude is likely to occur every 20–50 years (Giese and Franklin, 1996b). Hydrographs are shown in *Figures 2* and *3*.

River stage gradually began to rise (approximately 6 mm/d) in late December and continued through mid-March 1996, when stage began to rise at a rate of more than 9 mm/d in response to above-normal rainfall throughout the basin *(Figures 2* and *3)*. From about the end of February or early March until April 12, discharge at Branford was less than that at Ellaville, indicating that the river was losing water to groundwater *(Figure 3)*.

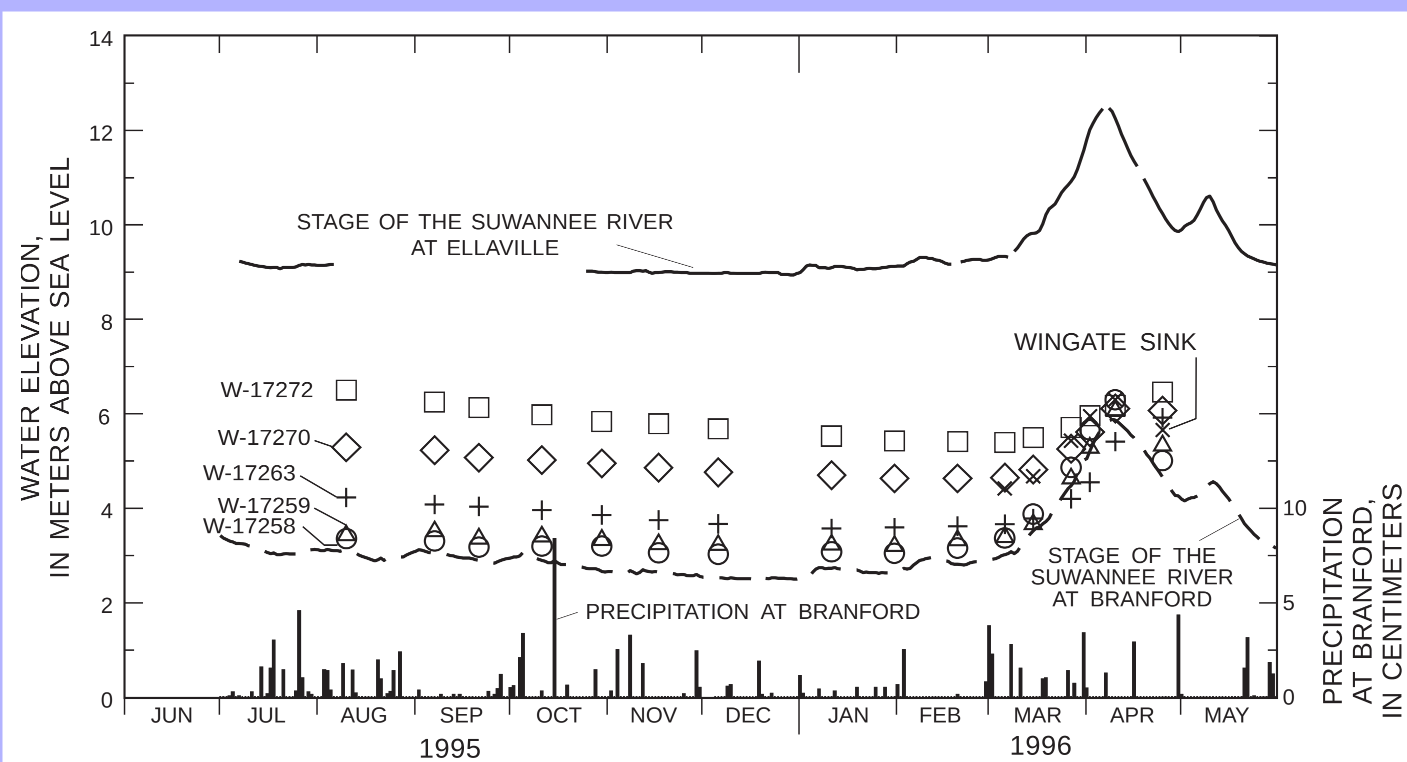

Figure 2. Stage of the Suwannee River at Ellaville and Brandford, Florida, daily rainfall, and water levels in selected wells during June 1995 through May 1966.

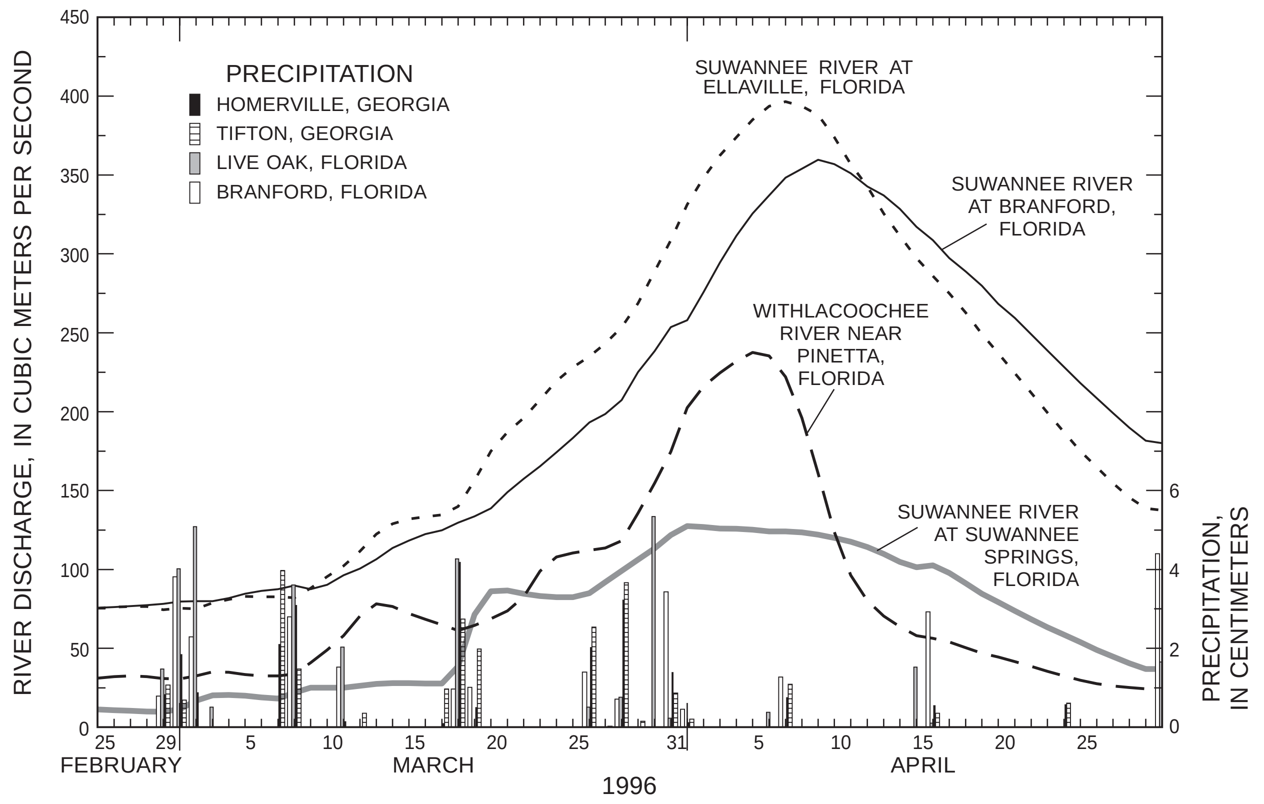

Figure 3. Suwannee River discharge at four locations in Florida, and daily rainfall measured at selected sites in the Suwannee River basin.

Discharge peaked in the upper basins between April 1–5 and peaked at Ellaville on April 7. Stage of the Suwannee River at Branford (the farthest downstream gaging station) peaked at 5.88 m on April 9 *(Figure 2)*. The peak in discharge was largely the result of March precipitation which averaged 5–13 cm above normal for the month over the entire Suwannee River basin (Owenby and Ezell, 1992) *(Figure 2)*. The corresponding instantaneous peak flow of 360 m^3/s was less than 20% of the maximum recorded instantaneous peak flow (Franklin and Meadows, 1996). A peak of this magnitude is likely to occur every 2 years or less on average (Giese and Franklin, 1996a). After April 12, discharge at Branford was equal to or it exceeded the discharge at Ellaville, indicating that the river discharge was receiving a considerable contribution from groundwater.

Changes in Groundwater Levels

Groundwater levels decreased continuously from July through December 1996. Minimum groundwater levels in wells 2 km or less from the river and Wingate Sink occurred between January 11 and February 20, about 1–2 months after minimum values of river stage *(Figure 2)*. The lowest groundwater elevation (3.05 m) was measured in well W-17258 on January 11. Groundwater levels in wells 3–4 km from the river did not reach their minimum elevations until early March. However, groundwater levels in most wells started to rise in mid to late February, when rainfall amounts increased and covered larger parts of the basin *(Figure 3)*.

On April 9, 1996, when river stage peaked at 6.31 m at Little River Springs and tannic-colored river water was observed flowing into Little River Springs, water levels at Wingate Sink and wells within 2.0 km of the river peaked almost synchronously with the river *(Figure 2)*. Groundwater levels in Wingate Sink and wells W-17258 and W-17260 were 6.30, 6.30, and 6.19m, respectively, on April 10, a rise of more than 3.2 m from low-flow values. Water levels in wells 3–5 km from the river were greater than 5.8 m during the high-flow period. For example, water levels in wells, W-17270 and W-17272 were and 6.11 and 6.18 m, respectively, on April 10 as shown in *Figure 4A*. A transient low or saddle was formed in the potentiometric surface approximately 1.6 km northeast of the river on April 9–10, as shown in *Figure 4B*. Groundwater levels in this area ranged from 5.41 m at W-17263 to 5.59 m in W-17262. Water levels in wells 3–5 km from the river continued to rise through April 25, when the last measurement was taken *(Figure 2)*.

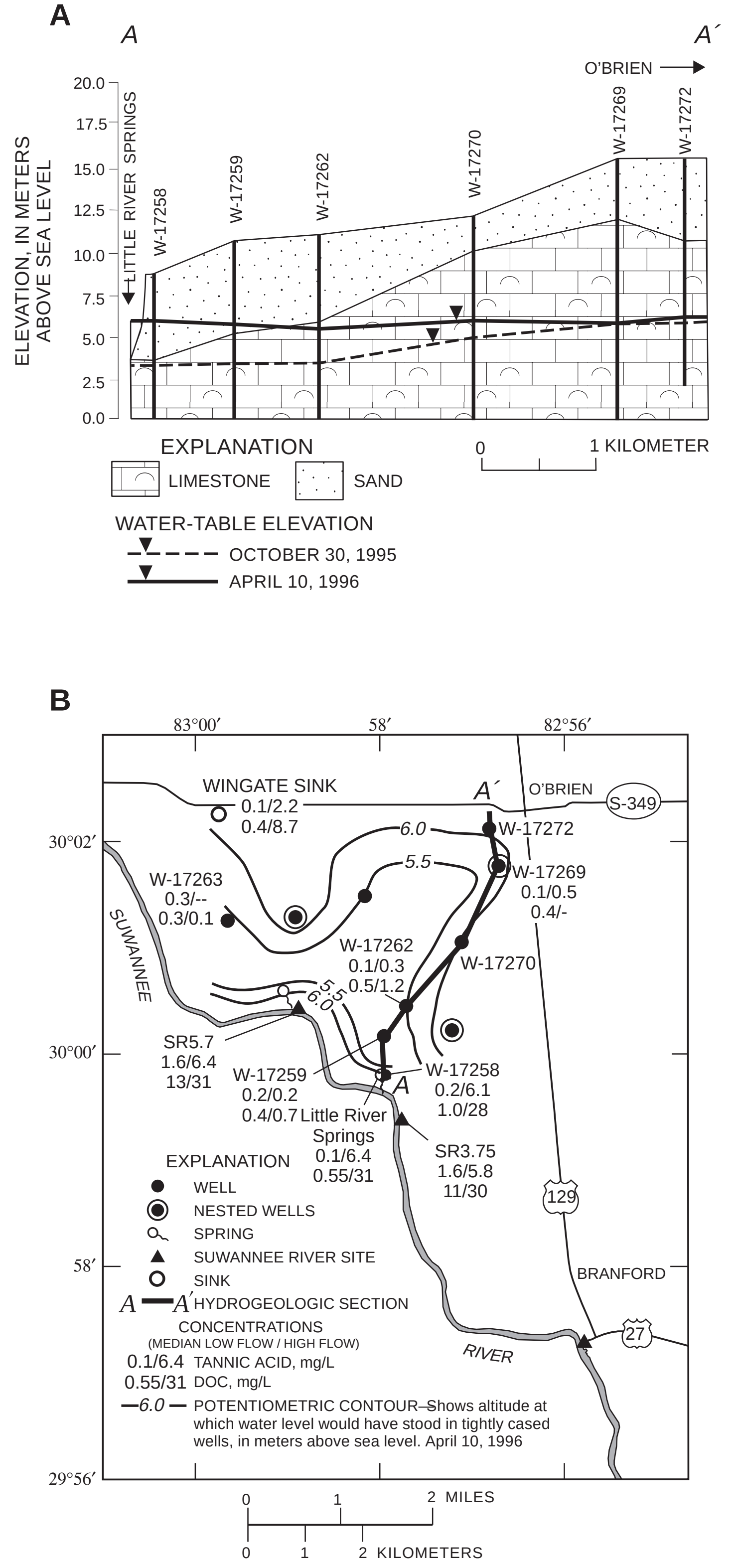

Figure 4.

(A) Hydrogeologic section A–A′ showing elevations of water levels during October 1995 and April 1996.

(B) Distribution of potentiometric head in the Upper Floridan aquifer during high-flow conditions, and concentrations of tannic acid and dissolved organic carbon in water samples from wells, Suwannee River and Little River Springs, Florida.

Water levels measured in nested wells W-17267 through W-17269 and W-17264 through W-17266 indicate that a relatively strong upward vertical gradient of 1–2 cm/m existed in the aquifer between March 27 and April 10. During the low-flow period, upward vertical gradients were usually less than 0.5 cm/m in the aquifer. The relatively strong upward movement of water in the aquifer probably occurred in response to a pressure increase in the aquifer during high flow from river inflow.

Chemistry of Groundwater and River Water During Low-Flow Conditions

Groundwater and river water were of calcium-bicarbonate type during the low-flow period, but the concentrations of major ions varied considerably from well to well. Results of chemical analyses are shown in *Tables 1* and *2* and are plotted in *Figure 5*. Water in the Upper Floridan aquifer evolves under open-CO_2 conditions (Katz, 1992). Rapid recharge rates in the study area, which result from percolation through highly permeable sands, facilitate the downward transport of oxygen and dissolved DOC from the unsaturated zone. The chemical character of water from the Upper Floridan aquifer can be quite variable because of short groundwater residence times, high recharge rates, and varying amounts of direct recharge to the aquifer through sinkholes and other solution features (Sprinkle, 1989; Katz, 1992).

Table 1. Median and range of pH and concentrations of selected constituents in samples of groundwater and water from the Suwannee River, Florida, collected in October 1995 and April 1996

[Units in milligrams per liter unless otherwise noted; low-flow river water includes samples from the Suwannee River at Branford, N, number of samples; DS, dissolved solids; DOC, dissolved organic carbon; pCi/L, picocuries per liter]

Constituent	Groundwater		Suwannee River	
	Low Flow (N=49)	High Flow (N=6)	Low Flow (N=5)	High Flow (N=2)
pH	7.38 (7.0-7.8)	7.5 (7.1-7.8)	7.5 (6.9-8.1)	6.2 (6.1 -6.6)
Ca	65.0 (21-98)	47 (11-99)	41 (35-43)	5.85 (5.8-5.9)
Mg	4.9 (0.35-17)	4.85 (1.8-11)	8.2 (7.5-8.6)	1.9 (1.9-1.9)
Na	3.0 (2.2-8.7)	4.25 (1.8-5.8)	7.2 (4.9-8.7)	4.6 (4.6-4.6)
K	2.2 (0.3-21)	2.2 (0.2-6.9)	0.8 (0.6-1.1)	1.65 (1.6-1.7)
HCO_3	237 (110-383)	191 (37-252)	137 (121-154)	12.4 (12.4-12.4)
Cl	4.1 (2.4-9.7)	5.1 (2.8-10)	6.0 (5.9-6.1)	7.55 (7.5-7.6)
SO_4	9.0 (1.4-31)	7.8 (3.6-30)	19 (17-23)	5.4 (5.4-5.4)
Fe, µg/L	<3.0 (<3.0-180)	76.5 (<3-480)	180 (120-230)	775 (770-780)
SiO_2	6.5 (5.2-10.0)	6.1 (5.2-6.6)	8.3 (7.9-8.9)	5.4 (5.4-5.4)
NO_3-N	0.62 (<0.05-9.9)	0.215 (<0.05-6.9)	0.75 (0.70-0.83)	0.23 (0.08-0.39) (N=4)
DS	218 (66-329)	175 (97-308)	183 (174-191)	87.5 (87-88)
DOC	0.4 (0.1-1.1)	1.2 (0.1-28)	12 (9.3-15)	30 (30-31)
Tannic acid	0.2 (<0.1-0.7) (N=43)	0.35 (0.1-6.1)	2.8 (0.4-2.8)	6.1 (5.8-6.4)
Radon, pCi/L	480 (190-1000) (N=15)	200 (37-350)	105 (100-110) (N=2)	32 (29-35)

Groundwater and river water are near saturation with respect to calcite during low flow (-0.56 to 0.51). Waters that are undersaturated (a negative SI value, *Figure 5*) with respect to calcite and dolomite are capable of dissolving these minerals and probably are indicative of recent recharge water (Katz et al., 1998). Water recharging the Upper

Table 2. Concentrations of major dissolved species and properties of water from the Suwannee River, Little River Springs, and wells, Florida, July 1995—April 1996

[LRSprgs, Little River Springs; SR3.75 and SR5.7 Suwannee River at stations 3.75 and 5.7 (about 3.75 and 5.7 miles upstream from Highway 27 bridge at Brandord, respectively). DO, dissolved oxygen; DOC, dissolved organic carbon; DS, dissolved solids. Concentrations are reported in milligrams per liter except for pH (pH units); Temp, (°C); Fe (µg/L); radon (pCi/L); and tannins and lignins (mg/L tannic acid)]

Site Name	Date	Temp	pH	DO	Ca	Mg	Na	K	Cl	SO_4	HCO_3	DOC	SiO_2	Fe	DS	NO_3 as N	^{222}Rn	Tannic acid
W-17259	24-Jul-95	23.4	7.40	4.0	60	14	3.8	2.2	4.1	25	383	0.4	6.4	<3	235	--	--	0.2
W-17258	25-Jul-95	21.2	6.99	2.8	95	3.1	3.2	0.3	7.1	16	280	1	8.4	21	284	--	--	0.2
W-17262	26-Jul-95	22.1	7.55	0.1	69	4.9	4.4	5.2	4.5	7.9	234	0.5	6.7	180	218	--	--	0.3
W-17260	26-Jul-95	21.5	7.23	2.9	77	8.4	2.5	0.7	4	10	327	0.2	7.5	<3	247	0.61	--	<0.1
W-17261	26-Jul-95	21.4	7.28	5.0	68	5.1	3	3.1	2.9	8.3	237	0.3	6.9	<3	209	0.78	--	0.2
W-17270	27-Jul-95	22.0	7.46	0.2	61	5.9	2.6	0.4	4.9	8.7	205	--	7.3	<3	188	--	--	--
LRSprgs	27-Jul-95	21.9	7.3	--	64	7.6	2.5	0.6	5.6	19	199	--	6.8	5	211	1.4	--	--
W-17267	27-Jul-95	22.5	7.27	0.2	74	6.1	3.8	3.4	3.8	11	258	--	6.8	150	237	--	--	--
W-17268	27-Jul-95	22.7	7.72	0.1	69	3.3	5.7	12	5.1	23	227	--	6.4	57	224	--	--	--
W-17269	27-Jul-95	22.8	7.03	6.6	97	3.6	4.6	3.6	9.5	31	237	--	6.5	<3	329	--	--	--
W-17264	28-Jul-95	21.7	7.28	1.4	66	7	2.3	0.4	4.1	7.4	241	0.3	6.8	<3	212	0.71	--	0.2
W-17265	28-Jul-95	21.7	6.97	7.8	82	1.9	2.3	0.6	3.7	2.6	288	0.3	7.7	<3	229	0.33	--	0.2
W-17263	31-Jul-95	21.6	7.92	10.6	40	12	2.2	0.6	--	--	173	0.3	5.3	3	--	0.08	--	0.4
W-17270	1-Aug-95	22.4	7.44	0.1	--	--	--	--	--	--	276	0.7	--	--	--	0.76	--	0.3
W-17267	1-Aug-95	22.7	7.24	0.1	--	--	--	--	--	--	258	0.5	--	--	--	<0.05	--	0.5
W-17268	1-Aug-95	22.8	--	--	--	--	--	--	--	--	--	0.7	--	--	--	0.14	--	0.7
W-17269	1-Aug-95	22.8	7.13	6.5	--	--	--	--	--	--	237	0.5	--	--	--	9.9	--	0.7
W-17272	4-Aug-95	23.4	7.17	6.2	75	3.5	2.5	2.2	3.5	7	312	0.9	6.5	<3	260	0.72	--	0.3
Wingate Sink	4-Aug-95	22.1	7.31	1.4	60	5.6	2.7	0.9	5.5	10	217	0.4	6.3	8	202	1.9	--	0.1
W-71271	10-Aug-95	23.3	7.37	--	60	15	2.5	0.9	4.8	11	263	0.5	5.8	3	233	0.91	--	--
W-17258	24-Oct-95	20.9	7.20	1.8	93	2.5	3	0.5	7	11	278	1.1	8	26	262	0.07	480	<0.1
W-17259	24-Oct-95	25.0	7.61	3.2	48	11	7	7.1	3.9	21	249	0.4	5.4	<3	192	0.33	190	<0.1
W-17262	25-Oct-95	21.0	8.20	0.4	47	4.1	8.7	16	4.4	7	195	0.5	5.9	87	183	<0.05	290	<0.1
W-17261	25-Oct-95	21.7	7.45	4.6	61	4.8	3.6	4.2	3	8.9	219	0.4	6.6	<3	201	0.77	1,000	<0.1
W-17260	25-Oct-95	21.6	7.32	3.7	72	6.1	2.3	0.4	3.5	7.8	268	0.4	7.2	6	236	0.89	560	<0.1
W-17270	26-Oct-95	21.4	7.50	0.6	59	5.8	2.5	0.5	4.3	7	202	0.4	6.9	6	196	0.64	480	<0.1
W-71271	26-Oct-95	22.1	7.38	4.4	57	15	4	1.4	4.8	10	249	0.3	5.7	<3	224	0.98	490	<0.1
W-17263	30-Oct-95	21.5	7.71	6.7	62	9.3	2.4	0.6	4.9	12	166	0.5	6.2	11	218	0.93	--	<0.1
W-17265	31-Oct-95	21.5	7.20	7.4	73	1.8	2.8	2.1	3.7	2.1	227	0.1	7.5	<3	211	0.24	240	--
W-17264	31-Oct-95	21.3	7.39	1.4	29	3.4	7.6	14	2.5	9.2	217	0.3	10	50	212	0.57	910	--
W-17269	1-Nov-95	22.3	7.17	5.8	97	3.6	3.9	2.9	8.8	29	249	0.4	6.2	<3	321	8.9	330	<0.1
W-17268	1-Nov-95	22.4	7.60	0.2	59	3.7	6.5	21	4.7	24	217	0.4	5.5	61	230	<0.05	690	<0.1
W-17267	1-Nov-95	22.4	7.42	0.3	68	5.6	2.8	3.7	3.6	9.2	244	0.4	6.6	140	226	<0.05	310	<0.1
Wingate Sink	2-Nov-95	22.0	7.55	1.4	65	5.7	2.7	2.5	5.0	10.0	190	0.3	6.7	<3	196	1.7	340	<0.1
LRSprgs	3-Nov-95	21.8	7.60	1.4	60	7.1	2.4	0.5	5.1	17.0	190	0.8	6.2	4.0	203	1.1	410	<0.1
SR5.7	3-Nov-95	22.5	7.79	6.1	41	8.6	7.2	0.7	5.9	19.0	154	9.7	8.3	130	183	0.77	100	0.4
SR3.75	3-Nov-95	22.5	7.79	6.2	42	8.6	7.2	0.8	6.0	19.0	137	9.3	8.3	120	188	0.75	110	0.4
W-17272	7-Nov-95	22.6	7.20	5.5	72	3.2	2.3	2.3	3.1	5.2	224	0.8	6.3	<3	220	0.78	460	<0.1
W-17258	29-Jan-96	21.3	7.29	4.0	84	3.2	2.9	0.5	5.2	10.0	249	1.0	7.9	<3	250	0.18	--	0.3
W-17259	30-Jan-96	23.1	7.59	3.1	45	10	6.9	8.1	4.0	20.0	190	0.3	5.4	<3	190	0.40	--	--
W-17262	30-Jan-96	21.4	7.57	1.1	53	4.4	7.1	12	4.1	5.8	219	0.5	6.0	130	192	<0.05	--	0.3
W-17270	30-Jan-96	21.7	7.42	0.6	58	6.0	2.5	0.3	4.2	6.5	205	0.3	7.1	<3	189	0.62	--	<0.1
W-17260	31-Jan-96	21.3	7.27	3.2	78	8.8	2.4	0.3	3.9	8.4	261	0.3	7.4	<3	249	0.78	--	0.4
W-17261	31-Jan-96	21.7	7.71	5.3	61	4.7	3.8	4.9	2.7	8.5	205	0.2	6.5	<3	201	0.75	--	--
W-17272	31-Jan-96	23.3	7.26	5.1	68	3.2	3.9	5.3	3.1	6.5	234	0.4	6.5	4.0	209	0.81	--	<0.1
W-17267	1-Feb-96	21.1	7.30	0.8	69	6.0	2.6	1.8	3.4	7.4	239	0.2	6.3	150	225	<0.05	--	0.5
W-17268	1-Feb-96	21.3	7.39	0.5	68	3.7	5.0	9.6	4.2	22	363	0.3	5.4	100	235	<0.05	--	0.2
W-17269	1-Feb-96	21.9	7.04	5.2	98	3.6	4.9	2.6	9.7	26	244	0.3	6.5	<3	314	5.4	--	<0.1
W-71271	1-Feb-96	21.7	7.21	4.5	56	17	3.5	0.6	4.6	9.3	244	0.2	5.7	4.0	219	1.0	--	<0.1
W-17264	2-Feb-96	21.4	7.39	0.8	61	7.8	2.3	0.4	4.0	8.3	212	0.2	6.4	<3	207	0.67	--	0.2
W-17265	2-Feb-96	21.1	7.35	7.4	78	2.0	2.4	1.0	3.3	1.4	254	0.1	8.0	<3	227	0.32	--	0.3
W-17263	7-Feb-96	22.6	7.51	7.2	41	12	2.2	0.8	2.8	3.3	239	0.3	5.2	<3	150	0.08	--	0.3
Wingate Sink	7-Feb-96	22.7	7.33	1.6	59	5.9	2.6	0.5	4.9	9.1	188	0.4	6.7	<3	184	1.5	--	0.3
W-17258	9-Apr-96	19.7	7.09	5.1	11	1.8	4.4	1.7	7.3	5.0	37	28.0	5.2	480	97	0.05	37	6.1
W-17259	9-Apr-96	22.1	7.78	3.4	51	11.0	5.8	6.9	3.9	22	198	0.7	5.9	<3	209	0.35	160	0.2
W-17262	10-Apr-96	20.3	7.57	0.5	61	4.5	5.1	6.8	4.3	7.5	208	1.2	6.5	190	195	<0.05	280	<0.1
SR5.7	10-Apr-96	17.4	6.09	7.5	5.8	1.9	4.6	1.6	7.5	5.4	12.4	31.0	5.4	780	87	0.10	29	6.4
LRSpgrs	10-Apr-96	17.7	6.14	7.1	5.7	1.8	4.4	1.5	7.5	5.4	12.7	31.0	5.3	770	87	0.08	31	6.4
SR3.75	10-Apr-96	17.6	6.16	7.2	5.9	1.9	4.6	1.7	7.6	5.4	12.4	30.0	5.4	770	88	0.08	35	5.8
W-17263	10-Apr-96	21.6	7.52	7.0	43	11.0	1.8	0.2	2.8	3.6	184	0.1	5.4	<3	153	0.08	240	.
W-17270	11-Apr-96	21.6	7.46	0.2	--	--	--	--	--	--	--	--	--	--	--	--	--	0.2
W-17269	11-Apr-96	21.1	7.13	4.5	99	3.7	4.1	2.7	10.0	30.0	252	--	6.6	<3	308	6.9	350	0.5
Wingate Sink	11-Apr-96	21.8	7.39	0.2	40	5.2	3.3	0.9	5.9	8.1	143	8.7	6.3	150	155	0.68	140	2.2

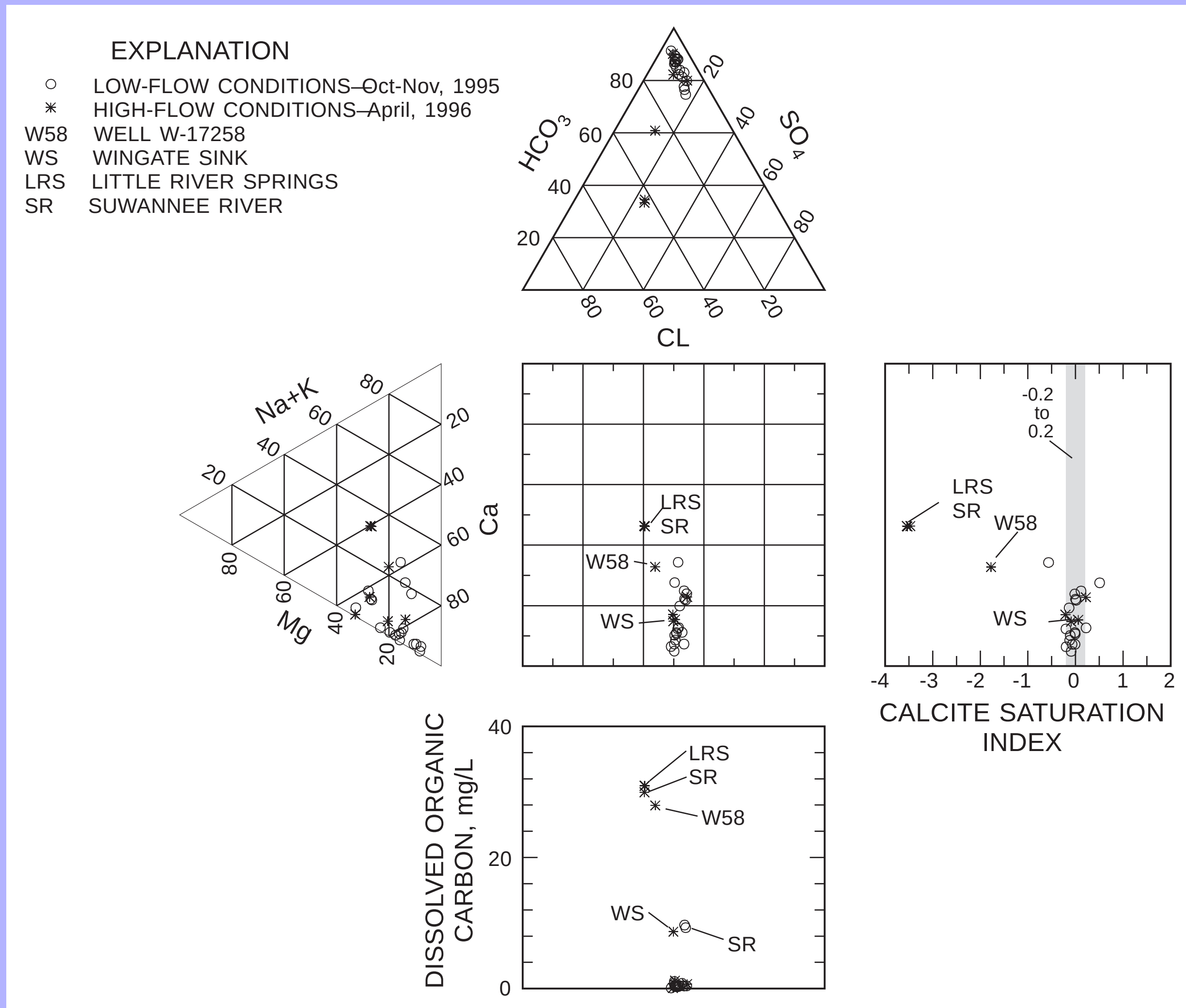

Figure 5. Durov plot showing major-ion composition, dissolved organic carbon, and calcite saturation index of groundwater, river water, and spring water.

Floridan aquifer in this area is usually elevated in carbon dioxide and organic acids, which promote the dissolution of carbonate bedrock material (Sprinkle, 1989). Other evidence of calcite dissolution in the Upper Floridan aquifer is (1) a substantial increase in the concentration of Ca^{2+} and HCO_3^- (dissolved inorganic carbon, DIC) compared to river water *(Table 1)*; and (2) an increase (enrichment) in $\delta^{13}C$ (DIC) in water from Little River Springs, -12.0 per mil during low flow (Katz and Hornsby, 1998) compared to $\delta^{13}C$ of DIC in water (-24.9 per mil) from the Little River, a disappearing stream in a tributary basin to the Suwannee River (Katz et al., 1998). Little River Springs, which intercepts water from large parts of the aquifer, derives its ^{13}C composition from nearly equimolar amounts of carbon from CO_2 ($\delta^{13}C$= -24‰ from degradation of organic material) and from dissolution of calcite ($\delta^{13}C$= 0‰), according to the equation.

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^- \qquad (1)$$

The Suwannee River is acidic as it emerges from the Okefenokee Swamp; pH values range from 4.0–4.5 units, due to the high concentration of humic and fulvic acids (Hull et al., 1981). The river water also has low concentrations of alkalinity and dissolved solids

(Berndt et al., 1996). As the river moves from the upper to lower part of the basin during low flow, increases occur in pH and specific conductance, as well as in concentrations of Ca, Mg, and HCO_3. A corresponding decrease occurs in organic carbon, reflecting the increasing contribution of groundwater to the total volume (Hull et al., 1981). Calcium, magnesium, and bicarbonate concentrations in Suwannee River water at Branford are generally two or three times the upstream concentrations during low flow (Hull et al., 1981). Overall, calcium, alkalinity, silica, dissolved solids, and radon concentrations were higher in groundwater than in river water. Concentrations of iron, DOC, and tannic acid typically were much higher in river water than in groundwater throughout the study period *(Table 1)*.

Changes in Chemistry of Groundwater and River Water During High-Flow Conditions

During the study period, differences in chemistry between the Suwannee River and groundwater were more pronounced during high-flow than low-flow conditions. For example, median dissolved-solids concentrations were 218 and 183 mg/L in groundwater and river water, respectively, during low flow, but concentrations were 175 and 88 mg/L in groundwater and river water, respectively, during high flow *(Table 1)*. During high flow, river water retains the chemical characteristics of its upstream basins, although this depends on the location and amount of recharge (Kincaid, 1998).

During high-flow conditions, the chemical composition of water from the river, Little River Springs, and well W-17258 changed from a Ca-HCO_3 type to a mixed water type *(Figure 5)*. Calcium content decreased from 60–70% of the total cation equivalents at low flow to about 30–40% of the total in water from the river, Little River Springs, and well W-17258. The content of Mg, Na, and K increased to about 60% of total cation equivalents, and Cl and SO_4 increased to about 60% of the total anion equivalents *(Figure 5)*. In contrast, the chemical composition of water from other wells did not change significantly, and calcium and bicarbonate remained the dominant ions *(Figure 5)*. Water from Wingate Sink remained a calcium-bicarbonate type during high flow; however, some small changes in chemical composition occurred, including a 10% decrease in Ca concentration and a small corresponding increase in Na and Mg concentrations.

Saturation indices of water from the Suwannee River, Little River Springs, Wingate Sink, and well W-17258 indicate undersaturation with respect to calcite and dolomite during high-flow conditions. Calcite SI values decreased from 0.10 to -0.45 in well W-17258, 0.17 to -0.30 in Wingate Sink, and 0.09 to -3.50 in the river during high flow. Saturation indices of water samples from other wells remained near 0.0 with respect to calcite and dolomite *(Figure 5)*.

DOC concentrations increased significantly in the Suwannee River, Little River Springs, Wingate Sink, and well W-17258 during high flow compared to low flow. DOC averaged 12 mg/L in the river during the low-flow period but increased to 30 mg/L during high flow *(Figures 4* and *5*, and *Table 2)*. DOC concentrations also increased from less than 0.1–28 mg/L and from 0.4–8.7 mg/L in water from well W-17258 and Wingate Sink, respectively, during high flow. The median DOC concentration in other groundwater samples was 0.7 mg/L during high flow compared to 0.4 mg/L for low flow. Large increases in DOC at Wingate Sink and well W-17258 indicate the likelihood of river water moving into the aquifer and mixing with groundwater at these sites. Other evidence for mixing of river water with groundwater at these two sites during high flow also is indicated by an increase in tannic acid (tannins and lignins). Tannins and lignins usually occur in the bark and leaves of plants such as cypress trees, and bottomland hardwoods such as those present in the Upper Suwannee River and Alapaha River basins *(Figure 1)*. Tannic-acid concentrations were generally low in groundwater (ranging from less than 0.1–0.7 mg/L) and in river water (0.4–2.8 mg/L) during low flow but increased significantly during high flow. Median tannic concentrations increased from 2.8–5.8 mg/L in river water, from 0.2–6.1 mg/L in well W-17258, and from 0.1–2.2 mg/L in Wingate Sink during high flow *(Figure 4* and *Table 2)*. Median concentrations of tannic acid in other groundwater was 0.2 mg/L during high flow.

Additional evidence for mixing of river water with groundwater at Wingate Sink, well W-17258, and Little River Springs is indicated by changes in concentrations of silica and radon (^{222}Rn). Silica concentrations generally increase when waters are in contact with aquifer materials containing silica due to the relatively long residence times of groundwater in the aquifer compared to the river water. Silica concentrations in the river, Little River Springs, Wingate Sink, and well W-17258 decreased during high flow. During low flow, ^{222}Rn concentrations ranged from 190–1000 pCi/L in groundwater and from 100–110 pCi/L in the river *(Table 1)*. However, during high flow, median ^{222}Rn concentrations decreased from 110–35 pCi/L in the river, 340–140 pCi/L in Wingate Sink, and from 480–37 pCi/L in well W-17258, respectively *(Table 2)*. Concentrations of ^{222}Rn remained nearly unchanged in other groundwater samples during high flow, ranging from 160–350 pCi/L *(Table 2)*. Radon concentrations tend to be elevated when waters are in contact with rocks or sediments containing uranium. When waters are open to the atmosphere ^{222}Rn degasses, resulting in concentrations of ^{222}Rn in river water that are typically 3–4 orders of magnitude lower than concentrations in groundwater (Wanty and Nordstrom, 1993).

Quantifying Hydrochemical Interactions Between Groundwater and River Water

The degree of mixing of river water and groundwater can be quite variable, depending upon such factors as (1) differences in the hydraulic head in the aquifer and hydrostatic pressure in the river, and (2) the degree of connectivity between parts of the

Table 3. Calculated river-water mixing fraction (f_{rw}, dimensionless) at sites W-17258 and Wingate Sink, using binary mixing model and naturally occurring chemical tracers

[Groundwater samples used in mixing models were collected during low flow conditions for the Suwannee River, October 1995–January 1996]

Chemical Constituent, Tracer	Well W-17258		Wingate Sink	
	October 1995	January 1996	October 1995	January 1996
Ca	0.94	0.93	0.42	0.36
Mg	--	--	0.13	0.17
Na	0.87	0.88	0.42	0.35
K	--	--	--	0.36
SO_4	--	--	0.41	0.27
Cl	0.50	0.87	0.36	0.38
HCO_3	0.91	0.90	0.27	0.26
SiO_2	--	--	0.31	0.31
DOC	0.93	0.93	0.27	0.27
Dissolved solids	0.95	0.94	0.38	0.30
^{222}Rn	0.99	--	0.65	--
Tannic acid	--	--	0.33	0.31
Median	0.93	0.91	0.35	0.31

aquifer and the river. To estimate the degree of mixing of river water and groundwater in well W-17258 and Wingate Sink during high-flow conditions, a two end-member mixing model was used. The fraction of river water (f_{rw}) in the mixture is calculated using the following expression:

$$f_{rw} = (Y_m - Y_{gw})/(Y_{rw} - Y_{gw}) \qquad (2)$$

where Y_m, Y_{gw}, and Y_{rw} denote the concentrations of a selected element in the mixture, groundwater, and river water, respectively.

Various chemical tracers were evaluated as to their effectiveness in quantifying mixing of groundwater and river water at W-17258 and Wingate Sink: SiO_2, DOC, ^{222}Rn, tannic acid, dissolved solids, and selected major ions (Ca, Mg, Na, K, Cl, HCO_3, SO_4). The effectiveness of a particular natural tracer in quantifying f_{rw} is related to the differences in tracer concentrations of the two end members, and how conservatively the tracer travels with the mixed water without subsequent changes in concentration due to chemical, physical, or biological processes. Mixing models were based on the following assumptions: (1) valid groundwater-flow patterns are derived from hydraulic-head data, (2) the concentrations of these tracers are not altered by chemical or biological processes after the mixing of river water and groundwater has occurred, and (3) hydrodynamic dispersion is minimal and does not affect the concentrations of natural tracers in mixed waters.

Two sets of mixing models were calculated for each site, based on chemical data for water samples collected in October 1995 and January 1996 (representing the groundwater end member composition during low-flow conditions) *(Table 3)*. The chemical composition of the river-water end member was represented by samples collected at river site SR3.75 (for well W-17258) and site SR5.7 (for Wingate Sink) in April 1996, and was selected based on the proximity of the river sites to the sink and well.

The fraction of river water (f_{rw}) that mixed with groundwater from well W-17258 ranges from 0.50–0.99 (median 0.92) during high flow using the aforementioned chemical tracers *(Table 3)*. In general, most tracers provided similar estimates of f_{rw} (0.87–0.99), with the exception of Cl (0.50). Chloride is typically considered a conservative tracer of water movement; however, differences between the Cl concentrations in the river and aquifer were small, which limited its effectiveness at this site. Median Cl concentrations were 4.1 and 6.0 mg/L in groundwater and river water, respectively. The f_{rw} calculated using ^{222}Rn concentrations gave a slightly higher value than other tracers (0.99). This higher value may result from degassing of ^{222}Rn to the atmosphere. A large cavity that was reported during drilling in the open interval of this well may have resulted in loss of ^{222}Rn due to degassing. F_{rw} could not be calculated using Mg, SO_4, and SiO_2, because the concentrations of these constituents were lower in the mixed water than those in the groundwater and river-water end members, which resulted in negative f_{rw} values. Again, the small differences in concentration of these constituents between groundwater and river water limited their effectiveness in quantifying mixing ratios. Alternatively, similar concentrations of these tracers in the two end-members and mixed waters may result from chemical reactions. The concentration of tannic acid in the water sample from well W-17258 was higher than that of both end members, resulting in an unrealistic f_{rw} (greater than 1.0) at this site. The higher tannic-acid concentration in water from well W-17258 compared to river water may have resulted from mixing with river water that had a higher concentration of tannic acid, possibly during the rising limb of the hydrograph.

At Wingate Sink, f_{rw} ranged from 0.13–0.65 (median f_{rw} values were 0.35 and 0.31 using data from October 1995 and January 1996, respectively). A relatively high degree of variability of f_{rw}, calculated using each tracer *(Table 3)*, may result from a greater distance of travel for river water (1.5 km from the river) and possible chemical reactions that occur prior to or after mixing with groundwater. Presumably, the long travel distance of river water in the aquifer may provide a greater opportunity for ^{222}Rn to degas, and other constituents to be exchanged, sorbed, diluted, or biologically altered. Most values of f_{rw} were within ±0.10 of the median, although f_{rw} values obtained using Mg and ^{222}Rn were outside of this range. It is possible that the river-water composition measured at SR7.5 is not representative of the river water that actually mixes with groundwater near Wingate Sink. If this is the case, an undetermined end-member composition for river water would complicate the assumption of a two-end member mixing model. Magnesium concentrations were lower in groundwater samples from Wingate Sink during high-flow conditions than would have been expected based on mixing ratios of other constituents. Mg can exchange for Na or can be sorbed on the aquifer matrix. Radon can degas to the atmosphere through nearby sinks and conduits during its travel through the aquifer. River-water mixing fractions using Cl (0.31–0.35) agreed well with values obtained using other tracers. A larger difference in Cl concentrations between groundwater from Wingate Sink (during low flow) and river water *(Table 2)* provided a better estimate of mixing than the similar Cl concentrations of groundwater and river water at well W-17258. Calculated values of f_{rw} using SO_4 and dissolved-solids concentrations varied slightly more than 10% for the

October and January samples, and these differences are most likely due to seasonal variations. Dissolved-solids concentrations were slightly higher in the October sample (220 mg/L) than in the January sample (184 mg/L). Mixing ratios based on SiO_2, DOC, and tannic acid were nearly identical using both sets of samples.

Changes in river chemistry may have occurred throughout the high-flow event. The sensitivity of f_{rw} to variations in river-water chemistry was evaluated for site W-17258 using a 10% uncertainty in the chemical composition of river water (Suwannee River at 3.75, 10-Apr-96, *table 2*). Mixing ratios, estimated from constituents where the concentrations of the river water and groundwater end members were similar in magnitude (Na, Mg, K, Cl, So_4, SiO_2), were significantly affected by a 10% change in river concentration and, so, provide less reliable estimates. Mixing ratios computed from constituents where the concentrations of end members were not similar in magnitude (Ca, tannic acid, DOC, ^{222}Rn, HCO_3) were not significantly affected by a 10% change in river concentration. For example, the fraction of river water (f_{rw}) varied from 0.93–0.95 using ±10% variation in calcium concentration in river water where there was a difference of 87.2 mg/L between the groundwater and river water end members. In contrast, f_{rw} varied from 0.84–1.0 using a ±10% variation in DOC concentrations in river water, where there was a difference of 28.9 mg/L between the two end members. Using a ±10% uncertainty in Cl concentration in river water, f_{rw}, mixing ratios ranged from 0.22 to mathematically unable to calculate, with a difference of only 0.60 mg/L between the two end members.

The effectiveness of naturally occurring solute tracers in quantifying interactions between river water and groundwater in the study area is highly dependent on the differences in end-member values and reactions that modify the chemical or isotopic composition after mixing has occurred. Solute tracers do not necessarily move conservatively with the water, and reactions such as dissolution of aquifer minerals (primarily calcite and dolomite), cation exchange, and sorption/desorption can significantly alter the solute composition depending on the travel time and/or distance between the river and sampling location (well, sink, or spring). Solute tracers, usually not as effective as oxygen and hydrogen isotopes in quantifying mixtures of river water and groundwater, provided reliable estimates of mixing of water from a sinking stream and groundwater in a mantled karst environment near the study area (Katz et al., 1998). The fact that f_{rw} values calculated using various dissolved species, such as Ca, Mg, Na, and K, are similar in water from well W-17258 and Wingate Sink indicates that chemical reactions involving these species have not occurred or are very minor. For example, even though the mixed water is undersaturated with respect to calcite, and dissolution of calcite is thermodynamically possible, the mixed-water composition does not reflect any measurable calcite dissolution.

DOC is an effective tracer for mixing of river water and groundwater in this karstic system due to (1) relatively large differences in end-member concentrations, and (2) insufficient time for microorganisms to degrade the DOC because flow is rapid (Gibert et al., 1994). Also, fewer sites for microorganisms exist along conduits and fractures in limestone compared to those in unconsolidated sediments, due to the smaller surface area to volume ratio. Similarly, tannic acid also is a good indicator of mixing between river water and groundwater in the study area. Using tannic-acid analyses offers two other advantages: (1) water samples can be analyzed relatively inexpensively in the field in about 30 min (Katz et al., 1998), and (2) tannic-acid concentrations can be used as a screening tool to determine if water samples should be collected for other chemical and isotopic analyses.

Possible Mechanisms for Mixing of River Water and Groundwater

An extensive network of conduits, both laterally and vertically in the Little River springs area, provides a means for rapid migration of river water into the aquifer. Groundwater levels in wells located 1.6–4.8 km from the river respond almost immediately to changes in river stage (Ceryak, 1977). Correlation coefficients between changes in river stage and water levels in wells 1–5 km from the river range from 0.60–0.98 and are highest for wells closest to the river (Hirten, 1996).

Even though the river did not overflow its bank during April 1996, river water most likely moves into the aquifer through two main mechanisms: (1) migration into the top of the aquifer adjacent to the river by expanded bank storage that consists of lateral migration of river water into the surficial sands adjacent to the river channel. This water eventually moves downward into the Upper Floridan aquifer through fractures and solution openings in the top of the limestone; and (2) migration directly into deeper parts of the aquifer through fractures, springs and/or conduit systems located along the river channel. These mechanisms are illustrated in *Figure 6*.

During high-flow conditions, chemical data indicate that the water from Little River Springs was river water. Water levels were at an altitude of 6.30 m in the Suwannee River, Little River Springs, Wingate Sink, and in wells 17258 and 17260 on April 10, 1996. River water was observed flowing into Little River Springs at that time. River water may have migrated into the aquifer to the vicinity of well W-17258 through conduits or fractures, which may connect the zone that well 17258 taps to the Little River Springs conduit system. During well drilling, cavities were identified in the open-interval of well W-17258 at depths ranging from 6–8 m. River water may have reached Wingate Sink to mix with groundwater through a complex network of fractures and conduits that are connected to the river channel, although river water was not detected in a shallow well located between the sink and the river (well W-17263).

Summary and Conclusions

During high-flow conditions in April 1996, water from the Suwannee River migrated directly into the karstic Upper Floridan aquifer, the source of water supply for northern Florida. Changes in the chemical composition of groundwater were investigated using naturally occurring geochemical tracers and mass-balance modeling techniques. Fifteen monitoring wells were installed open to the uppermost part of the aquifer in areas near Little River Springs, where numerous subterranean karst solution features were identified using ground-penetrating radar.

Following a period of sustained rainfall in the Suwannee River basin, the stage of the Suwannee River increased from 3.0–5.8 m (above mean sea level) in April 1996, and discharge of the Suwannee River peaked at 360 m^3/s. During high-flow conditions in the Suwannee River, the chemistry of water in a nearby monitoring well (W-17258), Wingate Sink, and Little River Springs changed, reflecting the mixing of river water and groundwater. Concentrations of calcium, silica, radon (^{222}Rn), and bicarbonate decreased, whereas concentrations of organic carbon, tannic acid, and chloride increased in water from these sites compared to low-flow conditions. The proportion of river water that mixed with groundwater ranged from 0.13–0.65 at Wingate Sink and 0.5–0.99 at well W-17258, based on binary mixing models using several solute tracers, including tannic acid, chloride, silica, ^{222}Rn, and dissolved organic carbon. The effectiveness of a particular natural tracer in quantifying mixing between river water and groundwater was related to differences in tracer concentrations of the two end members, and how conservatively the solute tracer travels in the mixed water without subsequent changes in concentration due to chemical, physical, or biological processes.

An extensive network of conduits, both laterally and vertically in the Little River Springs study area, provides a means for rapid migration of river water into the aquifer. River water most likely moves into the aquifer through two main mechanisms: (1) migration into the top of the aquifer adjacent to the river by expanded bank storage, and (2) movement into deeper parts of the aquifer through fractures, springs and conduit systems located along and beneath the river channel. The combination of naturally occurring geochemical tracers along with hydrologic data provides a better understanding of the hydrochemical interaction between surface water and groundwater. Knowledge of the processes controlling the chemical composition of water in these dynamic karst systems can help regulators to make informed environmental decisions for protection of the valuable groundwater and surface-water resources.

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