UNUSUAL CHEMISTRY AND ANTHROPOGENIC CONTAMINANTS IN UPPER FLORIDAN AQUIFER GROUNDWATER UNDERNEATH THE CHICKASAWHATCHEE SWAMP

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Abstract. In the karst landscape of the lower Flint River basin, there are large exchanges of water between wetland depressions such as the Chickasawhatchee Swamp and the Upper Floridan aquifer (UFA). At times, the creeks and wetlands within the swamp are a source of water to the aquifer, and at other times the aquifer is a source of water to creeks and wetlands. Groundwater chemistry was examined between January 2002 and December 2004 as part of a preliminary assessment of the role of the Chickasawhatchee Swamp in regional hydrology. Evidence for the influx of water from the overlying wetland was provided by the presence of high methane concentrations and anoxia in some areas of the aquifer. Large temporal variations in groundwater chemistry underneath the swamp were also attributed to the dynamic mixing between surface water and ground water in this area. The average apparent recharge age of the water underneath the swamp varied between 24 and 57 years when determined using the $^3H/^3He$ method. Chlorofluorocarbon (CFC) supersaturation was evident in both surface water and many ground water samples indicating an unidentified local source of CFC contamination. A large pulse of nitrate was observed in two wells that were down-gradient of an adjacent agricultural area. The nitrate pulse was much higher in concentration than other groundwater wells within the swamp, but similar to other parts of the UFA that have been contaminated by nitrate.

INTRODUCTION

The Chickasawhatchee Swamp is the second largest wetland in Georgia. This area has long been thought of as an area with dynamic surface water and groundwater exchanges. However, until recently, the area was not accessible for detailed study. The Chickasawhatchee Swamp is found within the Dougherty Plain which is one of the largest recharge features of the entire UFA system. The UFA is composed of upper Eocene Ocala limestone confined below by middle Eocene Lisbon Formation, and semiconfined above by undifferentiated Quaternary overburden (Hicks et al. 1987). This geology is classified as weathered karst and is characterized by dry and submerged limestone caves.

We hypothesized that if the Chickasawhatchee Swamp represents a substantial recharge feature of the UFA, then water in the aquifer underneath the swamp may have distinct water chemistry relative to the majority of the UFA which has been more extensively surveyed (Hicks et al. 1987). Here, we present a subset of results from a multi-disciplinary study to understand how regional hydrology and water quality may be influenced by this large wetland area. We present a synoptic from 2004 of oxygen, methane, $^3H/^3He$, and chlorofluorocarbons to look at heterogeneity of groundwater chemistry in the UFA and overburden. We also examine temporal trends in nitrate from selected groundwater wells over a three year period. These analyses indicate that human activities are influencing groundwater chemistry in this rural area in several different ways.

STUDY AREA

The Chickasawhatchee Swamp is located in the Dougherty Plain physiographic province of the southeast U.S. Coastal Plain which extends from southwest Georgia into the Florida panhandle (Fig. 1). Land cover within the swamp consists of bottomland hardwood forests and upland pine plantation. Large agricultural fields are located around the periphery of the swamp with a large cluster in the northwest corner.

Locations of surface water and groundwater sampling sites are given in Figure 2. The 2” wells were located in undifferentiated overburden and the 4” wells

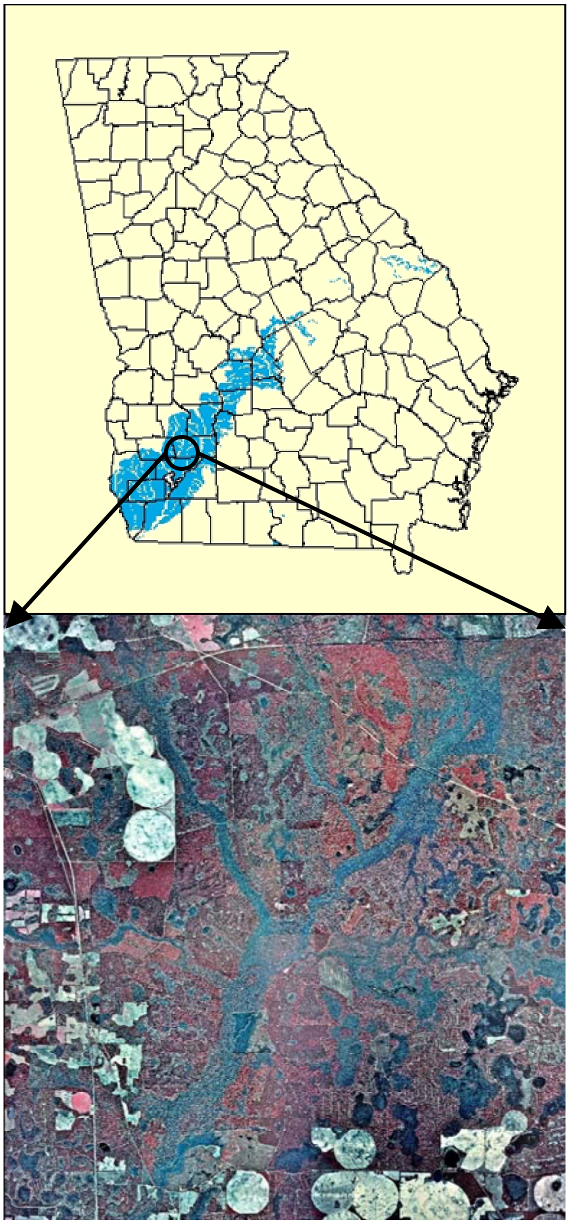

Figure 1. Location of the Dougherty Plain (upper, shaded blue) and satellite image of the Chickasawhatchee Swamp area (lower) in southwest Georgia.

were located in the UFA. The general hydrologic gradient is from the Northwest to the southeast with flow velocities ranging from cm/y for matrix flow to m/min for flow in large conduits (Hicks et al. 1987). Surface water samples were collected from Spring Creek and Chickasawhatchee Creek which both appear to be hydrologically connected to the UFA. An isolated wetland that is not hydrologically connected to the UFA was also sampled.

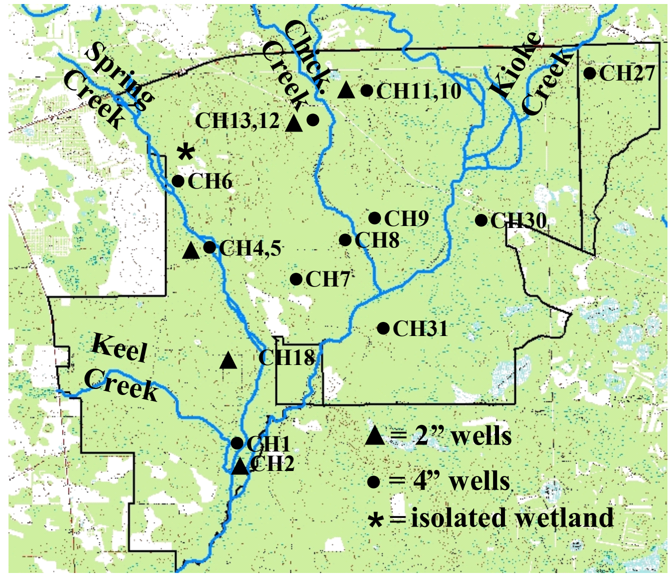

Figure 2. Groundwater and surface water sampling sites in the Chickasawhatchee Swamp.

METHODS

Groundwater wells were sampled for nitrate and dissolved oxygen on a regular basis between January 2002 and December 2004. Prior to sampling, each well was pumped with a Grunfos Redi-Flow pump fitted with Teflon tubing until at least three well volumes of water had passed. Dissolved oxygen was measured on outflow water from the pump in the field using a Hydrolab Quanta with a reported accuracy of ±0.20 mg/l. Samples for nitrate-N were filtered using Whatman GF75 filters and analyzed using a Latchet QuickChem 8000 analyzer. During July 2004, measurements of dissolved methane were also included. Water for methane analysis was collected in BOD bottles and measured by nitrogen headspace equilibration and flame ionization gas chromatography. In November 2004, both groundwater and surface water sites were sampled for $^{3}H/^{3}He$ and chlorofluorocarbons (CFC12, CFC11, CFC113) for estimating average apparent recharge ages as described by Happell et al (2006).

RESULTS AND DISCUSSION

Dissolved oxygen in groundwater ranged from 2.5 to 4.8 mg/L in the overburden and from 0.0 to 4.1 mg/L in the UFA wells (Fig. 3). Average concentrations were

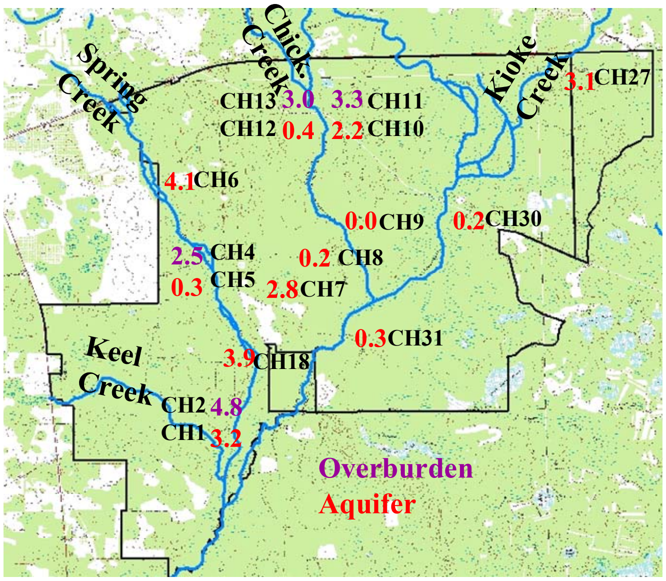

Figure 3. Dissolved oxygen concentration (mg/L).

much higher in the overburden (3.4 mg/L) in comparison to the UFA (1.7 mg/L). Six of the 12 wells in the UFA had oxygen concentrations below 1 mg/L indicating that suboxic or anoxic groundwater is widespread underneath the swamp.

Dissolved methane concentrations were elevated in some but not all overburden and UFA wells (Fig. 4). Wells CH4 and CH13 in the overburden had the highest methane concentrations. However, UFA wells CH8, CH9, and CH31 were also elevated indicating the presence of methane within the aquifer.

The average apparent recharge ages derived from $^{3}H/^{3}He$ determinations ranged from 16 to 36 y in the overburden and from 24 to 54 y in the UFA (Fig. 5).

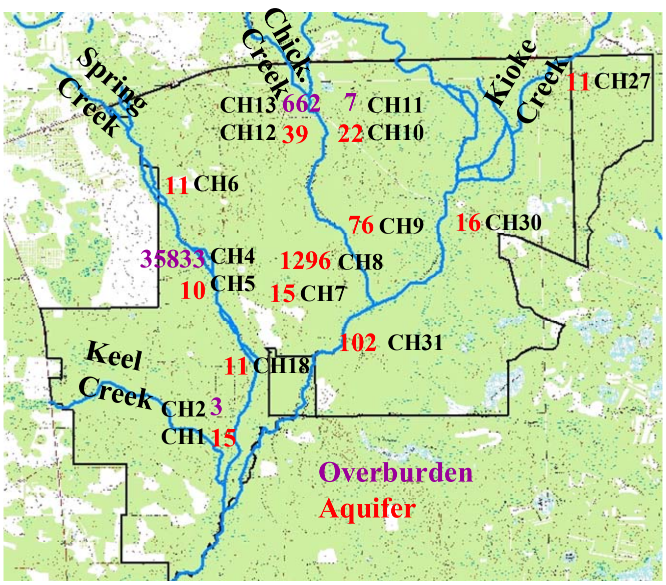

Figure 4. Dissolved methane concentrations (nM).

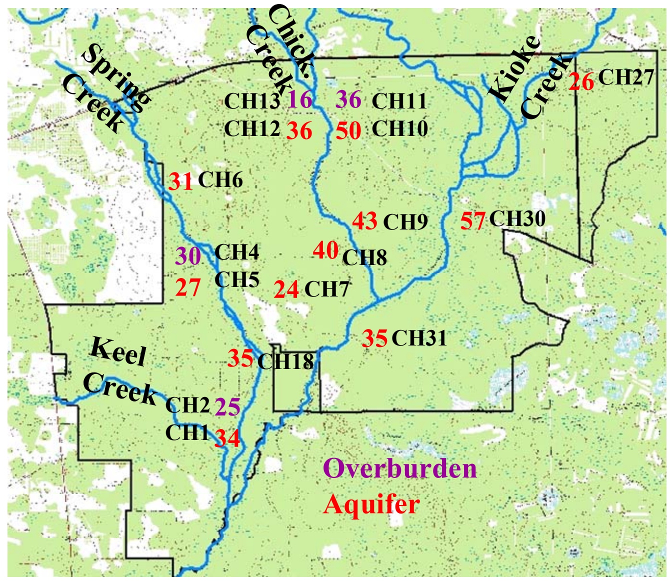

Figure 5. Average apparent recharge ages (y) in groundwater based on the $^{3}H/^{3}He$ method.

Average apparent recharge ages were lower in the overburden (27 y) in comparison to the UFA (37 y).

The average apparent recharges based on CFC concentrations could not be determined because six of 18 samples were contaminated in one or more CFC. Contamination refers to a situation in which concentrations were higher than would otherwise occur with normal equilibration between atmospheric CFCs and groundwater during recharge. Thus, there is an unidentified source of excess CFCs introduced to the UFA in this region. Possible sources of contamination include discarded appliances, automobiles, or leaky chemical containers containing CFC aerosols.

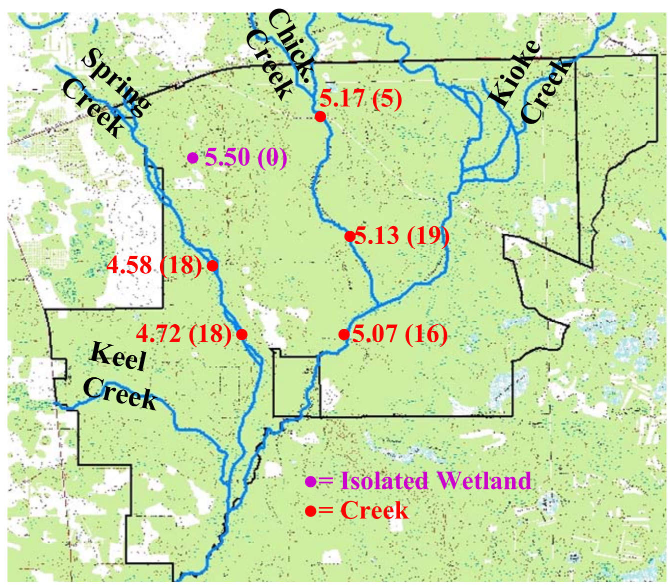

Figure 6. Average apparent recharge ages in surface water based on the $^{3}H/^{3}He$ method.

The tritium concentration and corresponding average apparent recharge estimate for the hydrologically isolated wetland (5.5 TU and 0 y) were consistent with a contemporary water source (i.e. rainfall) and little supplement from older groundwater (Fig. 6). The tritium concentrations in all of the creek stations were lower with an average apparent age of 5 to 19 y. This likely reflects a mixture of surface water runoff and older groundwater contributing to baseflow.

Concentrations of the three CFCs in the isolated wetland were all undersaturated relative to what would be predicted based on equilibration with the atmosphere (Table 1). In contrast, CFC12 and CFC 11 were supersaturated in all creek samples except CFC11 in SC Upper. CFC113 was undersaturated in all creek samples. We speculate that the CFC contamination in the creek comes from groundwater sources based on the fact that local groundwater wells showed widespread CFC contamination (primarily CFC12), and that these creeks are fed primarily by groundwater.

We examined trends in nitrate (Fig. 7) in four UFA wells (CH12, CH6, CH5 and CH1) that were hydrologically down-gradient of a major agricultural area (Figs. 1 and 2). Wells CH5 and CH6 showed high concentrations of nitrate whereas CH12 and CH1 had low nitrate concentrations. CH5 showed substantial temporal variability with concentrations ranging from <1 mg/L to 5 mg/l. Nitrate in well CH6 ranged from 0.2 to 1.4 mg/l. Both wells showed lowest values in May through August 2003. Nitrate concentrations above 1 mg/L are considered to be above background levels and indicate a human source of contamination. The proximity to a heavily fertilized area and a lack of substantial wastewater effluent regionally make it likely that fertilizer is the source of nitrate pulses that move through the groundwater system.

Table 1. Equivalent atmospheric concentration of CFCs (error given in parentheses) and the percent saturation relative to contemporary values[1] in surface water samples.

	CFC12		CFC11		CFC113	
	Atmospheric Equivalent (pmol/mol)	% Sat.	Atmospheric Equivalent (pmol/mol)	% Sat.	Atmospheric Equivalent (pmol/mol)	% Sat.
Isolated Wetland	275.4 (5.5)	50	45.2 (0.9)	18	11.8 (1.7)	15
SC Upper	718.3 (14.4)	132	252.8 (5.1)	98	50.8 (1.7)	64
SC Lower	774.3 (15.5)	142	286.9 (5.7)	111	55.2 (1.6)	69
CC Upper	835.0 (16.7)	153	310.4 (6.2)	120	60.7 (1.8)	76
CC Middle	859.8 (17.2)	157	321.1 (6.4)	124	63.4 (1.8)	79
CC Lower	803.1 (16.1)	147	300.2 (6.0)	116	59.2 (1.7)	74

[1]Contemporary CFC concentrations of 546, 258, and 80 pmol/mol were used for CFC12, CFC11, and CFC113, respectively.

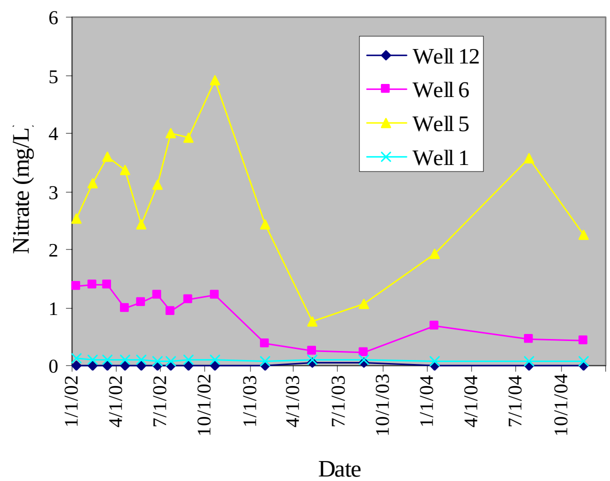

Figure 7. Nitrate-N concentrations (mg/L) from 2002 thorugh 2004.

CONCLUSIONS

Through this preliminary assessment, we have identified several types of human contaminants that are influencing water quality. Although CFC levels are below human health standards, they are indicative of contamination that is widespread throughout surface water and groundwater in the system. Nitrate contamination is also below human health standards but high concentrations in groundwater discharged to streams may negatively affect ecosystem health.

ACKNOWLEDGEMENTS

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