DETERMINATION OF THE RELATIONSHIP OF NITRATE TO DISCHARGE AND FLOW SYSTEMS IN NORTH FLORIDA SPRINGS

Sam B. Upchurch
SDII Global Corporation, 4509 George Road, Tampa, Florida 33634, USA, flwaterdoc@gmail.com

Abstract

The Suwannee River Water Management District has collected quarterly discharge and water quality data from 30 1st and 2nd magnitude springs in the Suwannee River Basin since 1998. These data were collected quarterly well into the late 2000s and constitute a valuable database for characterizing spring discharge behavior.

Trend and correlation analyses were used to compare the relationships of $NO_3^- + NO_2^-$ (nitrate in this paper), specific conductance, and spring discharge. Trends were considered significant if alpha levels of the trend slopes were ≤ 0.05.

Data from 50% of the springs show that nitrate concentrations increase as discharge from the spring increases. Forty-five percent of the remaining springs showed no correlation between discharge and nitrate, and only 5% (2 springs with poor data) have relationships where high discharge was related to lower nitrate concentrations.

Twenty percent of the springs had positive correlations of specific conductance with discharge, 37% showed no correlation, and 43% had negative correlations between specific conductance and discharge.

Most important in terms of understanding the plumbing of the conduit systems, 40% of the springs had positive correlations between nitrate and specific conductance, 48% showed no correlation, and 12% had negative correlations.

Introduction

The Suwannee River Water Management District is located in north Florida (Figure 1). There are more known first and second magnitude springs within this district than any other comparable area of North America. These springs constitute a major economic and ecological resource to north-central Florida.

In recent years, many of these springs have experienced increases of nitrate concentrations in discharge from the springs (Hornsby and Ceryak, 1998; Katz and Hornsby, 1998; Upchurch et al., 2007; Harrington et al., 2010). These increases in nitrate concentrations are causing eutrophication in some springs, spring runs, and receiving waters (rivers and streams) (Florida Springs Task Force, 2000; Stevenson et al., 2004).

As a result of concern for increasing nitrate concentrations in spring discharge, Florida's Department of Environmental Protection and Florida's water management districts initiated comprehensive water-quality sampling programs that continue today. The Suwannee River Water Management District began intensive spring sampling in 1998. This paper reports on an analysis of these data from 1998 through 2007.

Spring Discharge Considerations

The springs all occur in Oligocene or Eocene limestones that constitute the upper Floridan aquifer. Dolostone is locally present, but the majority of the rock in contact with the water is limestone.

The springs vary in setting from vents or groups of vents situated at the heads of spring runs up to several kilometers in length to vents located on the margins of their receiving waters, primarily the Suwannee and Santa Fe rivers.

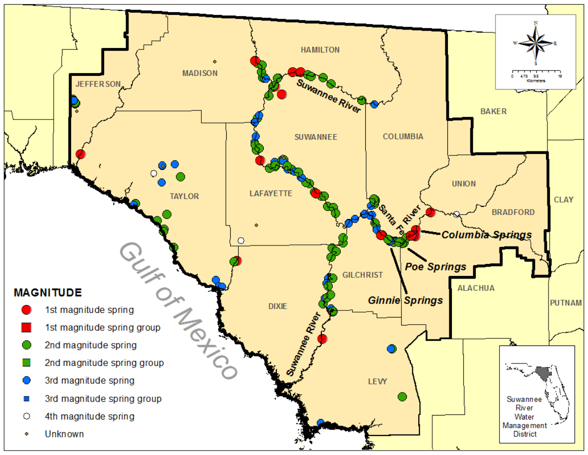

Figure 1. *Springs of the Suwannee River Water Management District by magnitude.*

Virtually all of these springs included in this investigation have been affected by increasing nitrate concentrations. For this reason, it is difficult to identify background nitrate concentrations. Upchurch (1992) reported that the mean nitrate as NO_3^- in rainfall was 0.97 mg/L (standard deviation = 1.01, n = 1373 samples), and in the upper Floridan aquifer groundwater in the Suwannee River Water Management District, he reported the median nitrate (NO_3^- as N) to be < 0.05 mg/L. Nitrate concentrations in many of the springs discussed in this paper exceed the "background" concentrations observed in regional Floridan aquifer water.

The typical time series for these springs (Figure 2; Upchurch et al. 2007) shows seasonal fluctuations in nitrate and specific conductance with time. However, the short-term variability is typically less than the long-term variability. In this paper, the relative behavior of nitrate, specific conductance, and discharge are of concern. Temporal trends, while present, do not affect the correlations discussed herein. For example, the relative behavior of nitrate and specific conductance at Manatee Springs (Figure 3) indicates a positive correlation that is significant at $\alpha = 0.05$ regardless of seasonal and long-term temporal trends in discharge or other causes of seasonality.

Hypotheses and Methods

It has long been understood that water derived by diffuse-flow in karst systems has higher calcium, hardness, and pH as a result of longer residence times and rock/water contact than rapidly recharged water in conduit-flow systems (White, 1988). Typically, calcium, hardness, and other rock-water interaction indicators in diffuse-flow systems have negative correlations with spring discharge (Basset and Ruhe, 1973) as a result of dilution under high discharge conditions.

In the eogenetic karst of Florida, this pattern is often complicated by complex matrix flow in the doubly porous limestone combined with connections of flow systems with swallets and siphons and with back-flooding during high stage events in the adjacent rivers. Many of the springs in the Suwannee River drainage basin are known to be connected to swallets and in-stream siphons (Hornsby and Ceryak, 1998; Butt et al., 2007). Others have unknown connections with surface-water sources. The majority of the Suwannee River basin springs are located on the shores of the rivers (Figure 1) and, depending on head/stage relationships, the springs act as estavelles.

In order to identify springs that are dominated by diffuse versus conduit flow and estavelles that are dominated by bank-storage events, correlation and trend analyses were undertaken comparing specific conductance (µS/cm), a surrogate for calcium, hardness, and other rock/water interaction indicators, with spring discharge (m^3/s). As a result of concerns about the sources of nitrate in the springs, correlation and trend analyses were also used to compare nitrate ($NO_3^- + NO_2^-$) with discharge and specific conductance.

Methods

All field analytes were obtained by trained staff, and the chemical and field analyses followed EPA and state protocols. Significance of correlations was determined by the coefficient of determination (R^2) and alpha level ($\alpha \leq 0.5$).

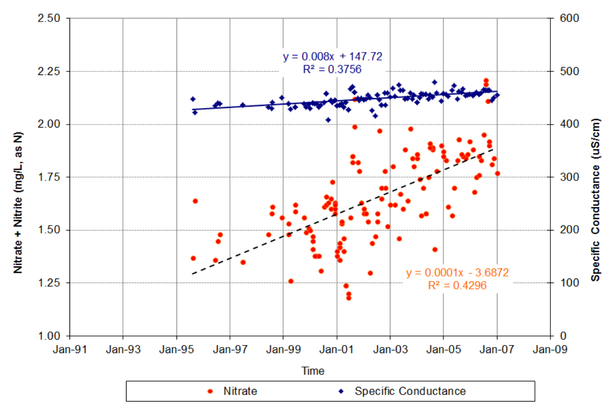

Figure 2. *Time series of nitrate and specific conductance at Manatee Springs, Levy County, Florida.*

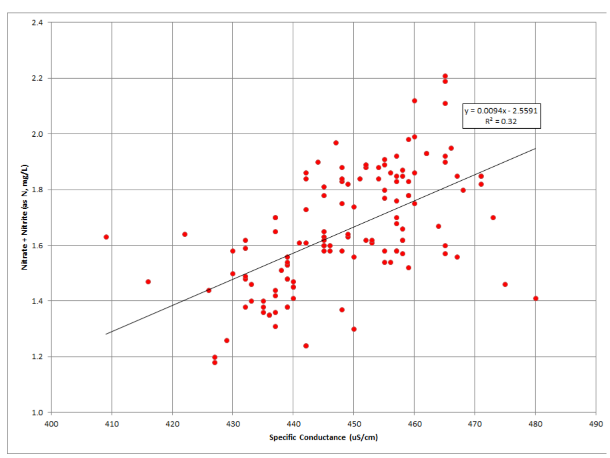

Figure 3. *Relationship of nitrate concentrations to specific conductance at Manatee Springs, Levy County, Florida.*

As noted above, unless stated otherwise, the term nitrate refers to nitrate plus nitrite ($NO_3^- + NO_2^-$) concentrations.

Hypothesis

It is proposed that the relationships between discharge, specific conductance, and nitrate should provide insight as to the dominant flow system and nitrate sources in each spring. Figure 4 presents the hypotheses used to rationalize the origins and flow systems.

In model A (Figure 4), it is hypothesized that a negative correlation and trend between discharge and specific conductance represents the dilution of diffuse flow water by rapidly recharged, conduit-flow water. The conduit flow could be derived from swallets or siphons distal to the spring or it may represent discharge of riverine water stored in the spring conduit system and, to some degree, intergranular porosity in the eogenetic limestone. The latter source should only occur shortly after a flood in the adjacent stream with sufficient stage to cause backflow of the spring.

A positive correlation would suggest that water contained in a diffuse flow system is flushed from the system with minimal dilution. This relationship may be complicated by the widespread use of high specific conductance, Floridan aquifer water for irrigation.

Model B (Figure 4) shows the hypothesized relationships of nitrate and spring discharge. If nitrate concentrations increase as discharge increases, the nitrate is contained in a surface-water source. A negative correlation suggests that the nitrate is stored in the soil or rock column and is diluted by conduit flow.

Model C (Figure 4) shows the proposed relationships between specific conductance (an indicator of diffuse flow) and nitrate (an analyte that originates at or near the land surface by human activity). A positive correlation between the two analytes suggests that the source of the nitrate is similar to the source of the total dissolved solids represented by the specific conductance. In other words, the nitrate is stored in the soil or rock column or applied upon irrigation. A negative correlation suggests that the nitrate is derived from a surface-water source and is entering the aquifer through a swallet or siphon or by backflow of riverine water into the spring conduiting.

Many of the springs in the Suwannee River basin are estavelles that take water when river levels are high. This complicates interpretation of the conduit-dominated models. If the spring discharges relatively elevated nitrate concentrations without high river levels, one can assume that the nitrate is derived from within the springshed and transported to the spring by conduit flow. However, if the elevated nitrate, low specific conductance discharge occurs in the waning phases or shortly after an episode of high river stage during which bank storage and estavelle action in the spring occurred, then the surface-water source may not be within the springshed.

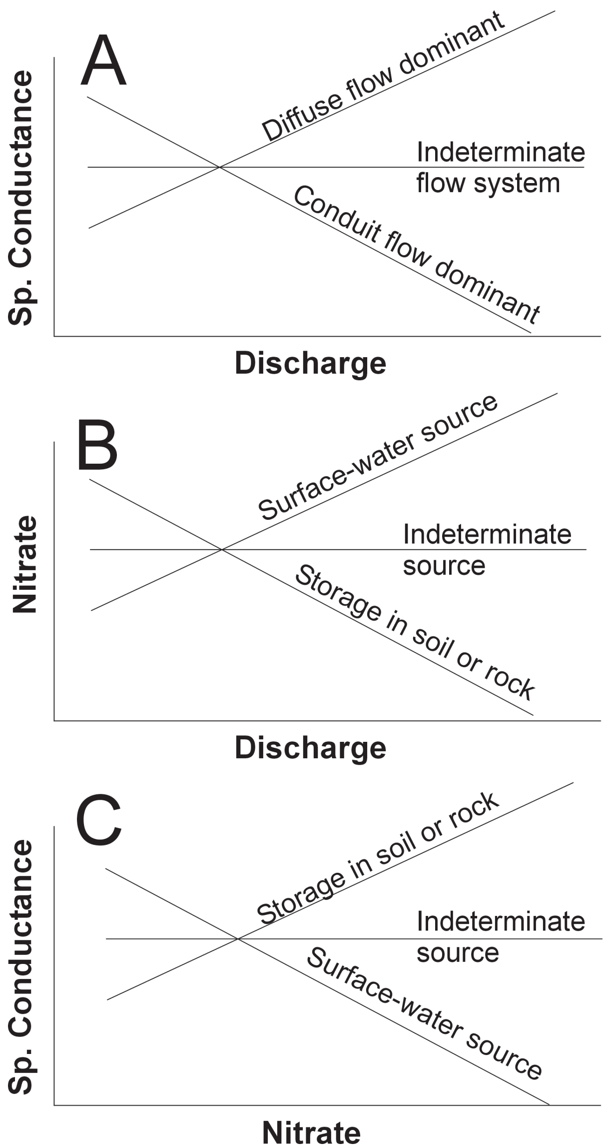

Figure 4. *Models suggesting the relationships of specific conductance and nitrate with discharge and with each other.*

Results

Table 1 summarizes the results of the correlation and trend analyses. Figure 5 illustrates the relationship of specific conductance to discharge in the springs for which there was sufficient data.

Trends of Specific Conductance with Discharge

For the most part, there is an expected negative correlation and trend between discharge and specific conductance. This pattern is consistent with the relationship identified by Bassett and Ruhe (1973). The cluster of springs in the middle Suwannee River (Figure 5) that showed positive trends can be explained by the proximity of the springs to several large farms that irrigate with Floridan aquifer water derived from the same horizon as the spring water.

Trends of Nitrate Concentrations with Discharge

Figure 6 depicts the trends of nitrate versus discharge in springs in the Suwannee River basin. With two exceptions (Table 1), the springs show either a positive trend or a non-significant relationship. This positive trend suggests that the sources of nitrate are related to surface water entering the limestone aquifer through swallets, siphons, or sinkholes that do not have associated streams, or drainage of riverine water from estavelles.

Model B (Figure 4) shows expected patterns of nitrate concentrations as a function of spring discharge. If the nitrate is stored in soil or rock, the Bassett and Ruhe pattern should appear. That is, nitrate should be slowly leached from the strata during low flow, but high discharge through conduits would be expected to dilute the nitrate. Conversely, rapid recharge of elevated nitrate surface water through a conduit or release of elevated nitrate riverine water stored in an estavelle should produce a trend with a positive slope.

Most of the springs had positive slope relationships between nitrate concentrations and discharge (Figure 6).

Correlation	Number of Springs		
	Positive Correlation	No Significant Correlation	Negative Correlation
Discharge v. nitrate	22	20	2
Discharge v. Sp. Conductance	9	17	20
Sp. Conductance v. Nitrate	21	25	6

Table 1. *Summary of correlations of discharge, nitrate, and specific conductivity.*

The two exceptions with negative slopes are located in an area of heavy irrigation and, apparently, high fertilizer use.

Figure 7 illustrates the positive trend relationship in a spring (Columbia Spring; Figure 1) that is known to be dominated by riverine recharge. Much of the water discharging from this spring enters the aquifer via a siphon on the Santa Fe River just upstream from the spring (Butt et al., 2007). In this system, discharge from the spring increases as stage in the river rises, so the nitrate concentrations reflect conditions in the river.

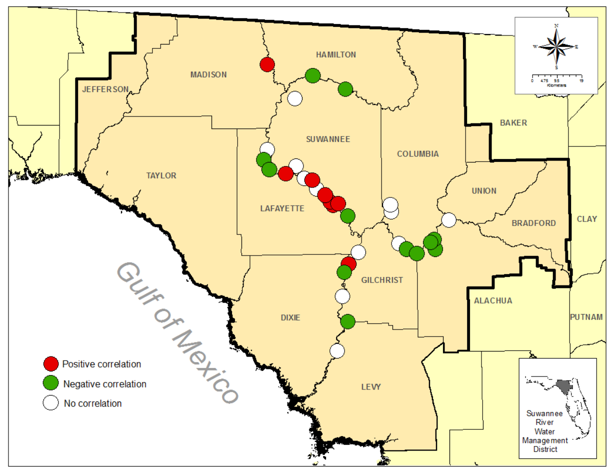

Figure 5. *Trends of specific conductance versus discharge in springs of the Suwannee River system.*

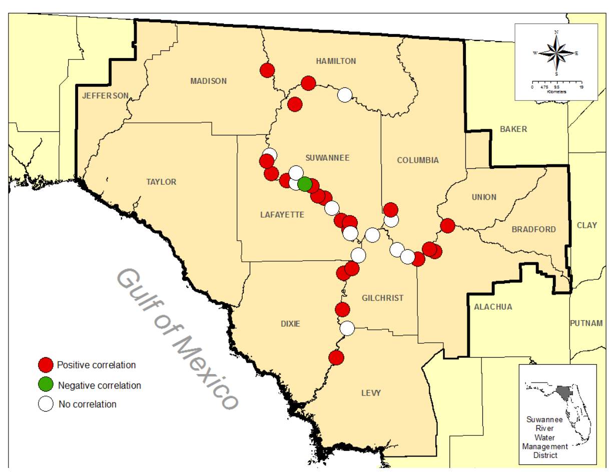

Figure 6. *Trends of nitrate (NO_3^- + NO_2^-) versus discharge in springs of the Suwannee River basin.*

Trends of Specific Conductance Compared to Nitrate Concentrations

When nitrate concentrations are compared to specific conductance through time, there is an interesting pattern (Table 1) of significant correlations. Figure 8 shows the distribution nitrate and specific conductance trends in the springs. According to the hypotheses (Figure 4C), those springs with statistically significant, positive correlations (red dots on Figure 8) should reflect concurrent flushing of pore water and nitrate during high discharge events. Almost half of the springs with statistically significant correlations (Table 1), showed this positive correlation between nitrate and specific conductance.

Figure 9 shows an example of the pattern of nitrate and specific conductance from a spring with a positive correlation between the analytes, and Figure 10 illustrates the behavior of these analytes through time. This spring, Ginnie Spring (Figure 1), is located in a resort with campgrounds and is down gradient from several dairies and other sources of nitrate. In this spring, elevated nitrate concentrations that are more-or-less synchronous with high specific conductance occur during low flow.

The low concentrations in late 2004 reflect a flood event in the adjacent Santa Fe River. In this case, low specific conductivity river water appears to have diluted the concentrations of groundwater discharging from the spring.

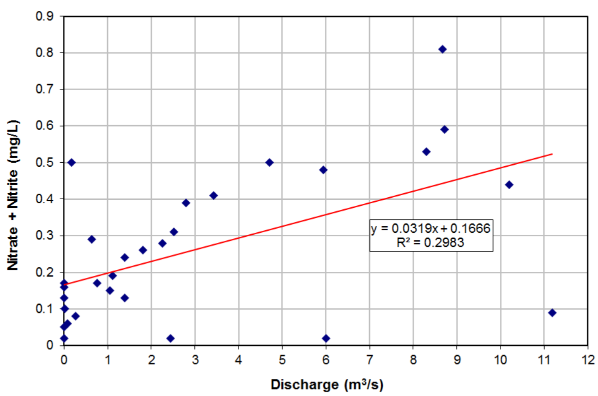

Figure 7. *Trends of nitrate (NO_3^- + NO_2^-) versus discharge in Columbia Spring, a known resurgence of the water derived from the Santa Fe River. The spring is located in Columbia County.*

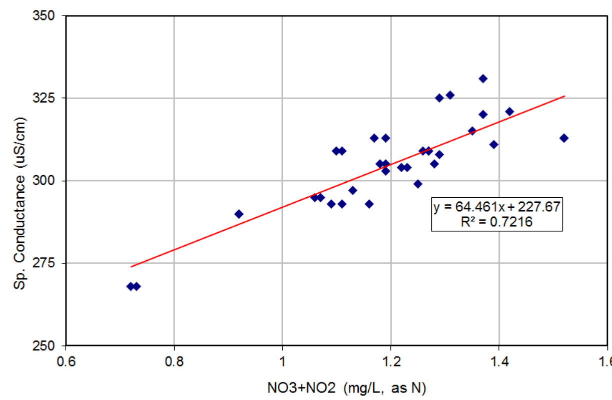

Figure 9. *Trends of nitrate (NO_3^- + NO_2^-) versus specific conductance in water discharging from Ginnie Springs, a second magnitude spring on the south side of the Santa Fe River in Gilchrist County.*

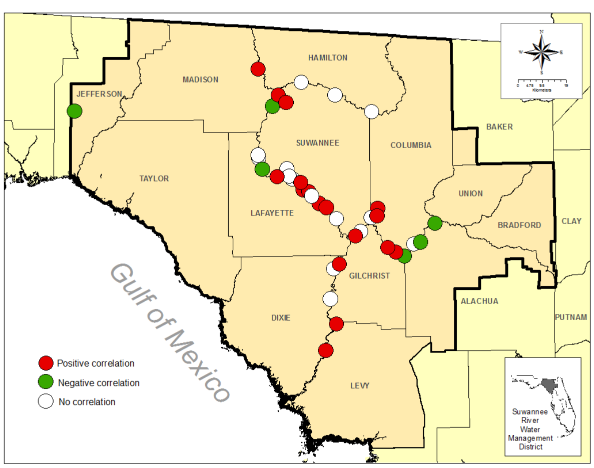

Figure 8. *Trends of nitrate (NO_3^- + NO_2^-) versus specific conductance in springs of the Suwannee River basin.*

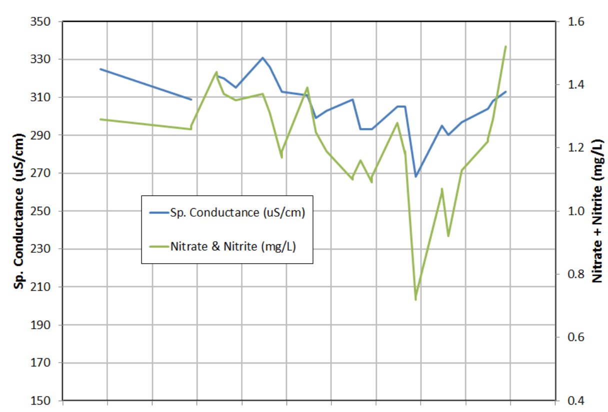

Figure 10. *Time series of nitrate and specific conductance at Ginnie Springs. Low concentrations of the analytes results during high discharge events.*

In contrast, those springs with negative correlations between nitrate and specific conductance reflect conduit flow (Figure 4C) and/or storage. Many of the springs with significant negative correlations have associated known swallets or siphons. In these springs, elevated nitrate discharge appears to reflect stormwater events within the springshed.

A few springs that exhibit negative correlations between specific conductance and nitrate do not have known swallets or siphons. One example is Poe Springs, a second magnitude spring located in a county park on the Santa Fe River in Alachua County. This spring (Figures 11 and 12) is located down gradient from farms with row crops and pasture land.

The negative correlation reflects episodes of discharge of low specific conductance, elevated nitrate water that correspond with flood events in the adjacent Santa Fe River (Figure 1) in 1998 and 2004. From this relationship with flooding, it appears that the low specific conductivity and elevated nitrate water (Figure 12) represents discharge of surface water stored in the aquifer during the flood. In other words, the data suggest that either Poe Springs is an estavelle or discharged water stored in the conduit system by a siphon located up gradient from the spring.

Summary and Conclusions

Investigation of the relationships between discharge, specific conductance, and nitrate in the springs of the Suwannee River basin suggests that the interactions of the aquifer flow system, adjacent rivers and streams, and diffuse versus conduit flow may strongly affect the patterns of nitrate release from springs. These data, which are derived from a doubly porous aquifer, clearly suggest that a simple assumption that nitrate is derived from a specific land use within the springshed may be erroneous.

Comparison of trends of time-series data allow for sorting out the myriad processes that affect spring discharge and water quality. In addition to measuring the discharge and water-quality parameters within a spring or spring run, it is advised that river discharge and stage relationships be considered and that inventories of swallets and siphons be included as part of a spring nitrate study.

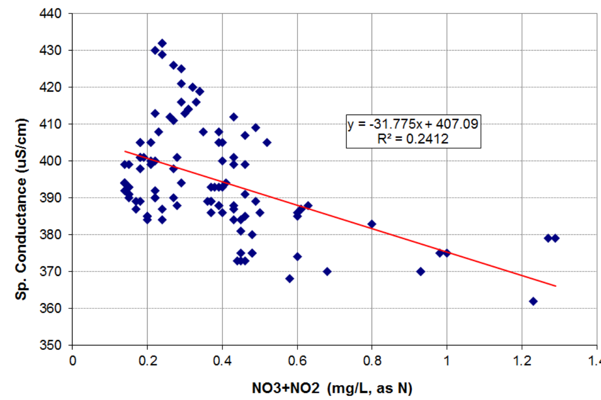

Figure 11. *Trends of nitrate ($NO_3^- + NO_2^-$) versus specific conductance in water discharging from Poe Springs, a second magnitude spring on the south side of the Santa Fe River in Alachua County.*

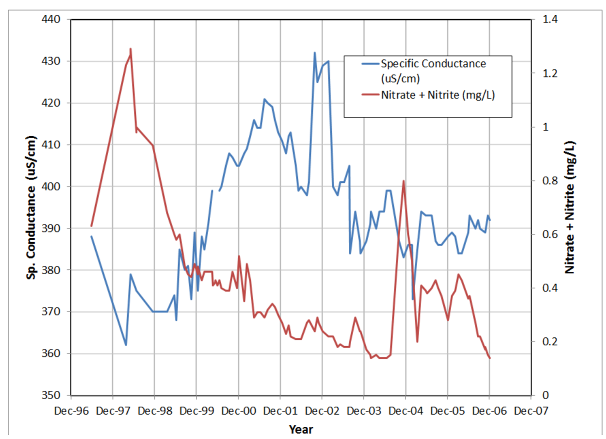

Figure 12. *Time series of nitrate and specific conductance at Poe Springs. Variations in the analytes reflect diffuse flow at low discharge and surface water inflows during high flows.*

References

Bassett JL, and RV Ruhe. 1973. Fluvial geomorphology in karst terrain. In: Morrisawa M, editor. Fluvial geomorphology. Binghamton, NY: State University of New York, p. 75-89.

Butt PL, Morris TL, and Skiles WC. 2007. Swallet/resurgence relationships on the lower Santa Fe River, Florida. High Springs (FL), Karst Environmental Services.

Florida Springs Task Force. 2000. Florida's springs: Strategies for protection & restoration. Tallahassee, Florida Department of Environmental Protection.

Harrington D, Maddox G, and Hicks R. 2010. Florida springs initiative monitoring network report and recognized sources of nitrate. Tallahassee, Florida Department of Environmental Protection, Bureau of Watershed Restoration, Ground Water Protection Section.

Hornsby D, Ceryak R. 1998. Springs of the Suwannee River Basin in Florida. Suwannee River Water Management District, WR99-02.
Katz BG, Hornsby HD. 1998. A preliminary assessment of sources of nitrate in spring waters, Suwannee River Basin, Florida. US Geological Survey Open File Report 98-0069.
Stevenson J, Pinowska A, Wang Y-K. 2004. Ecological condition of algae and nutrients in Florida springs. Florida Department of Environmental Protection, Tallahassee.
Upchurch, SB. 1992. Quality of waters in Florida's aquifers. In: Maddox GL, Lloyd JM, Scott TM, Upchurch SB, and Copeland R, editors. Florida Ground Water Quality Monitoring Program -- Volume 2, Background Hydrogeochemistry, Florida Geological Survey, Special Publication No. 34, Ch. IV, pp. 12-52, 64-84,90-347.
Upchurch SB, Chen J, Cain CR. 2007. Trends of nitrate concentrations in waters of the Suwannee River Water Management District, 2007. Live Oak (FL), Suwannee River Water Management District.
White W.B., 1988. Geomorphology and hydrology of karst terrains. New York (NY): Oxford University Press.