

**Hydrogeology of O'Leno State Park and Nitrate Loading from the River Rise, A First
Magnitude Spring**

**Comprehensive Project Report
DEP Agreement S0182**

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1 ABSTRACT

This document represents the Comprehensive Project Report for Springs Initiative project S0181. It includes data from that project, as well as data from previous projects S00060 and S0141. All three projects have two overall and complementary objectives, and thus this report attempts to integrate all of these data. The first objective is to determine the magnitude and mechanisms of surface and ground water mixing in the Sink-Rise system of the Santa Fe River in O'Leno State Park and River Rise State Preserve. The second objective builds on the first and is designed to determine sources of nutrients and magnitudes of nutrient loading to the Lower Santa Fe River. The implications of these studies are important for the Springs Initiative because recharge to the Upper Floridan Aquifer, and the water quality of the recharged water, will impact many springs located near the Cody Escarpment in north-central Florida.

When available, continuous discharge measurements at the River Sink and River Rise show that at high discharge more water flows into the River Sink than discharges from the River Rise. This water may be stored in the intergranular matrix porosity or fractures until released at low flow conditions, or where there is a shallow water table may recharge wetlands at the land surface. The magnitude of discharge allowing excess water to flow into the River Sink could not be determined because of discontinuous measure of water levels at the River Sink, which prevented determination of the discharge at the River Sink at intermediate stages of the river. Dye trace experiments which complimented the discharge measurements suggest that the rating curve may overestimate the magnitude of discharge from the River Rise by up to 50% at high flow conditions and by around 17% at low flow conditions. If less water discharges from the River Rise than indicated by the rating curve, excess water may flow into the River Sink at even lower stage than estimated by the available data. Travel time for dye to flow from the River Sink to the River Rise also confirms earlier measurements of travel times that are based on tracing temperature pulses along the flow path. Smooth breakthrough curves at the River Rise indicate a single conduit connects Sweetwater Lake to the River Rise.

Major element concentrations and Sr concentrations and isotope ratios are useful to separate water in the O'Leno State Park region into separate end members and to determine how these end members mix through time and with varying discharge conditions. The major element concentrations show that two types of ground water exist in the vicinity of O'Leno State Park, one with primarily a Ca-HCO₃ composition and the other with primarily a Ca-SO₄ composition. These two water types are separated geographically, but ground water compositions indicate they mix through time in the subsurface. The Ca-SO₄ end member is confined to the western portion

of O'Leno State Park but known conduits are located mostly in the eastern portion of the park. Mixing calculations indicate that at high flow conditions, water at the River Rise originates primarily from water flowing to the River Sink. At low flow conditions, however, water from the Ca-SO₄ and Ca-CO₃ ground water end members mix in variable proportions with water flowing into the River Sink. These mixing calculations indicate that water drains from the western region of the field area where there are few known conduits, as well as from the eastern edge of the field area where most conduits have been mapped. At high flow conditions, surface water is dominated by Na and Cl, which is likely derived from salts contained in rainwater that is derived from sea spray. Ground water in the region has Sr isotope ratios reflecting dissolution of Eocene aged carbonate or sulfate minerals. At high discharge conditions, surface water has Sr isotope ratios that are elevated above modern seawater value. These high values reflect flow from the Hawthorn Group and the confined regions above the Cody Escarpment.

Nutrient concentrations respond to variations in flow conditions differently than the major element concentrations and appear to have different sources and sinks from the major element concentrations. Water flowing from the confined portion of the aquifer has elevated PO₄ concentrations, most likely from interactions with the Hawthorn Group. The PO₄ concentrations do not correlate with flow suggesting a local source of PO₄ to the system that is not diluted by rain water. NO_x concentrations show a rough inverse correlation with flow, suggesting there is not a source of NO_x in water flowing off of the confined region, and reflecting a limited source of NO_x that is diluted as flow increases. As water flows from the River Sink to the River Rise, NO_x concentrations increase by up to nearly an order of magnitude while PO₄ concentrations decrease slightly by around 10%. The increase in NO_x concentrations could originate from oxidation of NH₃ which is elevated in the Ca-SO₄ ground water end member in the western portion of the region. The eastern conduits drain areas where improved pasture and row crops are the primary land uses and thus increased NO₄ concentrations could also originate from this source. Direct sampling of water in the eastern conduits would be needed to confirm this possible source. The decrease in PO₄ concentrations along the flow path may reflect adsorption of PO₄ by the carbonate minerals. The compositions and changes in concentration along the flow path are reflected in N/P ratios that decrease with discharge and are elevated at the River Rise over values at the River Sink. Most N/P molar ratios are lower than about 10, which suggest that N is the limiting nutrient in the system. Changes in river stage are closely tied to mixing of the surface and ground water as well as nutrient concentrations. To understand the processing of these nutrients along the Santa Fe River and the relationship with ground water at springs, it will be necessary to make high frequency measurements of NO_x and PO₄ at closely spaced locations along the river channel.

2 INTRODUCTION

2.1 Background

This report is the Comprehensive Project Report for DEP project S0181. Project S0181 is a continuation of two earlier Springs Initiative projects: DEP projects S0141 and DEP project S0060. Results from the first two projects have previously been presented in separate Comprehensive Project Reports for each project, but because of the similar nature of the three projects, data from all three are included and discussed in this report. Sampling for Project S0060 occurred between November 22, 2002 and May 31, 2003, and for Project S0141 between December 30, 2003 and May 31, 2004. Comprehensive Project Reports were submitted on December 23, 2003 and December 31, 2004 for Projects S0060 and S0141, respectively.

Project S0181 consists of three annual phases. Sampling and analysis for Phase I was initiated on December 1, 2004 and ran through June 30, 2005. Sampling and analysis for Phase II was initiated July 1, 2005 and ran through June 30, 2006. Sampling and analysis for phase III was initiated July 1, 2006 and ran through June 30, 2007. Phase III continued through December 31, 2007 to allow time for synthesis of the data collected and writing of this Comprehensive Project Report. Data from all three projects are included in appendices and data from all the projects have been used in construction of the figures for this report.

2.2 Project Objectives

There are two overall objectives of this and the earlier projects. The first objective can broadly be described as determining what influence mixing of surface and ground water has on

water quality along the Cody Escarpment (geomorphology of the region is described in Brooks, 1981), using the region of the Santa Fe River Sink-Rise as an extreme end member example of this mixing. The interaction between surface and ground water, both physical and chemical, is significant because of the high potential for contaminated surface water to recharge ground water in karst regions (e.g., Field, 1988; Field, 1993; Pretty et al., 2006). Depending on the type of storage of the recharged surface water, for example in conduits, fractures, or primary matrix porosity of the aquifer, ground water may be contaminated for variable periods of time (Katz et al., 1997; Martin and Dean, 2001; Martin and Sreaton, 2001). As described in detail below in section 2.4, the Santa Fe River Sink-Rise provides a good location to study the influence that surface water may have on ground water chemical compositions because there is a large amount of allogenic recharge of surface water into the subsurface (i.e. direct recharge into the River Sink), providing for a highly dynamic system, with significant amount of variation in flow and water quality (e.g., Hunn and Slack, 1983). In addition, autogenic recharge (i.e. diffuse recharge through the overlying soil and epikarst (Jones et al., 2004) is also important in the region because of a lack of a confining unit (Scott, 1988). The variable amounts of allogenic and autogenic recharge means that the relationship between precipitation, runoff and recharge may also be important to the hydrology and hydrogeology of the region and could influence water quality. Consequently, this portion of the study also focuses on precipitation and runoff records.

The second objective of these projects was to monitor nitrate and phosphate loading to the lower Santa Fe River from discharge at the Santa Fe River Rise. The Santa Fe River Rise was recently classified as a first magnitude spring by the Florida Geological Survey (Scott et al., 2002), and thus the water quality of this spring has direct implications to goals of the Springs Initiative. Nitrate has been identified as a major pollutant of concern in north-central Florida (Katz, 2004; Katz et al., 2001; Katz et al., 1999; Mytyk and Delfino, 2004) and nitrate concentrations could be closely related to land use (Lamsal et al., 2006; Schlesinger et al., 2006). There are long term records of increasing nitrate concentrations in springs around Florida and these changes correspond with increased growth of algae in the spring systems. Although these two changes in spring water chemistry and ecosystems correspond in time, because of the complex nature of ecosystems, it is not clear that they are directly related, or if they are related, what the connections may be. For example, other nutrients, such as phosphorous, should also play a role in the ecosystems of the springs, or oxygen concentrations in the water may control

the types of algal grazers. The goals of this work are not to link nutrient concentrations with ecosystem functioning, but rather to provide a time-series record of the absolute concentrations, as well as relative differences in concentrations of phosphorous and nitrogen at the Santa Fe River Sink Rise, and through the first objective to link temporal changes in concentrations with changes in flow.

2.3 Karst Hydrogeology and Relationship to North Central Florida

Conservation and wise use of water resources of karst aquifers, and the relationship between the water quality of the ground water and spring discharge, require characterization of the flow and storage properties of the conduits, fractures, and intergranular matrix porosity, physical coupling between these three components, and the chemical reactions between water and aquifer rocks (Sauter, 1992; Sauter, 1994; Smart and Ford, 1986b; White, 1999; White, 2002; Worthington, 1999; Worthington et al., 2000). Understanding of the coupling between these components has been improved through extensive observations and developments of deterministic and stochastic models of the aquifers, which have realized great advances recently through increased computational abilities (e.g., Palmer et al., 1999, and references therein).

Commonly, numerical and conceptual models of karst aquifers are based on European and Appalachian aquifers which have conduits embedded in a matrix with a network of fine fractures but with otherwise low intergranular porosity (e.g., White, 1988; Ford and Williams, 2007). These aquifers have been labeled “telogenetic” aquifers by Vacher and Mylroie (2002). Understanding is less advanced for karst aquifers that retain high intergranular porosity, termed “eogenetic” karst by Vacher and Mylroie (2002), where spongework and ramiform cave systems dominate (Palmer, 1991), and which is exemplified by the Floridan Aquifer of north-central Florida (e.g., Martin et al., 2002). Although both telogenetic and eogenetic aquifers have low storage and rapid, turbulent flow within conduits and large fractures, eogenetic aquifers are characterized by high storage coupled with large magnitude of diffuse, laminar flow in the matrix porosity. The high storativity coupled with large amounts of flow through the matrix porosity is important because of the potential for contamination of this commonly used water resource (Boyer and Pasquarell, 1995; Field, 1988; Vaute et al., 1997; Zuber and Motyka, 1994). Chemical composition and residence time of matrix water also effects karstification,

speleogenesis, evolution of the aquifer, and engineering problems such as sinkhole formation (Beck, 1986; Dreybrodt, 1981; Dreybrodt, 1988; Gabrovsek et al., 2004; Romanov et al., 2003).

Similar to residence time of water, the residence times of nutrients, including nitrate and phosphate, will depend on where it is stored within the aquifer (e.g. within conduits, fractures, or matrix porosity). The residence time should vary widely depending if water flows rapidly from the surface through conduits to the spring, if water infiltrates and flows through fracture systems, or if water flows primarily within porous matrix of the aquifer rocks (Martin and Screaton, 2001). Residence time should influence the concentrations of nitrate at springs because of its reactivity, for example, denitrification reactions may reduce nitrate concentrations if there are sufficient electron donors present in the subsurface (e.g. Schlesinger et al., 2006). Concentrations of nitrate, and changes of the concentrations with time, is thus likely to differ greatly between eogenetic and telogenetic karst systems. Residence time could also be important to phosphate concentrations because phosphate reacts with carbonate minerals, which thus may reduce its concentrations in the ground water (von Wandruszka, 2006). Other processes affecting the phosphate concentrations include reaction with ferric iron and thus any dissolved iron in the ground water could extract phosphate from the water (e.g. Hyacinthe and Van Cappellen, 2004). Because much work in karst systems has been done on telogenetic karst with much less work on eogenetic carbonates, it is important to provide primary observations of both flow and nutrient concentrations of the Floridan Aquifer as is one of the objective of the projects described here.

The rate of exchange of surface and ground water will also influence the rate of change for water quality of the spring discharge. The vulnerability of springs to water quality changes, and the rate that surface and ground water exchange, will determine the techniques that are needed to modify or moderate contaminants in spring discharge. Although this project does not directly describe techniques aimed at remediation, an understanding of how a system functions is required for remediation, and this understanding of dynamic systems, such as karst, comes from long time-scale observations of the system. For example, considering two end member situations, contaminants that enter intergranular porosity of the aquifer, through diffuse recharge through the soil layer and epikarst, will discharge at springs over long periods of time. In contrast, water that flows directly into sinkholes and rapidly through conduits to discharge points at springs will have a rapid impact on water quality of springs. The magnitude of the autogenic and allogenic recharge is thus critical to their impacts on contaminant delivery to the springs.

Contaminants in matrix porosity may have a long-term impact on water quality of springs, but their concentrations may be moderated by interactions with the aquifer material or through dilution by water in the aquifer. Contaminants introduced to conduit systems will have a rapid impact and rapidly be flushed from the system, but their concentrations may not be greatly altered by interactions with aquifer rocks. These two mechanisms for the introduction of contaminants to spring discharge will require distinctly different management and remediation protocols.

2.4 Brief Description of Field Area

Field work for studies of the two primary objectives of this project requires a location where there is good information about the hydrologic and hydrogeologic systems, clearly defined conduits, and favorable sites for comprehensive sampling of both conduits and ground water. An ideal site for this type of work occurs along a short stretch of the Santa Fe River in O'Leno State Park where the river completely sinks into the subsurface and returns to the surface about 6 km to the south.

2.4.1 Field Site and Geological Setting

The Floridan Aquifer is the primary aquifer in the Santa Fe River Sink-Rise area and is composed of Oligocene and Eocene carbonate rocks. The Floridan Aquifer extends across the entire Florida platform and northward into Alabama, Georgia, and South Carolina. On northern peninsular Florida, the aquifer is confined to the northeast by Miocene and younger mixed siliciclastic and carbonate rocks of the Hawthorn Group (Miller, 1986; Scott, 1988), but is unconfined to the west where these rocks have been removed by erosion (Figure 2-1). The erosional edge forms the boundary between the confined and unconfined Floridan aquifer and is referred to as the Cody Escarpment (Brooks, 1981). Surface water is common to the northeast of the scarp where the Hawthorn Group confines the Floridan Aquifer. As exemplified by the Santa Fe River Sink-Rise system, most water flowing off of the eastern highlands sinks into the subsurface and consequently, surface water is missing in the unconfined area to the southwest. Among all streams flowing across the Cody Escarpment, only the Suwannee River does not completely sink into the subsurface, although it does become a losing stream as it crosses the

escarpment. This sinking water has a major impact on the ground water chemistry in the region (Upchurch and Lawrence, 1984).

As the Santa Fe River crosses the Cody Escarpment, it flows into a 36 m deep sinkhole at the River Sink and re-emerges at the River Rise approximately 6 km south of the River Sink (Figure 2-2). Numerous karst windows, mostly large sinkholes, exist between the River Sink and River Rise. A variety of techniques, including injected tracers (Hisert, 1994); natural chemical and physical tracers (Martin and Dean, 1999; Martin and Dean, 2001; Martin et al., 2006; Sreaton et al., 2004a), and cave dive exploration (M. Poucher, pers. comm., 2005) have shown that most of these karst windows are connected to extensive conduit development in the system. The cross sectional area of the conduits has been modeled to be as large as 280 m² (Sreaton et al., 2004b).

Many lines of evidence indicate that the River Sink is not the sole source of water for the River Rise. Discharge at the River Rise has been found at times to be greater than the volume of water flowing into the River Sink (Sreaton et al., 2004a). Cave dive exploration has shown that a conduit, sufficiently large to swim through, enters the region for sinkholes located east of the Park (Figure 2-1). Unlike the River Sink, this eastern conduit system is not connected to perennial surface streams. It most likely represents a drain for water stored in matrix porosity and fractures located east of the main conduit system during dry periods, but it also could accept surface water runoff during storms. Although the boundaries of the system are fairly well constrained, all sources of water to the River Rise are not known for certain. In addition, the time variations are unknown for contributions from the various sources, including the River Sink, from surface infiltration, from the eastern conduit, as well as from deep within the stratigraphic sections (e.g., Jones et al., 1993)

2.4.2 Preliminary Hydrologic Studies

Mixing of surface and ground water across the Cody Escarpment has previously been demonstrated through observations of discharge at the River Rise (Skirvin, 1962), and with variations in chemical composition of water sources (Hunn and Slack, 1983; Upchurch and Lawrence, 1984). Streams flowing across the unconfined portion of the Floridan Aquifer tend to have higher concentrations of Ca, Mg, and HCO₃, and less tannic acid, than the streams flowing across the confined aquifer (Hunn and Slack, 1983). These differences in water chemistry reflect

a source of water from ground water that has equilibrated with the limestone of the Floridan Aquifer in the unconfined region, or surface water that has interacted with soils in the confined region. The composition of the surface water, particularly its saturation state with respect to carbonate minerals is important because it influences the distribution of karst features such as sinkholes (Upchurch and Lawrence, 1984). In one of the earliest studies to focus on the Santa Fe River as it flows through O'Leno State Park, Skirvin (1962) used tannic coloring of water to estimate the underground flow path of the river. Although the tannic color of the water at the River Rise suggested that much of the water flowing into the River Sink discharged from the River Rise, Skirvin (1962) noted that water continued to discharge from the River Rise even after the river was dammed above the River Sink during the construction of Interstate 75. These observations indicated that the Santa Fe River Rise discharges both surface water from the River Sink, but also acts as an important drain for ground water in the region. Except for the early work of Skirvin (1962), the control of variations in river discharge on the mixing between surface and ground water has not been thoroughly quantified (Martin and Dean, 2001).

2.4.3 Travel times

Travel times have been measured for water flowing through the conduits using both natural tracers and two injected tracer tests. The injected tracer used was SF₆, a highly insoluble gas (Hisert, 1994). The gas was injected into the River Sink, connecting the Sink to seven intermediate karst windows and Sweetwater Lake, but in this injection no gas was detected at the River Rise. Because of the lack of return of gas to the River Rise, a second injection of gas was made into Sweetwater Lake, which was connected to the River Rise. Both injections reflected flow velocities of several kilometers per day, but these velocities must be considered approximate because the injection occurred over a period of two hours, ending with a slug of tracer. These tracer results led Hisert (1994) to suggest that a single conduit exists between the River Sink and Jim's Sink, a karst window intermediate between the River Sink and River Rise, and two or more conduits exist between Jim's Sink and the River Rise. Subsequent cave dive exploration has confirmed multiple conduits north of Sweetwater Lake, but only a single conduit has been found so far in cave dive exploration between the River Rise and Sweetwater Lake (Figure 2-1).

Travel times that were measured using the injected gas have been confirmed using temperature of the water as a natural tracer. Dean (1999) was able to correlate measured temperature variations at the River Sink, Sweetwater Lake, and the River Rise and from the lag in arrival times for the fluctuations, was able to estimate the flow rate of the water (see also Martin and Dean, 1999; Martin and Dean, 2001; Sreaton et al., 2004a). Temperature tracing of flow rates provided a significantly higher temporal resolution than using injected tracers and showed that water flowed from the Sink to the Rise in about 30 hours at the highest river stage measured (~15 m above sea level at the River Sink), but flow required more than seven days at the lowest river stage measured (~10 m above sea level at the River Sink).

2.4.4 Exchange of conduit and matrix water

Comparison of discharge at the Sink with discharge at the Rise indicates that there are periods when more water flows into the River Sink than out of the River Rise, and suggests that some of this water may be stored in the aquifer prior to discharge to the surface. Because there is no permanent monitoring of discharge from the River Rise, however, comparisons of flow to the River Sink and from the River Rise have previously been made only during specific studies. For example, Hisert (1994) showed that flow into the River Sink was 31.3 m³/s but only 27.4 m³/s discharged from the River Rise at the time his SF₆ tracer experiment. Combining discharge estimates and flow rates based on temperature data, Sreaton et al. (2004a) was able to show that the relative discharge of the River Sink and River Rise depends on the flow conditions and that the amount of discharge from the River Rise typically exceeds discharge to the River Sink except during periods of high flow.

Hydraulic head in monitoring wells located tens of meters from the conduits are typically higher than heads in the conduit during low flow, but this gradient can reverse during high flow (Martin, 2003; Martin et al., 2006). During high flow, hydraulic head in the conduits are greater than heads in the monitoring wells, suggesting that water flows from the conduits to the surrounding matrix rocks due to the head gradient from the conduits into the porous matrix. Flow could be into primary porosity, fractures, and other conduits that might be located above the water table, and water could recharge wetlands if the water table rises to elevations above the land surface. As the hydraulic head in the conduits decreases when the river stage drops, water stored in the matrix would be expected to flow to the conduits and thus to the River Rise. One

dimensional model simulations of water flow into and out of the matrix following a storm pulse have been made using estimated hydraulic conductivity of the Floridan aquifer in the region and measured head gradients between the conduit and monitoring wells (Martin et al., 2006). These models suggest migration distances of ~0.45 and 8.5 m into the matrix with residence times in the matrix ranging between 19 and 21 days. Because these estimated travel distances and residence times are based on bulk hydraulic conductivity estimates, they are likely to underestimate zones of high permeability if there are large conduits and/or fractures that could deliver water from the major conduits into the matrix porosity.

Additional evidence that water may flow from conduits to the matrix during floods comes from the chemical composition of a water supply well located approximately 2 km down the hydraulic gradient from the conduit (Martin and Dean, 2001). Concentrations of conservative solutes (Cl, Na, and SO₄) were found to decrease in water from this well over a six month period following a major flooding event of the river. The decreases in concentrations are linear with time and approach the concentration of these solutes in the conduit at the time of the flood. Martin and Dean (2001) interpreted these changes in composition to reflect dilution of well water by water that flowed from the conduit following the flood, and if true, the observation suggests that conduit water may travel farther away from the source than indicated by the modeling results of Martin (2006). The dilution observed at the monitoring well could be a result from input of water from other sources, however, including other conduits or from infiltration through the soil and epikarst. In contrast to the decrease in the concentrations of conservative solutes, both the Ca concentrations and saturation state of the well water with respect to calcite varied little with time (Martin and Dean, 2001). This observation suggests that regardless of the source of the diluting water, calcite dissolved as water flowed along the flow path or mixed with water at equilibrium with respect to calcite.

2.5 Summary

The following report presents new and compiled data from throughout the Santa Fe River Sink-Rise system. These data are used to assess the nature of flow of water through system as the Upper Santa Fe River flows underground and re-emerges on the surface as the Lower Santa Fe River. In particular, the data reflect how chemical compositions may be used to help determine the movement of water in the system. The data include discharge variations through

time at the Sink and Rise, chemical compositions of major dissolved components and Sr isotope ratios in the water throughout the system, concentrations of various nitrogen and phosphorous species in the water, and the results of two injected dye traces. The report is divided into a methods chapter (Chapter 3), which describes field and analytical techniques and any problems associated with the techniques. The subsequent chapter (Chapter 4) addresses directly the flow objective of the study and the next chapter (Chapter 5) addresses the chemical analyses made on samples collected in the field area. Because the chemical compositions can be used to address both objectives of the project, namely the flow through the system and the nutrient distribution in time and space in the system, this chapter includes discussion of these two objectives. The final chapter attempts to summarize the entire project.

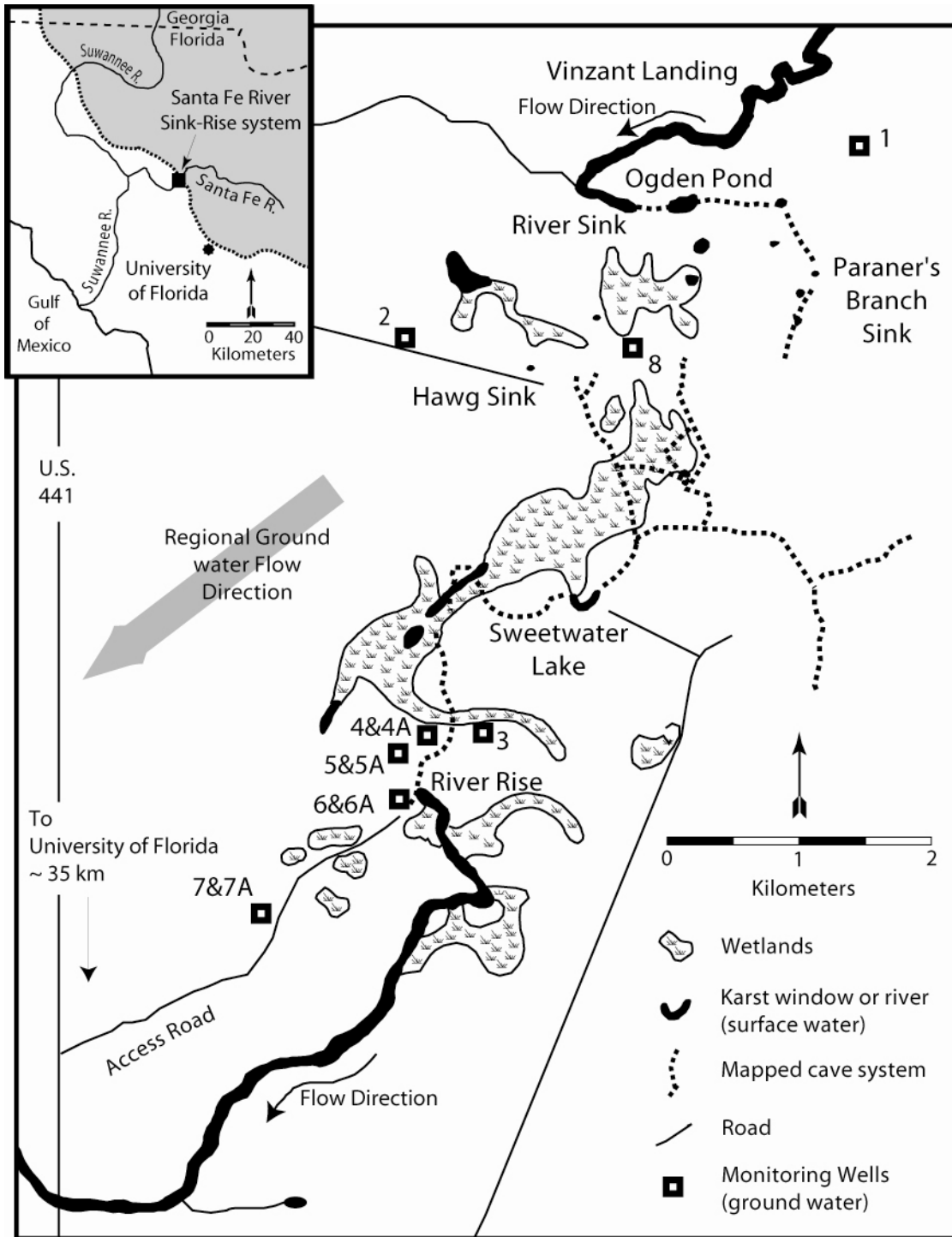
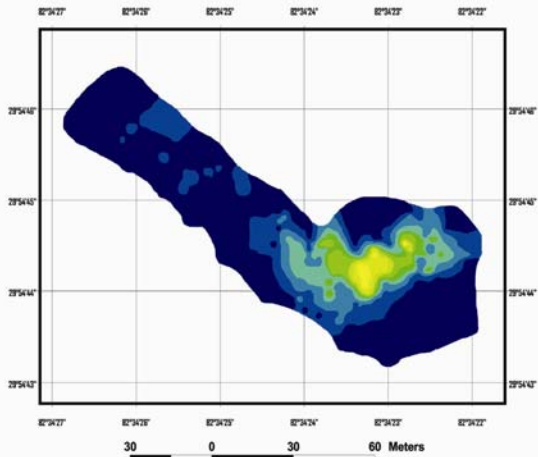
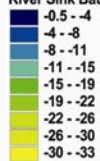


Figure 2-1. Location of sampling points for chemical studies and dye tracing. The small inset map shows the relationship between the field area and the location of the Cody Escarpment, i.e. the division between confined and unconfined Floridan Aquifer.

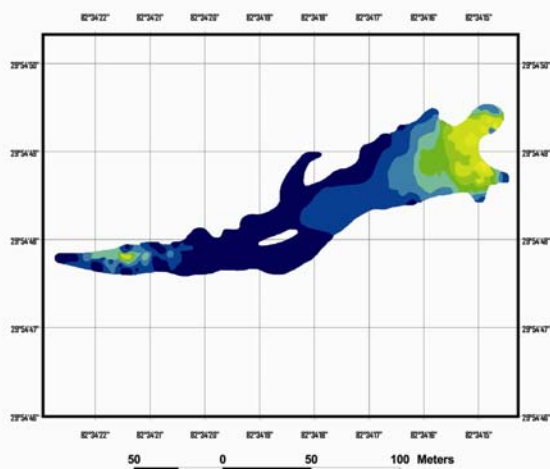


River Sink Bathymetric Contours

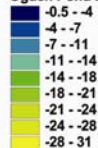


Bathymetric contours collected on 01/25/2006.
Santa Fe River stage at O'Leno State Park
was 10.80 meters above sea level.

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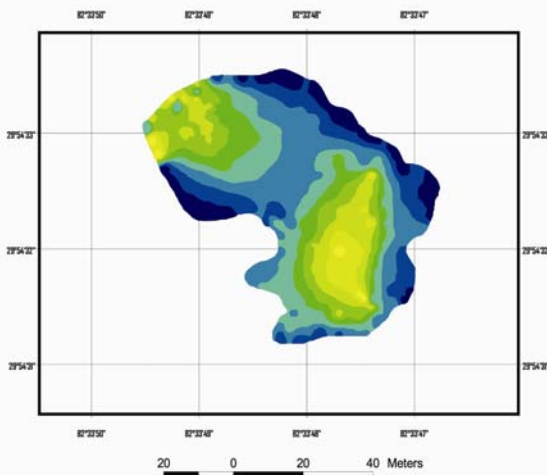


Ogden Pond Bathymetric Contours

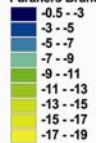


Bathymetric contours collected on 01/25/2006.
Santa Fe River stage at O'Leno State Park
was 10.80 meters above sea level.

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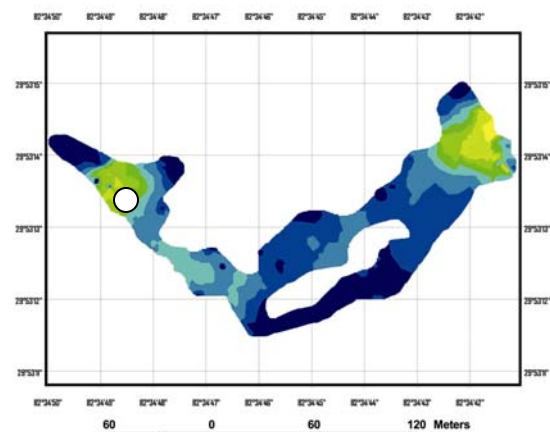


Paroners Branch Bathymetric Contours

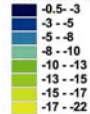


Bathymetric contours collected on 01/25/2006.
Santa Fe River stage at O'Leno State Park
was 10.80 meters above sea level.

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Sweetwater Lake Bathymetric Contours



Bathymetric contours collected on 03/09/2005.
Santa Fe River stage at Hwy. 441 near High Springs, FL was 9.99 meters above sea level.

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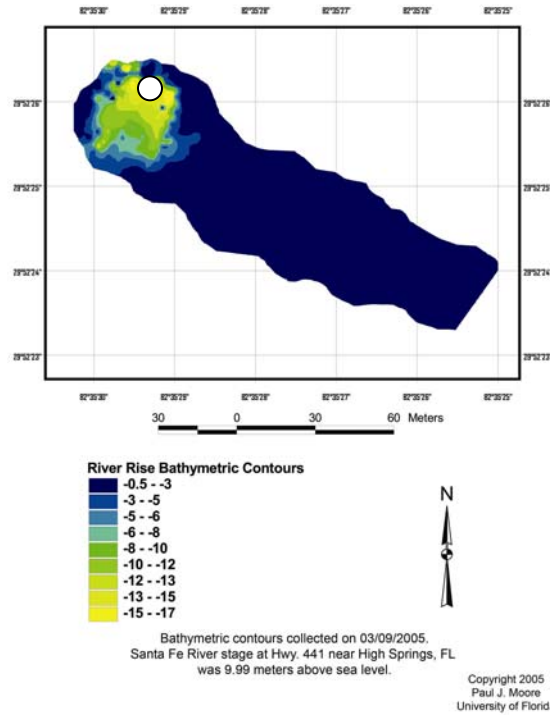


Figure 2-2. Bathymetry of the River Sink (upper left), River Rise (bottom) and intervening sinkholes from upper left to lower right: Ogden Pond, Paraner’s Branch, and Sweetwater Lake. Contour interval in meters. The white dot at Sweetwater Lake and the River Rise represent the location of the dye injection and dye monitoring stations, respectively. Note that each map has a distinct scale.

3 METHODS

3.1 Introduction

Field and analytical work for this project included installation of monitoring wells, sampling water for chemical analyses from surface water locations and the newly installed monitoring wells, measuring field parameters during sampling, monitoring water levels at the River Rise, collating data of water levels and precipitation at the River Sink, two dye trace studies, and laboratory analyses of chemical composition and isotopic ratios of selected dissolved components of the sampled water. Daily precipitation data was collected from within the Park using an automatic rain gauge monitored by the Suwannee River Water Management District (SRWMD), and water level at the River Sink were measured at the swinging bridge approximately 500 m upstream from the River Sink by park personnel. Water level at the River Rise was collected using an automatic pressure transducer initially installed during Project S0060. Field parameters measured during sampling included temperature (T), pH, specific conductance (SpC), dissolved oxygen (DO), and turbidity. Subsequent laboratory measurements of the water samples include Na, K, Ca, Mg, Cl, SO₄, NO₂, NO₂+NO₃, NH₃, total Kjeldahl nitrogen (TKN), total phosphorus (TP), orthophosphorus (OP), alkalinity, and silica concentrations of all samples. Selected samples were measured for their Sr concentrations and ⁸⁷Sr/⁸⁶Sr isotope ratios.

3.2 Compiled and Measured Flow and Rainfall Data

Data related to flow and rainfall through O'Leno State Park has been measured as part of this project and has been compiled from various sources. Daily precipitation data was collected in the park using an automated rain gauge maintained by SWRMD and water levels at the River Sink were measured by park personnel at the swinging bridge approximately 500 m upstream from the River Sink. The staff gage at this location is not continuous across all ranges of river stage, so some water elevations, primarily at intermediate stages of the river, are missing from this record. Stage information upstream from the River Sink has been converted to discharge based on a rating curve provided by the Suwannee River Water Management District.

In addition to the River Sink stage provided to this project by park personnel, continuous water levels have been monitored at the River Rise since August 2001 using an automatic Van Essen CTD Diver pressure transducer (accuracy of ± 0.03 m) installed approximately 200 m downstream from the River Rise at a location that provides a secure location for the transducer and, at the request of park personnel, minimizes its impact on park visitors. The pressure transducer is placed in a stilling well constructed of 2-inch diameter polyvinylchloride (PVC) pipe and securely fastened to a large tree on the side of the river. The level of the transducer is referenced to a benchmark installed at the River Rise by the Suwannee River Water Management District. The water levels are recorded in 10 minute intervals and are downloaded approximately monthly to bimonthly. During each download, water levels are measured from a staff gage at the River Rise and are compared with the measured water levels. River stage at the River Rise is converted to discharge based on a rating curve provided by the Suwannee River Water Management District. In addition to the pressure transducer, a SRWMD gauging station located at the Highway 441 bridge, approximately 2 miles downstream from the River Rise, was used to supplement water level data collected at the River Rise.

3.3 Construction of Monitoring Wells

Twelve monitoring wells were constructed and their water chemistry was sampled during this project. Four of the monitoring well sites consist of two nested wells. Within the well nests, the deep wells were drilled and screened (20 ft, 250 μ m PVC screening material) to depths of 100 ft below the land surface, or approximately at the depth of the conduits. The shallow wells were constructed in a similar manner, but have only 10 ft of screening that extends across the

water table. All wells are constructed from 2 inch diameter PVC casing that extends to the screened interval at the base of the well. Construction of the wells included a sand pack filling the well annulus surrounding the screening, with several feet of bentonite above the sand pack, and cement to the surface.

The wells became available for sampling sequentially as they were drilled: Wells 1, 2 and 7 were first sampled February 2003, Wells 3, 4, and 6 were first sampled March 2003, Well 5 was first sampled January 2004, Well 8 was first sampled May 2004 and the four shallow wells within the well nests (Wells 4A, 5A, 6A, and 7A) were first sampled July 2006. Six of the deep wells (Wells 1, 2, 3, 4, 6, and 7; Figure 2-1) and all of the shallow wells were drilled and completed by a commercial well drilling company (Clyatt Well Drilling). The other two wells (Wells 5 and 8) were drilled and continuously cored by the Florida Geological Survey as part of their study of the stratigraphy of peninsular Florida. Information about the wells is included in Table 3-1.

3.4 Water Sampling

3.4.1 Sampling Frequency and Techniques

Sampling for Project S0181 occurred at quarterly intervals for the surface waters and wells as they became available, but during Projects S0060 and S0141, the sampling was compressed into shorter intervals during the winter and spring, with long gaps between the sampling intervals (Figure 3-1 and Table 3-2). Sites that were sampled during the quarterly sampling event included six surface water sites and all of the monitoring wells that were available at the time of sampling. Two sets of samples were collected at higher frequency from wells 3, 4, 5, 6, 7 and from the River Rise. One of these sets of samples was collected during Project S0141 in April and May 2004 and the second set was collected during Project S0182 in April and May 2005 (Table 3-3). In 2004, samples were collected at a rate of approximately 2 to 3 sampling events per week. In 2005, samples were collected at a rate of approximately 1 to 2 sampling events per week. One of the quarterly sampling events occurred during the high resolution sampling event in 2004 (e.g. compare Table 3-2 and Table 3-3) and are included in analyses of both the quarterly sampling events and the high resolution events.

The timing of the quarterly sampling of all sites is listed in Table 3-2. To sample all of the sites usually required two days in the field, although if bad weather was encountered, more than two days were required. Occasionally all sites could be sampled in a single day. Previous work has shown that the time required for water to flow from the River Sink to the River Rise varies from a little more than a day to more than 10 days depending on river stage (Martin and Dean, 2001; Screamon et al., 2004b). The sampling strategy used for this study thus did not allow collection of a single parcel of water as it flowed from the River Sink to the River Rise. During most of the sampling times, the river stage was low with long travel times. During low flow conditions and slow flow rates, chemistry of water at any one location along the flow path shows little variation through time (Martin and Dean, 2001) and thus variations in composition of the samples is unlikely to result from the delay in sampling water along the flow path. Information provided by the long-term sampling events should be useful for assessment of the water quality of surface and ground water throughout the park and any gradual changes in water quality through time.

The high resolution sampling sites include wells 3, 4, 5, 6, and 7, which are located in a line that trends approximately perpendicular to the orientation of the conduit that is the source of the River Rise (Figure 2-1). High resolution samples were collected once during Project S0141 and once during Project S0182. The high resolution sampling was designed to observe changes in composition of the water during the recession limb of the hydrograph (e.g. Hess and White, 1988; Ryan and Meiman, 1996; Shuster and White, 1971; Shuster and White, 1972). Although no major floods occurred during the time available for sampling, the discharge was very different during the two sampling events. During the first high resolution sampling event, discharge at the River Sink averaged around 5 m³/sec, nearly an order of magnitude lower than discharge during the second high resolution sampling event (Table 3-3). During the second high-resolution sampling event, the discharge at the River Rise decreased from around 69 m³/sec to 32 m³/sec during the tail of the recession limb of a minor increase in discharge (Table 3-3).

General quality assurance procedures included regular collection of duplicates and field blanks. Duplicates were collected from one well and one surface water site during each of the quarterly sampling events. Duplicates were collected from one of the wells sampled during each of the high frequency sampling events. Field blanks were collected at the end of each day of sampling by passing deionized water (18 Mohm) through all of the equipment (e.g. pumps and

tubing) used to sample the wells and a surface water sites. The distilled water was brought to the field in 20 L Nalgene polyethylene jugs which are used only to carry distilled water. Collection tubing was never inserted into the jugs. The distilled water blanks were collected and preserved in identical sample bottles as those used to collect the samples.

3.4.2 Surface Water

Surface water was collected from several locations including the River Sink and River Rise and selected karst windows that include from north to south, Ogden Pond, Hawg Sink, Paraner's Branch, and Sweetwater Lake (Figure 2-2). These karst windows were selected for sampling because prior results of dye tracing and chemical analyses suggested they represent sites that are connected to the main conduit connecting the River Sink and River Rise.

Surface water samples were collected from the shore using a 12-V variable-speed peristaltic pump (Geotech Geopump 2) connected to a small 12-V automobile battery and PVC tubing. The tubing was attached to floats and the floats were pushed offshore using 1/2" threaded PVC piping. The end of the tubing was weighted so that it hung below the floats approximately 0.5 ft below the surface of the water. Once the tubing was located at the correct sampling location and depth, typically close to spring boils when visible, or in the deepest part of the sinkhole if no boil was present, water was pumped onshore into a free-flow cell constructed of a 500 ml PVC bottle. The tube was attached to the base of the container with a barbed PVC fitting and allowed to fill from the bottom of the container to overflowing. Prior to recording the values of the field parameters and collecting and preserving the samples, the entire system was flushed with at least 2 L of ambient water, which represents in excess of 4 times the tubing volume. Following flushing, calibrated field meter probes were placed into the free-flow cell, allowed to stabilize, and the values were recorded for various field parameters including SpC, pH, DO, and T. Samples were preserved in a variety of containers. These samples were transferred into the containers by removing the tubing from the base of the free flow cell and allowing water to flow directly into the sampling containers from the end of the tubing. Each container and its top were rinsed with the sample water at least three times prior to the final filling of the container. The end of the tubing was never inserted into the bottles and the bottles were not completely filled to provide room for the addition of preservatives.

Water samples for analyses of Sr isotope ratios were collected in 30 ml HDPE Nalgene bottles. All other samples were collected in polyethylene bottles ranging in size from 125 ml to 1L. Samples for the OP analyses were filtered in the field using 0.45 μm pore size Geotech engineering dispos-a-filters. These filters are certified to be free of 48 different metals. The filters were flushed and completely filled with the sample water prior to filling the sample bottles. A new filter was used at each sample site. The $\text{NO}_3 + \text{NO}_2$, NH_3 , TP, and TKN samples were acidified with measured volumes of sulfuric acid to a pH value of < 2 . The sample for the total metals was acidified with nitric acid to a pH value of < 2 . Concentrated acid was transferred into the samples using a graduated transfer pipette and the volume of acid added to the samples was recorded. After adding the acid, the bottles were gently shaken to distribute the acid within the bottle. The pH of all the acidified samples was tested by pouring a small aliquot of the acidified sample from the bottle onto thin strips of small-range pH paper and comparing the color change to the color chart on the package of pH paper. All samples were stored in zip-lock plastic bags on wet ice in a cooler until they were delivered to the laboratory, where they were stored in a refrigerator at $\sim 4^\circ\text{C}$.

3.4.3 Ground Water

Ground water was sampled from the monitoring wells using a Grunfos Redi-flo2 2” variable-speed submersible pump. The pump was powered by a 5800W generator that was loaded in the back of the field vehicle. The weight of the generator prevented its removal from the vehicle and restrictions on off-road use of the vehicle in the park limited the distance that the generator could be located from the well heads. Use of a 100 ft extension cord allowed the generator to be located at least 75 ft from the well during sampling.

Prior to sampling each well, water level was measured and recorded. The pump was then set approximately three feet below the water level in the well. Water level was recorded at selected times during purging of the wells. The deep wells were purged at a rate of 1 to 1.5 gallons per minute until one well volume had been removed from the well. The shallow wells were purged at a rate of 0.5 gallons per minute until one well volume had been removed from the well. Following this initial purge of both the shallow and deep wells, field parameters of T, pH, SpC, DO, and turbidity, as well as the water level were measured approximately every 3 minutes until the values stabilized. The purge was considered complete once three consecutive

measurements remained within a specified criteria, specifically $\pm 0.2^{\circ}\text{C}$ for T, within ± 0.2 pH units for pH, $\pm 5.0\%$ for SpC. Further specified criteria are that DO does not exceed 20% of saturation at the field measured temperature, and turbidity does not exceeding 20 NTUs. Samples were collected once acceptable values were reached. Drawdown was also calculated by the change in the water levels. All wells experienced only minor amounts of drawdown, typically at most a few inches which occurred between the initiation of the purge and the first measurement of the water level during purging. Once drawdown was established during the initial purge, there was no further drawdown of the water levels at the rates the wells were pumped.

3.5 Analyses

3.5.1 Field Measurements

During projects S0060 and S0141, measurements of all field parameters were made using four separate field instruments. These instruments included an Orion portable pH meter Model #250A for measurement of pH values, an ATI Orion portable conductivity meter Model #130 for measurement of T and SpC, a YSI model 55 handheld dissolved oxygen meter for measurement of DO, and a LaMotte 2020 turbidimeter for measurement of turbidity. The pH and oxygen meters were calibrated in the field at the start of the sampling day and the calibration was verified during the day with a check standard, typically immediately prior to sampling each new site. The conductivity meter and turbidity meter were calibrated in the laboratory prior to each sampling trip according to the manufacturer's specification. The pH and oxygen meter were verified more frequently than conductivity and turbidity meter because they were found to have greater amount of instrumental drift. The turbidity and conductivity meters are stable through time. During project S0182 a YSI multiprobe model 556 was used to make field measurements of pH, T, SpC, and DO values. This probe was calibrated in the laboratory prior to the field trips and except for the DO value, calibration was checked several times while in the field. Because of drift in the DO measurement, this value was checked and calibrated prior to measurement at each sample site.

3.5.2 Laboratory Analyses

Concentrations of the major components (Na, K, Ca, Mg, Cl, and SO₄), nutrients (NO₂, NO₂+NO₃, NH₃, TKN, TP, OP, and silica), and alkalinity were analyzed at PPB Environmental Laboratories, Inc., in Gainesville, Florida, a NELAP certified laboratory (Florida Department of Health #E82001). In February 2007, the name of PPB Environmental Laboratory changed to Advanced Environmental Laboratory, but retained the same NELAP certification from the Florida Department of Health. The analyses were determined using standard procedures (Table 3-4). The precision, accuracy and detection limits are shown in Table 3-5 for each of the analytes.

The ⁸⁷Sr/⁸⁶Sr ratios were measured in the laboratories of the Department of Geological Sciences at the University of Florida. Standard methods for analysis of these isotope ratios have not been adopted by the FDEP. Standard methods that are used in the Department of Geological Sciences, University of Florida are described below.

The Sr isotope ratios were measured on a thermal ionization mass spectrometer (TIMS) following extraction Sr from each sample by cation exchange. The procedure involved pipetting sufficient sample to provide approximately 1 µg of Sr into a clean Teflon beaker and then spiking the sample with precisely determined amounts of ⁸⁴Sr. The liquid samples were dried to completion and the resulting salts were dissolved in 50 µl of ultra-pure 3.5 N HNO₃. Strontium was separated using Sr-selective crown ether resin (Sr-Spec). The separated Sr was loaded onto tungsten filaments and analyzed in the Department of Geological Sciences at the University of Florida for measurement of the Sr concentrations and ⁸⁷Sr/⁸⁶Sr isotope ratios using a VG Micromass 354 triple collector TIMS that was run in dynamic mode. Instrumental mass fractionation was corrected to the natural ratio of ⁸⁶Sr/⁸⁸Sr of 0.1194. Strontium concentrations are calculated from the deviations from the global value of the ⁸⁴Sr/⁸⁸Sr ratio caused by the addition of the ⁸⁴Sr spike. Standardization and quality assurance is achieved by analyzing the NIST standard 987 at least every tenth sample. The average of repeated measurements over the past several years of this standard is 0.710240 (reported value is 0.710250) and the external precision ±0.000023 (2σ). The Sr blank for the technique is ~100 pg.

3.6 Dye Trace Study

Two quantitative dye traces were conducted between Sweetwater Lake and the River Rise in May 2005 and March and April 2007. The dye trace studies were conducted to determine flow characteristic over this section of the river and two studies were done to compare results at different flow levels.

3.6.1 Dye Trace 1

A week before injection of the dye, background fluorescence values were continuously monitored with a Turner 10AU Fluorometer at the River Rise between 1057 hrs on May 18, 2005 and 0640 hrs on May 19, 2005. Monitoring was accomplished by pumping water from 10 ft below the surface at the location of the deepest portion of the River Rise (white dot, Figure 2-2), using a submersible pump (commercial bilge pump). The pumping depth is below the lip delineating the edge of the spring, and thus discharged water should be well mixed and would represent average dye concentrations in the water flowing to the surface from the River Rise. The average background fluorescence over this preliminary monitoring time was 0.200 ppb with a standard deviation of 0.04. The Fluorometer was standardized with a three-point calibration with standards made of Rhodamine WT dye that was diluted with river water.

Approximately 20 hours prior to injection of the dye, the fluorometer was re-installed at the River Rise (Figure 2-2) to monitor background fluorescence. Background fluorescence was 0.125 ppb with a standard deviation of 0.02 between the time of installation and when fluorescence increased following the return of the dye at 0158 hrs on March 24, 2005. For the monitoring of background and during the dye trace, the fluorometer recorded 1-minute averages of 2-second cycle readings. The fluorometer was calibrated at 1020 hrs on May 23, 2005 with standards made with river water immediately prior to injection of the dye.

The dye trace consisted of injection of 18.14 kg of 20% Rhodamine WT solution, which represents 3.63 kg of active ingredient, directly into the sinkhole that drains Sweetwater Lake at 1200 hrs on May 23, 2005. The dye injection point at Sweetwater Lake and monitoring point at the River Rise are shown in bathymetric maps in Figure 2-2. The dye trace occurred when discharge from the River Rise average about 26 m³/sec. Dye was injected into Sweetwater Lake by dumping the dye into the sinkhole from a small raft directly over the deepest portion of sink

that drains Sweetwater Lake. Because the dye solution is approximately 20% more dense than the water, most dye immediately sank out of sight below the water surface. The dye container was rinsed several times with lake water until no dye remained in the container. Some of the rinsed dye remained on the surface of the lake for several hours after the initial injection, but the amount of dye remaining on the surface appeared to be a small fraction of the total dye. Within several hours following injection, all of the dye had disappeared into the sinkhole. As described below, there is no indication of this subsequent injection of dye while monitoring for the return of the dye.

3.6.2 Dye Trace 2

The second dye trace was conducted between Sweetwater Lake and the River Rise. Discharge from the River Rise during this dye trace averaged about 3.7 m³/sec or approximately 14% of the discharge during the first dye trace. A Turner 10AU Fluorometer was installed at the River Rise on March 11, 2007 at 1600 hrs to measure background fluorescence prior to injection of the dye. The measured background fluorescence was a value of 0.0 ppb with a standard deviation of 0.01. Approximately 24 hours after installation of the fluorometer, on March 12, 2007 at 1230 hrs, 18.14 kg of 20% Rhodamine WT solution, which represents 3.63 kg of active ingredient, was injected into Sweetwater Lake at the same location as the initial dye trace (Figure 2-2). Injection was directly over the deepest portion of the sink at Sweetwater Lake and was accomplished by pouring the dye through 2" diameter PVC pipe to a depth of about 10 feet below the surface. This injection represented a slight modification to the technique used in the initial dye injection, but did not alter the introduction rate of the dye. This modification improved the efficiency of dye injection by immediately introducing the dye into sinking water. An improved outcome of this change was that little dye remained on the surface of the lake following injection, which would be important for dye traces that occur in areas with large number of visitors.

Fluorescence was monitored continuously for 2 weeks after the initial injection. The fluorometer recorded 1-minute averages of 2-second cycle readings. Monitoring was ended on March 25, 2007 at 1100 hrs at which time the fluorescence in the river had returned to background values. Check standards for the Turner Fluorometer were measured daily during the dye trace and the instrument was calibrated as needed.

3.7 Description of Quarterly Sampling Trips

The following section describes field logistics, sampling, timing and any problems encountered during the 10 quarterly sampling trips that were completed during Project S0182. Dates of each of the sampling trips are reported in Table 3-2. Although data from projects S00060 and S0141 are included in this report, information concerning samples and sampling from those projects are not reproduced here. Information concerning those sampling trips can be found in comprehensive project reports for those projects. Overall, there have been few problems with sampling or with chemical analyses of the water samples. Results presented in the Appendices of this report use standard qualifiers to qualify any of the data that have problems. These qualifiers include samples with analyte concentrations below the detection limits (U), analyte concentrations below the practical quantification limit (I, four times the detection limit), analytes that were measured outside of the holding time (Q #, with # representing the time over the holding time). In addition blank values and duplicate values are listed in the appendices. The following discussion describes specific problems encountered with the analyses.

Sampling for the quarterly sampling trips was initiated on January 19 and 26, 2005. No problems were encountered during this sampling trip. All samples were delivered to the analytical lab within 24 hours of collection and all laboratory QA/QC analyses are acceptable. Method blanks are below detection limits. The spike recoveries are all within control limits. The range and %RSD of duplicate samples and internal standards are within control limits. Field blanks are all below detection limits with the exception of Cl which was found to be about 3 times the MDL, but below the PQL.

For the second quarterly sampling trip, samples were collected on March 14, 2005 from sites in the northern portion of the park including Wells 1 and 2, River Sink, Ogden Sink, Hawg Sink, and Paraner's Branch. Samples were collected on March 18, 2005 from Wells 3, 4, 5, 6, 7, Sweetwater Lake and River Rise. No problems were encountered during either sampling trips. All samples collected in the field were delivered to the analytical laboratory within 24 hours of collection and on March 14 were delivered approximately 60 minutes following the final sample collection. Some of these samples were reported by laboratory personnel as arriving at the laboratory at temperature of 20.6°C, even though the samples were stored on wet ice in a cooler while in the field and during transportation to the laboratory. The cause of the elevated

temperature is unknown, but the short time between sample collection and delivery to the laboratory may have prevented the samples becoming completely chilled. All subsequent samples were submerging completely in an ice-water bath to chill them more rapidly than with crushed ice as had been the previous practice.

Laboratory QA/QC analyses are acceptable for the second sampling trip. The method blanks are all below detection or practical quantification limits. The spike recoveries are all within control limits. The range and %RSD of duplicate samples are all within the range and %RSD control limits. Internal standards are all within the control limits. One sample (Well 3 collected on March 18, 2005) was not analyzed for alkalinity because of lack of volume of solution. All other samples had, and have had in the past, sufficient volume for all analyses, but following this sampling trip, twice the original volume was collected to ensure complete analyses.

No problems were encountered during the third quarterly sampling trip which was completed in its entirety on July 18, 2005. Because the analytical laboratory was closed by the time that sampling was completed, all samples were stored overnight in an ice-water bath and delivered to the laboratory on the morning of July 19, 2005. All laboratory QA/QC analyses were acceptable. The method blanks are all below detection or practical quantification limits. Except for alkalinity, the spike recoveries are all within control limits. The range and %RSD of duplicate samples are all within the range and %RSD control limits. Internal standards are all within the control limits. All field blanks are below detection or practical quantification limits. Analyses of all field duplicate samples reproduced to within 20% relative percent difference (RPD) except for the ammonia concentrations in the Paraner's Branch samples and TKN concentrations in the Well 1 sample. It is unknown why these duplicates fall outside the limits.

No problems were encountered during the fourth quarterly sampling trip, which was completed in its entirety on October 27, 2005. Because the analytical laboratory was closed by the time that sampling was completed, all samples were stored overnight in an ice-water bath and delivered to the laboratory the morning following sampling trip. Most laboratory QA/QC analyses were acceptable and all analytical problems that were encountered have been corrected. These problems included poor duplicate measurements for sodium and poor spike recoveries for two alkalinity samples. A re-analysis of the sodium sample corrected this problem and produced a %RSD for the duplicates of 0.29%. Re-analyses produced acceptable spike recoveries of 92%

and 80% for the alkalinity samples. A Ca spike recovery of 126% was measured on a digested spike. A rerun of the analytical spike (post digestion spike) yielded an acceptable 96% recovery. Elevated TKN spike recoveries (201% and 221%) were a result of double spiking the sample. Rerun of the spikes yielded acceptable values of 100% and 110%. Sodium reference recoveries were entered into the Laboratory Information Management system (LIMS) incorrectly and the actual recoveries have been corrected in the laboratory's corrected report.

No problems were encountered during the fifth quarterly sampling trip, which was completed in its entirety on January 17, 2006. Because the analytical laboratory was closed by the time that sampling was completed, all samples were stored overnight in an ice-water bath and delivered to the laboratory the morning following the sampling. All laboratory QA/QC analyses have been reviewed and are acceptable.

No problems were encountered during the sixth quarterly sampling trip, which was completed on April 11 and 12, 2005. Samples were delivered to the analytical laboratory the day following their collection. The samples were stored in an ice-water bath while in the field and in a refrigerator at 4°C in the laboratory until they were delivered to the laboratory. All blank values are either below the method detection limits or practical quantitation limits with the exception of calcium in the well blank. This value was 0.06 mg/L or 6 times the method detection limit and 50% above the practical quantitation limit. Calcium concentrations of the well water range from 50 to > 150 mg/L or more than 3 orders of magnitude greater than the blank. All duplicate samples had reproducible values of <5% and most were less than 2%. All laboratory QA/QC analyses have been reviewed and are acceptable.

No problems were encountered during the seventh quarterly sampling trip, which was completed on July 12 and 13, 2006. All samples were kept on wet ice and were delivered to the analytical laboratory on the days following their collection. All field blank values are either below the method detection limits (MDL) or practical quantitation limits (PQL) with the exception of ammonium in the well blank. This value was 0.06 mg/L or about 7 times the MDL and about 50% above the PQL. Ammonium concentrations of the well water range from 0.32 mg/L to below PQL. All duplicate samples with concentrations above the PQL had relative percent differences (RPD) of <5% and most were less than 2%, with the exception of Total Phosphorus of the Well 1 duplicate, which varied by 31% from the average value. Laboratory

quality control measures (lab blanks, duplicates, matrix spikes and references) fall into the acceptable range.

No problems were encountered during the eighth quarterly sampling trip, which was completed on October 10 and 12, 2006. Samples were kept on wet ice while in the field, and were delivered to the analytical laboratory on the days of their collection. The only analytical problem encountered was a laboratory blank of 0.5 mg/l in the Cl analysis for samples collected on October 12. (The reporting limit for Cl is 0.1 mg/l). The measured values have not been corrected for the laboratory blank, but these values are qualified in the appendix. The field blank for the wells was collected on October 12 and this field blank equals the laboratory blank suggesting that the measured excess Cl in the blank derives from the laboratory analyses. The laboratory Cl blank that was measured with samples collected on October 10 is below detection limit. All other field blanks are either below the PQL or the MDL.

No problems were encountered during collection of samples during the ninth quarterly sampling trip, which was completed on January 15 and 17, 2007. Samples were kept on wet ice until they were delivered to the analytical laboratory on the days following their collection. Two problems were encountered in the laboratory analyses, one with alkalinity and the other with potassium concentrations. The alkalinity problem consisted of a faulty automatic titrator at the laboratory. These samples were measured in duplicate and triplicate to correct the problem. During analyses of potassium concentrations, the laboratory substituted borosilicate glass tubes for the standard polyethylene tubes for analysis. As a result, potassium was leached from the borosilicate glass tubes during analysis, thereby causing an elevated potassium blank. All other QA/QC metrics measured were acceptable.

No problems were encountered during collection of samples for the tenth and final quarterly sampling trip, which was completed on April 10, 2007. These samples were kept on wet ice until they were delivered to the analytical laboratory on the day following collection. All blank values are either below the method detection limits or practical quantitation limits with the exception of nitrate-nitrite in both the surface water and well water blanks. This value was 0.019 mg/L for the surface blank and 0.02 mg/L for the well blank. The hits are about 6 times the method detection limit and 40% above the practical quantitation limit. Nitrate-nitrite concentrations of the well water range from 0.021 to 0.172 mg/L, and surface water range from 0.07 to 0.228 mg/L. An additional analytical problem was encountered with duplicate

measurements of Cl concentrations of 8 mg/L and 15 mg/L between Paraner's Branch and Paraner's Branch (DUP), respectively. The samples were rerun with accepted values of 15 mg/L for Paraner's Branch and 16 mg/L for Paraner's (DUP).

Table 3-1. Well numbers, locations, depths and descriptions

Well	Latitude	Longitude	Depth	Top of Limestone**	Screened interval
	(°N)	(°W)	(ft.)	(ft.)	(ft.)
1	29°54'57.0"	82°33'37.7"	75	56	75-55
2	29°54'09.5"	82°35'07.9"	100	20	100-80
3	29°52'34.4"	82°35'25.2"	93	10	93-73
4	29°52'34.1"	82°35'32.8"	97	15	97-77
4A	29°52'34.1"	82°35'32.8"	32	17	32-22
5	29°52'31.9"	82°35'32.9"	98	18	98-78
5A	29°52'31.9"	82°35'32.9"	27	10	27-17
6	29°52'28.9"	82°35'34.0"	102	16	102-82
6A	29°52'28.9"	82°35'34.0"	18	13	18-8
7	29°52'07.6"	82°36'00.8"	98	18	98-78
7A	29°52'07.6"	82°36'00.8"	25	8	25-15
8	29°54'19.1"	82°34'12.0"	100	10	100-80

* Locations relative to the 1927 North American Datum.

** Top of Limestone based on drillers judgment.

Table 3-2. Sampling periods, sampling dates and corresponding river stage

Project Number	Year	Date	Discharge (m ³ /sec)*		
			Sink	Rise	
S0060	2003	January 15-16**	11.1	12.2	
		February 5***	3.2	6.7	
		March 3 and 5**	43.2	40.6	
		March 19 ***	76.7	71.5	
		April 28 and May 1**	4.4	12.2	
		April 30***	4.6	12.0	
S0141	2004	January 22 – 23	0.5	5.2	
		March 8 – 9	5.3	9.6	
		May 4 and 5	0	6.1	
S0181	2005	January 19 and 26	8.7	18.0	
		March 14 and 18	9.5	20.2	
		July 18	35.3	49.5	
		October 27	3.8	15.7	
	2006	January 17	20.8	30.4	
		April 11 and 12	2.6	10.3	
		July 12 and 13	0	7.5	
		October 10 and 12	0	5.2	
		2007	January 15 and 17	0	3.9
			April 10	0	3.6

* For multiple days, the discharge value is average over those days. Where discharge data is missing, the value represents an average measurement surrounding the day. Maximum measured discharge during sample period = 193 m³/sec for the River Sink and 199 m³/sec for River Rise.

** Surface water

*** Wells

Table 3-3. Sampling periods, sampling dates and corresponding river stage for high resolution sampling

	Year	Date	Discharge* (m ³ /sec)
S0141	2004	April 26	4.65
		April 28	5.21
		April 30	5.24
		May 4***	4.94
		May 7	5.40
		May 10	5.16
		May 14	4.96
S0182	2005	April 18	69.22
		April 22	47.93
		April 28	36.08
		May 6	37.49
		May 11	40.42
		May 18	31.85

* Stage at staff gauge in O’Leno State Park, maximum discharge during sampling period = 193 m³/sec.

** N/D = no data

*** Complete quarterly sampling trip

Table 3-4. Matrix and analytical methods for analytes measured at PPB Laboratories

Analyte	Matrix¹	Method²
Alkalinity	GW, SW	EPA 310.1
Ammonium	GW, SW	EPA 350.1
Calcium ³	GW, SW	EPA 200.7
Chloride	GW, SW	EPA 325.2
Magnesium ³	GW, SW	EPA 200.7
Nitrate plus nitrite	GW, SW	EPA 353.2
Nitrite	GW, SW	EPA 353.3
Orthophosphate	GW, SW	EPA 365.2
Potassium ³	GW, SW	EPA 200.7
Silica	GW, SW	EPA 370.1
Sodium ³	GW, SW	EPA 200.7
Sulfate	GW, SW	EPA 375.4
Total Kjeldahl nitrogen	GW, SW	EPA 351.2
Total phosphorous	GW, SW	EPA 365.3

¹GW = Groundwaters; SW = Surface waters

²All methods for environmental waters from Methods for Chemical Analysis of Water and Wastes, EPA-600-79-020, Revised March 1983, and /or Standard Methods for the Examination of Water and Wastewater, 18th Edition, Revised 1992.

³ Digestion of metals will follow EPA METALS-EPA Methods for Chemical Analysis of waters and wastes EPA-600/4-79-020 Revised March 1983

Table 3-5. Precision, accuracy, and detection limits

Analyte	Precision (%RSD)¹	Accuracy LCL- UCL²	MDL³ (mg/L)
Alkalinity	0–10 L, 0–5 M, 0–5 H	80-120	0.5
Ammonium	0–15 L, 0–5 M, 0–10 H	80-120	0.005
Calcium	0–10 L, 0–8 M, 0–6 H	80-120	0.02
Chloride	0–20 L, 0–5 M, 0–5 H	90-120	0.4
Magnesium	0–10 L, 0–8 M, 0–6 H	80-120	0.02
Nitrate plus nitrite	0–20 L, 0–10 M, 0–10 H	75-125	0.004
Nitrite	0–20 L, 0–10 M, 0–10 H	80-120	0.004
Orthophosphate	0–10 L, 0–5 M, 0–5 H	80-120	0.004
Potassium	0–30 L, 0–10 M, 0–12 H	80-120	0.02
Silica	0–5 L, 0–5 M, 0–5 H	80-120	0.2
Sodium	0–8 M, 0–6 H	80-120	0.15
Sulfate	0–20 L, 0–20 M, 0–10 H	80-120	1.5
Total Kjeldahl nitrogen	0–20 L, 0–10 M, 0–15 H	70-130	0.07
Total phosphorous	0–30 L, 0–10 M, 0–10 H	80-120	0.004

¹L, M, and H refer to the low, medium, and high segments of the linear calibration range, respectively.

²Lower Control Limit – Upper Control Limit in percent of spike recovered.

³Method detection limits are determined in accordance with 40 CFR Part 136 Appendix B.

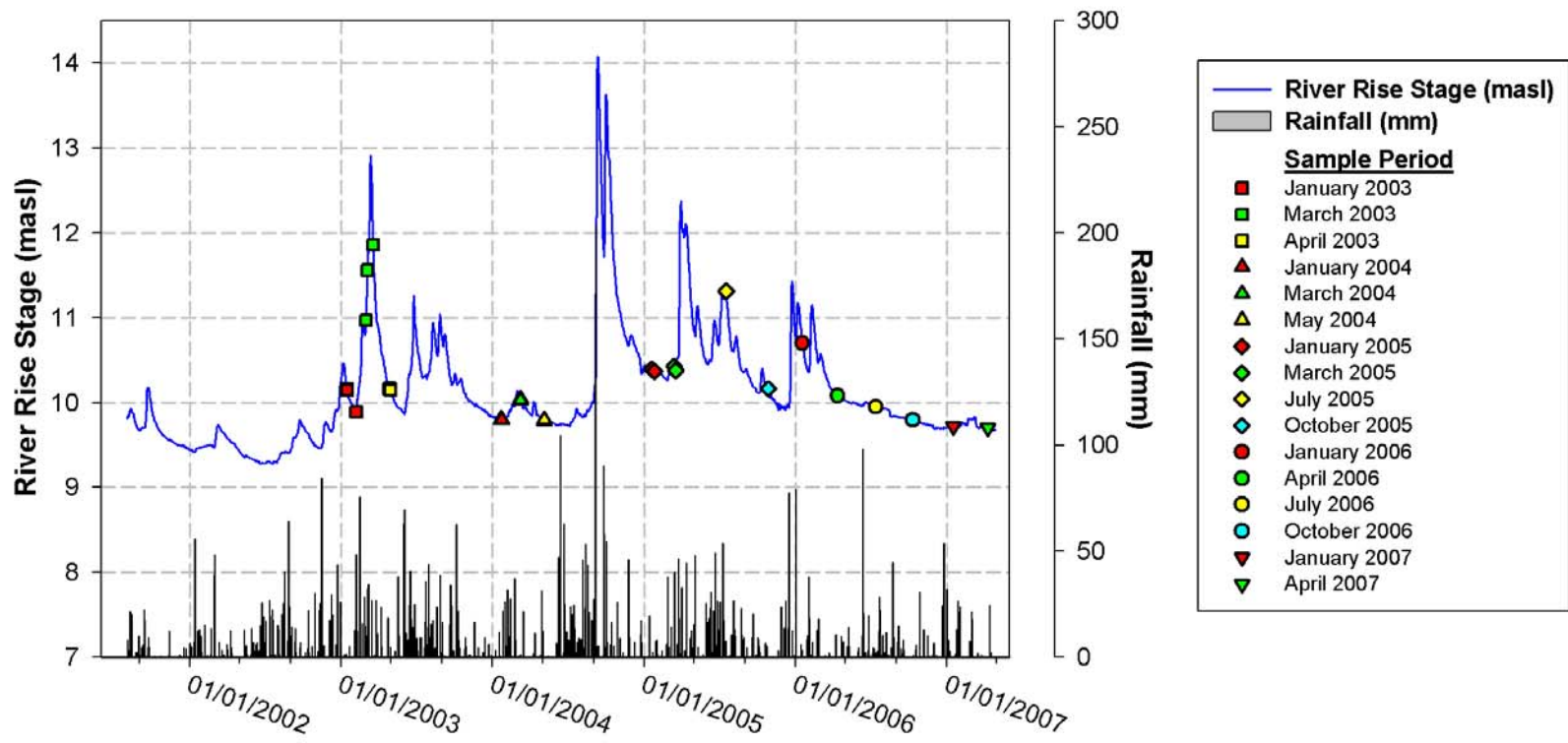


Figure 3-1. Hydrograph at the River Rise and rainfall as measured at O’Leno State Park. Markers on hydrograph represent sample periods when water was collected during this study.

4 FLOW AT O'LENO STATE PARK

To understand the fate and transport of dissolved solutes through a watershed, it is necessary first to describe the flow of water in the watershed. Such descriptions require multiple observations of flow at a variety of conditions and ultimately the development of a conceptual model of flow that can serve as a framework for flow of dissolved solutes in the watershed. To initiate development of such a conceptual model for the Santa Fe River Sink-Rise system at O'Leno State Park, multiple types of new data have been collected as part of this study. Data collected include river stage at the River Rise as well as quantitative dye traces between Sweetwater Lake and the River Rise. Additional archived data have been compiled from other sources, including rainfall measurements and river stage at the River Sink. These compiled and collected data are described below. The flow data were collected and collated at high resolution and are used to compliment the water quality data, which were collected at discrete intervals and which are described in detail in Chapter 5 of this report.

4.1 Precipitation Events and Variations in River Stage

Baseflow of a river can be defined as the groundwater contribution to a river (Fetter, 2001). This value is difficult to determine in karst settings because in many instances, including at the River Rise, all water flowing to the river is ground water regardless of the magnitude of precipitation or stage of the river. Consequently, it may be more useful in settings such as along the Santa Fe River to use as a benchmark the average flow rather than baseflow as is strictly defined. During the entire project, the average stage at the River Rise was 10.2 meters above sea level (masl) and its average discharge was 16.3 m³/sec (Figure 3-1). In this same time interval, the river stage at the River Rise varied from a low of 9.0 masl on August 9, 10, and 11, 2002 to a high of 14.1 masl on September 10, 2004. The lowest stage occurred following an extreme

drought during the preceding three years, when the area received approximately half of its average annual rainfall. The highest stage occurred immediately following Hurricane Frances, which delivered a total of 457 mm of rain to O'Leno State Park over an 11 day period between August 31 through September 11, 2004, with 375 mm of rain occurring on September 6 and 7, 2004 alone. This hurricane caused a rapid increase in river stage, which rose 4 m over a five day period to its peak. The flood recession lasted for 16 days before a second hurricane passed through the region. During the recession, the river stage fell 2.55 m to 11.35 masl from the flood crest when Hurricane Jeanne passed through the area on September 26 and 27, 2004. This hurricane dropped an additional 148 mm of rain and caused the river to rise 2.11 m to produce a second peak of river stage of 13.46 masl on October 1, 2004 (Figure 3-1).

The extreme rainfall amounts associated with these hurricanes clearly resulted in large and rapid increases in river stage, but other smaller storms also caused variable responses in stage. These additional smaller storms included convective storms during the summer as well as extra-tropical fronts during the winter. Over the period of this study, the correspondence between rainfall amount and the resulting change in river stage appears to be seasonal. The largest changes in river stage for a given amount of precipitation occurred during winter months, with smaller changes for similar magnitude rainfall in the summer (Figure 3-1). For example, in February and March 2003, six rain events produced a total of 285 mm of rain over a 34-day period. On February 16, 2003, a single 75 mm rainfall event caused a 3 m rise in the river stage. In contrast, in March 2005, 66 mm of rain over a four-day period and produced only about half of that rise, with an increase in river stage of 1.84 m. Even more extreme contrasts with these high rainfall events during the winter occur during the summer. For example, three rain events between June 4 and June 23, 2004, delivered a total of 256 mm of rain to the park, but had a negligible effect on the river stage. During this time, a single storm delivered 105 mm of rain on June 14, 2004 with little response in river stage to the precipitation. Similarly, no increase in the river stage occurred in June 2006, when 123 mm of rain was delivered to the park over three days (Figure 3-1).

Several variables may control the differences in responses of river stage to rainfall. The variability between river stage and rain events suggests antecedent conditions, such as soil saturation, may also influence how individual rain events affect river stage. If soils are saturated from earlier precipitation events, the river should respond rapidly to small rain events. In

general, soils would be expected to be most saturated during summer months because approximately half of the rainfall in the region occurs during the summer. If soil saturation is a primary variable controlling the relationship between rainfall and flow, the river should respond most rapidly to rainfall in the summer, but the opposite relationship is observed (e.g. Figure 3-1).

The correspondence between large amounts of rain and variations in river stage during winter, with a more muted response during the summer, suggests that other seasonal factors such as evapotranspiration and size of the storms may be important controls on the relationship between rainfall and river stage. Calculated evapotranspiration in the park can be as great as 14 cm/month in the summer but as low as 3 cm/month in the fall and winter (Ritorto, 2007). Consequently, although there may be overall more precipitation in the summer, the precipitation may be rapidly utilized by the vegetation and limit the amount of runoff to the river. In addition to evapotranspiration, summer convective thunderstorms tend to be more localized than winter extra-tropical fronts. As a result, large rainfall events that are observed at the rain gauge in the park may not be widespread across the basin, limiting the total amount of water available to increase the stage of the river. In contrast, extra-tropical fronts that pass through the area in the winter typically are large with widespread precipitation and consequently larger amounts of water entering the system. Over the period of this study, it appears that evapotranspiration and the spatial distribution of rainfall play an important role in the relationship between rainfall and flow.

4.2 Variations and Comparisons of Recharge to the River Sink and Discharge from the River Rise

Comparison of discharge measurements at the River Sink and River Rise during the study period shows that during most of the sampling times, more water discharges from the River Rise than flows into the River Sink (Figure 4-1). There are no sources of surface water to the River Rise and consequently discharge from the River Rise in excess of water flowing into the River Sink must result from additional sources of water in the subsurface. For example, visual observations of the river at the River Sink indicate that when river stage drops below 10.32 masl, most of the Santa Fe River is captured by a sinkhole at Vinzant's Landing located approximately 1 km upstream from the River Sink (Figure 2-1). The water captured at Vinzant's Landing could flow through unmapped conduits and contribute to discharge at the River Rise. In addition to

water captured at Vinzant's Landing, discharge at the River Rise during low river stage may originate from water released from storage in the matrix porosity of the Floridan Aquifer. Skirvin (1962) observed that water continued to discharge from the River Rise when flow in the Upper Santa Fe River was diverted to construct Interstate 75, which cuts across the region. During this time no water flowed into the River Sink or Vinzant's Landing.

At five discrete times during the sampling period, the instantaneous magnitude of flow into the River Sink is greater than the instantaneous magnitude of discharge at the River Rise. The length of time that flow into the River Sink exceeds discharge at the River Rise is variable, but in most cases this situation lasts several days (Figure 4-1). During these times water can flow from the River Sink to the River Rise in as little as one day as shown by variations in temperature of water along the flow path (Martin and Dean, 1999; Martin and Dean, 2001). Consequently, the rapid flow rates suggests the higher recharge into the River Sink than discharge from the River Rise can not be a result of an offset in timing for the flood pulse to pass through the system.

The most extreme example of this difference occurs when high discharge resulted from the extreme rain events of Hurricanes Frances and Jeanne in September 2004. Other times of excess flow into the River Sink occurred in March 2003, during fall 2003, and during spring 2006. Most of the events shown in Figure 4-1 are discontinuous because the stream gauge lacks an intermediate section, resulting in missing data for recharge into the River Sink. Unfortunately, these discontinuous records prevent quantitative assessment of the difference in the magnitude of discharge at the River Sink and Rise, which could provide a valuable tool to determine the vulnerability of the ground water in the region to surface contaminants. It is also impossible to determine from this record the stage when flow at the River Sink becomes greater than at the River Rise, although it is possible that the stage would vary depending on the elevation of the water table. Continuous stage measurements at both the River Sink and River Rise, coupled with well-constrained rating curves, would be valuable to determine the difference in discharge at the two locations.

Multiple mechanisms could allow more water to flow to the River Sink than discharges from the River Rise. During flooding, the head in the conduits becomes elevated above the head in the surrounding ground water which causes water to flow from the conduits into the matrix porosity (Martin et al., 2006). The excess water is unlikely to flow to air-filled conduits in the

region, since all conduits that capture the water flowing into the River Sink are located several tens of meters below the water table and there are no known dry caves in the region. The excess water that flows to the River Sink would thus displace water in the intergranular porosity, fractures, and other water filled conduits, resulting in a corresponding rise in the water table into the air-filled pore spaces of the vadose zone. An additional reservoir for the excess water could be wetlands in regions of low land-surface elevations and during times of extremely high water table.

Quantifying the difference in discharge between the River Sink and River Rise would be an important measurement of this system because it could represent a direct approach to determining the magnitude of loss of surface water to the subsurface. Although time is shorter when excess water flows into the River Sink than when excess water flows from the River Rise, it occurs during times when discharge of the river is several orders of magnitude larger than average. Consequently, these short term events could represent an important recharge mechanism for the matrix porosity along the reach of the river. And thus a long-term record of this flow could be used to assess the importance of flow of surface water into the subsurface regionally in the O'Leno State Park area. These records, when coupled with other rain gauge measurements, would also allow an assessment of the relative importance of autogenic recharge (i.e. diffuse flow through the vadose zone), compared with allogenic recharge into sinkholes. This information could be use in karst regions across north-central Florida and elsewhere. Additional information could be determined for the region as well as karst aquifers in general by developing rating curves at various karst windows along the flow path and monitoring stage (Figure 2-1). These observations would allow the determination of the magnitude of water flow at discrete locations along the flow path of the entire system. The relative magnitudes of water that recharges the ground water system through sinkholes compared with diffuse recharge is critical for water quality because water entering sinkholes would not have been modified by chemical interactions in the soil and vadose zones.

4.3 Stage and Discharge Variations during Quarterly Sampling Trips

A total of 16 quarterly chemistry sampling trips have been completed since this project was initiated in January 2003 (Figure 3-1). Changes in the chemical composition of the river depend strongly on flow at the time the water samples were collected (Martin and Dean, 1999;

Martin and Dean, 2001; Martin and Gordon, 2000), and thus the following section describes the variation in flow during each of the sampling trips. Most sampling occurred during times of average flow on the river with the stage at the River Rise of around 10.2 masl. Only two sampling times captured elevated flow, one in March 2003 and the other in July 2005. A third sampling time in January 2006 occurred when the river was elevated slightly above the average flow conditions (Figure 3-1). Most remaining samples were collect when the river was at average flow conditions or when the river was below average flow stage, e.g. during January, March and May 2004 and April and July 2006. The following section describes in detail the stage condition for each of the sampling trips and relates these stages to precipitation events prior to the sampling trip.

4.3.1 Project S0060.

Three sample trips occurred during Project S0060. The first set of samples were collected over three separate days on January 15, 16, and February 2, 2003; the second set of samples was collected on March 2, 5, and 19, 2003; and the third set of samples was collected on April 27, 29, and 30, 2003. During the first sampling times, the river stage at the River Rise was slightly below average dropping from 10.16 to 9.89 masl (Figure 3-1). In contrast with the first sampling trip, stage at the River Rise increased rapidly from 10.97 to 11.86 masl, which represents one of the highest river stages that was sampled. Stage values are missing from the River Sink during part of this time because of the lack of the stage gauge corresponding to the stage of the river. Consequently the record of difference between discharge at the River Sink and River Rise is discontinuous during this time (Table 4-2). Data for the River Sink are available between March 7 and 13, 2003, however, and indicate that flow into the River Sink was greater than discharge at the River Rise during the entire sampling time. Over the seven days when data are available from the River Sink and River Rise, an average difference in discharge between the River Sink and River Rise is about $29 \text{ m}^3/\text{s}$, or approximately $2.5 \times 10^6 \text{ m}^3/\text{day}$ (Table 4-2). During the third sampling trip, the stage at the River Rise was close to average, dropping slightly from 10.17 to 10.15 masl. During this time, discharge at the River Rise was greater by about $6.7 \times 10^5 \text{ m}^3/\text{day}$ than discharge at the River Sink.

4.3.2 Project S0141

As part of Project S0141, three quarterly sampling trips were completed in January, March, and May 2004. These sampling periods represent a long period of little rainfall, and consequently the river was below average stage for all three sampling events. A total of 335 mm of rain fell in O'Leno State Park between November 2003 and October 2004, resulting in a river stage that ranged from 9.75 to 10.14 masl over this time period (Figure 3-1). The first sampling trip occurred on January 22 and 23, 2004, at which time the stage at the River Rise was 9.80 masl and was discharging about $4.1 \times 10^5 \text{ m}^3/\text{day}$ more water than flowed to the River Sink (Table 4-2). In February 2004, prior to the second sampling trip, which occurred on March 8 and 9, 2004, 165 mm of rain fell in O'Leno State Park, but this rain caused only a slight increase in stage at the River Rise to about 10 masl (Figure 3-1). Although this rain represents the largest amount of precipitation during project S0141, there was only a slight decrease from the January sampling time in the difference in discharge between the River Sink and River Rise to about $3.8 \times 10^5 \text{ m}^3/\text{day}$ (Table 4-2). Following the February rain, the river continued to fall and during the final sampling time for project S0141, which occurred on May 4 and 5, 2004, stage at the River Rise was 9.79 masl on May 4, representing the lowest of all the stages. At this time the difference in discharge between the River Sink and River Rise was about $4.3 \times 10^5 \text{ m}^3/\text{day}$ and represents the greatest difference of all three sampling time.

4.3.3 Project S0181

Sampling for project S0181 was initiated in January 2005 and except for the second sampling trip continued at regular quarterly intervals through April 2007 (Figure 3-1). The most extreme precipitation event during the time represented by all three projects occurred in September 2004, when O'Leno State Park received 597 mm of rain, mainly due to Hurricanes Frances and Jeanne. Sampling was not carried out at this time because Project S0141 ended in May 2005 and Project S0181 did not start until January 2005. Nonetheless, the rain from Hurricanes Frances and Jeanne resulted in elevated river stage through the early part of 2005, which was sampled during the initial sampling trip for Project S0181. On March 25 and 30, 2005, 66 mm of rain fell in O'Leno State Park, which increased the stage at the River Rise by 1.86 m. This high flow event marks the third highest peak on the hydrograph shown in Figure

3-1, making this period one of the most variable times of river stage for the entire project, with the stage ranging from 9.90 to 12.41 masl. After the river stage was elevated by precipitation from Hurricanes Frances and Jeanne, and again later during the high flow in March 2005, flow into the River Sink was greater than flow into the River Rise (Figure 4-1). Unfortunately, stage data from the River Sink is missing from March 27 to April 17, 2005, and thus the total difference in discharge at the two locations can not be quantified.

The first sampling trip for project S0181 occurred on January 19 and 26, 2005 when stage at the River Rise was slightly above average at 10.40 and 10.37 masl, respectively. The difference in discharge between the River Sink and River Rise on January 19, 2005 was 7.9×10^5 m³/day, but the difference in discharge on January 26, 2005 can not be determined because stage data is missing for the River Sink (Table 4-2). The second sampling trip occurred on March 14 and 18, 2005, when the stage at the River Rise was 10.40 and 10.47 masl, respectively, and discharge at the River Rise was greater than discharge at the River Sink by an average of 8.1×10^5 m³/day (Table 4-2). Prior to the third sampling trip, 353 mm of rain fell in the park in June and early July 2005. This rain resulted in a high flow event so that the third sampling trip on July 17, 2005 occurred at one of the highest river stages of any of the sampling events when stage at the River Rise was 11.31 masl. Although this stage was elevated, discharge remained greater at the River Rise than at the River Sink by about 1.0×10^6 m³/day. The fourth sampling occurred on October 27, 2005, when the stage at the River Rise had fallen back to an average value of 10.17 masl and the River Rise discharged 7.3×10^5 m³/day more water than the River Sink.

The last concentrated rain fall of the project occurred between December 15, 2005 and January 3, 2006, when 276 mm of rain fell in the park. This rain elevated the stage at the River Rise by 1.22 m (Figure 3-1) and during the fifth sampling trip, which occurred on January 17, the stage at the River Rise was 10.70 masl (Table 4-1) and the River Rise discharged 4.9×10^5 m³/day more water than the River Sink. Between the fifth and sixth sampling trips, the stage at the River Rise dropped by about 0.7 m to around 10 masl. During the sixth sampling trip on April 11 and 12, 2006, the difference in discharge between the River Rise and the River Sink increased to around 7.3×10^5 m³/day. The seventh sampling trip occurred on July 12 and 13, 2006, and although 159 mm of rain fell in O'Leno in the month before sampling, with 123 mm of this rain occurring in three days, the precipitation had little effect on the river stage (Figure

3-1). During this sampling time, the stage at the River Rise was about 9.95 masl and the difference in discharge between the River Sink and River Rise was $6.8 \times 10^5 \text{ m}^3/\text{day}$.

River stage continued to fall between the seventh sampling trip and the end of the project. The stage for the eighth sampling trip, which occurred on October 10 and 12, 2006, was 9.80 masl for both days. Discharge was greater by $4.4 \times 10^5 \text{ m}^3/\text{day}$ at the River Rise than at the River Sink. River stage was 9.7 masl for the ninth sampling trip, which occurred on January 15 and 17, 2007 and remained at 9.7 masl for the tenth and final sampling trip, which occurred on April 10, 2007. During these sampling trips, approximately 3.7 m/sec more water flowed into the River Sink than discharged from the River Rise, which represents approximately $3.2 \times 10^5 \text{ m}^3/\text{day}$ drain from the matrix porosity.

4.4 Dye Trace – Results and Discussion

4.4.1 Dye Trace One: May 2005

Discharge was continuously monitored at the River Rise for fluorescence associated with Rhodamine WT dye following injection of the dye on May 23, 2005. The initial breakthrough of dye occurred at 0158 on March 24, 2005, 13 hours and 58 minutes after injection of the dye (Figure 4-2). The peak of dye concentration occurred at 0802 May 24, 2005, 20 hours and 2 minutes after injection of the dye with a concentration of 6.97 ppb. The centroid of the dye (the time when half of the dye had returned), which represents the average time for flow of water during the dye trace, occurred 22 hours and 31 minutes after injection of the dye. Assuming a conduit distance of 3 km between the injection point in Sweetwater Lake and the sampling location at the River Rise, this average flow is 0.038 m/s. Flow rates through the system have previously been measured by monitoring temperature of water at various karst windows, including Sweetwater Lake, and at the River Sink and Rise (Martin and Dean, 1999; Martin and Dean, 2001). The flow rate measured during this dye trace is similar to the temperature-derived rates. The fluorescence returned to a background value of ~ 0.1 ppb around noon on March 25, 2005. The shape of the breakthrough curve and its rapid return to background fluorescence reflect conduit flow with minimal dispersion of the dye.

By taking the concentration of dye and multiplying it by the discharge it is possible to estimate the mass of dye returned to the River Rise. This calculation shows that there was

approximately 5.3 kg of dye returned to the River Rise or about 46% more than the amount of dye injected into Sweetwater Lake (Table 4-3). This discrepancy may result from several possible problems including analytical error of the dye measurements or problems with measurement of discharge from the River Rise. Analytical errors in the measurements of dye concentrations seems unlikely because multiple standards were used to calibrate the fluorometer and check standards were measured every twelve hours (when batteries were changed) during monitoring of the dye. Check standards typically showed good values and if the check standards differed from the expected values the fluorometer was recalibrated. There are no large offsets in dye concentrations that indicate the recalibrations greatly altered the measured concentrations (Figure 4-2). Another source of analytical error could result if there is variations in the natural source of fluorescence in the water that discharge simultaneously with the dye. The constant background values for fluorescence and the smooth and nearly symmetric peak of dye return (Figure 4-2) suggests there is little extra fluorescence in the water.

An alternate cause for the difference in dye injected and dye return would be if dye free water flows to the river between the location of measurements of the dye concentrations and measurements of river stage. Stage at the River Rise is monitored several hundred meters downstream from the discharge measurements (at the lower end of Figure 2-2). If additional water flows to the river in this interval, it would be included in the estimate of discharge containing dye, but would not have diluted the dye prior to sampling. This explanation seems unlikely however as there are no obvious large springs between where dye concentrations were measured at the River Rise and where stage monitoring downstream. Any extra discharge of dye-free water would have to be through seepage or through fracture flow across the river bottom, which would be unlikely to provide sufficient water to increase the amount of estimated dye return by 46%.

A final possible explanation for the difference in the amount of injected and returned dye could happen if the estimates of discharge values are in error, for example if the rating curve used to estimate discharge from flow is no longer valid. The rating curve was constructed several years prior to the dye trace and changes in the shape of the river channel might alter the discharge estimates. Assuming that all dye injected was recovered, then the discharge can be estimated from the following equation

$$Q = \frac{1}{A} * M$$

4-1

where Q is discharge, A is area under the breakthrough curve and M is the mass of the dye injected. The assumption of 100% dye recovery is reasonable considering the rapid flow rate, smooth breakthrough curve and rapid return to back ground values, and that there appears to be only a single conduit connecting Sweetwater Lake and the River Rise. Furthermore, as discussed below in section 4.4.3, there is little evidence in fluorescence of water collected from monitoring wells that dye was lost to the matrix porosity. Equation 3-1 suggests that at the time of the dye trace, the discharge was around 17.5 m³/s rather than 26.3 m³/s as indicated by the measured stage and the rating curve (Table 4-3). If the rating curve is too high, comparisons in the difference in flow to the River Sink and discharge from the River Rise (e.g. Figure 4-1) would have errors of the same magnitude as the error in the rating curve. Determining the relative magnitudes of flow into the River Sink and discharge from the River Rise is important for estimating the amount of water that may exchange between conduits and the matrix porosity of the Floridan Aquifer in this area, and consequently, it will be important in the future to check and calibrate the rating curve at the River Rise.

4.4.2 Dye Trace Two: March 2007

The second dye trace was conducted at significantly lower flow conditions than the first dye trace (Table 4-3). Discharge was estimated to be around 3.7 m³/s based on stage measurements at the River Rise of around 9.7 masl and from the River Rise rating curve. This lower flow condition was reflected in a longer transit time from the injection point at Sweetwater Lake to the monitoring point at the River Rise. Dye was injected at 1230 hr with the initial dye return at the River Rise on March 14, 2007 at 2100 hrs. The peak concentration of 4.87 ppb occurred on March 16, 2007 at 0726 hrs and the centroid of the dye return was on March 17, 2007 or around 111 hours after the injection. This travel time indicates flow rates were around 0.0077 m/s. Stage of the river was lower than stage reported in Martin and Dean (1999) and the travel time is longer than any observed using temperature tracers and consequently a direct comparison can not be made between the two different techniques at this flow condition. This

dye trace indicates that flow continues through the system even during extremely low stages of the river and provides a quantitative measure of the rate of flow.

Estimates of the mass of dye recovered based on the discharge and concentration of dye indicates that approximately 4 kg of dye was recovered or about 12% more than injected (Table 4-3). If this discrepancy results from a change through time in the rating curve, the dye trace suggests that there is less difference between actual discharge and the discharge estimated from the rating curve. The rating curve estimates discharge to be around $3.7 \text{ m}^3/\text{s}$, but assuming 100% dye recovery and using equation 3-1 suggests that discharge should be around $3.2 \text{ m}^3/\text{s}$.

4.4.3 Ground water fluorescence

Following the first dye trace, Wells 3, 4, 5, 6, and 7 were sampled intermittently eight times for nearly two months following the dye injections to check for return of the dye to the wells (Figure 4-3). The wells were purged following standard chemical protocols and water was collected in opaque glass bottles, which were kept in the dark until they were returned to the laboratory. The water was measured for fluorescence in the laboratory using the same Turner 10 AU that had been calibrated with standards made of river water and an aliquot of the Rhodamine dye used for the dye trace.

No fluorescence measurements of the well water were taken prior to injection of the dye as a measure of their background fluorescence, but the wells were pumped the day after dye injection. At that time, three wells (3, 4, and 6) showed no fluorescence while wells 5 and 7 displayed some fluorescence (Figure 4-3). Continued sampling of the wells showed increases to maximum measured fluorescence at Well 7 of nearly 0.5 ppb on May 25, 2005 and at Wells 5 and 6 of nearly 0.7 ppb and 0.45 ppb respectively on June 3, 2005. The fluorescence declined at the wells since that time except for Well 7, which had a slight increase on June 13, 2005. Wells 3 and 4 show no fluorescence during the entire sampling time.

Following the second dye trace, water was also collected from Wells 3, 4, 5, and 6 on March 12, 16, and 19, 2007 to check for fluorescence resulting from the injected dye. These dates include the day of the injection, the day the maximum dye return was found at the River Rise, and three days after the fluorescence returned to background values. Rather than measuring the samples with the Turner 10 AU fluorometer, however, samples were measured for fluorescence on a Hitachi F9000 scanning spectrofluorophotometer. Because of smaller optical

slit widths (as small as 0.5 nm) found in scanning spectrofluorophotometer over the field fluorometer, scanning spectrofluorophotometers have the advantage of minimizing background interferences. With this more precise instrumentation, no background fluorescence was found within the water samples collected from wells following the second dye trace.

It is not clear if the fluorescence measured at the wells following the first dye trace is natural background fluorescence causing interference with any fluorescence that would result from dye flowed from the conduits to the wells. Such interference could result from wide optical slit widths (20 nm) that would detect fluorescence over a larger range than from the scanning spectrofluorophotometer. The long time for the increase in fluorescence at Wells 5, 6, and 7 is what would be expected for dye flow through the porous matrix of the aquifer (Figure 4-3). Interestingly, the wells that show no fluorescence are located closest to the conduits and thus would be expected to have the most rapid response to dye flow and also possibly the highest concentration of dye. As described below in Chapter 5 these wells have some of the lowest variation in the natural chemical composition, suggesting that they may be located in relatively low permeability sections of the aquifer. Such low permeability would limit the flow of dye to these wells. It is important, however, to make sure that the fluorescence observed in the wells is from Rhodamine rather than variations in natural fluorescent material contained in the water. Because the second dye trace was conducted during low flow conditions, the head gradients at the time were likely from the matrix into the conduit (e.g., Martin et al., 2006). Consequently, dye would not be expected at the wells during these conditions. Similar experiments carried out at high flow conditions would be useful to determine the magnitude of exchange between the conduits and the wells.

Table 4-1. Sample dates and stage at River Rise for each sample period.

Sample Period	Sample Date	Stage at River Rise (masl)
January 2003	01/15/2003	10.16
	01/16/2003	10.15
	02/06/2003	9.89
March 2003	03/02/2003	10.97
	03/05/2003	11.56
	03/19/2003	11.86
April 2003	04/27/2003	10.17
	04/29/2003	10.16
	04/30/2003	10.15
January 2004	01/22/2004	9.80
	01/23/2004	9.80
March 2004	03/08/2004	10.05
	03/09/2004	10.02
May 2004	05/04/2004	9.79
	05/05/2004	9.80
January 2005	01/19/2005	10.40
	01/26/2005	10.37
March 2005	03/14/2005	10.40
	03/18/2005	10.47
July 2005	07/18/2005	11.35
October 2005	10/27/2005	10.17
January 2006	01/17/2006	10.70
April 2006	04/11/2006	10.08
	04/12/2006	10.07
July 2006	07/12/2006	9.95
	07/13/2006	9.96
October 2006	10/10/2006	9.80
	10/12/2006	9.80
January 2007	01/15/2007	9.72
	01/17/2007	9.71
April 2007	04/10/2007	9.71

Table 4-2. Differences in discharge between the River Sink and River Rise and net gain (+), or loss (-) at the River Rise

Sampling Period	Date	Difference in discharge (m³/s)	Gain (+), or loss (-), at River Rise (m³/day)
January 2003	01/15/2003	0.74	6.4 x 10 ⁴
	01/16/2003	1.2	1.0 x 10 ⁵
	02/02/2003	3.3	2.9 x 10 ⁵
March 2003	03/02/2003	-0.82	-7.0 x 10 ⁴
	03/07/2003 – 03/13/2003	-29*	-2.5 x 10 ⁶
April 2003	04/27/2003	8.1	7.0 x 10 ⁵
	04/29/2003	7.7	6.7 x 10 ⁵
	04/30/2003	7.4	6.4 x 10 ⁵
January 2004	01/22/2004	4.7	4.1 x 10 ⁵
	01/23/2004	4.7	4.1 x 10 ⁵
March 2004	03/08/2004	3.9	3.4 x 10 ⁵
	03/09/2004	4.8	4.1 x 10 ⁵
May 2004	05/04/2004	4.9	4.2 x 10 ⁵
	05/05/2004	5.1	4.4 x 10 ⁵
January 2005	01/19/2005	9.2	7.9 x 10 ⁵
	01/26/2005	n.d.	
March 2005	03/14/2005	9.6	8.3 x 10 ⁵
	03/18/2005	9.1	7.9 x 10 ⁵
July 2005	07/18/2005	11.8	1.0 x 10 ⁶
October 2005	10/27/2005	8.5	7.3 x 10 ⁵
January 2006	01/17/2006	5.7	4.9 x 10 ⁵
April 2006	04/11/2006	n.d.	
	04/12/2006	8.4	7.3 x 10 ⁵
July 2006	07/12/2006	7.8	6.7 x 10 ⁵
	07/13/2006	8.0	6.9 x 10 ⁵
October 2006	10/10/2006	5.1	4.4 x 10 ⁵
	10/12/2006	5.2	4.5 x 10 ⁵
January 2007	01/15/2007	3.9	3.4 x 10 ⁵
	01/17/2007	3.7	3.2 x 10 ⁵
April 2007	04/10/2007	3.7	3.2 x 10 ⁵

* = Difference in discharge for seven consecutive days was averaged to estimate discharge data for the River Sink on 03/05/2003 and 03/19/2003 due to missing stage measurements on those days.

n.d.= No stage date for the River Sink, so discharge cannot be determined.

Table 4-3. Dye Trace results from Sweetwater to River Rise.

Tracer Dates	May 2005	March 2007
Average River Stage (masl)	10.69 ± 0.02	9.71 ± 0.02
Average Discharge (m ³ /s)	26.25 ± 0.61	3.71 ± 0.25
Time of Injection	5/23/2005 12:00	3/12/2007 12:30
Breakthrough	5/24/2005 1:58	3/14/2007 21:00
Elapsed time for Breakthrough	13h 58m	54h 35m
Peak Concentration (ppb)	6.97 @ 3/24/2005 08:02	4.87 @ 3/16/2007 07:26
Mean Travel Time (hours)	22.52	111.41
Mean Flow Velocity (m/s)	0.038	0.0077
Dye Injected (kg)	3.63	3.63
Dye Recovered (kg)	5.33	4.06
Excess Recovered Dye (%)	47	12
Area Under Curve (ug*s/l)	206597	1110889
Average Discharge (m ³ /s) from Tracer Test	17.57	3.27

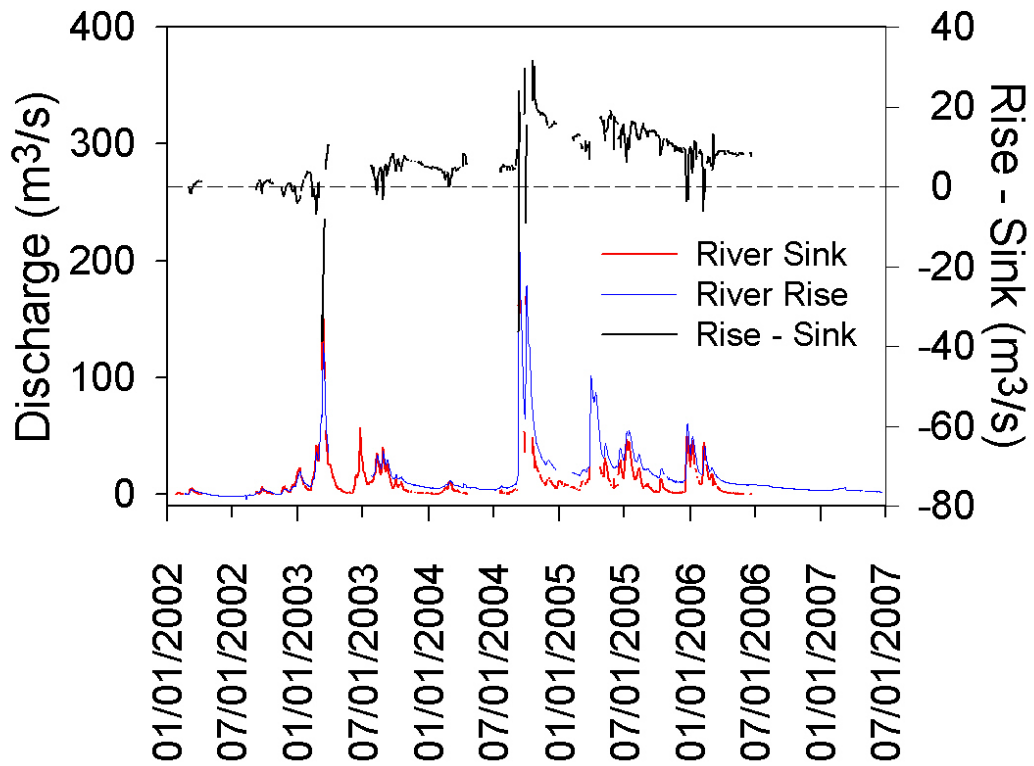


Figure 4-1. Comparison between discharge at the River Sink and the River Rise. Red and blue lines represent discharge at the River Sink and River Rise, respectively, and black line shows when discharge at the River Rise is greater than discharge at the River Sink (i.e., above dashed line), and, conversely, when discharge at the River Sink is greater than discharge at the River Rise (i.e., below dashed line).

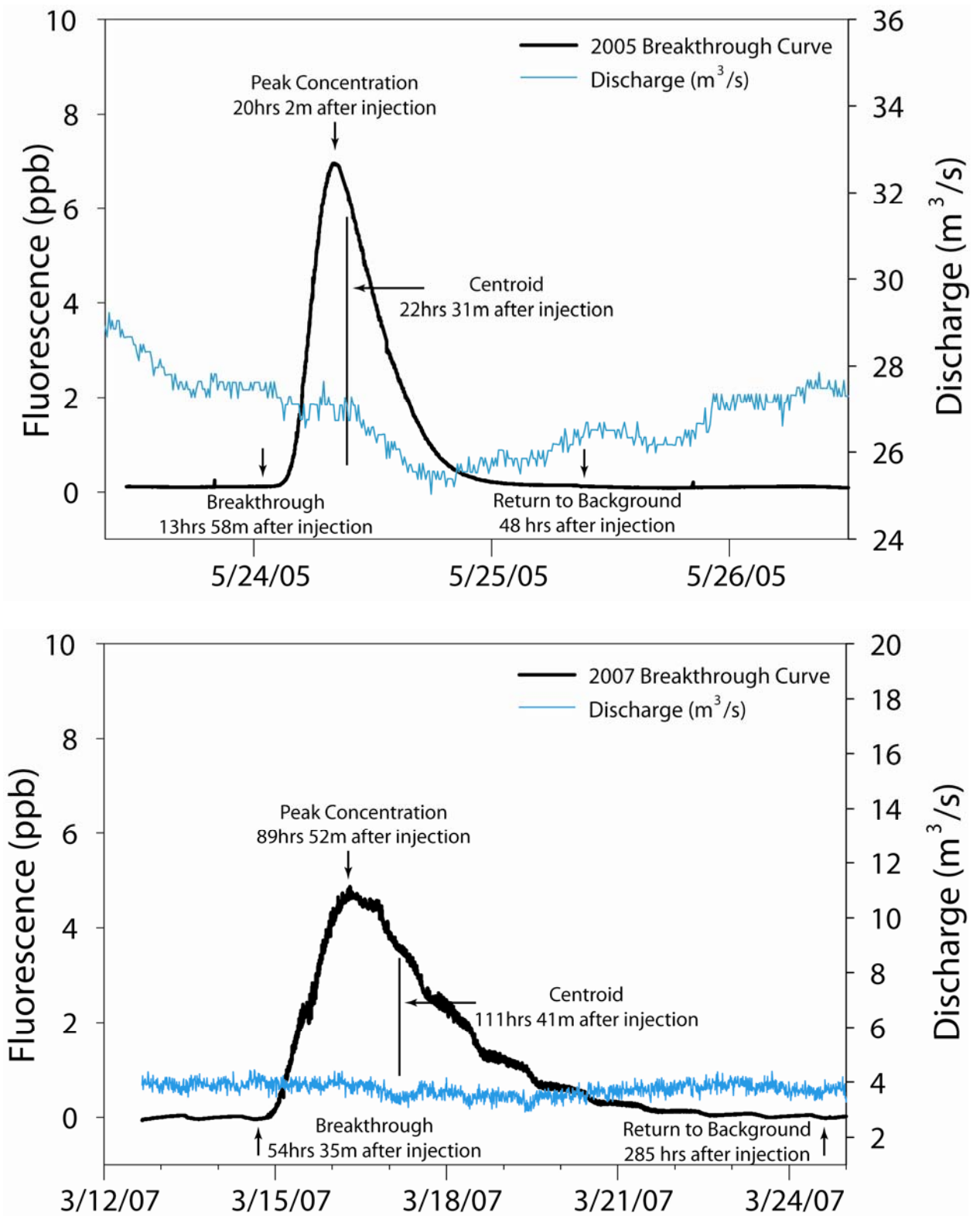


Figure 4-2. Breakthrough curves of tracer test conducted in A. May 2005 and B. May 2007 between Sweetwater Lake and the River Rise.

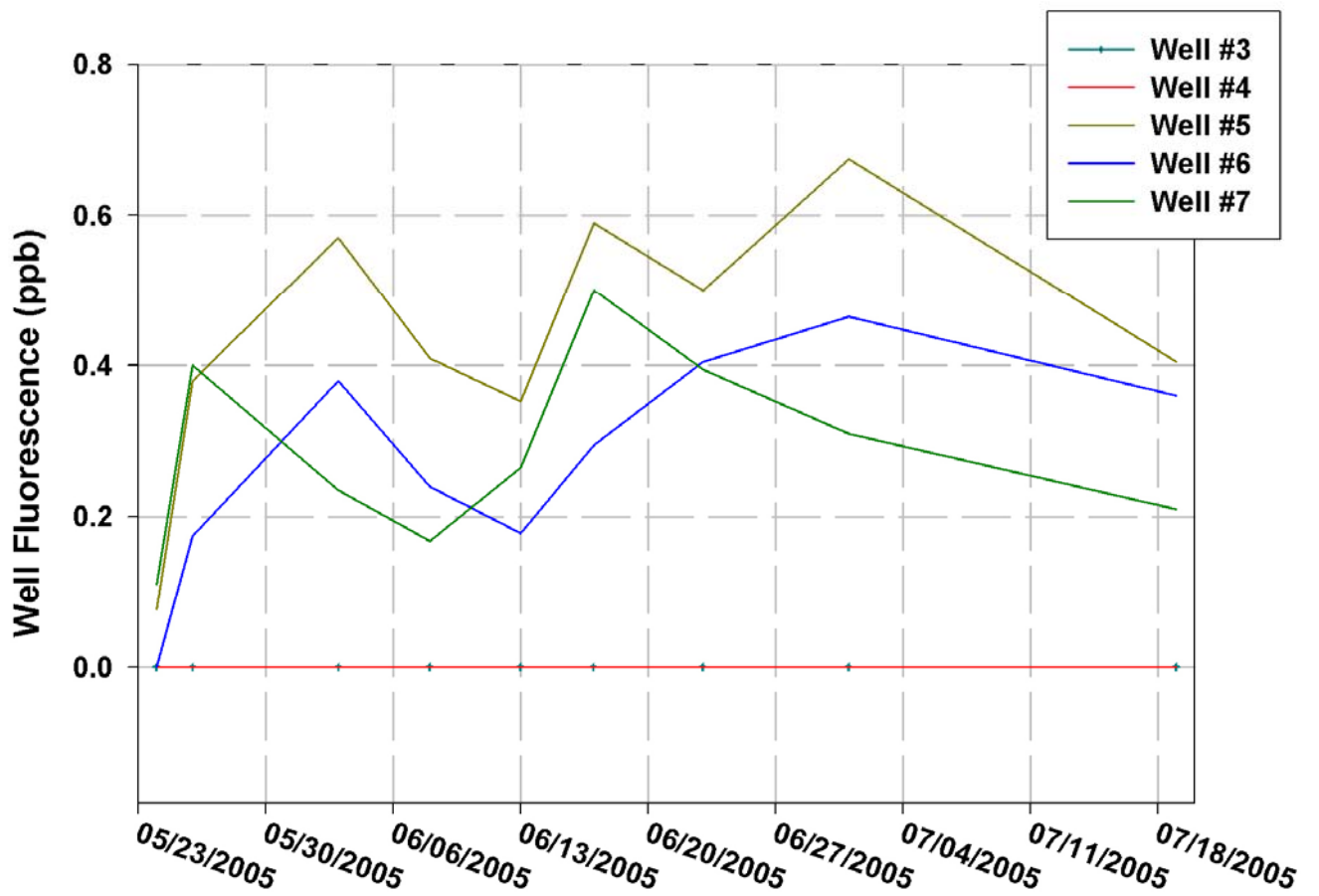


Figure 4-3. Fluorescence measured in five wells following injection of dye into Sweetwater Lake during the May 2005 dye trace. Wells 5, 6, and 7 show increases in fluorescence following dye injection, while wells 3 and 4 show none.

5 WATER CHEMISTRY

5.1 Introduction

Field sampling methodology is important for the quality of all subsequent analyses. Specific sampling methods used for collecting water samples are presented in Chapter 3 and are not repeated here. In general, field sampling of water for chemical analyses has followed DEP Standard Operating Procedures that were in place at the time of the sampling. These Standard Operating Procedures include SOP FS1000 – General Field Sampling, DEP-SOP FS2000 General Aqueous Sampling, and DEP-SOP FS2100 - Surface Water Sampling and DEP-SOP FS2200 Ground Water Sampling, particularly the section on collecting samples with pump and tubing. The specific SOPs used for sampling are described in several Sampling and Analysis Plans revised each year of the project and approved by DEP prior to sampling.

The data used to describe the temporal and spatial variations in chemical composition of water flowing through the Santa Fe Sink-Rise system comes from 16 sampling trips to six surface water and eight ground water sampling sites (Figure 2-1). The details of each sampling trip are also described in Chapter 3. The surface water sites include from north to south: River Sink, Ogden Sink, Hawg Sink, Paraner’s Branch, Sweetwater Lake, and River Rise. The surface water sites located between the River Sink and River Rise are karst windows where water flows from conduits to the surface at a spring and returns to the subsurface through sinkholes that are located within at most a few hundred meters from the spring (e.g. Figure 2-2). Although O’Leno State Park contains many of these karst windows, the karst windows that were sampled for this

project showed large variations in chemical compositions during the early projects, indicating they may intersect different portions of the aquifer.

Ground water was sampled from eight wells screened approximately at the depth of the conduits and four shallow wells that penetrate the surface of the water table. Not all of the wells were sampled throughout the project because they were drilled in stages. The first wells to be drilled include Wells 1, 2, 3, 4, 6, and 7 and these have the longest sampling record. The final wells to be drilled were the water table wells, which were completed during the final year of the project and consequently have been sampled only four times. The locations of the wells were selected to provide a distribution as wide as possible of ground water samples throughout the park and along the presumed ground water flow path within the park. Consequently, Wells 1, 2, and 8 are located in the northern portion of the park, while Wells 3, 4, 5, and 6 are closely spaced (separated by distances of 100 to 200 m) near the River Rise in the southern section of the park along the subsurface path of the conduit that connects Sweetwater Lake with the River Rise. Well 7 is located about 0.5 km from this grouping of wells (Figure 2-1). The closely spaced wells are designed to observe variations in chemical composition that may result if water flows from the conduits to the matrix porosity. The shallow water-table wells are located immediately adjacent to Wells 4, 5, 6 and 7.

5.2 Major Element Concentrations, End Member Compositions and Mixing

All chemical data from the 16 quarterly sampling trips and two high-resolution trips are presented in the appendices to this report. The appendices are divided into four major sections labeled Appendices A through D that are divided by calendar year and by subsection if they were collected as the long term sampling pattern (e.g. nominally quarterly) or at high temporal resolution. Appendices A1-A3 provide data from samples collected during the quarterly sampling trips in 2003. Appendices B1-B3 provide data from samples collected during the quarterly sampling trips in 2004, and Appendices BA-BF provide data from high resolution sampling trips from that year. Appendices C1-C4 provide data from samples collected during the quarterly sampling trips in 2005, and Appendices CA-CF provide data from high resolution sample trips from that year. Appendices D1-D4 provide data from samples collected during the quarterly sampling

trips in 2006. Appendices E1-E2 provide data from samples collected during the quarterly sampling trips in 2007.

All of the data from the long-term sampling is presented as a piper diagram to describe the spatial variation in major element chemistry (Figure 5-1). The high resolution data are not included in the diagram because they show little change through time. Piper diagrams plot the relative concentrations in percentages of meq/L of the major element concentrations of a particular water sample and thus do not show total concentrations of the ions, but rather the relative concentrations and changes in concentrations. For this reason, they are valuable for observing trends in changes in composition of waters and to observe mixing between water with distinct compositions.

The major element chemistry of water at O'Leno State Park shows two major mixing trends between what appear to be three primary end member compositions (Figure 5-1). One of these two trends extends between two end members, one with primarily a Ca-HCO₃ composition to another with Ca as the primary cation, but with more SO₄ and less HCO₃ as the charge balancing anion. Both of these end members are found in samples collected from the monitoring wells and thus represent the extreme variations in the composition of ground water. The other trend extends between an end member that is composed largely of Na-Cl concentrations with another end member composed of water with a composition that appears to be a mixture of the Ca-HCO₃ and Ca-SO₄ end members. This other trend is confined to water sampled from the surface water sites. The wide range in compositions of water reflects extensive mixing between all three end members.

5.2.1 Ground water compositions

Mixing between the Ca-HCO₃ and Ca-SO₄ end members are clearly shown in a piper diagram of chemical composition of water from the monitoring wells without the complimentary data from the surface water locations (Figure 5-2). The Ca-SO₄ end member is largely restricted to Well 2 and all of the other wells have compositions that are close to the Ca-HCO₃ end-member. Although only Well 2 defines the Ca-SO₄ end member, its concentration varies through time toward the Ca-HCO₃ end member. Similarly, some of the wells that are defined mostly by the Ca-HCO₃ end member,

primarily Wells 7 and 8, show slight variations in time that trend toward the Ca-SO₄ end member. These variations define the mixing line between the two compositions in the ground water at O'Leno State Park. Not all wells show this mixing, however, particularly, Wells 3, 4, 5 and 6 have concentrations that vary little through out the time they were sampled.

Well 2 is located in the northwestern portion of the park and is separated from the other wells by several kilometers (Figure 2-1). This separation suggests the two ground water end-member waters also are physically separated. Although the different compositions may result from local interactions with the aquifer rocks, the strong trend in compositions between the wells suggests that even with geographic separation, water flows between the locations of the ground water. To improve the understanding of how water flows through the subsurface and interacts with surface water at O'Leno State Park, an important question to resolve will be under what conditions could mixing occur between the two end members. An important ancillary question to consider would be whether variations in river levels could impact the mixing of the two end members and if variations in composition can be observed at the River Rise. Even though the Ca-SO₄ end member was observed in only one monitoring well, this end member appears to make up much of the surface water flow in the system (e.g. Figure 5-1), suggesting that SO₄ is an important component of the system. Because this end member is defined by the composition of Well 2, located in the northwestern portion of the region, the geographic distribution of the pool of Ca-SO₄ water appears not to be defined by the available monitoring wells.

The Ca-HCO₃ ground water end member can be explained as a result of dissolution of carbonate minerals of the Floridan Aquifer, but the source of sulfur to the Ca-SO₄ end member has several possible origins relating to interactions with aquifer minerals. Two possible reactions that could cause elevated SO₄ concentrations are dissolution of sulfate minerals such as gypsum or anhydrite, or from the oxidation of sulfide minerals such as pyrite. Sulfate minerals are common in the lower formations comprising the Floridan Aquifer, including the Avon Park Formation. If sulfur originates from the Avon Park Formation, then it would suggest upward flow from deeper portions of the aquifer around Well 2. Oxidation of sulfide minerals would have important

implications for dissolution and speleogenesis of the Upper Floridan Aquifer because oxidation of H_2S forms sulfuric acid, which could dissolve the carbonate minerals. These data are insufficient to resolve the potential sources of sulfur to the Floridan Aquifer, but this question could possibly be resolved through measurements of sulfur isotope ratios of the dissolved sulfate.

5.2.2 Surface water compositions

Compositions of the surface waters collected from the River Sink, River Rise, and intermediate karst windows also reflect mixing between end member compositions, but end members that differ from the ground water end members (Figure 5-3). Most of the surface water samples have compositions intermediate between the two ground water end members, with elevated Ca concentrations but variable SO_4 concentrations. These intermediate compositions suggest that they originate from mixing of the two ground water end members. None of these water samples has compositions that extend completely into the range of compositions of either of the ground water end member compositions, which indicates that the surface waters are not dominated by one or the other of the ground water end members. Water samples with these compositions were found only during low flow conditions; water that was sampled during high flow has a distinct composition with elevated Na and Cl concentrations. Samples with the largest fraction of the Na-Cl end member occur at the highest flow conditions (e.g. trends to the right in Figure 5-3). This elevated Na and Cl concentrations in the surface water defines the third end member of the system. No ground water sample has elevated Na and Cl concentrations, suggesting that fresh water input from precipitation controls the occurrence of the Na-Cl end member. There are no known Na or Cl bearing minerals in the rocks making up the Santa Fe River basin, and thus the most likely source of elevated Na and Cl concentrations would be from seawater, which could become entrained in precipitation as storms move inland from the coast (e.g., Drever, 1997).

The relationship between flow and mixing between the surface water end members is most clearly shown by the water composition at the River Sink, where Cl concentrations increase and SO_4 concentrations decrease as river stage increases (Figure

5-4). When stages at the River Sink are ≤ 10.5 masl, composition of water at the River Sink falls along the mixing line between the Ca-HCO₃ and Ca-SO₄ end members of ground water. Its composition appears to be approximately equal amounts of the Ca-HCO₃ and Ca-SO₄ end members, although it is offset slightly toward the Ca-HCO₃ end member (e.g. Figure 5-2). This distribution of composition shows a clear contribution of ground water to the River Sink at low flow conditions.

As the river stage increases, the composition moves toward enriched Cl and Na with lower relative concentrations of SO₄ and Ca, while the relative Mg and HCO₃ concentration remain approximately constant. Two samples have approximately 10% more Na relative to the mixing line defined by most of the samples (Figure 5-4). These two samples were collected January 15 and March 2, 2003 at river stages of 10.81 and 11.73 masl, respectively. These high flow events were caused by 183 mm of rain that fell between December 1, 2002 and January 14, 2003 after the region had experienced several years of extreme drought. The elevated Na and Cl concentrations may be linked to drought followed by rain, although the physical mechanism that would control the linkage is unknown. Possible linkages could include elevated evaporation during the drought and precipitation of salts, reactions with clay minerals, or incorporation of greater amounts of sea spray in the precipitation. Additional data would be required to separate these possible mechanisms.

A similar correspondence occurs between river stage and water composition at Sweetwater Lake and the River Rise as was found at the River Sink, but there is considerably more scatter in the mixing trend (Figure 5-5). At the highest flow conditions, water at both Sweetwater Lake and the River Rise has similar elevated concentrations of Na and Cl as water at the River Sink. At low flow conditions, however, the compositions that fall on the mixing line of the two ground water end members (i.e. the Ca-HCO₃/SO₄ end members) for Sweetwater Lake and the River Rise are offset from the composition at the River Sink and appear to be more influenced by the Ca-SO₄ end member defined by water composition at Well 2 (Figure 5-2). Sweetwater Lake and the River Rise are located farther from Well 2 (Figure 2-1), which defines the Ca-SO₄ end member and consequently it would be expected that the River Sink would have a larger influence from this end member.

This distribution of compositions suggests that water flowing from the River Sink to the River Rise entrains additional ground water from the northwestern portion of the region from the end member defined by the water composition of Well 2. This source of ground water to the River Rise is surprising considering that the mapped conduits are largely concentrated in the eastern portion of the field area (e.g. Figure 2-1). Particularly noteworthy is the large conduit that extends from the eastern boundary of O'Leno State Park and intersects the conduits that flow directly into Sweetwater Lake and the River Rise. Although the composition of water in this conduit is unknown, the difference in compositions of water at Wells 2 and 8 suggests that water draining toward the conduit would have compositions similar to the Ca-HCO₃ end member found at the other monitoring wells (e.g. Figure 5-2).

5.2.3 Calculations of Mixing of Ground and Surface Water

The concentrations of major elements of both the surface and ground water reveal the multiple possible sources of water in the O'Leno State Park system including Ca-HCO₃ water as exemplified by water from Well 4, Ca-Mg-SO₄ water as exemplified by water from Well 2, and Na-Cl water as exemplified by water at the River Sink during high flow conditions (e.g. Figure 5-1). All of these water sources are up gradient from the River Rise and consequently, water discharging from the River Rise should be composed of various fractions of these sources. The fractions of these sources are likely to change through time depending on flow conditions. The changes in composition at the River Rise and the changes in fractions of the sources of water can be observed qualitatively in the changes in major element chemistry of the water at the River Rise through time (e.g. Figure 5-5). During high flow, water at the River Rise has a similar composition to water at the River Sink but during low flow, composition of water from the River Rise deviates from composition of water at the River Sink as the relative proportion of ground water increases with declining stage.

Each water type is chemically distinct due a number of reasons including the amount of contact and length of time of the contact between water and the aquifer rocks. For example, sources of Mg in water flowing to the River Sink water may be dissolution of dolomite in the Hawthorn Group, which is the major water-bearing units in the

Hawthorn Group in this area of Florida (Maddox et al., 1992). For water flowing into the River Sink, sources of SO₄ are more likely from pyrite oxidation, since gypsum is not reported in the Hawthorn Group in this area (Scott, 1988). In contrast, chemical composition of water at Well 2 is about 2 orders of magnitude closer to equilibrium with respect to gypsum compared to Well 4 (Figure 5-6A), suggesting water is upwelling from deeper portions of the aquifer where gypsum is known to exist (Miller, 1986). The elevated SO₄ concentrations in the end member water near Well 2 thus may reflect upward flow of deep water. The dissolution of gypsum with the increase in Ca and SO₄ concentrations also may drive dedolomitization reactions (Jones et al., 1993), which would elevate the Mg concentrations of the water. Evidence for dedolomitization reactions is found in elevated and correlated Mg²⁺ and SO₄²⁻ concentrations (Figure 5-6B). Variations in Mg²⁺/SO₄²⁻ ratio suggest that water at the River Rise is variably influenced by water from the River Sink, Well 2 and Well 4.

The relative fraction of these waters discharging from the River Rise can be calculated based on a mass balance approach using Mg and SO₄ concentrations. The calculations are made assuming three end-member mixing of River Sink, Well 2, and Well 4 water where

$$(\text{SO}_4)_R = X(\text{SO}_4)_S + Y(\text{SO}_4)_{W2} + (1-X-Y)(\text{SO}_4)_{W4} \quad (5-1)$$

$$(\text{Mg})_R = X(\text{Mg})_S + Y(\text{Mg})_{W2} + (1-X-Y)(\text{Mg})_{W4} \quad (5-2)$$

In this model, *X* represents the fraction of river water entering the River Sink, *Y* represents the fraction of ground water from Well 2, SO₄ and Mg represent the concentrations of SO₄ and Mg in surface water at the River Rise (R), the River Sink (S), and ground water at Well 2 (W2) and Well 4 (W4), respectively. This model assumes only three contributing end members represented by concentrations of SO₄²⁻ and Mg²⁺ at the River Sink, Well 2 and Well 4, which results in two equations with three unknowns (i.e. the fractions of water from the various end members). A third equation can be found by recognizing that the total amount of water is the sum of water contributed from all three end members so that water originating from Well 4 is equal to 1-X-Y. These three

equations can be solved by substitution of $1-X-Y$ for the fraction of water from Well 4 and rearranging equations (5-1) and (5-2) to yield two new equations

$$(\text{SO}_4)_R - (\text{SO}_4)_{W4} = X((\text{SO}_4)_S - (\text{SO}_4)_{W4}) + Y((\text{SO}_4)_{W2} - (\text{SO}_4)_{W4}) \quad (5-3)$$

$$(\text{Mg})_R - (\text{Mg})_{W4} = X((\text{Mg})_S - (\text{Mg})_{W4}) + Y((\text{Mg})_{W2} - (\text{Mg})_{W4}) \quad (5-4)$$

These equations were solved simultaneously using Matlab to find X and Y . Solutions to these two equations provide the fraction of end-member water types contributing to the discharge at the River Rise (Table 5-1).

These calculations indicate that the fraction of water discharging from the River Rise that originates from the River Sink relative to the two ground water end members, as well as the fraction of water from the two ground water end members discharging from the River Rise, depends strongly on stage of the river (Table 5-1). During the highest discharge times, for example March 5, 2003 and July 18, 2005, the model calculations suggest that nearly all water discharging from the River Rise originated from the River Sink. The fraction of water flowing from the River Sink to the River Rise is more variable during low flow conditions. For example on January 17, 2007, with a discharge of $3.9 \text{ m}^3/\text{sec}$, nearly twice as much water flowed from the River Sink to the River Rise (70%) than on April 10, 2007, when discharge was $3.6 \text{ m}^3/\text{sec}$ (43%). The remainder of water discharging from the River Rise is nearly an even mixture of the two ground water end members.

These results reflect the importance of the River Rise as a drain for the Floridan Aquifer in the vicinity of O'Leno State Park. Clearly at low flow, water input into the system at the River Sink is less important for water quality of the River Rise and Lower Santa Fe River than during high flow events. Although no real flood conditions were sampled (e.g. Figure 3-1), the fact that during relatively small flood events, ground water has little control on the water composition of the River Rise suggests that the River Sink could be an important control on the composition of the ground water in region (e.g., Upchurch and Lawrence, 1984; Martin and Dean, 2001)

5.3 Sr Isotope Ratios

Strontium isotope ratios and concentrations, along with the major element chemistry, can also be used to separate different water sources and mixing between the sources (e.g., Martin and Moore, in press). Because Sr isotopes are reported as a ratio, the mixing between two end members is a hyperbola when plotted against concentrations, but is a straight line when plotted against 1/Sr concentrations (Faure, 1986). When all $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios are plotted against their 1/Sr concentrations, a clear mixing line is observed in the surface water data, although there are a few outliers (Figure 5-7). The mixing line is between water with high $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios, but low Sr concentrations (high 1/Sr ratios) and water with low $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios but high Sr concentrations (low 1/Sr ratios). In contrast, the well data show little mixing between these two end members, and instead tend to cluster around the end member characterized by high Sr concentrations and low $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios. The end member with high $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios was sampled from the River Sink and Sweetwater Lake during high flow conditions in March 2003, when water at the River Sink would have been dominated by water flowing off the Hawthorn Group confining unit, which may have contributed the elevated Sr isotope ratios. The Hawthorn Group is rich in phosphate minerals that could contain high concentrations of ^{87}Rb and thus provide a source for the radiogenic ^{87}Sr . High flow conditions would also have the effect of diluting the rainwater in minor element concentrations, thus reducing Sr concentrations derived from solid phases. Because of the low concentrations, there would be little change in the isotope ratios of the sampled water.

The outlier in surface water composition (i.e. those with low $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios and low Sr concentrations) was sampled at the River Rise during the same period of the highest flow conditions that defines the end member with elevated $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios and low Sr concentrations. The 1/Sr concentration and Sr isotope ratio at Sweetwater Lake is 25 g/ μg and 0.709101, respectively, during this time and differs greatly from the isotope ratio of the River Rise. These extremes in Sr isotope ratios with little change in Sr concentrations suggest that the isotopic composition of the water changes, but there is little change in the Sr concentrations, as it flows from the River Sink to River Rise. These changes may reflect the introduction of Sr derived from carbonate

minerals in the Floridan Aquifer to the water, but is diluted by nearly Sr free water from the high flow event. The greatest amount of change occurs between Sweetwater Lake and the River Rise, which may indicate the location with the greatest input of ground water along the flow system. This change suggests there is more mixing in this stretch of the conduits than is represented by the dye trace study (e.g. Figure 4-2).

The largest instantaneous change in $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios is shown as a plot of isotope ratios versus distance along the flow path from the River Sink to River Rise (Figure 5-8) during the high flow event in March 2003. This figure shows that even when elevated $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios occur at the River Sink, the elevated $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios do not emerge from the River Rise. One explanation for these variations in isotope ratios and concentrations could be from dilution of the ground water as water flows directly through the epikarst to the matrix porosity. Strontium dissolved in rain water would not alter the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios because of its low concentration, but rain water would be expected to rapidly dissolve carbonate minerals in the epikarst because of its undersaturation with respect to calcite. Strontium derived from the mineral phases would have the same low isotope ratios as minerals in the Floridan aquifer. Alternatively, water sampled at the River Rise may not have had sufficient time to flow from the River Sink through the conduit to the River Rise at the time of sampling. One way to resolve these issues would be to take similar samples from these locations during the recession curve of a flood hydrograph to determine if water with elevated $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios from the River Sink eventually reaches the River Rise. The Sr and its isotope ratios would thus act as a natural tracer of the flow of water and solutes through the system.

Introduction of rainwater through the epikarst may also explain why Sr concentrations vary at most of the monitoring wells, but $^{87}\text{Sr}/^{86}\text{Sr}$ ratios remain approximately constant through time (Figure 5-9). Although the wells show much less variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios and concentrations than the surface water, their variation tends to fall along the two mixing lines. Wells 2 and 7 have the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios and the highest Sr concentrations suggesting the greatest amount of interaction with the carbonate rocks. These wells also contain water with the highest sulfate concentrations. If sulfate were derived from gypsum dissolution in the Avon Park

Formation, then there would be longer flow paths for Sr exchange with the carbonate minerals as the water flows upward. In addition, gypsum typically contains high Sr concentrations, and because of their older age would have lower Sr isotope ratio values than the Ocala Limestone. Well 1 shows the greatest range of Sr isotope ratios of all the wells, with the greatest range in values occurring during sampling in 2003 when there was the greatest range in flow. In contrast with Well 1, Wells 4 and 5 show identical Sr isotope ratios within error, but slightly variable concentrations (Figure 5-9).

These results reflect mixing that was identified by the major element concentrations, but also provide new information about the sources of the water. The high Sr isotope ratios show that water flowing off of the confining unit contributes important solutes to the Santa Fe River Sink-Rise system, but that the local diagenetic reactions, i.e. dissolution of the aquifer minerals, is important to the water quality. The large differences in ground water Sr concentrations and isotope ratios in the ground water suggest that the end member compositions of the ground water could be more variable than as is suggested by the major element chemistry (e.g. Figure 5-2). Such variability in the ground water composition may reflect heterogeneity of the aquifer permeability so that certain areas of the aquifer would largely be controlled by local diagenetic reactions, such as wells 1, 4, and 5 (Figure 5-9), while others with high permeability would allow extensive mixing and homogenization of the water compositions, such as Wells 2 and 7.

5.4 Nutrient Concentrations

All nutrient species (nitrate plus nitrite, nitrate, and soluble reactive phosphate (SRP)) are reported in Appendices A-E. Nearly all samples have nitrite concentrations below method detection limits or practical quantification limits (Appendices A-E), and thus nitrite concentrations have not been subtracted from the nitrate plus nitrite concentrations in the following figures that report nitrogen concentrations. For simplicity, these values will be referred to as NO_x concentrations within the report. Unless otherwise stated, the plotted value of NO_x and PO₄ represent mass of the element, N or P, respectively, per liter of water.

5.4.1 Time variations and relationship to stage

Both major element concentrations and Sr isotope ratios reflect the importance of river stage to the concentrations because of dilution by rain water and from reactions with the aquifer minerals. Nutrient concentrations could also be influenced by river stage, but changes in their concentrations are complicated by differences in sources and sinks from the non-nutrient elemental concentrations. To show the variation in time and relationship to discharge conditions, nitrate and phosphate concentrations are plotted versus time in Figure 5-10 and Figure 5-11 along with the magnitude of the loading of each of the species that have been calculated by multiplying their concentrations by the discharge measurements at the River Sink and River Rise. These values of the loading of dissolved constituents depend on the accuracy of the discharge measurements. If the rating curve for the River Rise overestimates the actual discharge, as suggested by the dye trace experiments, then the loading values would be less than shown in figures Figure 5-10 and Figure 5-11. For comparative purposes, the discharge at the River Rise is included on these plots to show periods of average flow and flood conditions and to provide a visual comparison of the effects of river stage on the nutrient concentrations. Although sampling was fairly widely separated in time (quarterly during the later part of the project and concentrated in late winter and spring during the early part of the project), some patterns emerge between flow conditions and nutrient concentrations (Figure 5-10 and Figure 5-11).

The highest flow conditions that were sampled occurred in March 2003, July 2005, and January 2006 when the river stage was approximately 11.5, 11.4, and 10.7 masl, respectively, at the River Rise. Several other periods of flow were greater than average occurred during the project, but were not sampled. NO_x concentrations at all of the surface water sites are near their highest values when samples were collected immediately following times of elevated flow, but are generally lower during the elevated flow conditions (Figure 5-10). During long periods of low flow conditions, NO_x concentrations are more variable than during high flow events, but typically have lower concentrations than following the high flow events. The clearest reflection of low concentrations during long periods of low flow is over the final year of the project when NO_x concentrations remain constant between 0.1 and 0.2 mg/L depending on the

sampling location (Figure 5-10). The correspondence between high discharge and high concentrations make times of elevated discharge when the greatest loading occurs, reaching a maximum of around 500 kg/day of NO_x in January 2005 immediately after the hurricanes.

Unlike NO_x concentrations, PO₄ concentrations are elevated during most high discharge events (Figure 5-11). The exception to this observation occurs during high flow in January 2006, when the PO₄ concentrations drop to nearly their lowest values at all sites except for Hawg Sink. Although discharge is fairly constant over the low flow period during the final year of the project, the PO₄ concentrations are nearly as variable as during the early part of the project when there was variable flow. Because of the combination of high flow and high concentrations, the highest amount of phosphate loading occurs during the high flow event in March 2003, reaching a maximum of around 800 kg/day, or about 50% greater than the maximum loading value of NO_x.

Comparisons of NO_x concentrations versus discharge at the River Sink and River Rise show a large amount of scatter, but there is a weak inverse correlation between these two variables (Figure 5-12A and B). This relationship reflects some dilution of NO_x that occurs during high flow events, but the scatter in the plot indicates that other factors may also play an important role in controlling the NO_x concentrations. Because of the opposite effects of decreasing concentrations during elevated flow, loading of NO_x to the lower Santa Re River shows no relationship to discharge at either the River Sink or the River Rise (Figure 5-12C and D). In contrast with NO_x concentrations, PO₄ concentrations show little correlation with discharge at the River Sink, but are weakly correlated with discharge at the River Rise (Figure 5-13A and B). Unlike relationships between concentrations of both NO_x and PO₄ and flow, there is a strong positive correlation between PO₄ loading and discharge at both the River Sink and River Rise (Figure 5-13C and D). This relationship reflects the compounding effect of having PO₄ concentrations increase during high flow events.

Differences in the relationship between concentrations and loading of NO_x and PO₄ and the flow conditions may reflect different sources of the two nutrients. If NO_x concentrations are largely anthropogenic from animal waste and/or fertilizers (e.g., Katz, 2004; Katz et al., 2001; Katz et al., 2004), increased flow is likely to deplete this limited

source of NO_x as well as dilute source. In contrast, PO₄ has a large natural source from apatite contained within the Hawthorn Group (Scott, 1988). Apatite is a Ca-phosphate mineral with highly variable stoichiometry, but which can roughly be represented as Ca(PO₄)₃(OH,F,Cl) (Deer et al., 1966). High flow and increased erosion and weathering of the Hawthorn Group, may release PO₄ to the river. Such erosion would be most active along the Cody Escarpment with its relatively high relief and could provide large amounts of PO₄ to the system.

5.4.2 Sources and modifications of NO_x and PO₄

The differences in NO_x and PO₄ concentrations in relationship with stage suggest that there are differences in the sources and delivery of these nutrients to the lower Santa Fe River. As shown by flow rates measured during the dye trace experiment (section 4-4 and temperature tracing (Martin and Dean, 2001), the amount of time it takes for water to flow from the River Sink to the River Rise varies from less than a day at high flow conditions to more than 10 days at low flow conditions. The rapid flow and consequently short residence time in the subsurface during floods suggests that low NO_x concentrations are unlikely to result from denitrification processes as nitrate flows through the conduits. The rapid flow would allow the water in conduits to remain relatively well oxygenated and shorten the length of time for microbial NO_x reduction to occur. Alternatively NO_x concentrations could be diluted by rain water containing little NO_x during high flow events, similar to dilution of the non-nutrient elements. Similarly, little water flows from the matrix porosity during the high flow events as shown by mixing calculations (e.g. Table 5-1) and thus the NO_x concentrations in the conduits are unlikely to be diluted by the low NO_x concentrations in the aquifer water shown by low concentrations in the monitoring wells.

The limitation of denitrification is suggested by plots comparing NO_x concentrations and loading at the River Sink to those at the River Rise (Figure 5-14). During all but two sampling times, the NO_x concentrations and loads are elevated in the River Rise over those values for the River Sink, and the amount that NO_x concentrations are elevated in the River Rise range up to nearly an order of magnitude over the concentrations at the River Sink. The concentrations usually decrease, however, from the

River Sink to the Paraner's Branch Sink and then increase at Sweetwater Lake and the River Rise (e.g. data shown in Appendices). This distribution of concentrations suggests that water flowing to Sweetwater Lake may contain the elevated NO_x concentrations and suggests that the ground water concentrations and/or land use in the region may provide sources of NO_x.

Only two of the wells, Wells 3 and 4 have measurable quantities of NO_x (see Appendices) and concentrations of NO_x in the ground water are typically lower than the NO_x concentrations in the conduits as sampled at the karst windows. Wells 3 and 4 are located closest to the conduit feeding the River Rise (Figure 2-1) and thus the NO_x concentrations in these wells likely relate to the NO_x in the porous matrix that could flow to the conduit. Because the other nearby wells (5, 6, and 7) have no measurable NO_x, it appears that the NO_x found in Wells 3 and 4 may derive from water lost from the conduit rather than contributing to the surface water. An alternate source of NO_x could be from oxidation of reduced forms of N, for example NH₃. Wells 3 and 4 have the highest concentrations of DO which could limit the magnitude of denitrification in these regions. The cause of elevated DO concentrations is unknown, but these elevated concentrations are consistent throughout the project. Oxygen concentrations in the water decrease systematically as it flows from the River Sink to the River Rise, suggesting that reduced dissolved species are oxidized along the flow path. Only a few wells, including Wells 2, 7 and 8, have elevated NH₃ concentration, but these wells are located on the western side of the field area, which was shown to be a potential source of water to the River Rise in the major element chemistry (Figure 5-1).

Alternatively, NO_x could be contributed to Sweetwater Lake by conduits that are known to extend beyond the eastern edge of O'Leno State Park (Figure 5-15A). These conduits have no perennial surface water flowing into them, but there is a major change in the land use at the boundary of the park (Figure 5-15B). Within the park boundaries, land use is largely hardwood and pine hammocks and wetlands, all of which would contribute large amounts of organic carbon and would be expected to drive large amounts of denitrification. On the eastern side of the park, land use changes mostly to improved pasture with some row field crops. If NO_x is applied to the surface in this region, it could rapidly flow into the conduits and discharge at the River Rise with little modification by

denitrification to its concentrations. The influence of the eastern conduits to the NO_x concentrations at the River Rise would require routine sampling of water quality directly from the conduits. This monitoring would have to occur at all discharge conditions because of the large variability in concentrations through time and at different flow conditions (e.g. Figure 5-10).

In contrast with the lack of NO_x correlations between the River Sink and River Rise, PO₄ concentrations and loading correlate well between the River Sink and River Rise (Figure 5-16). The slope of a linear regression correlation for PO₄ concentrations at the River Sink and River Rise is 0.82 with an R² value of 0.87. The slope of a linear regression correlation for PO₄ loading at the River Sink and River Rise is 1.34 with an R² value of 0.98. A slope of less than one for the regression lines for PO₄ concentrations indicates that on average, PO₄ concentrations at the River Rise are lower by about 10% than expected based on PO₄ concentrations at the River Sink, and this amount of PO₄ must be lost from the water during its passage from the River Sink to the River Rise. The change in concentrations could result from differences in concentration of the source water, particularly coming from the eastern conduit, but this source would also have to be confirmed through direct sampling of the water in the conduit. Alternatively, phosphate is highly reactive with carbonate minerals (e.g., von Wandruszka, 2006), and thus some of the loss of PO₄ concentration may be a result of adsorption to the carbonate minerals of the Floridan Aquifer. The slope of the regression line is greater than one when comparing PO₄ loading at the River Sink and River Rise, and indicates that the loading of PO₄ increases by about 35% between the River Sink and River Rise. Increases in loading comes from the increase in discharge, at least at average flow conditions, between the River Sink and River Rise. The increase in loading will also depend on the concentrations of PO₄ in water flowing to the conduit.

Comparisons of N/P ratios to river discharge show that the N/P ratio decreases at elevated discharge for both the River Sink and the River Rise (Figure 5-17). In general, the River Rise has higher N/P ratios than those at the River Sink at any one discharge, reflecting the higher nitrate concentrations at the River Rise than at the River Sink. The greater N/P ratios at the River Rise than at the River Sink suggests that there is loss of P or an increase in NO_x along the subsurface flow path. This increase in N/P ratio also

suggests there may be little denitrification along the subsurface flow path as reflected in changes in NO_x concentrations with time (Figure 5-10).

Regardless of possible changes to NO_x and PO₄ concentrations along the flow path, the absolute N/P molar ratio is significantly lower than the Redfield Ratio (Figure 5-17). The Redfield Ratio was defined for marine systems based on the average molar ratio of organic matter in sediments, which was found to equal approximately 16 (Redfield, 1958). Although defined for marine systems, the N/P ratio of 16 is a valuable indicator of the nutrient limitation in systems. In the O'Leno State Park region, where the highest observed N/P molar ratio is around 11 and many of the ratios are below 1, there is an excess of P in the system compared to N, at least relative to the Redfield Ratio. Consequently, in this location, N limitation may be important so that addition of N may alter ecosystem function. Consequently, it will be important to determine the cause and source of the elevated NO_x that discharges from the River Rise relative to the River Sink.

Table 5-1. Fraction of water discharging from the River Rise originating from the River sink and two ground water end members

Sample Date	Rise Discharge (m³/s)	River Sink (%)	Well 2 (%)	Well 4 (%)
3/5/03	40.60	96.7	0	3.3
4/30/03	12.00	38.3	26.1	35.6
1/23/04	5.20	84.8	19.1	0
3/8/04	9.60	74.1	5.6	20.3
5/5/04	6.10	58.3	22.2	19.5
1/19/05	18.00	84.4	20.5	0
3/18/05	20.20	73.3	14.9	11.8
7/18/05	49.50	96.6	3.8	0
10/27/05	15.70	75.8	12.2	12
1/17/06	30.40	65.8	4.2	30
4/12/06	10.30	72.9	22.1	5
7/13/06	7.50	57.5	17.1	25.4
10/10/2006	5.20	46.7	22.1	31.2
01/17/2007	3.9	69.5	17.7	12.8
04/10/2007	3.61	43.5	23.6	32.9

Table 5-2. NO₃ Loading at the River Sink and Rise

Sample Date	Sink			Rise			NO ₃ Change*
	Discharge	NO ₃ conc.	NO ₃ Load	Discharge	NO ₃ conc.	NO ₃ Load	
	(m ³ /s)	(mg/L)	kg/day	(m ³ /s)	(mg/L)	kg/day	
January-03	11.10	0.037	35	12.20	0.036	38	2.5
March-03	43.20	0.026	97	40.60	0.026	91	-5.8
April-03	4.40	0.361	141	12.00	0.370	384	243.0
January-04	0.50	0.175	8	5.20	0.363	163	155.5
March-04	5.30	0.144	66	9.60	0.059	49	-17.0
May-04	0.00	0.025	0	6.10	0.225	119	118.6
January-05	8.70	0.183	138	18.00	0.349	543	405.2
March-05	9.50	0.105	86	20.20	0.230	401	315.2
July-05	35.30	0.034	104	49.50	0.063	269	165.7
October-05	3.80	0.249	82	15.70	0.324	439	357.7
January-06	20.80	0.055	99	30.40	0.066	173	74.5
April-06	2.60	0.420	94	10.30	0.526	468	373.7
July-06	0	0.008	0	7.50	0.280	181	181.4
October-06	0	0.013	0	5.20	0.252	113	113.2
January-07	0	0.006	0	3.9	0.186	63	62.7
April-07	0	0.016	0	3.61	0.228	71	71.1

Table 5-3. PO₄ Loading at the River Sink and Rise

Sample Date	Sink			Rise			PO ₄ Change*
	Discharge	PO ₄ conc.	PO ₄ Load	Discharge	PO ₄ conc.	PO ₄ Load	
	(m ³ /s)	(mg/L)	kg/day	(m ³ /s)	(mg/L)	kg/day	
January-03	11.10	0.105	101	12.20	0.103	109	7.9
March-03	43.20	0.254	948	40.60	0.234	821	-127.2
April-03	4.40	0.181	52	12.00	0.137	142	90.0
January-04	0.50			5.20			
March-04	5.30			9.60			
May-04	0.00	0.118	0	6.10	0.098	52	51.6
January-05	8.70	0.143	107	18.00	0.15	233	125.8
March-05	9.50	0.113	93	20.20	0.105	183	90.5
July-05	35.30	0.187	570	49.50	0.18	770	199.5
October-05	3.80	0.181	59	15.70	0.134	182	122.3
January-06	20.80	0.093	167	30.40	0.096	252	85.0
April-06	2.60	0.14	31	10.30	0.104	93	61.1
July-06	0	0.107	0	7.50	0.097	63	62.9
October-06	0	0.083	0	5.20	0.081	36	36.4
January-07	0	0.113	0	3.9	0.105	35	35.4
April-07	0	0.151	0	3.61	0.098	31	30.6

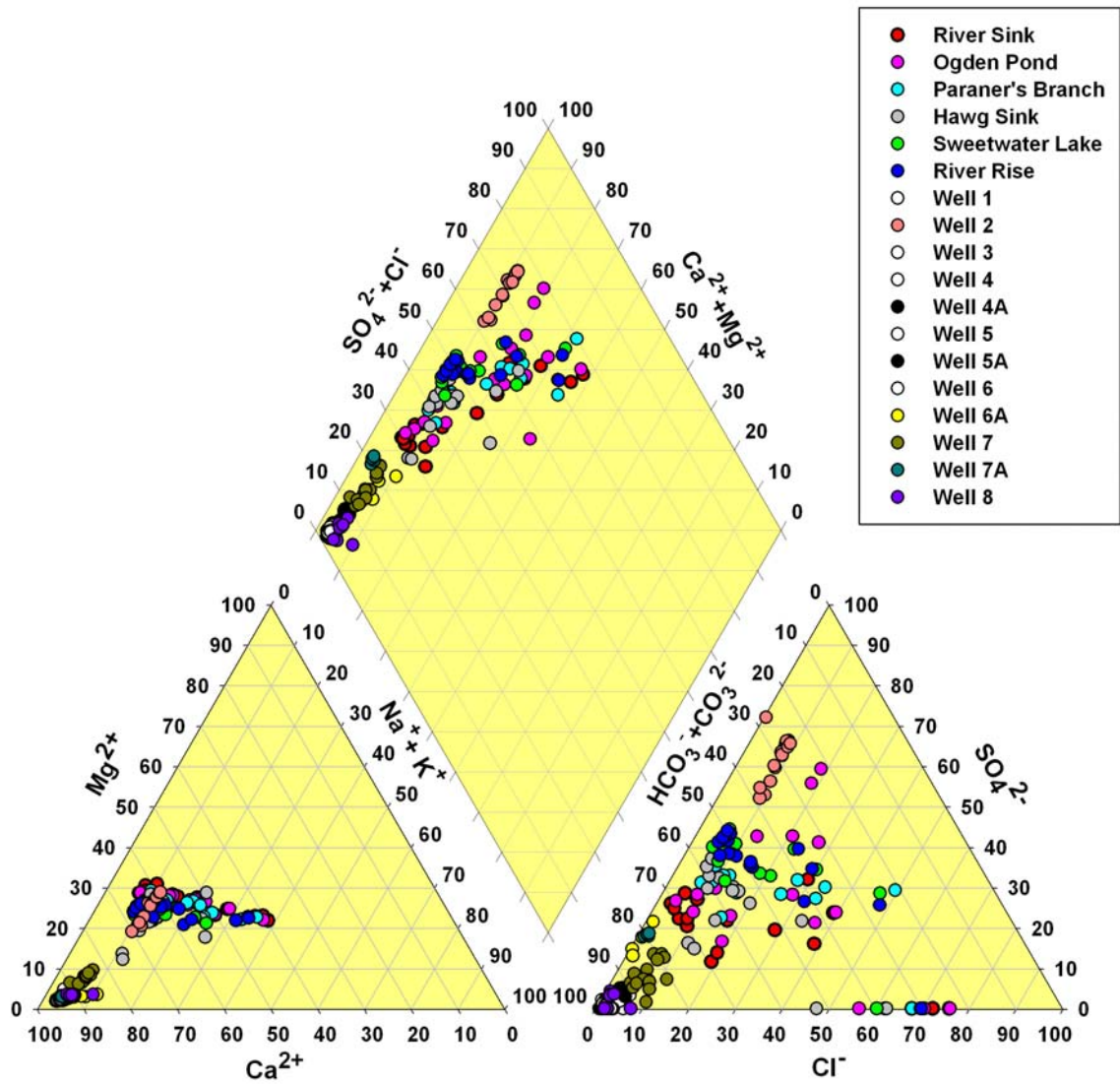


Figure 5-1. Piper diagram of major element chemistry for all quarterly sampling trips and at all sites including surface water from River Rise, River Sink and Karst windows and ground water from the monitoring wells.

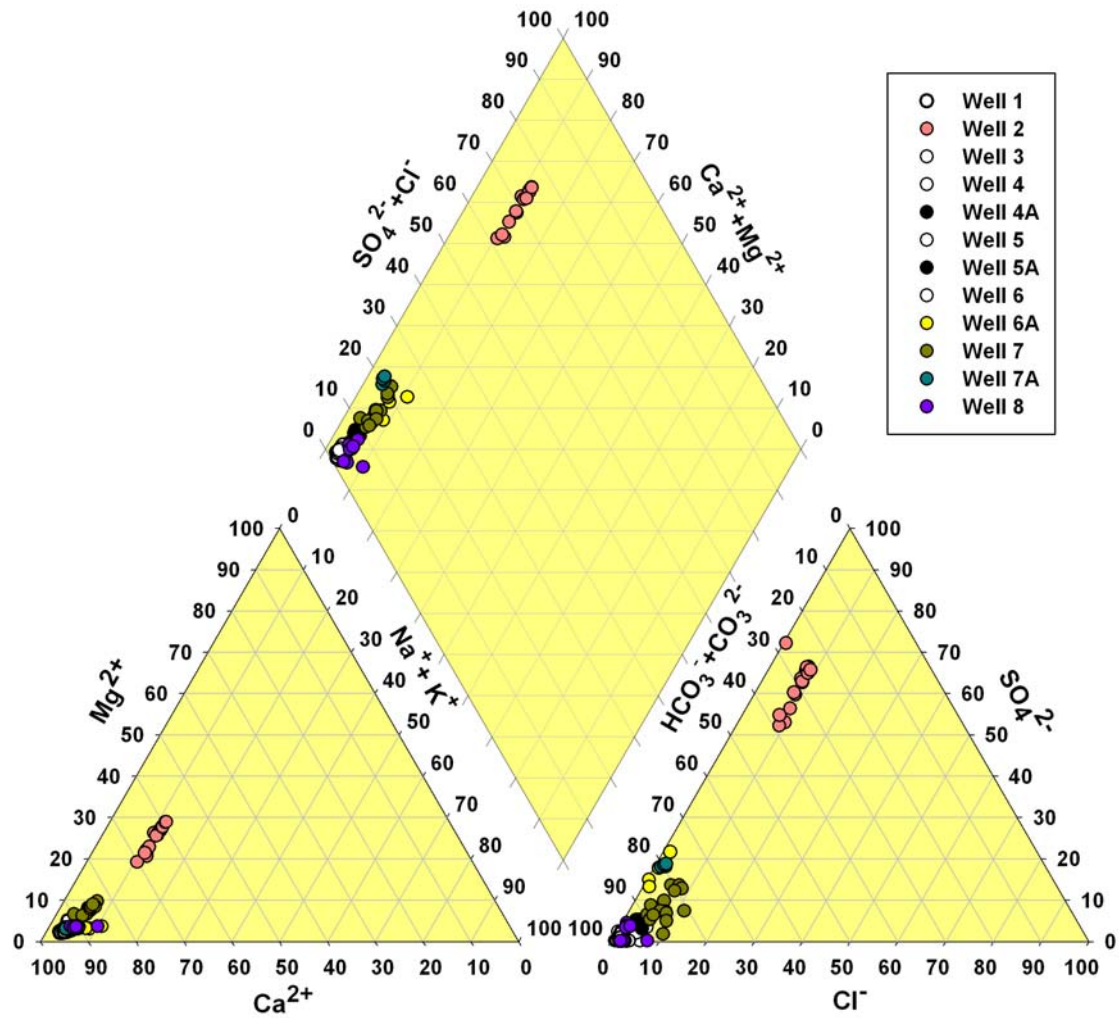


Figure 5-2. Piper diagram of major element chemistry for ground water sampled from eight monitoring wells. Wells with the letter A designation are shallow wells

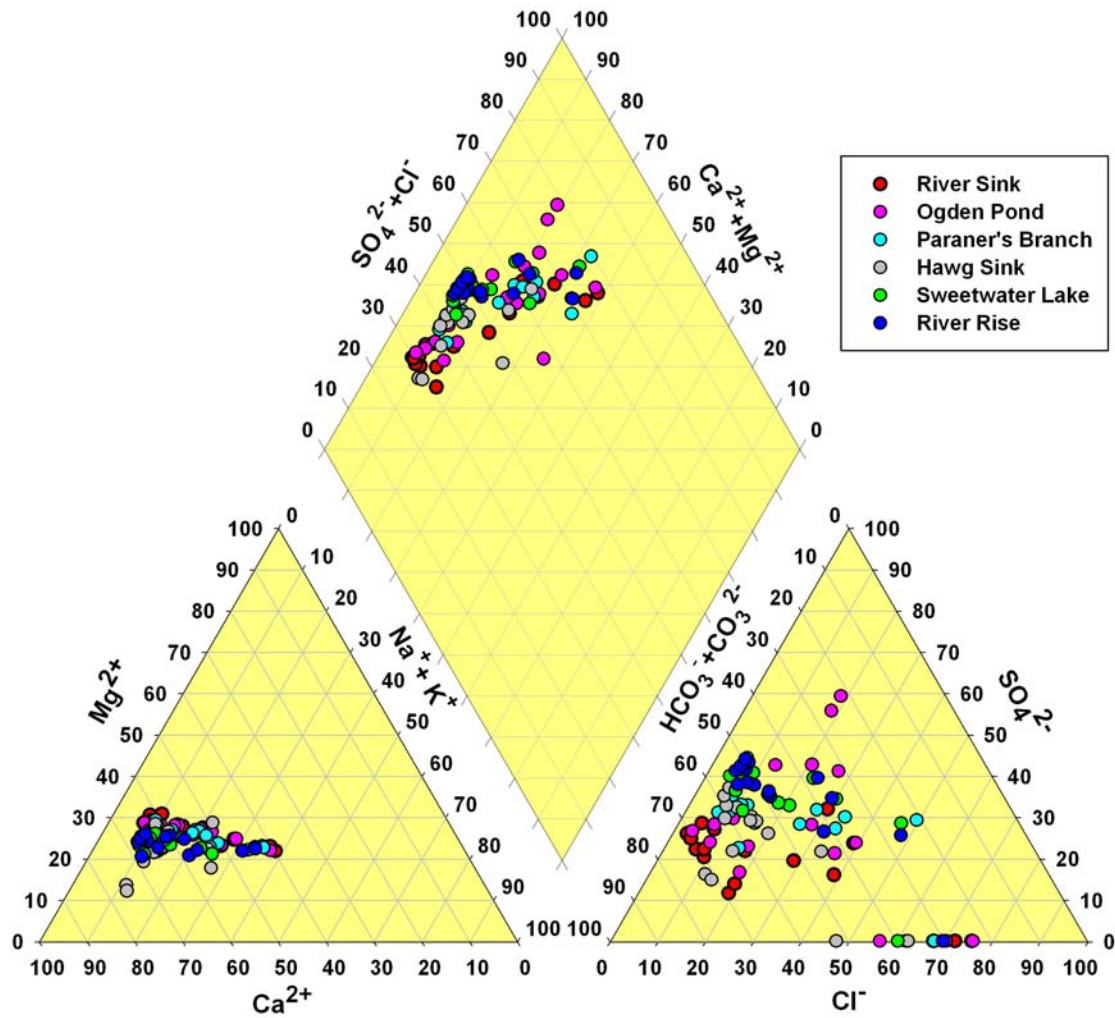


Figure 5-3. Piper diagram of major element chemistry for surface water sampled from the River Sink, River Rise, and intermediate karst windows.

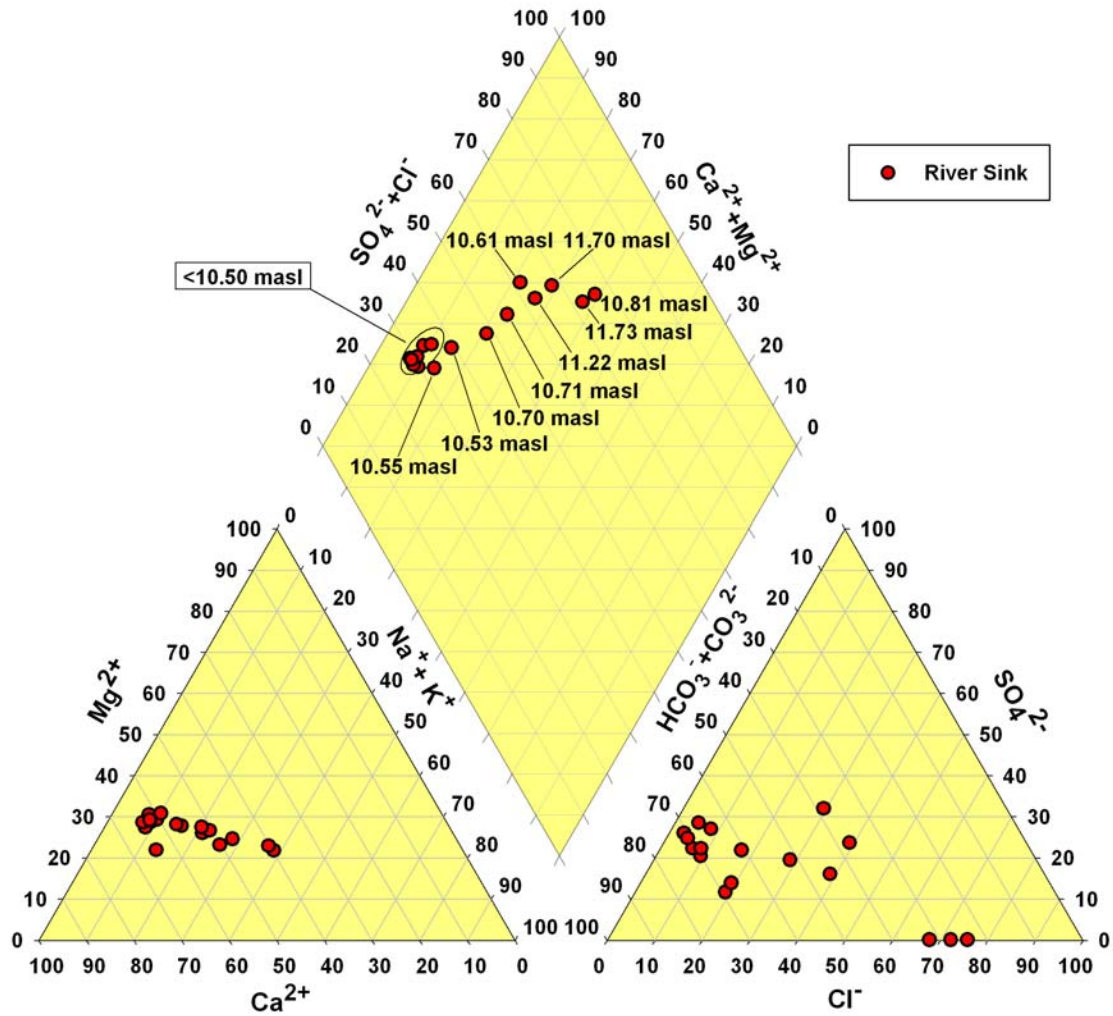


Figure 5-4. Piper diagram of major element chemistry from River Sink compared to river stage. Trend suggests water at the River Sink approaches a Na-Cl end member as river stage increases.

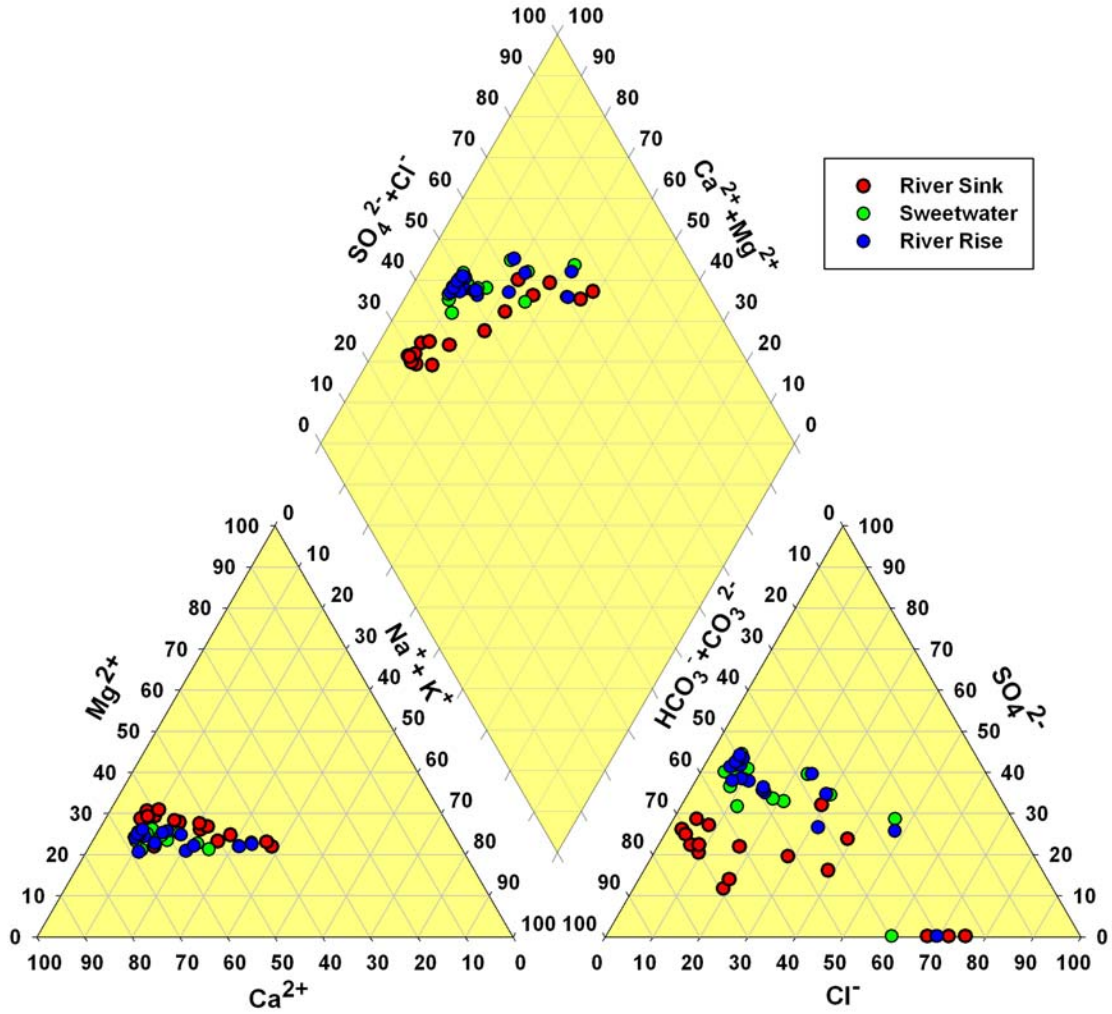


Figure 5-5. Piper diagram of major element chemistry from River Sink, Sweetwater Lake and River Rise. The figure shows increased fraction of the Na-Cl end member at Sweetwater Lake and the River Rise relative to the River Sink during low flow conditions. The fraction of the Na-Cl end member is similar between the Sweetwater Lake and the River Rise.

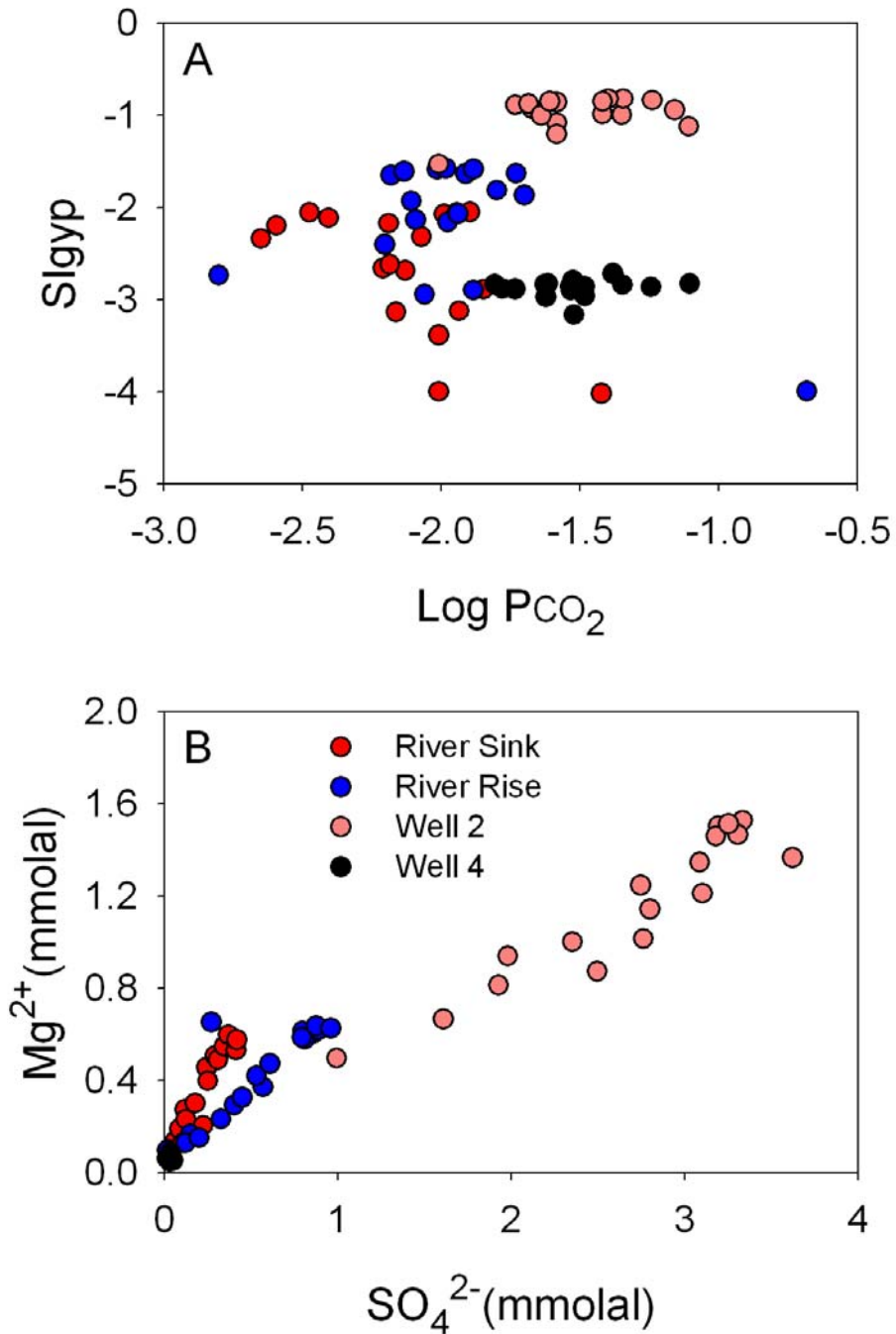


Figure 5-6. A. Plot of saturation index of gypsum to P_{CO2}. Ground water at Well 2 is about 2 orders of magnitude closer to equilibrium with gypsum than Ground water at Well 4 and 1 to 3 orders of magnitude above water at the River Sink. B. Comparison of Mg²⁺ and SO₄²⁻ concentrations showing spatial and temporal variation.

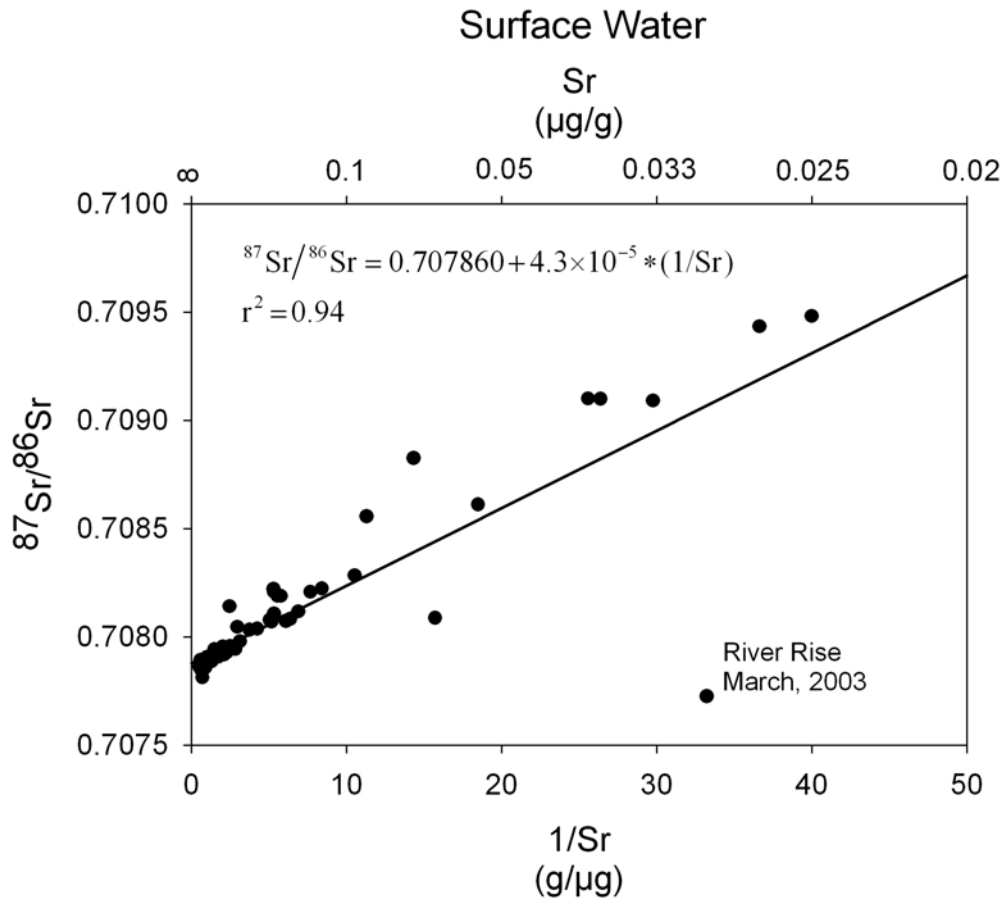


Figure 5-7. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios versus $1/\text{Sr}$ concentrations for surface water. The regression line shown includes excludes the value for the sample from the River Rise during the flood in March, 2003.

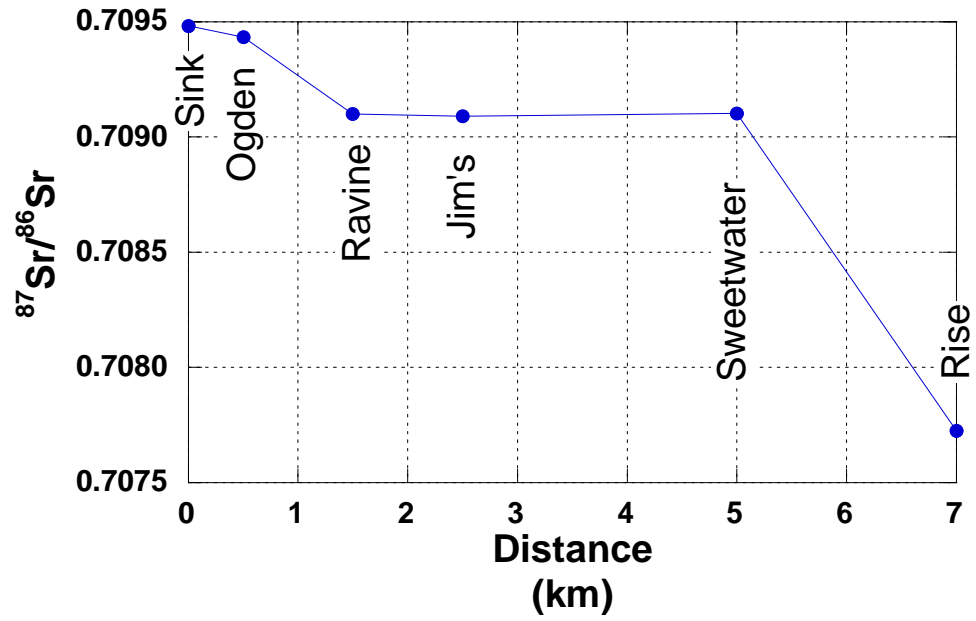


Figure 5-8. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios versus distance along the flow path at high flow conditions.

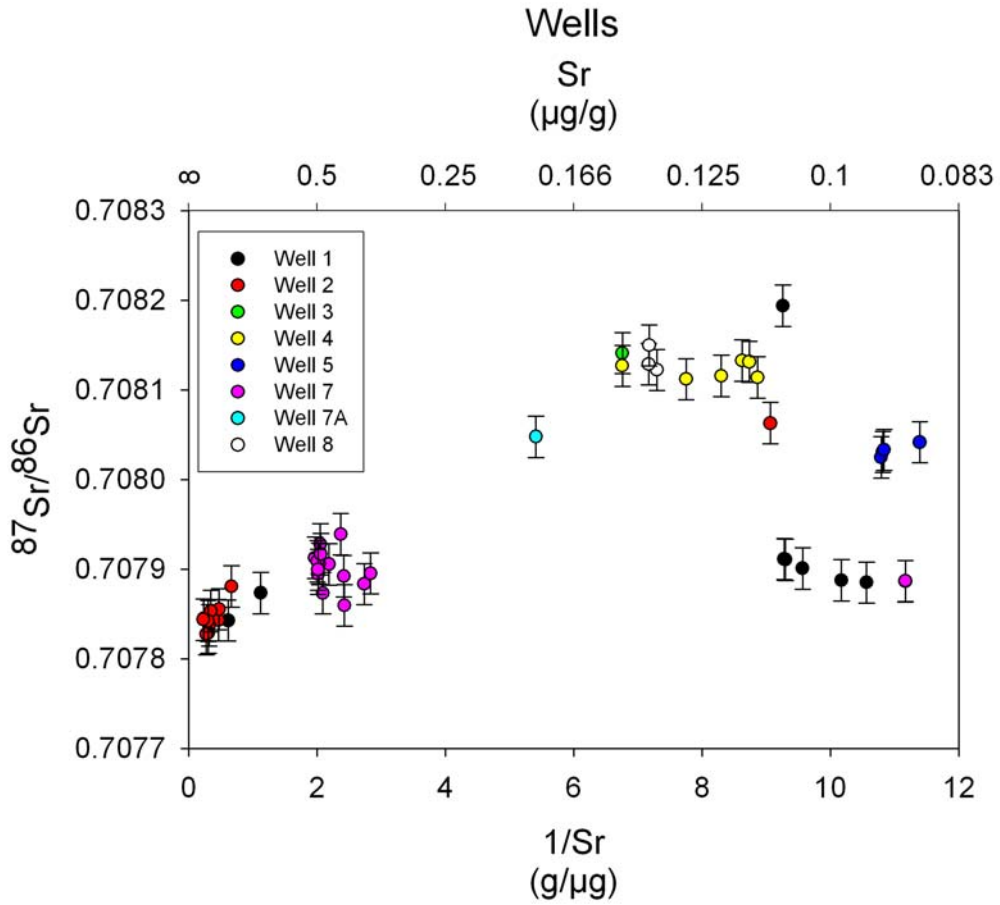


Figure 5-9. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios versus $1/\text{Sr}$ concentrations for ground water. Error bars represent 2σ error of isotope measurements (0.000023).

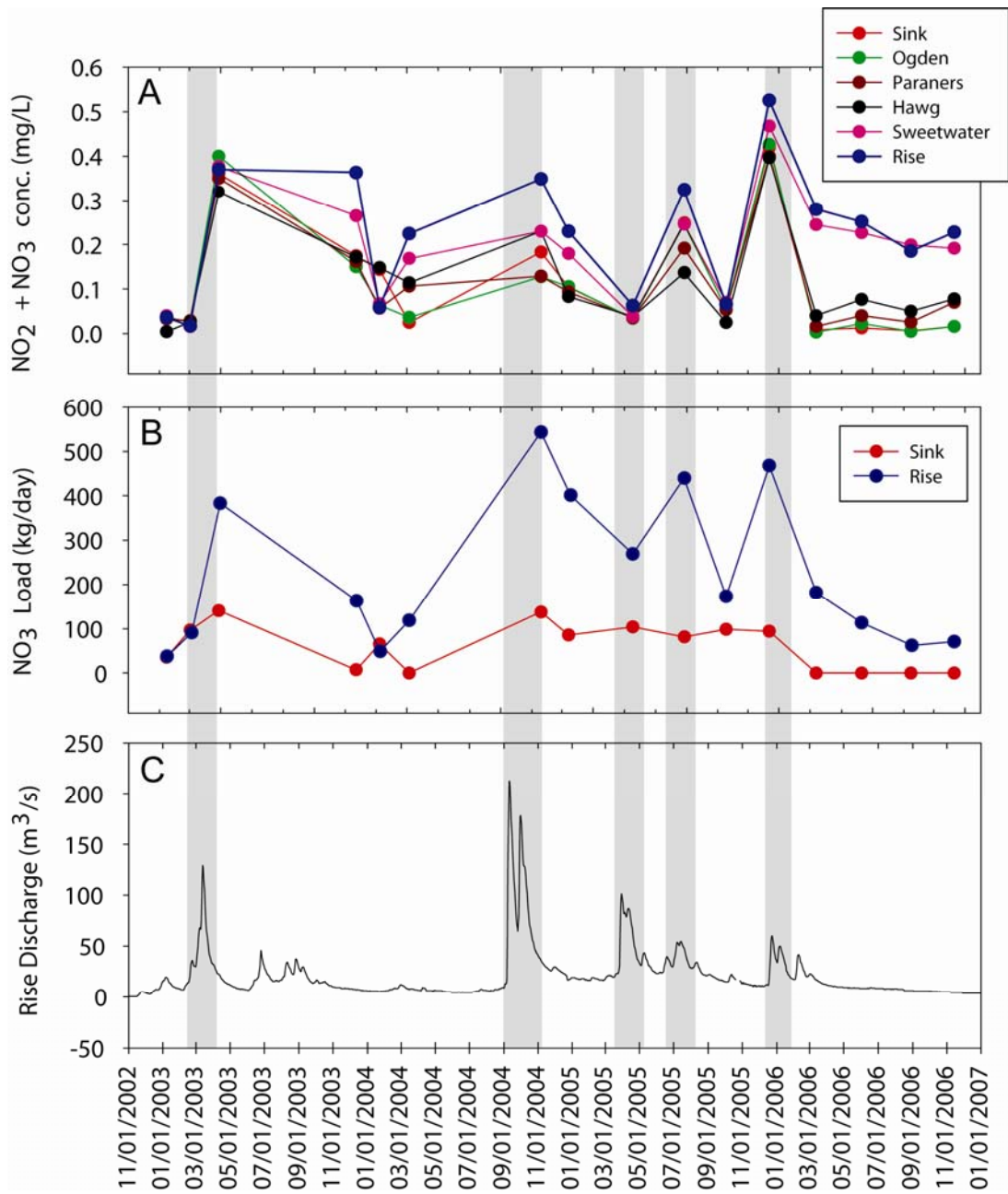


Figure 5-10. A. NO_x concentrations at the River Sink, Rise, and karst windows. B. NO_x loading at the River Sink and River Rise. C. Discharge at the River Rise. Vertical gray bars represent periods of high flow as shown in panel C.

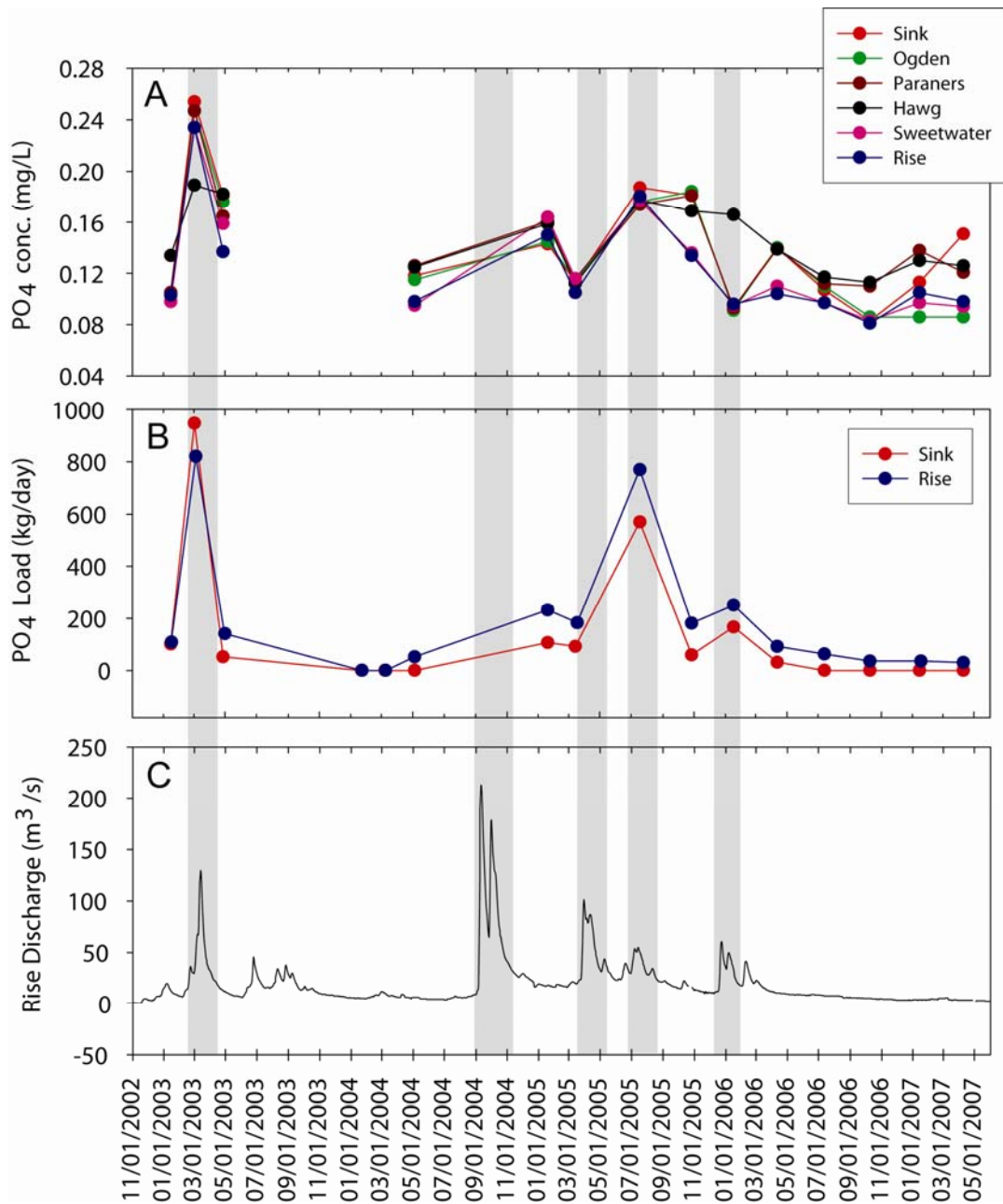


Figure 5-11. A. PO₄ concentrations at the River Sink, Rise, and karst windows. B. PO₄ loading at the River Sink and River Rise. C. Discharge at the River Rise. Vertical gray bars represent periods of high flow as shown in panel C.

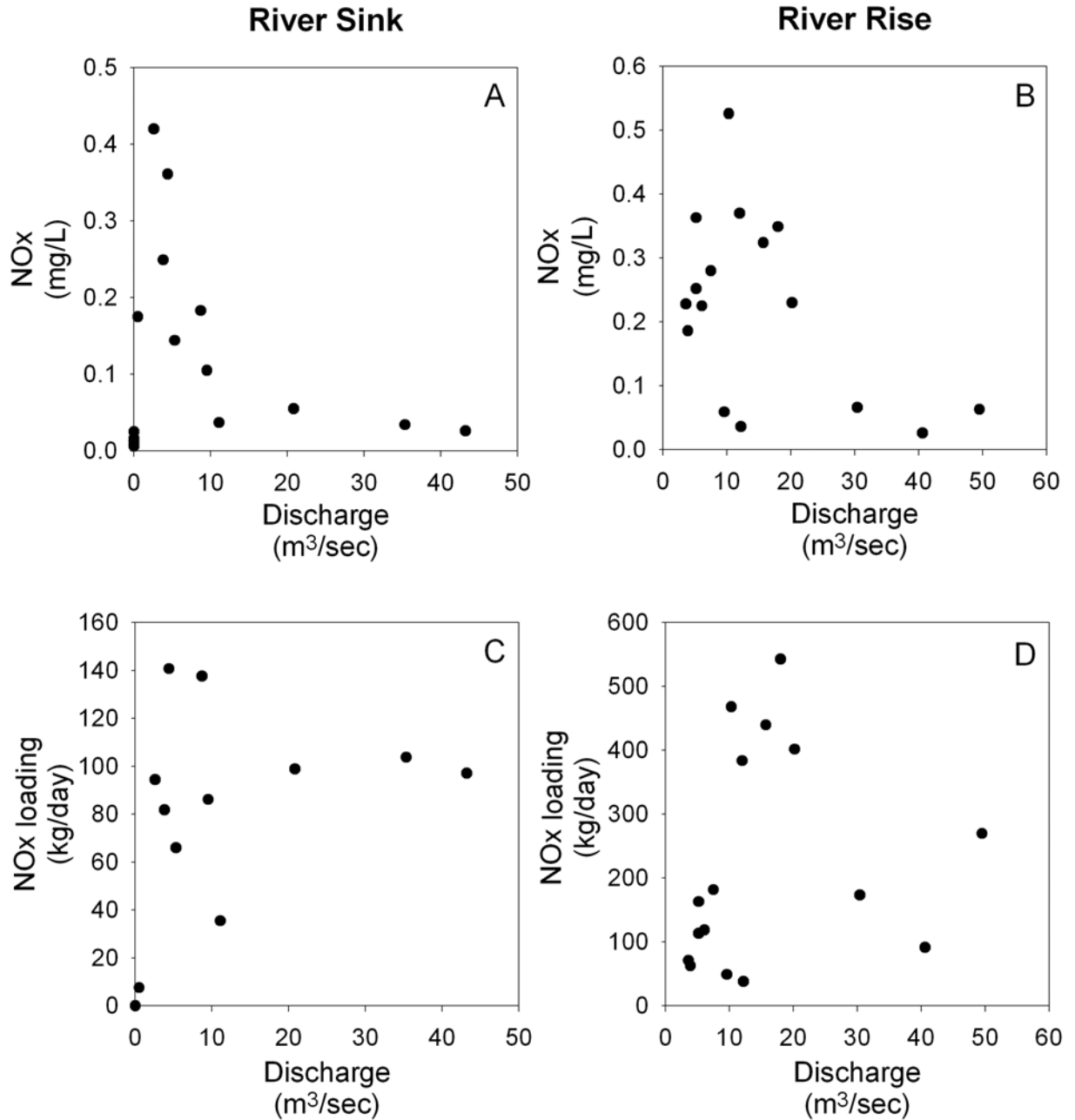


Figure 5-12. A. NO_x concentration versus discharge at the River Sink. B. NO_x concentration versus discharge for the River Rise. C. NO_x concentration versus discharge for the River Rise. D. NO_x loading versus discharge for the River Sink.

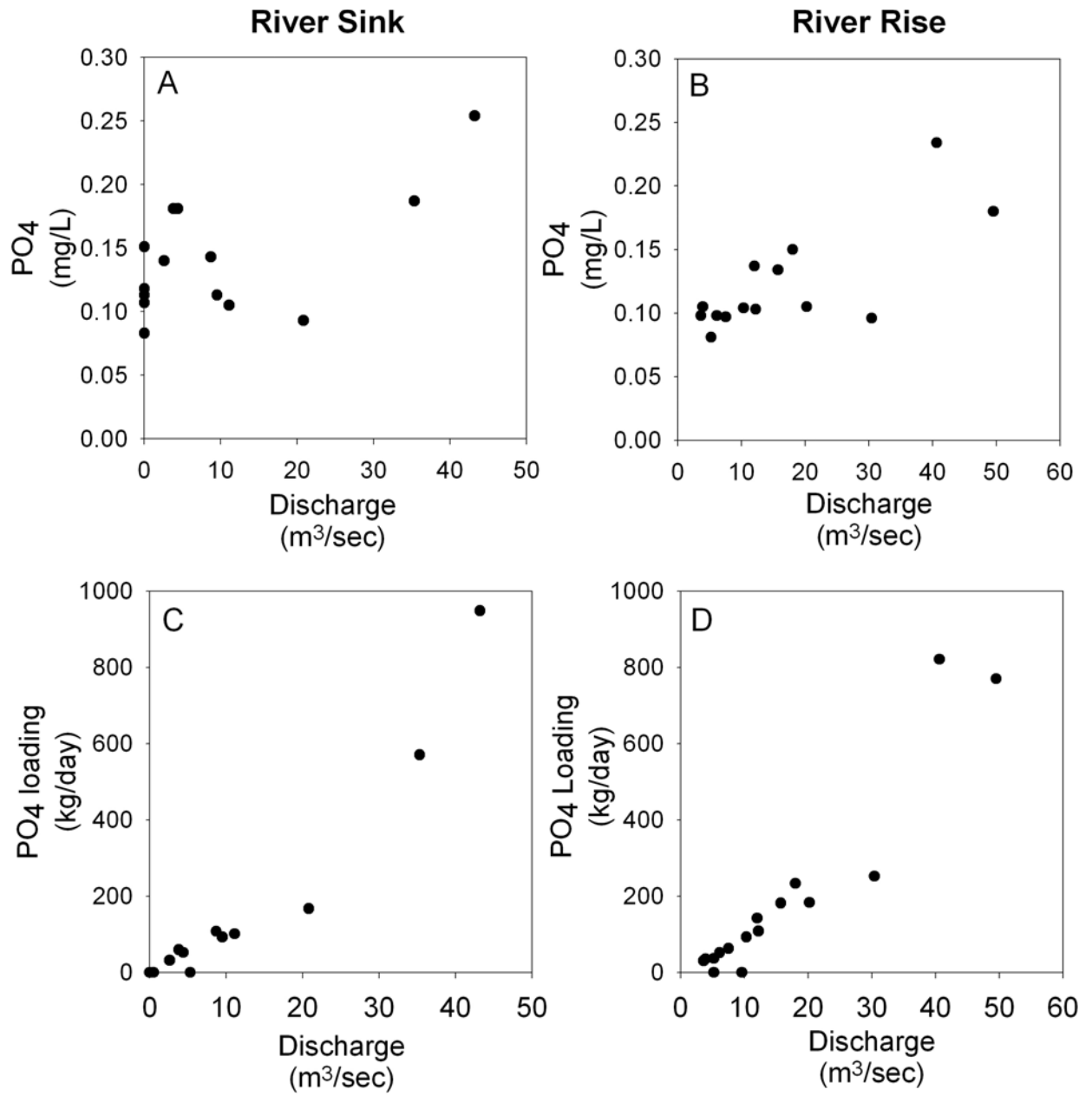


Figure 5-13. A. PO₄ concentration versus discharge at River Rise. B. PO₄ concentrations versus discharge at River Rise. C. PO₄ loading versus discharge at River Sink. D. PO₄ loading versus discharge at River Rise.

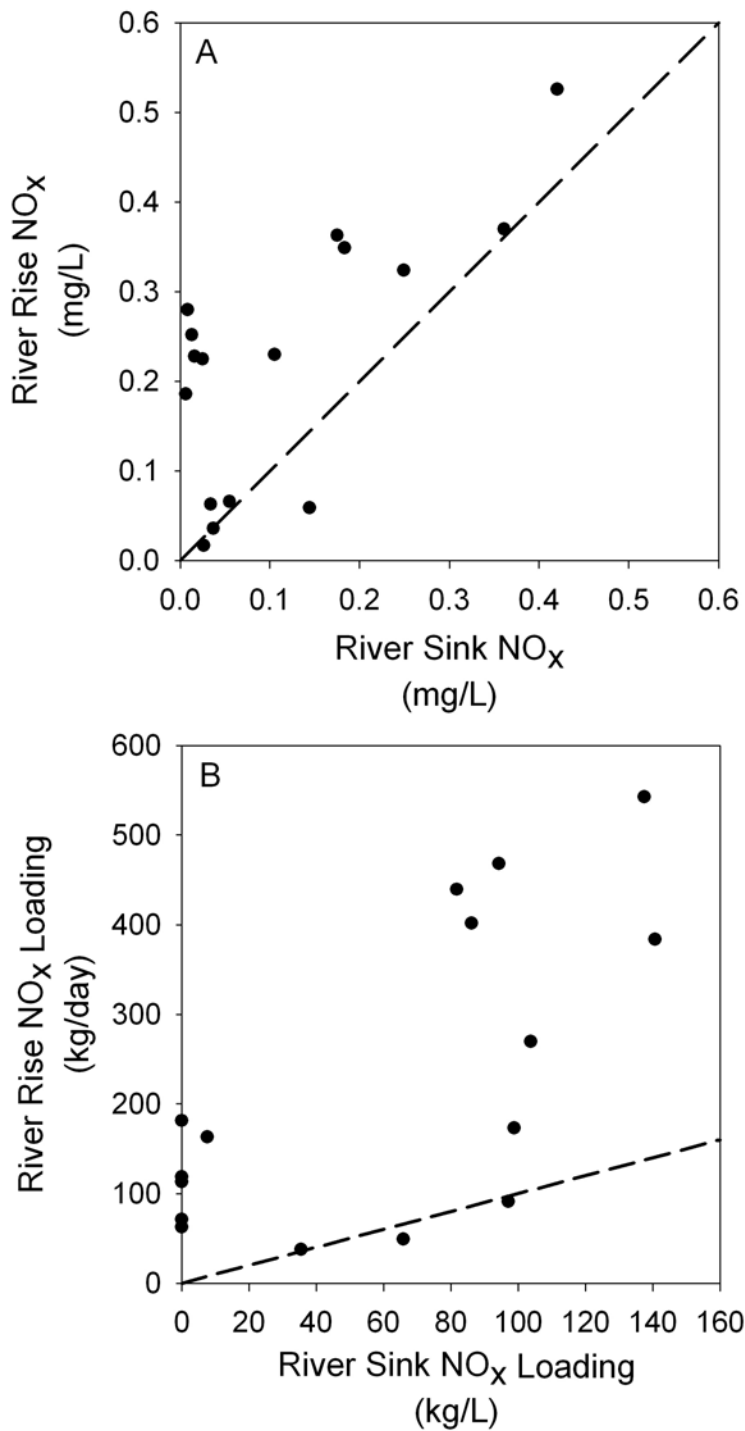
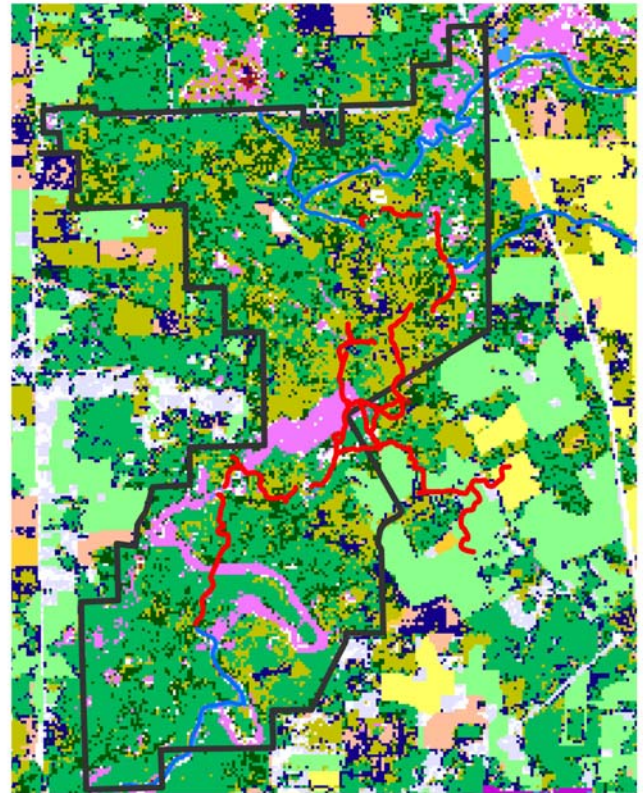
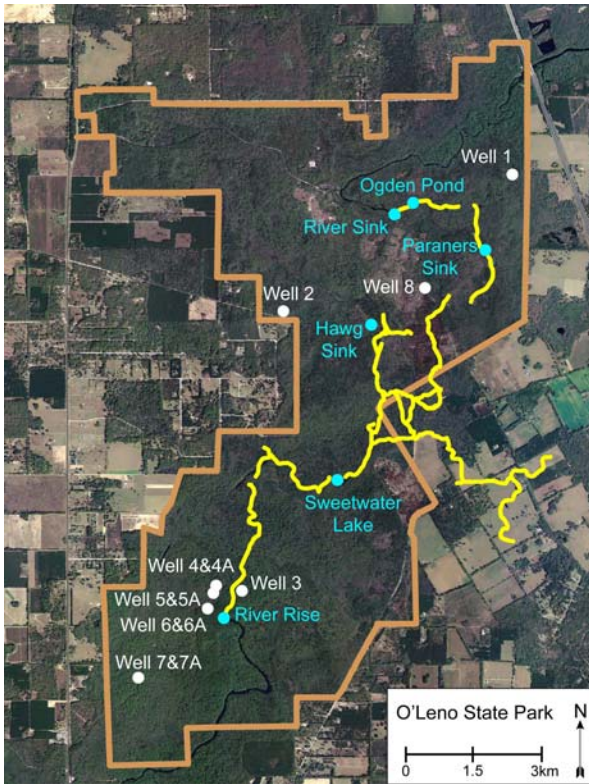


Figure 5-14. A. NO_x concentrations at the River Sink versus NO_x concentrations at the river rise. B. NO_x loading at the River Sink versus the NO_x loading at the River Rise. The solid lines represent identical concentrations and loading values at the two locations.



Vegetation Cover O'Leno State Park

Florida Vegetation and Land Cover Data
Derived from 2003 Landsat ETM+ Imagery
Florida Fish and Wildlife Conservation Commission

Legend

Mixed Pine & Hardwood	Row/Field Crops
Hardwood Hammocks	other Agric
Pinelands	High Impact Urban
Cypress Swamp	Low Impact Urban
Hardwood Swamp	Extractive
Open Water	Park Boundary
Shrub, brushland	Conduits
Bare soil, clearcut	
Imp Pasture	

0 1.5 3km



Figure 5-15. A. Aerial photograph of O'Leno State Park showing location of sampling sites and known conduits (yellow lines). B. Land use map in the region of O'Leno State Park with known conduits (red lines).

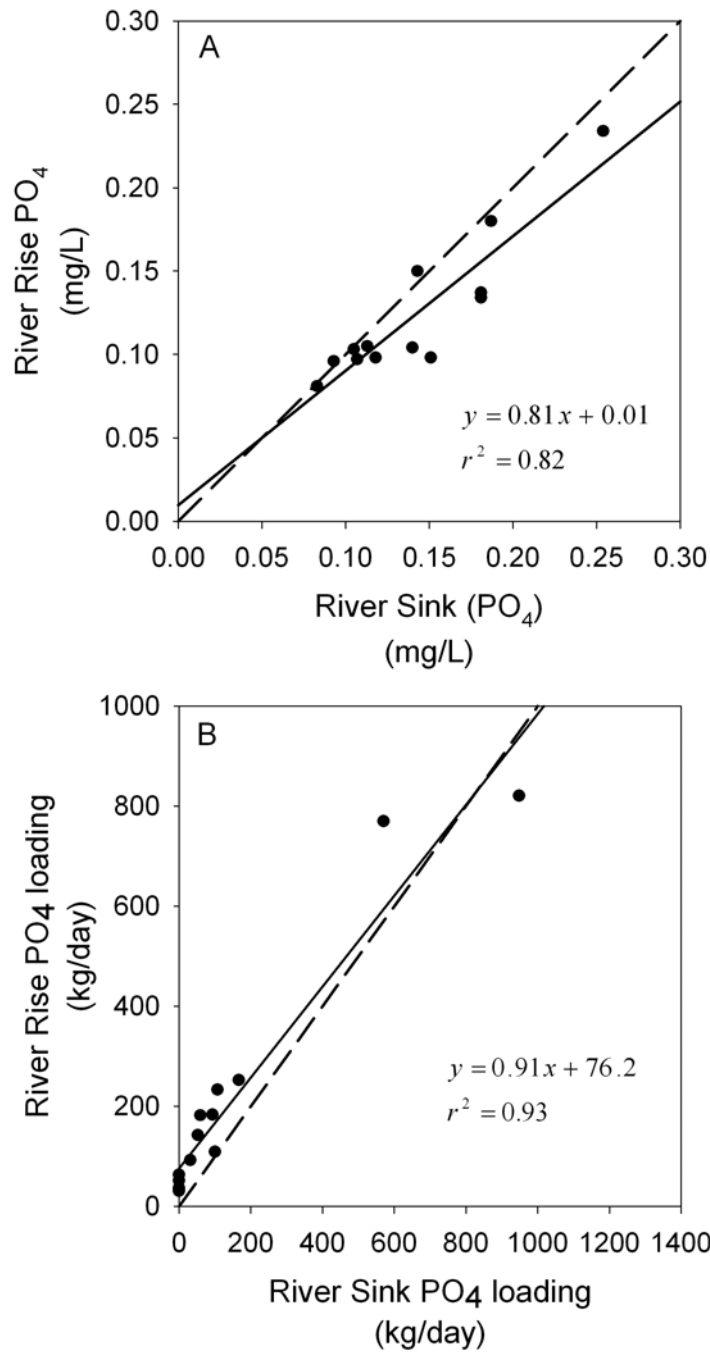


Figure 5-16. A. PO₄ concentrations at the River sink versus PO₄ concentrations at the river rise. B. PO₄ loading at the River sink versus the PO₄ loading at the river rise. The dashed lines represent identical concentrations and loading values at the two locations. The solid lines are linear regressions of the data with the R² values and equations shown on the plots.

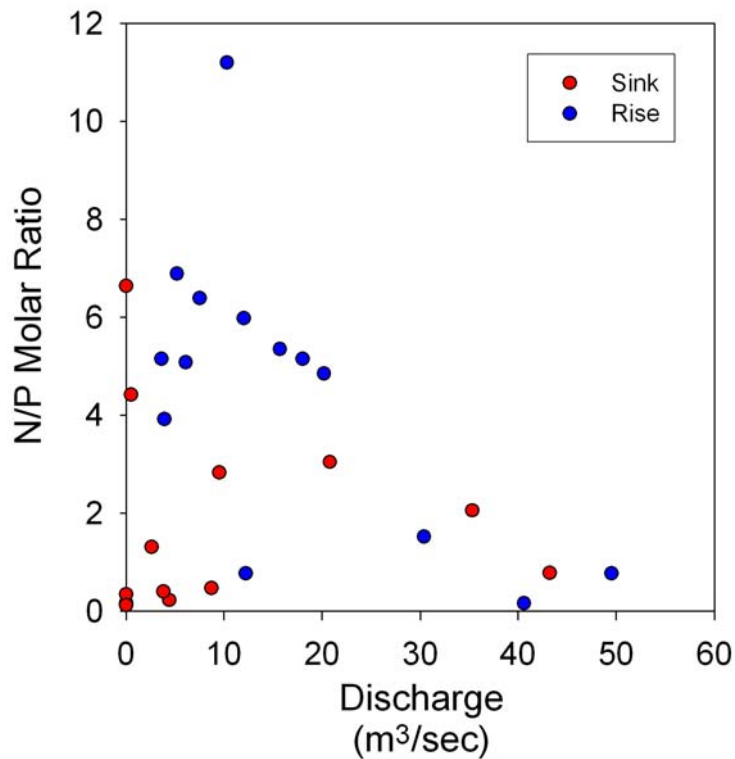


Figure 5-17. N/P molar ratios versus discharge at the Santa Fe River Sink and River Rise. A weak inverse correlation exists between discharge and N/P ratio indicating N concentrations are elevated and/or P concentration are reduced with increasing discharge. For any one discharge condition, the N/P ratio at the River Rise is typically elevated above the N/P ratio at the River Sink suggesting increase in N or loss of P as the water flows through the subsurface. Because at high flow conditions, water is lost to the matrix porosity from the conduits, these changes in N/P ratios reflect nutrient transformations along the flow paths. At low flow conditions, conduits gain water from the matrix porosity, so elevated N/P ratios should reflect contributions from the ground water.

6 SUMMARY AND CONCLUSIONS

Results of the flow measurements, major element compositions of water, dye trace results, and Sr isotope ratios indicate that mixing between the surface and ground water along the Cody Escarpment is complex, but that discharge of the river is a major control of water quality and flow through the system. At high flow, more water flows into the River Sink than from the River Rise indicating that some water leaves the conduits and because there are no known dry caves in the region is stored in the subsurface either in the intergranular matrix porosity or fractures, or on the surface in wetlands. During most flow conditions, however, water flows from the intergranular matrix porosity to the conduits and ultimately discharges from the River Rise, which represents the major drain in the region. Lack of continuous discharge measurements at the River Sink prevent identifying the stage (or stages) when this flow reversal occurs.

Major element chemistry indicates there are two primary types of ground water in the region. One end member has a Ca-HCO₃ composition that results from carbonate mineral dissolution. The other type of ground water has a Ca-SO₄ composition, and low Sr isotope ratios. The Ca-SO₄ end member is restricted to the northwestern portion of the field area and may be influenced by dissolution of gypsum and dedolomitization. These reactions suggest that the water at this location originates deep within the stratigraphic section and flows upward. Less than half of the surface water at the River Sink, River Rise and intermediate karst windows at low flow conditions is composed of variable amounts of these two water sources. The contribution from the Ca-SO₄ end member to

the River Rise indicates that the River Rise drains the western portion of the field area, although most of the conduits connected to the River Rise are located to the eastern side of O'Leno State Park.

Another surface water end member occurs at high flow conditions when the composition of the water varies toward a Na-Cl composition. The change in the composition of the water reflects dilution by precipitation that has elevated Na and Cl concentrations, and the most likely source of Na and Cl is from sea spray. Strontium isotope ratios and Sr concentrations are strongly correlated in the surface water and reflect two end members similar to the major element chemistry. One end member has high Sr concentrations and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios resulting from dissolution of the carbonate minerals. The other end member, which occurs at high flow conditions and corresponds to the Na-Cl end member, has low Sr concentrations but $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios elevated above modern seawater value. Low Sr concentrations in this end member reflect dilution by rain water but the radiogenic Sr isotope composition reflects interaction with the Hawthorn Group minerals, which are likely to have elevated ^{87}Sr concentrations from ^{87}Rb contained in the fine grained siliciclastic minerals. The dilute Sr concentrations and elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios reflect a significant input of water flowing off of the confined portion of the Floridan Aquifer.

Both NO_x and PO_4 concentrations respond to changes in flow through the system, but they respond in opposite ways. Precipitation and elevated discharge reduces NO_x concentrations, while PO_4 concentrations are unaltered by high flow. The reduction in NO_x concentrations is likely a result of dilution, similar to the major element compositions. The lack of change in PO_4 concentrations with river stage indicates that other processes besides dilution is important. Chemical interaction with Hawthorn Group minerals could play an important role in PO_4 distributions because of its high phosphorous content in the form of apatite, a phosphate-bearing mineral. The declining NO_x concentrations suggest that the source of NO_x , which is expected to relate largely to anthropogenic loading, is quickly flushed from the system with rainfall.

As water flows from the River Sink to the River Rise, NO_x concentrations can be increased by almost an order of magnitude, reflecting a source of NO_x to the conduit

system. In contrast, PO_4 concentrations decrease slightly (by about 10%) as they flow from the River Sink to the River Rise reflecting a loss of PO_4 along the flow path. There are at least two possible sources for the increase in NO_x from the River Sink to the River Rise. One source is from oxidation of elevated NH_3 concentration in the Ca- SO_4 end member in the western portion of the region. Another possible contribution of NO_x to the River Rise could be from conduits that drain the areas to the east of O'Leno State Park boundary. The high source of phosphorous to the area makes the N/P ratios at all times lower than the Redfield Ratio of 16. This low ratio indicates that the limiting nutrient in the region is N and that addition of nitrate may have detrimental effects to ecosystems. The high phosphorous concentrations will be carried downstream away from its solid source and where encountering high nitrate concentrations could be important to systems downstream.

All surface and ground water mixing along the Cody Escarpment depends on river stage, and is critically important for the chemical composition of the surface water. The mixing also must influence the composition of the ground water, but this influence is more subtle and difficult to observe than the influence on the surface water composition. The change in the ground water composition, particularly the water contained in the intergranular porous matrix of the Floridan Aquifer is what will be most important for the composition of water discharging from springs in the vicinity of the Cody Escarpment. The distribution of nutrient concentrations is also influenced by the Cody Escarpment, in particular from the source of phosphate from the Hawthorn Group. The relationship between NO_x concentrations, PO_4 concentrations, distance from the scarp and variations in concentrations with flow are important aspects of this system and the springs it contains. In particular, it is critical to know how the nutrient concentrations vary with stage of the river and the processes that alter their concentrations.

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8 APPENDIX A

APPENDIX A1. WATER CHEMISTRY DATA JANUARY 15, 16, 20, AND FEBRUARY 5, 2003

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
Vinzants Landing	23.0	6.5 I	11.2	10.40	3.39	1.22	12.0	0.006 I	0.035	0.071	1.23	0.108
Vinzants (dup)	23.0	6.8 I	11.5	10.70	3.45	1.25	12.0	0.005 I	0.041	0.068	1.20	0.106
River Sink	22.8	6.5 I	11.1	10.50	3.37	1.23	12.0	0.006 I	0.037	0.065	1.22	0.105
Ogden Pond	23.1	7.8 I	11.9	10.70	3.56	1.25	12.0	0.005 I	0.036	0.075	1.24	0.103
Big Sink	23.6	17.7	14.9	10.60	4.04	1.19	16.0	0.005 I	0.036	0.068	1.28	0.106
Ravine Sink	23.8	17.6	16.1	11.20	4.33	1.23	16.0	0.012 I	0.042	0.072	1.28	0.075
Paraner's Branch	23.3	17.4	15.0	10.70	4.09	1.20	16.0	0.005 I	0.033	0.069	1.15	0.105
Jim Sink	23.6	16.4	16.0	11.00	4.29	1.23	16.0	0.012 I	0.043	0.067	1.26	0.085
Jug Sink	23.1	18.8	16.0	11.10	4.30	1.24	16.0	0.012 I	0.040	0.064	1.24	0.095
Hawg Sink	16.7	24.0	60.0	9.17	6.26	0.94	136	0.005 I	0.004 U	0.005 I	0.45	0.134
Two Hole Sink	26.3	28.7	28.7	12.10	5.57	1.43	52.0	0.014 I	0.018	0.038	1.15	0.114
Sweetwater Lake	23.5	18.1	16.0	10.70	4.22	1.21	20.0	0.012 I	0.040	0.064	1.24	0.098
River Rise	22.8	15.3	15.5	10.40	4.08	1.21	20.0	0.012 I	0.036	0.074	1.19	0.103
Hornsby Spring	19.7	35.7	32.6	9.93	5.97	1.24	56.0	0.009 I	0.039	0.047	0.97	0.095
Treehouse Sink	26.2	20.1	19.1	11.00	4.62	1.26	24.0	0.010 Q(0.1)	0.051	0.050	1.22	0.112 Q (0.3)
Surface Blank	0.4 I	2.0 U	0.03 I	0.15 U	0.01 U	0.02 U	4.0 Q(1)	0.004 U	0.004 U	0.005 I	0.1 U	0.008 I
Well #1	8.4	2.0 U	107	3.79	3.25	0.24	252	0.004 U	0.004 U	0.105	0.1 U	0.043
Well #2	46.0	305	152	26.9	27.4	1.71	206	0.010 I	0.075	0.093	0.1 U	0.062
Well #7	13.4	14.6	101	7.06	5.41	0.62	262	0.005 I	0.004 U	0.371	0.55	0.162
Well #7 (dup)	13.4	14.9	102	7.29	5.57	0.65	236	0.005 I	0.007 I	0.351	0.55	0.134

APPENDIX A1. WATER CHEMISTRY DATA JANUARY 15, 16, 20, AND FEBRUARY 5, 2003

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
Vinzant's Landing	0.140	7.9			10.4	5.2	131.1	4.3	8.7
Vinzant's (dup)	0.140	7.8							
River Sink	0.140	7.8	0.707922	0.468	10.0	6.1	131.1	4.1	8.8
Ogden Pond	0.146	7.6	0.708825	0.070	10.2	6.4	136.0	4.0	8.6
Big Sink	0.146	8.2			10.0	6.0	160.7	3.8	8.2
Ravine Sink	0.146	8.6	0.708221	0.189	11.0	5.2	164.9	5.5	8.3
Paraner's Branch	0.142	7.8			10.0	6.2	160.7	3.6	8.3
Jim Sink	0.151	8.7	0.708208	0.188	10.6	6.3	164.8	4.1	8.1
Jug Sink	0.146	8.8			10.9	6.0	163.9	3.8	5.6
Hawg Sink	0.163	13.3	0.708189	0.174	15.5	6.7	368.0	2.1	1.6
Two Hole Sink	0.163	10.5	0.708046	0.338	12.0	6.7	235.0	6.5	3.1
Sweetwater Lake	0.142	8.5	0.708107	0.188	10.0	6.2	165.4	3.7	4.6
River Rise	0.146	8.6	0.708190	0.180	11.0	6.2	161.9	3.4	4.3
Hornsby Spring	0.131	10.0			13.2	6.5	252.0	2.9	2.5
Treehouse Sink	0.147	8.8			11.1	6.5	182.4	4.9	7.3
Surface Blank	0.004 U	1.0 U							
Well #1	0.094	10.5	0.707843	1.626	21.5	6.7	485.0	10.7	0.2
Well #2	0.059	15.0			26.3	6.8	1009.0	2.9	2.3
Well #7	0.135	9.1	0.707928	0.488	20.4	6.5	530.0	12.1	0.2
Well #7 (dup)	0.132	9.4							

U = Result below detection limit.

I = Result below practical quantitation limit (four times the method detection limit).

Q = Sample analyzed out of holding time (number of days).

APPENDIX A2. WATER CHEMISTRY DATA FEBUARY 24 AND MARCH 3, 5, AND 19, 2003

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
Vinzant's Landing	14.3	2.0 U	6.96	5.50	2.15	1.34	10.0	0.01 I	0.018	0.012 I	1.15	0.171
River Sink	12.7	2.0 U	7.64	6.29	2.41	1.72	8.0	0.01 I	0.026	0.017	1.20	0.254
Ogden Pond	12.8	2.0 U	7.59	5.76	2.32	1.55	16.0	0.012 I	0.027	0.016 I	1.23	0.247
Ravine Sink	12.8	2.0 U	7.92	5.82	2.36	1.53	10.0	0.013 I	0.033	0.019	1.25	0.252
Paraner's Branch	12.9	2.0 U	8.14	6.29	2.46	1.68	10.0	0.012 I	0.029	0.022	1.27	0.247
Paraner's (dup)	12.8	2.0 U	8.46	6.47	2.55	1.76	10.0	0.012 I	0.022	0.026	1.24	0.245
Jim Sink	13.1	2.0 U	8.31	6.16	2.48	1.69	8.0	0.012 I	0.024	0.020	1.24	0.247
Jug Sink	13.2	2.0 U	8.48	6.32	2.48	1.68	12.0	0.012 I	0.025	0.022	1.30	0.244
Hawg Sink	15.7	7.2 I	16.10	7.50	2.93	1.57	28.0	0.004 U	0.026	0.005 I	1.10	0.189
Sweetwater Lake	11.2	2.0 U	7.60	5.34	2.22	1.44	8.0	0.008 I	0.016 I	0.006 I	1.29	0.234
River Rise	11.3	2.0 U	8.12	5.71	2.32	1.60	8.0	0.005 I	0.017	0.026	1.24	0.234
Hornsby Spring	11.6	2.0 U	11.40	5.74	2.45	1.70	16.0	0.006 I	0.027	0.027	1.33	0.240
Surface Blank	0.8 I	2.0 U	0.02 U	0.15 U	0.01 U	0.02 U	4.0	0.004 U	0.011 I	0.01 I	0.1 U	0.004 U
Well #1	8.3	2.0 U	113.00	4.33	2.21	0.09	242	0.004 U	0.005 I	0.039	0.1 U	0.056
Well #1 (dup)	8.2	2.0 U	111.00	4.17	2.16	0.11	234	0.004 U	0.004 U	0.038	0.1 U	0.056
Well #2	21.3	114.0	79.10	14.10	13.80	1.43	102	0.004 U	0.004 U	0.092	0.61	0.088
Well #3	5.3	3.0 I	91.40	3.68	1.82	0.09	212	0.004 U	0.061	0.005 I	0.1 U	0.053
Well #4	8.2	4.4 I	91.00	5.08	2.18	0.24	206	0.004 U	0.038	0.005 I	0.1 U	0.053
Well #6	7.2	2.5 I	100.00	3.87	1.89	0.33	212	0.004 U	0.004 U	0.044	0.1 U	0.013
Well #7	13.1	17.7	87.20	7.53	5.78	0.57	196	0.004 U	0.004 U	0.375	0.72	0.138

APPENDIX A2. WATER CHEMISTRY DATA FEBUARY 24 AND MARCH 3, 5, AND 19, 2003

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
Vinzant's Landing	0.217	3.3 I			17.2	6.0	84.5	3.5	6.1
River Sink	0.286	3.4 I	0.709481	0.025	17.4	5.4	79.2	3.4	5.8
Ogden Pond	0.294	3.0 I	0.709434	0.027	17.2	5.0	79.0	4.0	5.7
Ravine Sink	0.294	3.1 I	0.709099	0.038	17.3	4.8	81.9	5.2	5.5
Paraner's Branch	0.294	3.0 I			17.1	5.0	82.0	4.0	5.5
Paraner's (dup)	0.297	3.0 I							
Jim Sink	0.300	2.6 I	0.709091	0.034	17.4	5.1	82.6	4.1	5.4
Jug Sink	0.292	2.7 I			17.6	4.9	84.3	3.7	5.5
Hawg Sink	0.253	3.0 I			18.4	5.6	123.2	3.2	2.9
Sweetwater Lake	0.305	2.9 I	0.709101	0.039	16.5	4.8	71.5	6.6	5.6
River Rise	0.338	2.8 I	0.707725	0.030	17.1	4.7	72.5	6.9	5.5
Hornsby Spring	0.292	3.1 I			18.8	5.1	86.8	4.4	4.4
Surface Blank	0.004 U	1.0 U							
Well #1	0.075	7.8	0.707874	0.890	21.9	6.8	484.0	0.9	0.3
Well #1 (dup)	0.064	7.8							
Well #2	0.142	1.4 I	0.708063	0.110	25.8	7.1	488.0	1.4	0.1
Well #3	0.063	10.0	0.708141	0.148	21.8	6.9	409.0	3.0	1.6
Well #4	0.063	8.2	0.708127	0.148	21.4	7.0	408.0	5.1	4.1
Well #6	0.078	6.1			21.1	6.8	435.0	11.0	0.2
Well #7	0.151	6.9	0.707939	0.422	20.7	7.0	422.0	8.3	0.2

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX A3. WATER CHEMISTRY DATA APRIL 28, 30, AND MAY 1, 2003

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
Vinzant's Landing	15.1	13.1	33.7	7.27	6.79	0.94	77.0	0.018	0.319	0.073	0.73	0.185
River Sink	15.5	12.8	35.0	7.38	6.8	0.94	78.9	0.017	0.361	0.062	0.67	0.181
River Sink (dup)	15.5	13.4	32.4	7.31	6.69	0.91	79.2	0.017	0.399	0.068	0.68	0.184
Ogden Pond	16.3	16.5	36.0	8.24	7.36	1.00	81.5	0.017	0.400	0.058	0.68	0.176
Ravine Sink	19.2	50.0	52.0	9.96	9.68	0.96	99.3	0.017	0.346	0.067	0.55	0.166
Paraner's Branch	17.5	27.9	43.1	8.57	8.23	0.96	97.2	0.014 I	0.350	0.062	0.60	0.165
Jim Sink	17.1	23.8	42.3	8.45	8.07	0.97	95.1	0.014 I	0.336	0.055	0.56	0.177
Jug Sink	17.3	27.7	40.0	8.31	7.64	0.96	90.7	0.011 I	0.406	0.059	0.61	0.163
Hawg Sink	18.7	37.5	43.8	8.85	8.23	0.96	90.0	0.013 I	0.320	0.024	0.70	0.182
Two Hole Sink	19.7	40.9	47.1	9.29	8.76	1.01	96.0	0.013 I	0.379	0.036	0.70	0.180
Sweetwater Lake	17.8	49.3	51.9	8.85	9.27	0.96	112	0.010 I	0.377	0.022	0.56	0.159
River Rise	18.2	62.9	57.1	9.36	9.82	0.96	108	0.010 I	0.370	0.019	0.47	0.137
Hornsby Spring	12.2	64.6	69.5	7.72	10.1	1.05	144	0.004 U	0.427	0.005 I	0.12 I	0.099
Treehouse	14.4	64	64.8	8.59	10.1	1.03	124	0.004 U	0.353	0.005 I	0.31 I	0.166
Surface Blank	0.6 I	2.0 U	0.07 I	0.15 U	0.01 U	0.02 U	1.0 U	0.001 I	0.018	0.016 I	0.1 U	0.004 U
Well #1	7.3	2.0 U	97.6	3.26	1.39	0.15	234	0.004 U	0.018	0.053	0.1 U	0.061
Well #2	40.7	242	148.0	25.2	27.8	1.87	188	0.004 U	0.026	0.107	0.12 I	0.059
Well #2 (dup)	41.2	243	144.0	24.8	27.2	1.88	178	0.004 U	0.016 I	0.102	0.16 I	0.061
Well #3	5.6	2.0 U	88.0	3.31	1.67	0.41	208	0.004 U	0.074	0.023	0.1 U	0.054
Well #4	8.2	2.0 U	94.5	4.41	1.51	0.31	208	0.004 U	0.058	0.030	0.1 U	0.054
Well #6	6.0	2.0 U	90.9	2.95	1.22	0.37	210	0.004 U	0.005 I	0.063	0.1 U	0.020
Well #7	14.9	11.6	111.0	4.41	4.61	0.62	256	0.004 U	0.039	0.421	0.70	0.138 Q(10)
Well Blank	0.4 I	2.0 U	1.25	0.15 U	0.01 U	0.02 U	6.0	0.004 U	0.008 I	0.019	0.1 U	0.004 U

APPENDIX A3. WATER CHEMISTRY DATA APRIL 28, 30, AND MAY 1, 2003

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
Vinzant's Landing	0.255	11.8			20.8	7.1	230	5.2	3.2
River Sink	0.258	12.2	0.708033	0.267	21.4	7.1	235	4.6	3.8
River Sink (dup)	0.244	12.0							
Ogden Pond	0.233	12.0			22.1	7.0	242	4.6	3.7
Ravine Sink	0.211	13.1	0.707894	0.796	22.7	7.0	225	3.3	3.7
Paraner's Branch	0.238	12.5			22.0	7.0	300	3.7	2.6
Jim Sink	0.241	12.6	0.707955	0.493	22.1	7.0	293	3.5	2.5
Jug Sink	0.227	12.4			22.1	7.0	287	3.3	2.1
Hawg Sink	0.227	11.9	0.707937	0.535	21.8	6.7	295	3.7	2.1
Two Hole Sink	0.238	12.2	0.707927	0.615	22.1	6.9	315	3.6	2.0
Sweetwater Lake	0.189	12.9	0.707887	0.764	22.1	6.8	338	2.7	1.7
River Rise	0.172	12.6			21.8	6.8	377	2.2	1.1
Hornsby Spring	0.153	13.2			23.1	7.0	420	0.2	0.3
Treehouse	0.180	12.8			22.4	7.1	400	1.4	2.0
Surface Blank	0.004 U	1.0 U							
Well #1	0.095	9.4	0.708194	0.108	26.0	6.9	448	1.8	0.2
Well #2	0.111	13.5	0.707843	2.160	22.0	6.9	907	1.4	0.1
Well #2 (dup)	0.114	13.7							
Well #3	0.078	10.5			21.8	6.9	416	0.6	1.3
Well #4	0.078	8.1	0.708112	0.129	21.7	6.9	423	0.4	2.1
Well #6	0.045	5.8			21.2	6.9	416	0.3	0.2
Well #7	0.149	10.2	0.707913	0.508	20.8	6.8	538	3.6	0.1
Well Blank	0.004 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

Q = Sample analyzed out of holding time (number of days).

9 APPENDIX B

APPENDIX B1. WATER CHEMISTRY DATA JANUARY 22 AND 23, 2004

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2+ NO3 (mg/L)	NH3 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)
River Sink	12.5	26.7	42.1	6.87	11.6	1.03	117	0.175	0.01 U	0.707915	0.565	15.0
Ogden Pond	17.8	50.0	50.0	9.13	13.3	1.08	127	0.150	0.01 U			16.4
Paraner's Branch	19.2	59.2	58.3	9.71	14.5	1.08	128	0.162	0.01 U			17.3
Hawg Sink	17.9	56.7	54.3	9.01	12.2	1.07	128	0.172	0.01 U			17.9
Sweetwater Lake	15.9	83.1	74.3	9.57	16.3	1.04	140	0.266	0.01 U	0.707857	1.372	19.3
Sweetwater (dup)	16.7	84.6	74.5	10.0	16.2	1.09	137	0.305	0.01 U			
River Rise	18.0	91.0	75.4	10.2	16.6	1.08	141	0.363	0.01 U	0.707863	1.341	19.0
Surface Blank [†]	0.6 l	2.0 U	0.04 l	0.15 U	0.01 U	0.02 U	0.5 U	0.531	0.01 U			
Well #1	7.5	2.0 U	101	3.67	1.27	0.21	239	0.004 U	0.01 U			21.2
Well #2	49.8	387	167	31.3	39.0	2.57	197	0.004 U	0.159	0.707837	3.141	24.9
Well #2 (dup)	49.1	374	168	31.7	38.9	2.58	201	0.004 U	0.138			
Well #3	6.2	2.0 U	92.9	3.69	1.79	0.32	232	0.004 U	0.046			21.0
Well #4	8.4	4.5 l	87.9	4.43	1.32	0.37	212	0.034	0.01 U	0.708133	0.116	20.9
Well #5	5.5	2.0 U	75.4	3.03	0.89	0.32	186	0.004 U	0.013 l	0.708031	0.092	20.8
Well #6	6.3	2.0 U	85.6	2.93	1.11	0.42	2.98	0.004 U	0.026 l			20.5
Well #7	11.0	21.7	69.1	5.32	3.87	0.79	165	0.004 U	0.401	0.707884	0.365	20.3
Well Blank [†]	0.6 l	2.0 U	2.97	0.15 U	0.02 l	0.02 U	128	0.004 U	0.01 U			

APPENDIX B1. WATER CHEMISTRY DATA JANUARY 22 AND 23, 2004

Location	pH	Conductivity (μS/cm)	Turbidity (NTU)	DO (mg/L)
River Sink	7.74	316	0.92	7.12
Ogden Pond	7.67	374	1.44	6.05
Paraner's Branch	7.47	409	1	1.89
Hawg Sink	7.37	407	0.65	1.89
Sweetwater Lake	7.41	466	0.6	2.66
Sweetwater (dup)				
River Rise	7.37	430	0.64	2.41
Surface Blank[†]				
Well #1	7.2	428	0.98	0.31
Well #2	7.08	1064	0.1	0.18
Well #2 (dup)				
Well #3	7.12	440	0.11	0.11
Well #4	7.19	425	0.99	1.18
Well #5	7.28	371	5.05	0.2
Well #6	7.19	423	0.15	0.23
Well #7	7.39	359	0.95	0.26
Well Blank[‡]				

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

† = Nitrite+Nitrate hit above field values

‡ = Calcium and alkalinity hits

APPENDIX B2. WATER CHEMISTRY DATA MARCH 8 AND 9, 2004

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	SiO2 (mg/L)	87Sr/86Sr
River Sink	17.8	23.3	18.4	7.22	5.14	1.20	35.7	0.010 I	0.144	0.01 U	7.3	0.708208
Ogden Pond	23.0	41.6	27.6	11.4	8.31	1.37	40.6	0.010 I	0.064	0.015 I	8.3	
Paraner's Branch	18.0	25.1	20.4	7.43	5.77	1.21	40.9	0.011 I	0.057	0.013 I	8.1	
Paraner's (dup)	17.5	24.8	20.4	7.46	5.78	1.23	38.2	0.011 I	0.056	0.011 I	8.3	
Hawg Sink	16.1	12.8	15.4	6.52	5.03	1.18	33.8	0.011 I	0.148	0.01 U	8.3	
Sweetwater Lake	17.2	34.8	25.3	7.47	6.26	1.18	42.3	0.008 I	0.067	0.01 U	9.4	0.707936
River Rise	17.4	34.2	24.2	7.35	5.92	1.20	40.5	0.008 I	0.059	0.019 I	8.8	0.707928
Surface Blank	0.4 I	2.0 U	0.08 I	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.004 U	0.01 U	1.0 U	
Well #1	7.4	2.0 U	98.4	3.38	1.19	0.18	230	0.004 U	0.013 I	0.01 U	7.6	0.707901
Well #1 (dup)	7.1	2.0 U	98.7	3.22	1.17	0.17	248	0.004 U	0.004 U	0.01 U	7.4	
Well #2	49.6	345	166	28.3	39.2	2.35	201	0.004 U	0.004 U	0.156	13.7	0.707829
Well #3	6.2	2.0 U	87.9	3.48	1.76	0.33	218	0.004 U	0.013 I	0.04 I	8.8	
Well #4	8.6	4.0 I	87.8	4.17	1.34	0.34	209	0.004 U	0.032	0.01 U	6.9	0.708116
Well #5	4.9	2.0 U	71.0	3.00	0.85	0.30	183	0.004 U	0.004 U	0.01 U	4.5	0.708025
Well #6	5.9	2.0 U	87.4	2.96	1.13	0.43	206	0.004 U	0.004 U	0.01 U	4.8	
Well #7	16.4	27.4	90.6	6.59	4.62	0.79	204	0.004 U	0.004 U	0.416	5.7	0.707873
Well Blank	0.4 I	2.0 U	0.02 I	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.008 I	0.01 U	1.0 U	

APPENDIX B2. WATER CHEMISTRY DATA MARCH 8 AND 9, 2004

Location	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Sink	0.130	19.0	6.83	139.6	2.3	5.64
Ogden Pond		19.0	6.81	155.2	2.3	5.57
Paraner's Branch		19.8	6.85	179.1	2.5	5.25
Paraner's (dup)						
Hawg Sink		18.4	6.78	166.1	2.4	5.05
Sweetwater Lake	0.463	19.0	6.88	211	2.2	5.15
River Rise	0.437	18.0	6.87	206	2.2	4.56
Surface Blank						
Well #1	0.105	21.7	7.01	417	0.55	0.31
Well #1 (dup)						
Well #2	3.251	25.0	7.03	1102	0.3	0.35
Well #3		21.3	7.08	430	0.55	0.38
Well #4	0.120	21.0	7.11	420	5.6	0.93
Well #5	0.093	21.0	7.23	273	2.9	0.32
Well #6		20.7	7.12	414	0.5	0.28
Well #7	0.478	20.3	7.12	413	1.2	0.29
Well Blank						

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX B3. WATER CHEMISTRY DATA MAY 4 AND 5, 2004

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Sink	11.2	32.8	50.2	7.03	13.1	0.97	133	0.004 U	0.025	0.01 U	0.23 I	0.118
Ogden Pond	13.9	47.4	55.6	9.40	14.7	1.01	137	0.005 I	0.036	0.01 U	0.17 I	0.115
Paraner's Branch	16.5	68.7	63.9	10.5	15.2	1.07	140	0.004 U	0.107	0.014 I	0.16 I	0.126
Paraner's (dup)	16.3	68.3	65.1	10.8	15.6	0.98	142	0.004 U	0.111	0.015 I	0.21 I	0.125
Hawg Sink	15.5	60.6	60.8	10.4	14.8	1.06	139	0.005 I	0.114	0.01 U	0.18 I	0.125
Sweetwater Lake	16.4	96.8	75.9	10.2	15.7	0.93	145	0.004 U	0.169	0.01 U	0.14 I	0.095
River Rise	18.3	99.4	76.4	11.9	16.6	0.96	144	0.004 U	0.225	0.01 U	0.1 U	0.098
Surface Blank	0.9	2.0 U	0.03 I	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.024	0.01 U	0.1 U	0.004 U
Well #1	7.5	2.0 U	106.0	3.86	1.3	0.23	246	0.004 U	0.101	0.01 U	0.1 U	0.125
Well #2	51.7	391	175.0	33.6	43.3	2.85	204	0.004 U	0.088	0.157	0.22 I	0.070
Well #3	5.8	2.0 U	93.4	3.77	1.81	0.27	223	0.004 U	0.039 V	0.01 U	0.1 U	0.092
Well #3 (dup)	5.7	2.0 U	91.0	3.63	1.76	0.26	221	0.004 U	0.025 V	0.01 U	0.1 U	0.087
Well #4	8.1	4.0 I	89.3	4.55	1.36	0.4	215	0.004 U	0.060	0.01 U	0.1 U	0.045
Well #5	5.1	2.0 U	77.9	2.92	0.94	0.34	186	0.004 U	0.111	0.01 U	0.11 I	0.019
Well #6	6.4	2.0 U	86.5	3.06	1.15	0.46	218	0.004 U	0.073	0.01 U	0.1 U	0.022
Well #7	9.9	15.5	82.1	6.30	4.12	0.83	200	0.004 U	0.030 V	0.394	0.76	0.125
Well #8 [†]	5.0	6.4	71.1	8.92	1.66	0.18	180	0.004 U	264	0.091	0.1 U	0.017
Well Blank	0.8 I	2.0 U	0.13	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.044	0.01 U	0.1 U	0.004 U

APPENDIX B3. WATER CHEMISTRY DATA MAY 4 AND 5, 2004

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Sink	0.132	10.0	0.707908	0.697	23.8	7.79	379	0.52	7.19
Ogden Pond	0.115	10.6			23.8	7.62	424	0.67	5.06
Paraner's Branch	0.134	13.5			23.5	7.40	480	0.69	2.49
Paraner's (dup)	0.135	13.5							
Hawg Sink	0.130	13.4			22.3	7.45	453	0.60	2.68
Sweetwater Lake	0.094	14.1	0.707859	1.604	23.7	7.36	543	0.49	1.62
River Rise	0.105	13.7	0.707849	1.614	23.4	7.59	549	0.39	5.70
Surface Blank	0.004 U	1.0 U							
Well #1	0.129	9.0			21.8	7.02	478	1.52	0.35
Well #2	0.073	15.9	0.707827	3.632	25.5	7.05	1315	0.97	0.27
Well #3	0.101	9.5			21.5	7.13	367	0.11	0.49
Well #3 (dup)	0.101	8.5							
Well #4	0.046	7.4	0.708131	0.114	21.4	7.17	390	2.63	1.27
Well #5	0.022	7.9			21.4	7.24	322	1.02	0.27
Well #6	0.028	6.1			21.0	7.15	371	0.63	0.28
Well #7	0.126	6.3	0.707860	0.412	20.6	7.22	306	2.32	0.27
Well #8†	0.039	14.2	0.708122	0.137	21.2	7.30	306	0.21	0.43
Well Blank	0.004 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

V = Result below blank value

† = Nitrite+Nitrate value due to nitric acid spike

APPENDIX BA. WATER CHEMISTRY DATA APRIL 26, 2004.

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Rise	19.6	92.0	69.0	10.6	14.5	1.03	139	0.009 I	0.252	0.01 U	0.2 I	0.106
Well #3	6.4	2.0 U	87.4	3.61	1.66	0.21	226	0.007 I	0.019	0.016 I	0.1 U	0.094
Well #4	8.8	4.3 I	85.1	4.29	1.30	0.36	213	0.007 I	0.079	0.01 U	0.1 U	0.049
Well #5	5.7	2.0 U	75.1	2.72	0.88	0.29	188	0.017	0.053	0.01 U	0.1 U	0.027
Well #6	6.8	2.0 U	84.1	2.94	1.11	0.41	215	0.012 I	0.004 U	0.015 I	0.1 U	0.019
Well #6 (dup)	6.5	2.0 U	85.5	2.96	1.13	0.42	214	0.010 I	0.004 U	0.013 I	0.13 I	0.022
Well #7	17.8	14.8	87.4	6.76	4.18	0.80	214	0.007 I	0.004 U	0.380	0.69	0.132

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Rise	0.103	14.5			22.2	7.36	509	0.40	1.87
Well #3	0.101	9.4			21.7	7.16	446	0.25	0.51
Well #4	0.046	7.4			21.7	7.21	432	0.55	1.14
Well #5	0.022	7.4			21.7	7.29	388	1.70	0.24
Well #6	0.027	6.7			21.1	7.18	420	0.40	0.30
Well #6 (dup)	0.025	7.0							
Well #7	0.125	6.1			20.8	7.21	481	2.40	0.31

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX BB. WATER CHEMISTRY DATA APRIL 28, 2004.

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Rise	20.0	91.1	68.3	10.8	14.8	1.11	139	0.004 U	0.230	0.01 U	0.21 I	0.102
Well #3	6.4	2.0 U	88.5	3.66	1.71	0.23	220	0.004 U	0.175	0.01 U	0.1 I	0.099
Well #3 (dup)	6.5	2.0 U	90.4	3.84	1.76	0.24	223	0.004 U	0.034	0.01 U	0.1 I	0.096
Well #4	9.0	4.2 I	91.0	5.02	1.43	0.42	214	0.004 U	0.063	0.01 U	0.1 I	0.048
Well #5	5.9	2.0 U	75.1	2.84	0.90	0.30	187	0.004 U	0.008 I	0.01 U	0.1 I	0.025
Well #6	6.3	2.0 U	87.2	3.11	1.16	0.44	214	0.004 U	0.015 I	0.01 U	0.1 I	0.026
Well #7	16.1	15.8	87.5	6.58	4.15	0.76	212	0.004 U	0.004 U	0.348	0.71	0.130

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Rise	0.100	14.2			22.3	7.47	519	0.55	2.80
Well #3	0.100	9.3			21.6	7.20	436	0.17	0.53
Well #3 (dup)	0.101	9.3							
Well #4	0.047	7.2			21.4	7.24	347	6.07	1.36
Well #5	0.021	7.6			21.4	7.30	368	1.97	0.25
Well #6	0.025	6.5			21.1	7.21	438	0.39	0.30
Well #7	0.120	6.0			20.9	7.23	457	2.27	0.29

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX BC. WATER CHEMISTRY DATA APRIL 30, 2004.

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Rise	18.2	94.4	70.9	10.8	15.1	1.15	139	0.004 U	0.252	0.01 U	0.14 I	0.104
Well #3	6.4	2.0 U	89.0	3.55	1.71	0.24	221	0.004 U	0.016 I	0.01 U	0.1 U	0.097
Well #4	1.9	4.0 I	93.0	4.87	1.42	0.42	214	0.004 U	0.090	0.01 U	0.1 U	0.053
Well #7	17.3	16.6	91.2	6.96	4.35	0.82	209	0.004 U	0.007 I	0.407	0.70	0.130
Well #7 (dup)	16.8	16.8	88.5	6.71	4.23	0.80	209	0.004 U	0.014 I	0.396	0.68	0.127

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Rise	0.107	13.9			22.0	7.32	507	0.41	1.63
Well #3	0.109	9.0			21.6	7.11	329	0.26	0.67
Well #4	0.051	7.1			21.3	7.16	267	5.60	1.44
Well #7	0.127	6.2			20.6	7.18	414	1.17	0.38
Well #7 (dup)	0.127	0.6 I							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX BD. WATER CHEMISTRY DATA MAY 7, 2004.

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
Rive Rise	17.5	99.1	74.4	10.7	15.7	0.96	145	0.004 U	0.180	0.01 U	0.11 I	0.098
Well #3	5.5	2.1 I	88.3	3.50	1.72	0.24	220	0.004 U	0.028	0.01 U	0.1 U	0.095
Well #3 (dup)	5.9	2.1 I	87.7	3.16	1.67	0.22	220	0.004 U	0.022	0.01 U	0.1 U	0.095
Well #4	8.3	4.1 I	87.6	4.51	1.35	0.36	210	0.004 U	0.047	0.01 U	0.1 U	0.048
Well #5	5.4	2.0 U	73.1	2.56	0.86	0.27	182	0.004 U	0.004 U	0.01 U	0.68	0.022
Well #6	7.0	2.0 U	84.5	2.87	1.12	0.40	214	0.004 U	0.016 I	0.02 I	0.1 U	0.027
Well #7	16.0	15.2	79.6	6.03	4.10	0.65	191	0.004 U	0.088	0.41	0.77	0.127

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
Rise	0.107	14.7			22.9	7.32	540	0.13	1.70
Well #3	0.104	9.7			21.6	7.10	447	0.01	0.60
Well #3 (dup)	0.104	9.7							
Well #4	0.052	7.4			21.4	7.13	393	2.88	1.31
Well #5	0.025	8.4	0.708042	0.088	21.5	7.22	345	0.81	0.34
Well #6	0.031	6.9			21.1	7.11	445	0.19	0.36
Well #7	0.127	6.1			20.6	7.24	407	1.61	0.34

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX BE. WATER CHEMISTRY DATA MAY 10, 2004.

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Rise	16.5	91.9	73.1	9.91	15.4	1.06	144	0.004 U	0.203	0.01 U	0.1 U	0.101
Well #3	5.9	2.0 U	91.0	3.36	1.75	0.27	221	0.004 U	0.023	0.01 U	0.1 U	0.090
Well #4	8.4	4.1 I	96.3	5.07	1.47	0.42	213	0.004 U	0.148	0.01 U	0.1 U	0.046
Well #5	5.4	2.0 U	81.4	3.11	0.96	0.34	184	0.004 U	0.009	0.01 U	0.1 U	0.019
Well #6	7.2	2.0 U	94.1	3.57	1.27	0.51	217	0.004 U	0.029	0.021 I	0.1 U	0.022
Well #7	17.2	14.9	78.7	5.84	4.07	0.78	190	0.004 U	0.004 U	0.397	0.71	0.120
Well #7 (dup)	17.3	15.3	77.3	5.60	3.98	0.76	189	0.004 U	0.004 U	0.397	0.69	0.120

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Rise	0.097	14.6			22.8	7.32	531	0.01	1.56
Well #3	0.092	9.3			21.6	7.09	385	0.26	0.52
Well #4	0.045	7.5			21.3	7.16	413	4.61	1.32
Well #5	0.02	7.9			21.3	7.25	365	0.92	0.29
Well #6	0.03	6.7			21.0	7.12	447	0.14	0.29
Well #7	0.113	6.8			20.6	7.25	366	2.27	0.34
Well #7 (dup)	0.114	6.6							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX BF. WATER CHEMISTRY DATA MAY 14, 2004.

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Rise	16.5	96.6	74.6	10.5	16	1.05	145	0.004 U	0.238	0.01 U	0.1 U	0.094
Surface Blank	0.9	2.0 U	0.03 I	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.013 I	0.012 I	0.1 U	0.005 I
Well #3	5.7	2.0 U	91.6	3.59	1.82	0.25	222	0.004 U	0.044	0.029 I	0.1 U	0.099
Well #3 (dup)	5.7	2.0 U	93.0	3.55	1.82	0.25	217	0.004 U	0.026	0.030 I	0.1 U	0.094
Well #4	8.3	4.2 I	92.5	4.82	1.46	0.38	210	0.004 U	0.050	0.01 U	0.1 U	0.045
Well #5	8.8	2.0 U	75.6	2.83	0.91	0.3	181	0.004 U	0.018	0.032 I	0.1 U	0.018
Well #6	6.7	2.0 U	93.7	3.4	1.28	0.45	217	0.004 U	0.044	0.036 I	0.11 I	0.023
Well #7	13.9	13.7	77.2	6.02	4.22	0.82	184	0.004 U	0.007 I	0.404	1.12	0.126

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Rise	0.089	15.4			22.7	7.25	540	0.09	1.17
Surface Blank	0.011 I	1.0 U							
Well #3	0.094	10.2			21.6	7.15	387	0.07	0.50
Well #3 (dup)	0.091	9.2							
Well #4	0.044	7.9			21.4	7.20	320	0.43	1.29
Well #5	0.017	6.7			21.4	7.29	370	0.62	0.32
Well #6	0.024	6.3			21.1	7.17	430	0.20	0.25
Well #7	0.111	6.2			20.6	7.33	335	5.25	0.33

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

10 APPENDIX C

APPENDIX C1. WATER CHEMISTRY DATA JANUARY 19 AND 26, 2005

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Sink	17.4	8.9	15.7	6.62	4.65	1.28	31.9	0.022	0.183	0.01 U	0.92	0.143
Ogden Pond	17.6	12.7	15.4	6.62	4.55	1.24	32.2	0.022	0.128	0.01 U	0.89	0.145
Paraner's Branch	18.8	18.7	18.6	7.52	5.14	1.39	34.2	0.019	0.129	0.023 I	0.98	0.161
Hawg Sink	16.8	25.2	33.1	7.34	6.76	0.98	66.3	0.018	0.230	0.020 I	0.67	0.159
Hawg Sink (dup)	17.3	25.1	31.8	7.2	6.64	0.98	66.9	0.016 I	0.285	0.016 I	0.81	0.156
Sweetwater Lake	17.1	30.9	30.4	7.59	6.65	1.34	55.2	0.018	0.230	0.023 I	0.92	0.164
River Rise	16.9	43.1	37.5	7.8	7.59	1.10	75.9	0.012 I	0.349	0.01 U	0.74	0.150
Surface Blank	0.6 I	2.0 U	0.02 U	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.004 U	0.01 U	0.1 U	0.004 U
Well #1	6.6	2.0 U	79.0	2.76	1.06	0.17	164	0.004 U, Q(18)	0.012 I	0.024 I	0.23 I	0.110
Well #1 (dup)	6.7	2.0 U	85.4	2.71	1.08	0.16	161	0.004 U, Q(18)	0.004 U	0.020 I	0.1 U	0.107
Well #2	34.4	192	125.0	19.5	19.50	1.37	182	0.004 U, Q(18)	0.004 U	0.154	0.23 I	0.075
Well #3	6.1	3.2 I	85.4	3.34	1.52	0.14	187	0.004 U, Q(17)	0.073	0.01 U	0.1 U	0.042
Well #4	9.2	4.3 I	86.0	4.26	1.30	0.35	158	0.004 U, Q(17)	0.052	0.01 U	0.1 U	0.037
Well #5	6.2	2.0 U	71.3	2.32	0.84	0.27	143	0.004 U, Q(17)	0.004 U	0.038 I	0.13 I	0.014 I
Well #6	6.8	2.0 U	80.8	2.72	1.07	0.42	165	0.004 U, Q(17)	0.008 I	0.038 I	0.12 I	0.011 I
Well #7	17.7	14.9	99.4	6.82	4.18	0.63	229	0.004 U, Q(17)	0.007 I	0.390	0.77	0.127 Q(18)
Well #8	5.4	4.4 I	67.9	4.54	1.39	0.10	149	0.004 U, Q(18)	0.004 U	0.121	0.1 U	0.074
Well Blank	0.6 I	2.0 U	0.06 I	0.15 U	0.01 U	0.02 U	1.3 I, Q(5)	0.004 U, Q(17)	0.004 U	0.01 U	0.1 U	0.004 U

APPENDIX C1. WATER CHEMISTRY DATA JANUARY 19 AND 26, 2005

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Sink	0.195	13.4	0.708223	0.119	11.59	6.46	140		7.42
Ogden Pond	0.192	13.1			12.94	6.49	144		7.25
Paraner's Branch	0.208	15.2			13.12	6.62	170		6.85
Hawg Sink	0.194	14.5	0.707952	0.378	18.43	6.70	232		3.23
Hawg Sink (dup)	0.197	12.7							
Sweetwater Lake	0.213	13.9	0.707919	0.477	16.51	6.78	223		4.67
River Rise	0.192	15.2	0.707909	0.572	18.65	6.91	280		3.43
Surface Blank	0.004 U	1.0 U							
Well #1	0.140	9.0			21.80	6.77	431	0.65	0.18
Well #1 (dup)	0.140	9.0							
Well #2	0.090	12.1	0.707881	1.494	24.81	6.91	838	0.85	0.16
Well #3	0.049	9.9			21.43	6.79	449	1.10	1.75
Well #4	0.051	7.8	0.708114	0.113	21.21	6.78	442	0.20	1.49
Well #5	0.026	7.8	0.708033	0.092	21.27	6.86	401	1.10	0.1
Well #6	0.018	7.7			20.97	6.80	443	0.00	0.11
Well #7	0.128	7.7	0.707906	0.491	20.67	6.70	550	2.10	0.11
Well #8	0.084	14.7	0.708129	0.140	21.22	6.67	372	0.05	0.18
Well Blank	0.004 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

Q = Sample analyzed out of holding time (number of days).

APPENDIX C2. WATER CHEMISTRY DATA MARCH 14 AND 18, 2005

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity [†] (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Sink	15.9	13.0	19.3	7.41	5.75	1.09	44	0.018	0.105	0.01 U	0.87	0.113
Ogden Pond	18.5	22.3	21.0	7.86	6.12	1.09	44	0.015 I	0.106	0.01 U	0.88	0.115
Paraner's Branch	16.5	21.7	23.6	8.06	6.38	1.04	45	0.013 I	0.094	0.01 U	0.78	0.113
Paraner's (dup)	16.7	21.7	23.7	8.01	6.36	1.02	45	0.012 I	0.097	0.01 U	0.84	0.113
Hawg Sink	15.2	24.6	44.9	7.89	7.24	1.02	91	0.009 I	0.083	0.01 U	0.60	0.112
Sweetwater Lake	18.0	37.1	36.0	8.06	8.17	1.00	67.7	0.015 I	0.180	0.01 U	0.55	0.116
River Rise	18.2	48.0	36.1	8.14	8.50	1.00	81.8	0.012 I	0.230	0.01 U	0.42	0.105
Surface Blank	0.4 I	2.0 U	0.04 I	0.15 U	0.01 U	0.02 U	2.0 U	0.004 U	0.004 U	0.01 U	0.1 U	0.004 U
Well #1	6.8	2.0 U	93.8	3.29	1.20	0.20	224	0.004 U	0.004 U	0.01 U	0.35 I	0.124
Well #2	41.7	290	155	27.2	30.7	2.10	194	0.004 U	0.004 U	0.165	0.33 I	0.082
Well #3	5.9	3.1 I	94.0	3.72	1.71	0.16	N/A	0.004 U	0.055	0.01 U	0.01 U	0.044
Well #4	9.2	4.2 I	90.2	4.68	1.40	0.38	214	0.004 U	0.037	0.01 U	0.01 U	0.041
Well #5	6.0	2.0 U	74.8	2.55	0.89	0.30	182	0.005 I	0.007 I	0.01 U	0.01 U	0.022
Well #6	6.5	2.0 U	85.2	2.98	1.14	0.44	221	0.005 I	0.005 I	0.01 U	0.01 U	0.019
Well #7	17.6	15.4	108	7.69	4.60	0.72	237	0.015 I	0.007 I	0.334	0.52	0.146
Well #8	5.8	4.6 I	69.2	5.08	1.49	0.12	164	0.004 U	0.030	0.103	0.27 I	0.076
Well # 8 (dup)	8.6	4.5 I	77.1	5.3	1.57	0.12	167	0.004 U	0.004 U	0.102	0.27 I	0.074
Well Blank	0.4 I	2.0 U	0.08 I	0.15 U	0.01 U	0.02 U	2.0 U	0.004 U	0.013 I	0.01 U	0.1 U	0.004 U

APPENDIX C2. WATER CHEMISTRY DATA MARCH 14 AND 18, 2005

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Sink	0.171	11.7	0.708075	0.193	18.20	6.55	172		6.55
Ogden Pond	0.168	10.4			18.25	6.75	186		6.75
Paraner's Branch	0.174	11.7			18.04	7.16	204		6.14
Paraner's (dup)	0.174	11.2							
Hawg Sink	0.157	9.8	0.707959	0.398	19.15	6.78	299		2.69
Sweetwater Lake	0.153	11.2	0.707920	0.605	18.89	7.00	280		3.89
River Rise	0.148	12.5			19.09	7.06	306		3.22
Surface Blank	0.004 U	1.0 U							
Well #1	0.177	8.9	0.707888	0.098	21.77	6.71	469	0.90	0.24
Well #2	0.096	12.7	0.707855	2.115	24.19	6.98	1034	0.00	0.30
Well #3	0.048	9.3			21.17	6.79	453	0.15	1.69
Well #4	0.043	7.2			21.01	6.87	449	0.75	1.39
Well #5	0.018	6.4			21.06	6.97	398	0.45	0.24
Well #6	0.015 I	8.1			20.74	6.92	447	0.10	0.22
Well #7	0.140	7.3	0.707895	0.496	20.45	6.85	549	2.90	0.16
Well #8	0.088	14.0			21.31	7.06	382	0.60	0.25
Well # 8 (dup)	0.082	12.0							
Well Blank	0.004 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

† = Well #3 not run for alkalinity due to insufficient volume

APPENDIX C3. WATER CHEMISTRY DATA JULY 18, 2005

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Sink	11.6	2.0 U	7.83	4.48	2.30	0.86	9.03	0.029	0.034	0.073	1.20	0.187
Ogden Pond	11.9	2.0 U	7.6	4.46	2.27	0.87	8.2	0.028	0.034	0.086	1.23	0.176
Paraner's Branch	11.9	2.0 U	10.2	4.93	2.69	0.91	11.9	0.019	0.035	0.087	1.16	0.174
Paraner's (dup)	11.9	2.0 U	8.55	4.63	2.46	0.89	11	0.020	0.049	0.045	0.99	0.174
Hawg Sink	11.9	2.0 U	11.2	4.81	2.63	0.94	11.7	0.020	0.038	0.037	1.19	0.177
Sweetwater Lake	12.4	2.0 U	11.1	5.13	2.49	0.90	13.3	0.022	0.038	0.075	1.01	0.177
River Rise	12.4	12.7	15.9	5.55	3.22	0.93	25.6	0.020	0.063	0.069	0.91	0.180
Surface Blank	0.7 I	2.0 U	0.02 U	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.004 U	0.01 U	0.10 U	0.004 U
Well #1	6.3	2.0 U	80.9	2.98	1.15	0.20	210	0.005 I	0.004 U	0.024 I	1.16	0.137
Well #1 (dup)	6.4	2.0 U	77.4	2.93	1.13	0.19	211	0.004 U	0.004 U	0.016 I	1.16	0.133
Well #2	45.0	335	136	25.3	32.2	2.16	191	0.004 U	0.004 U	0.137	0.14 I	0.057
Well #3	5.8	2.2 I	90.1	4.46	1.63	0.19	214	0.004 U	0.077	0.01 U	0.10 U	0.046
Well #4	8.6	4.5 I	89.4	4.88	1.31	0.40	206	0.004 U	0.045	0.01 U	0.10 U	0.045
Well #5	5.9	2.0 U	78.9	2.73	0.90	0.30	184	0.013 I	0.004 U	0.024 I	0.10 U	0.017
Well #6	6.1	2.0 U	90.3	3.21	1.18	0.48	201	0.014 I	0.006 I	0.011 I	0.19 I	0.016 I
Well #7	16.4	15.8	103	7.51	4.52	0.73	241	0.016 I	0.013 I	0.366	0.54	0.168
Well #8	11.6	4.4 I	61.8	4.13	1.42	0.12	168	0.004 U	0.010 I	0.105	0.35 I	0.080
Well Blank	0.6 I	2.0 U	0.05 I	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.004 U	0.01 U	0.10 U	0.004 U

APPENDIX C3. WATER CHEMISTRY DATA JULY 18, 2005

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Sink	0.236	18.2	0.708612	0.054	26.86	6.09	73		4.75
Ogden Pond	0.241	18.1			27.51	5.90	73		4.01
Paraner's Branch	0.246	18.0			27.30	6.30	85		4.25
Paraner's (dup)	0.243	18.2							
Hawg Sink	0.246	17.5	0.708557	0.089	27.06	6.58	88		3.11
Sweetwater Lake	0.241	18.0	0.708284	0.095	26.85	6.62	89		4.11
River Rise	0.238	17.6	0.708117	0.145	26.36	6.59	117		3.59
Surface Blank	0.004 U	1.0 U							
Well #1	0.154	12.1	0.707887	0.090	21.96	6.37	402	0.53	0.24
Well #1 (dup)	0.158	11.9							
Well #2	0.064	16.6	0.707853	2.881	24.84	6.69	991	0.20	0.21
Well #3	0.052	11.4			21.49	6.69	418	0.16	2.07
Well #4	0.043	8.8			21.54	6.48	415	1.51	1.51
Well #5	0.028	9.6			21.42	6.71	372	1.49	0.19
Well #6	0.026	9.4			21.07	6.45	411	0.16	0.19
Well #7	0.137	9.1	0.707887	0.090	20.91	6.53	520	3.08	0.17
Well #8	0.088	18.6			21.53	6.58	345	0.00	0.22
Well Blank	0.004 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX C4. WATER CHEMISTRY DATA OCTOBER 27, 2005

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Sink	13.3	18.9	27.0	6.39	7.58	1.82	67.1	0.010 I	0.249	0.01 U	0.62	0.181
Ogden Pond	13.6	20.2	27.8	6.73	7.77	1.82	66.7	0.011 I	0.246	0.01 U	0.64	0.184
Ogden (dup)	12.7	20.0	28.5	6.94	7.97	1.88	66.7	0.008 I	0.239	0.01 U	0.72	0.183
Paraner's Branch	14.5	28.9	33.6	7.76	8.73	1.55	71.2	0.008 I	0.192	0.01 U	0.71	0.181
Hawg Sink	13.8	29.8	33.8	7.37	8.04	1.27	72.9	0.010 I	0.137	0.01 U	0.22 I	0.169
Sweetwater Lake	15.0	57.4	48.9	7.93	10.80	1.12	98.7	0.006 I	0.246	0.01 U	0.37 I	0.136
River Rise	14.6	58.9	52.0	8.22	11.10	1.10	102	0.006 I	0.324	0.01 U	0.37 I	0.134
Surface Blank	0.6 I	1.0 U	0.02 U	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.004 U	0.01 U	0.1 U	0.004 U
Well #1	7.1	1.0 U	96.0	3.49	1.27	0.21	226	0.004 U	0.004 U	0.01 U	0.1 U	0.147
Well #1 (dup)	6.8	1.0 U	98.6	4.16	1.30	0.22	231	0.004 U	0.004 U	0.01 U	0.1 U	0.137
Well #2	53.1	410	189	36.5	48.2	3.21	200	0.004 U	0.004 U	0.145	0.13 I	0.061
Well #3	6.1	3.6 I	88.4	4.10	1.66	0.20	221	0.004 U	0.052	0.01 U	0.1 U	0.051
Well #4	9.0	4.2	87.6	4.63	1.37	0.39	207	0.004 U	0.035	0.01 U	0.1 U	0.046
Well #5	7.8	1.0 U	74.8	2.44	0.87	0.29	189	0.004 U	0.004 U	0.01 U	0.1 U	0.018
Well #6	6.2	1.1 I	90.0	3.10	1.21	0.47	210	0.004 U	0.004 U	0.011 I	0.1 U	0.018
Well #7	18.5	12.0	76.3	6.06	4.20	0.90	171	0.004 U	0.004 U	0.384	0.58	0.124
Well #8	5.3	4.5	68.4	4.26	1.51	0.11	173	0.004 U	0.004 U	0.102	0.17 I	0.082
Well Blank	0.6 I	1.0 U	0.04 I	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.004 U	0.01 U	0.1 U	0.004 U

APPENDIX C4. WATER CHEMISTRY DATA OCTOBER 27, 2005

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Sink	0.215	19.9	0.707980	0.320	17.36	7.06	214		5.24
Ogden Pond	0.215	19.8			18.10	7.06	219		5.30
Ogden (dup)	0.210	19.7							
Paraner's Branch	0.213	19.9			19.41	7.03	249		4.20
Hawg Sink	0.192	20.8	0.707918	0.488	21.84	7.01	255		1.82
Sweetwater Lake	0.155	20.8	0.707877	0.975	22.47	7.12	356		2.01
River Rise	0.152	19.4	0.707888	0.890	23.00	7.19	357		1.58
Surface Blank	0.004 U	1.0 U							
Well #1	0.171	13.0			21.80	6.57	459	0.48	0.17
Well #1 (dup)	0.171	12.9							
Well #2	0.069	20.3			24.68	6.59	1203	1.45	0.28
Well #3	0.050	11.5			21.31	6.83	442	0.52	2.01
Well #4	0.048	8.4			21.23	6.62	433	1.22	1.57
Well #5	0.024	9.5			21.29	6.79	381	0.77	0.09
Well #6	0.022	8.3			20.97	6.82	424	0.00	0.25
Well #7	0.126	8.8			20.66	6.93	395	3.79	0.06
Well #8	0.098	21.1			21.33	6.81	362	0.18	0.14
Well Blank	0.004 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX CA. WATER CHEMISTRY DATA APRIL 18, 2005.

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Rise	12.0	2.0 U	9.28	5.01	2.10	1.10	14.6	0.032	0.036	0.035 I	0.97	0.159
Well #3	5.85	3.7 I	97.8	4.03	1.75	0.18	226	0.004 U	0.067	0.028 I	0.1 U	0.046
Well #4	7.92	4.4 I	91.4	4.53	1.38	0.40	204	0.004 U	0.039	0.032 I	0.1 U	0.041
Well #5	5.75	2.0 U	83.8	2.59	0.92	0.31	188	0.004 U	0.004 U	0.01 U	0.1 U	0.014 I
Well #6	6.65	2.0 U	95.9	3.14	1.20	0.47	216	0.004 U	0.004 U	0.01 U	0.13 I	0.014 I
Well #7	16.6	14.0	86.2	6.36	4.22	0.86	180	0.004 U	0.005 I	0.390	0.75	0.120
Well Blank	0.4 I	2.0 U	0.06 I	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.004 U	0.01 U	0.1 U	0.004 U

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Rise	0.214	4.7			17.40	6.16	85		4.78
Well #3	0.046	10.3			21.38	6.77	463	0.15	1.24
Well #4	0.044	7.9			21.22	6.86	450	0.60	1.20
Well #5	0.020	7.6			21.29	6.91	392	1.40	0.12
Well #6	0.018	6.8			21.08	6.87	455	0.05	0.70
Well #7	0.122	6.3	0.707892	0.414	20.53	6.94	449	1.30	0.68
Well Blank	0.004 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX CB. WATER CHEMISTRY DATA APRIL 22, 2005.

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Rise	13.5	12.6	20.0	6.11	3.42	1.03	34.5	0.016 I	0.070	0.043	0.93	0.145
Well #3	5.8	3.8 I	95.2	4.06	1.75	0.18	219	0.004 U	0.067	0.01 U	0.1 U	0.051
Well #4	8.6	4.6 I	97.0	4.60	1.43	0.39	214	0.004 U	0.038	0.01 U	0.1 U	0.048
Well #5	6.0	2.0 U	82.0	2.56	0.92	0.31	182	0.004 U	0.004 U	0.01 U	0.1 U	0.021
Well #6	6.4	2.0 U	86.2	3.04	1.17	0.46	208	0.005 I	0.004 U	0.01 U	0.1 U	0.021
Well #7	16.9	15.5	94.9	7.05	4.49	0.79	205	0.004 U	0.004 U	0.425	0.64	0.130
Well #7 (dup)	17.1	16.2	97.2	6.91	4.47	0.76	210	0.005 I	0.004 U	0.403	0.63	0.131
Well Blank	0.4 I	2.0 U	0.07 I	0.15 U	0.01 I	0.02 U	1.0 U	0.004 U	0.004 U	0.01 U	0.1 U	0.004 U

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Rise	0.198	14.9	0.708073	0.164	18.91	6.76	135		3.41
Well #3	0.043	11.2			21.34	6.83	440	0.35	1.39
Well #4	0.046	8.4			21.32	6.77	430	0.95	1.27
Well #5	0.017	9.8			21.35	6.91	377	1.40	0.15
Well #6	0.017	5.4			21.07	6.86	433	0.45	0.43
Well #7	0.130	7.1	0.707905	0.457	20.48	6.91	476	4.60	0.46
Well #7 (dup)	0.132	7.0							
Well Blank	0.004 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX CC. WATER CHEMISTRY DATA APRIL 28, 2005.

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Rise	15.5	27.6	33.9	6.73	5.40	0.93	68.5	0.025	0.175	0.336	0.78	0.132
Well #3	5.8	3.7 I	86.8	3.66	1.58	0.16	216	0.004 U	0.064	0.01 U	0.1 U	0.046
Well #4	8.4	4.6 I	82.7	4.37	1.32	0.36	209	0.004 U	0.041	0.01 U	0.1 U	0.043
Well #5	6.0	2.0 U	76.2	2.30	0.84	0.28	181	0.004 U	0.005 I	0.01 U	0.12 I	0.019
Well #6	6.3	2.0 U	92.8	3.02	1.16	0.44	209	0.004 U	0.013 I	0.01 U	0.11 I	0.015 I
Well #7	19.2	14.9	109	7.63	4.46	0.68	244	0.004 U	0.006 I	0.01 U	0.72	0.131

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Rise	0.177	14.2	0.707944	0.351	19.66	7.11	232		2.48
Well #3	0.046	11.2			21.33	6.83	437	0.25	1.92
Well #4	0.056	7.8			21.29	6.73	430	1.30	1.28
Well #5	0.019	11.2			21.27	6.91	380	2.40	0.15
Well #6	0.016 I	9.0			20.98	6.83	435	0.20	0.26
Well #7	0.140	7.7	0.707906	0.492	20.56	6.70	529	5.70	0.22

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX CD. WATER CHEMISTRY DATA MAY 6, 2005.

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Rise	16.0	27.0	33.6	6.66	5.84	0.88	68.7	0.015 I	0.230	0.012 I	0.73	0.152
Well #3	5.5	3.6 I	91.7	3.58	1.53	0.15	206	0.004 U	0.062	0.01 U	0.1 U	0.047
Well #4	8.6	4.6 I	81.7	4.06	1.26	0.34	200	0.004 U	0.038	0.01 U	0.1 U	0.043
Well #5	5.6	2.0 U	71.7	2.28	0.84	0.26	186	0.004 U	0.004 U	0.01 U	0.1 U	0.017
Well #6	6.1	2.0 U	89.1	2.99	1.17	0.43	198	0.004 U	0.004 U	0.01 U	0.16 I	0.015 I
Well #7	17.6	15.4	115	7.16	4.31	0.63	240	0.006 I	0.004 U	0.374	0.59	0.134 Q(5)
Well Blank	0.4 I	2.0 U	0.05 I	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.004 U	0.01 U	0.1 U	0.004 U, Q(4)
Surface Blank	0.5 I	2.0 U	0.02 U	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.007 I	0.019 I	0.1 U	0.004 U

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Rise	0.181	9.2	0.707953	0.418	20.72	7.22	243		2.78
Well #3	0.045	10.2			21.26	6.93	431	0.00	1.82
Well #4	0.045	7.8			21.11	7.06	426	0.55	1.23
Well #5	0.022	6.7			21.15	6.73	378	1.10	0.17
Well #6	0.05	6.4			20.84	6.88	429	0.90	0.16
Well #7	0.139	8.3	0.707909	0.498	20.48	6.64	533	3.80	0.19
Well Blank	0.004 U	1.0 U							
Surface Blank	0.004 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

Q = Sample analyzed out of holding time (number of days).

APPENDIX CE. WATER CHEMISTRY DATA MAY 11, 2005.

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Rise	10.8	12.5	15.6	5.77	3.26	1.12	28	0.018	0.080	0.026 I	1.08	0.177 Q(21)
Well #3	5.1	3.4 I	87.0	3.83	1.62	0.17	213	0.005 I	0.070	0.01 U	0.1 U	0.050
Well #4	7.8	4.3 I	90.9	5.10	1.42	0.43	203	0.004 U	0.038	0.01 U	0.1 U	0.046
Well #5	4.5	2.0 U	75.6	2.83	0.94	0.34	177	0.004 U	0.004 U	0.015 I	0.1 U	0.019
Well #6	6.2	2.0 U	87.9	3.46	1.22	0.52	207	0.006 I	0.004 U	0.042	0.27 I	0.017
Well #6 (dup)	6.3	2.0 U	84.2	3.33	1.18	0.51	205	0.008 I	0.004 U	0.034 I	0.20 I	0.016 I
Well #7	13.1	15.7	103	8.50	4.70	0.86	230	0.012 I	0.006 I	0.403	0.75	0.137 Q(20)

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Rise	0.214	12.4	0.708087	0.064	20.57	6.36	128		4.84
Well #3	0.044	10.4			21.39	6.81	431	0.00	1.55
Well #4	0.041	7.8			21.21	6.90	427	2.09	1.36
Well #5	0.023	4.7			21.24	6.87	376	2.31	0.16
Well #6	0.016 I	7.0			20.88	6.83	426	0.45	0.28
Well #6 (dup)	0.018	6.2							
Well #7	0.146	7.2	0.707917	0.486	20.81	6.69	518	4.62	0.17

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

Q = Sample analyzed out of holding time (number of days).

APPENDIX CF. WATER CHEMISTRY DATA MAY 18, 2005.

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Rise	15.0	35.6	37.4	7.25	7.04	0.98	78.6	0.012 I	0.293	0.01 U	0.68	0.141
Well #3	5.4	3.4 I	89.0	4.06	1.69	0.17	217	0.004 U	0.073	0.01 U	0.1 U	0.044
Well #4	8.1	4.6 I	87.4	4.58	1.37	0.40	206	0.004 U	0.048	0.01 U	0.1 U	0.042
Well #5	5.2	2.0 U	76.4	2.55	0.87	0.28	182	0.005 I	0.004 U	0.01 U	0.12 I	0.013 I
Well #6	6.0	2.0 U	79.5	2.79	1.14	0.44	205	0.011 I	0.008 I	0.052	0.12 I	0.011 I
Well #7	16.9	23.9	102	7.59	4.51	0.70	236	0.012 I	0.012 I	0.338	0.63	0.160 Q(13)
Well Blank	0.4 I	2.0 U	0.07 I	0.15 U	0.01 U	0.02 U	1.0 U	0.004 U	0.004 U	0.016 I	0.1 U	0.004 U

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Rise	0.174	14.1			22.23	6.59	282		2.16
Well #3	0.044	10.1			21.49	6.81	439	0.12	2.32
Well #4	0.044	8.0			21.34	6.84	437	1.24	1.56
Well #5	0.018	8.0			21.48	6.63	389	0.75	0.75
Well #6	0.013 I	7.5			21.10	6.67	434	0.26	0.16
Well #7	0.131	8.2			20.70	6.59	550	2.52	0.20
Well Blank	0.004 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

Q = Sample analyzed out of holding time (number of days).

11 APPENDIX D

APPENDIX D1. WATER CHEMISTRY DATA JANUARY 17, 2006

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Sink	14.1	10.6	12.2	6.26	3.16	0.89	21.2	0.008 I	0.055	0.01 U	0.66	0.093
Ogden Pond	14.3	10.7	11.8	6.05	3.08	0.85	20.9	0.008 I	0.055	0.025	0.89	0.091
Paraner's Branch	14.9	16.1	14.8	6.66	3.59	0.92	24.4	0.008 I	0.053	0.01 U	0.91	0.093
Paraner's (dup)	15.2	16.3	14.6	6.56	3.55	0.90	24.0	0.008 I	0.055	0.01 U	0.92	0.093
Hawg Sink	9.2	10.7	29.4	4.46	2.72	1.08	65.6	0.004 U	0.025	0.01 U	0.55	0.166
Sweetwater Lake	15.1	20.9	16.7	6.70	3.88	0.95	27.4	0.008 I	0.070	0.01 U	0.88	0.095
River Rise	14.3	20.5	16.8	6.48	3.75	0.96	27.3	0.007 I	0.066	0.01 U	0.94	0.096
Surface Blank	0.6 I	1.0 U	0.3	0.20 U	0.08	0.02 U	1.0 U	0.004 U	0.007 I	0.01 U	0.1 U	0.004 U
Well #1	6.7	1.0 U	90.6	3.26	1.19	0.19	218	0.004 U	0.009 I	0.01 U	0.1 U	0.147
Well #1 (dup)	6.3	1.0 U	89.3	3.22	1.18	0.19	224	0.004 U	0.007 I	0.01 U	0.1 U	0.144
Well #2	49.1	347.0	157	29.00	36.20	2.33	201	0.004 U	0.004 U	0.128	0.24 I	0.07
Well #3	5.7	3.7 I	88.6	4.32	1.68	0.20	218	0.004 U	0.065	0.013 I	0.1 U	0.05
Well #4	8.7	4.5	86.1	4.44	1.34	0.38	206	0.004 U	0.034	0.01 U	0.1 U	0.044
Well #5	5.4	1.0 U	72.8	2.45	0.85	0.31	179	0.004 U	0.009 I	0.01 U	0.1 U	0.016 I
Well #6	5.9	1.9 I	86	3.03	1.15	0.47	210	0.004 U	0.005 I	0.011 I	0.1 U	0.015 I
Well #7	19.0	14.6	101	7.24	4.32	0.68	238	0.004 U	0.014 I	0.342	0.41	0.159
Well #8	5.5	4.7	66.5	4.26	1.44	0.10	170	0.004 U	0.006 I	0.114	0.19 I	0.081
Well Blank	0.8 I	1.0 U	0.05	0.20 U	0.01 U	0.02 U	1.0 U	0.004 U	0.005 I	0.01 I	0.1 U	0.004 U

APPENDIX D1. WATER CHEMISTRY DATA JANUARY 17, 2006

Location	TP (mg/L)	SiO ₂ (mg/L)	⁸⁷ Sr/ ⁸⁶ Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Sink	0.121	10.7			13.60	6.52	111		7.85
Ogden Pond	0.121	10.7			13.69	6.57	111		7.05
Paraner's Branch	0.121	10.4			13.71	6.92	128		6.50
Paraner's (dup)	0.121	10.9							
Hawg Sink	0.198	9.2	0.708083	0.157	15.73	7.05	181		0.82
Sweetwater Lake	0.131	10.8	0.708070	0.194	14.12	7.20	143		6.61
River Rise	0.131	10.8	0.708078	0.198	14.56	7.27	144		5.94
Surface Blank	0.004 U	1.0 U							
Well #1	0.162	9.5	0.707885	0.095	21.63	6.46	443	0.76	0.17
Well #1 (dup)	0.162	9.3							
Well #2	0.066	15.1	0.707842	3.320	25.00	6.52	1044	0.01	0.23
Well #3	0.043	9.7			21.33	6.80	436	0.00	1.62
Well #4	0.054	7.3			21.24	6.72	427	0.94	1.16
Well #5	0.017	6.8			21.28	6.55	367	0.79	0.17
Well #6	0.015 I	5.6			20.92	6.67	429	0.00	0.22
Well #7	0.134	7.1	0.707900	0.496	20.60	6.66	526	1.57	0.15
Well #8	0.095	14.1	0.708150	0.139	21.30	6.70	362	0.00	0.15
Well Blank	0.004 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX D2. WATER CHEMISTRY DATA APRIL 11 AND 12, 2006

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Sink	14.1	10.6	12.2	6.26	3.16	0.89	21.2	0.008 I	0.055	0.01 U	0.66	0.093
Ogden Pond	14.3	10.7	11.8	6.05	3.08	0.85	20.9	0.008 I	0.055	0.025	0.89	0.091
Paraner's Branch	14.9	16.1	14.8	6.66	3.59	0.92	24.4	0.008 I	0.053	0.01 U	0.91	0.093
Paraner's (dup)	15.2	16.3	14.6	6.56	3.55	0.90	24.0	0.008 I	0.055	0.01 U	0.92	0.093
Hawg Sink	9.2	10.7	29.4	4.46	2.72	1.08	65.6	0.004 U	0.025	0.01 U	0.55	0.166
Sweetwater Lake	15.1	20.9	16.7	6.70	3.88	0.95	27.4	0.008 I	0.070	0.01 U	0.88	0.095
River Rise	14.3	20.5	16.8	6.48	3.75	0.96	27.3	0.007 I	0.066	0.01 U	0.94	0.096
Surface Blank	0.6 I	1.0 U	0.3	0.20 U	0.08	0.02 U	1.0 U	0.004 U	0.007 I	0.01 U	0.1 U	0.004 U
Well #1	6.7	1.0 U	90.6	3.26	1.19	0.19	218	0.004 U	0.009 I	0.01 U	0.1 U	0.147
Well #1 (dup)	6.3	1.0 U	89.3	3.22	1.18	0.19	224	0.004 U	0.007 I	0.01 U	0.1 U	0.144
Well #2	49.1	347.0	157	29.00	36.20	2.33	201	0.004 U	0.004 U	0.128	0.24 I	0.07
Well #3	5.7	3.7 I	88.6	4.32	1.68	0.20	218	0.004 U	0.065	0.013 I	0.1 U	0.05
Well #4	8.7	4.5	86.1	4.44	1.34	0.38	206	0.004 U	0.034	0.01 U	0.1 U	0.044
Well #5	5.4	1.0 U	72.8	2.45	0.85	0.31	179	0.004 U	0.009 I	0.01 U	0.1 U	0.016 I
Well #6	5.9	1.9 I	86	3.03	1.15	0.47	210	0.004 U	0.005 I	0.011 I	0.1 U	0.015 I
Well #7	19.0	14.6	101	7.24	4.32	0.68	238	0.004 U	0.014 I	0.342	0.41	0.159
Well #8	5.5	4.7	66.5	4.26	1.44	0.10	170	0.004 U	0.006 I	0.114	0.19 I	0.081
Well Blank	0.8 I	1.0 U	0.05	0.20 U	0.01 U	0.02 U	1.0 U	0.004 U	0.005 I	0.01 I	0.1 U	0.004 U

APPENDIX D2. WATER CHEMISTRY DATA APRIL 11 AND 12, 2006

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Sink	0.121	10.7			13.60	6.52	111		7.85
Ogden Pond	0.121	10.7			13.69	6.57	111		7.05
Paraner's Branch	0.121	10.4			13.71	6.92	128		6.50
Paraner's (dup)	0.121	10.9							
Hawg Sink	0.198	9.2			15.73	7.05	181		0.82
Sweetwater Lake	0.131	10.8			14.12	7.20	143		6.61
River Rise	0.131	10.8			14.56	7.27	144		5.94
Surface Blank	0.004 U	1.0 U							
Well #1	0.162	9.5			21.63	6.46	443	0.76	0.17
Well #1 (dup)	0.162	9.3							
Well #2	0.066	15.1			25.00	6.52	1044	0.01	0.23
Well #3	0.043	9.7			21.33	6.80	436	0.00	1.62
Well #4	0.054	7.3			21.24	6.72	427	0.94	1.16
Well #5	0.017	6.8			21.28	6.55	367	0.79	0.17
Well #6	0.015 I	5.6			20.92	6.67	429	0.00	0.22
Well #7	0.134	7.1			20.60	6.66	526	1.57	0.15
Well #8	0.095	14.1			21.30	6.70	362	0.00	0.15
Well Blank	0.004 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

APPENDIX D3. WATER CHEMISTRY DATA JULY 12 AND 13, 2006

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO₃)	NO2 (mg/L)	NO2+ NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	SRP (mg/L)
River Sink	8	42.7	55.7	6.41	14.3	0.77	148	0.013 I	0.008 I	0.010 U	0.10 U	0.107
Ogden Pond	9	44.4	56.2	6.68	14.5	0.78	147	0.011 I	0.004 U	0.029 I, V	0.14 I	0.110
Paraner's Branch	14	68.5	66.6	9.96	16	0.99	145	0.012 I	0.016 I	0.010 U	0.36 I	0.112
Paraner's (dup)	14	69.9	64.3	9.62	15.3	0.95	142	0.009 I	0.004 U	0.010 U	0.23 I	0.112
Hawg Sink	14	68.5	66.2	9.87	15.7	1.02	145	0.012 I	0.040	0.010 U	0.27 I	0.117
Sweetwater Lake	14	88.2	75.3	9.5	15.4	0.96	154	0.008 I	0.245	0.010 U	0.20 I	0.097
River Rise	15	91.7	78.8	10.3	16	1.01	150	0.008 I	0.280	0.037 I, V	0.10 U	0.097
Surface Blank	1.0 U	1.0 U	0.03 I	0.20 U	0.01 U	0.02 U	1.0 U	0.005 I	0.004 U	0.010 U	0.10 U	0.004 U
Well #1	7	1.0 U	106	3.7	1.25	0.19	260	0.02	0.004 U	0.010 U	0.10 U	0.151
Well #1 (dup)	7	1.0 U	106	3.61	1.26	0.19	249	0.015 I	0.008 I	0.031 I, V	0.11 I	0.156
Well #2	54	429	191	36.9	49.6	3.1	214	0.008 I	0.004 U	0.111	0.15 I	0.049
Well #3	5	3.82 I	92.8	3.87	1.64	0.2	222	0.005 I	0.070	0.054 V	0.10 U	0.054
Well #4	8	4.54	90.6	4.66	1.35	0.36	211	0.005 I	0.041	0.01 U	0.10 U	0.044
Well #4A	10	9.4	101	5.74	1.72	0.31	241	0.004 U	0.094	0.042 V	0.10 U	0.100
Well #5	5	1.0 U	73.4	2.25	0.82	0.28	177	0.023	0.004 U	0.013 I, V	0.10 U	0.022
Well #5A	11	12.1	126	5.74	1.53	0.1	282	0.005 I	0.004 U	0.010 U	0.10 U	0.064
Well #6	6	2.07 I	96.2	3.54	1.28	0.47	226	0.023	0.004 U	0.010 U	0.10 U	0.018
Well #6A	6	30.1	94.4	6.47	1.79	6.15	220	0.022	0.004 U	0.066	0.10 U	0.091
Well #7	15	21.6	72.6	5.34	3.82	0.77	172	0.015 I	0.006 I	0.32	0.77	0.132
Well #7A	7	34.3	96	4.37	1.82	0.27	197	0.012 I	0.010 I	0.312	0.10 U	0.068
Well #8	5	4.43	70.8	4.26	1.44	0.1	167	0.019	0.008 I	0.06 V	0.35 I	0.080
Well Blank	1.0 U	1.0 U	0.05 I	0.20 U	0.01 U	0.02 U	1.0 U	0.005 I	0.004 U	0.06	0.10 U	0.004 U

APPENDIX D3. WATER CHEMISTRY DATA JULY 12 AND 13, 2006

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Sink	0.109	13.0			27.65	7.74	391		6.78
Ogden Pond	0.109	13.2			27.22	7.62	396		6.27
Paraner's Branch	0.116	13.2			27.1	7.55	464		6.23
Paraner's (dup)	0.119	13.2							
Hawg Sink	0.111	11.2			26.06	7.21	463		2.47
Sweetwater Lake	0.093	15.4			24.47	7.26	521		2.32
River Rise	0.090	15.0			24.27	6.98	532		1.15
Surface Blank	0.006 U	1.0 U							
Well #1	0.229	12.2			21.85	6.84	501	0.55	0.27
Well #1 (dup)	0.166	12.3							
Well #2	0.043	18.0			25.37	6.78	1258	0.28	0.28
Well #3	0.048	9.9			21.55	7	444	0.4	1.1
Well #4	0.041	7.6			21.51	7	442	0.2	2.13
Well #4A	0.093	8.3			21.29	6.89	501	3.06	4.34
Well #5	0.020 I	8.4			21.45	6.85	360	1.18	0.22
Well #5A	0.069	6.8			21.08	6.78	584	5.92	0.66
Well #6	0.020 I	9.3			21.13	6.69	462	0.59	0.23
Well #6A	0.098	4.7			20.45	6.97	490	11.6	0.62
Well #7	0.111	5.7			20.83	7.4	373	2.42	0.22
Well #7A	0.082	6.0			20.74	7.23	452	7.73	0.46
Well #8	0.088	19.1			21.56	7.04	369	0.24	2.89
Well Blank	0.006 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

V = Result below blank value

APPENDIX D4. WATER CHEMISTRY DATA OCTOBER 10 AND 12, 2006

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO ₂ [†] (mg/L)	NO ₂ + NO ₃ (mg/L)	NH ₃ (mg/L)	TKN (mg/L)	SRP (mg/L)
River Sink	10	41.9	55.2	6.94	15.6	0.88	152	0.010 U, Q(12)	0.013	0.009 U	0.89	0.083
Ogden Pond	34	117	82.8	20.9	22.8	1.43	154	0.010 U, Q(36)	0.022	0.009 U	0.26 I	0.086
Paraner's Branch	19	86.2	71.8	11.7	18.3	1.07	157	0.010 U	0.040	0.009 U	0.38	0.110
Paraner's (dup)	18	88.1	70.4	11.5	17.9	1.05	152	0.010 U, Q(10)	0.041	0.009 U	0.35	0.110
Hawg Sink	18	83.8	68.5	11.2	17.3	1.02	152	0.010 U, Q(24)	0.077	0.009 U	0.34	0.113
Sweetwater Lake	17	96.9	79.1	10.7	16.9	1.02	155	0.010 U	0.227	0.015 I	0.15 I	0.083
River Rise	18	103	80.2	11.1	17.1	1.04	156	0.010 U	0.252	0.009 U	0.17 I	0.081
Surface Blank	0.1 U	0.33 U	0.02 U	0.20 U	0.01 U	0.02 U	0.70 U	0.010 U	0.003 U	0.011 I	0.08 U	0.002 U
Well #1	9	0.33 U	107	4.11	1.28	0.23	255	0.010 U	0.003 U	0.009 U	0.25 I	0.156
Well #1 (dup)	8	0.33 U	108	3.98	1.27	0.22	253	0.010 U, Q(25)	0.003 U	0.009 U	0.30 I	0.150
Well #2	57	407	182	35.6	47.2	3.05	211	0.010 U, Q(50)	0.003 U	0.121	0.12 I	0.034
Well #3	6	4.01	92.4	4.77	1.7	0.23	224	0.004 U	0.111	0.029 I	0.16 I	0.052
Well #4	9	4.97	87.6	5	1.34	0.38	211	0.004 U	0.036	0.016 I	0.24 I	0.042
Well #4A	12	8.06	101	6.49	1.73	0.39	239	0.004 U	0.103	0.029 I	0.21 I	0.091
Well #5	5	0.33 U	72.7	2.52	0.84	0.33	177	0.004 U	0.005 I	0.009 U	0.36	0.018
Well #5A	12	12.4	125	6.28	1.53	0.11	284	0.004 U	0.009 I	0.009 U	0.37	0.065
Well #6	7	1.61	92.9	3.92	1.27	0.51	226	0.004 U	0.003 U	0.009 U	0.08 U	0.017
Well #6A	8	46.2	96.3	7.87	2.27	9.39	210	0.004 U	0.005 I	0.009 U	0.28 I	0.071
Well #7	14	7.16	67.7	5.68	3.86	0.8	164	0.004 U	0.003 U	0.365	0.86	0.097
Well #7A	8	33.1	91.3	4.29	1.73	0.29	187	0.004 U	0.003 U	0.009 U	0.45	0.062
Well #8	6	5.09	69.1	4.5	1.49	0.13	172	0.010 U	0.003 U	0.114	0.26 I	0.088
Well Blank	0.5	0.33 U	0.08	0.20 U	0.01 U	0.02 U	0.70 U	0.004 U	0.004 I	0.009 U	0.09 I	0.002 U

APPENDIX D4. WATER CHEMISTRY DATA OCTOBER 10 AND 12, 2006

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Sink	0.111	15.1	0.707902	0.967	22.72	7.24	396		4.01
Ogden Pond	0.106	16.1			25.09	7.22	631		2.42
Paraner's Branch	0.006 U	17.2			23.91	7.25	510		2.37
Paraner's (dup)	0.124	17.0							
Hawg Sink	0.121	15.8	0.707867	1.457	24.37	7.16	501		1.24
Sweetwater Lake	0.101	17.2	0.707861	1.869	23.84	7.19	544		1.28
River Rise	0.094	16.6			24.6	7.15	548		1.17
Surface Blank	0.006 U	1.0 U							
Well #1	0.199	10.6	0.707911	0.108	21.83	6.61	507	0.6	1.63
Well #1 (dup)	0.199	10.5							
Well #2	0.038	17.8	0.707844	4.347	25.92	6.8	1220	0.58	0.45
Well #3	0.053	9.4			21.4	6.92	439	0.26	2.26
Well #4	0.043	7.4			21.42	6.91	433	1.33	0.99
Well #4A	0.101	8.1			21.2	6.77	483	6.48	3.7
Well #5	0.023 I	7.7			21.37	7.03	350	2.2	0.26
Well #5A	0.071	6.5			21.25	6.75	566	5.35	0.51
Well #6	0.023 I	8.2			21.07	6.86	454	0.13	0.3
Well #6A	0.083	4.4			21.42	6.86	504	4.16	0.6
Well #7	0.096	5.4	0.707895	0.353	20.68	7.03	354	2.78	0.21
Well #7A	0.073	5.8	0.708048	0.185	21.07	7.04	421	5.7	0.28
Well #8	0.091	14.3			21.5	7	364	0.35	0.33
Well Blank	0.006 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

Q = Sample analyzed out of holding time (minutes).

† = Samples collected on 10/10/2006 were measured using EPA 300.0 method, and samples collected on 10/12/2006 were measured using EPA 353.2 method (not NELAC certified).

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APPENDIX E1. WATER CHEMISTRY DATA JANUARY 15 AND 17, 2007

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO ₂ [†] (mg/L)	NO ₂ + NO ₃ (mg/L)	NH ₃ (mg/L)	TKN (mg/L)	SRP (mg/L)
River Sink	10	45.8	51.4	6.94	13.8	1.06	136, Q(14)	0.008 I	0.006 I	0.004 U	0.33	0.113
Ogden Pond	94	341	143	52	37.9	2.72	161, Q(14)	0.008 I	0.005 I	0.072	0.34	0.086
Paraner's Branch	20	82.7	66.5	11.5	17.3	1.23	140, Q(14)	0.006 I	0.026	0.042	0.25 I	0.138
Paraner's (dup)	19	81	66	11.6	17.3	1.26	139, Q(14)	0.008 I	0.026	0.031 I	0.22 I	0.137
Hawg Sink	19	88.3	70.9	12	18	1.15	155, Q(14)	0.006 I	0.05	0.02 I	0.14 I	0.13
Sweetwater Lake	18	102	80.9	11.3	17.5	1.11	154, Q(13)	0.004 U	0.199	0.03 I	0.07 U	0.097
River Rise	17	101	81.1	10.7	17.4	1.05	156, Q(13)	0.004 U	0.186	0.004 U	0.07 U	0.105
Surface Blank	0.7 U	0.8 I	0.02 I	0.17 U	0.01 U	0.02 U	0.7 U, Q(13)	0.004 U	0.003 U	0.004 U	0.07 U	0.003 I
Well #1	8	0.79 I	104	3.67	1.18	0.21	259, Q(14)	0.015 I	0.003 U	0.047	0.13 I	0.175
Well #1 (dup)	8	0.88 I	103	3.74	1.18	0.22	242, Q(14)	0.017	0.005 I	0.045	0.12 I	0.164
Well #2	59	421	174	34.6	47.9	3.14	208, Q(14)	0.006 I	0.003 U	0.168	0.27 I	0.044
Well #3	6	3.09	91	4.02	1.65	0.22	226, Q(13)	0.004 U	0.056	0.004 U	0.07 U	0.06
Well #4	9	3.3	90	4.71	1.36	0.39	199, Q(13)	0.004 U	0.036	0.004 U	0.07 U	0.052
Well #4A	12	5.7	98.9	5.74	1.67	0.39	228, Q(13)	0.004 U	0.142	0.004 U	0.07 U	0.099
Well #5	5	0.74	71.4	2.39	0.82	0.33	170, Q(13)	0.025	0.003 U	0.025 I	0.07 U	0.087
Well #5A	12	10.1	122	5.44	1.47	0.14	267, Q(13)	0.004 U	0.007 I	0.014 I	0.07 U	0.073
Well #6	7	0.69	95.4	3.5	1.29	0.5	220, Q(13)	0.025	0.005 I	0.023 I	0.08 I	0.025
Well #6A	7	36.2	99.5	5.95	1.98	5.95	212, Q(13)	0.006 I	0.003 U	0.017 I	0.07 U	0.072
Well #7	12	18.4	69.4	5.08	3.89	0.79	156, Q(13)	0.006 I	0.003 U	0.408	0.68	0.112
Well #7A	7	32.8	88.7	3.51	1.57	0.26	181, Q(13)	0.007 I	0.012 I	0.052	0.26	0.075
Well #8	6	2.71	68.9	4.82	1.48	0.13	172, Q(14)	0.015 I	0.003 U	0.172	0.33	0.086
Well Blank	0.6 U	0.79 I	0.07 I	0.17 U	0.01 U	0.02 U	0.7 U, Q(13)	0.004 U	0.003 U	0.004 U	0.07 U	0.005 I

APPENDIX E1. WATER CHEMISTRY DATA JANUARY 15 AND 17, 2007

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Sink	0.119	9.8			16.17	7.06	365		2.88
Ogden Pond	0.095	17.2			21.51	7.18	1130		0.22
Paraner's Branch	0.14	16.3			19.64	7.43	479		2.84
Paraner's (dup)	0.135	15.9							
Hawg Sink	0.122	17.8			20.62	7.41	500		2.3
Sweetwater Lake	0.089	17.4			21.69	7.06	535		2.14
River Rise	0.086	18.5			21.41	7.26	528		1.36
Surface Blank	0.003 U	1.0 U							
Well #1	0.196	10.9			21.83	6.88	490	0.63	0.3
Well #1 (dup)	0.198	11.4							
Well #2	0.042	20			26.1	6.96	1184	0.24	0.31
Well #3	0.042	10.3			21.27	6.81	424	0.24	0.83
Well #4	0.039	7.8			21.16	6.84	420	0.61	1.03
Well #4A	0.076	8.4			20.81	6.77	460	3.77	2.75
Well #5	0.012	7.5			21.21	6.93	336	2.47	0.28
Well #5A	0.069	7.3			21.04	6.63	543	3.26	0.36
Well #6	0.028	6.5			20.83	6.89	436	1.68	0.26
Well #6A	0.068	5			20.28	6.85	473	13.6	0.85
Well #7	0.1	4.7			20.47	7.03	344	0.86	0.21
Well #7A	0.073	6.3			20.8	7.00	400	8.81	0.23
Well #8	0.1	17			21.52	7.14	353	0	0.27
Well Blank	0.003 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

Q = Sample analyzed out of holding time (days).

APPENDIX E2. WATER CHEMISTRY DATA APRIL 10, 2007

Location	Cl (mg/L)	SO4 (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Alkalinity (mg/L CaCO ₃)	NO ₂ [†] (mg/L)	NO ₂ + NO ₃ (mg/L)	NH ₃ (mg/L)	TKN (mg/L)	SRP (mg/L)
River Sink	15	46.6	50.4	8.51	15	1.2	142	0.004 U	0.016 I	0.058	0.33 I	0.151
Ogden Pond	72	248	109	39.7	30.7	2.14	146	0.004 U	0.016 I	0.057	0.22 I	0.086
Paraner's Branch	15	60.2	61.4	9.77	16.8	0.96	152	0.004 U	0.07	0.039 I	0.10 U	0.121
Paraner's (dup)	16	60.8	58.4	9.21	15.9	0.9	150	0.005 I	0.075	0.047	0.13 I	0.119
Hawg Sink	15	76.6	68	11.2	17.9	1.05	148	0.01 I	0.078	0.048	0.12 I	0.126
Sweetwater Lake	18	108	76	10.6	17.3	0.97	152	0.004 U	0.192	0.028 I	0.10 U	0.094
River Rise	18	110	75.6	10.9	17.3	1	158	0.004 U	0.228	0.030 I	0.12 I	0.098
Surface Blank	1.0 U	1.00 U	0.02 I	0.20 U	0.01 U	0.02 U	1.0 U	0.004 U	0.019	0.041	0.10 U	0.004 U
Well #1	8	1.00 U	98.1	3.56	1.18	0.19	256	0.01 I	0.042	0.055	0.10 U	0.178
Well #1 (dup)	8	1.00 U	99.6	3.61	1.19	0.19	248	0.01 I	0.02 V	0.044	0.10 U	0.174
Well #2	15	418	178	36.1	49.3	2.98	206	0.004 U	0.007 I	0.175	0.21 I	0.041
Well #3	6	3.12 I	86.4	3.9	1.64	0.19	214	0.004 U	0.067	0.013 I	0.10 U	0.056
Well #4	10	3.32 I	86.2	4.63	1.35	0.35	208	0.004 U	0.172	0.044	0.10 U	0.041
Well #4A	12	5.58	91.2	5.53	1.59	0.36	226	0.004 U	0.153	0.036 I	0.10 U	0.096
Well #5	5	1.00 U	68.7	2.22	0.82	0.3	166	0.015 I	0.062	0.077	0.10 U	0.019
Well #5A	12	9.65	118	5.54	1.48	0.13	276	0.004 U	0.004 U	0.044	0.10 U	0.068
Well #6	7	1.00 U	90.4	3.56	1.3	0.46	228	0.02	0.125	0.048	0.10 U	0.021
Well #6A	7	25.3	90.1	4.69	1.66	3.46	210	0.004 U	0.071	0.027 I	0.10 U	0.068
Well #7	14	2.31 I	61.5	4.63	3.69	0.67	158	0.004 U	0.021	0.368	0.63	0.106
Well #7A	7	31	79.5	3.2	1.46	0.21	168	0.004 U	0.119	0.061	0.18 I	0.071
Well #8	8	1.98 I	67.3	4.37	1.52	0.12	172	0.01 I	0.031	0.133	0.29 I	0.094
Well Blank	1.0 U	1.00 U	0.12	0.20 U	0.01 U	0.02 U	2.0 I	0.004 U	0.02	0.010 U	0.10 U	0.004 U

APPENDIX E2. WATER CHEMISTRY DATA APRIL 10, 2007

Location	TP (mg/L)	SiO2 (mg/L)	87Sr/86Sr	Sr (ppm)	Temp. (°C)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)
River Sink	0.171	4.9			18.44	7.14	412		0.35
Ogden Pond	0.1	10			21.60	7.17	939		0.63
Paraner's Branch	0.13	14.4			21.58	7.45	465		3.43
Paraner's (dup)	0.127	13.5							
Hawg Sink	0.135	13.3			21.92	7.35	502		2.02
Sweetwater Lake	0.108	15.7			22.50	7.34	564		1.32
River Rise	0.097	15.7			22.05	7.24	560		1.23
Surface Blank	0.006 U	1.0 U							
Well #1	0.206	10.4			21.69	6.82	505	1.37	0.30
Well #1 (dup)	0.203	11.5							
Well #2	0.048	18.3			26.08	6.98	1274	0.38	0.35
Well #3	0.072	9.7			21.33	6.96	441	0.77	0.91
Well #4	0.059	7.5			21.23	7.00	441	0.52	1.04
Well #4A	0.105	8.2			20.84	6.85	481	3.34	2.96
Well #5	0.026	7.4			21.29	7.12	351	2.98	0.35
Well #5A	0.078	6.6			20.91	6.79	570	4.46	0.38
Well #6	0.042	8.4			20.96	6.98	461	1.02	0.29
Well #6A	0.083	4.4			19.67	6.90	468	4.67	0.78
Well #7	0.105	5.2			20.58	7.27	354	6.35	0.27
Well #7A	0.078	5.6			20.59	7.11	417	7.35	1.11
Well #8	0.094	13.5			21.31	7.16	369	0.50	0.27
Well Blank	0.006 U	1.0 U							

U = Result below detection limit

I = Result below practical quantitation limit (four times the method detection limit).

V = Result at or below blank value