

CHEMICAL AND ISOTOPIC EVIDENCE FOR EXCHANGE OF WATER
BETWEEN CONDUIT AND MATRIX IN A KARST AQUIFER: AN EXAMPLE
FROM THE SANTA FE RIVER SINK/RISE SYSTEM

By

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Abstract of Thesis Presented to the Graduate School
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CHEMICAL AND ISOTOPIC EVIDENCE FOR EXCHANGE OF WATER BETWEEN
CONDUIT AND MATRIX IN A KARST AQUIFER: AN EXAMPLE FROM THE
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Karst aquifers are characterized by conduit porosity, fractures, and intergranular matrix porosity. Although classical karst aquifers have low matrix porosity, where permeability is high, ground water may exchange between conduits and matrix porosity. Because conduits can be filled with surface water entering through a sink or swallet this exchange may lead to contamination of the aquifer from the surface. An important process of karst hydrogeology is the extent that surface and ground water exchange, particularly by mixing of matrix and conduit water, and the processes that can control this mixing.

In North-central Florida the Upper Santa Fe River enters a 36m deep sinkhole at the River Sink. Less than 8 km south of the sink the headwaters of the Lower Santa Fe River occurs at the River Rise. Between the Sink and the Rise, numerous karst windows provide an opportunity to examine the movement of water between the conduit and the

matrix. In this study, the Sink, Rise, 12 karst windows, and 6 monitoring wells were sampled four times between May 2002 and May 2003 at drought, baseflow, and flood conditions. At drought conditions, high solute concentrations in water collected from the karst windows reflect evaporative loss of water and suggest that conduits contain water that originates from the matrix. Solute concentrations indicate 45-55% of the water originates from the matrix on the basis of two end-member mixing models. At flood conditions, concentrations reflect dilution and movement of surface water through the conduit and mixing models indicate the karst windows contain almost 100% surface water. At baseflow conditions the fraction of surface water depends on the antecedent conditions, specifically if baseflow is preceded by drought or flood conditions. Following drought conditions, low solute concentrations suggest that increasing water flow in the conduit and low hydraulic head of the matrix relative to the conduit allows loss of water to the matrix. At these conditions mixing models suggest that surface water makes up approximately 90-95% of the water in the karst windows. Following flood conditions, increased concentrations in the karst windows suggest water flows from the matrix to the conduit. Mixing models suggest the karst windows contain 75-80% surface water. Solute concentrations decrease by 50% in one of the wells in the study area during flooding and may be the result of flow along high permeability zones, which appears to be affected by loss of water from the conduit. All other wells have solute concentrations that change little during the study period and appear to be unaffected by surface water. Based on these data, the water chemistry in the karst windows appears to be affected by river levels and weather conditions to a greater extent than the water in the matrix.

CHAPTER 1 INTRODUCTION

Karst aquifers provide important water resources worldwide by providing water to more than 25% of the world's population. In the United States, karst terrains make up 20% of the land surface and karst aquifers supply 40% of the ground water used for drinking water (Karst Waters Institute, 2001). These aquifers are particularly vulnerable to contamination because they have a wide range of porosity. Unlike darcian-type aquifers, heterogeneous porosity develops in karst aquifers through dissolution of matrix rocks, resulting in large solution channels that typically have turbulent flow.

Karst aquifers are often considered a triple porosity system composed of fractures, conduits, and intergranular matrix porosity (Worthington, 1999). These three types of porosity may develop to different degrees depending on karst history and age. Conduits consist of dissolution features having large apertures, typically 10mm to tens of meters. Fracture porosity and the intergranular porosity typically have apertures of less than 10mm (White, 1999). Intergranular and fracture porosity can be difficult to distinguish, therefore, matrix will refer here to both fractures and intergranular porosity. In regions with low matrix permeability, conduits can transmit most of the potable water. In regions with elevated matrix porosity and permeability, large volumes of water can flow through the intergranular porosity of the matrix rocks (Smart and Ford, 1986) and in these areas most water may be stored in the matrix porosity.

Water can flow rapidly from the surface into sinkholes and then into conduits, thereby providing allogenic recharge (White, 1999). Mixing of water in conduits and

matrix can lead to rapid contamination of the water in the intergranular porosity, which may be a major source of potable water. Understanding the extent of exchange between the two different flow systems within karst aquifers is thus critical to determine the sources of spring waters and the potential for their contamination.

While there have been numerous studies focusing on karst aquifers, questions remain about the rates and extent of interactions between surface water and ground water and the mixing of water between the conduits and the matrix. The purpose of this study is to examine this interaction and to develop a better understanding of the hydrologic processes occurring in karst aquifers characterized by high matrix porosity. In addition, this study will develop techniques that incorporate natural chemical compositions, such as the use of $^{87}\text{Sr}/^{86}\text{Sr}$, as natural tracers in karst aquifers. This study attempts to answer several general questions:

1. How does variation in surface water levels influence mixing of water in conduits and matrix? What is the extent of mixing at various river water levels?
2. Can mixing models be developed for the extent of conduit/matrix exchange at various conditions?
3. How is the intergranular porosity water chemistry altered through water-rock interactions as water moves through the conduit and the matrix?
4. How does the distance from the conduit affect matrix water chemistry?
5. What role do antecedent conditions play in both conduit and matrix water chemistry?

Background Studies

Early studies using a variety of methods including potentiometric maps, dye-tracer studies, hydrographs, chemographs, and water chemistry (e.g., Shuster and White, 1971; Atkinson 1977; Thrailkill, 1985; Vervier, 1990; Thrailkill *et al.*, 1991; Padilla, 1994; and Halihan *et al.*, 1998) found that springs in karst aquifers can be divided into those that are

sourced from conduits in which water flows through large underground passages and those that are sourced by diffuse flow from intergranular porosity (Shuster and White, 1971 and Atkinson, 1977). Later work (Dean, 1999; Martin and Dean, 2001) showed that a gradation exists between the two types of springs.

In aquifers, potentiometric maps provide information about the ground water flow pattern. The presence of conduits in karst aquifers may alter the expected flow pattern determined by these maps (Thraillkill, 1985) and, as a result, dye-tracer tests are often used to determine ground water flow patterns in karst aquifers (e.g. Thraillkill, 1985; Thraillkill *et al.*, 1991). Fluorescein and RhodamineWT are often used as the tracer and are typically injected directly into a sink or swallet. These dye tracer experiments can define a ground water basin, conduit geometry, resurgence points from sinks and swallets, and response to storm events (Thraillkill, 1985 and Thraillkill *et al.*, 1991; Hisert, 1994). Resurgence of dyes provides information about the source of water at a given spring as well as linear travel time through the system. These studies cannot determine absolute flow paths, however, but instead provide a straight-line connection between the injection point and resurgence point.

Storm hydrographs and the chemistry of spring discharge provide additional information about flow in karst aquifers. Storm hydrographs represent the response of the spring to the influx of storm water and subsequent recession as springs return to baseflow conditions. Hydrographs can be compared with changes in spring water chemistry (chemographs) to distinguish between conduit springs and diffuse flow springs (Shuster and White, 1973). Chemical studies of spring discharge have also been used to study surface water/ground water exchange (Redwine and Howell, 2001). Precipitation

and ground water typically have different chemical concentrations as a result of water-rock reactions of the ground water. Precipitation typically has low concentrations of solutes and salts; however, ground water may have high solute concentrations due to water-rock interactions in the matrix.

In some karst aquifers, however, the geometry and geology of the region make chemical separation of spring types difficult. For example, in the Inner Bluegrass Karst Region in Kentucky both conduit and diffuse springs are recharged through limestone, but the conduit springs are associated with karst features, deep integrated conduit systems and large catchment areas while the diffuse springs are associated with shallow flow paths and small catchment areas (Scanlon and Thrailkill, 1987). The chemical compositions of both spring types are similar during low flow due to percolation and chemical reactions near the recharge zone. During high flow events the compositions are similar due to surface runoff through sinkholes recharging the conduit springs and short flow distances to the diffuse springs. Scanlon and Thrailkill (1987) concluded that the chemical composition of spring water is affected not only by conduit size but also by recharge type and flow path lengths in regions where the physiographical properties associated with springs do not differ between conduit-fed and diffuse-fed.

In recent years, isotopic compositions have been used to distinguish between surface water and ground water in karst aquifers. The primary isotope systems used are $\delta^{18}\text{O}$ and δD (e.g., Frederickson and Criss, 1999; Greene, 1997; Lakey and Krothe, 1996). The isotopes of oxygen and hydrogen have been used to trace lateral movements across a ground water basin (Greene, 1997) as well as spring discharge (Lakey and Krothe, 1996). When $\delta^{18}\text{O}$ and δD values are compared to the established meteoric water

line, sources of waters to springs and the influx of water following a storm can be determined (Lakey and Krothe, 1996).

Several studies have used $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios to study ground water in karst aquifers (Katz and Bullen, 1996; Katz *et al.*, 1997; Cao *et al.*, 1999; and Woods *et al.*, 2000). Strontium isotope ratios have been used in studies of surface/ground water mixing in carbonate systems (Katz and Bullen, 1996; Katz *et al.*, 1998; Cao *et al.*, 1999; Woods *et al.*, 2000; Dogramaci and Herczeg, 2002) and mixing with other ground water sources in non-carbonate systems (McNutt *et al.*, 1990; Johnson *et al.*, 2000). Strontium can be used for these studies because the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of dissolved Sr depends on the amount of dissolution of the solid aquifer material and its isotopic ratio. The only radiogenic Sr isotope is ^{87}Sr , which is the product of the decay of ^{87}Rb . Depending on their age, rocks containing abundant Rb-bearing minerals will have more ^{87}Sr and a higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than rocks with few Rb-bearing minerals, such as carbonates (Faure, 1986).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can be coupled with Sr^{2+} concentrations to provide a two end-member model. Woods *et al.* (2000) used such a model to provide evidence of mixing between water in the Upper Castle Hayne limestone aquifer with water in the younger Surficial Aquifer in the vicinity of the North Carolina coast. In Florida, the ratios have been used to discriminate ground water sources based on $^{87}\text{Sr}/^{86}\text{Sr}$ ratio-age plotting (Cao *et al.*, 1999) and to examine surface water/ground water interactions (Katz and Bullen, 1996; Katz *et al.*, 1997&1998). In the Leon Sinks Geological Area near Tallahassee, Florida groundwater samples from wells and the deepest sinkholes have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that plot along the Sr seawater age curve, suggesting the waters originate from the Oligocene-age limestones of the Upper Floridan Aquifer (Cao *et al.*, 1999). Samples

from shallow sinkholes have ratios above the modern seawater ratio of 0.70907, suggesting the waters originate from the younger clastics of the Water Table aquifer (Cao *et al.*, 1999). Katz and Bullen (1996) and Katz *et al.* (1997) examined lake water and ground water interactions in the mantled karst region of North Florida using the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios, and found ground water was associated with less radiogenic Sr than the water in the lakes. Ground water with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios was interpreted to either have a source from lake water or from rapid movement through the aquifer limiting equilibration with the limestone (Katz *et al.*, 1997).

While many methods have been employed in the study of karst aquifer systems, a number of these have focused on the discharge of a spring or springs to identify characteristics of the aquifer. In many of these studies, flow paths between surface water sources (i.e. a swallet) and the spring are unknown. In addition, there have been studies of surface water/ground water exchange but few studies focusing on the interaction of water in a porous matrix with water in conduits. A lack of abundant features along the flow path may be the reason for few detailed studies of conduit/matrix exchange. This study utilizes the major ion concentrations (Ca^{2+} , Mg^{2+} , Sr^{2+} , Na^+ , Cl^- , and SO_4^{2-}) and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios of water at known recharge and discharge points and from numerous karst windows and wells along the flow path connecting the recharge and discharge points. Consequently, the focus of this project is to examine the interaction of water in the matrix and water in the conduit where numerous karst windows provide access to the conduit water.

Study Area/Geologic Background

Study Area

The study area is along the Santa Fe River, in north-central Florida the second longest river flowing across north-central Florida and a major tributary to the Suwannee River (Figure 1-1). The river basin covers ~3500 km² and occurs in three physiographic regions, the Northern Highlands to the east and the Central Highlands and Gulf Coast Lowlands to the west (Hunn and Slack, 1983, Meyer, 1962). The river flows west from Santa Fe Lake for approximately 50 km then it disappears into a 36 m deep sinkhole known as the River Sink. Some of the water that enters the Sink eventually reemerges approximately 8 km downstream at the River Rise (Hisert, 1994); however, at times some fraction of this water appears to be lost to the matrix as the water travels through the conduit while at other times, water is gained from the matrix (Hisert, 1994; Dean, 1999; Martin, 2003; Smith *et al.*, 2002; Smith, 2004). The water discharging at the River Rise is probably a mixture of water flowing into the Sink and water lost from the matrix to the conduits (Hisert, 1994). Between the Sink and the Rise there are a number of karst windows present (Figure 1-2), and their water compositions reflect the physical and chemical processes that occur between the conduit and the matrix (e.g. Dean, 1999; Martin and Dean, 1999; Martin, 2003; Smith, 2002; Smith, 2004). This study extends the previous work through sampling and analysis of previously unsampled karst windows, as well as six wells recently drilled and completed at depths of the conduits.

Temperature and Climate

North-central Florida is classified as a humid sub-tropical climate (Meyer, 1962), with an average annual daytime temperature of 21°C. During January and December, the coldest winter months, the average daytime temperature is 14°C, and during August, the

warmest month, the daytime temperature averages 27°C. The average annual rainfall in the Santa Fe River basin is 140 cm (Hunn and Slack, 1983). Most rainfall occurs between June and September, and the least amount of rainfall occurs during the winter months (Meyer, 1962). In the summer, rainfall commonly comes from short afternoon thunderstorms that are the result of warm air rising over the land and drawing cool moist air inland from the Gulf of Mexico and the Atlantic Ocean. In the winter rainfall commonly comes from extra-tropical frontal systems. These storms typically last longer than the summer storms but do not occur as frequently.

The study area recently experienced a three-year drought that ended in the late fall and winter of 2002/2003. During the drought, the average yearly rainfall from January 1, 1999 to December 31, 2001 was 93 cm/year at O'leno State Park, which is approximately 33% less than the annual average (Suwannee River Water Management District archives). In contrast, in the years preceding the drought (1996-1998) the average rainfall at O'Leno was 147cm/yr. The river level at O'leno State Park for 1999 to the end of 2001 ranged between 9.6 and 10.3 meters above sea level (masl). Prior to that, the average river level at O'Leno State Park from 1994 through 1998 was 10.86 masl (SRWMD). For most of 2002, the river level was approximately 9.6 masl until mid-August when the river rose to 10 masl reaching a maximum at the end of December at 11 masl. In the first half of 2002 only 35 cm of precipitation occurred in the study area; however, between July and December 2002 an additional 70 cm of rainfall fell, resulting in 105 cm of rain for the year. During the fall and winter of 2002-2003 a moderate El Nino Southern Oscillation (ENSO) period caused greater than normal precipitation levels

throughout Florida and the Southeast with 60 cm of rain between November 1, 2002 and the end of March 2003.

Physiography

The Santa Fe River Basin is located along the Western Valley and the Northern Highlands physiographic provinces (White, 1970). The Western Valley is one of several large lowland areas within the Central Highlands. Several gaps within the valley allow drainage to the Gulf Coastal Lowlands, with the Santa Fe River flowing through the High Springs Gap to a confluence with the Suwannee River (White, 1970). The Northern Highlands represent the eastern portion of the river basin and have elevations greater than 30 masl. The eastern boundary of the basin is Trail Ridge, a north-south trending ridge that extends through central Florida. In the center of the basin lies an escarpment called the Cody Scarp that marks the boundary between the Western Valley and the Northern Highlands. This scarp is the erosional edge of the Miocene Hawthorn Group and marks the retreating edge of a formerly high plain that sloped northward. Similar to most streams crossing the Cody Scarp, the Santa Fe River flows into a sinkhole and reemerges at a first magnitude spring approximately 5km to the south (Fig. 1-2.).

Stratigraphy/Hydrostratigraphy

The lithology of Florida is composed of carbonate rocks that are pre-Miocene in age and mixed siliciclastic and carbonate rocks that are Miocene and younger (Table 1-1), with few outcrops. The oldest exposed units in the study area are Eocene carbonates of the Ocala Limestone. The lower Ocala is composed of grainstones to packstones and in some regions may be partially to completely dolomitized (Scott, 1992). The upper portion of the unit is muddy, granular limestones (packstones to wackestones) and can be soft and friable (Scott, 1992). Above the Eocene rocks of the Floridan Aquifer are the

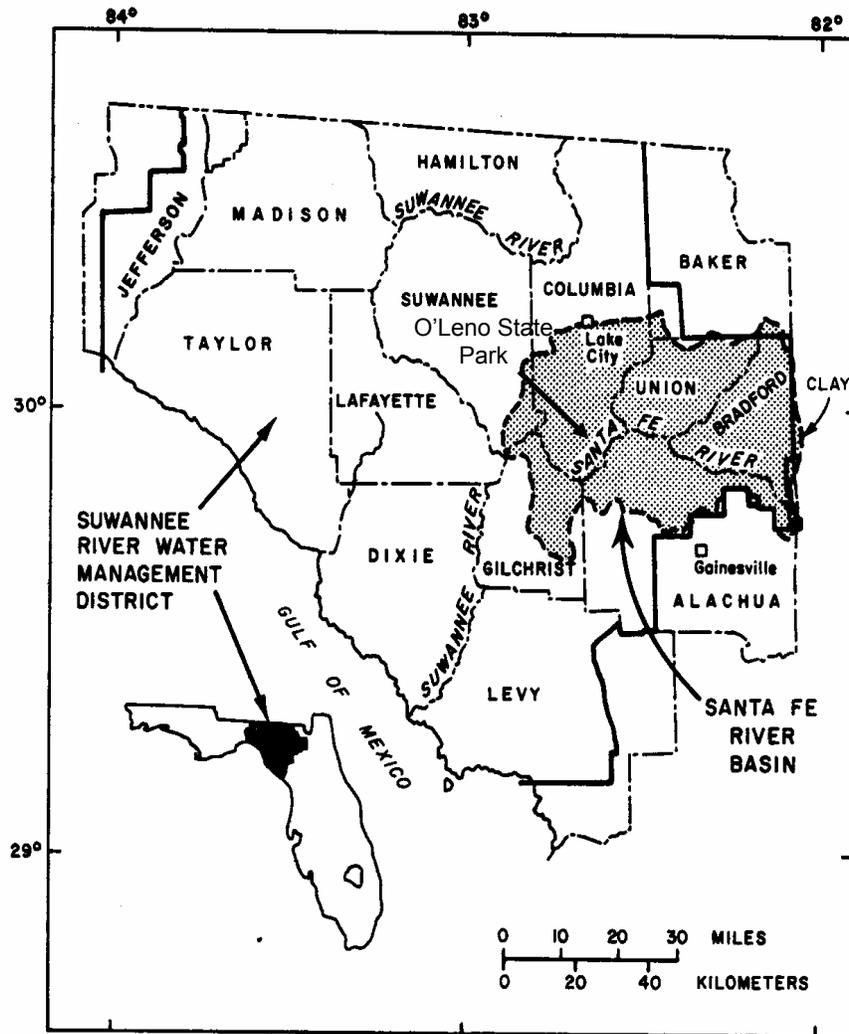


Figure 1-1. Map of the Santa Fe River Basin with the arrow showing O'Leno State Park and the study area, which is shown in detail in Figure 1-2. Modified from Hunn and Slack (1983).

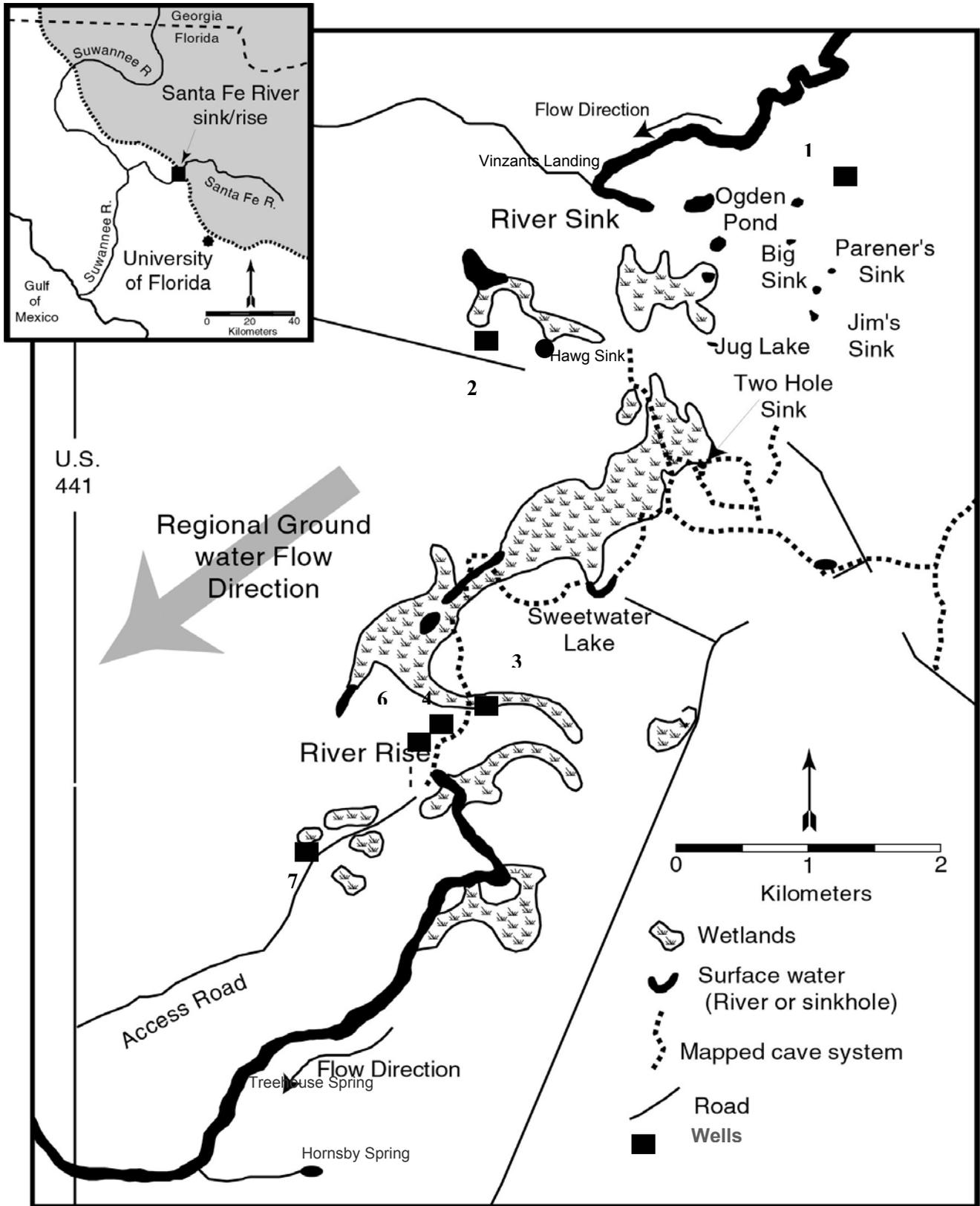


Figure 1-2. Map of the study area, including all of the karst windows and wells. Modified from Ginn (2002).

Miocene-age rocks of the Hawthorn Group. The Hawthorn Group contains primarily interbedded sands, clayey sands, sandy clays, clays, and carbonates (Grozos *et al.*, 1992) and is composed of the Hawthorn Formation and the Alachua Formation (Hunn and Slack, 1983). The upper most units in the study area are Pliocene-Pleistocene sediments that range from sands, sandy clays and carbonates and in North Florida include the Nashua Fm., Cypresshead Fm., Miccosukee Fm., and Undifferentiated Pleistocene-Holocene sediments. The undifferentiated sediments include marine sediments, eolian sand dunes, fluvial deposits, fresh water carbonates, and sediment mixtures that cover most of Florida (Scott, 1992).

Ground water is found in three aquifers that include, from upper to lowermost, the Surficial, Intermediate, and Floridan aquifers. The Surficial Aquifer is a water table aquifer within Pleistocene-Holocene sands (Hunn and Slack, 1983). Throughout most of the Santa Fe River basin, the water table is approximately 3 m below land surface; however, in the eastern portion of the basin the water table may be up to 9 m below land surface. Within the study area the Surficial Aquifer is approximately 5 m in thickness. Below the Surficial aquifer the Hawthorn Group carbonates contain the Intermediate Aquifer. Where present, the Hawthorn Fm. acts as a confining unit to the underlying Floridan Aquifer, but where missing, the Floridan Aquifer is unconfined and is recharged directly from the surface. The Floridan Aquifer is the primary source of drinking water for most of northern Florida. The aquifer consists of porous limestone that can be divided primarily into five units that are, from oldest to youngest, Lake City Limestone, Avon Park Limestone, and Ocala Limestone (all Eocene age), Suwannee Limestone

(Oligocene), and in some places lower Miocene limestones. The Eocene Ocala limestone is the major unit present in the study area.

Table 1-1. Stratigraphic and hydrostratigraphic units of the Santa Fe River Basin.

| Age | Stratigraphic Unit | Hydrostratigraphic Unit | Lithology | Thickness (m) |
|-------------------------------------|---|------------------------------------|---|---------------|
| Holocene Pleistocene Pliocene | Undifferentiated sediments | Surficial Aquifer | Fine sands and gravel | 0-25 |
| Pliocene to Miocene | Alachua Formation | Intermediate Aquifer/Confining Bed | Interbedded sands and clays Carbonates | 0-45 |
| Miocene | Hawthorn Formation | | | |
| Oligocene | Suwannee Limestone | Floridan Aquifer | Porous limestone and dolomite | 325-425 |
| Eocene | Ocala, Avon Park and Oldsmar Limestones | | | |
| Paleocene | Cedar Keys Formation | Sub-Floridan confining bed | Limestone with some clays and evaporites | ? |

Adapted from Meyer (1962), Hunn and Slack (1983), and Dean (1999).

Previous Studies of the Santa Fe River

In one of the earliest studies of the Santa Fe River basin in O'leno State Park Skirvin (1962) attempted to determine the underground flow path of the river after it sinks into the subsurface at the River Sink. Based upon the tannic color of water emerging at the Rise, he suggested that most water entering the Sink reemerges at the Rise. During this study, the river was temporarily dammed near the Sink, but water continued to flow from the Rise, suggesting groundwater enters the system between the Sink and Rise.

Hunn and Slack (1983) published a report on the hydraulic properties and water quality of the Santa Fe River basin, including the area within O'leno State Park. In the karstic region of the basin, the Floridan Aquifer is the primary groundwater source and is recharged directly through rainfall. They found that where the Floridan Aquifer is unconfined, it supplies groundwater to surface drainage features within the basin through large springs. In confined regions of the basin, however, discharge to streams is small and the Santa Fe River receives discharge only downstream from Worthington Springs. These sources of water are reflected in water quality in the confined and unconfined regions. Streams in the unconfined western region have greater concentrations of calcium, magnesium and bicarbonate, and are less tannic than streams in the confined region to the east. The higher chemical concentrations in the western region appear to reflect a water source from the Floridan Aquifer.

More comprehensive studies of the Santa Fe River between the Sink and the Rise have been conducted within the past ten years to better understand the underground flow of the river, the interaction of surface water and groundwater, and the exchange of water between conduits and matrix porosity (Hisert, 1994; Dean, 1999; Martin and Dean, 1999; Smith *et al*, 2002; Martin 2003; Smith, 2004). These studies have used various natural tracers including ^{222}Rn , $\delta^{18}\text{O}$ values, major element chemistry (i.e. Ca^{2+} , Mg^{2+} , Cl^-), and temperature and the injected tracer SF_6 (Hisert, 1994).

Hisert (1994) was able to determine a connection between the River Sink and Sweetwater Lake, using an injection of SF_6 , but required a second injection to connect Sweetwater Lake to the River Rise (Fig. 1-2). A connection with a single injection between the Sink and the Rise has never been obtained. Cave divers have recently

verified portions of this conduit system within the park (Old Bellamy Cave Exploration, 2001). In addition to SF₆ Hisert (1994) analyzed the chemical composition (Ca²⁺, Mg²⁺, Na⁺, K⁺, Al³⁺, δ¹⁸O, and ²²²Rn) at 23 locations between the Sink and Rise. Through the various experiments, Hisert (1994) determined that some mixing between surface water from the conduit and ground water in the matrix occurs. The fraction of ground water relative to surface water in the karst windows was not determined.

Dean (1999) measured the chemical composition of the water at the Sink, Sweetwater Lake, the Rise at various river levels and chemical compositions of two wells, one near the Sink and the other near the Rise. These data suggest that surface water and ground water mixing varied at different flow conditions with more surface water flowing into the matrix porosity during high flow periods. Dean (1999) suggested that high spatial and temporal resolution of surface and ground water sampling are needed to better understand the extent of mixing and the locations where mixing occurs in the system.

CHAPTER 2 METHODS

Measurements of physical hydrologic parameters and water chemistry included daily river stage, daily precipitation, and the chemical composition of 19 water samples. The staff at O'leno State Park collected the river stage data upstream from the Sink and precipitation data at the park entrance. These data were obtained through the Suwannee River Water Management District. Analysis of the water samples included field and laboratory measurements. Temperature, pH, specific conductance, dissolved oxygen (DO), and turbidity were each measured in the field. Major ions, dissolved species and isotopes were measured in the laboratory, including Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_2^{2-} , NO_3^{2-} , NH_3 , alkalinity, silica, Sr^{2+} concentration, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{18}\text{O}$ values.

Water Sampling

Surface Water

Water samples from the Sink, Rise, nine karst windows, a swallet upstream from the Sink, and two springs south of the Rise were collected four times between May 2002 and May 2003 at river stage levels varying between drought, high and intermediate discharge conditions (Table 2-1). The samples were collected over time periods ranging from several days to a few weeks with samples collected sequentially from upstream to downstream. The length of time for each sample period was, in some cases, dependent on weather conditions but an attempt was made to collect the same water parcel entering

the Sink and traveling through the conduit based on previously determined travel times between the Sink and Rise (Dean, 1999).

Samples were collected from a depth of approximately 0.5 meter and near the resurgence point of the spring, when possible. A Geotech Geopump 2 peristaltic pump was attached to PVC tubing to collect the water samples. Prior to sample collection, the tubing was purged with at least 2L of water from the karst window that was to be sampled. A free-flow cell was used to collect the purged water as well as to take field measurements. During each sample period two field duplicate and 1-2 field instrument blanks were collected. At each location, five separate containers were used to collect the samples. For the isotopic analyses, samples were collected in 30ml glass Qorpak bottles. All other samples were collected in polyethylene bottles ranging in size from 125 ml to 1L. Samples to be analyzed for alkalinity, Cl^- , orthophosphate, NO_2^- , and SO_4^{2-} had no preservatives added, but samples for silica and soluble reactive phosphorous were later filtered in the laboratory. The NO_x , NH_3 , total phosphorous and total Kjeldahl nitrogen samples were acidified with sulfuric acid to a pH level of <2 and the sample for the total metals was acidified with nitric acid to a pH level of <2 . All samples were kept in a cooler on wet ice while in the field and were then refrigerated at 4°C at the laboratory.

Table 2-1. Sample collection dates and the river stage at the time of collection.

| Sample Period | Date | River Stage (masl) |
|---------------|---------------------------|--------------------|
| 1 | May 8, 2002- June 5, 2002 | 9.8-9.6 |
| 2 | January 15 & 16, 2003 | 10.74- 10.71 |
| 3 | Feb. 24 – March 5, 2003 | 11.63- ~12 |
| 4 | April 28- May 1, 2003 | 10.49 |

Ground Water

In January 2003, six 2-inch monitoring wells were drilled throughout O'leno State Park. Three of the wells were installed along the regional ground water flow path and three were installed near the location of the conduit between Sweetwater Lake and the Rise, which has been mapped through cave diving exploration (Figure 1-2). The wells were drilled to approximately 30 m total depths and screened over a 6 m depth (Table 2-2).

Table 2-2. Total depth and location of the wells used in this project. Distance is unknown for wells 2 and 7.

| Well | Total depth of well (m) | Screened interval (m) | Direction to conduit | Distance from Conduit (m) |
|------|-------------------------|-----------------------|----------------------|---------------------------|
| 1 | 23 | 23-17 | NE | 475 |
| 2 | 30 | 30-24 | SW | |
| 3 | 28 | 28-22 | NE | 30 |
| 4 | 30 | 30-23 | W | 115 |
| 6 | 31 | 31-25 | W | 85 |
| 7 | 30 | 30-24 | SW | |

Between January and May 2003, three sets of water samples were collected from the monitoring wells. The January set included only wells 1, 2 and 7 while the other two sets included all six wells. During this time period, the river stage varied between intermediate river level and high river level (Table 2-3). The first and third sample periods took place during intermediate stage levels and the second sampling period took place during the March high river level (Table 2-1). The wells were sampled in conjunction with the surface water sample sets 2,3, and 4 (Tables 2-1&2-3) and were generally collected several days following the surface water collections.

The ground water samples were collected using a Redi-Flow2 variable speed submersible pump. Before sample collection the depth to the water level was measured to determine the depth at which to place the pump, which was set approximately 1m below the water table. Sampling followed purging of at least three well volumes.

The field measurements of temperature, pH, specific conductance, DO, and turbidity were made while the wells were purged. Purging was considered complete when all of the parameters stabilized such that three consecutive measurements of temperature were within $\pm 0.2^{\circ}\text{C}$, pH were within ± 0.2 standard units, specific conductance were within $\pm 5.0\%$ of the reading, DO was no greater than 20% of saturation at the field measured temperature, and turbidity was no greater than 20 NTUs. When stabilization occurred, five sets of samples were collected for each well in the same manner as previously described for surface water.

Table 2-3. River stage levels at the time of ground water sample collections.

| Sample Period | Date | River Stage |
|---------------|------------------|-------------|
| 2 | February 5, 2003 | 10.43 masl |
| 3 | March 19, 2003 | 13 masl |
| 4 | April 28, 2003 | 10.49 masl |

Analyses

Field Measurements

Measurements of the field parameters for both surface water and ground water were made with the same equipment. Measurement of pH was made with an Orion portable pH meter Model #250A calibrated at the start of each sampling period using 7.0 and 9.0 pH buffers. Specific conductance and temperature were measured with an ATI Orion portable conductivity meter Model #130. Dissolved oxygen and turbidity were measured

with YSI Model 55 handheld dissolved oxygen and temperature system and LaMotte 2020 turbidimeter, respectively.

Chemical and Isotopic Measurements

For the first sample period, the analyses of the Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , and SO_4^{2-} were carried out using an ion chromatograph at the University of Florida, Gainesville, Florida. For samples periods 2-4 analyses for the concentration of major ions, nutrients, alkalinity, and silica were carried out by PPB Environmental Labs, Inc. in Gainesville, Florida. Analyses were done according to Environmental Protection Agency regulations for each particular ion. Ca^{2+} , Mg^{2+} , and Na^+ were measured using an inductively coupled plasma (ICP) mass spectrometer and K^+ was measured by atomic adsorption.

The analysis of the $\delta^{18}\text{O}$ values of the samples was done using a Prism II Isotope Ratio Mass Spectrometer (IRMS) at the Department of Geological Sciences, University of Florida attached to an automated multiprep preparation system. Two hundred μL of each sample were pipetted into a glass vial and the headspace was filled with CO_2 gas within a glove bag. The water was equilibrated with CO_2 for 12 hours in the multiprep system and the samples were analyzed automatically by the mass spectrometer. Results are reported in standard delta notation relative to SMOW.

Strontium isotope measurements were made to determine the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios of the waters following separation of Sr using ion exchange columns. Concentration of Sr^{2+} was measured using isotope dilution. To determine both the Sr^{2+} concentration and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, samples were analyzed on a thermal ionization mass spectrometer (TIMS). The standard used was NBS 987, which had errors of 0.7-1.1%.

Computer Modeling

The Saturation Index values of the water samples were determined using the program PHREEQC (Parkhurst and Appelo, 1999). The program uses the chemical composition and temperature of each water sample to determine the saturation indices of various minerals including calcite for each sample. PHREEQC can also be used to determine the amount of calcite needed to dissolve in one liter of water to cause the water to reach saturation. Additionally, mixing two water samples in given proportions to calculate a mixture similar to measured samples can be measured to determine mixing fractions of surface water and ground water at various river levels and conditions.

CHAPTER 3 RESULTS

Stage, Precipitation and Discharge

Before the initial sampling period, the study area experienced a three-year drought, resulting in river stages ranging between 9.8-9.6 meters above sea level (masl) (Figures 3-1 and 3-2). During the El Niño event of autumn 2002 through early spring 2003, 114cm of precipitation fell, raising river stage levels to a maximum stage of 14.43 masl on March 13, 2003. Throughout the study period, the average river level was 10.35 masl. Based on this, river levels lower than 10 masl are considered low flow conditions and river levels above 11masl are considered high flow conditions. River levels of approximately 10.5 are considered baseflow conditions and are intermediate between low flow and high flow conditions.

Continuous water level measurements collected by Martin (2003) were used to determine discharge measurements for the Sink and Rise. The Sink discharge was based on a rating curve obtained from the Suwannee River Water Management District (Rating No 3. for Station No. 02321898, Santa Fe River at O'Leno State Park) and the discharge at the Rise was based on a rating curve determined by Sreaton *et al* (2004). During the drought conditions of May 2002, the calculations yield negative discharge rates at the Sink and the Rise (Table 3-1), indicating that the rating curves are not suitable for low water levels because the river is not actively flowing. During this time no water enters the Sink because the entire river was captured by the sinkhole at Vinzant's Landing. The

highest discharge measurements for the Sink and Rise occurred during the March flood event and were 45.41 and 40.2 m³/s, respectively.

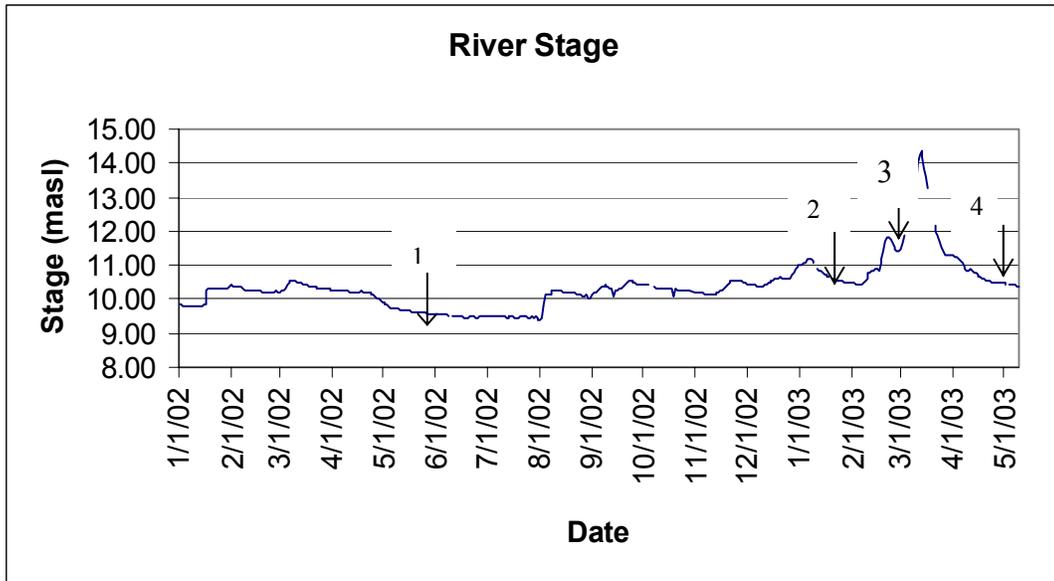


Figure 3-1. Graph of the Santa Fe River elevation collected at O'Leno State Park during the course of the study period. The arrows indicate the times of sampling.

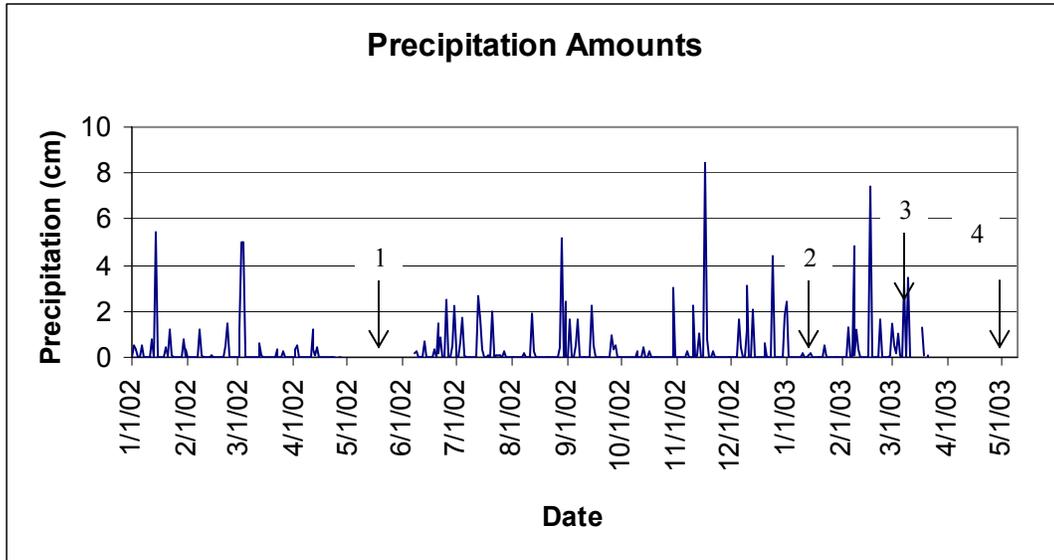


Figure 3-2. Graph of precipitation collected at O'Leno State Park during the study period. The arrows indicate the times of sampling.

Table 3-1. Water levels and discharge measurements at the Sink and Rise at the time of sampling.

| Location | Date | Water Level (m) | Discharge, Q (m ³ /s) |
|----------|---------|-----------------|----------------------------------|
| Sink | 5/14/02 | 9.76 | -11.42 |
| | 1/15/03 | 10.31 | 11.61 |
| | 3/3/03 | 11.95 | 45.41 |
| | 4/28/03 | 10.49 | 3.7 |
| Rise | 5/14/02 | 9.31 | -1.39 |
| | 1/17/03 | 10.11 | 11.2 |
| | 3/5/03 | 11.11 | 40.2 |
| | 5/1/03 | 9.94 | 7.71 |

Drought Stage

Field measurements

Vinzant's Landing, the River Sink, River Rise, eight karst windows and two springs were sampled during the drought conditions. Conductivity values ranged from a low of 319 μS at the Sink to a high of 645 μS at Ogden Lake. Water temperatures were 23°C - 28°C with the Rise having the lowest temperature and Treehouse Spring the highest. The lowest pH value was 7.03 at both Hawg and Twohole and highest pH value was 7.72 at Vinzants Landing. The dissolved oxygen (DO) content ranged from 0.1 mg/L at Ogden Lake, which at the time of sampling was nearly covered with duckweed, to 6.45 mg/L at Hornsby Spring.

Chemical and isotopic composition

The concentrations of cations were highest during the low river stage of the drought. The chemical compositions of the karst windows between the Sink and Rise were similar along the flow path with the exception of Ogden Lake, which had higher concentrations of all solutes compared with the other karst windows. In most cases, the lowest cation concentrations occurred at the River Sink or Vinzant's Landing. The

concentrations of most karst windows and springs fell between the values of the Sink or Vinzant's Landing and Ogden Lake values (Figs. 3-3a, 3-4a, 3-5a, and 3-6a). In addition, the concentrations are higher at Sweetwater Lake than at the Rise and the downstream springs. The anion concentrations follow a pattern similar to the cation concentrations with Vinzant's Landing and the Sink having the lowest concentrations of the solutes and Ogden Lake having the highest concentration (Figs. 3-7a and 3-8a). The alkalinity concentrations are more varied along the flow path than most of the solutes, and the lowest concentration occurs at Twohole sink and the highest at Hornsby Spring (Fig. 3-9a). Both the SO_4^{2-} and alkalinity concentrations are higher at Sweetwater Lake than the River Rise. Based on the cation and anion data all of the samples are at or near saturation with respect to calcite (Fig. 3-10a).

The isotopic data do not vary much along the flow path and have small ranges in values compared to the major elemental data. The lightest $\delta^{18}\text{O}$ concentration is -3.06‰ at Hornsby Spring and the Sink has the heaviest concentration of -1.71‰ (Fig. 3-11a), although most of the samples are between -2.6 to -2.1‰ . The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are lowest during this sample period with Paroners Branch Sink having the least radiogenic ratio and the Sink the most radiogenic (Fig. 3-12a).

Intermediate Stages

Surface Water

Field measurements

During the second sample period in January 2003, conductivity measurements were typically 130-160 $\mu\text{S}/\text{cm}$ with the exception of Hawg Sink, Twohole Sink and Hornsby Spring, which had higher values of 368, 235, and 252 $\mu\text{S}/\text{cm}$, respectively. In late

April/early May 2003, the conductivity in the karst windows is higher than in January, ranging from 225-420 μ S/cm with the highest values at Sweetwater Lake, the Rise, Treehouse Spring and Hornsby Spring. The pH values in January were approximately 6 while the pH in April was approximately 7. During the colder, winter event in January, the water temperature of the karst windows was 10-11 $^{\circ}$ C, but Hawg Sink is slightly warmer at 15.5 $^{\circ}$ C. In April the temperature of the surface waters increased to 21-23 $^{\circ}$ C. The DO content in January was 5.5-6, with Hawg having a very low level of 1.63, and was 1.1 to 3.8 in April.

Chemical and isotopic compositions

The chemical concentrations in January and April were intermediate compared to the concentrations during the drought and flood sample times. The concentrations in January were generally lower than the concentrations in April and were similar to the flood conditions while the concentrations in April were closer to the drought conditions. In January the Ca^{2+} , Mg^{2+} , and Sr^{2+} concentrations in the karst windows increase 63% between the River Sink and Ravine Sink and remain similar along the flow path. However, Hawg and Twohole Sinks and Hornsby Spring typically had higher concentrations (Figs. 3-3a, 3-4a, 3-5a, and 3-6a). The Na^{+} concentration at Hawg Sink, however, was lower compared with the other karst windows. In April, the concentrations of the cations were higher than the concentrations in January with the exception of Na^{+} , which was lower than January. The concentrations of most of the cations increased along the flow path from Paroners Branch Sink toward the River Rise, although the increase was small for Mg^{2+} and Sr^{2+} and there was no increase in Na^{+} (Figs. 3-3a, 3-4a, 3-5a, and 3-6a).

Both the SO_4^{2-} and alkalinity concentrations were lower in January than in April (Figs. 3-8a and 3-9a). The concentrations of these two solutes increase ~63% between River Sink and Ravine Sink and were relatively equal along the flow path. As with the cation concentrations, the SO_4^{2-} and alkalinity concentrations were higher at Hawg and Twohole Sinks as compared to the other karst windows along the flow path. In April the concentrations of the SO_4^{2-} and alkalinity increased along the flow path from Paroners Branch Sink toward the River Rise. In contrast to the SO_4^{2-} and alkalinity, the Cl^- concentrations in January did not decrease between the first and second sampling periods, but remained elevated and were equal along the flow path (Fig. 3-7a). Hawg Sink, however, had a lower concentration than other locations. In April, the Cl^- concentrations were lower than January. The concentrations were slightly higher in the karst windows than at Vinzant's Landing and the Sink but there is no increase in concentration along the flow path. However, there was a small spike in the concentration at Ravine Sink.

During January, most of the karst windows were undersaturated with respect to calcite (Fig. 3-10a), with Hawg Sink, Twohole Sink and Hornsby Spring being closest to saturation. In contrast, the samples in April were much closer to saturation with calcite and approached the saturation index values from May.

In contrast to the major element chemistry, the $\delta^{18}\text{O}$ values in January and April was similar along the flow path. The values in January were slightly depleted in $\delta^{18}\text{O}$ than in April from Vinzant's Landing to Paroners Branch Sink (Fig. 3-11a), but were enriched from Hawg Sink to Hornsby Spring. The ratios of $^{87}\text{Sr}/^{86}\text{Sr}$, however, were similar to the major element chemistry with the samples from January plotting closer to

the March data and the samples from April plotting closer to the May data (Fig. 3-12a). In January the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were more radiogenic than in April.

Ground Water

Field measurements

The field measurements of the ground water in the wells were similar for the two intermediate sample periods. The conductivity of the ground water was typically 415-530 $\mu\text{S}/\text{cm}$, although Well 2 had the highest conductivity value in January (1009 $\mu\text{S}/\text{cm}$) and Well 1 was highest in April (907 $\mu\text{S}/\text{cm}$). The average pH of the water during both events was 6.7 and the average temperature was 21-22°C. As with the conductivity, the temperature of Well 2 was highest in January (26°C) and Well 1 was highest in April (26°C). The DO content was low for most of the wells at 0.15-0.22mg/L.

Chemical and isotopic compositions

The chemical concentrations of the wells during January and April were similar for most of the wells; however, Well 2 had higher concentrations of all major elements during both sample events (Figs. 3-3b, 3-4b, 3-5b, and 3-6b). Wells 1 and 7 had higher concentrations than Wells, 3, 4 and 6 for Ca^{2+} and Well 7 had higher concentrations of Sr^{2+} and Mg^{2+} in April. The highest Sr^{2+} concentration in January was in Well 1. The Na^+ concentrations were similar between the wells in April; however, Well 7 had a slightly higher concentration. As with most of the cations, the anion concentrations of the ground water during sampling of the intermediate stages were similar between the two sampling periods (Figs. 3-7b, 3-8b, and 3-9b). Well 2 had the highest concentrations of Cl^- and Na^+ . The Cl^- concentrations were higher in Well 7 than Wells 1,3,4, and 6, but the SO_4^{2-} concentrations were similar in these 5 wells. The alkalinity concentrations

were lower in Well 2 than the other wells. The highest concentrations of alkalinity for both sample periods were in Well 7. During both January and April the ground water from each well was near saturation with respect to calcite, however, Well 7 was supersaturated with calcite in April (Fig. 3-10b).

The isotopic compositions for ground water during both intermediate stage periods were also similar. The $\delta^{18}\text{O}$ values were light in all of the wells in January and April and the values remained relatively unchanged (Fig. 3-11b). After several attempts, the ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ could not be calculated for Well 2 in January but were calculated from wells 1 and 7 (Fig. 3-12b). The ratio in Well 1 was less radiogenic in January than in April. In addition, Well 1 had the most radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in April as compared to the other wells.

Flood Stage

During the high water levels of the Santa Fe River at O'Leno State Park, all of the karst windows were sampled with the exception of Twohole sink and Treehouse Spring. These sites were inaccessible because of flooded roads and high waters and swift currents in the river. All of the wells were sampled at this time.

Surface Water

Field measurements

Field measurements of the karst windows during the flood stage were less variable than during the drought conditions. Conductivity was approximately 80 $\mu\text{S}/\text{cm}$ at most locations, and the temperature of the water was 17°C with the exception of Hornsby Spring, which was 18.8°C. The surface water pH levels were approximately 5 and DO levels were 6 mg/L, although Hawg was 2.88 mg/L.

Chemical and isotopic compositions

The solute concentrations in March are the lowest of the four sample periods. Unlike the low flow period, the concentrations at Ogden Lake were not anomalously higher than the other karst windows and, for the most part, the solute concentrations were similar at each location along the flow path (Figs. 3-3a, 3-4a, 3-5a, and 3-6a). Hawg Sink, however, had higher concentrations of Ca^{2+} , Mg^{2+} , and Na^+ than the other karst windows. As with the cations, the anion concentrations fell within a narrow range and were similar along the flow path (Figs. 3-7a, 3-8a, and 3-9a). Again, Hawg Sink had higher concentrations than the other karst windows. Based on the PHREEQC calculations all of the samples were undersaturated with respect to calcite (Fig. 3-10a).

The $\delta^{18}\text{O}$ values were the lightest during this sample period (Fig. 3-11a), with the exception of the Rise, Treehouse Spring, and Hornsby Spring. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were the most radiogenic and the Sink and Ogden Lake had the highest ratios (Fig. 3-12a). The low ratio at the River Rise may be due to error during Sr separation and analysis.

Ground Water

Field measurements

Field measurements of the physical parameters of the ground water in the wells were higher than those measured in the surface water. Conductivity of the wells was 408-488 $\mu\text{S}/\text{cm}$ and the temperature was 21°C except for Well 2 (25.8°C). The pH levels during flooding were close to 7 and the DO content of most of the wells was 0.13-0.33 mg/L. Well 3 and Well 4 had higher DO concentrations of 1.64 and 4.06 mg/L, respectively.

Chemical and isotopic compositions

All of the wells had similar chemical compositions except for Well 2, which had higher concentrations of some of the cations (Figs. 3-3b, 3-4b, 3-5b, and 3-6b), although the concentrations of these solutes in Well 2 were lower than during the intermediate sampling periods. The Ca^{2+} and Sr^{2+} concentrations were lowest in Well 2 during this sample period, however; the Mg^{2+} and Na^+ concentrations were higher in Well 2 than in the other wells. The Cl^- and SO_4^{2-} concentrations were highest in Well 2 (Figs. 3-7b and 3-8b). These concentrations were lower than those from the intermediate sampling periods. The alkalinity concentrations were similar in Wells 3,4,6 and 7 with Well 1 having the highest concentration and Well 2 the lowest (Fig. 3-9b). All of the ground water samples were at or near saturation with respect to calcite (Fig. 3-10b).

The isotopic data of the ground water were similar to the intermediate sample periods. The $\delta^{18}\text{O}$ values were lightest in Wells 3,4,6, and 7 (Fig. 3-11b). The ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ were less radiogenic than the surface water (Fig. 3-12b). Wells 2,3, and 4 had the highest ratios and Wells 1 and 7 had the lowest.

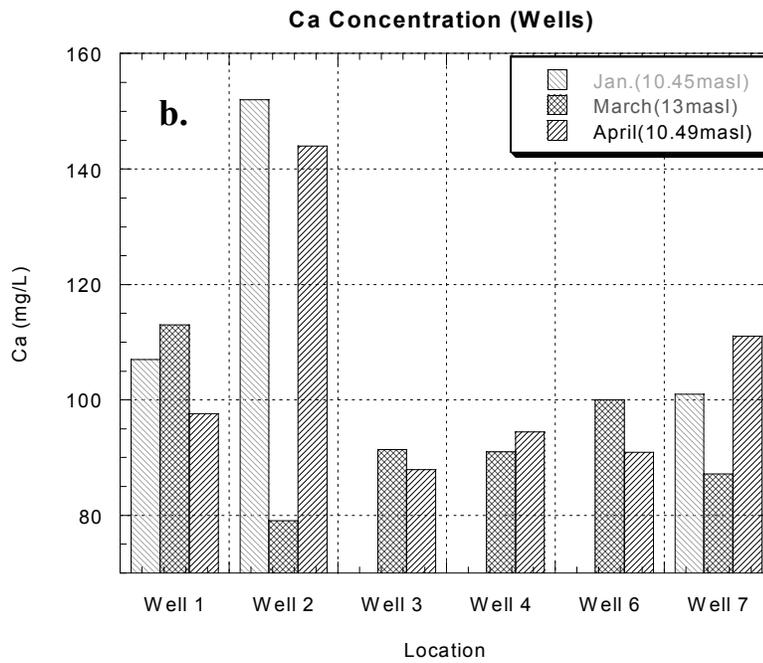
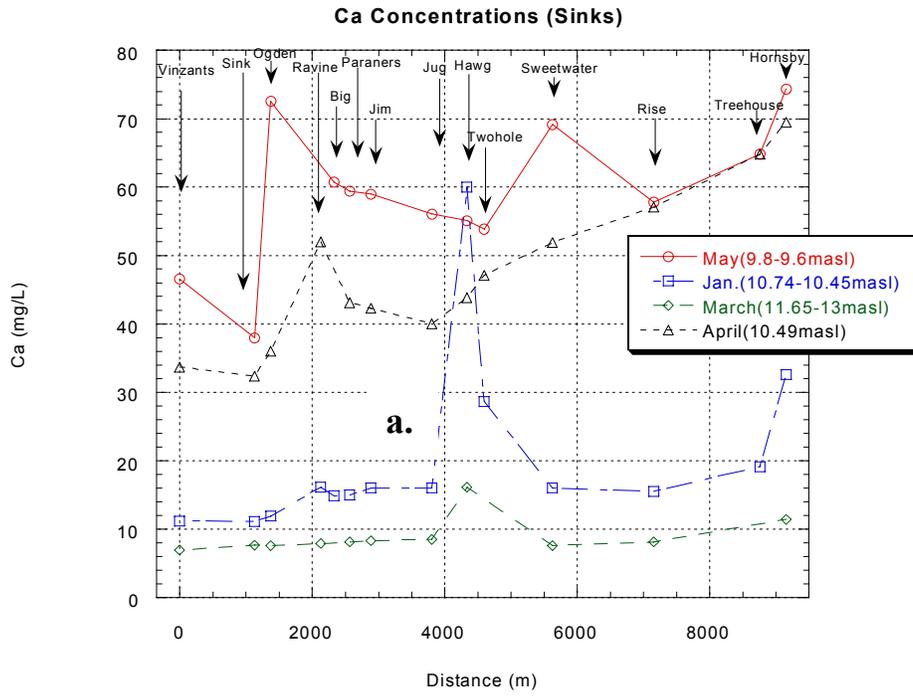


Figure 3-3 a. Ca^{2+} concentrations of karst windows vs. distance from Vinzants Landing for each sample set and b. Ca^{2+} concentrations of the wells for sample sets 2-4.

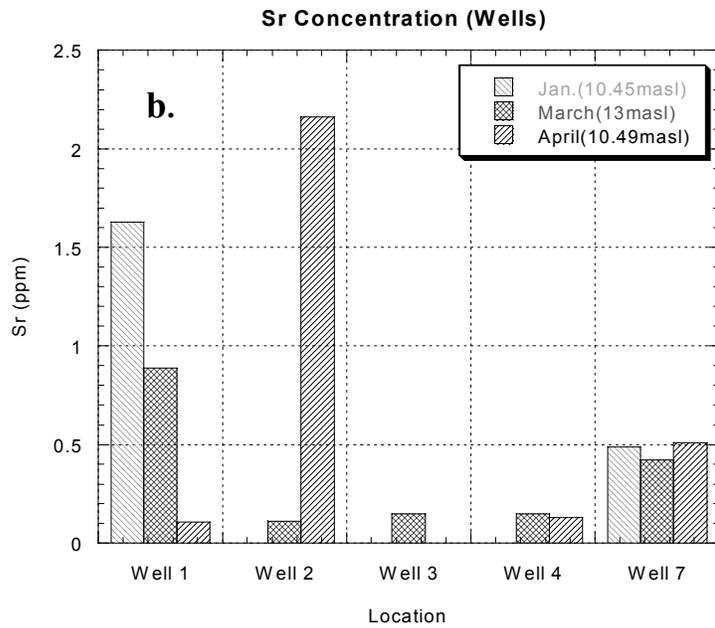
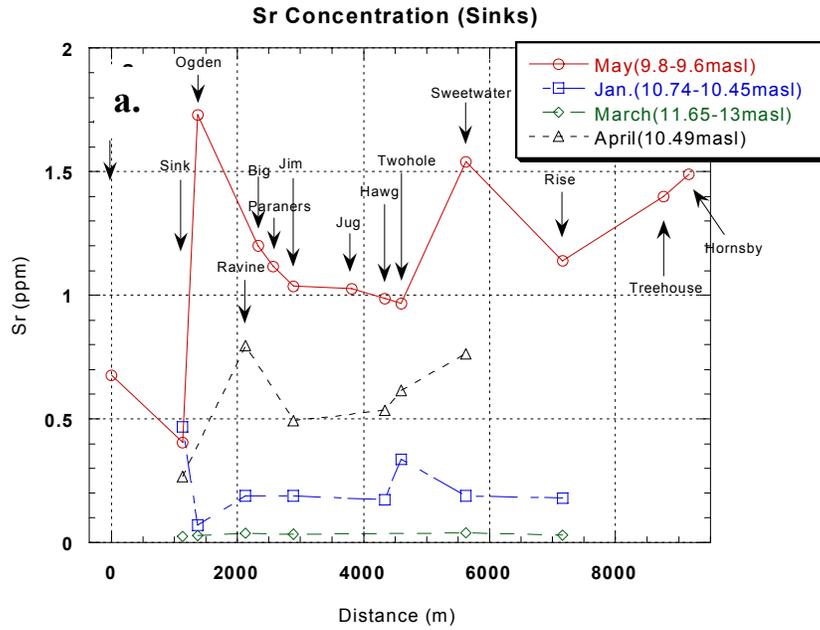


Figure 3-4a. The Sr^{2+} concentrations of the karst windows vs. distance from Vinzants Landing and b. the concentrations of Sr^{2+} in the wells for each sample period.

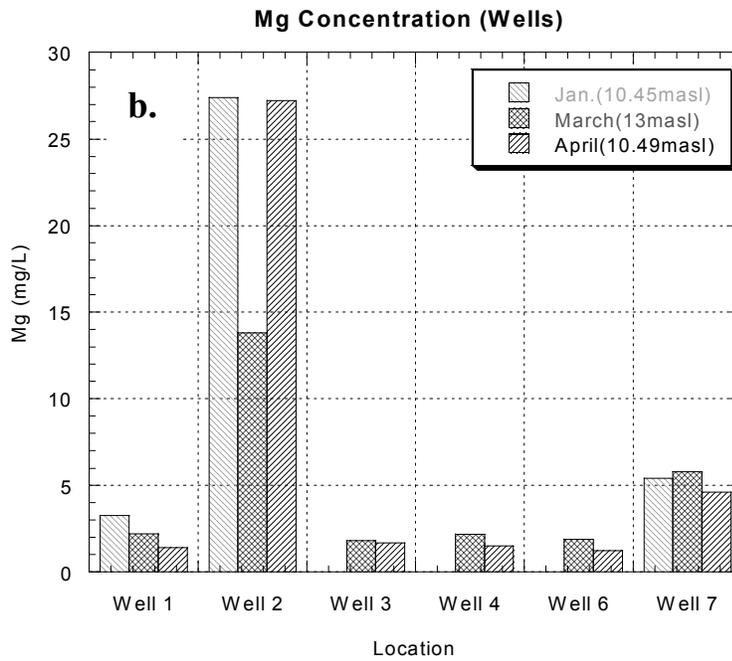
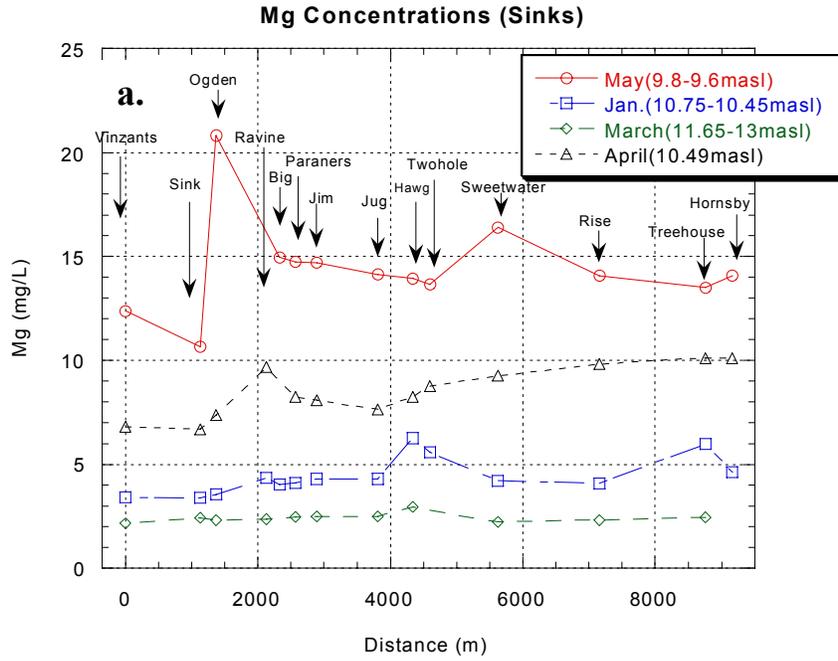


Figure 3-5a. The Mg^{2+} concentrations in the karst windows vs. distance from Vinzants Landing and b. the concentrations of Mg^{2+} of each well for each sample period.

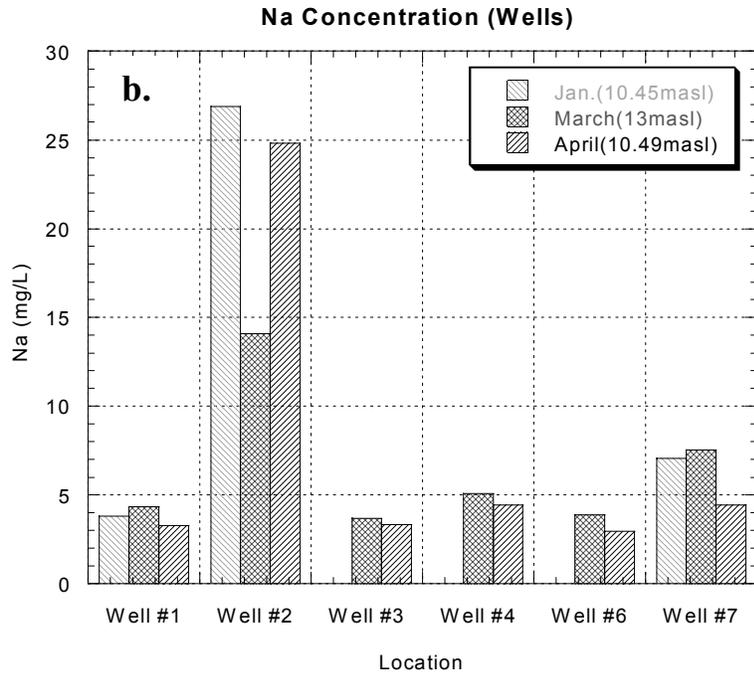
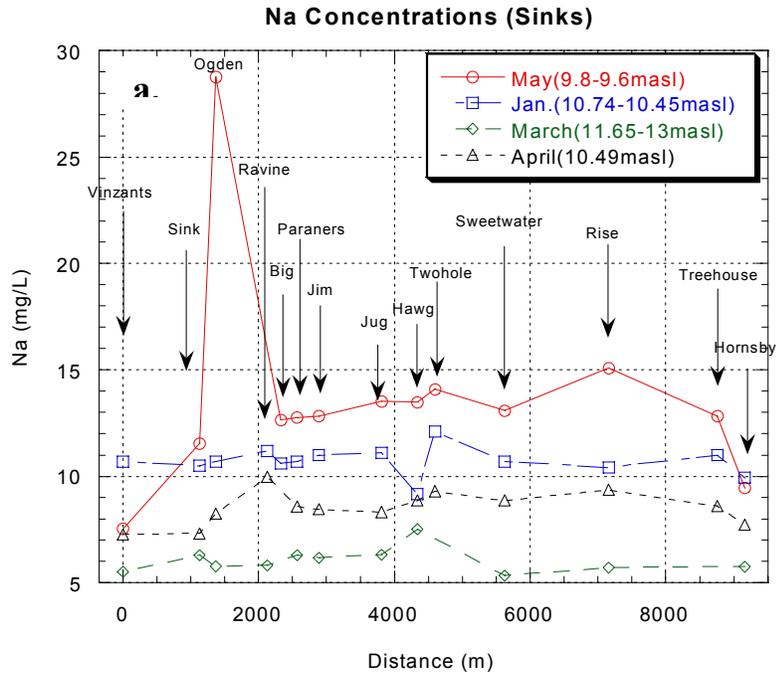


Figure 3.6a. The Na⁺ concentrations in the karst windows vs. distance from Vinzants Landing and b. Na⁺ concentrations of the wells for each sample period.

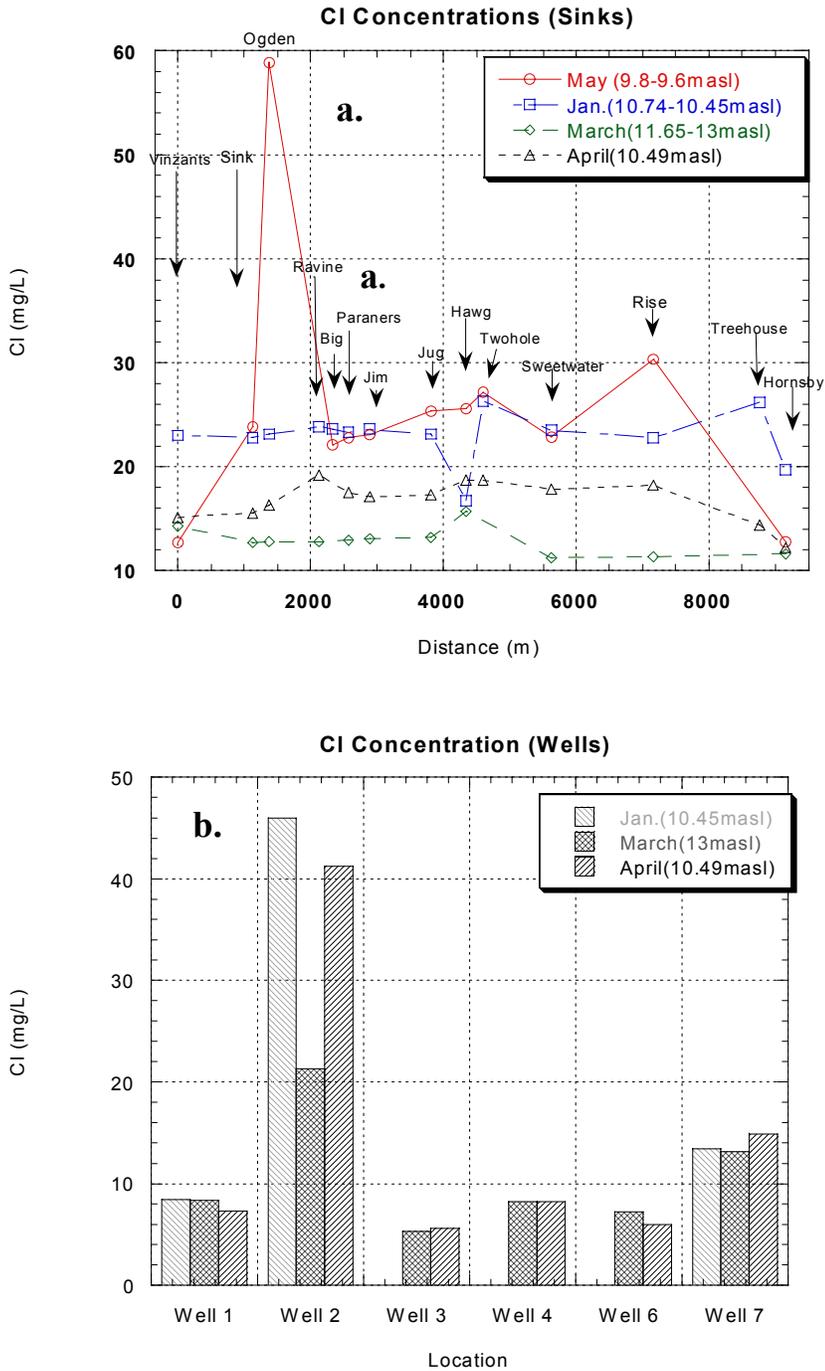


Figure 3-7a. The Cl⁻ concentrations in the karst windows vs. distance from Vinzants Landing and b. Cl⁻ concentrations in each well for each sample period.

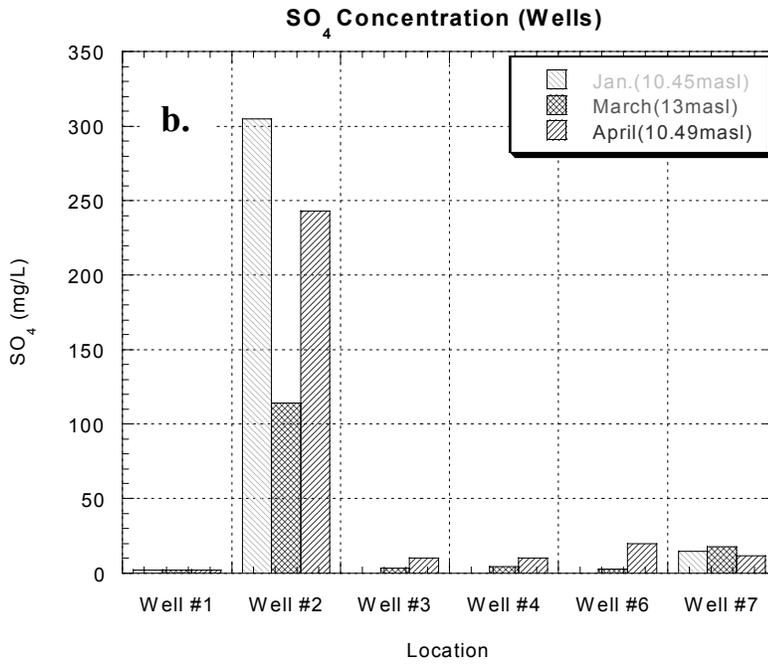
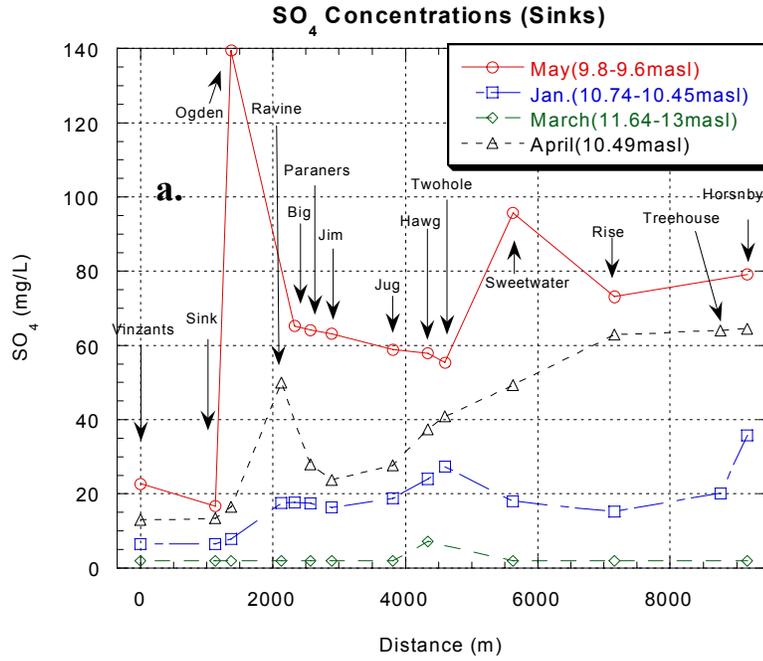


Figure 3.8a. The SO₄²⁻ concentrations in the karst windows vs. distance from Vinzants Landing and b. SO₄²⁻ concentrations of each well for each sample period.

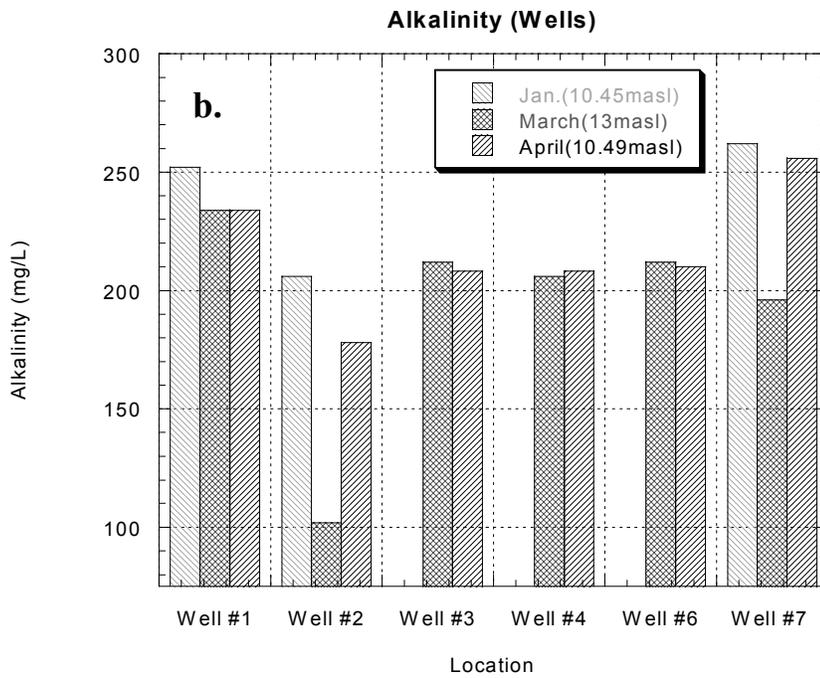
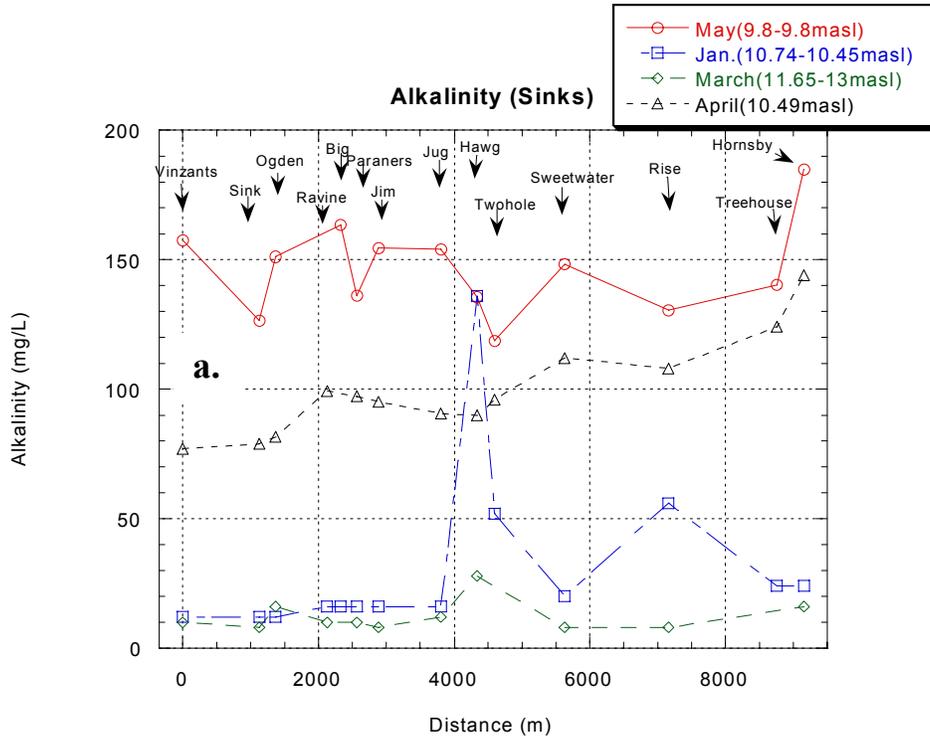
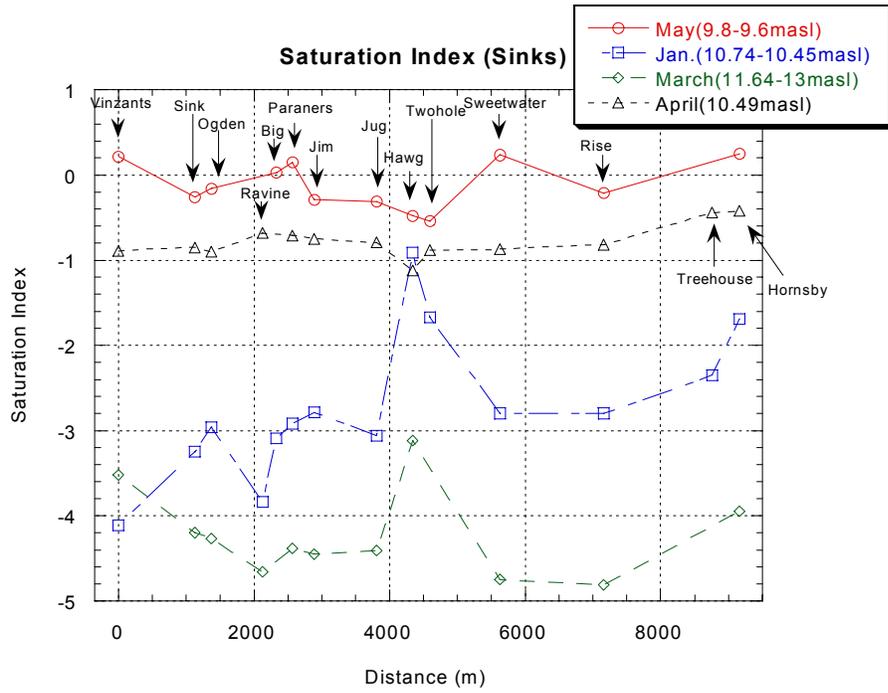
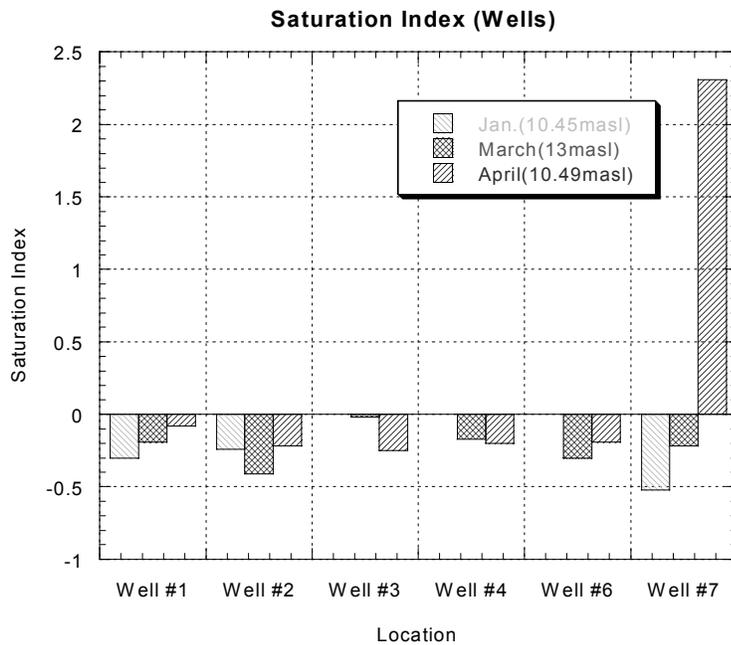


Figure 3-9a. The alkalinity concentrations of the karst windows vs. distance from Vinzants Landing and b. alkalinity concentrations of the wells for each sample period.



a.



b.

Figure 3-10a. The Saturation Index ratios of the karst windows vs. distance from Vinzants Landing and b. the Saturation Index ratios of the wells for each sample period.

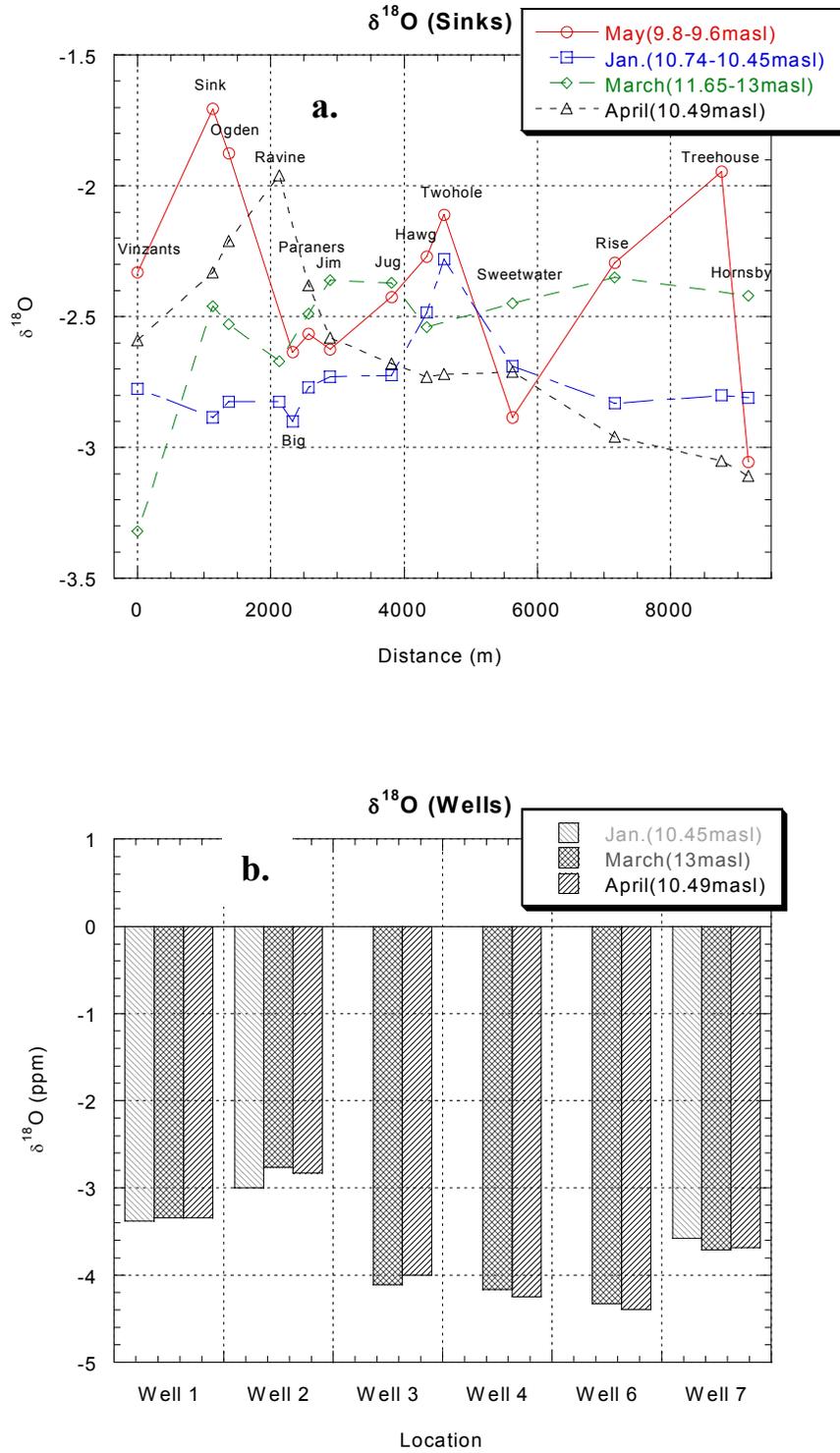


Figure 3-11a. $\delta^{18}\text{O}$ values of karst windows vs. distance from Vinzants Landing and b. The $\delta^{18}\text{O}$ values in each well for each sample period.

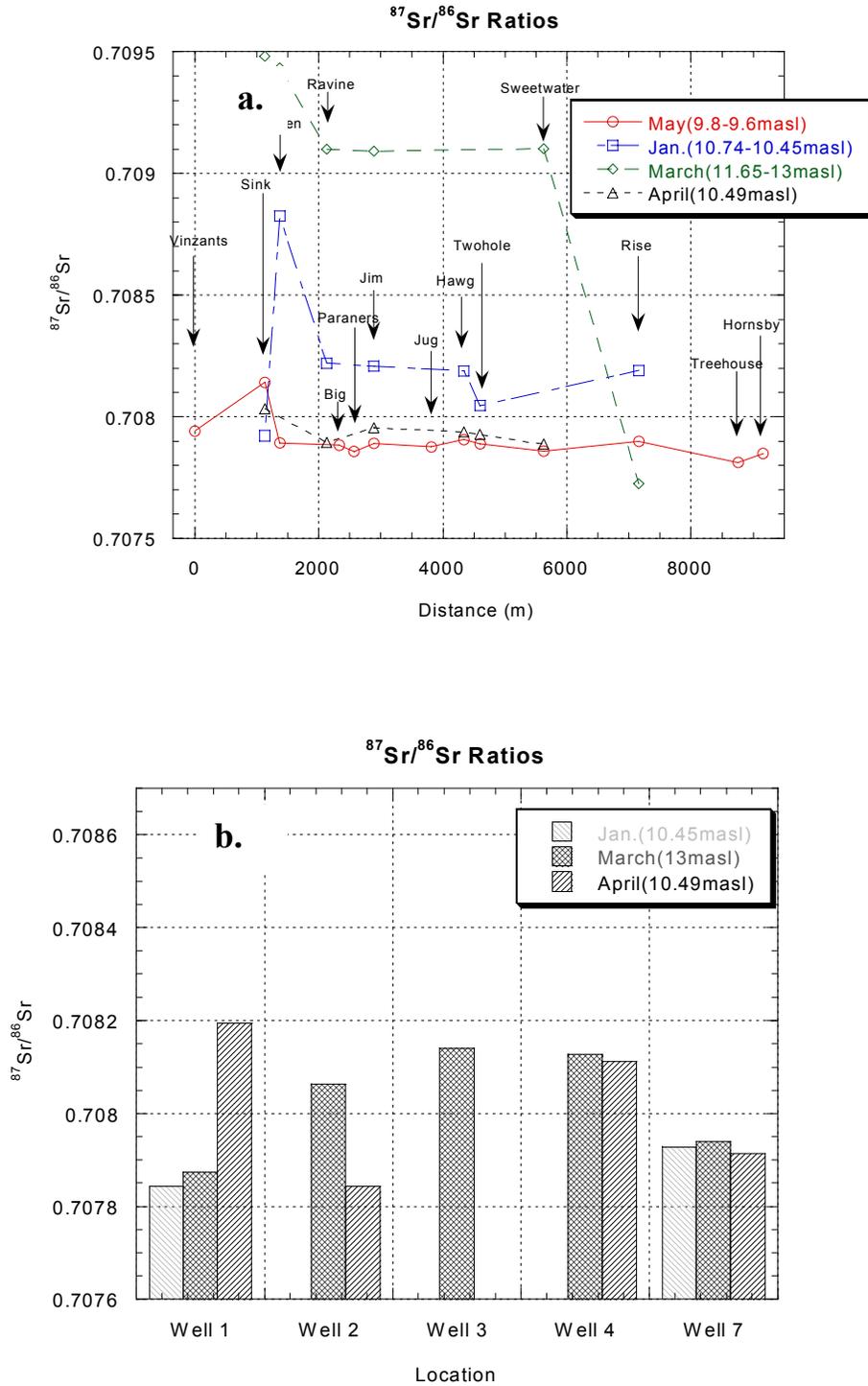


Figure 3-12a. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the karst windows vs. distance from Vinzants Landing for each sample period and b. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of each well for each sample period.

CHAPTER 4 DISCUSSION

Variation in Chemical and Isotopic Composition

The water in the matrix porosity can dissolve the limestone of the Floridan Aquifer increasing concentrations of Ca^{2+} , Mg^{2+} , and Sr^{2+} in the ground water. In contrast, conduit water may have low Ca^{2+} , Mg^{2+} , and Sr^{2+} concentrations if it comes directly from surface water. Consequently, the flow of water from the matrix to the conduit may increase Ca^{2+} , Mg^{2+} , and Sr^{2+} concentrations of the karst windows. Conversely water from the conduit flowing to the matrix will decrease these solute concentrations in the matrix. Therefore high solute concentrations in the karst windows may reflect flow of ground water from the matrix to the conduit while low solute concentrations may reflect flow of surface water through the conduit to the karst windows.

Chloride and sodium are chemically conservative during reactions with the carbonate rocks of karst aquifers and thus changes in their concentrations should be decoupled from changes in Ca^{2+} , Mg^{2+} , and Sr^{2+} concentrations. The main sources of Cl^- and Na^+ in the natural waters of Florida (Maddox, 1992) include 1) introduction from seawater along the coastal transition zone and 2) from marine aerosols in precipitation. Because the study area is located inland, introduction of seawater is negligible as a source of Cl^- and Na^+ , so their primary source in the study area is from marine aerosols in precipitation.

The concentrations of Cl^- and Na^+ can increase through evaporation or decrease by dilution from precipitation. Precipitation and evaporation should increase or decrease

concentrations of both solutes proportionately so that the Na/Cl ratio would not change. Sodium concentration may change through ion exchange with clays from the Hawthorn Formation. Chloride concentrations will not be effected by these reactions and thus changes in Na^+ by this process could be observed as variations in the Na/Cl ratio. The effects of cation exchange are likely to be much smaller than those caused by evaporative effects or dilution by precipitation.

The concentration of SO_4^{2-} can also be used as a tracer; however, like the Ca^{2+} , Mg^{2+} , and Sr^{2+} it is a non-conservative tracer involved in chemical reactions with the matrix rocks. The sources of SO_4^{2-} in Florida include 1) dissolution of gypsum and anhydrite 2) oxidation of rocks with sulfide-bearing minerals such as pyrite and 3) marine aerosols and acidic precipitation from airborne sulfur oxides (Maddox, 1992).

Chemical Variations in Karst Windows and Wells

The high concentrations of Cl^- , Na^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , and SO_4^{2-} in the karst windows in May 2002 may be due to introduction of water from the matrix that has higher solute concentrations, evaporation from the karst windows because of low precipitation, or a combination of the two. The high concentrations of Ca^{2+} , Sr^{2+} , Mg^{2+} , and SO_4^{2-} in the karst windows are expected for water that has reacted with aquifer rocks and flowed from the matrix to the conduit. However, the concentrations of Cl^- and Na^+ are higher than the concentrations in the ground water in the wells at baseflow indicating evaporation must also be occurring to increase the concentrations of these non-reactive solutes.

Another possible explanation for high concentrations of Ca^{2+} and SO_4^{2-} during this time may be from upwelling of water that has dissolved gypsum and anhydrite in the lower portions of the Floridan Aquifer. In Katz *et al* (1999) it was suggested that calcite

dissolution yields HCO_3^- and Ca^{2+} concentrations in a 2:1 ratio in the Upper Floridan Aquifer water according to the equation



Katz *et al* (1999) suggested that $\text{HCO}_3^-/\text{Ca}^{2+}$ ratios less than 2 were attributed to an alternative source of Ca^{2+} and SO_4^{2-} , such as gypsum. The $\text{HCO}_3^-/\text{Ca}^{2+}$ ratios in May are greater than two, however, ranging from 2.08 to 2.75 in the karst windows (Table 4-1) and 3.38 and 3.33 at Vinzants Landing and the River Sink, respectively. During this time all of the karst windows were at saturation or slightly supersaturated with respect to calcite (Fig. 3-10a). Extended periods of evaporation with little to no precipitation during the drought will concentrate the solutes in the water. Over time, these solutes can reach or exceed their saturation points, resulting in mineral precipitation. Calcite precipitation (e.g. reverse of reaction 1) would increase the $\text{HCO}_3^-/\text{Ca}^{2+}$ ratio and may cause the elevated $\text{HCO}_3^-/\text{Ca}^{2+}$ ratios at Vinzant's Landing and the Sink. Based on the concentrations of the reactive and non-reactive solutes, it appears that during the drought there was loss of water from the matrix to the conduit as well as evaporation in the karst windows resulting in the increased solute concentrations.

In January the increased concentrations in the karst windows from the Sink to the Rise suggest an input of water with higher solute concentrations downgradient from the River Sink. Dean (1999) found that at river stages of 10.74, 10.5 and 10.44 masl, SO_4^{2-} concentrations increased by 53.2%, 50.2% and 49.3% between the Sink and Sweetwater Lake, which he attributed to an input of water from the matrix to the conduit. The $\text{HCO}_3^-/\text{Ca}^{2+}$ ratios in January were, for the most part, less than two (Table 4-1) and could reflect upwelling of water that has dissolved gypsum. The SO_4^{2-} concentrations are low,

however, suggesting the ratios probably reflect mixing with dilute surface water (e.g. Katz *et al.*, 1999).

Table 4-1. The $\text{HCO}_3^-/\text{Ca}^{2+}$ ratios in the karst windows and the wells.

| Location | May | January | March | April |
|------------|------|---------|-------|-------|
| Vinzants | 3.38 | 1.07 | 1.44 | 2.28 |
| Sink | 3.33 | 1.08 | 1.05 | 2.25 |
| Ogden | 2.08 | 1.01 | 2.11 | 2.26 |
| Ravine | | 0.99 | 1.26 | 1.91 |
| Paraners | 2.29 | 1.07 | 1.23 | 2.26 |
| Jim | 2.62 | 1.00 | 0.96 | 2.25 |
| Jug | 2.75 | 1.00 | 1.42 | 2.27 |
| Hawg | 2.46 | 2.27 | 1.74 | 2.05 |
| Twohole | 2.2 | 1.81 | | 2.04 |
| Sweetwater | 2.14 | 1.25 | 1.05 | 2.16 |
| Rise | 2.26 | 1.29 | 0.99 | 2.89 |
| Hornsby | 2.16 | 1.72 | 1.40 | 2.07 |
| Treehouse | 2.49 | 1.26 | | 1.91 |
| Well 1 | | 2.36 | 2.14 | 2.40 |
| Well 2 | | 1.36 | 1.29 | 1.27 |
| Well 3 | | | 2.32 | 2.36 |
| Well 4 | | | 2.26 | 2.20 |
| Well 6 | | | 2.12 | 2.31 |
| Well 7 | | 2.59 | 2.25 | 2.31 |

In contrast to the other solute data, the Cl^- concentrations are not diluted in the karst windows in January and it is unclear at this time why the Cl^- concentrations remain elevated following the increased precipitation in the fall of 2002. Unlike the Cl^- concentrations, the Na^+ concentrations decrease by 16-30% between May 2002 and January 2003. The change in the Na^+ concentration compared to no change in Cl^- suggests that during drought conditions there may have been another source of Na^+ to the water other than the marine aerosols in precipitation. One possible source could be from cation exchange with the clay minerals of the Hawthorn Formation, which, in central Alachua County, have cation exchange capacities ranging between 6 and 46 meq/100 g (Rose, 1989). A possible explanation for the disproportionate decrease in the Cl^- and Na^+

concentrations in January is that during drought conditions Na^+ in the smectite may exchange with the high Ca^{2+} concentrations in the Santa Fe River, which would result in a high Na/Cl ratio (Fig. 4-1). With increased precipitation, the Ca^{2+} concentration in the river would be diluted, releasing the Ca^{2+} previously held in the exchange sites and uptaking Na^+ into the clays. This would result in a decrease in the Na/Cl ratio. The lower Na/Cl ratios in January further support cation exchange with the Hawthorn Group as a possible source of Na^+ during low flow.

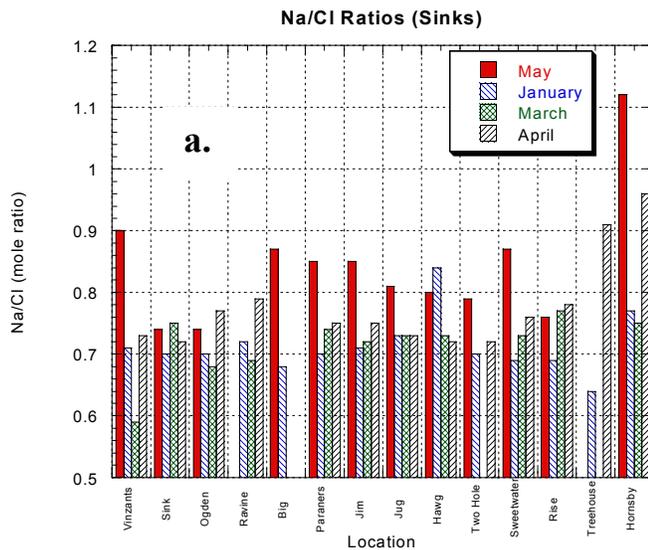


Figure 4-1. Graph of the Na/Cl ratios of the karst windows for each sample period.

Although the river stages were approximately the same in April and January the concentrations of Ca^{2+} , Mg^{2+} , Sr^{2+} , and SO_4^{2-} are higher in April than in January but the Na^+ and Cl^- concentrations are lower. Flooding in March may cause these differences in solute concentrations in April. During the flooding, water is lost from the conduit to the matrix and may be held in the matrix porosity, allowing the water to react with the carbonate rocks of the aquifer. As the floodwaters recede, the hydraulic head in the conduit becomes lower than the matrix (Martin, 2003) allowing the reacted water to flow

into the conduit. The lower concentrations of Cl^- and Na^+ in April may be a reflection of dilute floodwaters that were held in the matrix, with elevated Ca^{2+} , Mg^{2+} , and Sr^{2+} concentrations from dissolution reactions.

Solute concentrations do not change as much from one sample time to the next in water collected from all wells, as compared to the karst windows except Well 2 (Figs. 3-1b – 3-9b). Some of the wells, however, do have some small changes in concentrations between low and high flow with some solutes becoming more diluted and other solutes more concentrated. The changes in concentrations of the solutes are different for each well, suggesting that loss of water from the conduit is heterogeneous and varies at the local scale.

The $\text{HCO}_3^-/\text{Ca}^{2+}$ ratio of Well 2 ranges between 1.27 and 1.36 for the study period (Table 4-1), suggesting upwelling of deeper groundwater according to the model of Katz *et al* (1999). However, the lower concentrations of all of the solutes in March suggest the low $\text{HCO}_3^-/\text{Ca}^{2+}$ ratio reflects mixing with dilute surface water that has an $\text{HCO}_3^-/\text{Ca}^{2+}$ ratio of 1.05. The low solute concentrations in Well 2 in March suggest that at high discharge rates at the River Sink, surface water may leave the conduit and flow to the well, possibly along a zone of high permeability.

In January and April the $\text{HCO}_3^-/\text{Ca}^{2+}$ ratios in Well 2 are less than two and correspond with high SO_4^{2-} concentrations of 305 and 243 mg/L, respectively and indicate an alternative source of Ca^{2+} and SO_4^{2-} , such as gypsum, from water deep in the Floridan Aquifer. During intermediate, baseflow conditions, the water in Well 2 appears to represent ground water from the Floridan Aquifer. The solute concentrations in Well 2 are higher than the concentrations in the other wells and may reflect a deeper water

source. The differences in the ground water chemistry throughout the study area demonstrate the complex nature of karst aquifers in that the composition of ground water in karst terrains can vary on the local scale.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios as tracers in carbonate aquifer studies

Sr isotopes are particularly useful in studies of aquifers in marine carbonates because their $^{87}\text{Sr}/^{86}\text{Sr}$ reflects the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the seawater at the time of deposition (DePaolo and Ingram, 1985; Hess *et al.*, 1986). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater at the beginning of the Cretaceous was 0.7072. This value increased to 0.70775 at the Cretaceous-Tertiary boundary (Burke *et al.*; DePaolo and Ingram, 1985) and then decreased into the late Eocene to a value of 0.7076. From the late Eocene into the Quaternary the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater increased to the modern ratio of 0.70907 (Burke *et al.*, 1982; DePaolo and Ingram, 1985; Hess *et al.*, 1986). During the Oligocene and Eocene Periods, when many of the carbonate rocks of the Floridan Aquifer were deposited, the ratio remained relatively constant at 0.7077-0.7078. Thus, dissolution of this material should cause groundwater ratios to approach these low values.

Isotopic Variations in the Karst Windows and Wells

Water from the karst windows and wells appear to reflect mixing between Sr from the carbonates, Sr from rainfall and Sr from the Hawthorn Group rocks. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the wells are 0.7078 and 0.7079 prior to the flooding, which suggest that the ^{87}Sr in the water in the wells is enriched from dissolution of the calcite of the matrix rocks and the ratios are representative of ground water in the matrix. During low flow, the values of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the karst windows are 0.7078, similar to those of Eocene/Oligocene seawater and presumably the carbonate rocks of the Floridan Aquifer

(Fig. 3-12a). These values suggest that water in the karst windows originates from the matrix as has been suggested based on the solute concentrations.

During high flow conditions, the Sr isotope ratios in the karst windows reach the highest values of all the samples of 0.7091 to 0.7094. At the Sink and Vinzant's Landing the ratio is higher than the modern seawater value (0.70907) and may reflect the radiogenic ratios associated with the clays of the Hawthorn, which are present upstream from the River Sink. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in Well 1 remains within the Eocene/Oligocene seawater curve during high flow (Fig. 3-12b); however the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Wells 3,4, and 7 have slightly more radiogenic suggesting some mixing with water that has been in contact with radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios such as the clays of the Hawthorn Group.

During the two times of sampling during intermediate conditions, samples from the karst windows collected in January have more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than in April 2003. The differences in values suggest that the January samples are more influenced by the clays of the Hawthorn Formation than the April samples, which have ratios that reflect influence by the Floridan Aquifer carbonates. The karst windows in January 2003 are undersaturated with respect to calcite (Fig. 3-10a). This undersaturation implies there has been little dissolution of the carbonates of the Floridan Aquifer, thereby limiting the decrease in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and increase in Sr^{2+} concentrations. In April 2003, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the karst windows are closer to the values of Eocene/Oligocene seawater than in January, consistent with reactions with the carbonates of the Floridan Aquifer. These reactions may have occurred during flooding in March when water from the conduit would react with the high Sr^{2+} concentrations and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the aquifer rocks. As the floodwater recedes, the reacted water in the matrix would flow to

the conduit, causing the higher Sr²⁺ concentrations and less radiogenic ⁸⁷Sr/⁸⁶Sr ratios observed in April than in January. The slightly more radiogenic ⁸⁷Sr/⁸⁶Sr ratio of Well 1 in April may be a reflection of the floodwater held in the matrix that did not appear until sampling in April.

Sr Mixing Model

The Sr mixing model assumes two end-member mixing using the Sr²⁺ concentration and the ⁸⁷Sr/⁸⁶Sr ratios of selected end-members. One end member used for this model is the value of the River Sink sample during the flooding in March 2003. This value is assumed to represent the most pristine surface water sample and thus would be the closest to average precipitation in the region. The other end member used in the model is water from Well 1 in January 2003, due to its high solute concentrations and low radiogenic ⁸⁷Sr/⁸⁶Sr ratio, suggesting this water represents the ground water in the region. The strontium mixing model used is based on Faure (1986) and Woods *et al* (2000), assumes mixing of the end members of surface water and ground water following an equation in the form:

$$\left({}^{87}\text{Sr}/{}^{86}\text{Sr} \right)_M = \frac{a}{[\text{Sr}]_M} + b \quad (2)$$

where: $\left({}^{87}\text{Sr}/{}^{86}\text{Sr} \right)_M$ and $[\text{Sr}]_M$ are the ⁸⁷Sr/⁸⁶Sr ratio and concentration of the mixture, respectively, a is the slope of the line from the equation:

$$a = \frac{[\text{Sr}]_A [\text{Sr}]_B \left\{ \left({}^{87}\text{Sr}/{}^{86}\text{Sr} \right)_B - \left({}^{87}\text{Sr}/{}^{86}\text{Sr} \right)_A \right\}}{[\text{Sr}]_A - [\text{Sr}]_B} \quad (3)$$

and b is the y-intercept from the equation:

$$b = \frac{[\text{Sr}]_A \left({}^{87}\text{Sr}/{}^{86}\text{Sr} \right)_A - [\text{Sr}]_B \left({}^{87}\text{Sr}/{}^{86}\text{Sr} \right)_B}{[\text{Sr}]_A - [\text{Sr}]_B} \quad (4)$$

where $[Sr]_A$ and $[Sr]_B$ and $(^{87}Sr/^{86}Sr)_A$ and $(^{87}Sr/^{86}Sr)_B$ are the concentrations and ratios of end members A (the River Sink in March) and B (Well 1 in January) respectively.

The ratio of $^{87}Sr/^{86}Sr$ is plotted versus Sr and versus $1/Sr$ (Fig. 4-2). These figures suggest there is two end member mixing, but the extreme isotope values occur during extreme flood conditions. From the Sr isotope mixing model a quantitative percentage of surface water in a given sample can be determined by calculating the f parameter for mixing assuming a composition for the end members. In this model, f defines a mixture of two solutions A and B. The equation for f , based on Faure (1986), assumes two-component mixing using the formula:

$$f = \frac{(X_M)}{(X_A - X_B)} - X_B \quad (5)$$

where X_M , X_A , and X_B are the concentrations of Sr^{2+} for the sample and end members A (River Sink) and B (Well 1), respectively.

These calculations indicate that water with the lowest fraction sourced from the surface water occurred in the karst windows in May 2002 (Table 4-2) and averaged 32%. The highest proportion of water originating from the River Sink in the karst windows occurred in January, March, and April 2003 (Table 4-2). During the March flooding, the model suggests nearly 100% of the water in the karst windows is from the Sink. At river stages of 11.75 or greater, the travel time between the Sink and Rise is less than one day (Dean, 1999; Martin, 2003) meaning there is rapid flushing of water through the conduit. This rapid transport of water would prevent water from leaving the matrix and entering the conduit. Thus the low concentrations in the karst windows probably reflect dilution by precipitation.

The f parameter calculations indicate approximately 90% of water in the karst windows in January 2003 originated from the Sink surface water end member but in April 2003 52-71% originated from the Sink. Although the river stages were approximately equal during these sample times the karst windows in January contain 19%-38% more water from the Sink than in April. As the river level began to rise with increased precipitation in Fall 2002, water entered the Sink and flowed through the conduit. The hydraulic head in the conduit was higher than the matrix, allowing water to flow from the conduit to the matrix and result in water that is more dilute than in April. In contrast, the water in the karst windows in April reflects flow from the matrix to the conduit as the flooding receded. These results suggest that the antecedent conditions along with river stage are important for water chemistry.

From the f parameter calculation, the estimated proportion of water originating from surface water in Well 7 is similar between January, March and April 2003 (Table, 4-3) with only 25-30% of the water originating from ground water suggesting that surface water may reach this well. The well, however, is saturated with respect to calcite for each sample event and suggests that undersaturated surface water dissolves calcite as it moves through the matrix toward the well. Wells 3 and 4 also appear to have high percentages of water from the Sink end member for both March and April, which would lead to the more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and low Sr^{2+} concentrations in the wells at

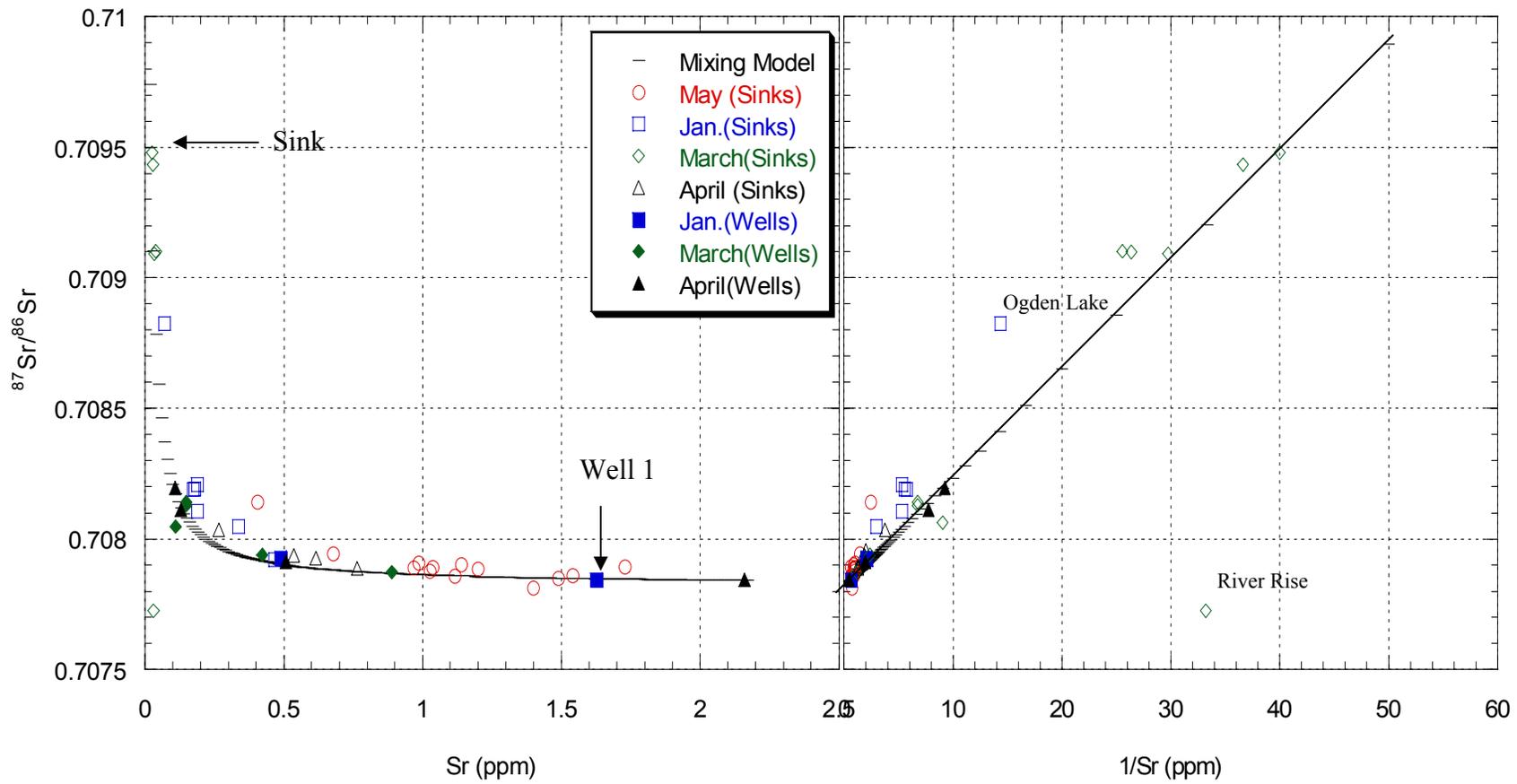


Figure 4-2. $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ vs. 1/Sr models for all karst windows and wells. The arrows indicate the end members.

Table 4-2. The calculations of the percentage of surface water in the karst windows.

| Location | May (%) | January (%) | March (%) | April (%) |
|------------|---------|-------------|-----------|-----------|
| Vinzants | 59 | | | |
| Sink | 76 | 72 | 100 | 85 |
| Ogden | -6 | 97 | 100 | |
| Ravine | | 90 | 99 | 52 |
| Big | 27 | 91 | | |
| Paraners | 32 | | | |
| Jim | 37 | 90 | 99 | 71 |
| Jug | 37 | | | |
| Hawg | 40 | 91 | | 68 |
| Twohole | 41 | 80 | | 63 |
| Sweetwater | 5 | 90 | 99 | 54 |
| Rise | 30 | 90 | 100 | |
| Treehouse | 14 | | | |
| Hornsby | 8 | | | |

those times. The mixing calculation suggests that Well 2 is composed of 95% surface water in March. This is supported by low solute concentrations at that time and suggests that at times of high flow in the river, water can be flushed toward the well. In April, the Sr^{2+} concentration in Well 2 is greater than the Well 1 end member, resulting in the negative f value at that time. Well 2 has higher concentrations of all of the solutes than Well 1 and suggests that water from deeper portions of the aquifer may be upwelling into Well 2. This possible source water for Well 2 is also evidenced by the low $\text{HCO}_3^-/\text{Ca}^{2+}$ ratios of less than two.

Saturation and Mixing Calculations

To better understand the composition of the water in Well 2, which appears to be more affected by flooding than the other wells, calculations of calcite dissolution and mixing

Table 4-3. The calculations of the percentage of surface water of the wells

| Location | January (%) | March (%) | April (%) |
|----------|-------------|-----------|-----------|
| Well 1 | 0 | 46 | 95 |
| Well 2 | | 95 | -33 |
| Well 3 | | 92 | |
| Well 4 | | 92 | 94 |
| Well 7 | 71 | 75 | 70 |

were done using PHREEQC. The program was used to simulate the reaction of one liter of a known solution of water with a given amount of calcite in order to determine how much calcite needs to dissolve to reach equilibrium. The saturation index of Well 2 in March is -0.40, which is close to saturation. For the simulation, water from the Sink in March with a saturation index of -4.2 was reacted with calcite until equilibrium was reached, which required dissolution of 1.4×10^{-3} moles of Ca^{2+} . In March, the water in Well 2 is greater by 1.7×10^{-3} moles of Ca^{2+} than the water in the Sink, similar to the amount calculated. This similarity suggests that Well 2 is a mixture of water from the Sink that has dissolved calcite and ground water from the matrix

The large decreases in solute concentrations in Well 2 in March were not seen at the other wells. Although the high solute concentrations in the well appear to reflect ground water from deep within the aquifer at baseflow conditions, the large changes during flooding suggest loss of water from the conduit to the matrix. For this reason, PHREEQC was used to check the fractions of surface water and ground water in Well 2 in March determined using the Sr^{2+} concentrations. The $^{87}\text{Sr}/^{86}\text{Sr}$ model suggests that the composition of Well 2 in March is approximately 95% surface water. Based on this, the same end-members used in the Sr model were mixed at varying proportions. The results show that a solution of 25-30% Sink water and 70-75% Well 1 water was closest to the

measured data, which is less than the 95% surface water estimated in the Sr model. This discrepancy may be due to the elements used in the calculation. The PHREEQC model takes into account the concentrations of all of the major elements in the solutions while the Sr model is based only on the concentrations of Sr^{2+} in the end-members and the mixture. The ground water in Well 2 differs from Well 1 and, therefore, the composition of Well 1 may not be an accurate representation of the waters that are mixing at Well 2. Because the Sr^{2+} concentrations of Well 1 and Well 2 are similar at baseflow conditions, the percentage of surface water in Well 2 calculated from the Sr model may be more accurate than the fractions determined using PHREEQC.

Nutrient Loading

The discharge at the Sink and Rise were calculated using water level data collected by Martin (2003) (Table 3-1) and, along with the NO_3^- and PO_4^- concentrations, were used to determine the amount of nutrient loading to the system (Tables 4-4 & 4-5). The discharge at the Sink in March ($45.41 \text{ m}^3/\text{s}$) is greater than the Rise ($40.2 \text{ m}^3/\text{s}$) indicating that water is lost to the matrix. The NO_3^- and PO_4^- loading at the Sink are $0.75 \times 10^3 \text{ mg/s}$ and $11.54 \times 10^3 \text{ mg/s}$, respectively and are $0.48 \times 10^3 \text{ mg/s}$ and $9.4 \times 10^3 \text{ mg/s}$ at the Rise. Less NO_3^- and PO_4^- discharges at the Rise than enters the Sink during the flooding, which is consistent with loss of water to the matrix. In January the discharge at the Rise is slightly less than the Sink ($11.2 \text{ m}^3/\text{s}$ vs. $11.6 \text{ m}^3/\text{s}$) so there is some loss of water to the matrix. This loss of water is reflected in the lower nutrient loading rates at the Rise (Tables 4-4 & 4-5). In April, however, the discharge at the Rise ($7.71 \text{ m}^3/\text{s}$) is greater than the Sink ($3.70 \text{ m}^3/\text{s}$) indicating water flows from the matrix to the conduit. If this additional water has higher NO_3^- and PO_4^- concentrations it would be expected that nutrient loading to the Rise is greater than at the Sink. In April, the nutrient loading at

the Rise (2.78×10^3 mg/s NO_3^- and 1.78×10^3 mg/s PO_4^{3-}) is nearly two times the loading at the Sink (1.27×10^3 mg/s NO_3^- & 0.67×10^3 mg/s PO_4^{3-}) even though the concentrations of the nutrients are similar between the two locations (Tables 4-4 and 4-5). There is a decrease in the PO_4^- concentration at both the Sink and the Rise in April compared to the concentrations in January and March. The decrease in PO_4^{3-} concentrations coupled with an increase in loading of both nutrients suggest that as water flows from the conduit with increasing discharge it is held in the intergranular porosity of the matrix. As the system returns to baseflow this water flows back into the conduit, increasing the nutrient loading to the Rise.

Table 4-4. The discharge and NO_3^{2-} loading calculations at the Sink and Rise.

| Location | Date | Water Level | Q | NO_3 | NO_3^- Loading |
|----------|---------|-------------|--------------------------|---------------|-------------------------|
| | | (m) | (m³/s) | (mg/L) | (mg/s x 1000) |
| Sink | 5/14/02 | 9.76 | -11.42 | 0.009 | -0.103 |
| | 1/15/03 | 10.81 | 11.61 | 0.031 | 0.36 |
| | 3/3/03 | 11.95 | 45.41 | 0.016 | 0.73 |
| | 4/28/03 | 10.49 | 3.70 | 0.344 | 1.27 |
| Rise | 5/14/02 | 9.31 | -1.39 | 0.077 | -0.107 |
| | 1/17/03 | 10.11 | 11.2 | 0.024 | 0.27 |
| | 3/5/03 | 11.11 | 40.2 | 0.012 | 0.48 |
| | 5/1/03 | 9.94 | 7.71 | 0.360 | 2.78 |

Table 4-5. The discharge and PO₄⁻ loading calculations of the Sink and Rise.

| Location | Date | Water Level | Q | PO4- | PO4-Loading |
|----------|---------|-------------|--------------------------|---------------|----------------------|
| | | (m) | (m³/s) | (mg/L) | (mg/s x 1000) |
| Sink | 5/14/02 | 9.76 | -11.42 | 0.132 | -1.5 |
| | 1/15/03 | 10.81 | 11.61 | 0.105 | 1.22 |
| | 3/3/03 | 11.95 | 45.41 | 0.254 | 11.54 |
| | 4/28/03 | 10.49 | 3.7 | 0.181 | 0.67 |
| Rise | 5/14/02 | 9.31 | -1.39 | 0.116 | -0.16 |
| | 1/17/03 | 10.11 | 11.2 | 0.103 | 1.15 |
| | 3/5/03 | 11.11 | 40.2 | 0.234 | 9.4 |
| | 5/1/03 | 9.94 | 7.71 | 0.137 | 1.06 |

CHAPTER 5 CONCLUSIONS

The heterogeneous characteristics of karst aquifer systems can leave ground water vulnerable to contamination from surface water. This heterogeneity allows water to move between the large solution channels of the conduit porosity and the smaller pore spaces of the intergranular porosity of the matrix. As water enters a conduit through a sink or swallet some of it may be lost to the matrix if the hydraulic head in the conduit is greater than the matrix. If, however, the hydraulic head is higher in the matrix than the conduit, water can flow from the matrix to the conduit.

Because surface water may contaminate ground water supplies it is important to understand the processes and circumstances that can allow surface water to enter the ground water matrix. Chemical analysis of surface water, in the form of sinks and springs, and ground water from wells can be used to evaluate the exchange of water from the two systems. In the Santa Fe River Sink/Rise system it appears that both the water level of the river as well as the antecedent conditions play a role in the movement of water between the conduit and the matrix.

Under low river levels and drought conditions, such as May 2002, no water enters the River Sink and flows through the conduit or out of the River Rise. As a result, the water chemistry in the karst windows reflects ground water from the matrix. As the river level rises with increased rainfall, more water enters the Sink and flows through the conduit. The hydraulic head in the conduit becomes higher than the matrix and surface water flows to the matrix. The increased amount of surface water in the subsurface is reflected in dilute solute

concentrations of the karst windows. During flooding in March 2003, water in the karst windows reflects a composition of nearly 100% surface water. As the flooding subsides, the system returns to baseflow conditions. Following flooding, water from the matrix enters the conduit and the karst windows. Because of the different circumstances preceding baseflow, the chemistry of the water in the karst windows is different. After prolonged periods of drought conditions an increased precipitation allows the conduit to quickly fill with water, increasing its hydraulic head, possibly over that in the matrix. However, following periods of high flow and flood conditions, the conduit quickly loses some water as precipitation decreases and discharge at the River Sink decreases. The response of the conduit and matrix to changes in precipitation and flow rates are important in understanding the hydrologic characteristics of karst aquifer systems.

The matrix appears less responsive to changes in the flow conditions and precipitation amounts than the conduit. The chemistry of ground water collected in the wells, for the most part, did not change much from one sample time to the next. However, the significant difference in the chemistry of Well 2 from baseflow to flood conditions indicates the complex, heterogeneous nature of karst aquifers. In addition, the Sr model indicates high percentages of surface water in the wells during the study period. Dissolution of matrix material can increase the solute concentrations in the ground water and making it appear that no surface water is present. Although there has been more extensive chemical analyses of the karst windows in the Sink/Rise system, it is now important to better understand the effects of flow conditions on the matrix with more sample collection at higher temporal resolutions.

APPENDIX A
DAILY PRECIPITATION AND STAGE RECORDS

| Daily Precipitation and Stage for 2002 | | | | | | | | |
|--|---------|-------|--------|-------|-------|--------|-------|-------|
| Month | ppt(cm) | masl | | | | | | |
| 1-Jan | 0 | 9.83 | 19-Feb | 0 | 10.22 | 9-Apr | 0 | 10.25 |
| 2-Jan | 0.508 | 9.82 | 20-Feb | 0 | 10.22 | 10-Apr | 0 | 10.24 |
| 3-Jan | 0.305 | 9.82 | 21-Feb | 0 | 10.22 | 11-Apr | 1.22 | 10.22 |
| 4-Jan | 0 | 9.81 | 22-Feb | 0.508 | 10.22 | 12-Apr | 0.36 | 10.22 |
| 5-Jan | 0 | 9.81 | 23-Feb | 1.473 | 10.21 | 13-Apr | 0.10 | 10.22 |
| 6-Jan | 0.508 | 9.81 | 24-Feb | 0 | 10.20 | 14-Apr | 0.41 | 10.22 |
| 7-Jan | 0 | 9.80 | 25-Feb | 0 | 10.22 | 15-Apr | 0 | 10.22 |
| 8-Jan | 0 | 9.80 | 26-Feb | 0 | 10.24 | 16-Apr | 0 | 10.22 |
| 9-Jan | 0 | 9.80 | 27-Feb | 0 | 10.23 | 17-Apr | 0 | 10.23 |
| 10-Jan | 0 | 9.80 | 28-Feb | 0 | 10.22 | 18-Apr | 0 | 10.23 |
| 11-Jan | 0 | 9.79 | 1-Mar | 0 | 10.22 | 19-Apr | 0 | 10.23 |
| 12-Jan | 0.813 | 9.79 | 2-Mar | 1.19 | 10.23 | 20-Apr | 0 | 10.22 |
| 13-Jan | 0 | 9.79 | 3-Mar | 5.03 | 10.24 | 21-Apr | 0 | 10.21 |
| 14-Jan | 5.461 | 9.79 | 4-Mar | 5.00 | 10.32 | 22-Apr | 0 | 10.20 |
| 15-Jan | 0 | 9.88 | 5-Mar | 0 | 10.43 | 23-Apr | 0 | 10.17 |
| 16-Jan | 0 | 9.87 | 6-Mar | 0 | 10.49 | 24-Apr | 0 | 10.15 |
| 17-Jan | 0 | 10.28 | 7-Mar | 0 | 10.52 | 25-Apr | | 10.13 |
| 18-Jan | 0 | 10.29 | 8-Mar | 0 | 10.53 | 26-Apr | 0 | 10.11 |
| 19-Jan | 0.432 | 10.30 | 9-Mar | 0 | 10.53 | 27-Apr | 0 | 10.05 |
| 20-Jan | 0.076 | 10.30 | 10-Mar | 0 | 10.53 | 28-Apr | | 10.01 |
| 21-Jan | 0.000 | 10.30 | 11-Mar | 0 | 10.51 | 29-Apr | 0 | 9.95 |
| 22-Jan | 1.219 | 10.30 | 12-Mar | 0 | 10.50 | 30-Apr | | 9.92 |
| 23-Jan | 0.076 | 10.32 | 13-Mar | 0.610 | 10.47 | 1-May | | 9.89 |
| 24-Jan | 0 | 10.33 | 14-Mar | 0.051 | 10.45 | 2-May | | 9.87 |
| 25-Jan | 0 | 10.34 | 15-Mar | 0 | 10.43 | 3-May | 0 | 9.84 |
| 26-Jan | 0 | 10.33 | 16-Mar | 0 | 10.42 | 4-May | | 9.81 |
| 27-Jan | 0 | 10.33 | 17-Mar | 0 | 10.40 | 5-May | | 9.75 |
| 28-Jan | 0 | 10.34 | 18-Mar | 0 | 10.40 | 6-May | | 9.74 |
| 29-Jan | 0.737 | 10.34 | 19-Mar | 0 | 10.39 | 7-May | 0 | 9.73 |
| 30-Jan | 0 | 10.40 | 20-Mar | 0 | 10.39 | 8-May | | 9.72 |
| 31-Jan | 0.305 | 10.43 | 21-Mar | 0 | 10.39 | 9-May | | 9.71 |
| 1-Feb | 0 | 10.40 | 22-Mar | 0.356 | 10.36 | 10-May | | 9.70 |
| 2-Feb | 0 | 10.39 | 23-Mar | 0 | 10.34 | 11-May | | 9.69 |
| 3-Feb | 0 | 10.39 | 24-Mar | 0 | 10.34 | 12-May | | 9.68 |
| 4-Feb | 0 | 10.38 | 25-Mar | 0 | 10.33 | 13-May | | 9.67 |
| 5-Feb | 0 | 10.37 | 26-Mar | 0.279 | 10.33 | 14-May | 1.07 | 9.69 |
| 6-Feb | 0 | 10.37 | 27-Mar | 0 | 10.32 | 15-May | | 9.67 |
| 7-Feb | 1.219 | 10.30 | 28-Mar | 0 | 10.31 | 16-May | | 9.66 |
| 8-Feb | 0.076 | 10.28 | 29-Mar | 0 | 10.30 | 17-May | | 9.65 |
| 9-Feb | 0 | 10.28 | 30-Mar | 0 | 10.29 | 18-May | | 9.64 |
| 10-Feb | 0 | 10.28 | 31-Mar | 0 | 10.28 | 19-May | 0.152 | 9.65 |
| 11-Feb | 0 | 10.28 | 1-Apr | 0 | 10.23 | 20-May | 0.051 | 9.63 |
| 12-Feb | 0 | 10.26 | 2-Apr | 0.356 | 10.26 | 21-May | 0 | 9.60 |
| 13-Feb | 0 | 10.26 | 3-Apr | 0.483 | 10.26 | 22-May | 0 | 9.62 |
| 14-Feb | 0.127 | 10.26 | 4-Apr | 0 | 10.26 | 23-May | 0 | 9.62 |
| 15-Feb | 0 | 10.25 | 5-Apr | 0 | 10.26 | 24-May | 0 | 9.62 |
| 16-Feb | 0 | 10.25 | 6-Apr | 0 | 10.26 | 25-May | 0 | 9.59 |
| 17-Feb | 0 | 10.25 | 7-Apr | 0 | 10.26 | 26-May | 0 | 9.59 |
| 18-Feb | 0 | 10.22 | 8-Apr | 0 | 10.25 | 27-May | 0.051 | 9.57 |

| | | | | | |
|--------|-------|-------|--------|-------|-------|
| 31-Oct | 0 | 10.20 | 21-Dec | 0 | 10.62 |
| 1-Nov | 0 | 10.20 | 22-Dec | 0 | 10.61 |
| 2-Nov | 0 | 10.19 | 23-Dec | 0 | 10.58 |
| 3-Nov | 0 | 10.19 | 24-Dec | 4.37 | 10.58 |
| 4-Nov | 0 | 10.18 | 25-Dec | 0.025 | 10.60 |
| 5-Nov | 0 | 10.17 | 26-Dec | 0 | 10.63 |
| 6-Nov | 0.279 | 10.16 | 27-Dec | 0 | 10.72 |
| 7-Nov | 0 | 10.14 | 28-Dec | 0 | 10.80 |
| 8-Nov | 0 | 10.13 | 29-Dec | 0 | 10.90 |
| 9-Nov | 0 | 10.14 | 30-Dec | 0 | 10.96 |
| 10-Nov | 2.210 | 10.14 | 31-Dec | 1.80 | 10.99 |
| 11-Nov | 0 | 10.14 | | | |
| 12-Nov | 0.051 | 10.14 | | | |
| 13-Nov | 1.02 | 10.17 | | | |
| 14-Nov | 0.025 | 10.19 | | | |
| 15-Nov | 0.000 | 10.23 | | | |
| 16-Nov | 8.407 | 10.25 | | | |
| 17-Nov | 0.737 | 10.30 | | | |
| 18-Nov | 0 | 10.35 | | | |
| 19-Nov | 0 | 10.43 | | | |
| 20-Nov | 0 | 10.49 | | | |
| 21-Nov | 0.279 | 10.54 | | | |
| 22-Nov | | 10.57 | | | |
| 23-Nov | | 10.57 | | | |
| 24-Nov | | 10.57 | | | |
| 25-Nov | | 10.57 | | | |
| 26-Nov | | 10.55 | | | |
| 27-Nov | | 10.53 | | | |
| 28-Nov | | 10.50 | | | |
| 29-Nov | | 10.48 | | | |
| 30-Nov | | 10.47 | | | |
| 1-Dec | | 10.45 | | | |
| 2-Dec | | 10.43 | | | |
| 3-Dec | | 10.42 | | | |
| 4-Dec | | 10.41 | | | |
| 5-Dec | 1.68 | 10.40 | | | |
| 6-Dec | 0.432 | 10.39 | | | |
| 7-Dec | 0 | 10.38 | | | |
| 8-Dec | 0 | 10.38 | | | |
| 9-Dec | 1.24 | 10.38 | | | |
| 10-Dec | 3.12 | 10.39 | | | |
| 11-Dec | 0.025 | 10.40 | | | |
| 12-Dec | 0.000 | 10.42 | | | |
| 13-Dec | 2.032 | 10.48 | | | |
| 14-Dec | | 10.50 | | | |
| 15-Dec | | 10.53 | | | |
| 16-Dec | | 10.57 | | | |
| 17-Dec | | 10.60 | | | |
| 18-Dec | | 10.62 | | | |
| 19-Dec | | 10.63 | | | |
| 20-Dec | 0.635 | 10.63 | | | |

| Daily precipitation and stage records for 2003 | | | | | | | | |
|--|----------|-------|--------|--------|-------|--------|--------|-------|
| Date | ppt (cm) | masl | | | | | | |
| 1-Jan | 2.4384 | 11.02 | 19-Feb | 0 | 11.42 | 9-Apr | | 10.85 |
| 2-Jan | 0 | 11.04 | 20-Feb | 0 | 11.72 | 10-Apr | | 10.86 |
| 3-Jan | 0.0254 | 11.05 | 21-Feb | 0 | 11.83 | 11-Apr | | 10.86 |
| 4-Jan | 0 | 11.09 | 22-Feb | 1.6002 | 11.84 | 12-Apr | | 10.85 |
| 5-Jan | 0 | 11.16 | 23-Feb | 0 | 11.78 | 13-Apr | | 10.80 |
| 6-Jan | 0 | 11.18 | 24-Feb | 0 | 11.63 | 14-Apr | | 10.75 |
| 7-Jan | 0 | 11.17 | 25-Feb | 0 | 11.54 | 15-Apr | | 10.71 |
| 8-Jan | 0 | 11.13 | 26-Feb | 0 | 11.48 | 16-Apr | | 10.68 |
| 9-Jan | 0 | 11.07 | 27-Feb | 0.1016 | 11.43 | 17-Apr | | 10.65 |
| 10-Jan | 0.1524 | | 28-Feb | 0.1778 | 11.40 | 18-Apr | | 10.62 |
| 11-Jan | 0 | 10.90 | 1-Mar | 1.4478 | 11.45 | 19-Apr | | 10.59 |
| 12-Jan | 0 | 10.84 | 2-Mar | 0.4826 | 11.65 | 20-Apr | | 10.56 |
| 13-Jan | 0.1016 | 10.81 | 3-Mar | 0.1524 | 11.87 | 21-Apr | | 10.55 |
| 14-Jan | 0.1524 | 10.77 | 4-Mar | 1.0414 | | 22-Apr | | 10.54 |
| 15-Jan | 0 | 10.74 | 5-Mar | 0.0508 | | 23-Apr | | 10.51 |
| 16-Jan | 0 | 10.71 | 6-Mar | 0 | | 24-Apr | | 10.50 |
| 17-Jan | 0 | 10.68 | 7-Mar | 3.2258 | 13.11 | 25-Apr | | 10.50 |
| 18-Jan | 0 | 10.65 | 8-Mar | 0 | | 26-Apr | | 10.48 |
| 19-Jan | 0 | | 9-Mar | 3.4544 | | 27-Apr | | 10.48 |
| 20-Jan | 0 | 10.60 | 10-Mar | 0.0254 | 13.41 | 28-Apr | | 10.49 |
| 21-Jan | 0 | 10.59 | 11-Mar | | 14.01 | 29-Apr | | 10.49 |
| 22-Jan | 0.5334 | 10.57 | 12-Mar | | 14.22 | 30-Apr | | 10.49 |
| 23-Jan | 0.0254 | 10.56 | 13-Mar | | 14.34 | 1-May | 0.4826 | 10.48 |
| 24-Jan | 0 | 10.54 | 14-Mar | | 14.16 | 2-May | | 10.45 |
| 25-Jan | 0 | 10.53 | 15-Mar | | 13.86 | 3-May | | |
| 26-Jan | 0 | 10.53 | 16-Mar | | 13.58 | 4-May | | 10.43 |
| 27-Jan | 0 | 10.49 | 17-Mar | 1.27 | 13.25 | 5-May | | 10.43 |
| 28-Jan | 0 | 10.50 | 18-Mar | 0.0508 | | 6-May | | 10.41 |
| 29-Jan | 0 | 10.48 | 19-Mar | | | 7-May | | 10.40 |
| 30-Jan | 0 | 10.48 | 20-Mar | 0.0762 | | 8-May | | 10.39 |
| 31-Jan | 0 | 10.46 | 21-Mar | 0.0254 | 12.19 | 9-May | | 10.39 |
| 1-Feb | 0 | 10.46 | 22-Mar | | 11.99 | 10-May | | |
| 2-Feb | 0 | 10.46 | 23-Mar | 0.1016 | 11.87 | 11-May | | |
| 3-Feb | 0 | 10.45 | 24-Mar | | 11.69 | 12-May | 0.2794 | |
| 4-Feb | 1.27 | 10.45 | 25-Mar | | 11.55 | 13-May | | |
| 5-Feb | 0 | 10.43 | 26-Mar | | 11.42 | 14-May | | |
| 6-Feb | 0 | 10.43 | 27-Mar | 2.54 | 11.32 | 15-May | | |
| 7-Feb | 4.826 | 10.46 | 28-Mar | | 11.27 | 16-May | | |
| 8-Feb | 0.0762 | 10.53 | 29-Mar | | 11.29 | 17-May | | |
| 9-Feb | 1.1684 | 10.60 | 30-Mar | | 11.32 | 18-May | 1.143 | |
| 10-Feb | 0.3556 | 10.78 | 31-Mar | 1.27 | 11.29 | 19-May | 3.6322 | |
| 11-Feb | 0 | 10.78 | 1-Apr | | 11.28 | 20-May | 0.254 | |
| 12-Feb | 0 | 10.83 | 2-Apr | | 11.25 | | | |
| 13-Feb | 0 | 10.86 | 3-Apr | | 11.25 | | | |
| 14-Feb | 0 | 10.87 | 4-Apr | | 11.19 | | | |
| 15-Feb | 0 | 10.88 | 5-Apr | | 11.12 | | | |
| 16-Feb | 7.3914 | 10.86 | 6-Apr | | 11.05 | | | |
| 17-Feb | 0.1778 | 11.04 | 7-Apr | | 10.97 | | | |
| 18-Feb | 0 | 11.16 | 8-Apr | | 10.90 | | | |

APPENDIX B
WATER CHEMISTRY DATA

Data collected between May 8,2002 to June 5, 2002

| Location | Cl | SO ₄ | Ca | Na | Mg | Alk. | SiO ₂ | δ ¹⁸ O | Sr | ⁸⁷ Sr/ ⁸⁶ Sr | NO ₃ | PO ₄ | Temp. | pH | Cond. | DO |
|-------------------|--------|-----------------|--------|--------|--------|--------|------------------|-------------------|--------|------------------------------------|-----------------|-----------------|-------|------|-------|------|
| | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (‰) | (mg/L) | | (mg/L) | (mg/L) | (°C) | | | |
| Vinzants | 12.7 | 22.7 | 46.6 | 7.5 | 12.4 | 157.5 | 14.0 | -2.3 | 0.7 | 0.707942 | 0.018 | 0.120 | 24.6 | 7.72 | 358 | 4.98 |
| Sink | 23.8 | 16.7 | 38.0 | 11.5 | 10.7 | 126.5 | 5.3 | -1.7 | 0.4 | 0.708141 | 0.009 | 0.132 | 26.6 | 7.37 | 319 | 1.72 |
| Ogden | 58.9 | 139.5 | 72.6 | 28.8 | 20.8 | 151.3 | 8.4 | -1.9 | 1.7 | 0.707892 | 0.009 | 0.132 | 26.6 | 7.21 | 645 | 0.1 |
| Big | 22.1 | 65.3 | 60.7 | 12.6 | 15.0 | 163.4 | 13.2 | -2.6 | 1.2 | 0.707882 | 0 | 0.122 | 25.2 | 7.42 | 463 | 2.78 |
| Paraners | 22.8 | 64.2 | 59.4 | 12.7 | 14.7 | 136.0 | 12.7 | -2.6 | 1.1 | 0.707858 | 0.02 | 0.125 | 26 | 7.61 | 456 | 1.33 |
| Jim | 23.1 | 63.2 | 59.0 | 12.8 | 14.7 | 154.6 | 13.1 | -2.6 | 1.0 | 0.707890 | 0 | 0.127 | 24.7 | 7.13 | 454 | 1.7 |
| Jug | 25.3 | 58.9 | 56.1 | 13.5 | 14.1 | 154.1 | 12.3 | -2.4 | 1.0 | 0.707877 | 0 | 0.122 | 24.4 | 7.14 | 440 | 2.64 |
| Hawg | 25.6 | 57.9 | 55.1 | 13.5 | 13.9 | 135.7 | 12.4 | -2.3 | 1.0 | 0.707907 | 0.009 | 0.127 | 24.3 | 7.03 | 437 | 0.51 |
| Twohole | 27.2 | 55.4 | 53.9 | 14.1 | 13.7 | 118.7 | 11.7 | -2.1 | 1.0 | 0.707888 | 0.105 | 0.131 | 24.6 | 7.03 | 429 | 0.23 |
| Sweetwater | 22.9 | 95.8 | 69.1 | 13.1 | 16.4 | 148.3 | 14.7 | -2.9 | 1.5 | 0.707859 | 0.119 | 0.103 | 24.1 | 7.65 | 512 | 0.72 |
| Rise | 30.3 | 73.2 | 57.8 | 15.1 | 14.1 | 130.5 | 11.4 | -2.3 | 1.1 | 0.707899 | 0.077 | 0.116 | 22.8 | 7.33 | 458 | 2.04 |
| Treehouse | | | 64.8 | 12.8 | 14.1 | 140.3 | | -1.9 | 1.4 | 0.707812 | | | 27.5 | 7.5 | 475 | 5.44 |
| Hornsby | 12.8 | 79.2 | 74.4 | 9.4 | 13.5 | 184.9 | 12.4 | -3.1 | 1.5 | 0.707849 | 0.067 | 0.052 | 23 | 7.54 | 498 | 6.46 |

Data collected between January 15,2003 and February 5,2003

| Location | Cl | SO ₄ | Ca | Na | Mg | K | Alk. | SiO ₂ | δ ¹⁸ O | Sr | ⁸⁷ Sr/ ⁸⁶ Sr | NO ₃ | PO ₄ | Temp. | pH | Cond. | DO |
|------------|--------|-----------------|--------|--------|--------|--------|--------|------------------|-------------------|--------|------------------------------------|-----------------|-----------------|-------|------|-------|-----|
| | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (‰) | (mg/L) | | (mg/L) | (mg/L) | (°C) | | | |
| Vinzants | 23.0 | 6.8 | 11.5 | 10.70 | 3.45 | 1.25 | 12 | 7.8 | -2.8 | | | 0.029 | 0.14 | 10.4 | 5.2 | 131.1 | 8.7 |
| Sink | 22.8 | 6.5 | 11.1 | 10.50 | 3.37 | 1.23 | 12 | 7.8 | -2.885 | 0.468 | 0.70792 | 0.031 | 0.14 | 10 | 6.1 | 131.1 | 8.8 |
| Ogden | 23.1 | 7.8 | 11.9 | 10.70 | 3.56 | 1.25 | 12 | 7.6 | -2.825 | 0.070 | 0.70883 | 0.031 | 0.15 | 10.2 | 6.36 | 136 | 8.6 |
| Big | 23.6 | 17.7 | 14.9 | 10.60 | 4.04 | 1.19 | 16 | 8.2 | -2.9 | | | 0.031 | 0.15 | 10 | 6.03 | 160.7 | 8.2 |
| Ravine | 23.8 | 17.6 | 16.1 | 11.20 | 4.33 | 1.23 | 16 | 8.6 | -2.825 | | | 0.03 | 0.15 | 11 | 5.23 | 164.9 | 8.3 |
| Paraners | 23.3 | 17.4 | 15.0 | 10.70 | 4.09 | 1.20 | 16 | 7.8 | -2.77 | | | 0.027 | 0.14 | 10 | 6.2 | 160.7 | 8.3 |
| Jim | 23.6 | 16.4 | 16.0 | 11.00 | 4.29 | 1.23 | 16 | 8.7 | -2.73 | 0.188 | 0.70821 | 0.031 | 0.15 | 10.6 | 6.29 | 164.8 | 8.1 |
| Jug | 23.1 | 18.8 | 16.0 | 11.10 | 4.30 | 1.24 | 16 | 8.8 | -2.725 | | | 0.028 | 0.15 | 10.9 | 6.02 | 163.9 | 5.6 |
| Hawg | 16.7 | 24.0 | 60.0 | 9.17 | 6.26 | 0.94 | 136 | 13.3 | -2.485 | 0.174 | 0.70819 | -0.001 | 0.16 | 15.5 | 6.66 | 368 | 1.6 |
| Two Hole | 26.3 | 28.7 | 28.7 | 12.10 | 5.57 | 1.43 | 52 | 10.5 | -2.28 | 0.338 | 0.70805 | 0.004 | 0.16 | 12 | 6.66 | 235 | 3.1 |
| Sweetwater | 23.5 | 18.1 | 16.0 | 10.70 | 4.22 | 1.21 | 20 | 8.5 | -2.69 | 0.188 | 0.70811 | 0.028 | 0.14 | 10 | 6.2 | 165.4 | 4.6 |
| Rise | 22.8 | 15.3 | 15.5 | 10.40 | 4.08 | 1.21 | 20 | 8.6 | -2.83 | 0.180 | 0.70819 | 0.024 | 0.15 | 11 | 6.19 | 161.9 | 4.3 |
| Treehouse | 26.2 | 20.1 | 19.1 | 11.00 | 4.62 | 1.26 | 24 | 8.8 | -2.8 | | | 0.041 | 0.15 | 11.1 | 6.48 | 182.4 | 7.3 |
| Hornsby | 19.7 | 35.7 | 32.6 | 9.93 | 5.97 | 1.24 | 56 | 10 | -2.81 | | | 0.03 | 0.13 | 13.2 | 6.54 | 252 | 2.5 |
| Well #1 | 8.4 | 2.0 | 107.0 | 3.79 | 3.25 | 0.24 | 252 | 10.5 | -3.38 | 1.626 | 0.70784 | 0 | 0.09 | 21.5 | 6.7 | 485 | 0.2 |
| Well #2 | 46.0 | 305.0 | 152.0 | 26.90 | 27.40 | 1.71 | 206 | 15 | -3 | | | 0.065 | 0.59 | 26.3 | 6.76 | 1009 | 2.3 |
| Well #7 | 13.4 | 14.6 | 101.0 | 7.06 | 5.41 | 0.62 | 262 | 9.1 | -3.58 | 0.488 | 0.70793 | 0.002 | 0.14 | 20.4 | 6.51 | 530 | 0.2 |

Data collected March 3, 2003 to March 19,2003

| Location | Cl | SO ₄ | Ca | Na | Mg | K | Alk. | SiO ₂ | δ ¹⁸ O | Sr | ⁸⁷ Sr/ ⁸⁶ Sr | NO ₃ | PO ₄ | Temp. | pH | Cond. | DO |
|------------|--------|-----------------|--------|--------|--------|--------|--------|------------------|-------------------|--------|------------------------------------|-----------------|-----------------|-------|------|-------|------|
| | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (‰) | (mg/L) | | (mg/L) | (mg/L) | (°C) | | | |
| Vinzants | 14.3 | 2 | 6.96 | 5.5 | 2.15 | 1.34 | 10 | 3.3 | -3.32 | | | 0.008 | 0.217 | 17.2 | 5.98 | 84.5 | 6.08 |
| Sink | 12.7 | 2 | 7.64 | 6.29 | 2.41 | 1.72 | 8 | 3.4 | -2.46 | 0.025 | 0.709481 | 0.016 | 0.286 | 17.4 | 5.35 | 79.2 | 5.77 |
| Ogden | 12.8 | 2 | 7.59 | 5.76 | 2.32 | 1.55 | 16 | 3 | -2.53 | 0.0273 | 0.709434 | 0.015 | 0.294 | 17.2 | 4.98 | 79 | 5.7 |
| Ravine | 12.8 | 2 | 7.92 | 5.82 | 2.36 | 1.53 | 10 | 3.1 | -2.67 | 0.0379 | 0.709099 | 0.02 | 0.294 | 17.3 | 4.75 | 81.9 | 5.52 |
| Paraners | 12.9 | 2 | 8.14 | 6.29 | 2.46 | 1.68 | 10 | 3 | -2.49 | | | 0.017 | 0.294 | 17.1 | 5.04 | 82 | 5.54 |
| Jim | 13.1 | 2 | 8.31 | 6.16 | 2.48 | 1.69 | 8 | 2.6 | -2.36 | 0.0336 | 0.709091 | 0.012 | 0.300 | 17.4 | 5.05 | 82.6 | 5.43 |
| Jug | 13.2 | 2 | 8.48 | 6.32 | 2.48 | 1.68 | 12 | 2.7 | -2.37 | | | 0.013 | 0.292 | 17.6 | 4.9 | 84.3 | 5.5 |
| Hawg | 15.7 | 7.2 | 16.1 | 7.5 | 2.93 | 1.57 | 28 | 3 | -2.54 | | | 0.022 | 0.253 | 18.4 | 5.58 | 123.2 | 2.88 |
| Sweetwater | 11.2 | 2 | 7.6 | 5.34 | 2.22 | 1.44 | 8 | 2.9 | -2.45 | 0.0391 | 0.709101 | 0.008 | 0.305 | 16.5 | 4.78 | 71.5 | 5.56 |
| Rise | 11.3 | 2 | 8.12 | 5.71 | 2.32 | 1.6 | 8 | 2.8 | -2.35 | 0.0301 | 0.707725 | 0.012 | 0.338 | 17.1 | 4.67 | 72.5 | 5.54 |
| Hornsby | 11.6 | 2 | 11.4 | 5.74 | 2.45 | 1.7 | 16 | 3.1 | -2.42 | | | 0.021 | 0.292 | 18.8 | 5.11 | 86.8 | 4.35 |
| Well #1 | 8.3 | 2 | 113 | 4.33 | 2.21 | 0.09 | 242 | 7.8 | -3.34 | 0.8899 | 0.7078735 | 0.001 | 0.075 | 21.9 | 6.8 | 484 | 0.33 |
| Well #2 | 21.3 | 114 | 79.1 | 14.1 | 13.8 | 1.43 | 102 | 1.4 | -2.76 | 0.1103 | 0.7080629 | 0 | 0.142 | 25.8 | 7.08 | 488 | 0.14 |
| Well #3 | 5.3 | 3 | 91.4 | 3.68 | 1.82 | 0.09 | 212 | 10 | -4.11 | 0.148 | 0.708141 | 0.057 | 0.063 | 21.8 | 6.93 | 409 | 1.64 |
| Well #4 | 8.2 | 4.4 | 91 | 5.08 | 2.18 | 0.24 | 206 | 8.2 | -4.16 | 0.148 | 0.708127 | 0.034 | 0.063 | 21.4 | 6.97 | 408 | 4.06 |
| Well #6 | 7.2 | 2.5 | 100 | 3.87 | 1.89 | 0.33 | 212 | 6.1 | -4.33 | | | 0 | 0.078 | 21.1 | 6.8 | 435 | 0.22 |
| Well #7 | 13.1 | 17.7 | 87.2 | 7.53 | 5.78 | 0.57 | 196 | 6.9 | -3.71 | | | 0.004 | 0.151 | 20.7 | 6.98 | 422 | 0.16 |

Data collected April 28, 2003 to May 1, 2003

| Location | Cl | SO ₄ | Ca | Na | Mg | K | Alk. | SiO ₂ | Sr | ⁸⁷ Sr/ ⁸⁶ Sr | δ ¹⁸ O | NO ₃ | PO ₄ | Temp. | pH | Cond. | DO |
|------------|--------|-----------------|--------|--------|--------|--------|--------|------------------|--------|------------------------------------|-------------------|-----------------|-----------------|-------|------|-------|------|
| | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | | (‰) | (mg/L) | (mg/L) | (°C) | | | |
| Vinzants | 15.1 | 13.1 | 33.7 | 7.27 | 6.79 | 0.94 | 77 | 11.8 | | | -2.59 | 0.301 | 0.255 | 20.8 | 7.06 | 230 | 3.24 |
| Sink | 15.5 | 12.8 | 35 | 7.38 | 6.8 | 0.94 | 78.9 | 12.2 | 0.267 | 0.708033 | -2.33 | 0.344 | 0.244 | 21.4 | 7.07 | 235 | 3.8 |
| Ogden | 16.3 | 16.5 | 36 | 8.24 | 7.36 | 1 | 81.5 | 12 | | | -2.21 | 0.383 | 0.233 | 22.1 | 6.99 | 242 | 3.74 |
| Ravine | 19.2 | 50 | 52 | 9.96 | 9.68 | 0.96 | 99.3 | 13.1 | 0.796 | 0.707894 | -1.96 | 0.329 | 0.211 | 22.7 | 6.99 | 225 | 3.74 |
| Paraners | 17.5 | 27.9 | 43.1 | 8.57 | 8.23 | 0.96 | 97.2 | 12.5 | | | -2.38 | 0.336 | 0.238 | 22 | 7.04 | 300 | 2.57 |
| Jim | 17.1 | 23.8 | 42.3 | 8.45 | 8.07 | 0.97 | 95.1 | 12.6 | 0.493 | 0.707955 | -2.58 | 0.322 | 0.241 | 22.1 | 7.02 | 293 | 2.45 |
| Jug | 17.3 | 27.7 | 40 | 8.31 | 7.64 | 0.96 | 90.7 | 12.4 | | | -2.68 | 0.395 | 0.227 | 22.1 | 7.02 | 287 | 2.1 |
| Hawg | 18.7 | 37.5 | 43.8 | 8.85 | 8.23 | 0.96 | 90 | 11.9 | 0.535 | 0.707937 | -2.73 | 0.307 | 0.227 | 21.8 | 6.67 | 295 | 2.1 |
| TwoHole | 19.7 | 40.9 | 47.1 | 9.29 | 8.76 | 1.01 | 96 | 12.2 | 0.615 | 0.707927 | -2.72 | 0.366 | 0.238 | 22.1 | 6.85 | 315 | 2.04 |
| Sweetwater | 17.8 | 49.3 | 51.9 | 8.85 | 9.27 | 0.96 | 112 | 12.9 | 0.764 | 0.707887 | -2.71 | 0.367 | 0.189 | 22.1 | 6.76 | 338 | 1.69 |
| Rise | 18.2 | 62.9 | 57.1 | 9.36 | 9.82 | 0.96 | 108 | 12.6 | | | -2.96 | 0.36 | 0.172 | 21.8 | 6.84 | 377 | 1.14 |
| Treehouse | 14.4 | 64 | 64.8 | 8.59 | 10.1 | 1.03 | 124 | 12.8 | | | -3.05 | 0.423 | 0.180 | 22.4 | 7.06 | 400 | 2 |
| Hornsby | 12.2 | 64.6 | 69.5 | 7.72 | 10.1 | 1.05 | 144 | 13.2 | | | -3.11 | 0.349 | 0.153 | 23.1 | 6.99 | 420 | 0.31 |
| Well #1 | 7.3 | 20 | 97.6 | 3.26 | 1.39 | 0.15 | 234 | 9.4 | 0.108 | 0.708194 | -3.34 | 0.014 | 0.095 | 26 | 6.92 | 907 | 0.22 |
| Well #2 | 40.7 | 242 | 148 | 25.2 | 27.8 | 1.87 | 188 | 13.5 | 2.16 | 0.707843 | -2.83 | 0.022 | 0.111 | 22 | 6.87 | 448 | 0.13 |
| Well #3 | 5.6 | 10 | 88 | 3.31 | 1.67 | 0.41 | 208 | 10.5 | | | -4 | 0.07 | 0.078 | 21.8 | 6.9 | 416 | 1.27 |
| Well #4 | 8.2 | 10 | 94.5 | 4.41 | 1.51 | 0.31 | 208 | 8.1 | 0.129 | 0.708112 | -4.25 | 0.054 | 0.078 | 21.7 | 6.92 | 423 | 2.08 |
| Well #6 | 6 | 20 | 90.9 | 2.95 | 1.22 | 0.37 | 210 | 5.8 | | | -4.39 | 0.001 | 0.045 | 21.2 | 6.94 | 416 | 0.17 |
| Well #7 | 14.9 | 11.6 | 111 | 4.41 | 4.61 | 0.62 | 256 | 10.2 | 0.508 | 0.7079129 | -3.68 | 0.035 | 0.149 | 20.8 | 6.79 | 538 | 0.14 |

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BIOGRAPHICAL SKETCH

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