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Microbial Influences on Karst Dissolution: The Geochemical Perspective, with a Chapter on Assessment of the Spreadsheets Across the Curriculum Project

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Microbial Influences on Karst Dissolution: The Geochemical Perspective, with a Chapter on Assessment of the Spreadsheets Across the Curriculum Project

by

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A dissertation submitted in partial fulfillment
of the requirements for the degree of
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DEDICATION

This dissertation could be dedicated to no one other than Sandra McGee, and Gail and Jim Carew. The result of this parenting triumvirate is a testament to the African proverb "*It takes a village to raise a child*", and I credit who I am and how far I've come to the unique brand of support, encouragement, and guidance provided by each. My mother taught me that love and devotion can get you through the hardest obstacles, and though her time was cut short, her perseverance is a continuous inspiration. I will never be able to express how extraordinarily fortunate and grateful I am to have an aunt and uncle who not only willingly stepped in as parents in her stead, but did so with more patience and dedication than could ever be expected under such circumstances. They picked up where my mother left off, shaping and molding like expert potters. My aunt is both my fiercest advocate and the toughest cookie I've ever met—any tenacity I draw upon to get what I want out of life, including this degree, is attributed directly to her. My uncle is the sage who taught me that it wouldn't matter in the end what I did, as long as I loved it. He never could have guessed I'd pick his field as my own, but I credit him for helping me realize my love for geology a bit faster than I probably would have on my own.

Here's to you guys.

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I'm indebted to Ray and Sharon Thornton, who for years, have graciously provided USF Karst researchers access to their cave for a variety of scientific and education endeavors. Lee Florea and Jason Polk (Western Kentucky University), Robert Brooks and Tom Turner (Florida Speleological Society), Erin Rothfus (Gerace Research Center), Dave DeWitt (Southwest Florida Water Management District), and graduate students Jon Sumrall and Glen Hunt were also vital to field operations and discussion for the karst component of this dissertation. Many thanks also go to Zac Atlas and Hanna Endale for their assistance (and moral support) during IRMS activities. Graduate students Christina Stringer and Sean Callihan were central to facilitating the collection and organization of data for the assessment component of this dissertation, and I'd also like to thank the students of Computational Geology for their participation and good sport. Finally, I'd like to thank Emily Lardner and Gillies Duncan (Evergreen State College) for their valuable input on the assessment process.

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NOTE TO READER

The original copy of this dissertation contains color necessary for interpreting and understanding many data figures, and is on file with the USF Library in Tampa, Florida. In addition, Chapter 2 was originally published in the journal *Carbonates and Evaporites* and is reprinted here with the kind permission of Springer Science + Business Media. Full citation of this paper can be found in the list of references provided at the conclusion of Chapters 1 and 2.

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ABSTRACT

Microbes are prevalent in geologic settings and a growing body of research suggests the roles they play in geologic processes may be more important than previously thought, and therefore underestimated. This dissertation addresses the influence of microbes on the dissolution of limestone in karst settings by analyzing the stable carbon isotopes and geochemistry of air and waters from three unique cave and karst settings: West-Central Florida, the Everglades (southern Florida) and The Bahamas. In Florida, these parameters as well as air/water temperature, rainfall, and water-level fluctuations were monitored for 22 and 10 months. In the Bahamas, geochemical data were collected from at varying time-intervals from a variety of cave and surface water bodies. Results showed that microbial respiration in these environments is an important source of carbon dioxide, which contributes to the formation of carbonic acid, which appears to be the major dissolving agent at each of these sites. At the same time, microbially-mediated oxidation of both organic matter and minerals exerts a secondary dissolution control by providing additional acid and inorganic ions that dissolve rock and/or inhibit limestone precipitation.

This dissertation also includes a chapter discussing the role of the USF Department Geology in the evolution of assessment for *Spreadsheets Across the Curriculum* (SSAC) project, which promotes quantitative literacy (QL) by teaching math in the context of other disciplines. Assessment occurred primarily in the Computational Geology course from 2005 to 2008 and showed that this teaching strategy fostered gains in math knowledge and positive math association. Simultaneously, instructors

learned that pre-planning and adaptability was central to developing a successful assessment strategy, which, when combined with the heterogeneity of subjects each year, presents challenges in the yearly comparison of results. These conditions are common in educational settings, illustrating the impracticality of standardized assessment instruments and practices, and the importance of the extensive preparation required in identifying assessment goals and the best strategies for achieving them in a given setting.

CHAPTER 1:

INTRODUCTION

The major breakthrough occurs when someone with a very young brain sees the world differently than all of these distinguished people with old brains.

--William B. White

1.1. Research Overview

In 2006, Dr. William White, one of the most esteemed karst researchers, was invited as the keynote speaker for the University of South Florida Karst Research Group's semi-annual Best of Karst Series. Dr. White graciously accepted and delivered a sweeping pictorial retrospective of his contributions to the fields of karst hydrogeology and geomorphology. When the talk concluded, an audience member raised their hand and asked Dr. White his thoughts on the future directions of karst research. After a brief pause, Dr. White smiled and stated that in his opinion, the Pandora's Box of karst research regarded the role microorganisms play in the physical and chemical processes governing speleogenesis and the evolution of karst landscapes. This newly expanding branch of karst research was one of very few he admitted having the fortitude to explore at this stage in his career, but he acknowledged that the growing awareness of the influence microorganisms exerted in certain geologic processes seemed to quietly stalk the models of hydrogeology and geomorphology built by him and his colleagues. In his mind, he felt it was the duty of the next generation of karst scientists to employ these new ideas in an effort to expand and improve upon the current understanding laid down by their predecessors. These thoughts were echoed in an interview he and his wife and research colleague Elizabeth provided for the Hydrogeology Time Capsule, a series of interviews of distinguished hydrogeologists, established by the editors of the Hydrogeology Journal (Simmons and Renard, 2008; Goldscheider et al., 2009).

Dr. White's call to action was one of the many inspirations that drove the majority of research presented in this dissertation, which utilizes a geochemical approach, specifically fluctuations in the stable isotopic compositions of carbon ($\delta^{13}C$) of water and rock, to explore the degree to which microorganisms influence the dissolution of limestone in caves. This research began with a pilot project in collaboration with The Gerace Research Centre was conducted from cave and surface waters on San Salvador Island, The Bahamas, to characterize their geochemical composition in relation to their environmental setting and their connectivity to the ocean through subsurface conduits (Chapter 2). These data were used to hypothesize the extent to which microorganisms influence limestone dissolution on this carbonate island, in light of research suggesting that previously established abiotic models of dissolution could not account for the formation of the island's larger cave systems. This chapter was originally published in *Carbonates and Evaporites* prior to the submission of this manuscript and is reprinted here with the kind permission of Springer Science + Business Media (McGee et al., 2010). The findings of this project, as well as data collection and analytical methods, were utilized at Thornton's Cave in West-Central Florida, which served as the primary site of investigation for this dissertation. A two-year study monitoring climate, hydrologic and geochemical parameters was conducted here to establish a model of biogenic dissolution driven by the acidification of water through CO_2 respiration and oxidation reactions (Chapters 3 and 4). A similar study was conducted in collaboration with a year-long United States Geological Survey Mendenhall postdoctoral research project by Dr. Lee Florea using geochemical data collected from southern Florida at Palma Vista Cave in Everglades National Park (Chapter 5).

Though exploration of the lesser-known paths of karst science served as the primary focus of this dissertation, the ability to conduct interdisciplinary research on this level would be impossible without the tools and skills gained through decades of education at all levels and across all disciplines (closely followed by the guidance and mentoring of those educators). It is this certain knowledge that inspired the second component of this dissertation, which focuses on the assessment of models and strategies of teaching as a means of not only establishing student learning gains, but also making them most effective at enhancing and improving the learning process. The origin of Spreadsheets Across the Curriculum (SSAC) in the USF Department of Geology, an NSF-funded project (DUE 0442629) aimed at increasing quantitative literacy (QL) among college students, provided a unique opportunity to investigate how student understanding of quantitative skills and concepts, as well as students' comfort levels utilizing them increased in response to being taught these skills and concepts in the context of a discipline other than math (Chapter 6). In addition, feedback provided by students in attitude and knowledge surveys associated with this teaching strategy was crucial in the identification of areas where this strategy could be improved. Given the major emphasis in the United States on improving student perceptions of, and abilities within, the science, technology, engineering and math (STEM) disciplines at both grade school and college levels, the successful implementation of projects such as SSAC are vital in educational settings. At the same time, they promote the development of future generations of scientists to carry the torches passed down from researchers like Dr. White, and one day, myself.

This dissertation is constructed as a series of independent research papers presented as chapters related by the two major themes discussed above. As such, the replication of objectives, ideas, and in some cases data, will occur between chapters, and therefore should be expected as they are read. These chapters will be followed by concluding remarks provided in Chapter 7.

1.2. References

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CHAPTER 2:

TRACING GROUNDWATER GEOCHEMISTRY USING $\delta^{13}C$ ON SAN SALVADOR ISLAND (SOUTHEASTERN BAHAMAS): IMPLICATIONS FOR CARBONATE ISLAND HYDROGEOLOGY AND DISSOLUTION

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2.1. Introduction

Karst regions comprise 15 to 20% of the earth's surface (Ford and Williams 2007). The formation of their landscapes and features are governed primarily by dissolution processes. Because limestone dissolution is largely driven by water geochemistry and because networks of conduits and fractures make the transmission of water from the surface and through limestone aquifers more rapid than sandstone aquifers, karst settings are a dynamic environment for the study of water-carbonate geochemical reactions and their influence on dissolution. Furthermore, the interplay between water and carbonate rock is also an important component of the global carbon cycle, as dissolution of carbonate rock may consume between 0.11 and 0.61 Pg of the total 3.6 Pg CO_2 drawn down from the atmosphere per year (Yuan & Zang eds. 2002; Liu et al. 2002).

Numerous studies have examined groundwater geochemistry and its impacts on surface and subsurface karst geomorphology (e.g. Dreybrodt 1988; White 1988; Ford and Williams 2007). These impacts are well demonstrated on carbonate islands where several groundwater models have been developed based on geochemical and hydrologic observations (Davis and Johnson, 1989; Vacher and Wallis 1992; Whitaker and Smart 1997a; Brooks and Whitaker 1997; Whitaker and Smart 2007a-b). For example, freshwater percolating through epikarst forms a lens perched atop marine-sourced groundwater, and it is widely accepted that the mixing of these sources at the halocline, which is developed at the lower boundary of the lens, intensifies limestone dissolution by lowering the calcite saturation state below levels that would not normally exist in either water mass (Wigley and Plummer 1976; Smart et al. 1988; Vacher et al. 1990; Jensen et al. 2006). This hypothesis implies that most dissolution at any given point in time occurs at the halocline boundary, which changes position during sea-level high- and lowstands. However, the presence of the halocline is wholly dependent upon the input of freshwater from the surface, which is governed by landscape, characteristics of the subsurface (i.e. shape of and connectivity between fractures and conduits), and climate. For example, on carbonate islands dominated by karst terrains with ample secondary porosity, water permeates quickly through the soils and epikarst such that surface streams are virtually non-existent and surface water only accumulates in topographic lows or in areas of low porosity (e.g. clay/paleosol horizons, dense organic deposits) that prevent downward water migration (Vacher 1988; Vacher and Mylroie 1991; Whitaker and Smart 1997a). This generally unrestricted flow permits a well-developed mixing zone; however, conduit flow may be irregular in the subsurface, preferentially channeling water to specific areas with higher conduit connectivity, preventing uniform halocline development throughout the island. Furthermore, the amount of freshwater input to the aquifer is affected by both precipitation and evaporation rates such that the net export of water from the surface to the subsurface is lower in regions with high evaporation rates (Whitaker and Smart 1997b). The degree to which each factor contributes to groundwater geochemistry varies both within and between islands, underscoring the need to utilize a holistic approach that integrates both physical and chemical analyses on a variety of spatial scales when studying groundwater dynamics.

In carbonate islands, such as The Bahamas, dissolution of limestone by the downward percolation of rainfall charged with atmospheric and/or soil CO_2 is considered limited due to the rapid buffering of water pH upon contact with the limestone, as well as the thin, nutrient-poor quality of the soils (Schwabe et al., 2008). As a result, mixing-zone corrosion has been cited as the primary mode of dissolution, including conduit and fracture widening (Back et al. 1986; Mylroie and Carew 1990; Carew and Mylroie 1995a, 1995b). Because some Bahamian caves formed during Oxygen Isotope Substage (OIS) 5e (ca. 125 ka), and that particular highstand only permitted mixing-zone dissolution to occur at the position of these caves for a period of less than 15 ka, it was assumed that those waters must have been particularly undersaturated with respect to calcite and aragonite, and that the majority of dissolution likely occurred at the discharging margins of the fresh-water lens where the lens was thinnest and the mixing waters were most corrosive (Mylroie and Carew 1990). Hydrologic studies, however, reveal the complex nature of water flow and mixing in the subsurface resulting in lens thickness variations throughout these islands (Whitaker and Smart 1997a; Martin and Moore 2008). In addition, tidal lags and variations in temperature and salinity observed in the surface, cave, and well waters on San Salvador Island illustrate the uneven hydraulic conductivity of water sources through the aquifer (Davis and Johnson 1989; Gamble et al. 2000; Crump and Gamble 2006), while geochemical and microbial observations from cave and conduit waters on the island suggest a biotic component to the mixing-dissolution model (Moore et al. 2006; Schwabe et al. 2008).

Though the general model of mixing-zone dissolution is theoretically viable, the specifics of this model assume relatively more uniform hydrologic conditions than observed on San Salvador Island, and call for more detailed studies of the island's surface and subsurface hydrology to address these differences. Stable carbon isotopes are often used as tracers of environmental processes due to the ubiquity of carbon in the environment in differing chemical states and the propensity of its fractionation during biotic and abiotic transformations from one species to another. Studies using $\delta^{13}C$ analyses, or the change in ratio between the isotopes ^{12}C and ^{13}C, have increasingly been used in cave and karst settings as indicators of paleoclimate and associated vegetal change, hydrologic sources and processes, and microbial impacts on speleogenesis (e.g. Dorale et al. 1998; Boston et al. 2006; Sumer 2001; Doctor et al. 2006; Polk et al. 2007). Because $\delta^{13}C$ studies have seldom been performed on San Salvador and because the island was the site of development for the prevailing dissolution models for carbonate islands, it serves as an ideal setting for this study investigating the utility of $\delta^{13}C$ analyses coupled with geochemical measurements in identifying water sources and hydrologic patterns on the island. In December 2007/January 2008, measurements of $\delta^{13}C$ from waters, atmosphere, and rocks at Crescent Top Cave were obtained and combined with geochemical analyses of the water as well as cave microclimate data to determine tidal effects on water geochemistry. In January 2009, the study was expanded to include $\delta^{13}C$ and geochemical measurements from a wider variety of surface and cave waters on the island in order to more fully document the geochemical characteristics of the island's hydrologic system and its role in mixing dissolution. This insight will help better constrain dissolution rates and thusly atmospheric CO_2 drawdown and flux on carbonate platforms, which is currently estimated at 0.011 Pg per year (Yuan and Zhang eds, 2002; Mylroie 2008).

2.2. Regional Geologic Setting

2.2.1. Overview

San Salvador Island is situated on an isolated carbonate platform along the eastern margin of the Bahamian Archipelago (Figure 2.1). The island is dominated by low, tropical scrub plains, surface lakes, ponds, lagoons, and dune-ridge complexes. Because of the platform's tectonic stability, the steepness of the carbonate platform margins, and the isolation from any significant siliclastic input, the development of the existing islands of the Bahamas has been largely controlled by depositional and erosional processes associated with Pleistocene-Holocene glacioeustatic sea-level changes (Mylroie and Carew 1997). As sea-level rose to a highstand, transgressive-phase eolianites formed as reef sediments were transported onto the platform by wave activity associated with rising sea-level. Marine subtidal and lagoonal facies developed to their greatest extent during the high-sea-level stillstands on the platform. Later, many of those deposits were overstepped by regressive-phase eolian facies as sea-level fell. Those deposits were later modified by pedogenic and karst processes during the lowstands of sea-level (below -20 m) when the platforms were subaerially exposed. A Quaternary stratigraphy of Bahamian islands is provided by Carew and Mylroie (1995a).

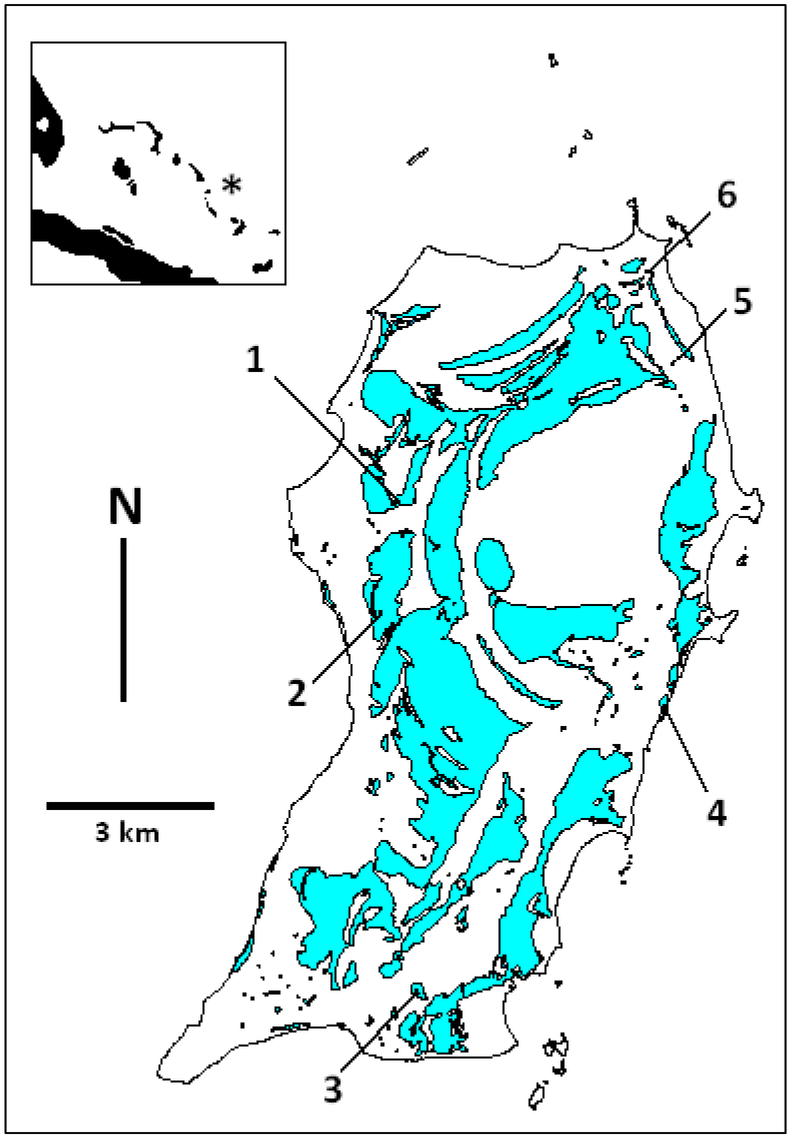

Figure 2.1. San Salvador Island, with inland lakes. Surface and cave sampling locations numbered as follows: 1) Major's Cave, 2) Little Lake, 3) Mermaid Pond, 4) Salt Pond, 5) Lighthouse Cave and Fresh Lake 6) northeastern lake cluster. *Adapted from Robinson and Davis, (1999).*

2.2.2. Surface and Subsurface Hydrology

San Salvador Island is classified as having a subtropical climate, with an annual temperature range of 22 to 28 °C, and a rainfall regime characterized by short, wet periods in the spring, wet summers and early autumns associated with hurricane season, and dry winters (Sealey 1994; Shaklee 1996). Given the relatively low rainfall in the southeastern Bahamas, annual evaporation exceeds rainfall, and, therefore, the net fresh-water budget on San Salvador Island is negative (Sealey 1994); however, during the wet seasons, rainfall exceeds evapotranspiration such that some freshwater percolates down to form a freshwater lens atop marine groundwaters (Davis and Johnson 1989; Shaklee 1996). Groundwater moves through Pleistocene limestones, and its flow is governed by secondary porosity with higher hydraulic conductivity than that seen in Holocene sand aquifers located in the northern Bahamas (Whitaker and Smart 1997a). Because hydraulic conductivity increases in older limestones due to greater degrees of karstification, circulation of marine water occurs through the platform (Whitaker and Smart 1990). Numerous investigations of the specifics of San Salvador's hydrologic regime have been undertaken; however, a precise understanding of how fresh and marine waters flow and interact in the island's subsurface is still under investigation (e.g., Davis and Johnson 1989; Crump and Gamble 2006; Gentry and Davis 2006; Martin and Moore 2008). Though the Dupuit-Ghyben-Herzberg principle is typically employed to explain fresh-water lens geometry, hydrologic surveys of surface and groundwater on the island, and regionally, have suggested the model's limited validity to only a few carbonate island settings (Vacher 1988; Vacher and Wallis 1992; Schwabe 1999). On San Salvador, the thickness of the fresh-water lens is highly variable and thought to reflect limestone heterogeneity; it may also be governed by the topography of the island (Vacher and Mylroie 1991). Davis and Johnson (1989) modeled the hydrology of the island and describe it as being comprised of six principal elements: rainfall, evapotranspiration, groundwater, inland lakes, tides, and conduits (including blueholes). Further, they found the permeability of most rocks sampled was typically below 10^{-6} cm/s, considered low as compared to other oolitic limestones and thought to contribute to high water tables and thick freshwater lenses. This led the authors to speculate that areas on the island with low water-levels and thinner freshwater lenses could be explained by nearby conduit flow, allowing water to migrate away from the area.

Surface water on San Salvador Island is found as inland lakes and ponds, with salinities ranging from brackish to hypersaline. The majority of these water bodies are situated in swales between eolianite dune ridges, and all water bodies, with the exception of blue holes, are generally ≤3 m in depth. Davis and Johnson (1989) classified the inland water bodies as being open or limited based on the degree of hydrologic exchange with tidal or groundwater marine sources. Under open exchange conditions, lakes are fed directly by or through a network of conduits and seeps such that salinity is at or near normal marine values. Since some lakes are slightly above sea-level during the average high tide, water usually discharges from the lakes through conduits to the ocean. During the highest tides, water surges into the lakes during the brief interval when sea-level is higher than the lake elevation, thereby regulating salinity and geochemistry throughout the year. Under limited exchange conditions, lakes are fed primarily by direct rainfall and groundwater seeps, with the majority of freshwater lost through evaporation leading to salinities anywhere from two to six times that of marine values. Although relatively rare, surface freshwater bodies have been documented at seven wetlands (Gentry and Davis 2006). Widespread karstification and low topographic relief coupled with the negative water balance preclude surface streams.

2.3. Methods

2.3.1. Locations

Crescent Top Cave, a shallow flank-margin cave (*sensu* Mylroie and Carew 1997) is located approximately 1 km south-southeast of the Gerace Research Centre on the northeastern corner of the island (Figs. 2-3). A single, low, narrow entrance connects the cave to the surface, and a seasonal temperature inversion exists such that the cave is cooler in the summer and warmer in the winter than average surface conditions (Gamble 2009). A pit containing a pool of normal-marine-salinity exists toward the rear of the main chamber, and it is hydrologically influenced by tidal fluctuations in the adjacent Crescent Pond. Crescent Pond is a shallow (maximum depth of 3 m) water body of marine salinity bounded by eolianite ridges. It is fed primarily through conduits and fractures that transport marine water and secondarily via direct rainfall as well as fresh-water seeps and runoff from the surrounding landscape (Crump and Gamble 2006). A temporal lag of approximately three hours exists between marine tidal fluctuations and corresponding water-levels at Crescent Pond and Crescent Top Cave.

To more comprehensively relate the data collected from Crescent Pond and Crescent Top Cave, nine surface samples from ponds and two samples from permanent water bodies in caves were sampled in January 2009. Reckley Hill, Crescent, Moonrock, Oyster, and Osprey ponds comprise a northeastern cluster of surface bodies and are each located less than 1 km south of the Gerace Research Centre (Figure 2.2). Fresh Lake, as well as Salt and Mermaid ponds are located on the eastern side of the island, with Little Lake on the west-central side just east of Cockburn Town. Lighthouse and Major's caves are the island's two largest flank-margin caves, located on the east and west sides of the island, respectively. Both are formed within rocks of the Owl's Hole Formation, which is hypothesized to have deposited during either OIS 7 (ca. 220 ka), 9 (ca. 320 ka) or 11 (ca. 410 ka) (Figure 2.4) (Carew and Mylroie 1985, 1995).

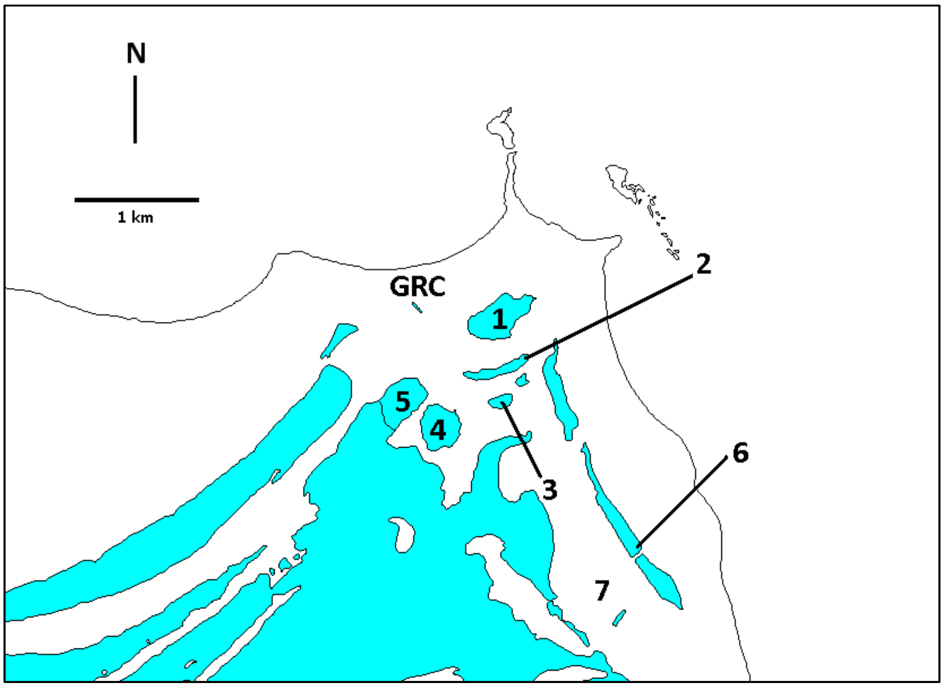

Figure. 2.2. Northeastern San Salvador Island, including Gerace Research Centre and lakes. Surface and cave sampling locations numbered as follows: 1) Reckley Hill Pond, 2) Crescent Pond/Crescent Top Cave, 3) Moonrock Pond, 4) Oyster Pond, 5) Osprey Pond, 6) Fresh Lake, 7) Lighthouse Cave and 8) Graham's Harbor. *Adapted from Robinson and Davis, (1999).*

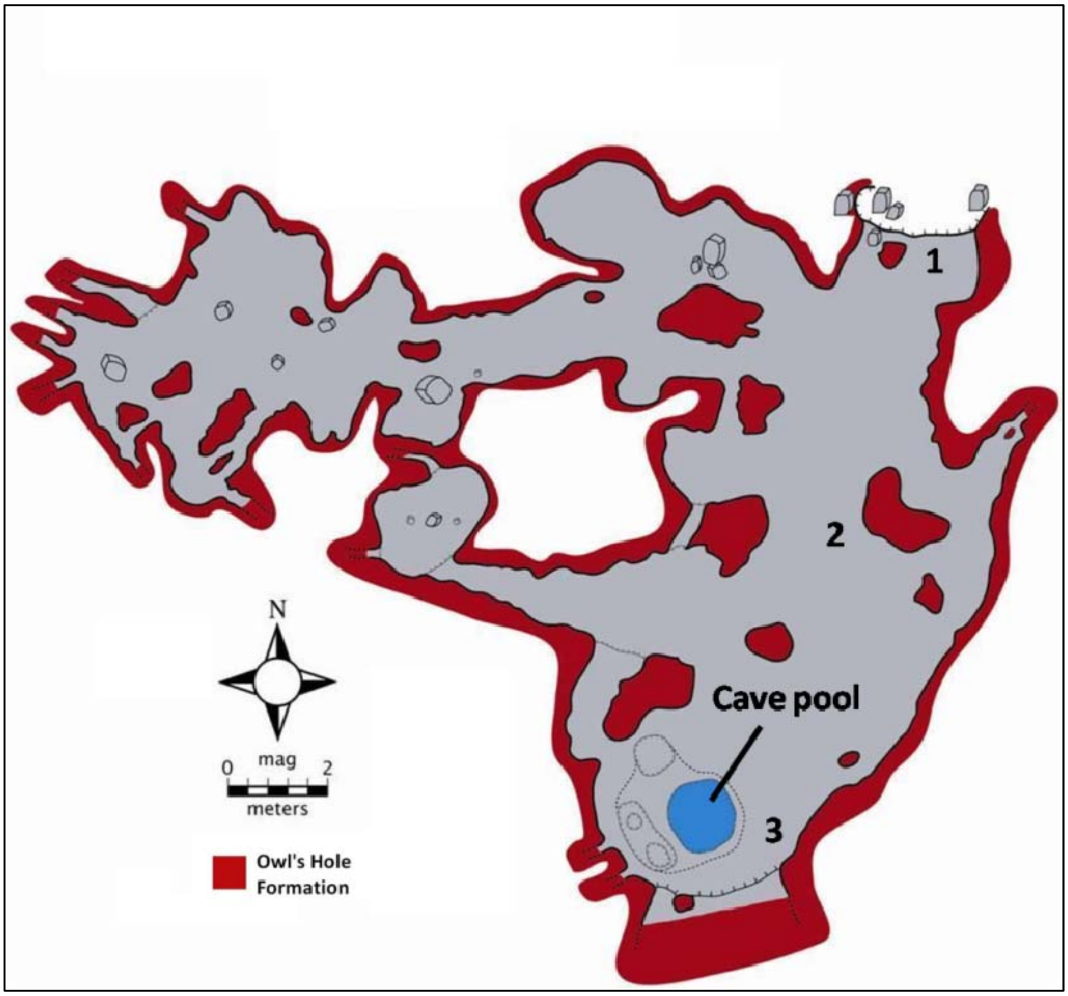

Figure 2.3. Crescent Top Cave, area = 116.4 m^2. Numbers indicate location of air temperature and CO_2 sampling stations: 1) Inside entrance, 2) Mid-passage and 3) Cave rear. *Adapted from Onac et al. (2008).*

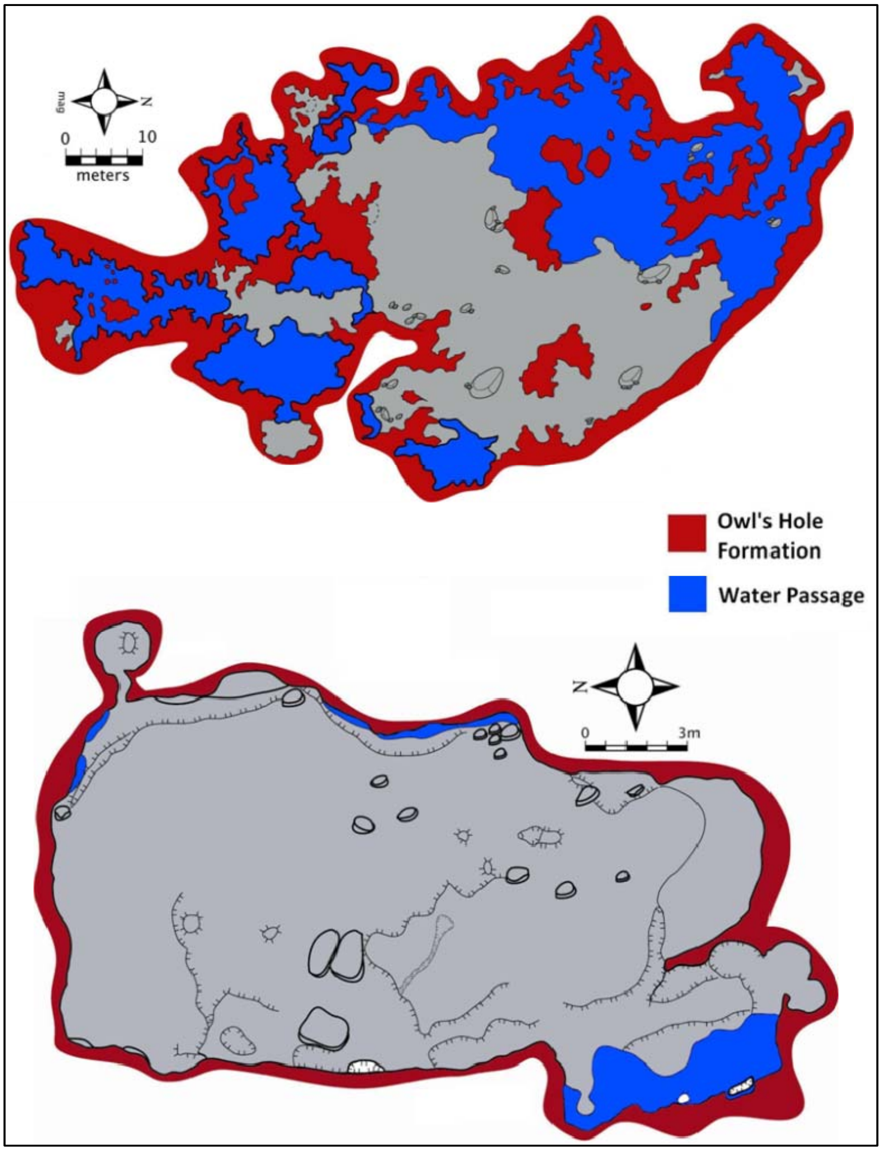

Figure 2.4. Top: Lighthouse Cave, area = 1378 m^2. Bottom: Major's Cave, area = 216 m^2. *Adapted from Onac et al. (2008).*

2.3.2. Sampling Methods

To monitor geochemical variability through 1.5 tidal cycles, waters at Crescent Top Cave and Crescent Pond were sampled at near-hourly intervals beginning at 10:00 am on December 30, 2007 and ending just after 12:00 am on December 31 (a total of 14 hours). This sampling period commenced with an initial low tide at 9:05 am, with additional high and low tides at 3:20 and 9:45 pm, respectively. All water samples analyzed for $\delta^{13}C$ of dissolved inorganic carbon (DIC) were collected using 11 mL vials pretreated with $HgCl_2$ to prevent further biotic reactions that might lead to changes in DIC concentration and resulting carbon isotope fractionation. Vials were sealed with Parafilm prior to capping to eliminate headspace and were refrigerated until analyses were performed. Atmospheric samples were collected in 10-mL septum-capped vials with Kel-F discs and wrapped in Parafilm to prevent leakage (Knohl et al. 2004). Samples were obtained by opening the vials and allowing them to equilibrate for a period of 30 minutes. This was performed at the start of the sampling period to prevent contamination by human respiration accumulating in the cave during hourly sampling intervals. Measurements of temperature, pH, and conductivity were recorded when water samples were collected. Salinity values were calculated using temperature and conductivity data, assuming standard air pressure (Fofonoff and Millard 1983). Temperature loggers were deployed at the surface and at progressively deeper locations inside the cave to monitor cave climate during the geochemical survey (Figure 2.3) and were retrieved on January 4, 2008. Samples of cave and surface atmosphere as well as cave wall rock were collected for $\delta^{13}C$ analyses of CO_2 and host rock, respectively.

Identical procedures were employed when surface waters as well as Lighthouse and Major's caves (Figure 2.4) and open-marine waters at Graham's Harbor were individually sampled in January 2009. When possible, additional measurements of salinity and alkalinity were recorded (when salinity could not be directly measured, it was calculated as above). Finally, water samples were collected in 60-mL polycarbonate bottles for analyses of total organic and inorganic carbon concentration (TOC and TIC, respectively).

2.3.3. Analyses

All $\delta^{13}C$ analyses of water, atmosphere, and rock samples were performed at the Stable Isotope Laboratory in the Department of Geology at the University of South Florida. Analyses of $\delta^{13}C_{DIC}$ were carried out using a gas-source isotope ratio mass spectrometer (IRMS) coupled to a Gasbench II peripheral combining the methods of Torres et al. (2005) and Assayag et al. (2006) and were standardized to VPDB. Analyses of $\delta^{13}C_{CO2}$ were performed using the same instrumentation following the methods of Tu et al. (2001). CO_2 concentration of each sample was determined by gas chromatography (GC) using the GC column built into the Gasbench II. The peak area of mass 44 for the first of 10 replicate peaks was used and standardized with a mixture of CO_2 in He with a concentration of ~3000 ppm.

The inverse values of the concentrations and $\delta^{13}C_{CO2}$ were plotted and fitted with a linear regression to estimate the $\delta^{13}C$ of the source CO_2 (Keeling 1958; Pataki et al. 2003). This estimate was used to help identify the dominant source of CO_2 in the cave. Calculations of pCO_2 from water samples were made using pH and alkalinity data from each site (where available) and the dissociation constants K_1 and K_{CO2} at 25 °C (Stumm and Morgan 1996). These values were plotted against $\delta^{13}C_{DIC}$, TIC, and TOC to identify any correlations that would help explain overall trends in carbon flux at these sites.

Rock samples were ground to produce a homogenized sample, sterilized with 20% hydrogen peroxide, and analyzed for $\delta^{13}C_{carb}$ by reaction with phosphoric acid (Révész and Landwehr 2002). Waters sampled for total carbon concentration were analyzed at the Gerace Research Centre's analytical laboratory using a Shimadzu Total Organic Carbon Analyzer (TOC-5050A). Total carbon and TOC concentrations were measured, with TIC concentrations estimated by subtracting the TOC fraction from the total carbon concentration. Though carbon concentrations were not measured during the 2007-2008 sampling cycle at Crescent Top Cave, DIC concentration was estimated using methods similar to that of CO_2 concentration. The peak area of mass 44 for the first of 10 replicate peaks for each sample was standardized with a mixture of $NaHCO_3$ with a concentration of ~24 µg/L and converted to mmol/L so units were consistent with TOC and TIC data.

2.4. Results

All isotope and geochemical data from Crescent Top Cave and Crescent Pond are summarized in Table 2.1. Similar data for cave and surface waters sampled in 2009 are summarized in Table 2.2.

At Crescent Top Cave and Crescent Pond, no clear geochemical trends were observed that could be related to tidal fluctuation, though water-levels in the pool at the cave fluctuated by approximately 0.5 m. Overall, cave-water temperatures were warmer and less variable than pond waters (Figure 2.5a). Cave water $\delta^{13}C_{DIC}$, conductivity, DIC concentrations, and pH were lower than the pond (Figs. 2b-e). A slight divergence in DIC concentration occurred after 8:30 pm when values at the pond increased whereas cave pool concentration remained relatively constant. The $\delta^{13}C$ value of carbonate wall rock collected from the Owl's Hole Formation in which the cave is dissolved measured -2.9‰.

Measured cave atmosphere temperatures, ranging from 24.4 °C at the cave entrance to 28.8 °C inside, were identical to those reported by Gamble et al. (2000). Values of $\delta^{13}C_{CO2}$ and CO_2 concentrations for replicate samples of surface and cave atmosphere deviated by 0.2‰ and 21 ppm or less, respectively. Replicate values were averaged and are reported in Table 2.1. The $\delta^{13}C_{CO2}$ value was higher at the surface, whereas in the cave the $\delta^{13}C_{CO2}$ values are isotopically more negative. CO_2 concentrations were higher in the cave, showing a slightly decreasing trend towards the rear of the cave. When $\delta^{13}C_{CO2}$ and the inverse of concentrations of replicate samples were displayed on a *xy* scatter plot, the $\delta^{13}C$ value of the *y*-intercept (indicating the primary CO_2 sources) was -23.1‰ (Figure 2.6).

Table 2.1. Water geochemical and atmospheric CO_2 data for Crescent Top Cave and Crescent Pond

Cave and Pond Water							
Cave Pool	Date	Tide Level	Temp (°C)	pH	Cond. (mS/cm)	$\delta^{13}C_{DIC}$ (‰)	DIC Conc. mmol/L)
	12/30/07	rising	28.6	6.93	48.1	-6.1	2.42
	11:15		28.6	7.01	48.6	-6.2	2.43
	12:15		28.6	7.07	48.2	-6.0	2.38
	13:25		28.6	7.34	48.3	-3.9	2.67
	14:40		28.6	7.26	48.2	-6.4	2.41
	16:10	falling	28.5	7.56	48.6	-6.4	2.63
	18:30		28.5	7.33	48.4	-6.1	2.61
	19:40		28.6	7.45	48.3	-5.7	2.45
	20:50		28.5	7.55	48.7	-5.8	2.60
	21:45	low	28.4	7.38	48.5	-6.0	2.39
	22:45	rising	28.5	7.33	48.2	-6.1	2.38
	23:45		28.6	7.61	48.8	-6.2	2.44
Mean			28.6	7.32	48.4	-5.9	2.48
Stdev			0.06	0.21	0.2	0.7	0.10
Crescent Pond	12/30/07	rising	26.2	7.74	52.5	-3.9	2.46
	11:45		26.9	7.70	52.5	-3.4	2.42
	12:30		27.2	8.05	51.6	-3.7	2.36
	14:10		27.9	7.94	52.2	-3.6	2.44
	15:45	high	27.7	7.96	52.7	-3.9	2.46
	17:15	falling	27.4	8.01	52.5	-3.8	2.60
	19:30		26.9	7.77	52.8	-3.8	2.53
	20:35		26.7	7.75	53.0	-4.0	2.47
	22:05	rising	26.5	7.87	52.5	-3.8	2.84
	12/31/07		26.7	7.89	53.0	-4.0	2.65
Mean			*27.0*	*7.87*	*52.5*	*-3.8*	*2.52*
Stdev			*0.1*	*0.12*	*0.4*	*0.18*	*0.13*

Atmospheric CO_2

Location	$\delta^{13}C_{CO2}$ (‰)	Stdev	CO_2	Stdev	1/conc
Surface	-7.5	0.2	379	11	0.00264
Inside	-16.3	0.2	857	21	0.00117
Mid-	-16.0	0.1	827	5	0.00121
Cave rear	-15.9	0.05	823	8	0.00121

Owl's Hole Formation

$\delta^{13}C_{Rock}$ = -2.9‰

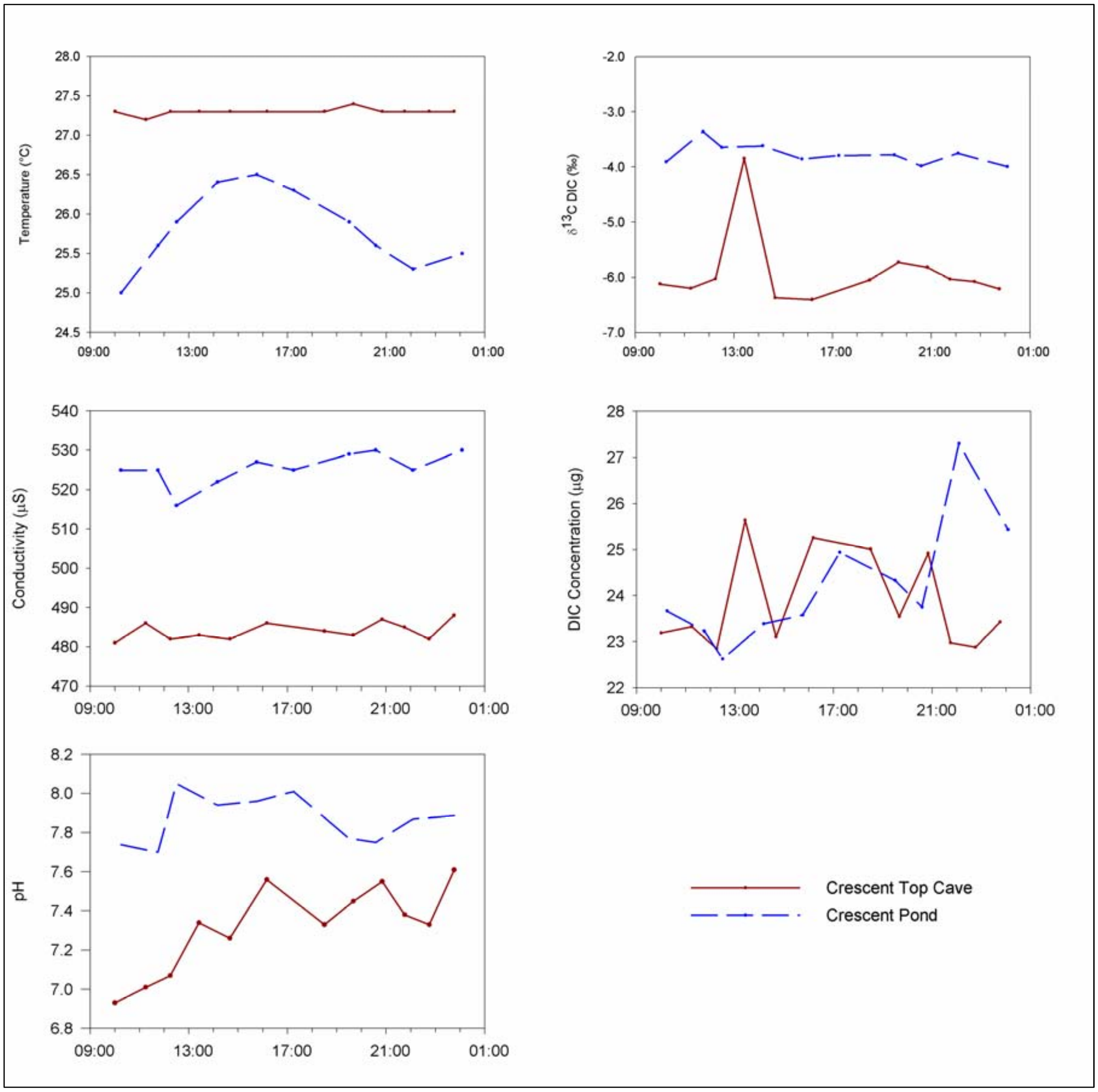

Figure 2.5. Temperature, $\delta^{13}C_{DIC}$, conductivity, DIC concentration and pH of Crescent Top Cave pool and Crescent Pond, December 30-31, 2007.

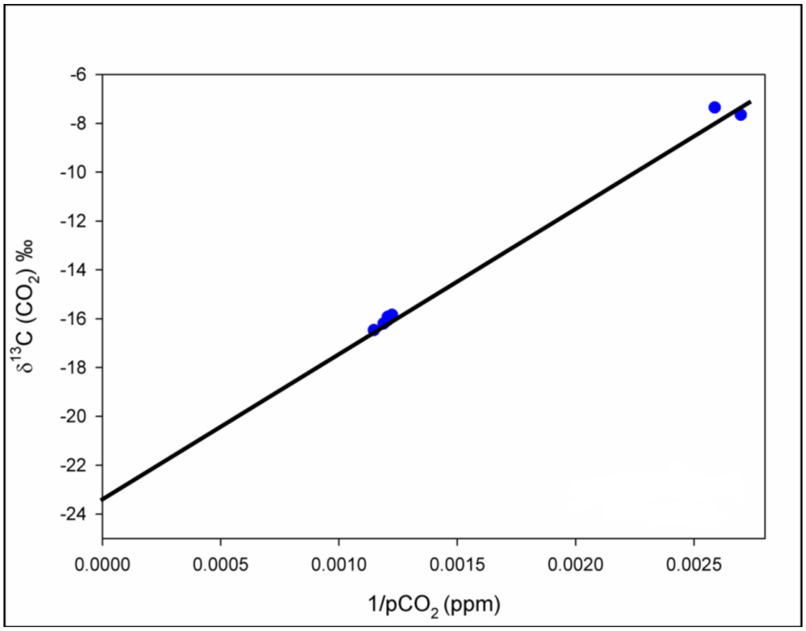

Figure 2.6. $\delta^{13}C$ of CO_2 versus concentration at Crescent Top Cave. Regression: $y = 5910x - 23.14$, $r^2 = 0.996$.

Isotope and geochemical data collected from cave and surface water bodies in January 2009 are summarized in Table 2.2. Salt Pond and Fresh Lake were geochemical outliers compared to the remaining surface water bodies, with the highest pH and carbon concentrations and lowest pCO_2. In addition, salinity and conductivity at Salt Pond was the highest, while $\delta^{13}C_{DIC}$ was the most negative. Despite their close proximity, ponds in the northeastern cluster displayed a variety of different isotopic and geochemical compositions, with salinities ranging from normal at Crescent, Moonrock, and Oyster ponds, to slightly hypersaline with higher pH, alkalinity, and TOC concentrations at Reckley Hill and Osprey ponds. Isotopic and geochemical characteristics at Lighthouse and Major's caves also differed from one another, with Lighthouse Cave having a much higher conductivity, lower pH, and the highest pCO_2 of any of the waters sampled in 2009. Carbon concentrations and alkalinity were similar at both caves, as were their $\delta^{13}C_{DIC}$ values, which were more negative than the remaining water bodies with the exception of Salt Pond.

Table 2.2. Geochemical summary of 2009 surface and cave samples. Fresh Lake and Lighthouse Cave collected 1/3/09; all remaining samples collected 1/4/09

Location	**Temp (°C)**	**Salinity (PSU)**	**Cond. (mS/cm)**	**pH**	**Alk. (mg/L)**	***p*CO_2 (atm)**	**TIC (mmol/L)**	**TOC (mmol/L)**	**$\delta^{13}C_{DIC}$ (‰)**
Reckley Hill	22.3	41.4	58.3	8.17	146	4.96E-11	1.66	0.47	-2.26
Crescent	23.2	36.2	53.6	7.85	128	1.18E-10	1.88	0.00	-3.69
Moonrock	24.3	36.4	54.1	8.06	125	7.46E-11	1.72	0.00	-3.53
Oyster	23.8	38.1	55.6	7.83	139	1.14E-10	1.94	0.00	-4.66
Osprey	24.8	55.2	78.8	8.12	141	5.76E-11	1.88	0.94	-1.34
Salt Pond	24.6	78.6	106.2	8.75	128	1.49E-11	0.83	2.55	-11.59
Mermaid	24.2	34.8	51.8	7.73	152	1.31E-10	1.83	0.03	-4.19
Little Lake	24.1	44.6	65.6	8.24	133	4.63E-11	1.77	0.54	-1.21
Fresh Lake	24.9	32.7	49.9	8.53	226	1.40E-11	3.43	3.59	-3.29
Lighthouse	26.6	33.0	52.0	7.21	177	3.73E-10	2.38	0.00	-6.51
Major’s	23.1	24.4	37.0	8.00	153	7.00E-11	2.10	0.00	-6.46
Graham’s	26.8	35.2	55.2	8.04	101	9.67E-11	1.38	0.02	0.31
Average	*24.4*	*40.9*	*59.8*	*8.04*	*146*	*9.66E-11*	*1.90*	*0.68*	*-4.04*
Stdev	*1.3*	*14.0*	*17.6*	*0.39*	*30*	*9.50E-11*	*0.61*	*1.18*	*3.13*

Geochemical plots showed few regressions illustrated any relationship between the specific geochemical parameters plotted; however, when geochemical outliers such as Salt Pond and Fresh Lake or the caves were omitted, r^2 values typically increased, illustrating the diversity of factors affecting the geochemical composition of waters on San Salvador Island (Table 2.3). With some exceptions, $\delta^{13}C_{DIC}$ values are correlated to TIC and TOC concentration, pCO_2, and conductivity, TIC concentrations are correlated to alkalinity, and TOC concentrations are correlated to pCO_2 and conductivity.

Table 2.3. Regressions for 2009 surface and cave water geochemical analyses

Variables		All Samples		Excluding Outliers		
x	*y*	Regression	r^2	Regression	r^2	Outliers
Conductivity	$\delta^{13}C_{DIC}$	*y*=-0.070*x*+0.18	0.16	*y*=0.14*x*-11.22	0.44	Salt Pond, Fresh
pCO_2	$\delta^{13}C_{DIC}$	*y*=-4.16E9*x*-3.11	0.016	*y*=-3.41E10*x*-0.11	0.78	Salt Pond, Fresh
TIC	$\delta^{13}C_{DIC}$	*y*=1.052*x*-6.033	0.043	*y*=-7.21*x*+10.10	0.72	Salt Pond, Fresh
TOC	$\delta^{13}C_{DIC}$	*y*=-0.76*x*-3.52	0.083	*y*=3.35*x*-3.93	0.82	Salt Pond, Fresh
Alkalinity	TIC	*y*=0.017*x*-0.62	0.77	*n/a*	*n/a*	*n/a*
Conductivity	TOC	*y*=0.030*x*-1.13	0.20	*y*=0.045*x*-2.37	0.96	All except
pCO_2	TOC	*y*=-5.95E9+1.25	0.23	*y*=-2.42E10*x*-2.55	0.66	Caves

2.5. Discussion

The complexity of San Salvador's hydrologic regime is well represented by the data generated in this study, yet some discernable trends are present and were similar to monthly conductivity and carbon concentration data collected by Rothfus following this study (2009, unpublished data). Overall, proximity to the ocean, proximity to one another, and water volume do not appear to be useful, independent predictors of geochemistry for water bodies on San Salvador Island, underscoring the intricacy and small-scale spatial variability of the island's hydrologic system; however, a few relationships between geochemical parameters can be discerned. Furthermore, the configuration of conduits and fractures in the subsurface and the source waters moving through them are probably not the only factors to consider when studying geochemical patterns of some of the island's water bodies. Whereas these conduits and fractures are important, surface geomorphologic factors, such as elevation, topography and water-basin geometry, geographic factors, such as landscape features and vegetation, and biotic factors, such as algal and bacterial respiration, also influence water geochemistry in the surface ponds and lakes. These influences may be transmitted to the subsurface directly through conduit flow, or indirectly through seepage, and affect mixing-dissolution processes.

2.5.1. Crescent Top Cave and Crescent Pond

At Crescent Top Cave and Crescent Pond, changes in water chemistry resulting from tidal fluctuation were not observed, though water-levels at the cave pool visibly changed during this time. Variability in water-level was not directly observed at Crescent Pond, although semi-diurnal variations in water-level up to 0.3 m were recorded here by Crump and Gamble (2006) representing approximately half the average tidal range in this area (see below). The presence of tidally influenced water-level fluctuations and the absence of concurrent geochemical changes support their hypothesis that water-levels at Crescent Pond fluctuate by hydrostatic pressure produced from tides, forcing water through the conduit from the ocean toward the pond. Though water is moving through the conduit, water and geochemical exchange between the ocean and the cave (and between the pond and the cave) may be minimal, except when water surges more forcefully through the conduit during the highest high tides as described by Davis and Johnson (1989), which are most likely to occur in association with spring tides and storm surges. The spring tide range reported by the National Oceanic and Atmospheric Administration at the San Salvador Airport is 0.85 m (referenced to Mean Lower Low Water, MLLW). High tide levels recorded during our sampling period varied between 0.61 and 0.64 m, well below the spring-tide range. Further, the last quarter phase of the moon occurred on December 31, indicating tides were in their neap range. This makes it unlikely that exchange in pond and marine water occurred during the sampling period, explaining the lack of geochemical fluctuation.

If little variation in geochemistry is occurring at the pond most of the time, it is unlikely much variation will be occurring in the pool at Crescent Top Cave. Though the cave and the pond are connected by a conduit (Gamble et al. 2000), the flow between them may be similar, albeit on a shorter spatial scale, to that between the pond and the ocean such that except during extreme high tides, little to no exchange occurs. This allows for the evolution of independent water geochemistries based on the differing processes affecting each body. Mean conductivity at the cave pool was 4.12 mS/cm lower than the pond and may be explained by the infiltration of freshwater from seeps flowing into the pond. Meanwhile, pool pH was 0.55 units lower than the pond and could be explained by diffusion of higher concentration atmospheric CO_2 from the cave into the pool. Groundwater $\delta^{13}C_{DIC}$ values are often lower than ocean and marine limestone values due primarily to the ^{13}C-depleted carbon produced by bacterial respiration (Clark and Fritz 1997). Though the majority of water in Crescent Top Cave is sourced from Crescent Pond, it is largely confined to the conduit and becomes part of the groundwater system and subject to the same redox reactions imparted by bacterial activity. If the bacteria are organotrophic, CO_2 would be released as a byproduct of the respiration, which would lower the pH and trigger dissolution. Migration of the seep-derived freshwater toward Crescent Pond may also influence dissolution by mixing with marine-derived conduit waters and lowering the saturation state. These hypotheses may explain why the average pH and conductivity at the cave are slightly lower at the cave relative to the pond.

2.5.2. Surface Ponds

Despite their close proximity, the geochemistry of the northeastern cluster of surface ponds (Reckley Hill, Crescent, Moonrock, Oyster, and Osprey ponds) varied from one another and even ponds with similar dimensions and volumes, such as Oyster, Osprey, and Mermaid, had varying geochemical signatures. Salt Pond was geochemically anomalous in salinity/conductivity, pH, TOC, TIC, $\delta^{13}C_{DIC}$, and pCO_2 (Tables 2.2-2.3). Fresh Lake was also an outlier in pH, alkalinity, TIC, TOC, and pCO_2. When data from these locations were removed from regression analyses, relationships between geochemical parameters became more apparent (Table 2.3). For example, the relationship between $\delta^{13}C_{DIC}$ and TIC concentration is obscured when all waters sampled are included, but r^2 improves from 0.043 to 0.72 when Salt Pond and Fresh Lake are omitted. At Salt Pond, $\delta^{13}C_{DIC}$ measured -11.59‰ and was much lower than all water bodies sampled, indicating dissolution of limestone by CO_2 of a biotic origin with a $\delta^{13}C$ value of approximately -23‰, representing C_3 vegetation (Salomons and Mook 1976). Concentration of TIC and alkalinity at Fresh Lake were the highest, measuring 3.43 mmol/L and 226 mg/L, respectively. Values of $\delta^{13}C_{DIC}$ did not appear to be related to pCO_2 at either water body, unlike the remaining inland surface waters (Table 2.3), though TIC did seem to be related to alkalinity regardless of location, largely due to the influence of HCO_3^- at this pH (Clark and Fritz 1997). At Salt Pond, conductivity/salinity was highest of all waters sampled (106.2 mS/cm and 78.6 PSU, respectively), despite being less than 75 m from the ocean, illustrating that no open-marine conduit exists and that conductivity/salinity is largely governed by evaporative concentration, although it may also be influenced by runoff from the surrounding landscape. Low pCO_2 and low TIC combined with high TOC suggests photosynthesis is occurring (likely by calcareous algae known to colonize the island's hypersaline lakes) simultaneously with the accumulation of organic matter, similar to conditions caused by algal blooms. This hypothesis is supported by a dissolved oxygen measurement obtained during this study, with a salinity-corrected saturation of 68%, indicative of algal bloom conditions (Lewis 2006). Although low pCO_2 and high pH preclude dissolution at Salt Pond at the time of sample collection, its $\delta^{13}C_{DIC}$ value suggests that dissolution utilizing biogenic CO_2 produced during organic decomposition does occur. Carbon concentration data collected at Salt Pond monthly from January to October 2009 by Rothfus (2009, unpublished data) show TIC concentrations increase in relation to TOC in the summer when salinity and conductivity was low, and might reflect dissolution (Figure 2.7a). Further geochemical analyses of pH and $\delta^{13}C_{DIC}$ would be necessary to confirm this hypothesis. In contrast, TIC and TOC concentrations at Fresh Lake are the highest of all water bodies sampled while $\delta^{13}C_{DIC}$ and conductivity/salinity falls within range of many surface-water bodies. Low pCO_2 suggests that primary productivity is high, evidenced by the high TOC concentration and the prevalence of algae and cyanobacteria visually observed in the water; however, high TIC concentration coupled with near-marine conductivity measured here sets Fresh Lake apart from the model of organic activity developed for Salt Pond. One explanation for this difference might be an increase in organic productivity resulting from direct or indirect input of pollutants from nearby residential development and the adjacent road, which parallels the lake along its western shore. This could be addressed by sampling nitrate, ammonia, and phosphate levels, along with testing for other water-quality parameters, such as fecal coliform counts, which would indicate whether pollutant sources, including septic systems, animal waste from pets and livestock (i.e., goats, feral cattle), leakage of fuel drums, and runoff of detergents and/or vehicle fluids, were affecting Fresh Lake.

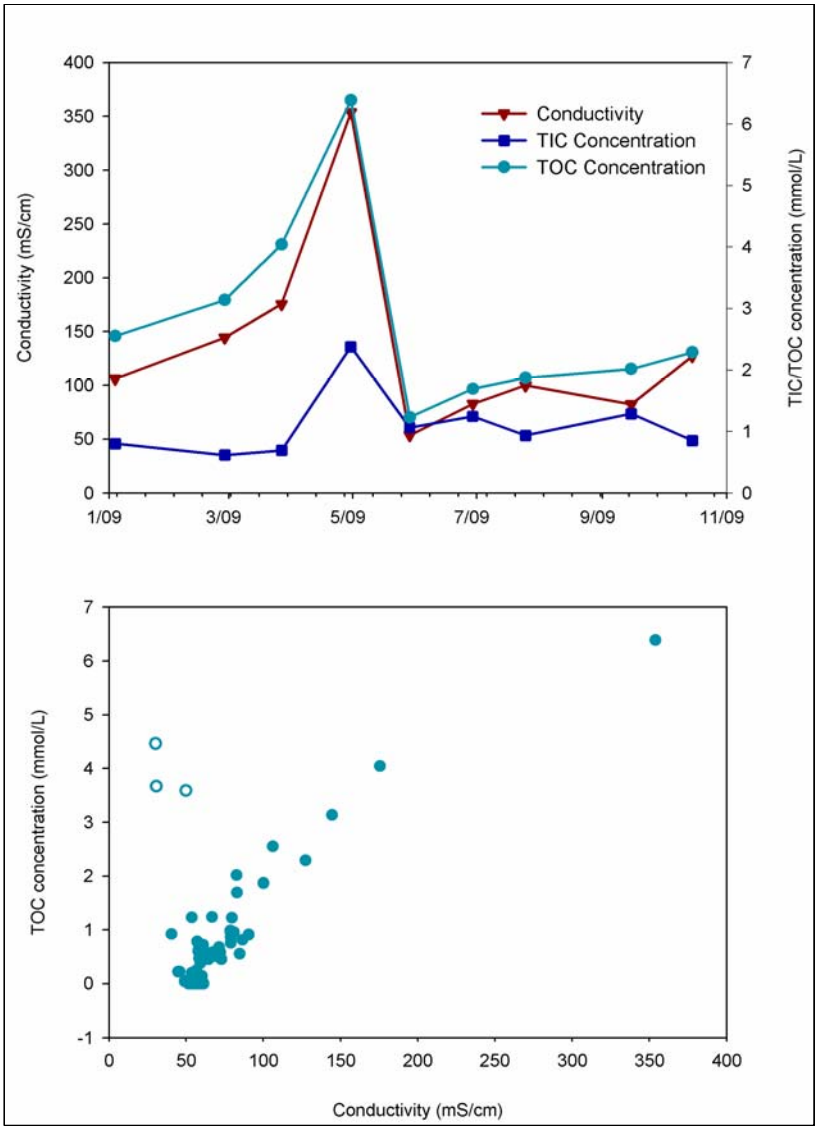

Figure 2.7. Top: Monthly conductivity (triangles), TIC (squares) and TOC concentrations (circles) for Salt Pond. Bottom: TOC versus conductivity for Reckley Hill, Osprey and Salt Ponds, and Little Lake (closed circles) and Fresh Lake (open circles). Regression (all data): $y = 0.37x - 11.34$, $r^2 = 0.45$. Regression excluding Fresh Lake: $y = 0.43x - 18.60$, $r^2 = 0.85$. *Unpublished data from Rothfus (2009).*

Apart from Salt Pond and Fresh Lake, connectivity to the ocean appears to exert the dominant control over conductivity/salinity of surface waters, with secondary influences provided by evaporation and runoff. This is evidenced by the near marine-conductivity/salinity values (~55 mS/cm and 36 PSU, respectively) of water bodies with known conduit connections to the ocean including Crescent Pond, Oyster Pond, Little Lake, and Reckley Hill Pond (Table 2.2). To a lesser degree, connectivity to the ocean is also associated with $\delta^{13}C_{DIC}$, as these values generally display a positive, though weak correlation with conductivity/salinity (Table 2.3); however, the low r^2 value of 0.44 suggests that other factors, including mixing of waters and/or biotic processes such as photosynthesis, also influence $\delta^{13}C_{DIC}$. $\delta^{13}C_{DIC}$ values of marine water are highest at 0.31‰, whereas subsurface waters sampled from the caves have the lowest values in the study (with the exception of Salt Pond) at -6.51 and -6.46‰ at Lighthouse and Major's caves, respectively, implying that surface ponds and lakes with intermediate $\delta^{13}C_{DIC}$ values represent mixing between these sources and/or the progressive alteration of marine values through water-mineral reactions or photosynthesis. Finally, due to the negative relationship between $\delta^{13}C_{DIC}$ and TIC (Table 2.3), each may be a useful predictor the other. This might be explained by pCO_2, which increases with decreasing $\delta^{13}C_{DIC}$ in the inland water bodies (Table 2.3). Since CO_2 is a component of both DIC and TIC and biotically sourced carbon has the lowest $\delta^{13}C$ values, we can interpret that the TIC in most inland water bodies is at least partially dependent on the availability of biotically sourced CO_2 in the water. A weak, negative relationship between TOC and pCO_2 exists that becomes much stronger (0.43 increase in r^2) when Lighthouse and Major's caves are omitted from the regression, illustrating that when TOC is high, pCO_2 is low (Table 2.3). This suggests photosynthesis is the cause, as this process is restricted in caves. It is also a clear indicator of which water bodies have organic activity dominated by photosynthesis, supported by the positive relationship between $\delta^{13}C_{DIC}$ and TOC concentration (Table 2.3). As the relative concentration of organic carbon increases, $\delta^{13}C_{DIC}$ comprised of biotically sourced CO_2 is decreasing due to consumption by photosynthesizers. The consumption of organic carbon increases the proportion of abiotically sourced inorganic carbon, such as HCO_3^- released during limestone dissolution, which is represented by higher $\delta^{13}C_{DIC}$ values. Consequently, we predict that primary productivity is highest in Fresh Lake and Salt Pond, and to a lesser degree, Osprey and Reckley Hill ponds, and Little Lake. With the exception of Fresh Lake, the above-mentioned water bodies also contain the highest conductivity/salinity, and a strong correlation exists between TOC and salinity/conductivity at these sites (Table 2.3) that is also present in the long-term data (Figure 2.7b). This is expected as algae, cyanobacteria, and other microorganisms visibly flourish in hypersaline ponds and lakes on San Salvador and affect their water color in aerial and satellite images.

2.5.3. Cave Pools

Waters at both Lighthouse and Major's caves are governed by marine conduit flow, with $\delta^{13}C_{DIC}$ values lower than surface waters and within the range of groundwater DIC influenced by open-marine water (Clark and Fritz 1997). Both have no measurable TOC, and are in the upper range of TIC concentrations for this study at 2.38 and 2.10‰ for Lighthouse and Major's caves, respectively. If TOC concentrations of the island's water bodies are driven by rates of primary productivity, no organic carbon would be expected to accumulate in caves devoid of sunlight unless it was transported from the surface. This assumption also suggests that organic carbon transported through the limestone from surface soils and organic mats at the bottom of water bodies via the downward migration of water is either trapped or consumed by bacteria in the pore space of the rock such that it has little influence on the geochemistry of water in fractures and conduits. Therefore, subsurface water geochemistry in these areas (typified by cave waters) might be governed more by the interactions between water and surrounding limestone than by interactions between meteoric water and soils and/or pore spaces. While marine water supplies some inorganic carbon to the groundwater, additional inorganic carbon would come from the dissolution of limestone by undersaturated waters, particularly at the halocline. In addition, if organic carbon from the surface is being consumed rather than trapped in the pore space of limestone, byproducts of this consumption (e.g., CO_2 and H_2S, depending on the bacterial communities present and redox conditions) may combine with pore water to cause dissolution within the rock itself, releasing DIC from the rock that it is carried by waters into conduits and fractures, including caves. A relatively low pH of 7.21 in conjunction with a relatively high pCO_2 of 3.73×10^{-10} atm at Lighthouse Cave suggests that dissolution is occurring in the cave, as evidenced by the corrosion of speleothems in some of its flooded passages. At Major's Cave, pH and pCO_2 are higher and lower than at Lighthouse Cave, respectively, suggesting that dissolution might be occurring elsewhere prior to the water being transported to the cave pool. Collectively, these data suggest active dissolution of the limestone is occurring in the subsurface, and might be attributed to CO_2 production by heterotrophic bacteria (Schwabe et al. 2008), as evidenced by low $\delta^{13}C_{DIC}$ values.

2.5.4. Geographic and Topographic Controls

Though subsurface hydrology represented by connectivity to the ocean affords a primary control on the geochemical characteristics of San Salvador's water bodies, the irregular configuration of subsurface conduits and fractures means that the proximity of surface water bodies to both the ocean and one another cannot be used to predict their geochemical composition. Likewise, though relationships exist between certain geochemical parameters as discussed above, their relatively low r^2 values suggest that other factors affecting the geochemistry of these waters are at work, such as complex mixing of various sources. This could be addressed by expanding this study to include a wider array of sampling locations, particularly on other carbonate islands, coupled with physical measurements of water flow patterns and velocities from conduits, caves, and wells. Surrounding landscape (i.e., ecological communities, human development) and topography (which controls the basin geometry of the surface-water bodies), also are important factors to consider. For example, despite their close proximity to one another, the geochemical composition of surface-water bodies in the northeastern cluster of ponds and lakes were quite variable. In particular, Osprey and Oyster ponds are located approximately 50 m apart, yet Osprey Pond has higher values for most geochemical parameters measured, particularly conductivity/salinity and TOC concentration. This geochemistry might be attributed to a more restricted connection to the open ocean as discussed above; however, Osprey Pond is loosely connected to an arm of the hypersaline Blue Pond at its southwestern margin. A man-made dam was constructed between the two in the 1800s and used as a walkway for British colonials navigating the island via its inland lakes. Because the dam is earthen, seepage of hypersaline water through the dam to Osprey Pond is the likely source of its additional conductivity/salinity. If Osprey Pond was not connected by a conduit to the ocean as is the case in the nearby Oyster Pond, we would expect that continuous seepage from Blue Pond would elevate conductivity/salinity beyond those values observed here. This regulation of conductivity/salinity is evidence for a marine conduit at Osprey Pond, which perhaps may be part of the same conduit feeding Oyster Pond. If this is the case, this conduit may have influenced the geochemistry of Blue Pond prior to the construction of the earthen dam, underscored by the dramatic water color difference between the two ponds.

Topographic control on surface water bodies is clearly visible by the distribution of linear ponds and lakes situated in swales with ridge elevations ranging from 6 to 24 m amsl. Crescent and Salt ponds and Fresh and Little lakes fall into this category, while the remaining surface-water bodies formed via collapse features in the karst landscape.

If the water body lacks a marine conduit to regulate salinity (such as that present at Crescent Pond and Little Lake), these water bodies become hypersaline. In addition, elongate catchment morphology funnels sediment runoff from the surrounding ridges into the swales, which should add to the supply of ions in the water, thus pushing conductivity levels even higher. To test this, major ion compositions of surrounding soils and their concentrations should be compared to that of the linear ponds and lakes to more effectively model the contribution of runoff to water geochemistry.

2.5.5. Biotically Influenced Dissolution

The data presented here suggest the geochemistry of both surface and subsurface waters on the island is more influenced by biotic processes than once thought. Primary productivity dominates surface waters on San Salvador Island; however, low $\delta^{13}C_{DIC}$ in the subsurface coupled with relatively higher inorganic carbon concentrations suggest that bacteria may be living in the pore spaces of the limestone which consume organic carbon filtered down from the surface, and whose byproducts might provide another source of dissolution. Heterotrophic bacterial activity has been previously documented within both quarry and building limestones, particularly near the interface of rock and air/water where geochemical exchange rates would be highest (Paine et al. 1933; Schwabe et al. 2008). Recent studies on San Salvador Island and in other areas of The Bahamas suggest that mixed groundwaters, such as those found at the halocline, are not as undersaturated as once thought (Moore et al. 2006), and that the role of bacteria on dissolution both in the phreatic and the vadose zones was potentially overlooked (Bottrell et al. 1991, 1993; Mylroie & Balcerzak 1992). Those authors suggested that bacteria, feeding on varied sources of carbon from the surface provide an unaccounted source of CO_2 sufficient to drive dissolution in the phreatic zone, and perhaps also in the vadose zone. Because rainwater pH is almost immediately buffered upon contact with limestone, and Bahamian soils are thin and nutrient-poor (supporting only C_3 scrub vegetation), dissolution via meteoric water and dissolved soil CO_2 by heterotrophic bacteria was considered minor, underscoring the importance of *in situ* production of CO_2 by heterotrophic bacteria in carbonic acid dissolution of limestone. Though soils are thin and poor, scrub forests are abundant on the island, as surface water basins and wetlands, collecting organic matter. This organic matter provides an ample source of carbon for heterotrophic bacteria living in the underlying limestone. Since aerobic heterotrophic bacteria require oxygen, we can estimate they are most abundant at rock/air or rock/water interfaces such as outcrops at the surface, cave walls, or conduits receiving oxygenated marine water. To better assess this, long-term observations of the geochemical parameters tested here coupled with calcite saturation indices should be carried out in both surface and subsurface waters. In addition, algal and bacterial species from each pond as well as vadose and phreatic rock samples (when possible), should be identified and enumerated to characterize the nature of the biota at each location and their impacts on the geochemistry.

2.5.6. Broader Application

Care should be taken when using these data to construct and interpret regional-scale hydrologic, dissolution, or carbon cycling models because the unique characteristics observed at the locations in this study demonstrate the heterogeneity of even small carbonate platforms. Minor variations in latitude, sea-level/elevation, and platform size can exert a significant control on the hydrologic regime, and by default, dissolution, by way of feedbacks between surface and groundwater and climate, geomorphology, and vegetation. Nevertheless, the results from this research suggest that the methods used are valuable as a comprehensive, first-order approach to tailoring existing or establishing new hydrologic and/or dissolution models for carbonate platforms. Coupling $\delta^{13}C$ analyses with a suite of geochemical parameters reveals indications of patterns and processes even in complex hydrologic regimes that may be further explored in more targeted studies. Furthermore, the methods utilized in this study are relatively simple and inexpensive, and can be applied to most, if not all, carbonate/karst settings.

2.6. Conclusion

Despite San Salvador Island's diminutive size relative to some karst settings, it is a dynamic environment with a complex suite of factors influencing the geochemistry of its waters. First and foremost of these is the water body's degree of connectivity to open marine water, which is not governed by proximity to the ocean or basin volume. Conduit flow and tidal flux are primary regulators of salinity and conductivity, and are influenced by island topography as well as subsurface geomorphology. Evaporation is a dominant control on salinity and conductivity in surface-water bodies where marine flow is restricted. Variations in salinity and conductivity as well as the location of the water body (at the surface or in the cave) influence the degree of photosynthesis in the surface waters, which in turn drive changes in TIC, TOC, and $\delta^{13}C_{DIC}$ of these waters. The second factor influencing the geochemistry of these waters may be explained by both natural and man-made variations in the landscape that influence runoff patterns and can provide a minor control on the connectivity of the water bodies. The degree of connectivity to the ocean and the surrounding landscape both seem to drive biologic processes, such that variations in salinity/conductivity as well as the location of the water body (at the surface or in the cave) influence the degree of photosynthesis in the surface waters, which in turn drive changes in TIC, TOC, and $\delta^{13}C_{DIC}$. Little to no TOC in cave waters compared to surface waters demonstrates that TOC leached from soils and organic mats by meteoric water at the surface is consumed prior to that water recharging the conduits and fractures. Relatively higher TIC concentrations and pCO_2 in the conduits suggests that some dissolution is happening in the subsurface. The absence of organic carbon in these waters combined with evidence of dissolution suggests organic carbon is consumed in the rocks by heterotrophic bacteria that in turn, acidify the water with metabolic byproducts (e.g., CO_2 by organotrophic communities). The biotic contribution to dissolution may require a revision to the mixing-dissolution models developed for carbonate islands and warrants further study to identify the magnitude of their influence. The methods utilized in this study can be applied as a simple, first-order approach to addressing this on other carbonate islands (and may also be used to address dissolution models in other carbonate settings). This more precise understanding of dissolution will allow for better estimates of dissolution rates on carbonate platforms, with implications for obtaining more accurate estimates of limestone dissolution's role on both CO_2 drawdown and the global carbon cycle.

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CHAPTER 3:

THORNTON'S CAVE PART 1: CLIMATE, HYDROLOGIC AND CARBON DIOXIDE PROFILES OF THORNTON'S CAVE, WEST-CENTRAL FLORIDA (USA)

3.1. Introduction

Speleogenesis and the evolution of karst terrains are dictated by a variety of factors including the depositional and geologic history of the landscape, climate and sea-level fluctuation, and local hydrology (Palmer, 2007). These factors work in concert to drive the geomorphology of cave systems and their understanding is critical to determining other cave processes, specifically the rainfall and dissolution of calcium carbonate and biogeochemical reactions. The availability and flow of water through a cave system is considered the primary agent governing these processes by serving as a primary vector of geochemical transport into and out of the cave. Air is another vector of geochemical transport, controlled by the degree of openness of the cave to the surface as well as surface climate, which drives the density and pressure contrasts that act to push air into and out of the cave. Surface climate also controls hydrologic patterns by governing hydrologic inputs and sea-level, which impact speleogenesis on a variety of time scales from the enlargement of existing caves to the deposition of sediments necessary to form the initial limestone settings which are then subjected to karstification and speleogenesis. Collectively, these processes establish the framework that governs the abiotic and biotic processes occurring in the cave—the latter of which is the primary focus of this dissertation. In this chapter we explore the climate, hydrologic and carbon dioxide (CO_2) profiles (including CO_2 production in cave substrates) of Thornton's Cave in West-Central Florida over a two-year period beginning in late March, 2007. These observations were critical in supporting the interpretations of a biogeochemical survey simultaneously conducted at this site, whose main objective was to determine whether microorganisms were contributing to the cave's dissolution (see Chapter 4).

3.2 Regional Setting

The karst region of West-Central Florida is part of a karst belt that extends from the Florida Panhandle to just south of Tampa Bay (Figure 3.1). Topographic highs in this region are dominated by the Brooksville Ridge and the larger Ocala Platform, which serve as regional boundaries for the Withlacoochee River basin. Surface stratigraphy is dominated by Middle Eocene to Late Oligocene limestones comprising the Avon Park Formation as well as the Ocala and Suwannee Limestones (Figure 3.2). In the Brooksville Ridge and Ocala areas, the uppermost portion of the Ocala Limestone, and in places, the Suwannee Limestone, were eroded during the Oligocene. This was followed by infilling of sinks and solution pits of the remaining Ocala Limestone with Miocene and younger sediments (Yon and Hendry, 1992). As a result, the highly porous Ocala Limestone is the primary unit containing the Floridan Aquifer in West-Central Florida, with active circulation of groundwater contributing to the region's karstification (Stringfield and LeGrand, 1966; Lane, 1986). With the exception of the Withlacoochee River, surface streams are precluded and the majority of surface waters exist as springs, sinkhole ponds, and wetlands adjacent to the river.

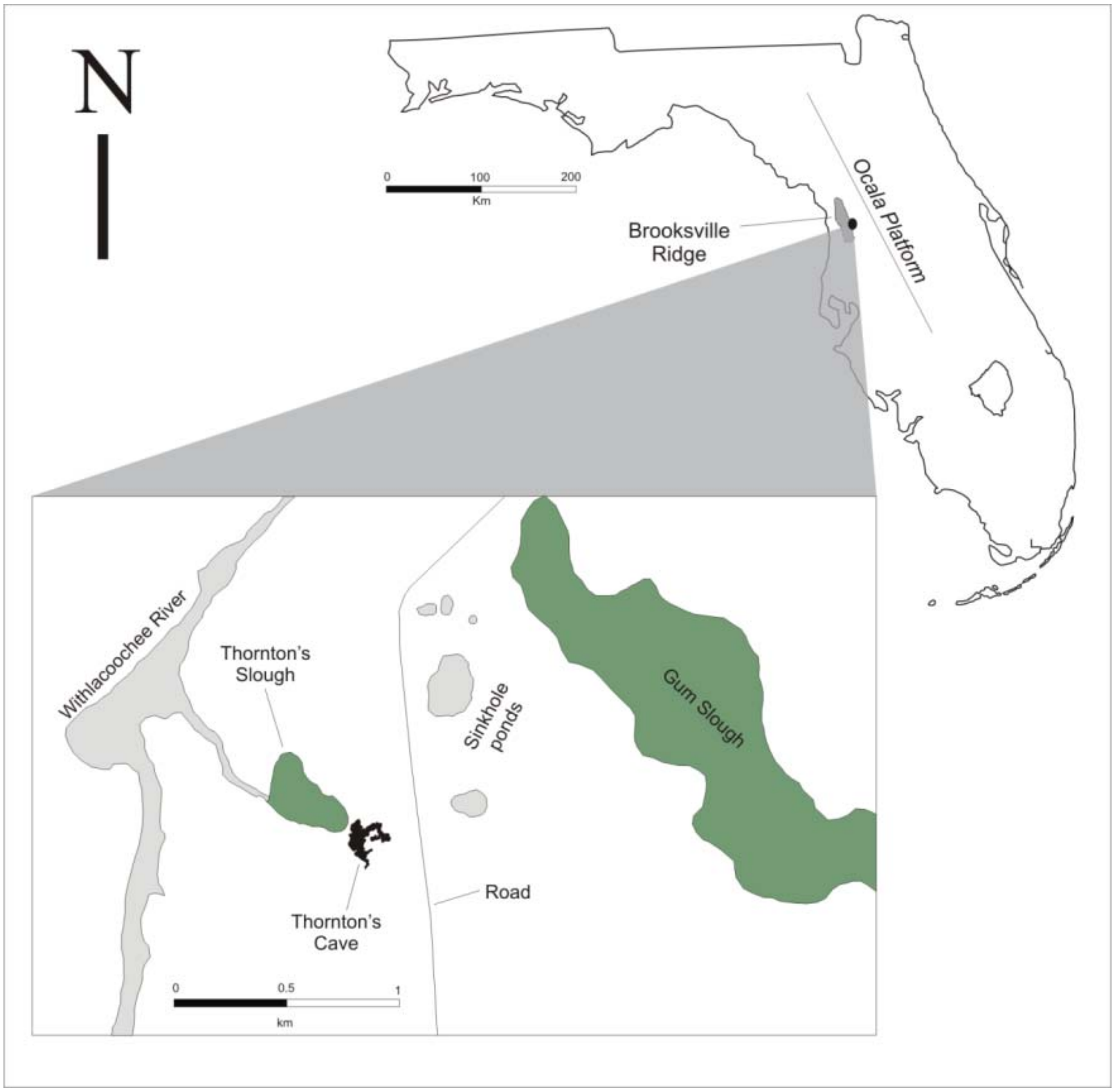

Figure 3.1. Regional map of Thornton's Cave area.

System	Series	Lithostratigraphy
Quaternary	Holocene and Pleistocene	Alluvium
		Undifferentiated Deposits (Caloosahatchee Marl and Bone Valley, Alachua, & Tamiami Formations)
Tertiary	Pliocene	
	Miocene	Hawthorne Formation
		Tampa Limestone
	Oligocene	Suwannee Limestone
	Eocene	Ocala Limestone
		Avon Park Formation
		Oldsmar Formation
	Paleocene	Cedar Keys Formation

Figure 3.2. Stratigraphy of West-Central Florida. *Adapted from Miller (1984) and Randazzo (1997)*.

Wet and dry caves of various sizes and morphologies occur throughout West-Central Florida (including submerged caves on the West Florida Shelf) and are largely aligned with marine terraces formed during sea-level high- and lowstands, indicating their formation was driven by glacioeustatic sea-level fluctuation (Florea et al., 2007). Local variations in lithology and the position of the groundwater table, however, are believed to exert a minor control on speleogenesis as well. In particular, Florea et al. (2007) hypothesized that recharge to the Floridan Aquifer by the Withlacoochee River combined with reduced permeability from riverine sediment infilling the pore space of the underlying limestone may locally raise the groundwater table such that dissolution in association with Plio-Pleistocene sea-level fluctuation is reactivated, allowing speleogenesis of caves in this area to occur over multiple generations.

3.3. Thornton's Cave

Thornton's Cave is in western Sumter County, Florida, less than 1 km east of the Withlacoochee River on privately owned land (Figure 3.1 and 3.3). Between the cave and the river is an open, seasonally flooded wet prairie (Thornton's Slough) fed directly by the river, and a narrow cypress stand. The cave is 14.4 m above mean sea-level within the Ocala Limestone and intersects the unconfined Upper Floridan Aquifer such that some passages are flooded throughout the year. The alignment of Thornton's Cave with the Talbott marine terrace (paleoshoreline) suggests the primary control on its formation was sea-level; however, local elevation of the groundwater table exerted by the Withlacoochee River is thought to issue a modern control, promoting further dissolution of the cave beyond that of other caves in the West-Central Florida region that are at similar elevations but farther from the river (Cook 1931, 1945; Florea et al., 2007).

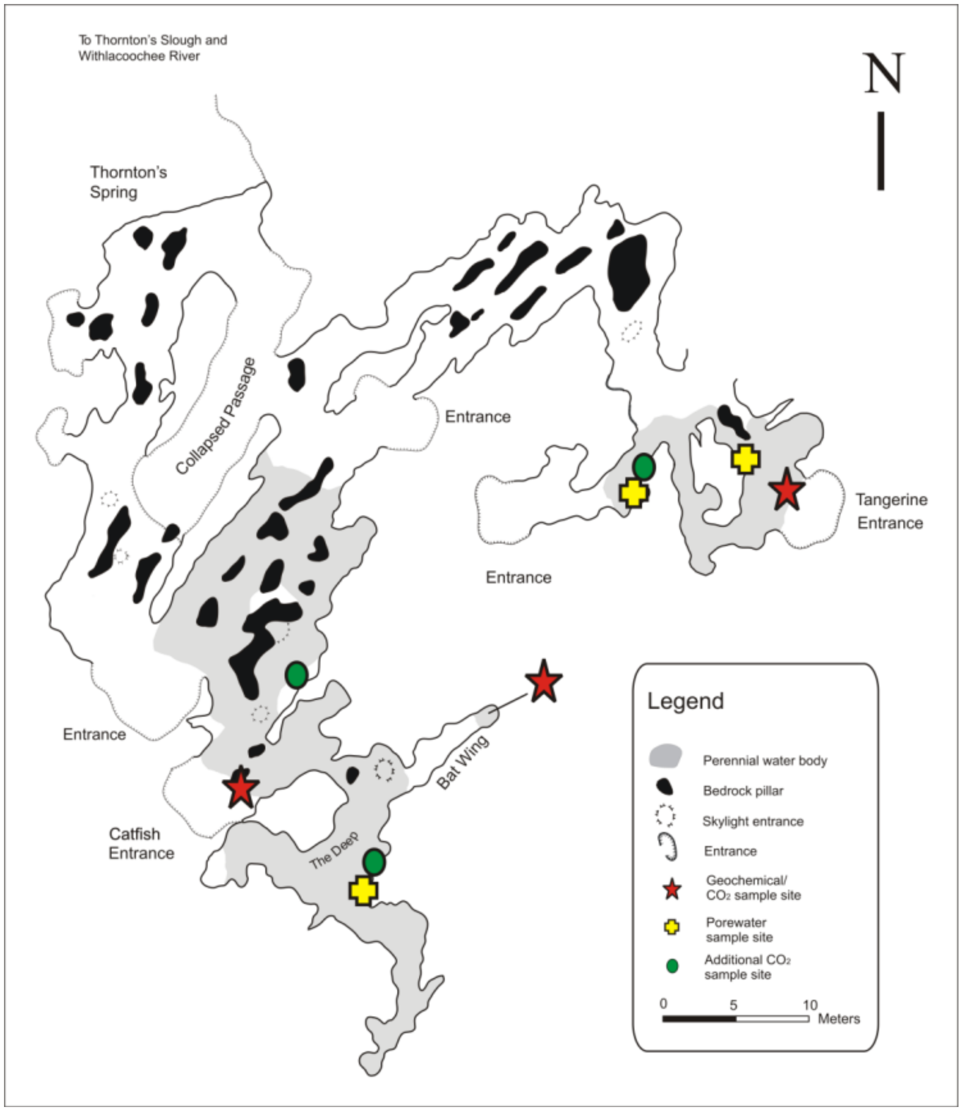

Figure 3.3. Thornton's Cave map. *Modified from Florea et al. (2006)*.

Approximately 315 m of the cave's dry passages have been mapped, while submerged passages remain relatively unmapped. Exploratory dives in the Tangerine Entrance documented a submerged vertical passage extending into the aquifer beyond 35 m, suggesting this area of the cave functions as a spring (Brooks et al., personal comm.). Periodic flooding of dry passages (and rising water-level in the flooded passages) occurs during the summer wet season, while high permeability and transmissivity measurements of the Ocala Limestone in this region (approximately 10^{-12} to 10^{-13} m^2 and 250,000 to 500,000 ft^2/day, respectively) support rapid recharge of the aquifer and therefore rapid response to surface rain events (Ryder, 1985; Budd and Vacher, 2004; Florea, 2006). The cave is also hypothesized to facilitate the transport of water between Gum Slough (<1 km to the west) and the Withlacoochee River (Florea et al., personal comm.). When water-level at Gum Slough is higher than the river, water is believed to drain westward through the cave and out from Thornton's Spring, through the cypress stand and Thornton's Slough toward the river, with the opposite effect occurring when the river level is higher; however, periodic droughts combined with increasing regional withdrawal on the aquifer for agricultural and development purposes appear to have restricted westward flow from Gum Slough, as water has not been observed flowing out of Thornton's Spring for at least five years prior to this study (Thornton, personal comm.; Ryder, 1985).

Collapse features and solution pits are exceptionally common at the cave due to its shallow position, just 1.7 m below the land surface. No fewer than 15 entrances, eight of human size, are present, subjecting the cave to year-round infilling of sediment and organic matter and rainfall from the surface. The cave also serves as a maternity roost for a breeding bat colony, typically along the Bat Wing (Figure 3.3), containing several thousand individuals from approximately late April to mid-August.

3.4. Methods

To establish a record of climate, hydrology, and CO_2 for this site, continual monitoring of these parameters took place over a two-year period both at various points within the cave, and at its surface. Temperature, rainfall, and water-levels were monitored using dataloggers (discussed below), while CO_2 concentration and $\delta^{13}C$

values were monitored seasonally by collecting atmospheric gas samples in the cave and at the surface. Fluctuations in CO_2 concentration and $\delta^{13}C$ values were of particular importance in estimating the contribution of biogenic CO_2, exhibited by ^{13}C-depleted CO_2 to the cave atmosphere (e.g., Craig, 1953; Ehleringer et al., 2000). Further, bench-top experiments sampling CO_2 produced and respired from cave substrates and sediments and surface soils were conducted to more specifically determine the contribution of heterotrophic microorganisms to cave atmospheric CO_2 profiles. Collectively, these data will be compiled with geochemical data presented in Chapter 4 to construct a biogenic model for carbonic acid (H_2CO_3) dissolution driven by the *in situ* production of CO_2 during microbially driven decomposition of organic matter.

3.4.1. Climate and Hydrologic Monitoring

Air temperature was monitored at the surface and inside the cave over the two-year monitoring period. Air temperature was continuously monitored at ten minute intervals at the surface using a Gemini Tinytag Plus 2 temperature datalogger (model TGP-4500, accuracy = ±3.0%) in a tree away from direct sunlight ~3 m from the Tangerine Entrance. Cave- air temperatures were continually monitored just inside the Catfish Entrance and in The Deep (~5 m southwest from the entrance to the Bat Wing passage) using Onset pendent temperature dataloggers (HOBO model UA-002-064, accuracy = ±0.54°). Water temperatures were continually monitored at The Deep (identical location as air temperature) and at the Tangerine Entrance. Surface soil temperature was monitored from January 2009 to April 2010 by burying a HOBO temperature logger approximately 20 cm below the soil surface outside the Catfish Entrance.

Water-levels were measured continually at the Tangerine Entrance using a Onset water-level logger (HOBO model U20-001-02, accuracy = 0.05% FS), which also collected the above-mentioned temperature data. The water-level logger was calibrated by measuring the depth at a fixed point in the cave; however, due to uneven cave-floor topography, particularly along the northeastern wall of the Tangerine Entrance where divers descended into the aquifer, water-level data could be used to measure trends only and not actual water-level at that entrance. Water-level fluctuations at the Withlacoochee River were collected from the Pineola gauging station, approximately 5 km upstream from the cave. This station is part of the National Water Information System (NWIS station ID 02312598) and is jointly monitored by the United States Geological Survey (USGS) and the Southwest Florida Water Management District (SWFWMD). Approved water-level data reported for this station were downloaded from the NWIS web interface (NWIS, 2010). Rainfall was measured using a HOBO RG3-M datalogger mounted in an open field on the property 20 m north of the cave. Because this gauge was deployed in late June 2008, rainfall rates between late March (when the study began) and the deployment date were determined using daily observations archived by the National Weather Service Precipitation Analysis database (USGS Water Resources Water-Data Support Team, 2010; National Weather Service, 2010).

All temperature and water-level loggers recorded measurements at hourly intervals. Water-level data for the Withlacoochee River were reported as daily averages. Rainfall data were post-processed to produce daily cm/day values.

Cross-correlograms were used to determine the relationship between water-level in the cave and the river. It was also used to analyze the degree to which water-levels at both sites respond to rainfall. All cross-correlation analyses were performed using R version 2.10.1 (R Development Core Team, 2009). Lag and correlation values are provided in Appendix III.

3.4.2. Cave CO_2: $\delta^{13}C$, Concentration, and Production Rates

Cave-air samples for seasonal analyses of $\delta^{13}C_{CO2}$ and CO_2 concentration were collected from the Tangerine and Catfish entrances and their nearby passages (and when accessible, the Bat Wing and The Deep), the surface, and on the hardwood forest floor using 12-mL septum-capped vials (Figure 3.3, Knohl et al. 2004). Replicate samples for each site were obtained by opening the vials and leaving them to equilibrate for a period of 30 minutes. Vials were then capped and wrapped in Parafilm to prevent leakage, and transported in a cooler chilled to approximately 25 °C to USF for analysis. Measurements of $\delta^{13}C_{CO2}$ were conducted using a Delta V gas-source isotope ratio mass spectrometer (IRMS) coupled to a Gasbench II peripheral following the methods of Tu et al. (2001). CO_2 concentration of each sample was determined by gas chromatography (GC) using the GC column built into the Gasbench II. The peak area of mass 44 for the first of 10 replicate peaks was used and standardized with a mixture of CO_2 in He with a concentration of ~3000 ppm. Two replicate values were averaged to obtain an overall value for each site. In July 2008, freshly deposited guano was also collected from the Bat Wing to document whether CO_2 respired from heterotrophic bacteria contributed to the atmosphere of the Bat Wing. Four replicate samples of a single guano pellet were placed in the above-mentioned septum-capped vials and flushed with CO_2-free air to remove ambient CO_2. Carbon dioxide production from the guano occurred over the time the samples (including cave atmosphere samples) were held for analysis and during the course of analysis prior to individual sampling by the IRMS (approximately 46 hours, total).

To estimate CO_2 production rates from cave substrates as indicative of bacterial respiration within these materials, bench-top experimentation using fresh samples collected from dry and submerged wall rock, dry and submerged cave sediments, and surface soils were conducted to obtain $\delta^{13}C$ and CO_2 concentration values. Samples were collected in early December with the assumption that cooler conditions should lead to lower CO_2 production rates such that rates measured in bench-top experimentation would yield minimum estimates. Substrates were placed in respiration chambers constructed using preserving jars with Swagelock® valves fitted with 2 mm septa affixed to the air-tight lids (Figure 3.4). Ambient CO_2 was flushed out of the jars using CO_2-free air prior to sealing. Respiration chambers were allowed to incubate for a period of 23.8 days prior to CO_2 sampling and measurement via IRMS analysis. Carbon dioxide was collected from chambers using a gas-tight syringe to extract 2.5 mL of gas, which was then inserted into a 12-mL septum-capped vial pre-flushed with He. Samples were analyzed using the above-mentioned methods to obtain $\delta^{13}C$ and CO_2 concentration values. To estimate the CO_2 flux/production rate for each chamber, substrate volume was calculated by filling the chambers to their headspace with a known volume of water (in mL, after IRMS analysis) after gas analyses and subtracting that value from the total volume of the chamber. Using the calculated substrate volume, CO_2 production was calculated per m^3 over the total incubation time using the Ideal Gas Law. Standard pressure and a lab temperature of 295.7 K were used to calculate a 24.26 L volume occupied by one mole of gas, or 24.26 mL occupied by1 mmol of gas. Using this volume, the gas concentration at the same pressure and temperature conditions was calculated as 0.04 mmol/mL (C_g). This value was then used to convert the concentration of CO_2 in µL/L (ppmV) in each septum-capped sampling vial to mmol CO_2, representing the amount of CO_2 in the gas sample in the vial. This amount was calculated using Eq. 1, where V_c is equal to the volume of the container in mL (in this case, the 12 mL vial):

$$\left(\frac{\mu L}{L}\ CO_2 \times \frac{1\ L}{1{,}000\ mL} \times \frac{1\ mL}{1000\ \mu L}\right) \times V_c\ mL \times C_g\ mmol/mL = mmol\ CO_2 \qquad \text{Eq. 1}$$

That value was converted back to µL/L using the reverse of the above equation and assuming the 2.5 mL volume of the gas-tight syringe as V_c to represent the concentration sampled from the each respiration chamber. To calculate the mmol/mL concentration of CO_2 in each respiration chamber, the µL/L concentration previously calculated was converted assuming the void space volume of each chamber as V_c. Finally, the CO_2 production rate in µmol m^{-3} s^{-1} was calculated using Eq. 2, where V_s is equal to the volume of the substrate in m^3, and t is equal to the total incubation time, in seconds:

$$\frac{\frac{mmol\ CO_2 \times \frac{1{,}000\ \mu mol}{mmol}}{V_s\ m^3}}{t\ sec} = \mu mol\ m^{-3}\ s^{-1} \qquad \text{Eq. 2}$$

Figure 3.4. CO_2 respiration chambers. Bottom: close-up of Swagelock© valve and septa.

3.5. Results and Discussion

Temperature, water-level, rainfall, and CO_2 data are each discussed below. Raw temperature and water-level data are reported in Appendices I and II. During a flood event in July 2009, the two dataloggers recording air and water temperature in The Deep were lost, restricting the dataset for that site.

3.5.1. Cave and Surface Temperature

Data collected from cave- and surface-air and water temperature dataloggers were smoothed using a running average and plotted in Figure 3.5. Diurnal fluctuations in air temperatures were also plotted in Figure 3.5. Long-term cave-air temperatures show strong seasonal trends, even in The Deep, one of the more remote passages farthest from an entrance. At the same time, cave-air temperatures were slightly cooler than surface temperatures during the summer and slightly warmer in the winter. Even so, long-term cave- and surface-air temperature differences were typically less than 2 °C, illustrating the openness of the cave and indicating the degree of exchange between cave- and surface-air. A temperature inversion at The Deep occurred during December 2008 that does not appear at the remaining sites. While it could be assumed that a localized area of increased temperature is indicative of temporary animal habitation, the duration of this event coincided with bi-weekly geochemical sampling trips during which no animal traces were observed. The cause of this inversion is therefore unknown.

An example of daily air temperature variation from July 1 to July 5, 2008 illustrate a diurnal variation in cave temperature that varies from approximately 0.5 to 1 °C (Figure 3.5). Not surprisingly, variations at the Catfish Entrance are more pronounced than The Deep. This suggests that though muted, cave-air temperatures do respond simultaneously to temperature changes at the surface.

Water temperature at the Tangerine Entrance displays a seasonal trend that varied by approximately 1°C for most of the sampling cycle (Figure 3.5). Tangerine Entrance temperature was 1 °C or less cooler than The Deep, and may be due to the greater degree of exposure of waters at the Tangerine Entrance to the surface. Like the air, water temperatures at The Deep increased slightly in December 2008 but stayed warmer through the winter before decreasing slightly in the late spring of 2009. The cause for this is unknown as no such observation is seen at the Tangerine Entrance. Just as enigmatic is the steady decrease of water temperature at the Tangerine Entrance beginning in late 2009 that appeared to level out at the end of the sampling cycle in early spring 2010. Water temperature throughout the dataset, including the negative excursion at the Tangerine Entrance, are representative of Floridan Aquifer temperature (Sprinkle, 1989) supporting the hypothesis that perennial water bodies in the cave intersect the aquifer, with water-levels varying more as a result of fluctuations in the water table than from direct surface runoff during rain events. Given this, and the hypothesis established through exploratory dive operations that the Tangerine Entrance acts as a spring, it is possible that cooler water upwelling from the aquifer occurred in late 2009 through early 2010, lowering the temperature at the Tangerine Entrance.

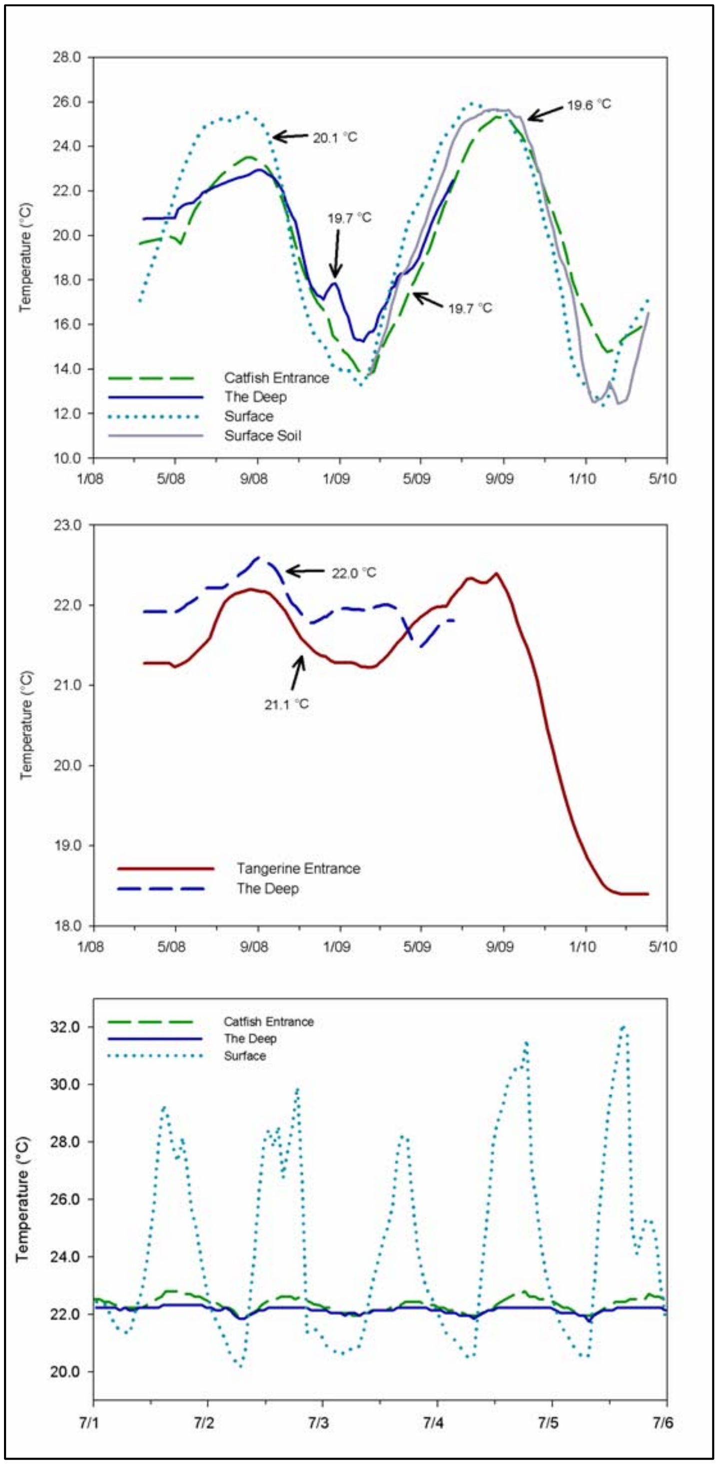

Figure 3.5. Air and water temperature profiles at Thornton's Cave. Top: long-term air temperatures, March 2008 to April 2010; Middle: long-term water temperatures, March 2008 to April 2010; Bottom: example of diurnal fluctuations in air temperature, July 2009. Arrows indicate mean annual temperature for each site.

3.5.2. Rainfall and Water-levels

Rainfall rates and changes in water-level at Thornton's Cave and the Withlacoochee River are illustrated in Figure 3.6. Visual comparisons of wet- and dry-season water-levels at sites sampled in this study are illustrated in Figures 3.7 and 3.8. Overall, rainfall data are indicative Florida's wet summer/fall and dry winter/spring climate, particularly in 2008. The passage of Tropical Storm Fay between August 21 and 22 brought the highest rainfall amount for the year, with the remainder of rainfall events driven by afternoon/evening convection systems in the summer/fall and frontal systems in the winter and early spring. The onset of El Niño in 2009 reduced tropical storm and hurricane activity but maintained rainfall rates through the summer due to frontal and local convection systems. Most notably, the El Niño event contributed to increased rainfall activity through winter 2009/2010, a stark contrast to the previous year. These conditions persisted through the spring of 2010 when this study concluded.

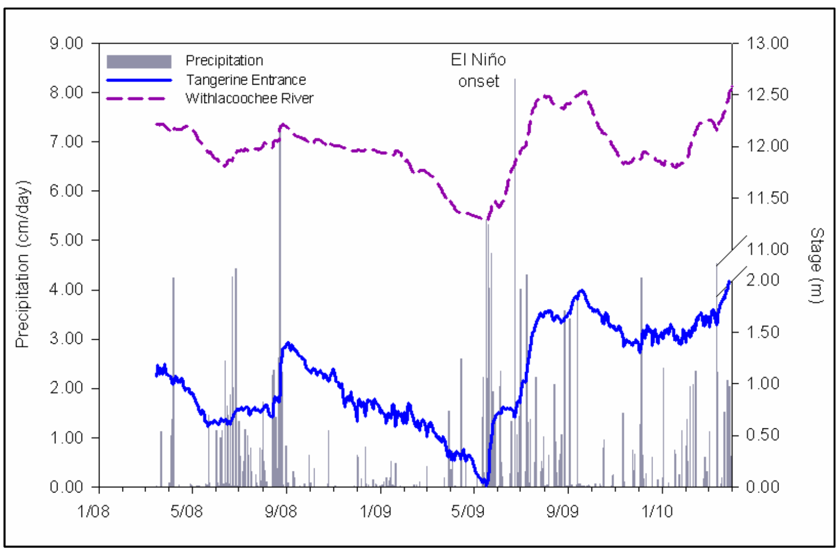

Figure 3.6. Rainfall and stage data for Tangerine Entrance and Withlacoochee River. Data for Tangerine Entrance should be interpreted as trends rather than actual stage due to uneven depths attributed by variations in cave floor topography and presence of vertical passages.

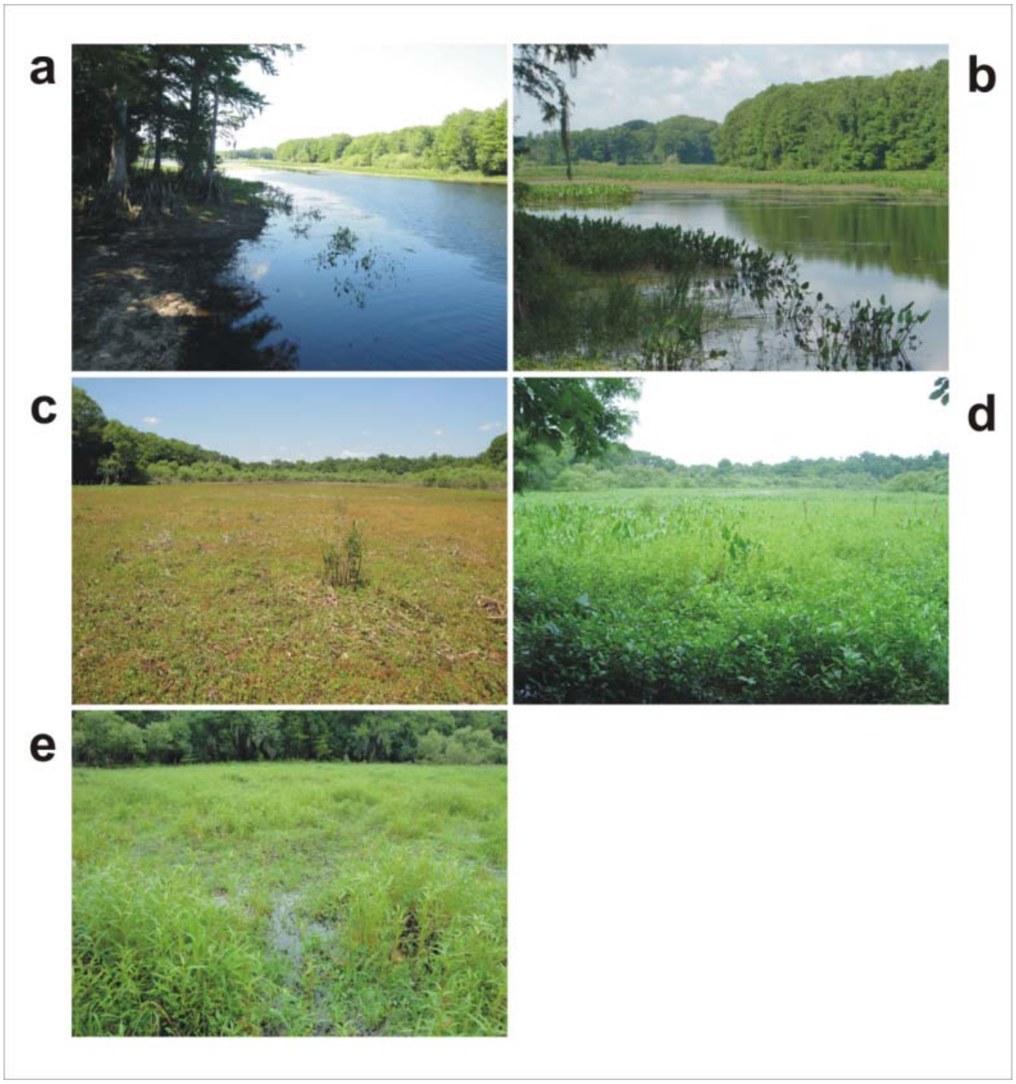

Figure 3.7. Seasonal images of Withlacoochee River and Thornton's Slough: a) Withlacoochee River, dry season (looking south); b) Withlacoochee River, wet season (same vantage); c) Thornton's Slough, dry season (looking west toward river; note dried aquatic vegetation amid grasses); d) Thornton's Slough, wet season (same vantage); e) Thornton's Slough, wet season (looking east toward cypress stand and cave).

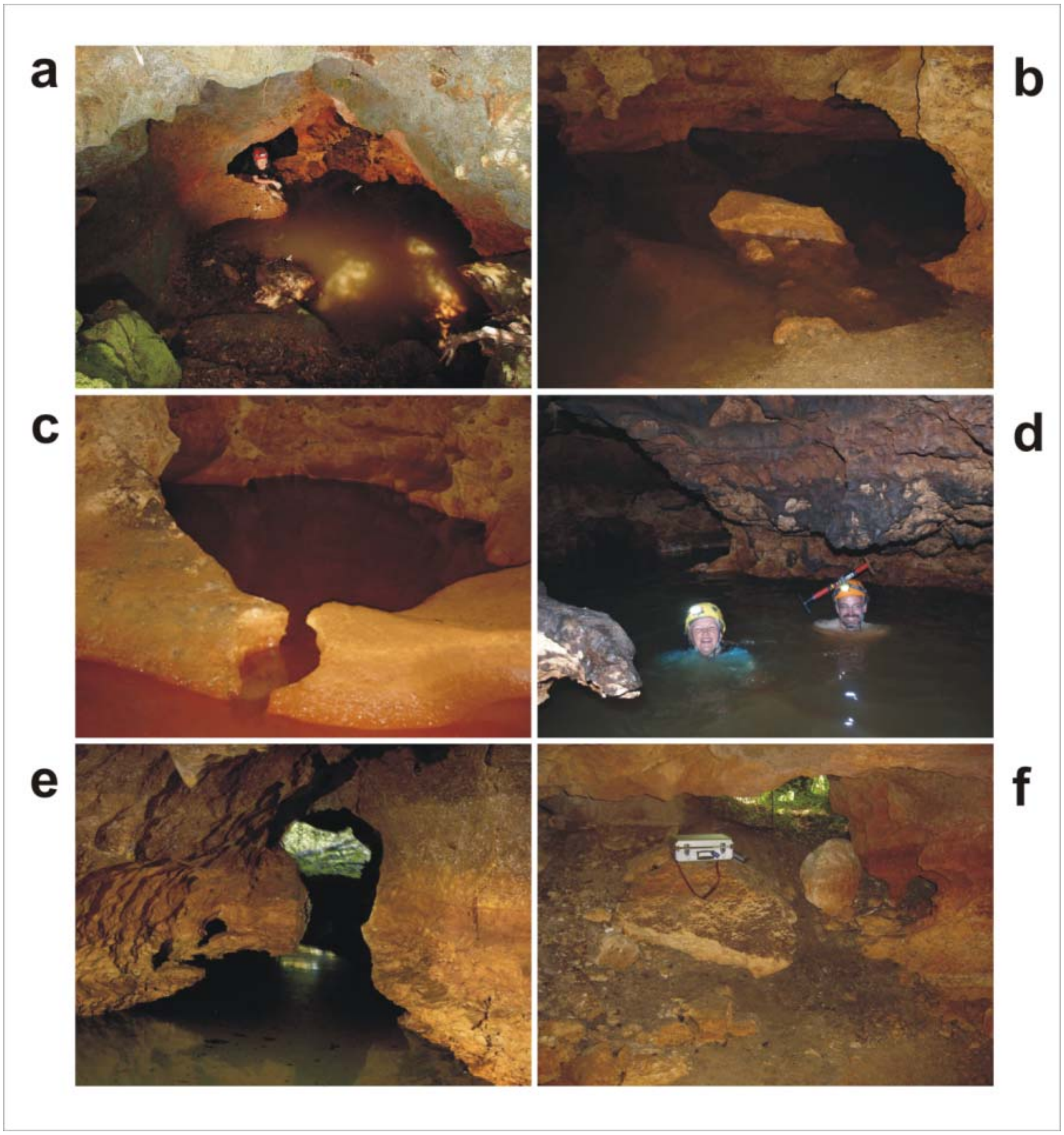

Figure 3.8. Thornton's Cave entrances and passages: a) Tangerine Entrance (pool depth exceeds 30 m at right); b) Catfish Entrance (passage to Bat Wing and The Deep on right); c) perennially flooded pool at terminus of Bat Wing; d) The Deep passage (note dark encrustations on cave ceilings and walls); e) perennially flooded passage west of Tangerine Entrance; f) typical dry cave entrance and passage. *Photos a, d, and e courtesy of T. Turner, J. Sumrall, and A. Palmer, respectively*.

Water-levels at both Thornton's Cave and the Withlacoochee River largely mirror one another and appear to respond rapidly to rainfall events (Figures 3.6, 3.9). Water-levels at both locations were on the decline from the start of the study to June 2008 when they began to rebound with the onset of the wet season, particularly with the passage of Tropical Storm Faye in late August. From August onward, water-levels decreased steadily through the following winter and spring, reaching their lowest points in mid-May 2009 before rising dramatically with the onset of frequent and heavy rain events occurring through the summer. The rapid increase in intense rainfall eventually caused Thornton's Slough (fed by the Withlacoochee River) to flood into the cave through the entrance at Thornton's Spring in early July 2009 (Figure 3.10), with water observably flowing through passages to the Catfish Entrance and The Deep and to the Tangerine Entrance until early August. Continuous rainfall through winter 2009/2010 maintained water-levels much higher than the previous year and in late March 2010 such that Thornton's Slough once again back-flooded into the cave along the same flow paths. This flooding continued through the end of this study in early April.

Steady rainfall and elevated water-levels from summer 2009 to spring 2010 coincide with the gradual decrease in water temperature at the Tangerine Entrance and may help explain this phenomenon. The continual recharge to the Floridan Aquifer over this time period may have gradually flushed cooler water from deeper in the aquifer upward toward the surface where it discharged at springs. Deeper waters should be cooler than waters at the Tangerine Entrance, which are influenced by surface air temperatures and direct exposure to sunlight (Figure 3.8a). This steady increase in upward flow from the aquifer would explain the steady decrease in water temperature at the Tangerine Entrance.

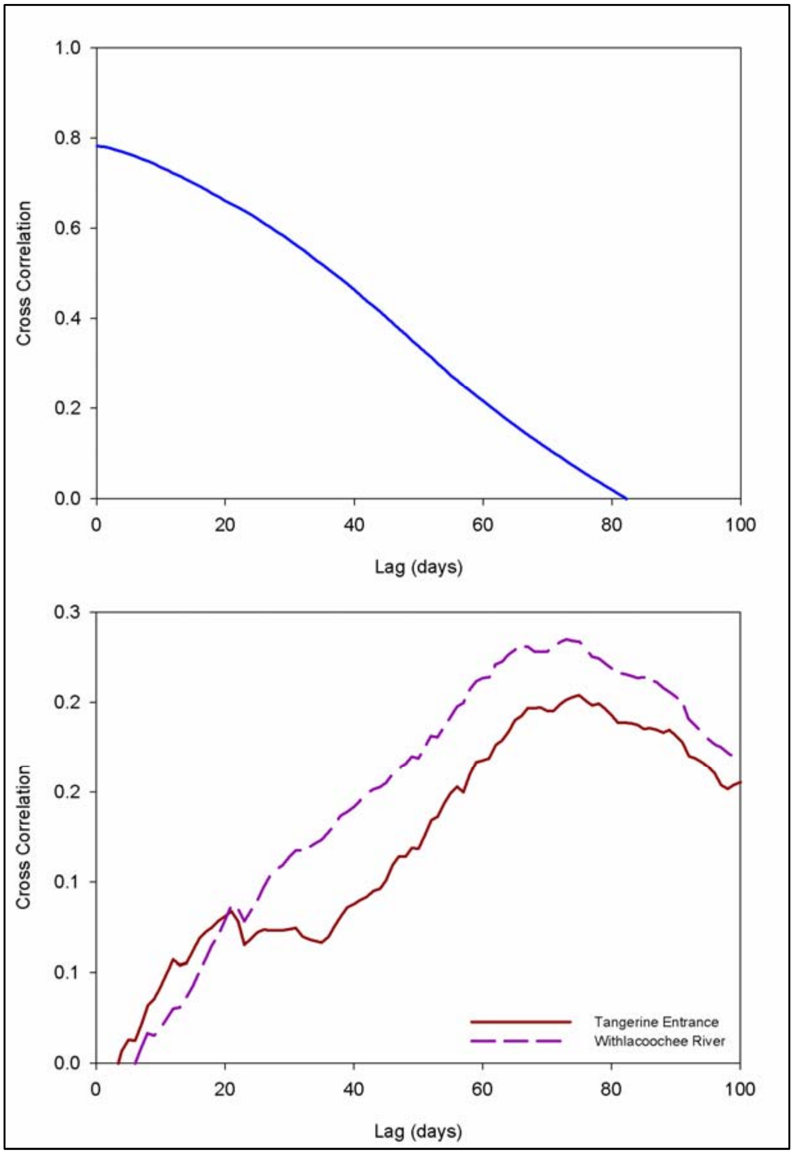

Figure 3.9. Cross-correlograms of water-level and rainfall data at the Tangerine Entrance and the Withlacoochee River. Top: Cross-correlation of water-levels at each site. Bottom: Cross-correlation of rainfall and water-level at each site.

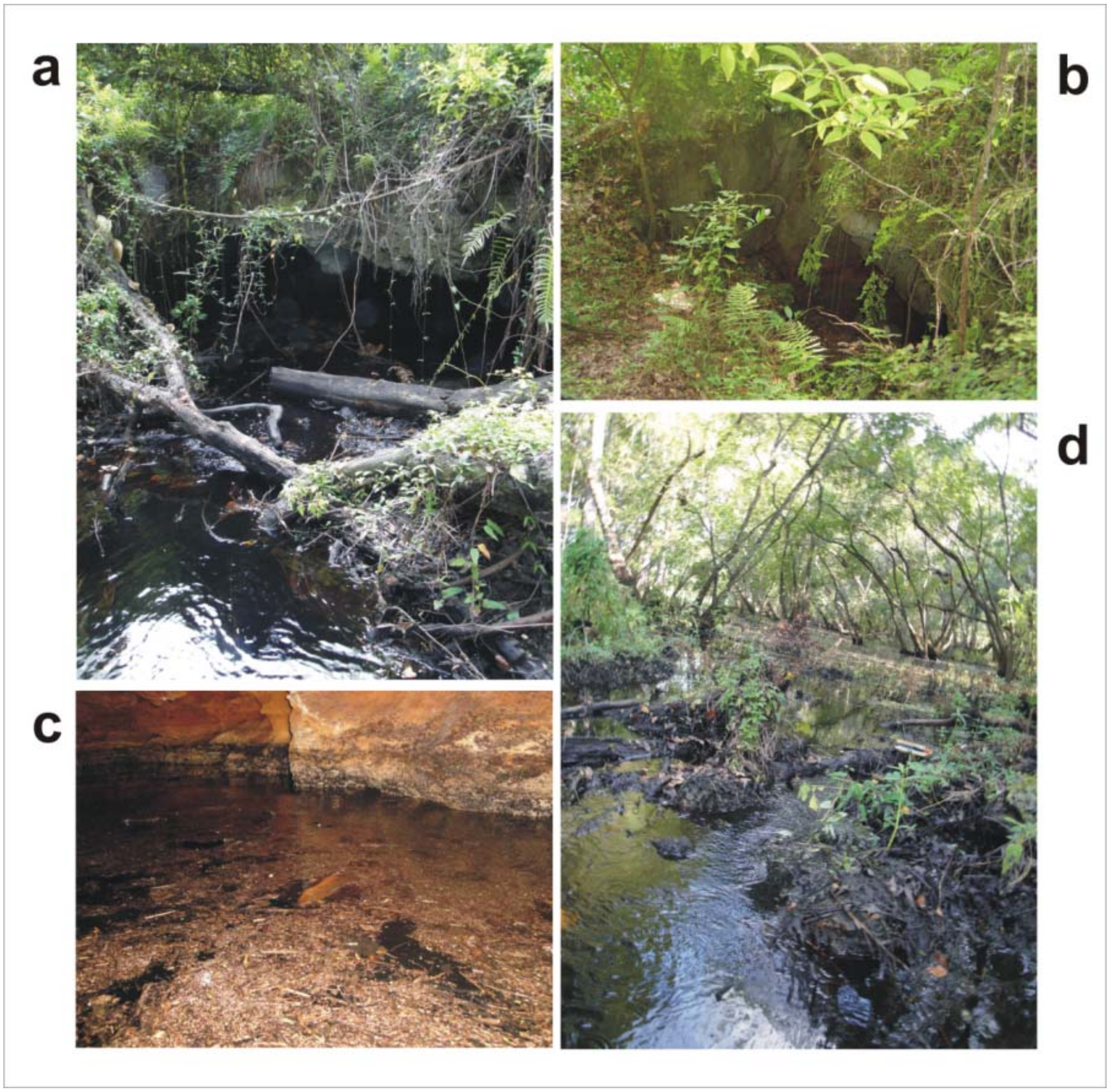

Figure 3.10. Summer 2009 flood images: a) flooded Thornton's Spring Entrance; b) Thornton's Spring Entrance (dry season comparison); c) flooded Catfish Entrance including surface debris (connection to The Deep & Bat Wing submerged along wall); d) flooded cypress hammock (view from Thornton's Spring west toward slough).

3.5.3. Cave-air CO_2

Seasonal cave-air CO_2 sampling from 2008 to 2010 show that CO_2 concentrations reach their peak in the late summer and fall, while at the same time, $\delta^{13}C_{CO2}$ values are at their lowest. These values range from ~450 ppm and ~11‰ at the entrances to ~1230 ppm and -19‰ in more remote passages (Table 3.1). During these months, CO_2 concentrations and $\delta^{13}C_{CO2}$ values at the Catfish Entrance are typically 200-300 ppm higher and 5‰ lower, respectively, than that of the Tangerine Entrance and likely result from the respiration of the breeding bat colony in the adjacent Bat Wing where CO_2 concentrations were highest (~1230 ppm) and $\delta^{13}C_{CO2}$ values were lowest (~ -19‰; Figure 3.11). In addition, decomposition of thick deposits of guano by microorganisms is likely providing an additional source of CO_2 to the Bat Wing, evidenced by CO_2 produced from four replicate samples of freshly collected guano. During the cooler months, CO_2 concentrations remain higher and $\delta^{13}C_{CO2}$ values lower in the more remote passages but typically stay below 500 ppm and above -12‰, respectively. Regardless of season, cave CO_2 concentrations were always higher and more ^{13}C-depleted than surface CO_2. These data suggest that despite ample ventilation to the surface, as suggested by temperature profiles, biogenic CO_2 accumulates in the cave, particularly during the summer months. This is evidence that that biotic activity from microbial respiration and/or that of macrobiota is greater during the warmer, wetter season and contributes a significant amount of CO_2 produced *in situ* to the cave system.

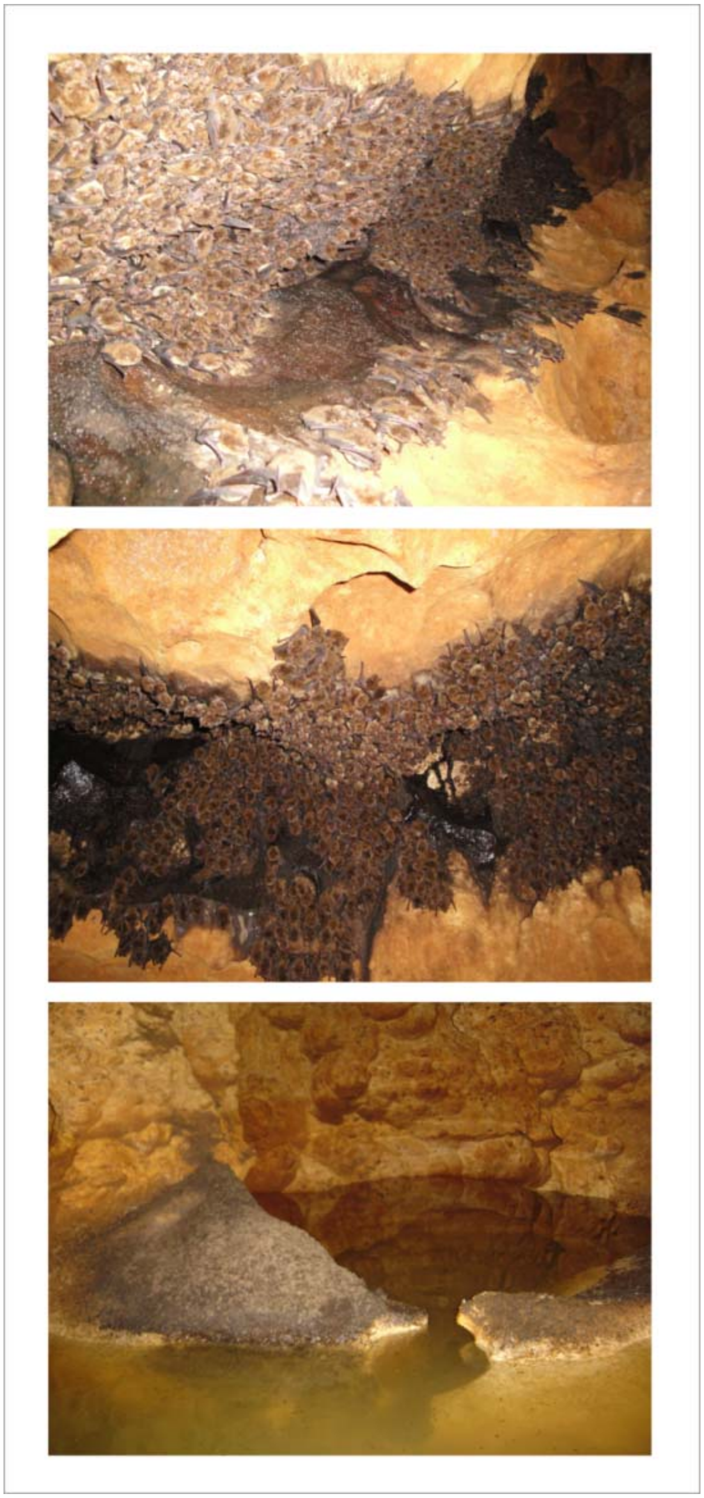

Figure 3.11. Bat Wing summer maternity roosting colony. Top - Middle: roosting colonies (individuals ~5-8 cm in length); Bottom: guano deposits on exposed surfaces below the colony. *Note: Limited photos taken under guidance of Jeff Gore, scientific advisor for the Florida Bat Conservancy. As of January 2010, white-nose syndrome (WNS) caused by the fungal species* Geomyces destructans*, not reported in Florida bat populations.*

While macroorganisms such as bats undoubtedly provide an important source of CO_2 in the summer, the microbial production of CO_2 within cave substrates is evidenced by low $\delta^{13}C_{CO2}$ values shown in Table 3.2, with production rates ranging from 0.10 to 0.23 μmol m^{-3} s^{-1} in the cave. Production rates calculated from surface soils were the highest (0.33 μmol m^{-3} s^{-1}) with a $\delta^{13}C_{CO2}$ value of -23.1‰, characteristic of soils from C_3-dominated vegetative environments (Ehrlinger and Cerling, 2000). Within the cave, production rates seemed to be driven first by substrate type and secondarily by moisture, as rates were first highest in cave wall rock and then in wet samples. This is an indicator that microorganisms may be thriving on dissolved organic carbon (DOC) leached through the rock by the infiltration of water from the soils above. If this is the case, respiration of CO_2 may be higher in the summer months as organic activity increases. Interestingly, $\delta^{13}C_{CO2}$ values observed from CO_2 produced in dry cave rock are at least 5‰ more enriched in ^{13}C than the remaining samples, which might suggest that the pore spaces of dry rock may contain relatively higher volumes of surface CO_2 with the characteristic $\delta^{13}C_{CO2}$ value closer to -8‰. Alternatively, this CO_2 could be derived from inorganic sources such as abiotic precipitation of $CaCO_3$.

Heterotrophic microbial production of CO_2 from rock has been documented as far back as the early 1900s when Paine et al. (1933) characterized and enumerated bacteria sampled from various building stones (typically limestones and marbles) and measured CO_2 respired from them in an attempt to determine the microbial contribution to the degradation of these stones. The combined works of Paine et al. (1933) and Schwabe et al. (2008) show that bacterial counts are highest in the first 2-5 cm depth from the surface, likely due to limitations in oxygen and nutrient availability. If we were to assume all the CO_2 produced in these experiments occurs in the outermost 5 cm of the rock and sediment, then we can compare production rates measured in this study to production rates calculated from soil CO_2 flux rates published in other studies. Common CO_2 flux rates measured in tropical forest, grassland and montane soils range from 1 μmol m^{-2} s^{-1} to 8 μmol m^{-2} s^{-1} (Janssens et al., 1998; Chen et al., 2002; Kao and Chang, 2009; Wei et al., 2010). Assuming this CO_2 is produced in the upper 5 cm of the soil column (i.e., multiplying the flux rate by a factor of 0.05) yields CO_2 production rates varying from 20 μmol m^{-2} s^{-1} to 160 μmol m^{-2} s^{-1}, well above the production rates measured for Thornton's Cave substrates. While it might be expected that CO_2 production rates in the cave would be lower than that of most surface soils, this does not account for the low production rate calculated for the soils collected from the forest overlying the cave in this study. At the same time, the CO_2 production rates measured in this study are within the lower range of modeled production rates from soils in a montane region in Utah, USA (Solomon and Cerling, 1987). We should therefore interpret CO_2 production rates calculated from published soil CO_2 flux rates with caution by acknowledging the differences in bacterial community distribution between the pore spaces of rocks and that of soils, and their effects on the depth to which CO_2 is produced. Regardless, these bench-top studies document that CO_2 production of heterotrophic microorganisms in soils and rock do contribute to atmospheric CO_2 in the cave and should be assessed under field conditions to establish more reliable rates of production and efflux. They also implicate microorganisms as potential factors influencing dissolution by contributing to CO_2 that can acidify vadose water in both the rock and sediment pore spaces, as well as acidify wall condensate as CO_2 degasses from these substrates to the cave atmosphere.

Table 3.1. Summary of seasonal CO_2 $\delta^{13}C$ and concentration variations, by site

	July 08		February 09		June 09		October 09		December 2009	
	$\delta^{13}C_{CO2}$ (‰)	Conc. (ppm)	$\delta^{13}C_{CO2}$ (‰)	Conc. (ppm)	$\delta^{13}C_{CO2}$ (‰)	Conc. (ppm)	$\delta^{13}C_{CO2}$ (‰)	Conc. (ppm)	$\delta^{13}C_{CO2}$ (‰)	Conc. (ppm)
Tangerine Entrance	-10.5	466	-9.60	409	-11.41	440	-13.78	515	-9.05	431
Tangerine Ent. Passage	-12.3	525	-9.62	411	-11.02	437	-15.73	620	-12.74	611
Catfish Ent	-15.8	805	-11.39	470	-10.97	419	-17.01	727	-9.52	445
Catfish Ent. Passage	-12.6	534	-9.92	417	-11.10	431				
Bat Wing	-19.4	1234	-11.39	481	-18.96	1232				
Forest Floor	-8.8	391	-12.09	488	-14.74	545	-18.16	762	-8.81	417
Surface Atmosphere	-8.6	381	-9.39	405	-9.59	384	-9.72	383	-8.26	397
Guano	-22.8	1056								

Table 3.2. Results from bench-top CO_2 production experiments

	$\delta^{13}C$ (‰)	CO_2 Production, by particle volume (excl. pore space) ($\mu mol\ m^{-3}\ s^{-1}$)
Wet cave rock	-18.5	0.23
Dry cave rock	-13.2	0.18
Wet cave sediment	-21.1	0.15
Dry cave sediment	-20.3	0.10
Surface soils	-23.1	0.33

3.6. Summary and Conclusions

Climate, hydrologic and CO_2 data collected from Thornton's Cave exhibits a strong degree of connectivity between surface and subsurface processes, which is to be expected given the cave's proximity and openness to the surface. Long-term trends in temperature data at the cave's entrances and more remote passages are not dissimilar to surface temperatures, both in actual values and seasonality. Diurnal variation in cave temperatures occur on a shorter time-scale at both the entrances and remote passages as well, though the temperature range is much smaller than that observed at the surface. These data support that the cave responds simultaneously to both long- and short-term temperature flux at the surface. Water temperatures at the Tangerine Entrance and The Deep are more consistent with a mild seasonal trend and are probably regulated more so by the Floridan Aquifer than air temperature. At the same time, water-levels at the cave are well-correlated to both rainfall and variations in water-level at the Withlacoochee River. Water-levels at the cave respond rapidly to rainfall at the surface, owing to the high permeability and transmissivity of the Ocala Limestone and to a lesser degree, runoff from the surface.

Seasonal surveys of atmospheric CO_2 at the cave suggest that during the wet season, CO_2 concentrations both increase and are more influenced by biotic sources compared to the dry season when CO_2 concentrations are lower and more similar to surface atmospheric values. The marked accumulation of CO_2 in the cave atmosphere during the wet season combined with its lower $\delta^{13}C$ values is evidence that cave CO_2 is produced *in situ* at a rapid enough rate to allow for accumulation despite the cave's ample ventilation to the surface. Though a significant portion of this CO_2 is likely sourced from the breeding bat colony occupying the Bat Wing during the summer (as well as degassing from guano deposits), CO_2 may also be degassed from cave wall rock and floor sediment, particularly in the wetter regions of the cave. This CO_2 is sourced from the respiration of microorganisms living in the sediment and pore spaces of the rock as they break down organic matter. This is a strong indicator that microorganisms could be contributing to the dissolution of the cave by providing ample CO_2 to diffuse and dissolve into water to produce H_2CO_3, a common corrosion agent in many limestone systems. Collectively, these data provide a background upon which this mode of dissolution can be further explored in Chapter 4.

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CHAPTER 4:

THORNTON'S CAVE PART 2: THE ROLE OF BIOTICALLY DRIVEN CARBONIC ACID DISSOLUTION AND OTHER MICROBIALLY MEDIATED PROCESSES ON SPELEOGENESIS IN WEST-CENTRAL FLORIDA (USA)

4.1. Introduction

Carbonate rocks are the world's largest crustal reservoir of carbon and account for approximately 15% of earth's exposed land surface (Houghton & Woodwell, 1989; Amiotte Suchet et al., 2003; Ford and Williams, 2007). As such, dissolution of carbonates exert san important control on the global carbon cycle by providing 90% of the calcium carbonate ($CaCO_3$) in the world's oceans and accounting for approximately 40% of the total atmospheric CO_2 drawn down by rock weathering, which removes an estimated 0.11 and 0.41 Pg/C per year from the atmosphere (Liu and Zhao, 2002; Amiotte Suchet et al., 2003; Konhauser, 2007). These characteristics of carbonate rocks, as well as their capacity to serve as important reservoirs for water and hydrocarbon resources, are largely responsible for the prevalence of models describing limestone dissolution processes and kinetics in carbonate and karst literature; however, only within the last two decades have studies begun to specifically address the role that biota, namely microorganisms, may play in such processes (reviewed in Sand, 1997; Northup and Lavoie, 2001; Barton and Northup, 2007). Particular attention has been paid to the impacts of iron, manganese, and sulfur oxidizers involved in sulfidic systems such as those in the Guadalupe Mountains region of New Mexico and Texas, the Kane Caves in Wyoming, Frasassi Gorge in central Italy, and eastern Europe (e.g., Davis, 1980; Egemeier, 1981; Hill, 1990, 2000; Galdenzi and Menichetti, 1995; Hill, 1987, 1990; Onac et al., 1997; Spilde et al., 2005; Macalady et al., 2006; Engel, 2007; Porter et al., 2009). In these karst settings, sulfuric acid (H_2SO_4) is an important, if not primary, dissolution agent; however, comparatively fewer studies researched the role of microorganisms in karst settings where dissolution is driven by carbonic acid (H_2CO_3), the principal agent in many fundamental dissolution models (e.g., Roques, 1962, 1964; Dreybrodt, 1987; Palmer, 1991; Dreybrodt et al., 1996; White, 1997).

One likely explanation for this is the interdisciplinary nature of cave and karst science itself, which, not unlike geological research, led to the fragmentation of karst research across the natural and social sciences, and in gray and white literature (Florea et al., 2007a; Fratesi, 2008). Though the influence of microorganisms on the dissolution of limestone have been documented since at least the 1930s (Paine et al., 1933), early geomicrobiological research in caves was dominated by microbial taxonomy and culture-dependant studies and did not shift toward the investigation of their specific speleogenetic roles until the 1990s, long after the more fundamental dissolution models were established (see review by Northup and Lavoie, 2001 and Barton and Northup, 2007). At the same time, parallel observations of the microbial affects on carbonates in both laboratory settings and natural environments were slowly unveiling the impact of biota on dissolution through their influence on water geochemistry and contributions to geochemical cycling (e.g., Kitano and Hood, 1965; Berner 1967; Reddy, 1977; Inskeep and Bloom; 1986; James, 1994; Takasaki et al., 1994; Luttge and Conrad, 2004; Bennet and Engel, 2005; Macalady et al., 2006).

Here, I present the results of a 20-month study monitoring aqueous geochemistry and limestone dissolution rates in the surface and subsurface at a cave in West-Central Florida (USA), with the following purposes: 1) to determine the degree to which microbial activity influences H_2CO_3 dissolution, and 2) to identify other potential dissolution mechanisms that may be microbially mediated. If microorganisms are contributing to dissolution via H_2CO_3 or other mechanisms, we should expect to see evidence of this in stable carbon isotope ($\delta^{13}C$) profiles of dissolved inorganic carbon (DIC) as well as in nitrogen, sulfur, iron, and phosphorous ion concentrations as they oxidize organic matter and/or mediate mineral redox reactions, releasing these ions into solution. By combining these data with climate, hydrologic, and CO_2 respiration data reported and discussed in Chapter 3, I provide a multi-dimensional view of dissolution in this cave setting, which can be adapted and applied to caves worldwide, and considered in current and future limestone dissolution models.

4.2. Thornton's Cave

Thornton's Cave is located in southeastern Sumter County in West-Central Florida, and is part of the Western Florida karst belt that extends from the Florida Panhandle to just south of Tampa Bay (Figure 4.1). The cave lies 1.7 m below the land surface and has multiple entrances; it intersects the water table and contains a range of passages, some of which are perennially and intermittently flooded. As a result, organic matter is continually supplied to the cave by direct infilling from the hardwood forest above and flooding from an adjacent wetland and river in the wet season. Additional organic matter is also supplied by *in situ* production from macroorganisms such as bats, which charge the system with a source of energy and nutrients and ions from guano and urea. Since the supply of organic matter is abundant whereas light is limited (in most passages), microbial communities are assumed to be primarily organotrophs, a hypothesis that is supported by CO_2 production experiments and data discussed in Chapter 3. This point separates Thornton's and potentially other similar caves from the afore-mentioned sulfidic caves, where the supply of organic matter is limited, such that microbial communities tend to be chemolithoautotrophic, utilizing reduced ions such as H_2S and elemental S as their primary energy source (Sarbu et al., 1996; Engel, 2007; Porter et al., 2009). These characteristics of Thornton's Cave therefore make it an excellent environment in which to study the effects of biotic activity on H_2CO_3-driven dissolution processes; however, because organic matter is prevalent in this system, and because other sources of chemical energy from reduced ions (e.g., NH_4^+, SO_4^{2-}, S^{2-}, S, and Fe^{2+}) are prevalent in the limestones and groundwaters of this region (Miller, 1986; Sprinkle, 1989), minor inputs of acidity from other microbially driven oxidation reactions (e.g., nitrification, iron and sulfide oxidation) are also postulated to potentially contribute to limestone dissolution.

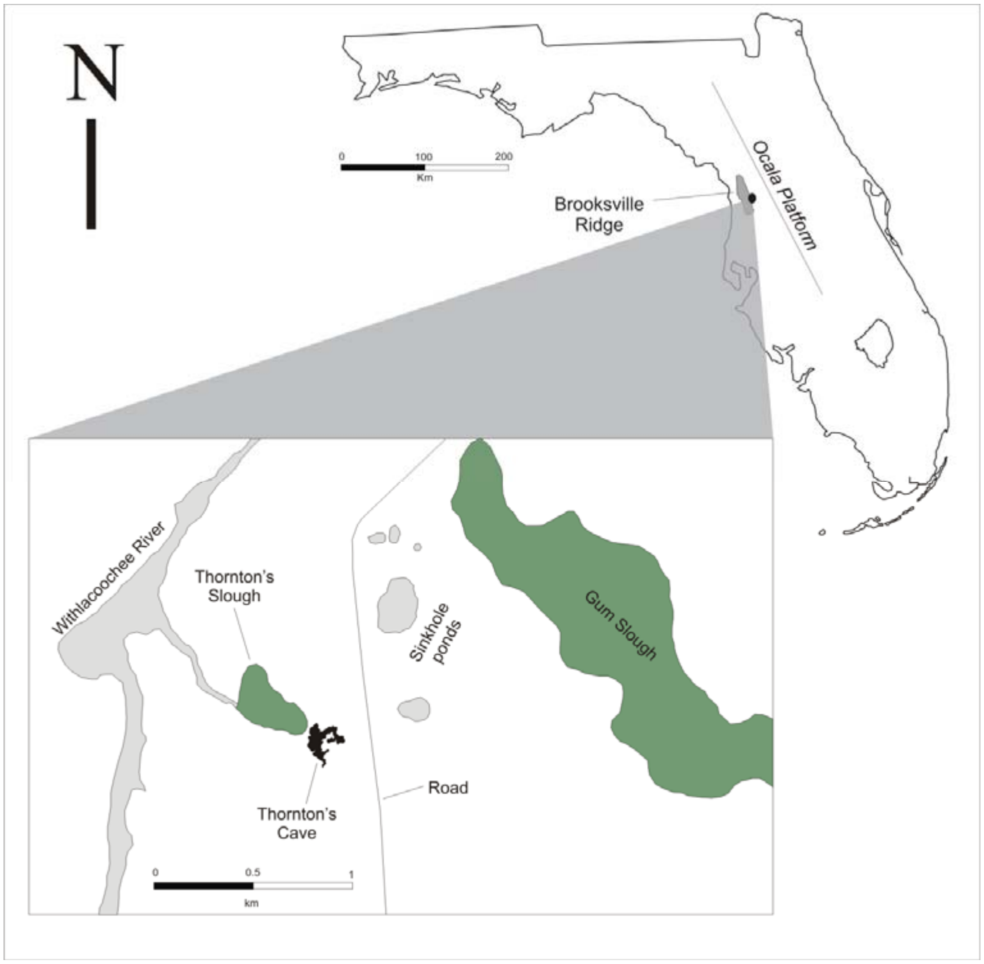

Figure 4.1. Regional map of Thornton's Cave area.

4.2.1. Regional Geology

The karst region of West-Central Florida is marked by the area's high density of sinkholes, springs, and caves (Figure 4.1). The Brooksville Ridge and the larger Ocala Platform are the most significant topographic highs, and they serve as regional boundaries for the Withlacoochee River Basin (Maddox, 1992). Surface stratigraphy is dominated by Middle Eocene to Late Oligocene limestones comprising the Avon Park Formation, as well as the Ocala and Suwannee limestones (Figure 4.2). In the Brooksville Ridge and Ocala areas, the Ocala and Suwannee limestones are most prevalent at the surface, with karst features, such as sinks and solution pits, commonly infilled by Miocene and younger sediments (Yon and Hendry, 1972). With the exception of the Withlacoochee River, surface streams are absent, and the majority of surface waters exist as springs, sinkhole ponds, and wetlands adjacent to the river. The highly porous Ocala Limestone is the principal unit containing the Floridan Aquifer in West-Central Florida, with active circulation of groundwater contributing to the region's karstification (Stringfield and LeGrand, 1966; Lane, 1986).

System	Series	Lithostratigraphy
Quaternary	Holocene and Pleistocene	Alluvium
		Undifferentiated Deposits (Caloosahatchee Marl and Bone Valley, Alachua, & Tamiami Formations)
Tertiary	Pliocene	
	Miocene	Hawthorne Formation
		Tampa Limestone
	Oligocene	Suwannee Limestone
	Eocene	Ocala Limestone
		Avon Park Formation
		Oldsmar Formation
	Paleocene	Cedar Keys Formation

Figure 4.2. Stratigraphy of West-Central Florida. *Adapted from Miller (1984) and Randazzo (1997)*.

Wet and dry caves of various sizes and morphologies occur throughout West-Central Florida (including submerged caves on the West Florida Shelf) and are largely aligned in terms of depth with marine terraces formed during sea-level high- and lowstands, indicating their formation was driven by glacioeustatic sea-level fluctuation (Florea et al., 2007b). Local variations in lithology and the position of the groundwater table, however, are believed to exert a minor control on speleogenesis as well. In particular, Florea et al. (2007b) hypothesized that recharge to the Floridan Aquifer by the Withlacoochee River combined with reduced permeability from riverine sediment infilling the pore space of the underlying limestone may locally raise the groundwater table such that dissolution in association with Plio-Pleistocene sea- level fluctuation is reinitiated, allowing speleogenesis of caves in this area to occur over multiple generations.

4.2.2. Environmental Setting and Previous Research

Thornton's Cave is less than 1 km east of the Withlacoochee River in Sumter County (Figure 4.1). Between the cave and the river is an open, seasonally flooded wet prairie (hereafter referred to as Thornton's Slough) fed directly by the river. This slough is adjacent to a narrow cypress stand (Figure 4.3). The cave is 14.4 m above mean sea-level and dissolved into the Ocala Limestone. It intersects the unconfined Upper Floridan Aquifer such that some passages are flooded throughout the year. The alignment in elevation between Thornton's Cave and the Talbott marine terrace (paleoshoreline) suggests the primary control on its initial formation was that of sea-level; however, locally, the groundwater table is elevated by the position of the Withlacoochee River and is thought to constitute a modern control, promoting further dissolution of the cave beyond others situated in the West-Central Florida region at similar elevations but located farther from the river (Cook 1931, 1945; Florea et al., 2007b).

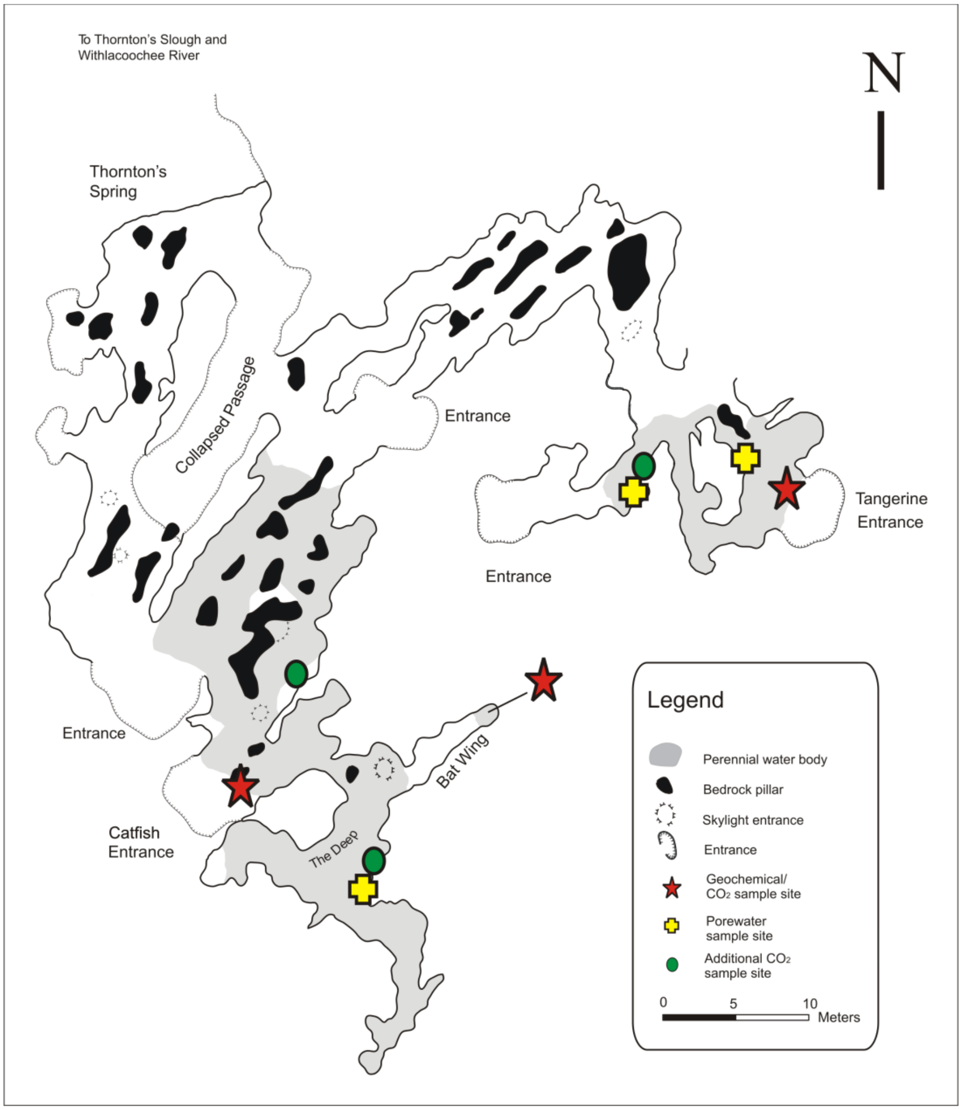

Figure 4.3. Thornton's Cave map. *Modified from Florea et al. (2006)*.

4.2.2.1. Geomorphology and Hydrogeology

Thornton's Cave passages are typically low and wide, with ceiling heights seldom exceeding 2-3 m except at its deeper, perennially flooded areas (Figure 4.3-4.4). Approximately 315 m of the cave's dry passages have been mapped, while submerged passages remain relatively unmapped. Exploratory dives in the Tangerine Entrance documented a submerged vertical passage extending into the aquifer beyond 35 m depth (Brooks et al., personal comm.). Periodic flooding of dry passages (and rising water-level in the flooded passages) is largely associated with increased rainfall in the summer and fall months due to local convection systems as well as tropical systems, including hurricanes (Figure 4.5; Chapter 3). High permeability and transmissivity measurements of the Ocala Limestone in this region (approximately 10^{-12} to 10^{-13} m^2, and 23,226 to 46,452 m^2/day, respectively) support rapid recharge of the aquifer, and therefore rapid response to surface rain events (Ryder, 1985; Budd and Vacher, 2004; Florea and Vacher, 2006). These data are supported by cross-correlation analyses of water-levels at both the Withlacoochee River and the cave's Tangerine Entrance, which show a near-symmetric curve with a lag = ~0, and a rapid, positive response when water-levels at each site were correlated with rainfall (Figure 4.6; Chapter 3). The cave is also hypothesized to facilitate the transport of water between Gum Slough (<1 km to the west) and the Withlacoochee River (Figure 4.7; Florea, personal comm.). When water-level at Gum Slough is higher than the river, water is thought to drain westward through the cave and out from Thornton's Spring and to the river via Thornton's Slough, with the opposite effect occurring when river levels are higher. However, recent droughts combined with increasing regional withdrawal from the aquifer for agriculture and development appears to have restricted westward flow from Gum Slough, as water has not been observed flowing out of Thornton's Spring for at least five years prior to this study (Thornton, personal comm., Ryder, 1985). The summer wet season of 2009, marked by the onset of El Niño-Southern Oscillation, brought more frequent heavy rain events than that of 2008, which caused water-levels at the Withlacoochee River and Thornton's Slough to rise sufficiently to flood into the cave through the Thornton's Spring Entrance (Figure 4.8; Chapter 3). Flooding was observed from early July through mid-September, but due to higher-than-average rainfall through the dry season, water-levels in the cave remained higher than the previous year. In late March 2010, the cave was once again flooded by rising waters at the Withlacoochee River and Thornton's Slough. This event was attributed to the passage of relatively frequent, high-precipitation winter frontal systems associated with the El Niño event, which continued through early-April.

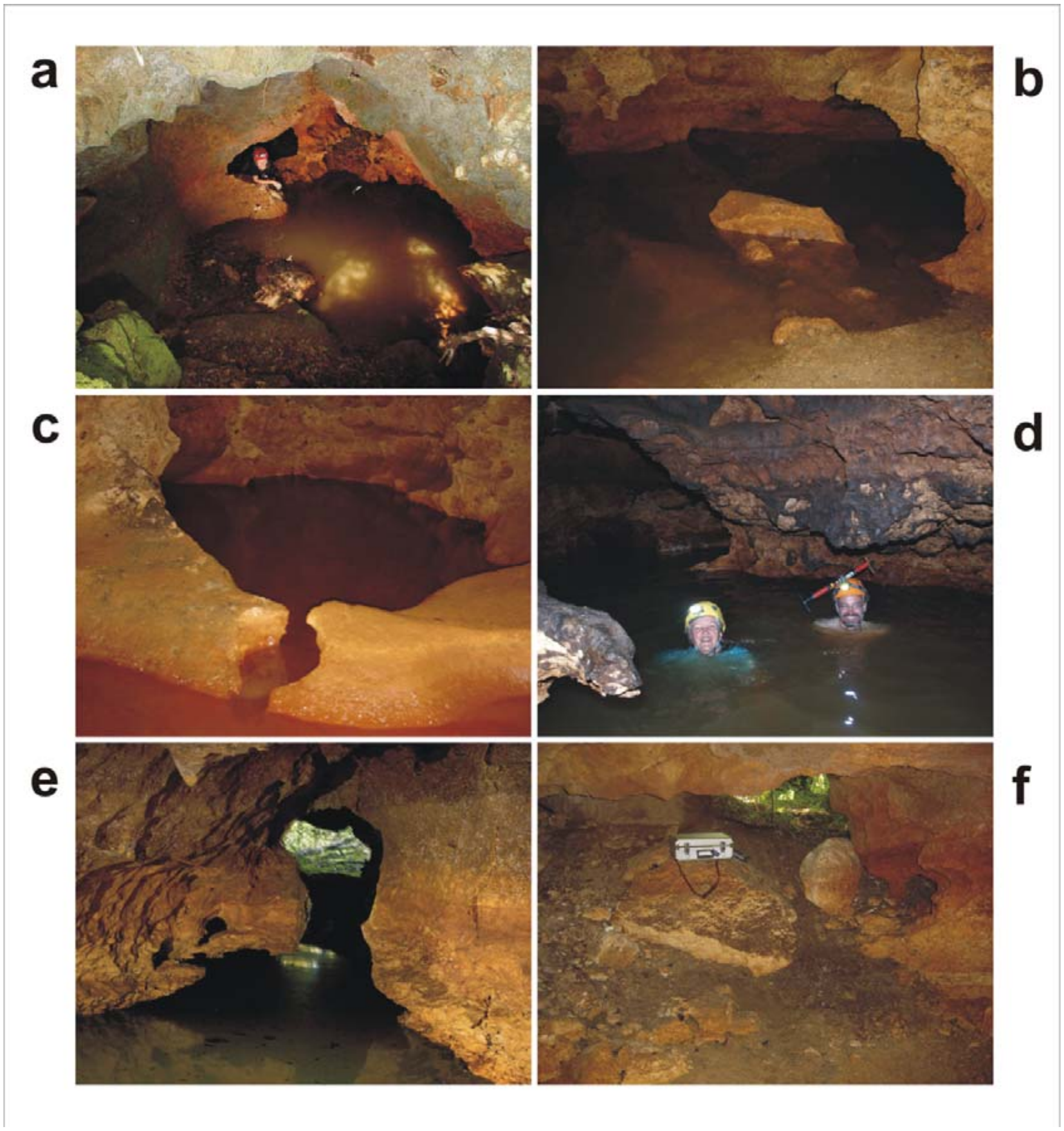

Figure 4.4. Thornton's Cave entrances and passages: a) Tangerine Entrance (pool depth exceeds 30 m at right); b) Catfish Entrance (passage to Bat Wing and The Deep on right); c) perennially flooded pool at terminus of Bat Wing; d) The Deep passage (note dark encrustations on cave ceilings and walls); e) perennially flooded passage west of Tangerine Entrance; f) typical dry cave entrance and passage. *Photos a, d, and e courtesy of T. Turner, J. Sumrall, and A. Palmer, respectively*.

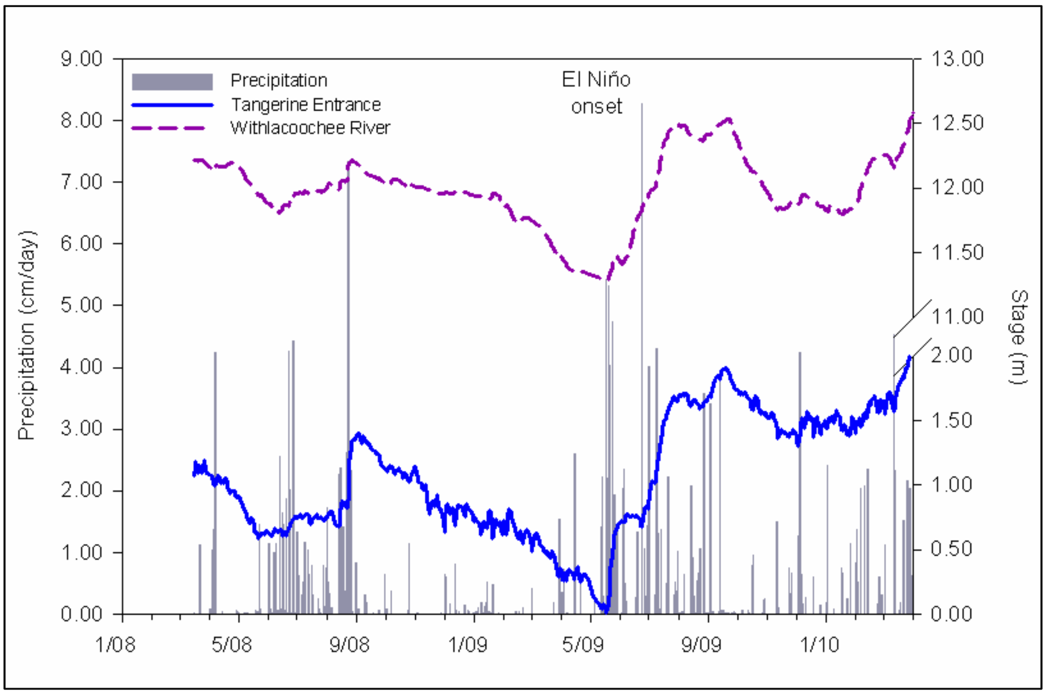

Figure 4.5. Rainfall and stage data for Tangerine Entrance and Withlacoochee River. Note: data for Tangerine Entrance should be interpreted as trends rather than actual stage due to uneven depths attributed by variations in cave floor topography and presence of vertical passages.

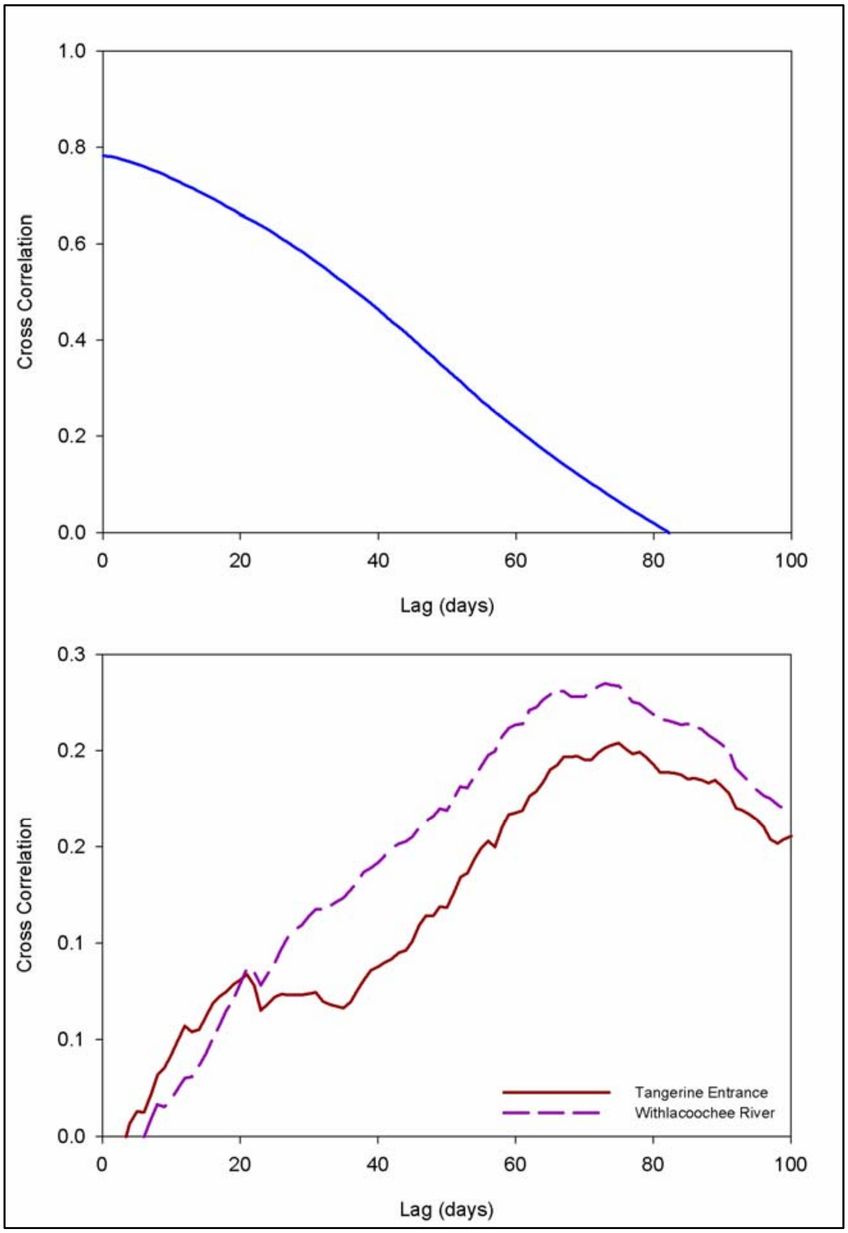

Figure 4.6. Cross-correlograms of water-level and precipitation data at the Tangerine Entrance and the Withlacoochee River. Top: Cross-correlation of water-levels at each site. Bottom: Cross-correlation of rainfall and water-level at each site.

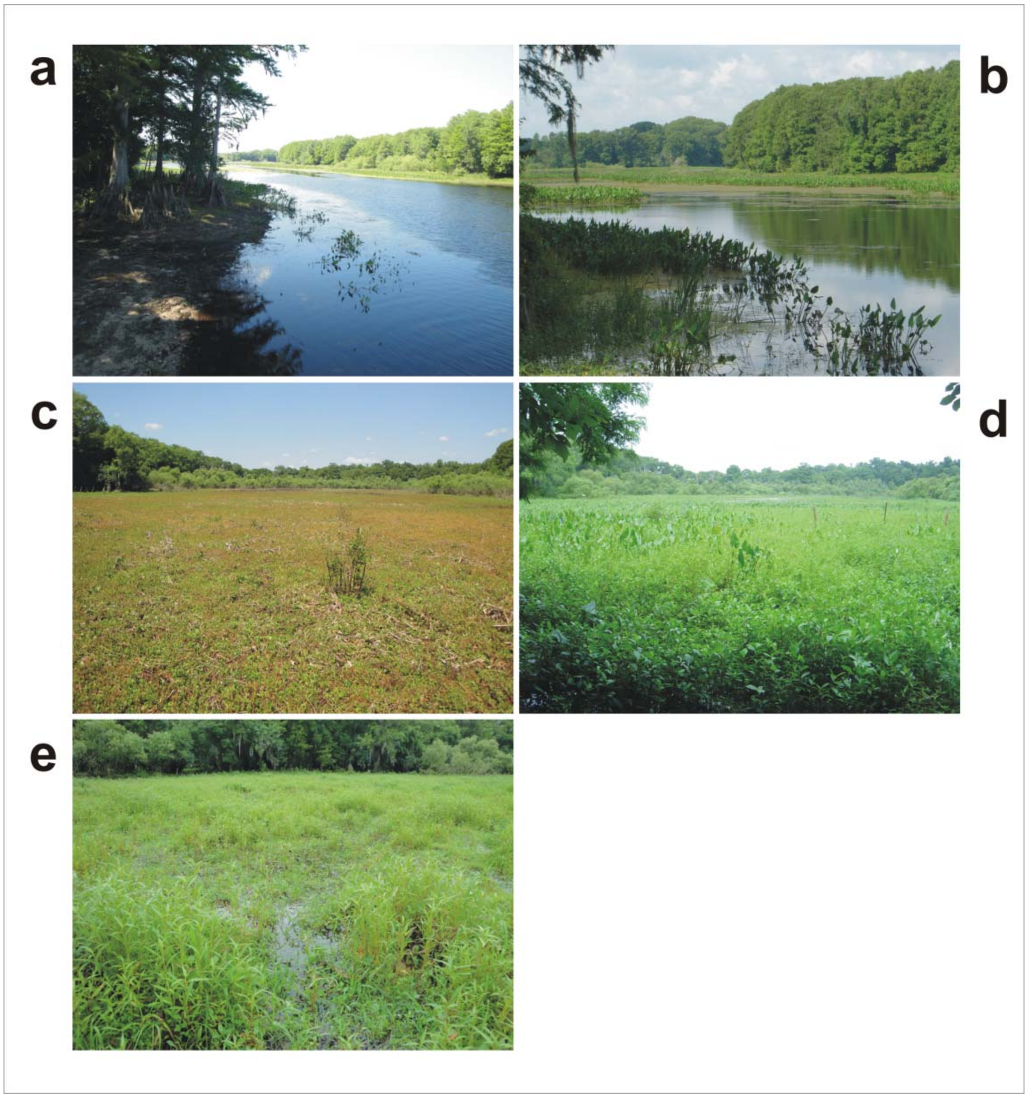

Figure 4.7. Seasonal images of Withlacoochee River and Thornton's Slough: a) Withlacoochee River, dry season (looking south); b) Withlacoochee River, wet season (same vantage); c) Thornton's Slough, dry season (looking west toward river; note dried aquatic vegetation amid grasses); d) Thornton's Slough, wet season (same vantage); e) Thornton's Slough, wet season (looking east toward cypress stand and cave).

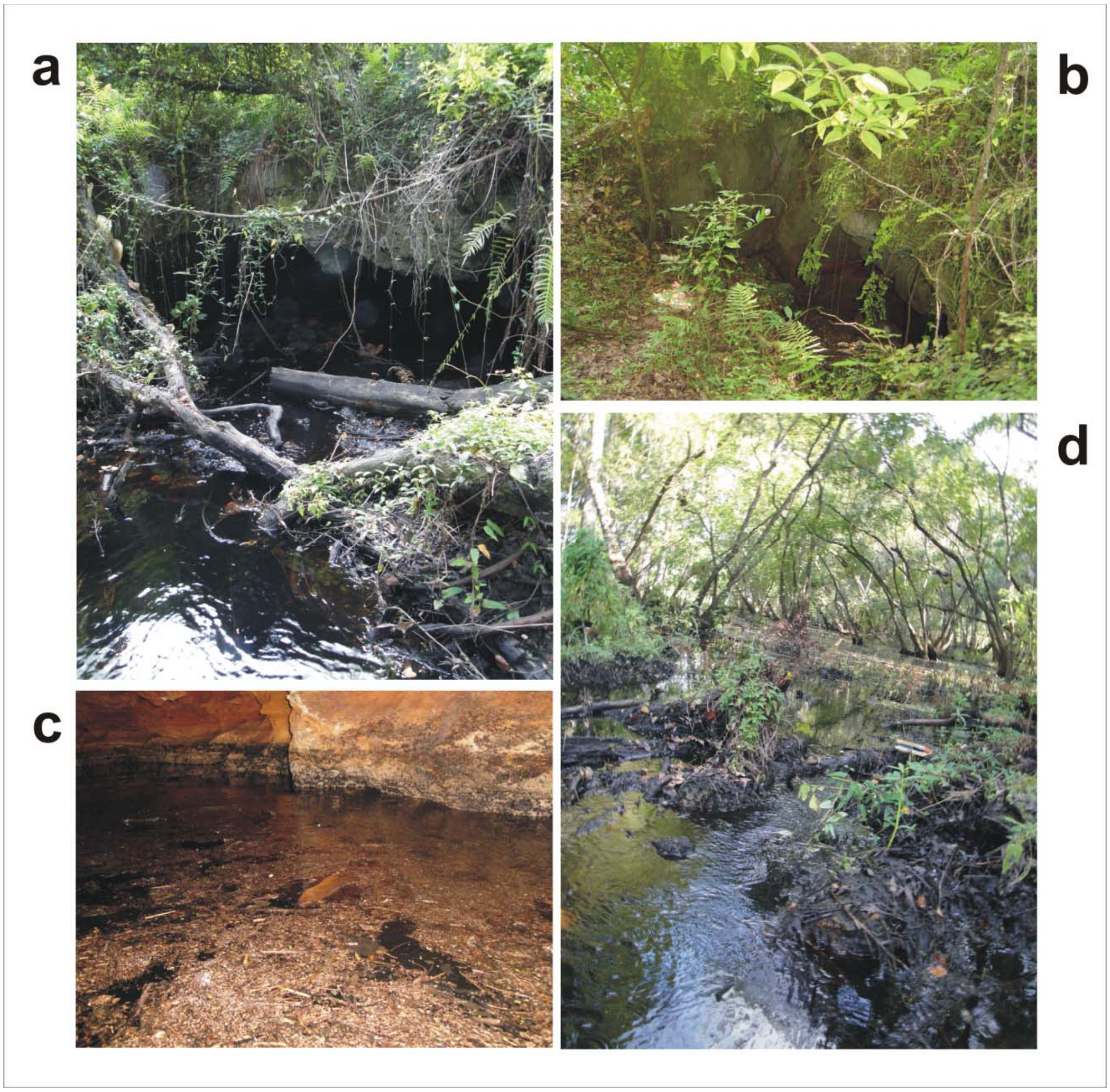

Figure 4.8. Summer 2009 flood images: a) flooded Thornton's Spring Entrance; b) Thornton's Spring Entrance (dry season comparison); c) flooded Catfish Entrance including surface debris (connection to The Deep & Bat Wing submerged along wall); d) flooded cypress hammock (view from Thornton's Spring west toward slough).

4.2.2.2. Cave and Surface Temperatures

Cave air temperatures are generally cooler in the summer and warmer in the winter relative to surface temperature, and exhibit a seasonal lag in temperature change of several weeks (Figure 4.9; Chapter 3). Soil temperatures above the cave are usually intermediate between cave and surface temperatures, such that average values were slightly higher than the cave and had a slightly shorter seasonal lag. Water temperatures at the Tangerine Entrance were more stable with minor seasonal variation but showed a marked decrease beginning in Fall 2009 that appeared to stabilize toward the end of the sampling cycle.

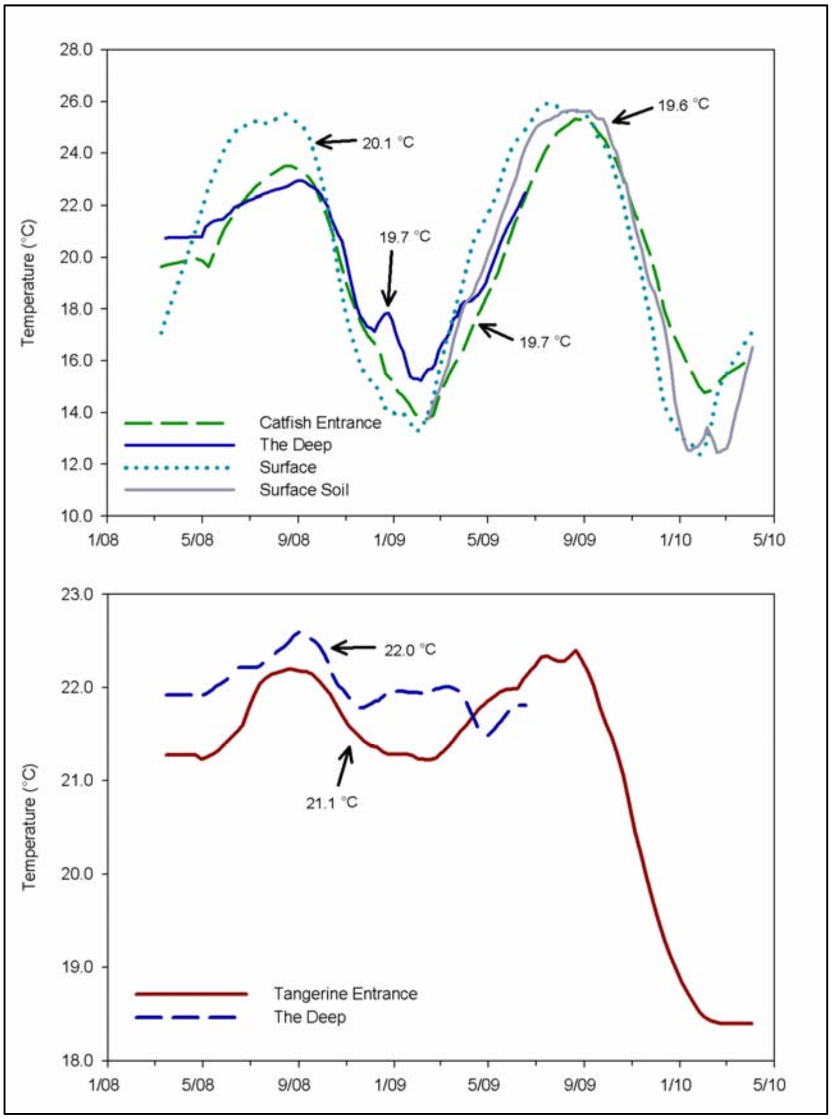

Figure 4.9. Air and water temperature profiles at Thornton's Cave. Top: long-term air temperatures, March 2008 to April 2010; Bottom: long-term water temperatures, March 2008 to April 2010. Arrows indicate mean annual temperature for each site.

4.2.2.3. Organic Matter Sources

Because Thornton's Cave is just 1.7 m below the land surface, collapse features and solution pits have made the cave exceptionally open to the surface, with no fewer than fifteen entrances (eight of human-size). As a result, the cave is subject to both year-round infilling of surface sediments and detrital organic matter from the hardwood forest above, and runoff from rainfall. In addition, the cave serves as a maternity roost for a breeding bat colony (hypothesized to be the eastern pipistrelle, *Perimyotis subflavus*, or the southeastern myotis, *Myotis austroriparius*) of several thousand individuals from approximately late April to mid-August (Figure 4.10). Preferred roosting passages appear to vary from year to year, estimated by extensive diagenetic alteration of ceiling rock due to limestone-bat excrement and urine reactions, yielding black (presumably Fe and/or Mn) crusts throughout the cave's more remote passages. The preferred roosting location observed during the two breeding seasons examined in this study was a passage near the Catfish Entrance, referred to as the Bat Wing (Figure 4.3). Thick deposits of guano combined with showers of urea accumulate on all exposed surfaces at this site, and are input directly into cave waters in a permanent pool at the distal margin of the Bat Wing, as well as the waters along the floor of the passage during seasonal flooding (Figure 4.4c, Figure 4.11).

Figure 4.10. Bat Wing summer maternity roosting colony with associated ceiling encrustation: a-b) roosting colonies (individuals ~5-8 cm in length); c) Bat Wing ceiling following breeding season (note light-colored fungal growth); d) close-up of ceiling encrusting deposits. *Note: Limited photos taken with under guidance of Jeff Gore, scientific advisor for the Florida Bat Conservancy. As of January 2010, white-nose syndrome (WNS) caused by the fungal species* Geomyces destructans*, not reported in Florida bat populations.*

Figure 4.11. Guano deposits in Bat Wing. Top: Guano deposition along passage floor and exposed rock below colony in late April, 2009. Bottom: Rear of same passage in late May 2009 during the onset of the wet season.

4.2.2.4. Cave CO_2

Cave CO_2 surveys from 2008 to 2010 and bench-top respiration experiments show that despite the ventilating conditions of the cave imparted by its numerous openings to the surface, biotic respiration exerts a significant control on CO_2

concentrations in the cave, perhaps more so than ambient atmospheric CO_2 from the surface (Tables 4.1-4.2). Surface CO_2 concentrations and $\delta^{13}C_{CO2}$ values at Thornton's Cave range from 380 to 405 ppm and -8.2 to -9.7‰, respectively, with a 10-20 ppm increase and 0.4 to 1.3‰ decrease from the summer (June-September) to the winter (December-March) months (Table 4.1). By comparison, CO_2 concentrations and $\delta^{13}C_{CO2}$ values in the cave are lowest and highest, respectively, during the cooler winter months, with little variation between cave entrances and cave passages. During this time, concentrations range from 400-500 ppm, whereas $\delta^{13}C_{CO2}$ values range from -10 to -12‰. The opposite effect occurs in the warmer summer months (June through August), when CO_2 concentrations and $\delta^{13}C_{CO2}$ values are highest and lowest, respectively. This summer CO_2 and $\delta^{13}C_{CO2}$ pattern is particularly evident at the Bat Wing, where respiration of the breeding bat colony yields values of approximately 1230 ppm and -19‰. From here, CO_2 is ventilated out through the Catfish Entrance, raising its CO_2 concentration and lowering its $\delta^{13}C_{CO2}$ value beyond that measured at the Tangerine Entrance.

Bench-top experiments to document and calculate CO_2 production from samples of cave rock and sediments from dry and flooded passages, as well as surface soils, showed that CO_2 of biogenic origin was derived, in varying quantities, from each substrate (Table 4.2). These data demonstrated that production of CO_2 by microorganisms was occurring within each of the cave substrates and in the cave, was most productive in sediments and when substrates were water-saturated. Production rates in the cave fell within the lower range of those modeled by Solomon and Cerling (1987) for montane soils in Utah, USA, and suggest that while CO_2 flux from substrates such as wall rock and sediments is moderate compared to that from surface soils, it may nonetheless be an important contribution of CO_2 in caves when organic matter and water are not limiting.

Table 4.1. Summary of seasonal CO_2 $\delta^{13}C$ and concentration variations, by site

	July 08		February 2009		June 2009		October 2009		December 2009	
	$\delta^{13}C_{CO2}$ (‰)	Conc. (ppm)	$\delta^{13}C_{CO2}$ (‰)	Conc. (ppm)	$\delta^{13}C_{CO2}$ (‰)	Conc. (ppm)	$\delta^{13}C_{CO2}$ (‰)	Conc. (ppm)	$\delta^{13}C_{CO2}$ (‰)	Conc. (ppm)
Tangerine Entrance	-10.5	466	-9.60	409	-11.41	440	-13.78	515	-9.05	431
Tangerine Ent. Passage	-12.3	525	-9.62	411	-11.02	437	-15.73	620	-12.74	611
Catfish Ent	-15.8	805	-11.39	470	-10.97	419	-17.01	727	-9.52	445
Catfish Ent. Passage	-12.6	534	-9.92	417	-11.10	431				
Bat Wing	-19.4	1234	-11.39	481	-18.96	1232				
Forest Floor	-8.8	391	-12.09	488	-14.74	545	-18.16	762	-8.81	417
Surface Atmosphere	-8.6	381	-9.39	405	-9.59	384	-9.72	383	-8.26	397
Guano	-22.8	1056								

Table 4.2. Results from bench-top CO_2 production rate experiments

	$\delta^{13}C$ (‰)	CO_2 Production Rate (μmol m^{-3} s^{-1})
Wet cave rock	-18.5	0.23
Dry cave rock	-13.2	0.18
Wet cave sediment	-21.1	0.15
Dry cave sediment	-20.3	0.10
Surface soils	-23.1	0.33

4.3. Methods

Geochemical data collection at Thornton's Cave, Thornton's Slough, and the Withlacoochee River took place over a period of twenty months, from April 2008 to December 2009. These data consisted of $\delta^{13}C$ analyses of cave limestone and observations of its dissolution over time made from tablets deployed in the cave, and bi-weekly measurements of aquatic geochemistry. Statistical and multivariate analyses of aquatic geochemical data were performed to provide insight as to the major geochemical processes occurring at each site, and to determine the degree of similarity between sites.

4.3.1. Limestone Dissolution

To approximate dissolution rate in the water and at the soil/limestone interface at the cave, small limestone tablets (~36 cm^3) cut from a larger sample of Ocala Limestone collected from the cave were deployed for 16 months between December 2008 and April 2010 (Figure 4.12). Deployment took place at the Tangerine Entrance and ~20 cm deep in the thin soil veneer above the Catfish Entrance. Tablets were cut from the interior of the sample to obtain the least altered material and initially treated with 20% hydrogen peroxide to remove organic matter and human-introduced carbon. After rinsing with DI water and drying for 36 hours at 75 °C, tablets were then treated with 20% HCl to create a fresh limestone surface, then thoroughly rinsed and re-dried. Tablet weights were obtained to three decimal places using a microbalance prior to deployment in mesh bags (facilitating air/water exchange) at both locations. Upon retrieval, samples were once again cleaned with hydrogen peroxide following the above-mentioned procedure. They were then re-weighed using the same microbalance to determine change in mass.

Figure 4.12. Limestone tablets cut from samples of Ocala Limestone.

4.3.2. Aquatic Geochemistry

Water samples were collected approximately biweekly from permanent pools at both the Tangerine and Catfish Entrances of Thornton's Cave. Water-levels permitting, samples were also collected in the Bat Wing to observe the impact of bat colonies on the water geochemistry. Samples were also collected in Thornton's Slough just east of the cave and at a gauging station on the Withlacoochee River approximately 5 km upstream from the cave. This station is part of the National Water Information System (NWIS station ID 02312598) and is jointly monitored by the United States Geological Survey (USGS) and the Southwest Florida Water Management District (SWFWMD). Approved water-level data reported for this station were downloaded from the NWIS web interface (USGS Water Resources Water-Data Support Team, 2010). Seasonal samples were also collected for analyses of $\delta^{13}C_{DOC}$ and carbon/nitrogen (C/N) ratios. In 2008, porewater samples were collected from wall rock at various locations in the cave.

4.3.2.1. pH, Conductivity, and DIC

Biweekly samples were analyzed on-site for pH and conductivity using a Eutech EcoScan pH 5 and Oakton Acorn CON6 conductivity meters. Samples collected for $\delta^{13}C_{DIC}$, and DIC concentration analyses were contained in 11-mL vials and fixed with $HgCl_2$ to prevent further bacterial production. Vials were covered with Parafilm to eliminate headspace and then refrigerated. Analyses of $\delta^{13}C_{DIC}$ were carried out at the University of South Florida's Isotope Geochemistry lab using a Delta V gas-source isotope ratio mass spectrometer (IRMS) coupled to a Gasbench II peripheral using the methods of Torres et al. (2005) and Assayag et al. (2006). They were then standardized to Vienna Pee Dee Belemnite (VPDB):

$$\delta^{13}C_{sample}(‰) = \left[\frac{({}^{13C}/_{12C})\ sample}{({}^{13C}/_{12C})\ VPDB} - 1\right] \cdot 1000 \qquad \text{(Eq. 1)}$$

The DIC concentration of each sample was estimated by standardizing the peak area of mass 44 for the first 10 replicate peaks for each sample using a $NaHCO_3$ solution with a known concentration of ~24 μg/L.

4.3.2.2. Alkalinity, Hardness, Major Ions, and *p*CO_2

Additional analyses of alkalinity began in early December 2008, and hardness in mid-May, 2009, with both continued through to the end of the water sampling cycle. Both were calculated for $CaCO_3$ and measured in the field by digital titration with detection limits of 10-4000 mg/L. Major ion analyses (total Fe, ferrous iron (Fe^{2+}), SO_4^{2-}, NO_3^-, NH_3, and PO_4^{3-}) were conducted over a five-month period from mid-May to late October, 2009. Samples were collected, chilled in the field, and transported to the University of South Florida's Aquatic Geochemistry Lab for immediate analyses (within

2-3 hours) using a Hach DR/2400 spectrophotometer. Detection limits for ion methods utilized are as follows: total Fe (0.02-3 mg/L), Fe^{2+} (0.02-3 mg/L), SO_4^{2-} (2-70 mg/L), NO_3^- (0.01-10 mg/L), NH_3 (0.4-50 mg/L), PO_4^{3-} (0.02-2.5 mg/L). Dilution was necessary for some NH_3 and total Fe samples that exceeded detection limits. Bicarbonate concentration was assumed using alkalinity data and was calculated by multiplying alkalinity values by a factor of 1.22, the stoichiometric ratio of 2 moles of HCO_3^- produced per mole of $CaCO_3$. The summed equivalent concentration of Ca^{2+} and Mg^{2+} was measured using hardness data. This calculation was done by multiplying hardness values by 0.4, or the mass fraction of Ca^{2+} in $CaCO_3$, and converting this value to millequivalent concentration. Magnesium substitution in this case is considered limited due to the minimal concentrations of Mg^{2+} in both the Ocala Limestone and in the Floridan Aquifer compared to Ca^{2+} (Miller, 1986; Sprinkle, 1989). Calculations of pCO_2 were made using pH and alkalinity data, using the dissociation constants K_1 and K_{CO2} at 25 °C (Stumm and Morgan, 1996).

4.3.2.3. $\delta^{13}C_{DOC}$ and C/N Ratios

One-liter water samples from each site (when available) were filtered using 0.45 µm membranes and fixed with 30% HCl to prevent further bacterial production. Dissolved organic carbon was physically separated from the sample by evaporative concentration of the entire liter. This method produced varying amounts of dry DOC, ranging approximately from 30 to 150 mg. This DOC was then treated with sulfurous acid to remove any inorganic carbonate minerals, and dried for 36 hours at 75 °C. For $\delta^{13}C_{DOC}$ analyses, at least 5 mg of DOC from each sample was measured into tin capsules and loaded into an auto-sampler. Analyses of $\delta^{13}C$, %C, and %N were carried out using a Costech elemental analyzer coupled to the above-mentioned IRMS and standardized to Fergie CN (containing sucrose, KNO_3, SiO_2, and kaolinite), and B2155 (protein). Percentages of C and N reported in analyses were used to calculate C/N ratios. This procedure was not performed for limestone and soil pore water DOC, as insufficient water could be extracted for analysis.

4.3.2.4. Limestone and Pore Water $\delta^{13}C_{DIC}$

To obtain the $\delta^{13}C$ of the Ocala Limestone, small samples were collected from the walls of Thornton's Cave and ground to produce a homogenized powder. These powders were sterilized with 20% hydrogen peroxide to remove organic matter and analyzed for $\delta^{13}C$ by reaction with 85% phosphoric acid using the above-mentioned IRMS (Révész and Landwehr, 2002). Four replicates of these samples were analyzed and averaged to produce a single $\delta^{13}C$ value.

Pore waters were extracted from wall rock at the Tangerine Entrance, along a passage immediately to the west of the Tangerine Entrance, and in The Deep in April 2008 (Figure 4.3). To collect pore waters, a 4- to 5-cm-wide hole was drilled into the cave wall approximately 8 cm deep. A UMS SG soil porewater sampler connected to a pump was adapted to collect porewater by inserting it into the hole and packing it with quartz sand to create a vacuum. Water was collected in 11-mL vials fixed, sealed, and analyzed for $\delta^{13}C_{DIC}$ and DIC concentration using the above-mentioned methods.

4.3.2.5. Statistical Analyses

All statistical analyses were performed using a combination of PAST, version 2.00, and R, version 2.10.1 (Hammer et al., 2001; R Development Core Team, 2009). Significance tests of results between sites were performed using the Mann-Whitney test for paired, non-parametric distributions, with results reported within the 95% confidence interval.

Multivariate data reduction of aquatic geochemical measurements was performed using correlation matrices and principal component analyses (PCA) to identify the degree of geochemical similarity between sites and to determine specific processes contributing to geochemical variation at each individual site. Only geochemical parameters sampled at biweekly intervals were used in multivariate analyses; therefore, data collected from the Bat Wing at Thornton's Cave was omitted from all PCAs as sampling was limited due to passage flooding that restricted access to this location. Because alkalinity, hardness, pCO_2, and major ions were sampled later in the study, two separate PCAs were needed for bulk and individual site analyses. In PCA-A, water-level, pH, conductivity, $\delta^{13}C_{DIC}$, and DIC concentration for each sampling date were included. In PCA-B, all parameters sampled from May 20 to October 29, 2009 were included. Because PCA requires square data matrices, missing data points for a given geochemical parameter were replaced with their averages calculated for the sampling duration. This only affected PCA-A, as no data were missing from the time period analyzed in PCA-B.

In all PCAs, water-levels were included to elucidate any affects of concentration and dilution on geochemical parameters. Because water-level data recorded at the Tangerine Entrance was higher in resolution than the geochemical data, linear interpolation was utilized to obtain 33 values corresponding to the 33 total sample dates. Since Withlacoochee River water-levels measured by the USGS/SWFWMD were reported on a daily basis, water-levels for each sampling date were applied to the dataset for this location. Finally, due to high substantial differences in average water-levels between wet and dry seasons identified and discussed in Chapter 3, PCA-A was rerun for each sampling site to analyze only those samples collected during the wet and dry seasons (PCA-A_w and PCA-A_d, respectively). This method was done to further elucidate the impact of water-level on the geochemical variation at these sites. Based on rainfall data collected for this study reported in Chapter 3 and long-term data (1971-2000) reported by Florida State University's Florida Climate Center for West-Central Florida, the wet season was defined by elevated rainfall rates between May and September, with the remaining months considered as part of the dry season (Florida Climate Center, 2010). Once PCAs were complete, principal components explaining geochemical relationships were chosen using the Kaiser-Guttman rule, eliminating all principal components with eigenvalues ≥1 (Guttman, 1954; Kaiser, 1960).

4.4. Results

Active dissolution of limestone at Thornton's Cave was observed, with tablets located at both the Tangerine Entrance and the soil column above the Catfish Entrance demonstrating a loss in mass over the course of their deployment (Table 4.3). The mass of the Tangerine Entrance tablet was reduced the most (by 0.941g), equating to 3.497% of its original mass, while the soils tablet lost 2.504% of its mass (0.778 g).

Table 4.3. Limestone tablet masses before and after deployment

Location	Initial Mass (g)	Final Mass (g)	Diff.	% Lost
Tangerine Entrance	26.908	25.967	0.941	3.497
Soils	31.076	30.298	0.778	2.504

Geochemical data measured from each site in this study are summarized in Tables 4.4-4.6 and Figures 4.13-4.16. Bulk PCA-A results indicate little difference in geochemical variation between them, particularly between the Tangerine and Catfish

Entrances (Figure 4.17). Similar results were returned in PCA-B despite the more limited dataset. Individual site results are discussed below, and grouped by location into cave and surface sites. Values of these bulk PCAs are reported in Appendices IV and V.

Table 4.4. Geochemical data collected for Thornton's Cave and Slough, and the Withlacoochee River, April 2008 to December 2009

	Date	pH	Cond (µS)	Hard. (mg/L)	Alk. (mg/L)	pCO_2 (atm)	$\delta^{13}C_{DIC}$ (‰)	DIC Conc (µg/L)	Fe^{2+} (mg/L)	Total Fe (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	NH_3 (mg/L)	PO_4^{3-} (mg/L)
Tangerine Entrance														
	4/14/08	6.12	449	*	*	*	-5.7	21.39	*	*	*	*	*	*
	4/26/08	6.06	450	*	*	*	-5.0	33.66	*	*	*	*	*	*
	6/14/08	6.31	460	*	*	*	-3.8	24.78	*	*	*	*	*	*
	6/27/08	6.46	466	*	*	*	-5.8	30.29	*	*	*	*	*	*
	7/6/08	6.41	454	*	*	*	-6.7	30.57	*	*	*	*	*	*
	7/19/08	6.33	463	*	*	*	-3.3	21.90	*	*	*	*	*	*
	7/26/08	6.30	465	*	*	*	-5.9	28.02	*	*	*	*	*	*
	8/14/08	6.52	474	*	*	*	-5.8	25.00	*	*	*	*	*	*
	9/3/08	6.44	472	*	*	*	-6.8	27.33	*	*	*	*	*	*
	9/28/08	6.57	467	*	*	*	-4.6	28.60	*	*	*	*	*	*
	10/25/08	6.50	477	*	*	*	-5.8	29.11	*	*	*	*	*	*
	11/12/08	6.34	480	*	*	*	-5.3	26.15	*	*	*	*	*	*
	12/6/08	6.44	480	*	204	1.91E-03	-5.8	26.90	*	*	*	*	*	*
	12/17/08	6.52	483	*	210	1.54E-03	-0.1	26.34	*	*	*	*	*	*
	1/17/09	6.49	483	*	231	1.50E-03	-5.9	30.68	*	*	*	*	*	*
	1/30/09	6.48	482	*	241	1.47E-03	-7.5	38.17	*	*	*	*	*	*
	2/13/09	6.74	487	*	217	8.98E-04	-6.8	36.63	*	*	*	*	*	*
	2/24/09	6.60	488	*	214	1.26E-03	-4.8	32.63	*	*	*	*	*	*
	3/20/09	6.78	499	*	214	8.30E-04	-4.6	28.26	*	*	*	*	*	*
	4/10/09	6.38	507	*	212	2.10E-03	-4.8	28.41	*	*	*	*	*	*
	4/27/09	6.56	506	*	258	1.14E-03	1.0	24.99	*	*	*	*	*	*
	5/20/09	6.40	495	205	198	2.15E-03	-4.4	32.46	0.25	2.52	19.00	0.10	0.43	0.49
	6/5/09	6.57	486	256	239	1.21E-03	-5.4	37.43	0.00	2.18	6.00	0.00	0.46	0.47
	6/17/09	6.28	489	250	276	2.04E-03	-4.8	26.72	0.02	2.11	8.00	0.00	0.41	0.60
	7/6/09	6.41	475	285	225	1.85E-03	-2.5	28.93	0.04	2.11	0.00	0.00	0.20	0.64
	7/22/09	7.15	197	150	76	9.97E-04	-6.3	1.52	0.05	1.82	0.00	0.00	0.02	0.96
	8/12/09	6.92	131	200	110	1.17E-03	-5.8	3.27	0.07	1.75	0.00	0.00	0.14	0.71
	8/27/09	7.18	194	85	69	1.02E-03	-5.6	3.80	0.05	2.41	0.00	0.00	0.12	0.83
	9/17/09	5.77	130	125	48	3.79E-02	-8.6	2.40	0.11	1.39	0.00	0.00	0.01	0.51
	10/1/09	6.15	195	140	60	1.26E-02	-7.1	1.13	0.11	2.30	0.00	0.00	0.32	1.09

	Date	pH	Cond (µS)	Hard. (mg/L)	Alk. (mg/L)	pCO_2 (atm)	$\delta^{13}C_{DIC}$ (‰)	DIC Conc (µg/L)	Fe^{2+} (mg/L)	Total Fe (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	NH_3 (mg/L)	PO_4^{3-} (mg/L)
T.E. cont'd	10/29/09	7.23	305	150	166	3.80E-04	-4.6	14.15	0.08	4.21	0.00	0.00	0.64	2.00
	11/14/09	7.25	419	270	184	3.27E-04	-4.6	17.59	*	*	*	*	*	*
	12/7/09	6.61	489	281	215	1.22E-03	-5.1	20.05	*	*	*	*	*	*
	Mean	6.52	424	200	184	3.60E-03	-5.1	23.92	0.08	2.28	3	0.01	0.28	0.83
	StDev	0.33	115	69	69	8.25E-03	1.9	10.56	0.07	0.76	6	0.03	0.21	0.46
Catfish Entrance														
	4/14/08	6.14	450	*	*	*	-5.5	22.11	*	*	*	*	*	*
	4/26/08	5.99	451	*	*	*	-5.0	31.63	*	*	*	*	*	*
	6/14/08	6.28	461	*	*	*	-3.2	15.50	*	*	*	*	*	*
	6/27/08	6.45	460	*	*	*	-5.7	26.98	*	*	*	*	*	*
	7/6/08	6.25	451	*	*	*	-7.9	37.41	*	*	*	*	*	*
	7/19/08	6.24	460	*	*	*	-5.5	25.08	*	*	*	*	*	*
	7/26/08	6.56	469	*	*	*	-5.7	28.91	*	*	*	*	*	*
	8/14/08	6.59	427	*	*	*	-4.3	20.22	*	*	*	*	*	*
	9/3/08	6.56	450	*	*	*	-4.5	22.78	*	*	*	*	*	*
	9/28/08	6.55	470	*	*	*	0.9	21.82	*	*	*	*	*	*
	10/25/08	6.5	480	*	*	*	-5.4	27.87	*	*	*	*	*	*
	11/12/08	6.33	480	*	*	*	-5.6	27.56	*	*	*	*	*	*
	12/6/08	6.42	482	*	212	1.92E-03	-6.7	31.89	*	*	*	*	*	*
	12/17/08	6.63	482	*	215	1.17E-03	-5.6	27.03	*	*	*	*	*	*
	1/17/09	6.54	488	*	221	1.40E-03	-5.8	29.09	*	*	*	*	*	*
	1/30/09	6.55	482	*	216	1.40E-03	-7.2	38.10	*	*	*	*	*	*
	2/13/09	6.54	487	*	210	1.47E-03	-5.0	25.69	*	*	*	*	*	*
	2/24/09	6.46	487	*	208	1.78E-03	-7.6	42.28	*	*	*	*	*	*
	3/20/09	6.76	500	*	215	8.65E-04	-6.0	34.38	*	*	*	*	*	*
	4/10/09	6.59	498	*	209	1.32E-03	-7.3	36.23	*	*	*	*	*	*
	4/27/09	6.51	505	*	228	1.45E-03	-4.6	37.38	*	*	*	*	*	*
	5/20/09	6.65	489	203	209	1.15E-03	-5.3	35.57	0	2.22	21	0.1	0.68	0.35
	6/5/09	6.61	487	251	226	1.16E-03	-3.1	32.07	0.04	3.24	7	0	0.45	0.17
	6/17/09	6.45	486	245	252	1.51E-03	-6.2	33.88	0.15	2.2	12	0.01	0.49	0.65
	7/6/09	6.62	483	238	295	8.70E-04	-5.4	34.23	0.11	2.32	0	0.11	1.49	0.59
	7/22/09	7.24	202	110	95	6.48E-04	-6.1	1.72	0.05	1.6	0	0	0.03	0.91
	8/12/09	6.95	131	335	85	1.41E-03	-8.9	2.23	0.1	1.59	0	0	0.15	0.74

	Date	pH	Cond (µS)	Hard. (mg/L)	Alk. (mg/L)	pCO_2 (atm)	$\delta^{13}C_{DIC}$ (‰)	DIC Conc (µg/L)	Fe^{2+} (mg/L)	Total Fe (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	NH_3 (mg/L)	PO_4^{3-} (mg/L)
C.E. Cont'd	8/27/09	7.31	225	135	102	5.14E-04	-5.7	4.55	0.01	2.4	0	0	0.36	1.05
	9/17/09	6.36	128	155	52	8.99E-03	-8.4	1.71	0.12	1.57	0	0	0.01	0.39
	10/1/09	5.92	138	215	94	1.37E-02	0.6	1.55	0.01	2.26	0	0	0.34	1.01
	10/29/09	7.28	288	180	118	4.76E-04	-6.5	16.74	0.03	4.13	0	0	0.8	1.94
	11/14/09	7.37	392	240	192	2.38E-04	-4.5	15.98	*	*	*	*	*	*
	12/7/09	6.52	473	205	210	1.54E-03	-2.8	12.33	*	*	*	*	*	*
	Mean	6.57	419	209	184	2.14E-03	-5.3	24.32	0.06	2.35	4	0.02	0.48	0.78
	StDev	0.34	117	60	65	3.18E-03	2.1	11.81	0.05	0.80	7	0.04	0.44	0.50
Bat Wing														
	4/14/08	*	*	*	*	*	*	*	*	*	*	*	*	*
	4/26/08	*	*	*	*	*	*	*	*	*	*	*	*	*
	6/14/08	*	*	*	*	*	*	*	*	*	*	*	*	*
	6/27/08	*	*	*	*	*	*	*	*	*	*	*	*	*
	7/6/08	*	*	*	*	*	*	*	*	*	*	*	*	*
	7/19/08	*	*	*	*	*	*	*	*	*	*	*	*	*
	7/26/08	*	*	*	*	*	-5.7	26.48	*	*	*	*	*	*
	8/14/08	6.71	437	*	*	*	-5.2	22.86	*	*	*	*	*	*
	9/3/08	*	*	*	*	*	-5.0	22.70	*	*	*	*	*	*
	9/28/08	6.61	445	*	*	*	6.4	15.07	*	*	*	*	*	*
	10/25/08	6.62	481	*	*	*	-6.0	28.68	*	*	*	*	*	*
	11/12/08	6.61	483	*	*	*	-5.0	23.71	*	*	*	*	*	*
	12/6/08	6.55	481	*	215	1.40E-03	-6.3	28.36	*	*	*	*	*	*
	12/17/08	6.68	483	*	222	1.01E-03	-5.7	28.48	*	*	*	*	*	*
	1/17/09	6.63	492	*	218	1.15E-03	-7.8	36.75	*	*	*	*	*	*
	1/30/09	6.47	483	*	210	1.73E-03	-8.1	37.67	*	*	*	*	*	*
	2/13/09	6.54	493	*	212	1.46E-03	-0.9	20.78	*	*	*	*	*	*
	2/24/09	6.48	488	*	217	1.63E-03	-5.2	30.87	*	*	*	*	*	*
	3/20/09	6.67	503	*	209	1.10E-03	-5.6	31.48	*	*	*	*	*	*
	4/10/09	6.42	499	*	216	1.88E-03	-8.7	42.45	*	*	*	*	*	*
	4/27/09	6.54	510	*	228	1.35E-03	0.5	26.29	*	*	*	*	*	*
	5/20/09	6.47	493	246	222	1.63E-03	-7.3	45.10	0.03	3.05	21	0	0.75	1.27
	6/5/09	6.59	492	321	252	1.09E-03	-5.9	37.24	0.01	2.32	7	0	0.51	0.28
	6/17/09	6.29	490	405	272	2.02E-03	-4.6	34.32	0.03	3.01	11	0	0.64	0.63
	7/6/09	6.48	487	225	246	1.44E-03	-5.5	36.60	0.02	2.85	0	0.07	2.3	1.04

	Date	pH	Cond (µS)	Hard. (mg/L)	Alk. (mg/L)	pCO_2 (atm)	$\delta^{13}C_{DIC}$ (‰)	DIC Conc (µg/L)	Fe^{2+} (mg/L)	Total Fe (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	NH_3 (mg/L)	PO_4^{3-} (mg/L)
B.W. cont'd	7/22/09	*	*	*	*	*	*	*	*	*	*	*	*	*
	8/12/09	*	*	*	*	*	*	*	*	*	*	*	*	*
	8/27/09	*	*	*	*	*	*	*	*	*	*	*	*	*
	9/17/09	*	*	*	*	*	*	*	*	*	*	*	*	*
	10/1/09	*	*	*	*	*	*	*	*	*	*	*	*	*
	10/29/09	*	*	*	*	*	*	*	*	*	*	*	*	*
	11/14/09	*	*	*	*	*	*	*	*	*	*	*	*	*
	12/7/09	*	*	*	*	*	*	*	*	*	*	*	*	*
	Mean	6.55	485	299	226	1.45E-03	-4.8	30.31	0.02	2.81	10	0.02	1.05	0.81
	StDev	0.11	18	82	19	3.17E-04	3.5	7.77	0.01	0.34	9	0.04	0.84	0.44
Thornton's Slough														
	4/14/08	*	*	*	*	*	*	*	*	*	*	*	*	*
	4/26/08	*	*	*	*	*	*	*	*	*	*	*	*	*
	6/14/08	6.44		*	*	*	-2.0	16.64	*	*	*	*	*	*
	6/27/08	6.40	358	*	*	*	-5.3	11.54	*	*	*	*	*	*
	7/6/08	6.27	385	*	*	*	-4.1	11.37	*	*	*	*	*	*
	7/19/08	6.03	351	*	*	*	3.8	26.87	*	*	*	*	*	*
	7/26/08	*	*	*	*	*	*	*	*	*	*	*	*	*
	8/14/08	6.36	258	*	*	*	-12.9	43.21	*	*	*	*	*	*
	9/3/08	6.35	306	*	*	*	-11.1	12.13	*	*	*	*	*	*
	9/28/08	6.48	327	*	*	*	-6.1	18.93	*	*	*	*	*	*
	10/25/08	6.34	371	*	*	*	-6.6	15.21	*	*	*	*	*	*
	11/12/08	6.36	383	*	*	*	-5.1	14.71	*	*	*	*	*	*
	12/6/08	6.52	389	*	136	2.38E-03	-4.9	16.68	*	*	*	*	*	*
	12/17/08	6.88	422	*	177	7.97E-04	-8.9	21.21	*	*	*	*	*	*
	1/17/09	6.87	404	*	161	8.97E-04	-7.5	25.80	*	*	*	*	*	*
	1/30/09	6.90	458	*	185	7.28E-04	-9.1	29.61	*	*	*	*	*	*
	2/13/09	6.62	523	*	212	1.21E-03	0.1	25.79	*	*	*	*	*	*
	2/24/09	*	*	*	*	*	*	*	*	*	*	*	*	*
	3/20/09	*	*	*	*	*	*	*	*	*	*	*	*	*
	4/10/09	*	*	*	*	*	*	*	*	*	*	*	*	*
	4/27/09	*	*	*	*	*	*	*	*	*	*	*	*	*
	5/20/09	6.24	634	344	158	3.90E-03	-9.9	61.02	0.04	0.7	134	0.3	0.23	1.62

	Date	pH	Cond (µS)	Hard. (mg/L)	Alk. (mg/L)	*p*CO_2 (atm)	$\delta^{13}C_{DIC}$ (‰)	DIC Conc (µg/L)	Fe^{2+} (mg/L)	Total Fe (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	NH_3 (mg/L)	PO_4^{3-} (mg/L)
T.S. cont'd	6/5/09	6.24	521	427	160	3.85E-03	-8.6	61.84	0.07	0.8	345	0.3	0	0.21
	6/17/09	6.53	448	273	183	1.73E-03	-8.3	40.45	0.05	0.46	75	0	0.01	0.93
	7/6/09	6.32	390	250	162	3.16E-03	-9.9	42.39	0.05	2.9	23	0	0.01	1.72
	7/22/09	7.07	230	240	87	1.05E-03	-2.8	3.18	0.05	2.51	0	0	0.03	0.84
	8/12/09	6.72	136	175	183	1.11E-03	-9.8	9.65	0.09	2.46	0	0	0.07	1.09
	8/27/09	7.01	214	150	84	1.25E-03	-4.6	13.71	0.15	6.1	0	0	0.05	0.98
	9/17/09	6.06	147	55	42	2.22E-02	-8.8	8.67	0.07	1.35	0	0	0	0.39
	10/1/09	5.73	127	150	64	3.11E-02	-5.8	7.5	0.14	4.02	0	0	0.02	0.63
	10/29/09	6.80	328	190	166	1.02E-03	-2.2	18.76	0.02	2.2	0	0	0.04	1.15
	11/14/09	7.46	377	204	226	1.64E-04	-4.5	35.7	*	*	*	*	*	*
	12/7/09	6.72	510	180	213	9.58E-04	-3.6	33.96	*	*	*	*	*	*
	Mean	6.53	360	220	153	4.56E-03	-6.1	24.10	0.07	2.35	58	0.06	0.05	0.96
	StDev	0.37	126	97	54	8.54E-03	3.7	15.63	0.04	1.73	110	0.13	0.07	0.48
Withla-coochee River														
	4/14/08	*	*	*	*	*	*	*	*	*	*	*	*	*
	4/26/08	*	*	*	*	*	*	*	*	*	*	*	*	*
	6/14/08	*	*	*	*	*	*	*	*	*	*	*	*	*
	6/27/08	6.35	320	*	*	*	-5.5	14.45	*	*	*	*	*	*
	7/6/08	6.28	339	*	*	*	-5.5	9.26	*	*	*	*	*	*
	7/19/08	6.31	366	*	*	*	-5.5	40.22	*	*	*	*	*	*
	7/26/08	*	*	*	*	*	*	*	*	*	*	*	*	*
	8/14/08	6.56	372	*	*	*	-8.0	65.65	*	*	*	*	*	*
	9/3/08	6.38	320	*	*	*	-7.6	11.85	*	*	*	*	*	*
	9/28/08	6.60	259	*	*	*	-2.2	12.72	*	*	*	*	*	*
	10/25/08	6.73	312	*	*	*	-1.5	11.82	*	*	*	*	*	*
	11/12/08	6.52	493	*	*	*	-4.8	14.85	*	*	*	*	*	*
	12/6/08	7.42	401	*	177	2.30E-04	-2.3	18.85	*	*	*	*	*	*
	12/17/08	7.21	396	*	157	4.20E-04	-1.9	18.92	*	*	*	*	*	*
	1/17/09	7.20	384	*	153	4.41E-04	-2.4	17.33	*	*	*	*	*	*
	1/30/09	7.16	379	*	132	5.61E-04	-3.7	19.03	*	*	*	*	*	*
	2/13/09	7.18	387	*	151	4.68E-04	0.9	15.98	*	*	*	*	*	*
	2/24/09	7.02	525	*	94	1.09E-03	-2.6	12.49	*	*	*	*	*	*

	Date	pH	Cond (µS)	Hard. (mg/L)	Alk. (mg/L)	*p*CO_2 (atm)	$\delta^{13}C_{DIC}$ (‰)	DIC Conc (µg/L)	Fe^{2+} (mg/L)	Total Fe (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	NH_3 (mg/L)	PO_4^{3-} (mg/L)
W.R. cont'd	3/20/09	7.59	430	*	142	1.94E-04	-3.7	20.23	*	*	*	*	*	*
	4/10/09	7.86	380	*	83	1.78E-04	-4.9	15.42	*	*	*	*	*	*
	4/27/09	7.61	358	*	74	3.55E-04	4.5	5.67	*	*	*	*	*	*
	5/20/09	6.84	323	153	67	2.31E-03	-0.9	9.67	0	0.9	70	0.4	0.08	0.12
	6/5/09	7.68	446	178	143	1.56E-04	-6.5	28.26	0.01	0.9	139	0.3	0	0.18
	6/17/09	6.48	347	188	96	3.69E-03	-4.0	20.80	0.02	0.11	82	0.2	0	0.45
	7/6/09	5.84	240	152	83	1.86E-02	-5.4	13.74	0.05	1.17	0	0	0.13	0.96
	7/22/09	6.81	148	65	56	2.96E-03	-12.6	4.01	0.08	1.21	0	0	0.10	0.44
	8/12/09	6.50	141	160	31	1.09E-02	-6.8	2.53	0.06	1.17	0	0	0.07	0.67
	8/27/09	6.50	149	90	94	3.60E-03	-4.7	4.91	0.05	0.71	0	0	0.07	0.52
	9/17/09	6.68	117	85	38	5.89E-03	-12.6	4.97	0.06	0.9	0	0	0.03	0.57
	10/1/09	5.61	154	70	45	5.84E-02	-2.0	2.74	0.11	1.01	0	0	0.05	0.51
	10/29/09	6.63	266	25	14	1.79E-02	2.9	6.69	0.01	0.58	0	0	0.01	0.54
	11/14/09	7.32	305	194	126	4.07E-04	-4.4	24.29	*	*	*	*	*	*
	12/7/09	7.21	333	189	129	5.12E-04	-5.6	30.34	*	*	*	*	*	*
	Mean	6.83	324	129	99	6.16E-03	-4.1	16.47	0.05	0.87	29	0.09	0.05	0.50
	StDev	0.55	105	58	47	1.32E-02	3.7	12.86	0.04	0.33	50	0.15	0.04	0.24

Table 4.5. $\delta^{13}C_{DOC}$ and C/N data for Thornton's Cave, Thornton's Slough, and the Withlacoochee River, Spring 2008 to Winter 2009

	Spring 2008		Summer 08		Summer 09		Winter 09	
	$\delta^{13}C_{DOC}$ (‰)	C/N (ratio)	$\delta^{13}C_{DOC}$ (‰)	C/N (ratio)	$\delta^{13}C_{DOC}$ (‰)	C/N (ratio)	$\delta^{13}C_{DOC}$ (‰)	C/N (ratio)
Tangerine Entrance.			-21.2	8.6	-25.8	7.2	-26.2	6.7
Catfish Entrance	-25.9		-25.7	2.1	-25.8	5.7	-26.1	8.6
Bat Wing			-25.2	1.1	-24.6	4		
Thornton's Slough			-26.6	13.9	-26.6	9.6	-27.1	13.6
Withlacoochee River			-26.1	14.8	-25.9	14.3	-25.9	17.1

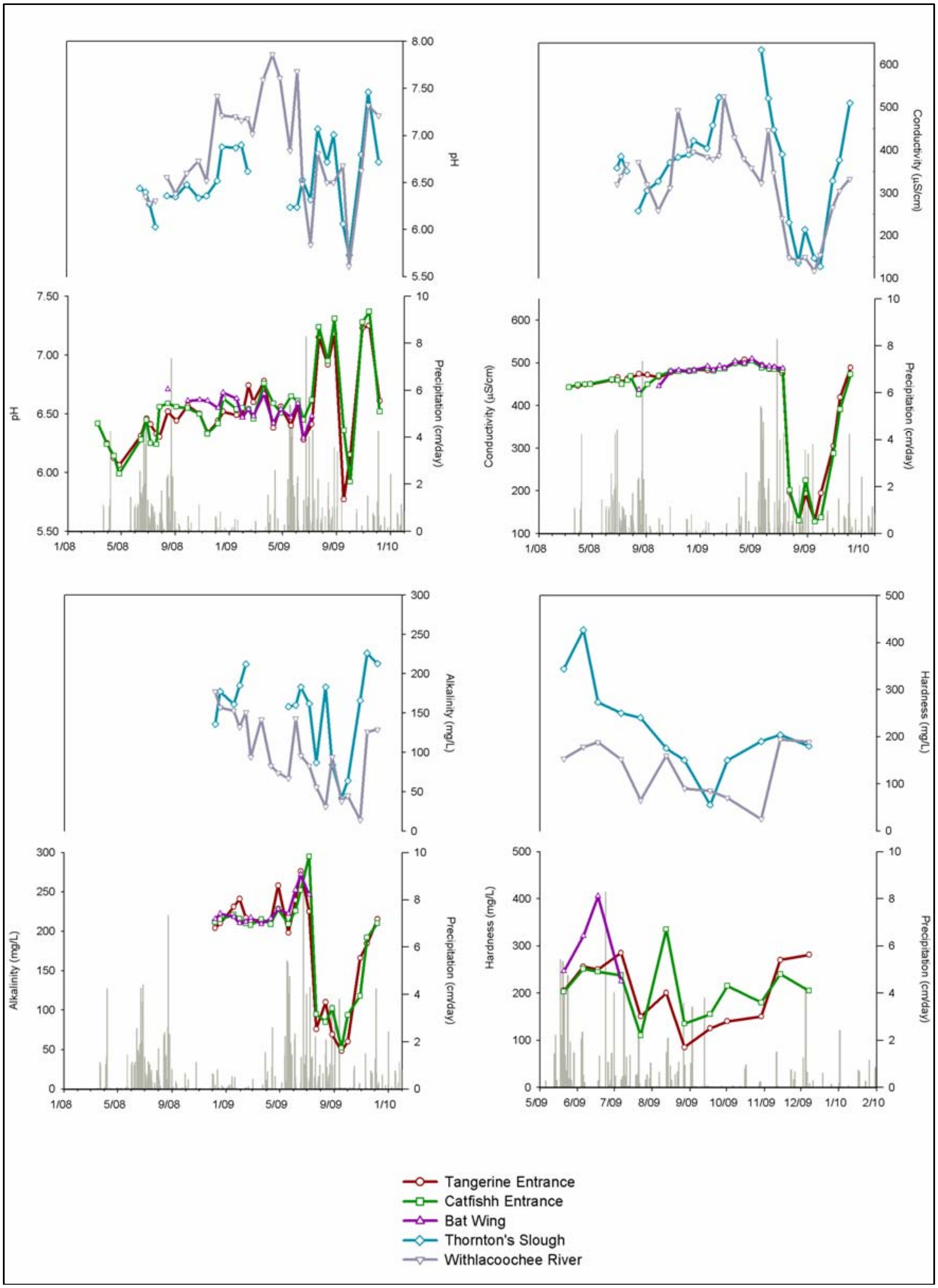

Figure 4.13. Geochemical trends in pH, conductivity, alkalinity and hardness. Surface locations plotted in upper graphs, cave locations plotted in lower graphs. Note *x*-axis scale change for hardness data.

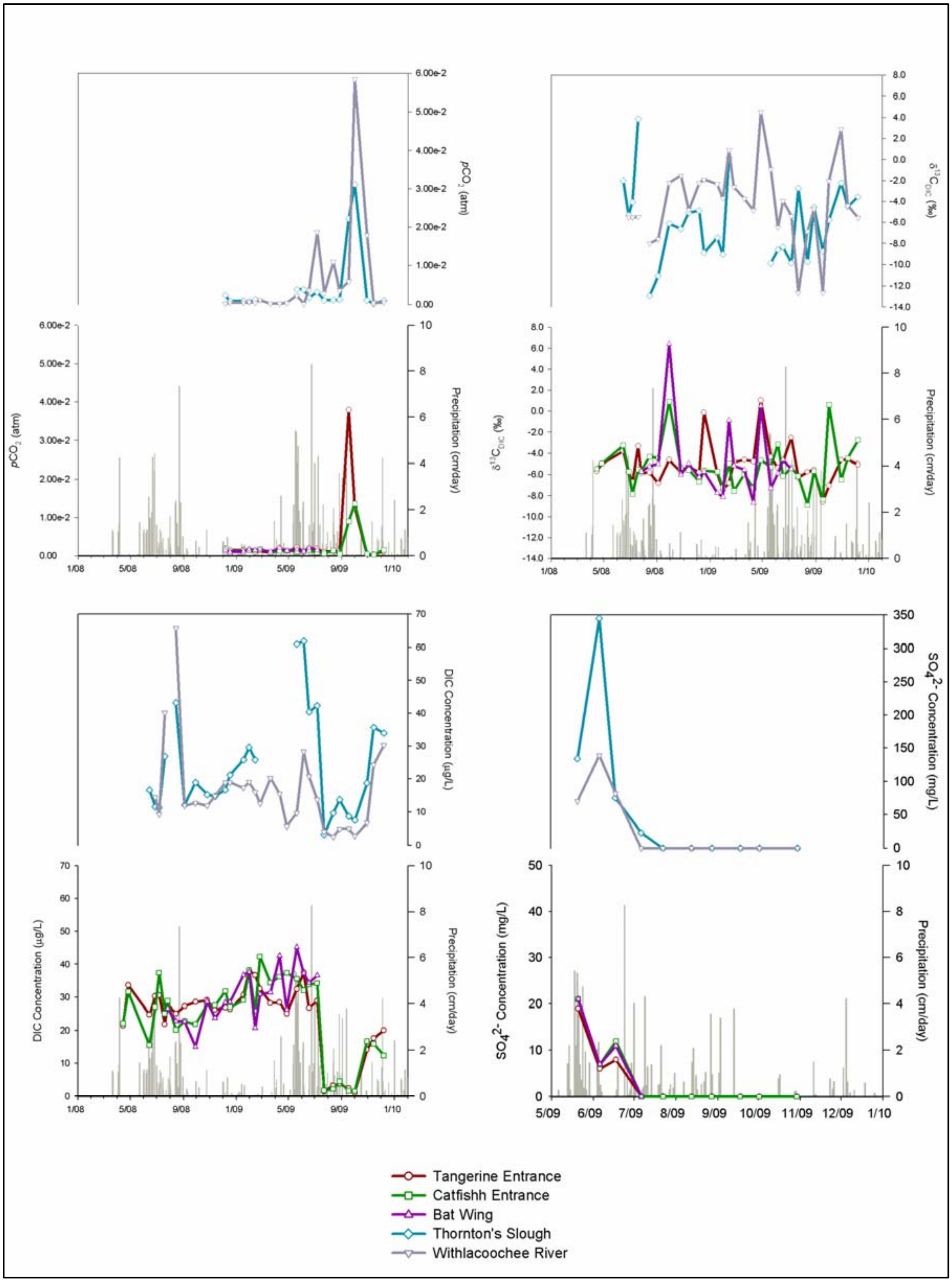

Figure 4.14. Geochemical trends in pCO_2, $\delta^{13}C_{DIC}$, DIC concentration and SO_4^{2-}. Surface locations plotted in upper graphs, cave locations plotted in lower graphs. Note *y*-axis scale changes for SO_4^{2-} data.

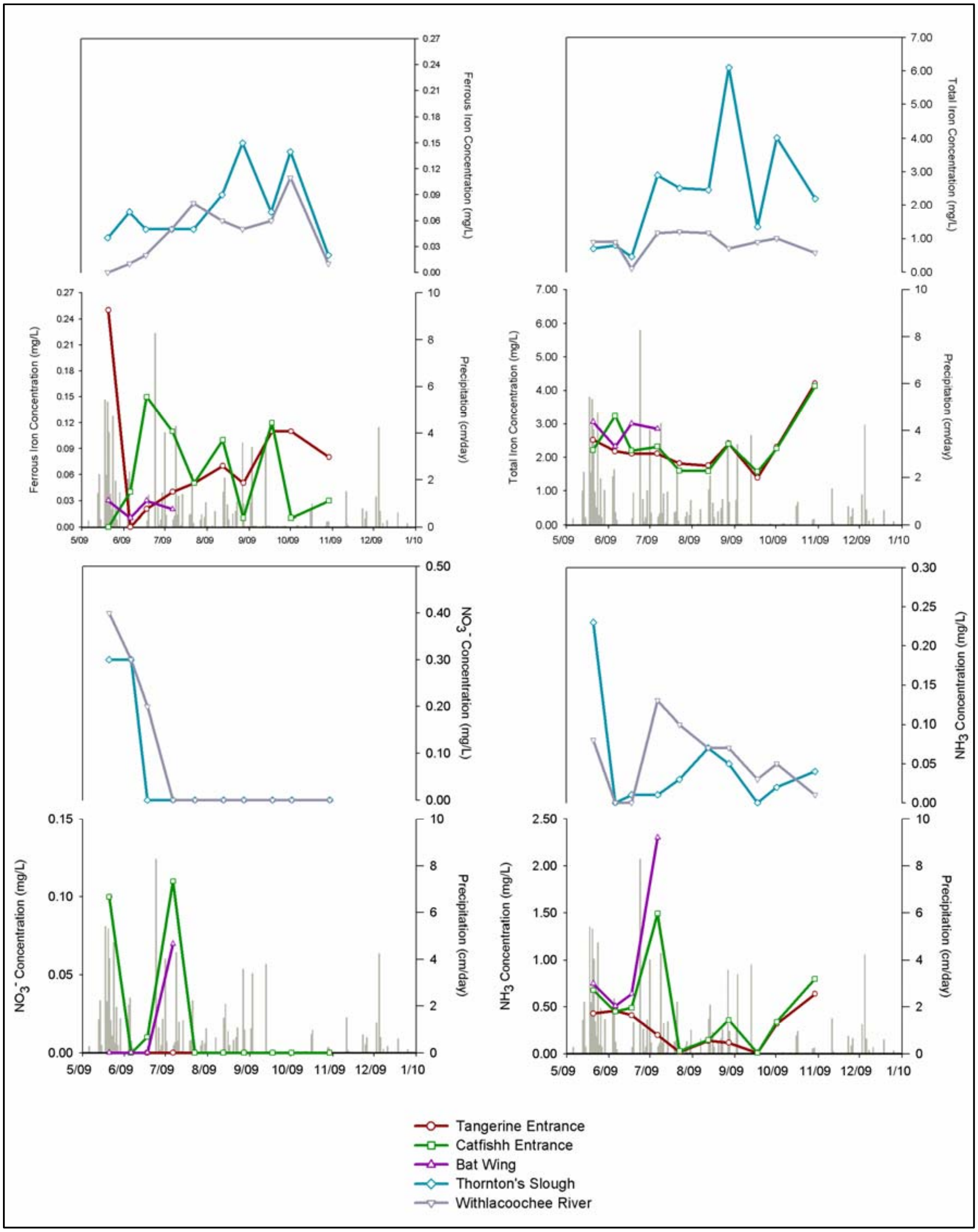

Figure 4.15. Geochemical trends in ferrous Fe, total Fe, NO_3^- and NH_3. Surface locations plotted in upper graphs, cave locations plotted in lower graphs. Note *y*-axis scale changes for NO_3^-, and NH_3 data.

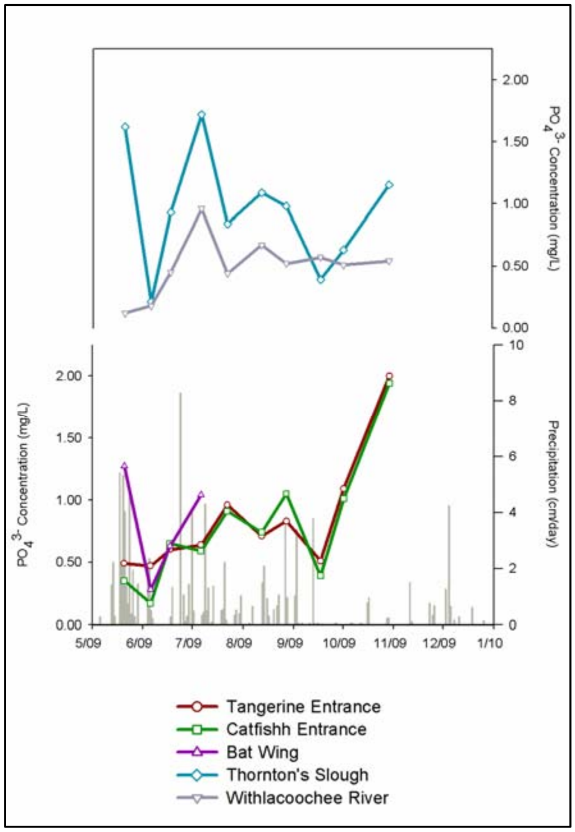

Figure 4.16. Geochemical trends in PO_4^{3-}. Surface locations plotted in upper graphs, cave locations plotted in lower graphs.

Table 4.6. Ocala Limestone $\delta^{13}C$ values. $\delta^{13}C_{DIC}$ and DIC concentration data for pore waters and $\delta^{13}C$ of Ocala Limestone

Porewater Location	**$\delta^{13}C_{DIC}$ (‰)**	**DIC Concentration (µg/L)**	**Ocala Limestone**	**$\delta^{13}C_{Carbonate}$ (‰)**
The Deep	-1.6	27.37	Replicate 1	-2.3
Tangerine Entrance	-0.2	40.31	Replicate 2	-2.5
Tangerine Passage	-0.4	14.20	Replicate 3	-2.8
Mean	-0.7	27.3	Replicate 4	-3.0
StDev	0.8	13.1	Replicate 5	-2.6
			Mean	-2.6
			StDev	0.3

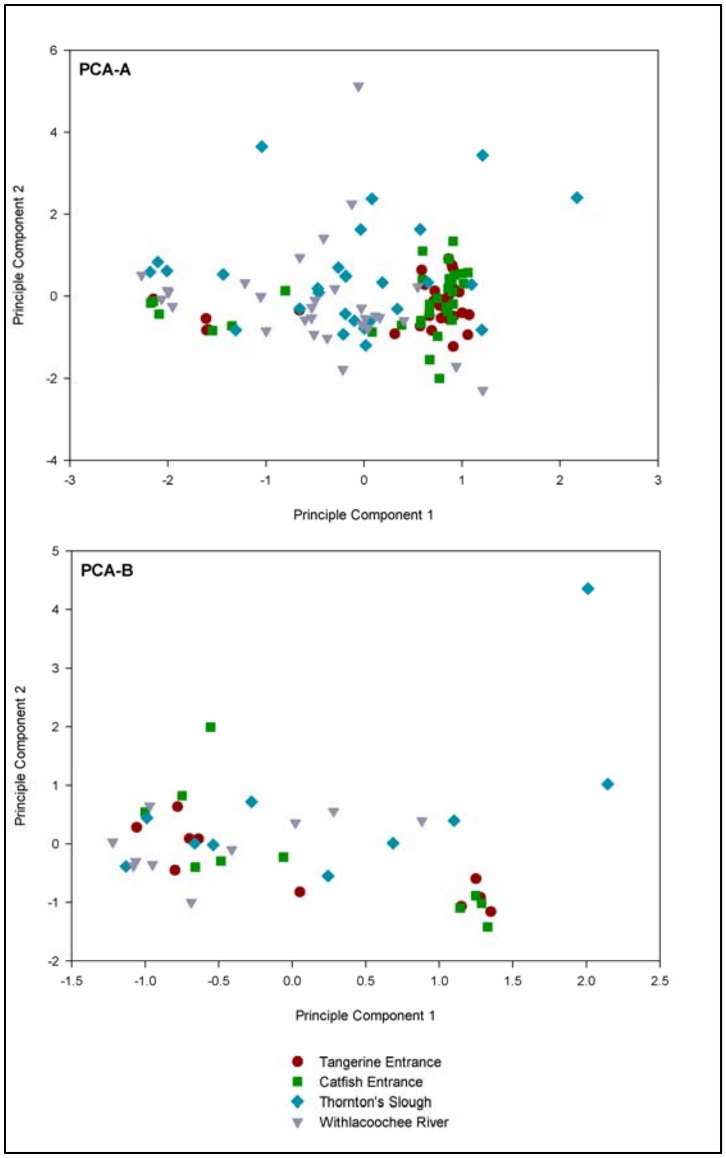

Figure 4.17. Bulk PCA analyses of Thornton's Cave, Thornton's Slough, and the Withlacoochee River geochemical data. Top: PCA-A (water-level, pH, conductivity, $\delta^{13}C_{DIC}$ and DIC concentration from April 2008 to December 2009). Bottom: PCA-B (all geochemical data measured from May to October, 2009).

4.4.1. Thornton's Cave

The geochemical trends shown in Figures 4.13-4.16 for the Tangerine and Catfish entrances reflect similarities in the mean values of their parameters (including those for the Bat Wing), reported in Table 4.4. Mann-Whitney significance tests comparing parameters between sites yielded no significant differences except in that of conductivity between the Bat Wing and the Catfish and Tangerine entrances (p = 0.0020 and 0.0046, respectively) and NH_3 between the Bat Wing and the Tangerine Entrance (p = 0.029). Regular seasonal variations in geochemical parameters were limited due to the summer 2009 flooding event, though in general, pH, conductivity, and DIC concentration values appeared somewhat lower during the wet season of 2008 compared to the dry season of 2008-2009, the result of dilution from increasing water-levels (Figures 4.13-4.14). Values of $\delta^{13}C_{DOC}$ and C/N were not statistically different between sampling sites ($p > 0.3$ for all), and represented organic matter dominated by C_3 vegetation comprised of softer-tissue species (Table 4.5). Porewater $\delta^{13}C_{DIC}$ ranged from -1.6 to -0.19‰, and was slightly more ^{13}C-enriched than the Ocala Limestone, which averaged -2.6 ± 0.3‰ (Table 4.6).

Rapid variation in pH, conductivity, alkalinity, and pCO_2 existed at each cave site during the wet season of 2009, coinciding with cave flooding by the Withlacoochee River through Thornton's Slough (Figures 4.13-4.14). While pH displayed a wider range in overall values rather than an obvious trend, conductivity, alkalinity and DIC concentration decreased. Like pH, values of pCO_2 demonstrated wider variation, but were typically higher during the flood event. At the conclusion of flooding, conductivity, alkalinity, and DIC concentration values gradually rebounded while pCO_2 approached pre-flood values. Values of pH continued to demonstrate large fluctuation with no clear trend. No obvious impact of flooding was observed in $\delta^{13}C_{DIC}$ values.

Major ions showed variable responses during the 2009 wet season. Ferrous Fe concentrations at the Tangerine Entrance fell sharply in late May before slowly rising again thereafter, while concentrations at the Catfish Entrance and Bat Wing demonstrated no apparent trend. An overall decrease in total Fe occurred through the wet season before rising again in late September, coinciding with decreasing water-levels. Sulfate and NO_3^- values varied slightly before falling below detection limits in early July when the cave was flooded by the Withlacoochee River. While all three cave sites showed similar trends in PO_4^{3-} concentrations (a general rise through the wet season), NH_3 concentrations varied such that the Catfish Entrance and Bat Wing increased prior to cave flooding, while concentrations at the Tangerine Entrance decreased. As the cave flooded, fluctuations in NH_3 were more similar at the Catfish and Tangerine entrances (with concentrations slightly higher at the Catfish Entrance), exhibiting an overall increase as water-levels fell.

Results of PCA-A were identical for both sites, with PC1 controlled by changes in water-level, conductivity, and DIC concentration (accounting for 56.2% of the total variation) while PC2 was dominated by changes in pH and $\delta^{13}C_{DIC}$ (accounting for 24.2% of the total variation). Identical results were returned when PCA-A was subdivided into wet and dry season data (PCA-A_w and PCA-A_d, respectively); however, correlation matrices for these data yielded very different results for each entrance (Tables 4.7-4.9). At the Tangerine Entrance, water-level was more correlated to the remaining parameters during the wet season, with differences in water-level between the wet and dry seasons exerting the strongest impact on the correlation between conductivity and DIC concentration. During the wet season, these parameters exhibited a strong, positive correlation (r = 0.96), which diminished to a weak positive correlation (r = 0.39) in the dry season. At the Catfish Entrance, water-levels had a mixed relationship to the other parameters such that correlations to conductivity and DIC concentration were higher during the dry season, while correlations to pH and $\delta^{13}C_{DIC}$ were higher during the wet season. This phenomenon had little impact on the relationship between conductivity and DIC concentration, though the relationship between DIC concentration and $\delta^{13}C_{DIC}$ values went from no correlation during the wet season (r = 0.17) to becoming somewhat strongly, inversely correlated during the dry season (r = -0.67).

Table 4.7. PCA-A results for Tangerine and Catfish Entrances (water-level, pH, conductivity, $\delta^{13}C_{DIC}$ and DIC concentration from April 2008 to December 2009)

Tangerine Entrance						Catfish Entrance					
PC	Eigen	%Var		PC1	PC2	PC	Eigen	%Var		PC1	PC2
1	2.89	57.71	WL	-0.91	-0.04	1	2.81	56.17	WL	-0.92	0.11
2	1.14	22.87	pH	-0.30	0.79	2	1.21	24.22	pH	-0.43	-0.62
			Cond	0.95	0.01				Cond	0.93	0.06
			$\delta^{13}C_{DIC}$	0.45	0.70				$\delta^{13}C_{DIC}$	-0.07	0.88
			DIC Conc	0.92	-0.14				DIC Conc	0.95	-0.17

Table 4.8. PCA-A results subdivided into wet (PCA-A_w) and dry (PCA-A_d) season values for Tangerine and Catfish Entrances

PCA-A_w						PCA-A_d					
Tangerine Entrance											
PC	Eigen	%Var		PC1	PC2	PC	Eigen	%Var		PC1	PC2
1	3.20	64.01	WL	-0.92	-0.07	1	2.62	52.47	WL	-0.92	-0.02
2	1.09	21.87	pH	-0.41	0.82	2	1.18	23.68	pH	-0.15	0.73
			Cond	0.97	-0.02				Cond	0.93	0.06
			$\delta^{13}C_{DIC}$	0.60	0.64				$\delta^{13}C_{DIC}$	0.30	0.77
			DIC Conc	0.95	-0.10				DIC Conc	0.90	-0.22
Catfish Entrance											
PC	Eigen	%Var		PC1		PC	Eigen	%Var		PC1	PC2
1	3.28	65.59	WL	-0.89		1	3.29	65.76	WL	-0.91	0.22
			pH	-0.68		2	1.13	22.54	pH	0.11	0.98
			Cond	0.98					Cond	0.88	-0.07
			$\delta^{13}C_{DIC}$	0.48					$\delta^{13}C_{DIC}$	-0.86	-0.32
			DIC Conc	0.92					DIC Conc	0.96	-0.13

Table 4.9. Correlation matrices of wet and dry season values for Tangerine and Catfish Entrances

Tangerine Entrance									
Wet Season					Dry Season				
	WL	pH	Cond	$\delta^{13}C_{DIC}$		WL	pH	Cond	$\delta^{13}C_{DIC}$
pH	0.28				pH	-0.02			
Cond	-0.84	-0.36			Cond	-0.78	0.23		
$\delta^{13}C_{DIC}$	-0.52	0.09	0.51		$\delta^{13}C_{DIC}$	-0.16	0.44	0.28	
DIC Conc	-0.82	-0.38	0.96	0.41	DIC Conc	-0.62	-0.14	0.39	-0.34
Catfish Entrance									
Wet Season					Dry Season				
	WL	pH	Cond	$\delta^{13}C_{DIC}$		WL	pH	Cond	$\delta^{13}C_{DIC}$
pH	0.28				pH	-0.19			
Cond	-0.63	-0.09			Cond	-0.92	0.25		
$\delta^{13}C_{DIC}$	-0.55	0.01	0.53		$\delta^{13}C_{DIC}$	0.51	-0.25	-0.43	
DIC Conc	-0.55	-0.20	0.78	0.17	DIC Conc	-0.86	0.01	0.75	-0.67

The results of PC1 in PCA-A were replicated in PCA-B (Table 4.10); however, minor variations in the remaining patterns also distinguish the Tangerine and Catfish entrances. Namely, fluctuations in hardness, $\delta^{13}C_{DIC}$, SO_4^{2-}, and total Fe concentrations were important to the geochemistry of the Tangerine Entrance, while NO_3^- concentrations appeared more important at the Catfish Entrance. At the Tangerine Entrance, hardness values were strongly, positively correlated to conductivity, alkalinity, and DIC concentration (r = 0.79, 0.87, and 0.81, respectively), while $\delta^{13}C_{DIC}$ values were positively correlated to conductivity and alkalinity as well (r = 0.73, and 0.74, respectively; Table 4.11). Sulfate exhibited a moderately strong, positive correlation to conductivity and DIC concentration (r = 0.67 for both), and a strong, positive correlation to NO_3^- (r = 0.88). Total Fe exhibited a strong, positive correlation to NH_3 and PO_4^{3-} (r = 0.78 and 0.82, respectively) while Fe^{2+} was best correlated to NO_3^- (r = 0.78). At the Catfish Entrance, NO_3^- was most strongly correlated to NH_3 (r = 0.76) and moderately positively correlated to conductivity, alkalinity, and DIC concentration (r = 0.62, 0.67, and 0.65, respectively). Like the Tangerine Entrance, SO_4^{2-} demonstrated a similar relationship to conductivity and DIC concentration but was only weakly correlated to NO_3^- (r = 0.43). Ammonia was better correlated to alkalinity and DIC concentration compared to the Tangerine Entrance (r = 0.76 and 0.70, respectively); though, unlike the Tangerine Entrance, it was weakly correlated to total Fe (r = 0.46). Hardness concentrations and $\delta^{13}C_{DIC}$ values exhibited moderate correlations at best with the remaining parameters.

Table 4.10. PCA-B results for Tangerine and Catfish Entrances (all geochemical data measured from May to October, 2009)

Tangerine Entrance								**Catfish Entrance**							
PC	**Eigen**	**Var %**		**PC1**	**PC2**	**PC3**	**PC4**	**PC**	**Eigen**	**%Var**		**PC1**	**PC2**	**PC3**	**PC4**
1	6.54	46.71	**WL**	-0.95	0.23	-0.10	0.12	1	5.88	42.03	**WL**	-0.93	0.05	-0.03	0.33
2	3.22	23.03	**pH**	-0.06	0.79	0.10	-0.55	2	2.54	18.15	**pH**	-0.16	0.88	-0.36	-0.21
3	2.31	16.47	**Cond**	0.96	-0.03	-0.15	0.12	3	2.09	14.91	**Cond**	0.97	0.10	0.02	-0.03
4	1.14	8.18	**Hard**	0.77	-0.10	-0.52	0.06	4	1.35	9.65	**Hard**	0.35	-0.33	-0.21	0.46
			Alk	0.92	0.10	-0.31	0.15				**Alk**	0.95	-0.01	-0.01	0.21
			pCO_2	-0.54	-0.62	0.07	0.52				pCO_2	-0.45	-0.68	0.49	0.15
			$\delta^{13}C_{DIC}$	0.77	0.39	-0.16	-0.23				$\delta^{13}C_{DIC}$	0.12	-0.26	0.90	0.02
			DIC Conc	0.95	-0.08	-0.17	0.13				**DIC Conc**	0.98	0.05	0.02	0.05
			Fe^{2+}	0.14	-0.42	0.86	-0.05				Fe^{2+}	0.09	-0.34	-0.71	0.49
			Tot-Fe	0.29	0.77	0.48	0.29				**Tot-Fe**	0.27	0.63	0.50	0.25
			SO_4^{2-}	0.77	-0.41	0.42	-0.11				SO_4^{2-}	0.73	-0.18	0.01	-0.54
			NO_3^-	0.55	-0.40	0.69	-0.24				NO_3^-	0.75	-0.05	-0.02	0.02
			NH_3	0.66	0.44	0.29	0.46				NH_3	0.71	0.29	0.18	0.49
			PO_4^{3-}	-0.23	0.83	0.37	0.28				PO_4^{3-}	-0.42	0.69	0.28	0.30

Table 4.11. Correlation matrices for Tangerine and Catfish Entrances

Tangerine Entrance													
	WL	**pH**	**Cond**	**Hard**	**Alk**	***p*CO_2**	**$\delta^{13}C_{DIC}$**	**DIC Conc**	**Fe^{2+}**	**Tot-Fe**	**SO_4^{2-}**	**NO_3^-**	**NH_3**
pH	0.16												
Cond	-0.90	-0.17											
Hard	-0.67	-0.24	0.79										
Alk	-0.80	-0.08	0.93	0.87									
***p*CO_2**	0.43	-0.71	-0.44	-0.37	-0.49								
$\delta^{13}C_{DIC}$	-0.61	0.31	0.73	0.66	0.74	-0.74							
DIC Conc	-0.90	-0.18	0.97	0.81	0.92	-0.38	0.68						
Fe^{2+}	-0.29	-0.26	0.00	-0.23	-0.19	0.22	-0.09	0.00					
Tot-Fe	-0.10	0.49	0.23	-0.11	0.23	-0.43	0.41	0.18	0.12				
SO_4^{2-}	-0.90	-0.24	0.67	0.37	0.54	-0.21	0.30	0.67	0.59	0.06			
NO_3^-	-0.71	-0.15	0.41	0.11	0.21	-0.12	0.24	0.41	0.86	0.11	0.88		
NH_3	-0.51	0.10	0.62	0.33	0.63	-0.42	0.45	0.60	0.10	0.78	0.44	0.26	
PO_4^{3-}	0.42	0.54	-0.26	-0.39	-0.20	-0.21	0.06	-0.33	-0.04	0.82	-0.40	-0.26	0.43
Catfish Entrance													
	WL	**pH**	**Cond**	**Hard**	**Alk**	***p*CO_2**	**$\delta^{13}C_{DIC}$**	**DIC Conc**	**Fe^{2+}**	**Tot-Fe**	**SO_4^{2-}**	**NO_3^-**	**NH_3**
pH	0.14												
Cond	-0.90	-0.08											
Hard	-0.27	-0.31	0.22										
Alk	-0.80	-0.19	0.95	0.35									
***p*CO_2**	0.43	-0.77	-0.51	-0.06	-0.43								
$\delta^{13}C_{DIC}$	-0.14	-0.52	0.14	-0.03	0.18	0.49							
DIC Conc	-0.90	-0.16	0.99	0.31	0.94	-0.45	0.11						
Fe^{2+}	0.08	-0.22	0.09	0.36	0.24	-0.05	-0.53	0.14					
Tot-Fe	-0.19	0.24	0.37	-0.01	0.25	-0.26	0.27	0.38	-0.38				
SO_4^{2-}	-0.91	-0.21	0.69	0.16	0.52	-0.24	0.07	0.70	-0.11	0.03			
NO_3^-	-0.64	-0.14	0.62	0.13	0.67	-0.25	0.02	0.65	0.00	-0.06	0.47		
NH_3	-0.45	-0.02	0.67	0.21	0.76	-0.32	0.16	0.70	0.03	0.46	0.14	0.76	
PO_4^{3-}	0.48	0.48	-0.36	-0.28	-0.37	-0.06	-0.01	-0.36	-0.29	0.51	-0.45	-0.33	0.09

4.4.2. Surface Waters

Despite the direct connection between the Withlacoochee River and Thornton's Slough, the geochemical trends appear to vary more between these sites than the cave sites, with significant differences existing in their pH, hardness, alkalinity, $\delta^{13}C_{DIC}$, total Fe, and PO_4^{3-} values (p <0.05 for each). At the Withlacoochee River, pH was higher and demonstrated more elevated values during the dry season and fell sharply at the onset of heavy rains during the 2009 wet season, while pH values at Thornton's Slough were more similar to cave values (Figure 4.13). Though alkalinity and hardness values were higher and lower at the river, respectively, their overall fluctuations were similar to the slough. Values of $\delta^{13}C_{DIC}$ were lower at the river and also show similar fluctuations as the slough until the onset of the 2009 wet season (Figure 4.14). Phosphate and total Fe concentrations were higher at the slough than the river, with episodic similarities in their fluctuation patterns (Figures 4.15-4.16). Of the remaining major ions, SO_4^{2-} and NO_3^- were below detection limits with the onset of the 2009 wet season, while Fe^{2+}, NH_3, and PO_4^{3-} concentrations fluctuated (Figures 4.14-4.16). At times, these fluctuations appeared to be coincident with rainfall activity, though this relationship was not consistent. Values of $\delta^{13}C_{DOC}$ and C/N were not statistically different between the river and slough (p = 0.1, respectively), nor were they significantly different from cave values (p >0.30 for DOC and >0.1 for C/N; Table 4.5). Overall, $\delta^{13}C_{DOC}$ values were lower at the surface compared to the cave while C/N values were higher, representing C_3-vegetation comprised of relatively tougher and/or woodier tissues.

Water-level and conductivity played an important role in PC1 at both sites (indicated by both PCAs); however, DIC concentration was an additional parameter of importance in PC1 at the slough, while pH was more important in PC1 at the river (Tables 4.12-4.14). Results of PCA-B demonstrated that alkalinity, SO_4^{2-}, and NO_3^- were also important geochemical parameters in PC1 (Table 4.15). From there, both sites varied, such that pH and Fe^{2+} appeared in PC1 and $\delta^{13}C_{DOC}$ in PC2 at the river, and PO_4^{3-} exerted a minor influence in PC3 at the slough. Few parameters seemed to exhibit a major influence on the geochemistry in PC3 at the river. At Thornton's Slough, strong, positive correlations between conductivity, hardness, and DIC concentration existed (r = 0.85-0.95), while alkalinity exhibited only a somewhat strong, positive correlation to these parameters (r = 0.60 – 0.62; Table 4.16). Sulfate and NO_3^- were strongly, positively correlated to both one another (r = 0.87), as well as to conductivity and hardness (r = 0.71 – 0.85). pH and pCO2 were strongly, inversely correlated (r = -0.79), while NH_3 and PO_4^{3-} showed only moderate correlations at best to one another and other parameters (r <0.57). At the Withlacoochee River, conductivity was well correlated to DIC concentration (r = 0.91), Fe^{2+} (r = -0.78), SO_4^{2-} (r = 0.91), and NO_3^- (r = 0.81), and only moderately well correlated to alkalinity (r = 0.66); however, alkalinity was well correlated to DIC concentration (r = 0.82) and SO_4^{2-} (r = 0.76; Table 4.16). Of the parameters in PC1, pH was best correlated to SO_4^{2-} (r = 0.67), and moderately correlated to conductivity and NO_3^- (r = 0.54 and 0.56, respectively).

Table 4.12. PCA-A results for Thornton's Slough and the Withlacoochee River (water-level, pH, conductivity, $\delta^{13}C_{DIC}$ and DIC concentration from April 2008 to December 2009)

Thornton's Slough						**Withlacoochee River**					
PC	**Eigen**	**%Var**		**PC1**	**PC2**	**PC**	**Eigen**	**%Var**		**PC1**	**PC2**
1	2.41	48.23	**WL**	-0.89	-0.09	1	2.54	50.86	**WL**	-0.89	0.13
2	1.14	22.87	**pH**	0.02	0.60	2	1.20	24.05	**pH**	0.74	-0.02
			Cond	0.90	0.25		0.67	13.49	**Cond**	0.86	0.20
			$\delta^{13}C_{DIC}$	-0.16	0.82		0.31	6.18	**$\delta^{13}C_{DIC}$**	0.54	-0.68
			DIC Conc	0.89	-0.21		0.27	5.42	**DIC Conc**	0.39	0.83

Table 4.13. PCA-A results subdivided into wet (PCA-A_w) and dry (PCA-A_d) season values for Thornton's Slough and the Withlacoochee River

PCA-A_w						**PCA-A_d**					
Thornton's Slough											
PC	**Eigen**	**%Var**		**PC1**	**PC2**	**PC**	**Eigen**	**%Var**		**PC1**	**PC2**
1	2.99	59.89	**WL**	-0.96	-0.14	1	2.59	51.84	**WL**	-0.55	0.01
2	1.05	20.95	**pH**	-0.57	-0.16	2	1.02	20.44	**pH**	0.86	-0.18
			Cond	0.93	0.21				**Cond**	0.83	0.14
			$\delta^{13}C_{DIC}$	-0.24	0.98				**$\delta^{13}C_{DIC}$**	0.14	0.98
			DIC Conc	0.91	-0.21				**DIC Conc**	0.92	-0.10
Withlacoochee River											
PC	**Eigen**	**%Var**		**PC1**		**PC**	**Eigen**	**%Var**		**PC1**	**PC2**
1	2.61	52.13	**WL**	-0.93	0.15	1	2.43	48.69	**WL**	-0.75	0.59
2	1.09	21.84	**pH**	0.37	0.56	2	1.64	32.79	**pH**	0.91	-0.23
			Cond	0.93	0.12				**Cond**	0.74	-0.03
			$\delta^{13}C_{DIC}$	0.63	-0.72				**$\delta^{13}C_{DIC}$**	-0.28	-0.89
			DIC Conc	0.58	0.48				**DIC Conc**	0.64	0.66

Table 4.14. Correlation matrices of wet and dry season values for Thornton's Slough and the Withlacoochee River

Thornton's Slough									
Wet Season					**Dry Season**				
	WL	**pH**	**Cond**	**$\delta^{13}C_{DIC}$**		**WL**	**pH**	**Cond**	**$\delta^{13}C_{DIC}$**
pH	0.31				**pH**	-0.27			
Cond	-0.90	-0.36			**Cond**	-0.33	0.58		
$\delta^{13}C_{DIC}$	-0.07	0.19	-0.01		**$\delta^{13}C_{DIC}$**	-0.04	0.00	0.19	
DIC Conc	-0.67	-0.35	0.68	-0.34	**DIC Conc**	-0.39	0.80	0.66	0.06
Withlacoochee River									
Wet Season					**Dry Season**				
	WL	**pH**	**Cond**	**$\delta^{13}C_{DIC}$**		**WL**	**pH**	**Cond**	**$\delta^{13}C_{DIC}$**
pH	-0.19				**pH**	-0.79			
Cond	-0.74	0.06			**Cond**	-0.48	0.33		
$\delta^{13}C_{DIC}$	-0.59	0.10	0.21		**$\delta^{13}C_{DIC}$**	0.01	-0.13	-0.12	
DIC Conc	-0.59	0.02	0.85	0.20	**DIC Conc**	-0.20	0.47	0.22	-0.53

Table 4.15. PCA-B results for Thornton's Slough and the Withlacoochee River (all geochemical data measured from May to October, 2009)

Thornton's Slough								Withlacoochee River							
PC	**Eigen**	**Var %**		**PC1**	**PC2**	**PC3**	**PC4**	**PC**	**Eigen**	**%Var**		**PC1**	**PC2**	**PC3**	**PC4**
1	6.89	49.18	**WL**	-0.97	0.08	0.00	-0.08	1	7.50	53.59	**WL**	-0.90	0.15	-0.25	-0.28
2	2.64	18.88	**pH**	-0.13	0.86	-0.38	0.18	2	2.02	14.46	**pH**	0.70	0.34	-0.56	0.11
3	1.49	10.62	**Cond**	0.96	0.06	0.02	0.07	3	1.49	10.64	**Cond**	0.94	-0.15	0.19	0.01
4	1.24	8.84	**Hard**	0.90	0.00	-0.26	0.20	4	1.08	7.74	**Hard**	0.64	0.35	0.48	-0.16
			Alk	0.70	0.45	0.00	-0.19				**Alk**	0.71	0.36	0.31	-0.27
			***p*CO_2**	-0.46	-0.80	0.27	-0.10				***p*CO_2**	-0.53	-0.52	0.43	0.03
			$\delta^{13}C_{DIC}$	-0.48	0.36	-0.47	0.21				**$\delta^{13}C_{DIC}$**	0.22	-0.86	0.25	0.27
			DIC Conc	0.95	-0.14	0.05	0.08				**DIC Conc**	0.87	0.10	0.25	-0.32
			Fe^{2+}	-0.56	-0.36	0.08	0.63				**Fe^{2+}**	-0.82	0.19	0.14	-0.14
			Tot-Fe	-0.68	0.18	0.09	0.62				**Tot-Fe**	-0.47	0.57	0.21	0.49
			SO_4^{2-}	0.79	-0.41	-0.39	0.20				**SO_4^{2-}**	0.96	0.08	0.06	-0.05
			NO_3^-	0.83	-0.32	-0.02	0.33				**NO_3^-**	0.89	0.01	0.08	0.35
			NH_3	0.46	0.22	0.61	0.35				**NH_3**	-0.50	0.47	0.46	0.44
			PO_4^{3-}	0.26	0.65	0.66	0.02				**PO_4^{3-}**	-0.68	0.05	0.40	-0.39

Table 4.16. Correlation matrices for Thornton's Slough and the Withlacoochee River

Thornton's Slough

	WL	pH	Cond	Hard	Alk	pCO_2	$\delta^{13}C_{DIC}$	DIC Conc	Fe^{2+}	Tot-Fe	SO_4^{2-}	NO_3^-	NH_3
pH	0.21												
Cond	-0.97	-0.09											
Hard	-0.87	-0.01	0.86										
Alk	-0.63	0.21	0.60	0.62									
pCO_2	0.35	-0.79	-0.45	-0.48	-0.69								
$\delta^{13}C_{DIC}$	0.38	0.51	-0.34	-0.26	-0.33	-0.06							
DIC Conc	-0.96	-0.27	0.95	0.85	0.60	-0.33	-0.54						
Fe^{2+}	0.47	-0.14	-0.56	-0.39	-0.52	0.44	0.06	-0.40					
Tot-Fe	0.61	0.27	-0.59	-0.50	-0.45	0.12	0.44	-0.56	0.76				
SO_4^{2-}	-0.78	-0.26	0.71	0.85	0.37	-0.19	-0.36	0.80	-0.18	-0.51			
NO_3^-	-0.82	-0.28	0.78	0.79	0.30	-0.16	-0.39	0.81	-0.22	-0.49	0.87		
NH_3	-0.44	0.02	0.47	0.28	0.24	-0.22	-0.22	0.35	-0.17	-0.16	0.08	0.53	
PO_4^{3-}	-0.22	0.22	0.33	0.11	0.47	-0.44	-0.17	0.24	-0.33	0.08	-0.32	-0.04	0.57

Withlacoochee River

	WL	pH	Cond	Hard	Alk	pCO_2	$\delta^{13}C_{DIC}$	DIC Conc	Fe^{2+}	Tot-Fe	SO_4^{2-}	NO_3^-	NH_3
pH	-0.46												
Cond	-0.93	0.54											
Hard	-0.58	0.24	0.57										
Alk	-0.56	0.43	0.66	0.64									
pCO_2	0.32	-0.75	-0.32	-0.38	-0.38								
$\delta^{13}C_{DIC}$	-0.46	-0.22	0.39	-0.08	-0.12	0.36							
DIC Conc	-0.76	0.51	0.91	0.67	0.82	-0.37	0.07						
Fe^{2+}	0.81	-0.61	-0.78	-0.39	-0.34	0.63	-0.42	-0.61					
Tot-Fe	0.34	-0.11	-0.43	-0.13	-0.19	0.20	-0.42	-0.39	0.51				
SO_4^{2-}	-0.84	0.67	0.91	0.67	0.76	-0.40	0.11	0.89	-0.64	-0.37			
NO_3^-	-0.92	0.56	0.81	0.61	0.55	-0.40	0.25	0.65	-0.70	-0.28	0.87		
NH_3	0.26	-0.43	-0.45	-0.03	-0.13	0.07	-0.23	-0.43	0.38	0.70	-0.51	-0.27	
PO_4^{3-}	0.59	-0.68	-0.53	-0.14	-0.34	0.31	-0.13	-0.33	0.44	0.25	-0.70	-0.79	0.45

When PCA-A was split into wet- and dry-season values, both sites showed somewhat different responses to changes in water-level. At Thornton's Slough, water-level had a reduced impact on conductivity and DIC concentration during the dry season, while pH became a more important factor in PC1 and was positively correlated to DIC concentration (r = 0.80; Tables 4.13-4.14). The Withlacoochee River behaved similarly, in that water-level had a dampened impact on conductivity and DIC concentration in the dry season; however, although pH was also a more important parameter in PC1 during the dry season, it had a strong, negative correlation to water-level (*r* = -0.79). Additionally, during the dry season, the correlation between conductivity and DIC concentration decreased from 0.85 to 0.22.

4.5. Discussion

Dissolution is an active process at Thornton's Cave, evidenced by the substantial loss in mass of the limestone tablets over a relatively short interval of observation, and is occurring both at the limestone/soil interface, and within the cave at the limestone/water interface. Geochemical data here, combined with field observations and previous CO_2 research support the hypothesis that organic activity is available to fuel dissolution driven by H_2CO_3, as well as other mechanisms (to be discussed below). While carbonate equilibrium reactions appear to drive the bulk of geochemical change at the surface and within the cave and are most likely attributable to the *in situ* production of CO_2, it is clear that a variety of biogeochemical reactions can influence the DIC pool, and, therefore, limestone dissolution reactions, to varying degrees at each site.

An overview of geochemical variation demonstrated by bulk PCA analyses shows significant overlap between the geochemical characteristics of Thornton's Cave, the Withlacoochee River, and Thornton's Slough (Figure 4.17), supporting the hypothesis that the river influences the elevation of the Upper Floridan Aquifer and that two water sources influence the subsurface water bodies sampled here (Figure 4.17). The waters of Thornton's Cave are the most similar geochemically, which suggests that the Upper Floridan Aquifer acts as a first-order control that not only provides the majority of the water to the system, but promotes a homogenized geochemical composition for cave waters. Results of PCA-B are typically similar to those of PCA-A, suggesting that despite the short-term dataset from which PCA-B was constructed, it was nevertheless representative of the longer-term geochemical variation; however, PCA-B exhibited minor variations between sites in terms of variations in major ion concentrations, which suggest localized differences in organic activity. These localized differences may stem from site-specific and/or seasonal variations in the contribution of specific dissolution pathways (to be discussed below). Localization of geochemical variation is exemplified at the Bat Wing by the statistically higher conductivity and NH_3 concentration in its waters, imparted by the passage's seasonal occupation by a breeding bat colony. Taken as a whole, geochemical variation at all sites seems to be influenced primarily by water-level and calcite equilibrium reactions and secondarily by microbial reactions involving H_2S, SO_4^{2-}, Fe^{2+}, Fe^{3+}, NO_3^-, and NH_3 (to be discussed below).

4.5.1. Water-level

Water-level exerted a primary influence on geochemical composition year-round at all sites, with the exception of the dry season at Thornton's Slough, the only site to completely dry out (Table 4.4). Tables 4.9 and 4.14 show that correlation between water-level and other parameters generally diminished between the wet and dry season; however, there were two exceptions. At the Catfish Entrance, negative correlations between water-level and both conductivity and DIC concentration became more strong between the wet and dry season, suggesting that some process other than water-level influences these parameters during the wet season. The second exception is found at the river, where the negative correlation between pH and water-level becomes dramatically stronger during the dry season, enough to elevate pH into PC1 (Table 4.14). The most likely process that would raise pH under these conditions is the concentration of DIC as water-levels decrease, which would make waters more alkaline through the increase in HCO_3^-concentration, and potentially increase calcite saturation. This hypothesis is supported by higher loadings for DIC concentration during the dry season, and the increase in correlation from wet to dry season pH and DIC concentration (from $r = 0.02$ o $r = 0.47$). This correlation is only mild, however, suggesting that other reactions consuming acidity, such as denitrification and ammonification, are also contributing to the rise in pH.

4.5.2. Carbonate Equilibrium Reactions

In carbonate systems, equilibrium reactions between calcite and the surrounding waters drive variations in acidity that promote or inhibit limestone precipitation and dissolution. In most dissolution models, biogenic CO_2 sourced from the decomposition of organic matter in soils is dissolved into and hydrated by meteoric water to produce H_2CO_3. Carbonic acid then corrodes the underlying limestone in the following dissolution reaction (Eq. 2):

$$H_2CO_3 + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad \text{(Eq. 2)}$$

Bicarbonate produced in this reaction is derived from carbon of both biogenic (CO_2) and abiotic (limestone) sources. Plant and microbial metabolic processes kinetically fractionate the stable isotopes of carbon by the preferential incorporation of ^{12}C such that the stable isotopic composition of biogenic CO_2 tends to be ^{13}C-depleted (~23‰ and below; Craig, 1953). Alternatively, marine carbonate precipitates in isotopic equilibrium with DIC, which in marine settings, is at or near 0‰. When dissolution combines these two carbon sources, the resultant $\delta^{13}C_{DIC}$ value of the water is intermediate between these two sources, reflecting the ratio of ^{13}C-enriched (lithogenic) and ^{13}C-depleted (biogenic) carbon. In open systems, this ratio is closer to 1 due to infinite supplies of biogenic CO_2 and a relatively temperature-independent fractionation factor of ~8-9‰, yielding $\delta^{13}C_{DIC}$ values of ~-14 to -12‰ (Clark and Fritz, 1997). In contrast, closed systems become CO_2-limited such that once the available $CO_{2(aq)}$ has been reacted, equilibration of the water with the surrounding limestone progressively enriches the water with ^{13}C to produce $\delta^{13}C_{DIC}$ values that are more positive, approaching a biogenic:lithogenic DIC ratio of 0.5 (Clark and Fritz, 1997; Böttcher, 1999). Finally, when dissolution is driven by carbonate equilibrium reactions without the influence of biogenic CO_2, the DIC produced will be purely lithogenic, with $\delta^{13}C_{DIC}$ nearly identical to that of the host limestone (~0‰, in most cases) due to a fractionation factor of ~1.5‰ (Clark and Fritz, 1997). Though Berner and Morse (1974) argue that H_2CO_3 production through the hydration of biogenic CO_2 is a less efficient, and consequently a less common dissolution mechanism than the addition of H^+ to $CaCO_3$, $\delta^{13}C_{DIC}$ analyses of groundwaters from a variety of karst settings continually yield values more depleted than marine limestone values (often by at least 4-5‰) supporting H_2CO_3-dissolution as an important DIC source (e.g., Deines et al., 1974; Lojen et al., 2004; Doctor et al., 2008).

Conductivity, DIC concentration, and alkalinity (when included) were important parameters in PC1 of each PCA, illustrating the influence of carbonate equilibrium reactions at each site (Table 4.7-4.8, 4.10, 4.12-4.13, 4.15). Hardness concentrations were also important in PC1 at each site, with the exception of the Catfish Entrance (Table 4.10). Considerable overlap exists in the $\delta^{13}C_{DIC}$ values at all sites, with the most variability exhibited by the Withlacoochee River, Thornton's Slough, and inside the cave at the Bat Wing (Figure 4.14). $\delta^{13}C_{DIC}$ values below that of the Ocala Limestone are evidence that biogenic CO_2 contributes to dissolution at each site, and are supported by the results of PCA-A (largely echoed by PCA-B) which document $\delta^{13}C_{DIC}$ as a contributor to geochemical change at each site. These data are also supported by CO_2 surveys and respiration studies, documenting that biogenic CO_2 is produced in the cave, particularly during the wet season, by degassing from cave sediments and rock, breeding bat colonies, and the microbial decomposition of bat guano, and probably contributes to H_2CO_3 production (Chapter 3). The exception to this hypothesis is Thornton's Slough, where PCA-B results show minimal contribution by $\delta^{13}C_{DIC}$ to geochemical change when part of a more complex dataset (compared to PCA-A, where it influences PC2). This suggests that multiple processes are responsible for influencing the DIC pool. It also suggests that the DIC pool is unlikely to be driven solely by carbonate dissolution and precipitation reactions, which should be expected given that slough waters are not in direct contact with limestone. By comparison, PCA-B results for the remaining sites show $\delta^{13}C_{DIC}$ as a primary contributor to geochemical change at the Tangerine Entrance, a secondary contributor at the Withlacoochee River, and a tertiary contributor at the Catfish Entrance. At the Tangerine Entrance, $\delta^{13}C_{DIC}$ values are strongly and positively correlated to conductivity and alkalinity (Table 4.11), further evidence that the primary process contributing to $\delta^{13}C_{DIC}$ variation is tied to carbonate equilibrium reactions. At the river and Catfish Entrance, $\delta^{13}C_{DIC}$ values are only moderately correlated to other parameters at best, suggesting that while carbonate equilibrium reactions are important (as demonstrated by PCA results), other processes are influencing the DIC pool as well, and are likely explained by the significance of other major ions in PCA-B results for each site. Unlike Thornton's Slough, however, where $\delta^{13}C_{DIC}$ fluctuations exerted little impact on overall geochemical variation, the combined influence of carbonate equilibrium reactions and $\delta^{13}C_{DIC}$ fluctuations exhibited by PCA-B results for the river and Catfish Entrance suggest that $\delta^{13}C_{DIC}$ values are influenced primarily by limestone dissolution and precipitation and secondarily by other processes (to be discussed below).

4.5.3. Sulfur-based Reactions

Sulfur in its most reduced form (sulfide, H_2S, S^o, S^{2-} or HS^-) is often sourced from sulfate-reducing bacteria which oxidize organic carbon as an energy source and use oxidized sulfur (SO_4^{2-}) as an electron acceptor (Konhauser, 2007). This process is particularly common under anoxic conditions found in wetland and marine sediments after reactions such as denitrification and Fe and/or Mn reduction are complete. Sulfate may be provided by marine limestone rocks and as such, is a common constituent of Floridan groundwaters, as SO_4^{2-} is assimilated into the limestone during deposition, or through post-depositional leaching from surface soils, by mineralization with other free ions (Sprinkle, 1989). During weathering in the oxidizing environment of the vadose zone, sulfide minerals and dissolved sulfide are oxidized (either biotically or abiotically) to release SO_4^{2-} in an acid-producing reaction. Sulfuric acid is produced directly by aerobic oxidation of sulfides, ultimately derived from microbially mediated sulfate reduction. Limestone dissolves in the presence of H_2SO_4 by the following reaction:

$$2CaCO_3 + H_2SO_4 \rightarrow 2Ca^{2+} + 2HCO_3^- + SO_4^{2-} \qquad \text{(Eq. 3)}$$

Because all of the carbon in HCO_3^- produced during H_2SO_4-dissolution is lithogenic, $\delta^{13}C_{DIC}$ values will reflect that of the limestone itself and therefore be more enriched in ^{13}C than DIC produced through H_2CO_3-dissolution facilitated by biogenic CO_2. Further, evidence of H_2SO_4-dissolution can also be seen by comparing the ratio of the summed equivalent concentrations of HCO_3^- and SO_4^{2-} to the equivalent concentration of Ca^{2+} + Mg^{2+}. Because the stoichiometric ratio of these products is fixed, any excursion below a unity line (in chemical equivalents) suggests this dissolution mechanism is contributing to the DIC pool.

Values of $\delta^{13}C_{DIC}$ cannot be used to distinguish $H_2CO_3^-$ and H_2SO_4-dissolution processes; however, when crossplots of hardness versus $HCO_3^-+SO_4^{2-}$ were constructed, each site exhibited minor excursions below the unity line (Figure 4.18). Nevertheless, because SO_4^{2-} was only a minor contributor to *x*-values at the three cave sites, identical plots omitting SO_4^{2-} yielded little difference in their trends, eliminating H_2SO_4 as a significant dissolution agent there. The opposite trend was seen at

Thornton's Slough and the Withlacoochee River, with many points shifting to lower *x*-values when SO_4^{2-} was omitted, reflecting the higher concentrations of this ion at these two sites prior to the major rainfall events associated with the 2009 wet season (Figure 4.14). While this suggests that at least for part of the year, H_2SO_4-dissolution may be adding SO_4^{2-} to the geochemistry at these surface sites, this method does not specifically identify H_2SO_4-dissolution as a SO_4^{2-} source. Sulfur isotope analyses combined with analyses of major sulfur ions in surrounding sulfur reservoirs (e.g., minerals, organic matter, industrial emissions) would be a practical method for specifically identifying sulfur sources and their contributions to the surface and cave waters.

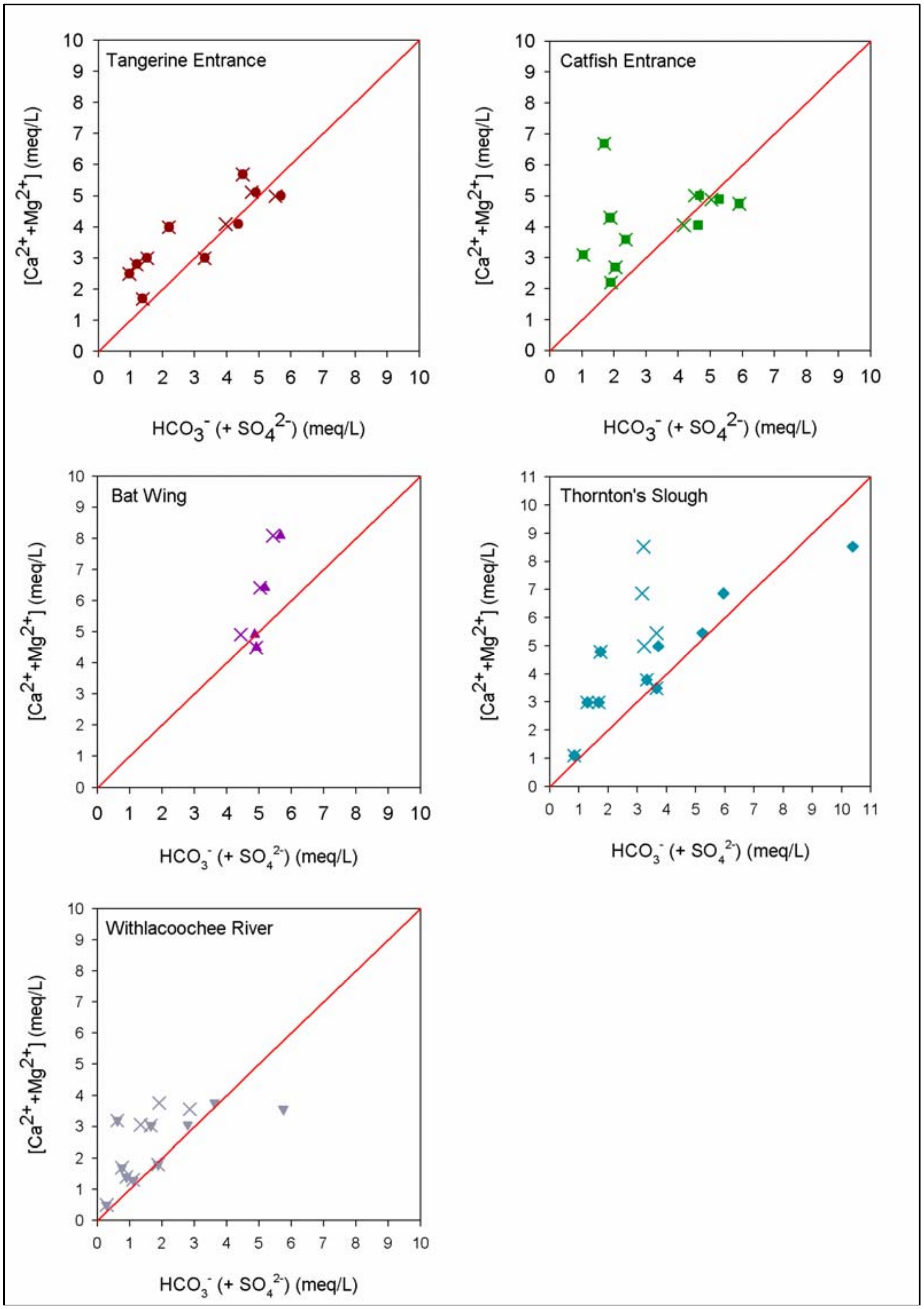

Figure 4.18. H_2SO_4-dissolution plots for Thornton's Cave, Thornton's Slough, and the Withlacoochee River. Crosses: [Ca^{2+}+ Mg^{2+}] concentrations versus HCO_3^- concentrations. Solid points: Ca^{2+} concentrations versus summed millequivalent concentrations of HCO_3^- + SO_4^{2-}.

Another potential source of SO_4^{2-} at each site could come from the dissolution of gypsum ($CaSO_4$ $2H_2O$). Gypsum readily dissolves in water (Hill and Forti, 1997; Palmer, 2007) in the following reaction:

$$2HCO_3^- + CaSO_4 \cdot 2H_2O \rightarrow CaCO_3 + CO_2 + SO_4^{2-} + 3H_2O \qquad \text{(Eq. 4)}$$

Determining whether gypsum dissolution contributes SO_4^{2-} to these sites can be done by using the stoichiometric ratio of SO_4^{2-} to [Ca^{2+}+ Mg^{2+}], the products of gypsum dissolution, which yield a 1:1 relationship (with Mg^{2+}included to account for any ion substitution for Ca^{2+} in the limestone, or the presence of dolomite) . Because the source of HCO_3^- consumed to produce $CaCO_3$ is unknown and can come from biotic or abiotic origins, the use of $\delta^{13}C_{DIC}$ values is not likely to distinguish gypsum dissolution from other processes impacting the DIC pool.

When SO_4^{2-} versus [Ca^{2+}+ Mg^{2+}] concentrations are plotted, the waters of Thornton's Slough and the Withlacoochee River both demonstrated evidence of periodic gypsum dissolution within the river basin, giving correlation between SO_4^{2-} and [Ca^{2+}+ Mg^{2+}] beyond the "calcium excess" (in excess of gypsum dissolution; Jin et al., 2010; Figure 4.19). At the river, further evidence of gypsum dissolution is also provided by the positive correlation between SO_4^{2-} and DIC concentration (r = 0.89) and alkalinity (r = 0.76). Sulfate was also well correlated to DIC concentration and hardness at Thornton's Slough (r = 0.80 and 0.85, respectively), but not to alkalinity (r = 0.37). This suggests that reactions other than gypsum dissolution (which produces CO_2 and SO_4^{2-} and consumes the alkalinity component HCO_3^-) may influence the slough's alkalinity levels. For example, runoff of PO_4^{3-} from fertilizers applied to local agricultural lands may also attribute to the slough's alkalinity levels (evidenced by PCA-B and correlation in Tables 4.14-4.15).

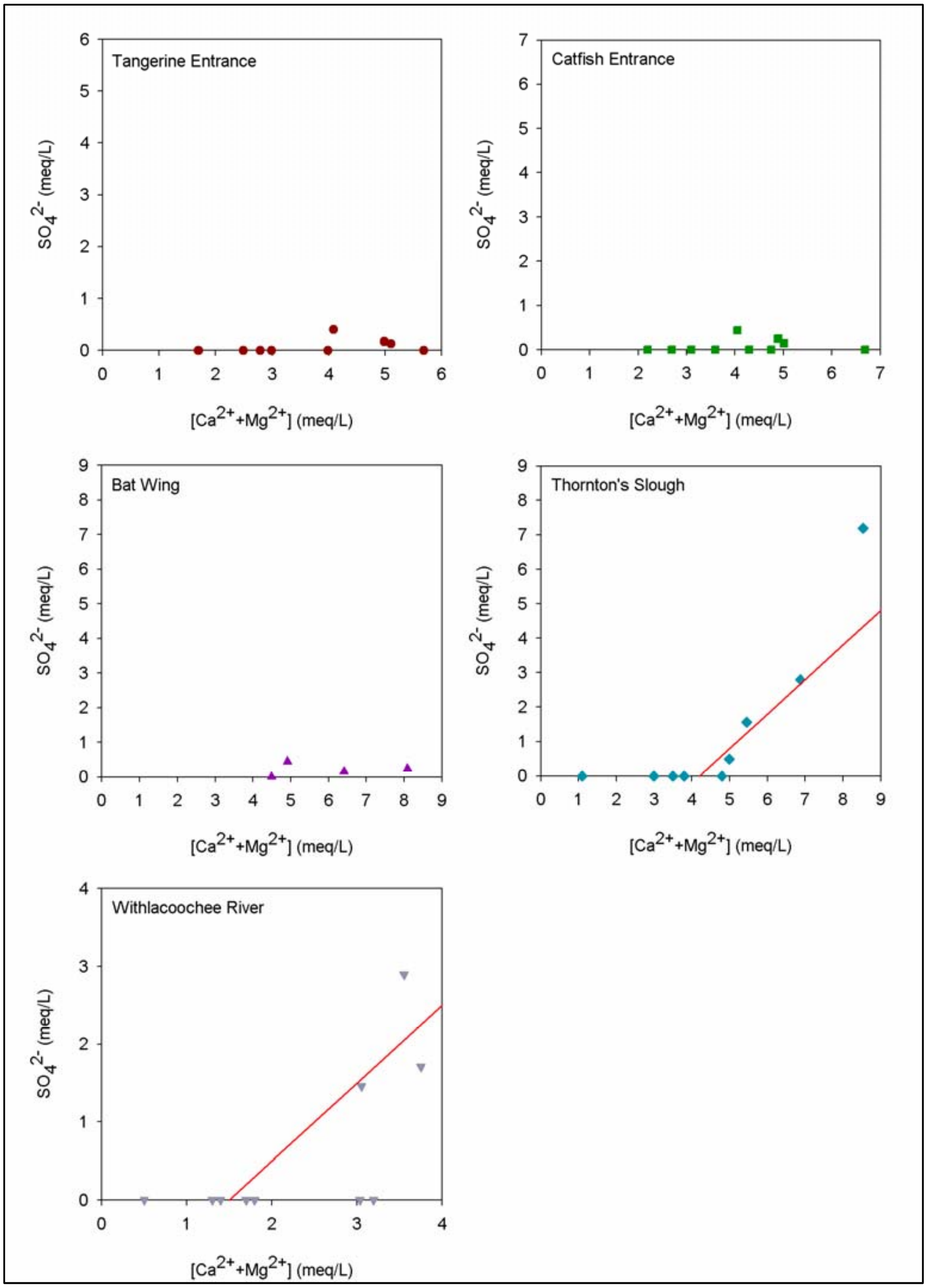

Figure 4.19. Gypsum dissolution plots for Thornton's Cave, Thornton's Slough and the Withlacoochee River. Calcium excess indicated by points plotting to the left of the unity line.

Evidence of gypsum dissolution at the cave sites was difficult to identify due to their waters' inherently lower SO_4^{2-} concentrations relative to the surface, and perhaps also to the limits of the dataset; however, the high water:rock ratio for the cave is likely to preclude much evaporite mineral formation, which could preclude gypsum dissolution as a major influence in the geochemistry of the water. Nevertheless, fluctuation in SO_4^{2-} was an important parameter in PC1 of both the Tangerine and Catfish entrances and can likely be attributed to its natural abundance in the Floridan Aquifer (Sprinkle, 1989). Alternatively, if anoxia occurs in cave sediments, sulfate-reducing bacteria could be removing SO_4^{2-} from solution keeping concentrations low, while contributing to higher alkalinity values in cave waters compared to that of the surface as displayed in the following reaction:

$$SO_4^{2-} + 2CH_3COO^- + H_2O \rightarrow H_2S + 2HCO_3^- + OH^- \qquad \text{(Eq. 5)}$$

The high ratio of Ca^{2+} to SO_4^{2-} at each site argues that though sulfate-based reactions are occurring and may influence alkalinity and DIC concentrations, considerable Ca^{2+} excess means that limestone dissolution is the main contribution to hardness. Though H_2SO_4-dissolution, gypsum dissolution, and sulfate-reduction each influence the DIC pool through the contribution or utilization of HCO_3^-, excess Ca^{2+} can only come from carbonate dissolution. Because carbonate dissolution also produces HCO_3^-, we can assume the influence of sulfate-based reactions is moderate, and at best, secondary to carbonate dissolution, further suggesting H_2CO_3-dissolution and carbonate equilibrium reactions are important controls on the variation of these ions.

4.5.4. Iron-based Reactions

Iron is a common mineral constituent of marine limestones and is provided to carbonate environments primarily by riverine or windblown transport of minerals weathered from continental rocks and is recycled by the *in situ* decomposition of organic matter, which cycles weathered Fe through the biosphere. Pyrite (FeS_2) is the most prevalent Fe mineral in marine limestones, and is a major sink for sulfide minerals. It is produced by the bacterial reduction of SO_4^{2-} in reducing diagenetic conditions (Eq. 5) with abundant energy provided by organic carbon substrates (Rickard and Luther, 2007):

$$2H_2S + Fe^{2+} \rightarrow FeS_2 + 4H^+ \qquad \text{(Eq.6)}$$

Equation 6 combines two separate reactions where H_2S first binds with Fe^{2+} to produce iron monosulfide (FeS), which then reacts with H_2S to form FeS_2. At low temperatures (<100 °C), the second reaction can proceed only in solutions super-saturated with FeS due to the high activation energies required for pyrite nucleation.

When pyrite-bearing limestones are weathered or subject to microbial oxidizers, pyrite is oxidized to form oxides, hydroxides, and oxyhydroxides such as ferric hydroxide, $Fe(OH)_3$, and H_2SO_4 in the following example:

$$FeS_2 + 3.75O_2 + 3.5H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4 \qquad \text{(Eq. 7)}$$

In the intermediate steps of this reaction, Fe^{2+} is hydrolyzed to Fe^{3+} to precipitate $Fe(OH)_3$, while sulfoxy anions, S_2OH^-, are oxidized to SO_4^{2-}. Similar reactions occur in the oxidation of other iron-sulfide minerals, such as marcasite, chalcopyrite, and arsenopyrite. The net effect of these combined reactions is the release of protons, which lower pH and promote limestone dissolution. Research of ferromanganese deposits produced from the oxidation of Fe and Mn in the caves of the Guadalupe Mountains region of New Mexico strongly implicate iron- and manganese-oxidizing bacteria, such as *Pedomicrobium manganicum* and *Leptothrix*, as facilitators, if not major contributors, to this process (Cunningham, 1991; Cunningham et al., 1995;

Northup et al., 2003; Spilde et al., 2005). The formation of $Fe(OH)_3$ is the precursor to the formation of various other iron oxides including goethite, lepidocrocite, and limonite, which may form precipitate crusts as the underlying limestone is corroded. In particular, *Acidovorax* sp., a nitrate-reducing oxidizer of Fe^{2+} facilitates the formation of these minerals, especially under elevated carbonate and humic acid concentrations (Larese-Casanova et al., 2010).

In Florida limestones, Fe is most prevalent as secondary pyrite (Randazzo, 1997), whose oxidation is likely the main contributor of Fe to the Floridan Aquifer system (Sprinkle, 1989). In caves such as Thornton's that are open to the surface, additional Fe would also be supplied by infilling of surface soils rich in Fe minerals, organic matter (through Fe bioaccumulation) and surface water (containing dissolved Fe species). The results of PCA-B show that total Fe and/or Fe^{2+} was important to the geochemical change at each site. Total Fe concentrations were typically 14+ times greater than the concentrations of Fe^{2+}, illustrating its higher solubility and mobility compared Fe^{3+} and suggesting its conversion to Fe^{3+} is a rapid process in cave waters. Conversely, Fe^{3+} is less soluble and mobile than Fe^{3+}, allowing it to accumulate more readily in cave waters and remain longer. At the cave, total Fe played an important role in PC2 at the Tangerine Entrance, and to a slightly lesser degree at the Catfish Entrance, while Fe^{2+} was important in PC3 of both sites (Table 4.10). The moderate to strong, positive correlation between total Fe and PO_4^{3-} at both entrances is evidence of the affinity of iron hydroxides for PO_4^{3-} adsorption (e.g., Griffioen, 1994), and probably accounts for the geochemical variation in PC2 for both sites. Though the Eocene limestones of Florida have relatively low abundances of phosphate-bearing minerals, PO_4^{3-} is a common geochemical constituent in the Floridan Aquifer due to its abundance in Miocene limestones, as well as runoff from phosphate mines, fertilizers, and sewage effluent (Miller, 1986; Sprinkle, 1989). At Thornton's Cave, the decomposition of bat guano provides a more localized source, and is likely a factor in its contribution to geochemical variation in PC2 at the Catfish Entrance, if not at both entrances.

The role of Fe^{2+} in PC3 is less clear. At the Tangerine Entrance, Fe^{2+} was best correlated to NO_3^- (r = 0.86), which contributed a secondary influence on geochemical variation in PC3, suggesting that the decomposition of organic matter may be contributing both to the water column, followed by oxidation of Fe^{2+}, accounting for its lower concentration relative to that of total Fe. Additionally, Fe^{2+} oxidation by nitrate-reducing bacteria could be contributing to the relationship between Fe^{2+} and NO_3^-, serving to reduce the concentration of both over time and possibly explaining the low and high overall concentrations of NO_3^- and Fe^{3+}, respectively (Benz et al., 1998; Larese-Casanova et al., 2010). This process was not evident at the Catfish Entrance, where Fe^{2+} exhibited the strongest correlation to $\delta^{13}C_{DIC}$ values (r = -0.53). Aerobic decomposition of organic matter could also account for this relationship by producing ^{13}C-depleted CO_2 as decomposition releases Fe^{2+}; however, because Fe^{2+} demonstrates no correlation to pCO_2, the $Fe^{2+}/\delta^{13}C_{DIC}$ correlation is probably an artifact of separate processes impacting each of their values.

At both the Withlacoochee River and Thornton's Slough, Fe^{2+} and total Fe demonstrate a moderate to strong positive relationship to one another and to water-level and an inverse relationship to most other parameters that experience dilution when water-levels are high, notably conductivity, hardness, alkalinity, and DIC concentration. These relationships would explain why PCA-B results suggest that both Fe^{2+} and total Fe have a moderate to strong influence on geochemical variation in PC1. The most probable explanation for increasing Fe concentrations during the wet season is soil runoff into both the river and the slough, with the slough receiving additional Fe from river flooding, exhibited by its higher overall concentrations (Table 4.4, Figure 4.15). Fluctuation in Fe^{2+} was more important to the geochemical variation at the river, and may result from rates of reduced mineral inputs exceeding rates of oxidation in river waters. The variation in the hydrologic and vegetative regime at the slough is probably responsible for the more balanced contribution of total Fe and Fe^{2+} at this site, exhibited by their moderate loadings in PC1 and their strong correlation to one another (r = 0.76). Because water-level at the slough is wholly dependent on flooding by the river, the slough floods during the wet season and becomes totally dry when river stage falls during the dry season. This change causes a floral turnover in the slough from dense growth of aquatic macrophytes in the wet season, to short grasses and small herbaceous plants in the dry season and provides a setting of continual growth and decomposition that promotes *in situ* Fe cycling, with additional Fe provided by runoff during the wet season.

Combining the interpretations of both Fe and SO_4^{2-} in this study, we see that though pyrite oxidation can contribute a significant source of Fe and SO_4^{2-} to the Floridan Aquifer, the primary source of these ions to Thornton's Cave and nearby surface waters is likely runoff from surface soils. The absence of H_2SO_4-dissolution evidence at the cave combined with evidence for gypsum dissolution in surface waters yielded by SO_4^{2-} data support this hypothesis and implicate organic matter and gypsum, respectively, as primary SO_4^{2-} sources at each site. Nevertheless, brown to black encrustations (Figure 4.10) on the ceilings and "cornflake"-like precipitants observed in the cave's more remote passages suggest precipitation of Fe, and perhaps also Mn provided by the dissolution of minerals bearing these elements from the limestone. Energy dispersive x-ray (EDX) analysis performed on cornflake precipitates showed they were comprised primarily of Fe and calcium (Figure 4.20; Florea, personal comm.). These data suggest that although sulfide oxidation exerts little control on the aquatic geochemistry of the cave, it is nevertheless an active process, and may in part be attributed to reactions associated with bat roosting, where these features are most commonly found. According to observations of roosting sites made during this study and by those of residents living on the cave property, the summer breeding bat colony is located primarily along a transect extending from the Bat Wing to The Deep, one of the more remote areas of the cave(Figure 4.3). It is also here that ceilings have the highest occurrence of encrustation, and where cornflake precipitants are most commonly observed. Because the composition of bat guano can include a variety of elements including Fe, and because bat excrement is known to produce a variety of minerals in caves, this fuels the hypothesis that these encrustations may result from microbially mediated excrement- and urea-limestone reactions (Studier et al., 1994; Karkanas et al., 2002; Shalhack-Gross et al. 2004). In addition, elevated concentrations of atmospheric CO_2 documented at the Bat Wing during the breeding season by colony respiration, and possibly by the microbial breakdown of guano deposits (Chapter 3) could be dissolving into surface condensate on cave walls and promoting corrosion. Similar hypotheses have been suggested to explain “bell-hole” dissolution cavities and associated crusts identified in the ceilings of tropical caves in Belize, the Bahamas, and Jamaica, and implicate bats as important, and at times major contributors to CO_2 levels and cave microclimate (King-Webster & Kenny, 1958; Harris, 1970; Miller, 1990, 1996; Lauritzen et al., 1997; Wicks and Engeln, 1997; Lundberg and McFarland, 2009). This dissolution of the limestone would expose relatively insoluble metallic residues susceptible to auto-oxidation as well as iron-oxidizing bacteria akin to those produced in the caves of the Guadalupe Mountains of New Mexico and Romania (Onac et al., 1997; Northup et al., 2003). Regardless of the relative contribution of Fe from surface soils, bat excrement, and limestone, the stability and insolubility of the Fe^{3+} ion might explain its much higher concentration compared to Fe^{2+}, which readily converts to Fe^{3+} under oxidizing conditions.

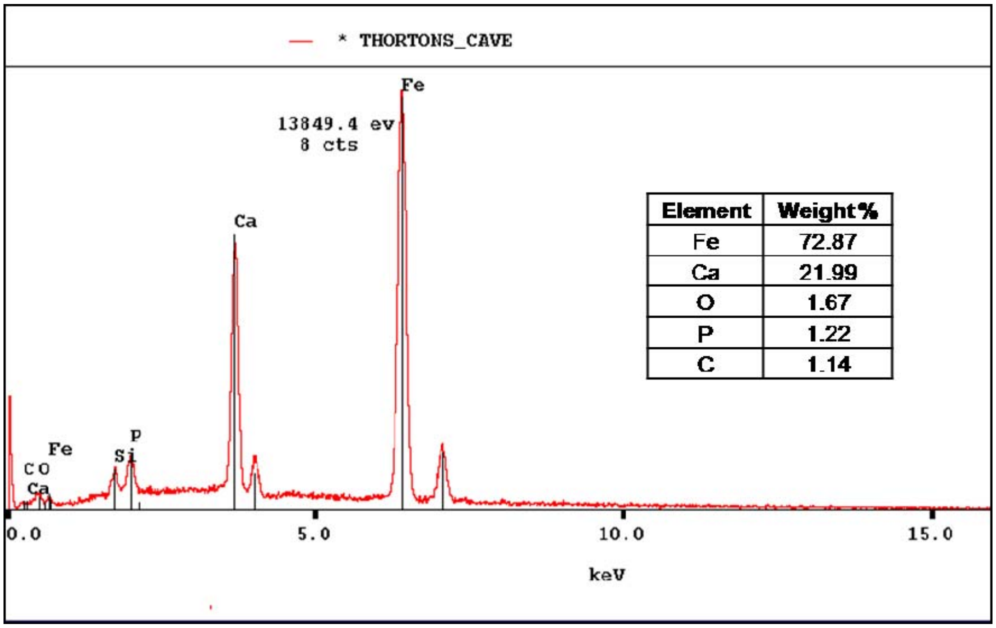

Figure 4.20. EDX analysis of “cornflake” precipitants collected from Thornton’s Cave.

4.5.5. Nitrogen-based Reactions

Nitrogen is a critical component of biochemical cycling, and its availability, as well as that of carbon and phosphorus, is a significant control on biogeochemical processes in the biosphere. The oxidation of NH_3 (or NH_4^+) to NO_3^- during nitrification is a two-step process (Eq. 8-9):

$$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^- \qquad \text{(Eq. 8)}$$

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \qquad \text{(Eq. 9)}$$

Oxidation of NH_3 and NH_4^+ in the first step is facilitated by the genera *Nitrosomonas*, *Nitrosospira*, and *Nitrosolobus*, while oxidation of NO_2^- to NO_3^- in the second step is facilitated by *Nitrobacter*, *Nitrospina*, and *Nitrococcus*. Each of these nitrifying microorganisms consumes CO_2 as a carbon source for growth. Ammonia, N_2, NH_4^+, and

NO_3^- are assimilated into plants, then decomposed and converted back to free inorganic forms and other minerals. Denitrification is one method, in which nitrate reducers, including *Pseudomonas*, *Escherichia coli*, *Staphyloccocus carnosus*, and *Thiobacillus denitrificans* convert NO_3^- to N_2 and NH_4^- (Eq. 10 and 11, respectively):

$$CH_2O + 0.8NO_3^- + 0.8H^+ \rightarrow 0.4N_2 + CO_2 + H_2O \qquad \text{(Eq. 10)}$$

$$CH_2O + 0.5NO_3^- + H^+ \rightarrow CO_2 + 0.5NH_4^+ + H_2O \qquad \text{(Eq. 11)}$$

Acidification caused by nitrification will cause dissolution of limestone, producing lithogenic DIC that enriches the DIC pool in ^{13}C. In carbonate settings, continual nitrification will cause positive excursions in $\delta^{13}C_{DIC}$ values that could exceed that of the host limestone as NH_3 concentrations and pCO_2 decrease and NO_3^- concentrations increase. Similarly, ammonia volatilization, commonly facilitated by species of the bacterial genus *Helicobacter* at a pH range of 6.5 to 8 (the most common range observed at each site in this study), converts urea ($(NH_2)_2CO$) to NH_3 and carbamic acid (H_2NCOOH) using the enzyme urease (Eq. 12). Ammonia gas is formed from the breakdown of carbamic acid, unless the NH_3 reacts with water to form NH_4^+ (Eq. 13).

$$(NH_2)_2CO + H_2O \rightarrow NH_3 + H_2NCOOH \rightarrow 2NH_{3(g)} + CO_{2(g)} \qquad \text{(Eq. 12)}$$

$$NH_{3(g)} + H_2O \rightarrow NH_4^+ + OH^- \qquad \text{(Eq. 13)}$$

Conversely, denitrification and ammonification contribute ^{13}C-depleted CO_2 back into the DIC pool, lowering $\delta^{13}C_{DIC}$ values as NH_3 concentration and pCO_2 increase and NO_3^- concentrations decrease.

Results of PCA-Bs show that nitrogen cycling is an important agent of geochemical variation at each site, demonstrated by its high loadings of NO_3^- and/or NH_3

in PC1. Nitrate appeared to influence the geochemistry more at the Withlacoochee River and Thornton's Slough, while NH_3 concentrations were more significant at both entrances of the cave. Prior to dilution associated with the 2009 wet season, NO_3^- concentrations in the surface waters were higher than NH_3 concentrations, suggesting that nitrification reactions were dominant (or that denitrification was limited to the subsurface), illustrated by $\delta^{13}C_{DIC}$ values that occasionally exceeded that of Ocala Limestone; however, NO_3^- concentrations did not show an inverse correlation to NH_3 concentrations, nor did they show a positive correlation to $\delta^{13}C_{DIC}$ values. This indicates that fluctuations in these ions were not due solely to *in situ* nitrification and denitrification/ammonification reactions, and like Fe, may be due to episodic runoff of organic matter from the surrounding landscape. In addition to local organic matter inputs, inputs to the river from forested, agricultural, and residential areas upstream will deliver any surplus NO_3^- and NH_3 to the sites sampled in this study. These inputs would generate a heterogeneous mixture of NO_3^- and NH_3 contributed by multiple sources with potentially unique nitrogen cycling dynamics, making any assumptions regarding *in situ* nitrogen dynamics difficult to assess.

At the cave, NH_3 fluctuations contributed to more geochemical variation and NH_3 concentrations generally exceeded that of NO_3^- (Figure 4.15, Table 4.4); however, NH_3 and NO_3^- concentrations measured from each entrance do not show the expected correlations to $\delta^{13}C_{DIC}$ values and pCO_2, or the negative correlations to one another, that are indicative of nitrification, denitrification, ammonia volatilization and ammonification (Table 4.11). Instead, each exhibit mild to moderate positive correlations with the remaining geochemical parameters in PC1 and to one another, and inverse correlations to water-level. While these correlations are not evidence against nitrogen cycling, the periodic excursions of $\delta^{13}C_{DIC}$ values above that of the Ocala Limestone suggest that nitrification is impacting the DIC pool. These results could be indicative of both the limitations of the major ion dataset and the complex nature of nitrogen dynamics at the cave, which likely undermine any direct relationships between nitrogen species and $\delta^{13}C_{DIC}$ values and pCO_2 concentrations.

To illustrate, NO_3^- was rarely detected at the Tangerine Entrance, and, despite the proximity between the Bat Wing and Catfish Entrances, it was only documented at the Bat Wing beginning in early July. At the same time, NH_3 concentrations were gradually declining at the Tangerine Entrance while rising dramatically at the Catfish Entrance and Bat Wing. This increase was undoubtedly in response to the occupation of the Bat Wing by the breeding bat colony, beginning in mid-May, 2009. When colonization initiated, water-levels at the cave were still relatively low such that the accumulation of guano in the Bat Wing tended to occur on the muddy passage floor and upon exposed benches directly below the colony (Figure 4.11). It was not until the colony size increased in early June that individuals began to roost directly above the perennial pool at the rear of the Bat Wing where water samples were collected. This may account for the delay in the rise of NO_3^- at the Bat Wing compared to the Catfish Entrance, the primary access point for bats travelling in and out of the cave. The growth in colony size between May and July also explains the sharp increase in NH_3 concentrations over this time period, evidence of nitrogen fixation and/or ammonia volatilization. The odor of ammonia gas also grew steadily during this time and could be sensed at the surface up to 10 m from the Catfish Entrance. No signs of bat colonization were visible at the Tangerine Entrance. The lack of bat colonies at the Tangerine Entrance was supported by the absence of similarity between its geochemical profile and that of the Catfish Entrance and the absence of guano deposits and NH_3 odors. Cave flooding in July 2009 appeared to homogenize NH_3 and NO_3^- concentrations between sites, evidenced by their similar fluctuations in NH_3 and the absence of detectible NO_3^-. Though flooding should have rinsed all accumulations of guano and any associated NO_3^- into the water column, particularly at the areas nearest the Bat Wing, the dilution of NO_3^- during flooding of this magnitude combined with the rapid uptake of NO_3^- through a variety of organic processes probably explains why it could not be detected. It is assumed that the flood event caused the maternity colony to abandon the cave, as no direct observation of individuals or traces of their presence were observed thereafter.

Collectively, PCA results, fluctuations in the concentrations of nitrogen species, and direct observations support several conclusions regarding nitrogen dynamics at Thornton's Cave. First, the hydrologic connection between the Catfish and Tangerine Entrances must be restricted at best, allowing independent, seasonal evolution of nitrogen profiles at the Catfish Entrance driven by bat colonization during the summer breeding season. Second, nitrogen sources appear to become more similar when the bat colony vacates and/or when the cave is flooded, such that the primary sources at both sites are derived from the decomposition of organic matter from surface infilling. Third, the inherent complexity of nitrogen cycling combined with the variations in sourcing described above preclude any direct geochemical relationships between nitrogen species and $\delta^{13}C_{DIC}$ values associated with CO_2 sources. This is not to say nitrification and denitrification/ammonification reactions at the cave exert no influence on the DIC pool. Periodic excursions of $\delta^{13}C_{DIC}$ values above those of the Ocala Limestone certainly suggest that nitrification is occurring, and nitrogen cycling associated with the abundant seasonal loading of bat guano and urea undoubtedly exerts some influence on dissolution through the colonization of microorganisms. The release of acidity through the oxidation of organic matter releases organic acids and other humic substances, as well as inorganic ions (e.g., PO_4^{3-} and Fe^{3+}), that are each known to act as inhibitors of calcite precipitation, if not direct promoters of dissolution (Berner, 1975; Reddy, 1977; Dove and Hochella, 1993; Takasaki et al., 1994; Hoch et al., 2000; Sand, 1997; Northup et al., 2000). Further, oxidation of reduced ions associated with other organic processes, notably the oxidation of Fe^{2+} to Fe^{3+} during bacterially mediated nitrate reduction could also be contributing to dissolution through acid production (Benz et al., 1998; Larese-Casanova et al., 2010), while increasing Fe^{3+} concentrations and decreasing NO_3^- concentrations. A longer-term, more directed study using major ions in conjunction with carbon and nitrogen isotopes, as well as a study identifying the presence of absence of microorganisms involved in the nitrogen cycle is therefore suggested to better elucidate the dynamics of nitrogen cycling and its potential role in limestone dissolution processes.

4.6. Conclusion

Dissolution is an active process at Thornton's Cave, and analyses of geochemical variations in the cave and surface waters suggest that the production of H_2CO_3 is an important agent of limestone dissolution. Ample sources of CO_2 provided to the cave environment have been documented, and with the exception of atmospheric CO_2 flowing into the cave from the surface, all are biotic in origin, contributing to $\delta^{13}C_{DIC}$ values commonly below that of the Ocala Limestone:

1. Perennial diffusion of CO_2 from surface soils, elevated during the wet season
2. Perennial respiration of CO_2 from cave sediments and to a lesser degree, wall rock through the oxidation of organic matter, elevated in wet sediments and rock, and most likely elevated further during the wet season
3. Seasonal CO_2 inputs from direct respiration of breeding bat colonies and the microbial decomposition of guano deposits

Though not specifically determined here, we can hypothesize that oxidation of organic matter as well as the surface atmosphere are major sources of CO_2 in surface waters.

The prevalence of microbially driven reactions that produce and consume CO_2, as well as other microbial reactions that influence acidity also support the dissolution of limestone through mechanisms other than H_2CO_3-dissolution. Though H_2SO_4-dissolution was not evident at the cave, H_2CO_3-dissolution that exposes pyrite to oxidizing conditions, and perhaps manganese minerals to oxidizing conditions may enhance dissolution through the release of H^+ in these reactions. The same can be said of for oxidation of other sulfide minerals, nitrification, and the oxidation of organic matter, each of which are supported by data presented in this study.

Further, microorganisms can contribute to dissolution in other ways. Active weathering processes include exfoliation of rock as species probe grain boundaries for mineral resources, while endolithic bacteria actively bore into rocks in search of minerals (e.g., Golubic et al., 1970; Pentecost, 1992). Passive weathering processes include the excretion of extrapolymeric substances on mineral faces by microorganisms as a protective layer, which lock in water, and perhaps acids, that corrode the underlying material through hydrolysis or chemical weathering, respectively. Paine et al. (1933) documented and enumerated heterotrophic bacteria respiring CO_2 from both buildings and quarry limestone, and later documented dissolution of sterile limestones treated with nutrient broths and inoculated with nitrifying and sulfide-oxidizing bacteria. Similarly, a variety of autotrophic and heterotrophic bacteria have been identified colonizing the pore spaces of limestone, many of which assumed to be contributing to corrosion as they metabolize nutrients and produce organic acids (Cunningham et al., 1995; Laiz et al., 1999; Spilde et al., 2005; Schwabe et al., 2008).

In all, microbial dissolution of limestone can be achieved through a variety of means, and while the production of H_2CO_3 by CO_2 respiration may be the chief mechanism identified in this study, the complex geochemistry of these waters suggest that multiple dissolution processes likely played roles. The evidence for this hypothesis lies mainly in the observation that the traditional model of limestone dissolution wherein CO_2 of unknown (but probably biotic) origin, and particularly H^+ alone, is the primary dissolving agent is no longer sufficient to explain the evolution of karst landscapes over time. By choosing to ignore the sources of CO_2 and their contributions, as well as the impacts of other biogeochemical reactions, important details regarding the dissolutional history of carbonate rocks, particularly dissolution rates (e.g., punctuated versus continual, susceptibility to disturbance by localized or global environmental change) and the influence of carbonate weathering on global carbon cycles, are lost. Though the integrative methods utilized in this study are not feasible for reconstructing karst development and speleogenesis in the past, assessments of the modern development of karst systems can be applied to older systems. In doing so, we are better capable of generating more accurate models of their dissolutional history, thereby developing a broader perspective on karst evolution.

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CHAPTER 5:

CHARACTERIZING BIOTICALLY DRIVEN LIMESTONE DISSOLUTION MECHANISMS IN A MODERN TROPICAL WETLAND (EVERGLADES NATIONAL PARK, USA)

5.1. Introduction

Limestone dissolution is an important geochemical process contributing to the formation of the world's more productive aquifers, upon which an estimated 20 to 25% of the world's population relies as a principal water source (Ford and Williams, 2007). Classic models of limestone dissolution cite the flow of mildly acidic waters through the pore space and/or along fractures as the primary mechanism of the formation and evolution of karst landscapes (summarized in White, 1988). These waters can be acidified several ways. In most karst regions, the acid is often assumed to be produced by dissolution of soil CO_2 to generate carbonic acid (H_2CO_3) as meteoric waters migrate through soil toward the limestone, or by the mixing of two water bodies saturated with respect to calcite to form an undersaturated solution (Wigley and Plummer, 1976; Ford and Williams, 2007). Sulfuric acid (H_2SO_4) is a common agent of dissolution in karst areas influenced by geothermal activity, or anywhere sulfate minerals such as pyrite and gypsum undergo redox reactions (Hill and Forti, 1997; Ford and Williams, 2007). Biogenic organic compounds such as humic substances and some inorganic ions (e.g., PO_4^{3-}, Mg^{2+}, and iron) released during the decomposition of organic matter have also been implicated in limestone dissolution reactions as they have been known to inhibit calcite precipitation and/or promote acidification of meteoric water (Paine et al., 1933; Berner et al., 1978; Inskeep and Bloom, 1986; de la Torre et al., 1993, Hoch et al., 2000; Schwabe et al., 2008; McGee et al, 2010). In one example, acidity is produced in the first step of nitrification during the oxidation of NH_3 or NH_4^+ to NO_2^- by the bacteria *Nitrosomonas (*discussed in Konhauser, 2007). Though such dissolution mechanisms are mediated by biotic reactions, they are commonly overlooked in dissolution models, underscoring the need to assess their influence on both limestone dissolution and the evolution of karst landscapes.

Though enhanced porosity in some karst regions can preclude the accumulation of water at the surface, wetlands are relatively common in lowland karst where groundwaters are near the surface. Wetlands themselves are among the most biodiverse and productive of ecosystems, making those in karst regions unique settings for the study of biotic influences on dissolution. By identifying and characterizing biotic dissolution mechanisms in these modern environments, we are better able to identify the temporal geomorphic evolution of these environments. The Everglades of southern Florida represents such a setting where an expansive freshwater wetland, composed primarily of marshes, sloughs, and wet prairies, overlies Pleistocene eogenetic limestone (Hoffmeister et al., 1967; Cunningham et al., 2009). Unlike other freshwater karst wetlands, such as the turloughs of western Ireland where groundwater surges in the winter and floods the surface to form seasonal lakes, the Everglades are flooded year-round, fed by rainfall and slow southward flow from Lake Okeechobee. This perennial wetland supports a diverse floral community attracting a diverse native and migrant fauna. The highly productive ecosystem provides ample carbon cycling, making it an ideal area in which to study biotically driven dissolution processes. Drainage of the Everglades for land use and water supply have altered its hydrologic regime such that previously thick deposits of peat (up to 3.7 m thick in the lower-lying sloughs) are exposed to aerobic decomposition (Gleason and Stone, 1994). This oxidation of organic matter releases both nutrients and oxidized forms of carbon, nitrogen, and sulfur into surface waters resulting in acidification, which has the potential to accelerate dissolution rates in areas where limestone is at or near the surface, as well as in places where previously buried limestone becomes exposed. Therefore, the Everglades region also serves as a useful site in which to study human impacts on the natural dissolution of these environments.

The ubiquity of carbon in the environment makes it a powerful tracer, and it is often employed to identify and characterize biotic and abiotic processes, such as primary productivity and weathering, on a variety of time and spatial scales (e.g., Keeling, 1958; Berner, 1998; Aucor et al., 1999; Berner and Kothavala, 2001; Romanov et al., 2008; Scholze et al., 2008). In particular, stable isotopes of carbon are used to identify carbon sources and sinks due to fractionation effects as C moves from one species to another during biogeochemical reactions (summarized in Schlesinger, 1997). As a result, stable carbon isotope ratios (^{12}C and ^{13}C, or $\delta^{13}C$), are commonly used to reconstruct modern and/or ancient climates and ecologies and are becoming more common in hydrologic and karst research to characterize dissolution and precipitation processes (Hullar et al., 1996; Sumner, 2001; Doctor et al., 2006; Dorale et al., 2010; McGee et al., 2010). The ratio of carbon to nitrogen (C/N) of organic matter is also used to constrain inputs of organic carbon sources based on their tissue structure, with high and low ratios indicating inputs by taxa with tougher, woodier and from softer-tissues, respectively. Finally, carbon concentrations are used to establish contributions of particular carbon sources identified by $\delta^{13}C$ and C/N analyses to construct an overall model of carbon flux for a given system. In this study, we combine direct observation of dissolution processes using limestone tablets, $\delta^{13}C$ of organic and inorganic carbon, dissolved inorganic carbon concentration, and C/N analyses with geochemical measurements of pH, conductivity, alkalinity, dissolved oxygen (DO), calcite saturation indices (SI) and major ion concentrations from a nine-month monitoring project to establish a model of dissolution in limestones at or near the land surface within the Everglades. The purpose of this study is threefold: 1) to identify and characterize the role of biota on the natural dissolution of limestone in this freshwater karst environment, 2) to estimate how natural dissolution might be affected by the decomposition of peat in the drained regions of the Everglades to the north, and 3) to provide a better understanding of the variety of dissolution processes in modern and ancient carbonate environments that may be relevant to hydrology, paleoenvironmental reconstruction, paleoclimatology, and petroleum exploration.

5.2. The Everglades

The Everglades region lies at the southernmost end of the Florida Peninsula, within the ~28,000 km^2 Kissimmee-Okeechobee-Everglades drainage basin (Figure 5.1; Light and Dineen, 1994). The primary feature of this basin is the Everglades Depression, a linear trough extending southwest from Lake Okeechobee (Wanless et al., 1994). Maximum elevation change in the depression is 4.3 m between Lake Okeechobee and Florida Bay and facilitates the slow sheetflow of water from the lake southward along Shark River Slough toward the Cape Sable region and Taylor Slough to Florida Bay (Thornberry-Ehrlich, 2008). Diversion of this flow by canalization to the Miami-Dade metropolitan area and drainage for agricultural development has dramatically reduced the volume of water in the Everglades since the late 1800s, with the only relatively pristine landscape remaining in its southern region at Everglades National Park. The park, including the northeastern expansion area added in 1989, is just over 6,100 km^2, representing approximately one-fifth of the Everglades' original area and extends south from the Tamiami Trail to Florida Bay (Davis and Ogden, 1994; National Park Service, 2009).

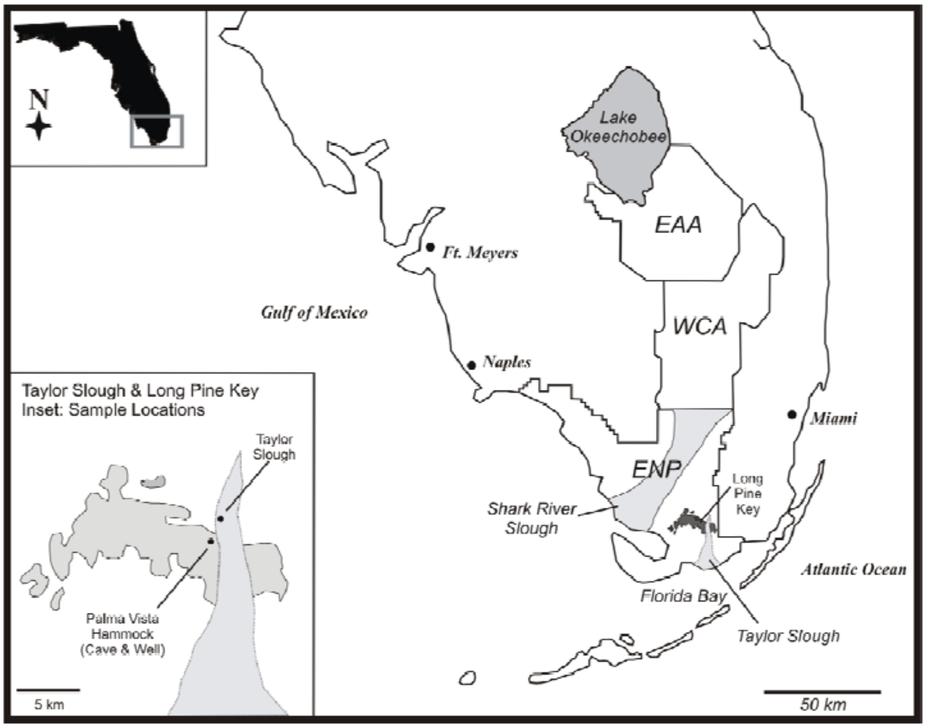


Figure 5.1. The Everglades of South Florida. Inset: Taylor Slough. Boundaries shown for Everglades National Park (ENP), Water Conservation Area (WCA) and Everglades Agricultural Area (EAA).

Seasonal temperature fluctuation in this region of south Florida is low, with average daytime highs in the winter months ranging between the mid 20s (°C) and the lower 30s during the summer (Florida Climate Center, 2010). However, seasonal variation in rainfall is large: from May to June mostly local convection systems produce ~8-24 cm/month, with a brief decrease in July (~18 cm), followed by high rainfall from August to September (~ 20-22 cm/month) from the passing of tropical low-pressure systems such as tropical depressions/storms and hurricanes (Florida Climate Center, 2010). Rainfall is lowest during the winter and early spring (November through March), varying from 3 to 5 cm/month (Florida Climate Center, 2010).

The Everglades landscape is subdivided into eight ecosystem units, differentiated by hydrologic and vegetative regimes: tropical hardwood hammocks, rockland pine forests, cypress domes, mangroves, freshwater sloughs, marl prairies, coastal lowlands, and marine/estuarine environments (Lodge, 1994; Thornberry-Ehrlich, 2008). Forces shaping the distribution and scale of these units are driven by disturbances such as fires, storms and droughts, as well as naturally occurring long- and short-term fluctuation such as climate/sea-level change and hydroperiod, respectively (DeAngelis, 1994). Because water is not a limiting factor for photosynthesis in the Everglades, most native plants utilize the C_3 photosynthetic pathway, which yields organic matter with $\delta^{13}C$ values between -23 and -27‰ due to continual, preferential uptake of the ^{12}C isotope during carbon fixation (Schlesinger, 1997; Ehleringer and Cerling, 2002). A notable exception is the C_4 plant sugarcane (*Saccharum* sp.), a non-native crop introduced in the late 1800s, adapted to more arid conditions and grown in drained soils. Because this pathway is adapted to fix less CO_2 in photosynthesis than the C_3 pathway, its $\delta^{13}C$ values are between -10 and -14‰ (Schlesinger, 1997; Ehleringer and Cerling, 2002).

5.2.1. Geology

The majority of the Everglades subprovince is underlain by the Miami Limestone, a dual-porosity eogenetic limestone of Sangamon age (70-125 ka) (Hoffmeister et al., 1967; Cunningham et al., 2009). The Miami Limestone contains a peloidal/bryozoan facies distinguished by areas of high and low porosity: high porosity (50-80%) facies are dominated by interconnected ichnogenic vugs representing the callianassid shrimp burrows (i.e., *Ophiomorpha*) during deposition as well as biomoldic porosity from the dissolution of mollusk shells, and these are interbedded between lower porosity (<30%) facies (Cunningham, 2009). These high-porosity, very permeable facies allow for rapid response of the Biscayne Aquifer to droughts and rainfall and make it particularly susceptible to pollution transport, sourced largely from agricultural and urban runoff (Harvey et al., 2008; Renken et al., 2008; Shapiro et al., 2008). A detailed description of the Miami Limestone in association with the Biscayne Aquifer is discussed Cunningham et al. (2009).

Epikarstic features, such as solution holes are found throughout Everglades National Park, and are often subject to infilling by organic and marl sediments, which are estimated to lower pH through decomposition and accelerate dissolution (Thornberry-Ehrlich, 2008). These solution holes also act as habitats and watering holes for plant and animal species, particularly during drier winter months. In the upland regions, notably the Atlantic Coastal Ridge subprovince, the Miami Limestone outcrops at the surface exposing these solution holes as shallow pits and caves and other collapse features (Figure 5.1; Cressler, 1993; Thornberry-Ehrlich, 2008). This subprovince intersects the Everglades to form Long Pine Key in Everglades National Park, with elevations varying from 1.5 to 6 m (Gleason and Stone, 1994).

5.2.2. Taylor Slough and Palma Vista Hammock

Taylor Slough is a small, wedge-shaped slough cutting perpendicularly across the Atlantic Coastal Ridge, widening as it reaches Florida Bay (Figure 5.1). Sedimentary environments in the slough are dominated by freshwater marls in its northern reaches, transitioning to freshwater peat, then mangrove peat as it flows southward (Wanless et al., 1994). Vegetation in the slough varies and is dominated by C_3-plant species including: the aquatic macrophytes *Nymphaea odorata* (white water lily), *Thalia geniculata* (alligator flag), *Cladium jamaicense* (sawgrass), and various terrestrial shrubs in localized patches of higher elevation. Periphyton is common in the water column, and is comprised of photosynthetic microorganism communities (various algal and cyanobacterial species, along with diatoms, heterotrophic microorganisms, and detritus) that adhere to submerged surfaces and are an important base constituent in the Everglades food web (Browder et al., 1994). Calcareous periphyton, comprised of mostly blue-green algal species, is common in waters saturated with respect to $CaCO_3$ and precipitates calcite in the algal matrix (Lodge 1994; Browder et al. 1994). Organic flocculent (hereafter referred to as floc) and detritus are also common in the water column.

The northern reaches of Taylor Slough are surrounded by rocky pinelands where it transects the Atlantic Coastal Ridge, with interspersed tropical hardwood hammocks situated along its entire length (Thornberry-Ehrlich, 2008). Palma Vista Hammock, located approximately 1 km southwest of Taylor Slough's northern margin is one such hammock, and is dominated by tree species such as live oak (*Quercus virginiana*), gumbo limbo (*Bursera simaruba*), and wild tamarind (*Lysiloma latisiliquum*), and less common species including mahogany (*Swietenia mahogany*) and sugarberry (*Celtis laevigata*) (Gunderson, 1994). These trees create dense canopies that prevent the growth of herbaceous ground species, though epiphytes are relatively common (Gunderson, 1994). The Miami Limestone crops out throughout the hammock to form several epikarstic features, including a shallow collapse structure providing access to Palma Vista Cave, a small, horizontal passage intersecting the water table (Cressler, 1993; Florea and Yuellig, 2007). The cave entrance is water-filled, with the passage exposed only during the winter dry season. As such, the cave has only been surveyed to a length of 12 m and measured to a depth of 2.8 m below the land surface and is hypothesized to be larger in extent (Florea and Yuellig, 2007). Approximately 6 m northwest of the cave is Palma Vista Well, monitored by the United States Geological Survey (USGS). Though a physical connection has not been documented between the cave and well, water poured onto the land surface adjacent to the well could be heard dripping into the cave passage within 3 minutes when soils were dry, and 15 seconds when soils were saturated (Florea and McGee, 2010). Permeability of the Miami Limestone at this location ranges from $10^{-12.4}$ to $10^{-13.5}$ m^2 (Florea and McGee, 2010).

5.3. Methods

Water was sampled from Taylor Slough and Palma Vista Hammock at two USGS gauging stations, which are also included in the National Water Information System (NWIS) network (Figure 5.1). At Taylor Slough (NWIS station ID 252404080362401), water was collected for stable isotope analyses of organic and inorganic carbon (including DIC concentration and C/N ratios of organic matter) biweekly from April 2007 to January 2008. Hourly rainfall rate and water-levels were also recorded at this site. Waters were simultaneously collected at Palma Vista Hammock from both the cave and well, which share the same gauging station (NWIS station ID 252312080371901), with water-levels also recorded at the well.

Additional geochemical parameters (discussed below) were recorded at each site during sample collection. These data were reported and discussed in Florea and McGee (2010) and are utilized here to further elucidate factors affecting trends in carbon flux.

5.3.1. $\delta^{13}C_{DIC}$ and DIC Concentration

Eleven-mL water samples from each of the three sites were collected and fixed with $HgCl_2$ to prevent further biological production. Vials were covered with Parafilm to eliminate headspace and refrigerated. Analyses of $\delta^{13}C_{DIC}$ were carried out at the University of South Florida's Isotope Geochemistry lab using a Delta V gas-source isotope ratio mass spectrometer (IRMS) coupled to a Gasbench II peripheral combining the methods of Torres et al. (2005) and Assayag et al. (2006) and were standardized to

VPDB. The DIC concentration of each sample was estimated by standardizing the peak area of mass 44 for the first 10 replicate peaks for each sample using a $NaHCO_3$ solution with a known concentration of ~24 μg/L.

5.3.2. $\delta^{13}C_{DOC}$ and C/N Ratios

One-liter water samples from each of the three sites were filtered using 0.45-μm membranes and fixed with 30% HCl to prevent further bacterial production. Dissolved organic carbon was physically separated from the sample by evaporative concentration of the entire liter. This separation produced varying amounts of dry DOC, ranging from approximately 30 to 150 mg. For $\delta^{13}C_{DOC}$ analyses, at least 5 mg of DOC from each sample was measured into tin capsules and loaded into an auto-sampler. Analyses of $\delta^{13}C$, %C, and %N were carried out using a Costech elemental analyzer coupled to the IRMS and standardized with respect to two internal standards using the VPDB scale for isotopic composition. Percentages of C and N reported in analyses were used to calculate C/N ratios on a mass basis.

5.3.3. Geochemistry and Dissolution

Geochemical data consisting of pH, dissolved oxygen (DO), conductivity, and alkalinity were collected on site at the time of sample collection. Additional analyses of major ion concentrations of NO_3^-, Mg^{2+}, total Fe, Ca^{2+}, Na^+, K^+, Cl^-, and SO_4^{2-}, took place at the National Water Quality Lab in Denver, Colorado. Concentrations of Ca^{2+} combined with pH, temperature, and alkalinity data were used to calculate calcite saturation indices. Calculations of pCO_2 were made using pH and alkalinity data, using the dissociation constants K_1 and K_{CO2} at 25 °C (Stumm and Morgan, 1996).

To document active dissolution during the sampling period, micro-polished calcite tablets were deployed at Palma Vista Cave and Taylor Slough from July 18, 2007, to

January 17, 2008. Tablets were housed in microbial diffusion chambers designed and constructed by John Lisle at the United States Geological Survey in St. Petersburg, Florida, and launched in sets of four at the surface (0.1 m) and bottom of the water columns at both sites (cave floor and 0.7 m depth at the slough; Figure 5.2). Two diffusion chambers served as controls, investigating the impact of water alone on dissolution. This was done using a 0.2-μm diffusion membrane sealed with an o-ring that allowed water to flow through the chamber while isolating the tablet from microorganisms. The two remaining chambers were left open, allowing direct contact to the tablet by water and microorganisms.

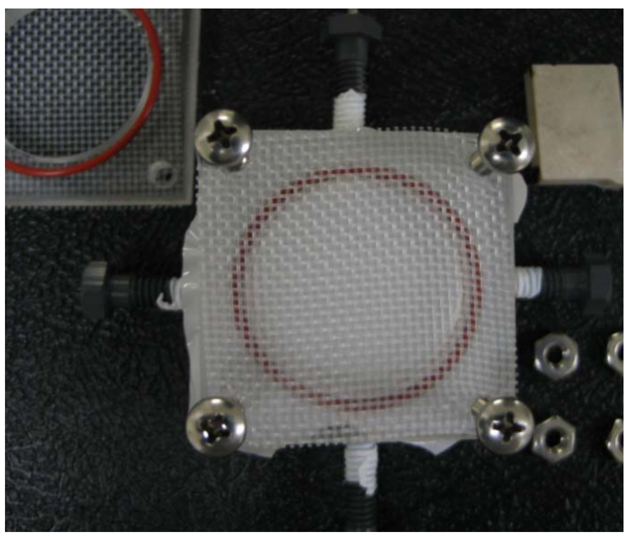


Figure 5.2. Plexiglass limestone tablet diffusion chambers. Control chamber (center) fitted with 0.2 μm Teflon membrane to restrict macroalgal and microorganism growth.

Prior to deployment, tablets were heated to 900 °C for four hours to remove organic matter and autoclaved for further sterilization. Tablets were also imaged using scanning-electron microscopy (SEM) at the University of South Florida-St. Petersburg to document the overall surface appearance and texture, which would be later compared to similar images taken following tablet retrieval. When tablets were retrieved, two processes were utilized to prepare samples for SEM analysis. Of the four tablets from each site, one each of the filtered and unfiltered tablets were cleaned using sodium dodecyl sulfate (SDS) solution to remove all biofilms and organic matter that might have accumulated during deployment, and sputter-coated with Au-Pd prior to SEM imagery. Biofilms and organic matter that might have accumulated on the remaining filtered and unfiltered tablets were preserved using the methods of Fratesi et al. (2004).

Several diffusion chambers and/or filters were damaged during the six-month such that only tablets recovered from the bottom waters of the cave could undergo both cleaning and fixation processes prior to SEM analyses. The remaining tablets were all cleaned with SDS prior to SEM analysis, with the exception of tablets deployed in the surface waters of Taylor Slough. At this location, it was assumed that biofilms and microalgae growth would be more abundant due to the tablets' exposure to more sunlight (compared to tablets deployed in the at 0.7 m depth). These tablets were therefore chosen to be fixed.

5.3.4. Statistical Analyses

Significance tests of results between sites were performed using the Mann-Whitney test for paired, non-parametric distributions, with results reported within the 95% confidence interval. Multivariate data reduction was performed using correlation matrices and principal component analyses (PCA) to identify processes contributing to the most geochemical variation. Because C/N data could not be measured for a total of four sampling dates, and because the variation in these values precluded the reliable use of means as data replacements, this parameter was omitted from multivariate analyses. Further, as $\delta^{13}C_{DOC}$ values were used to characterize the nature of vegetation inputs rather than dissolution processes, incorporation of this parameter was not necessary in multivariate analysis. Cross-correlation was used to determine the association of rainfall rates and water-levels at each site and to determine how water-levels at the slough and well co-vary. Water-levels were included in PCAs to elucidate any effects of concentration and dilution on certain geochemical parameters. Because water-level data had higher temporal resolution than geochemical data, downsampling of the former was utilized to reduce the dataset to 22 values for both the slough and well that were applied to their respective sites (with well data applied to the cave site). Principal components explaining geochemical relationships were chosen using the Kaiser-Guttman rule, eliminating all principal components with eigenvalues ≤1 (Guttman, 1954; Kaiser, 1960). Rainfall data collected at Taylor Slough was applied to multivariate analyses of all three sites, and Palma Vista Well water-level data were applied to both the cave and well analyses. All statistical analyses were performed using PAST, version 2.0.0 and R, version 2.10.1 (Hammer et al., 2001; R Development Core Team, 2009).

5.4. Results

Limestone tablets each lost between 1 and 4 mg of mass during deployment, evidence that dissolution was active at these sites for at least part of the deployment period (Figure 5.3-3.4). Each tablet also exhibited visible surface alteration: etching along crystalline boundaries was most commonly observed in tablets deployed at the cave (Figure 5.4a-d), with secondary precipitation of calcite (confirmed by EDX) most common on tablets in the cave bottom water (Figure 5.4c-d). This precipitation is consistent with the observation of floating calcite debris at the cave when tablets were retrieved in January 2007. Periphyton growth was observed on both tablets deployed in the surface waters of Taylor Slough, due to a breaking of the filtered tablet's filter (Figure 5.4e-f). The unfiltered tablet collected from the slough at 0.7 m illustrated considerable secondary calcite precipitation, obscuring the surface of the tablet itself (Figure 5.4g). The filtered tablet from the same location was not recovered. Due to the precipitation of calcite and periphyton biofilms on most samples regardless of cleaning or fixation, it is assumed that the loss in mass measured upon retrieval is likely underestimated.

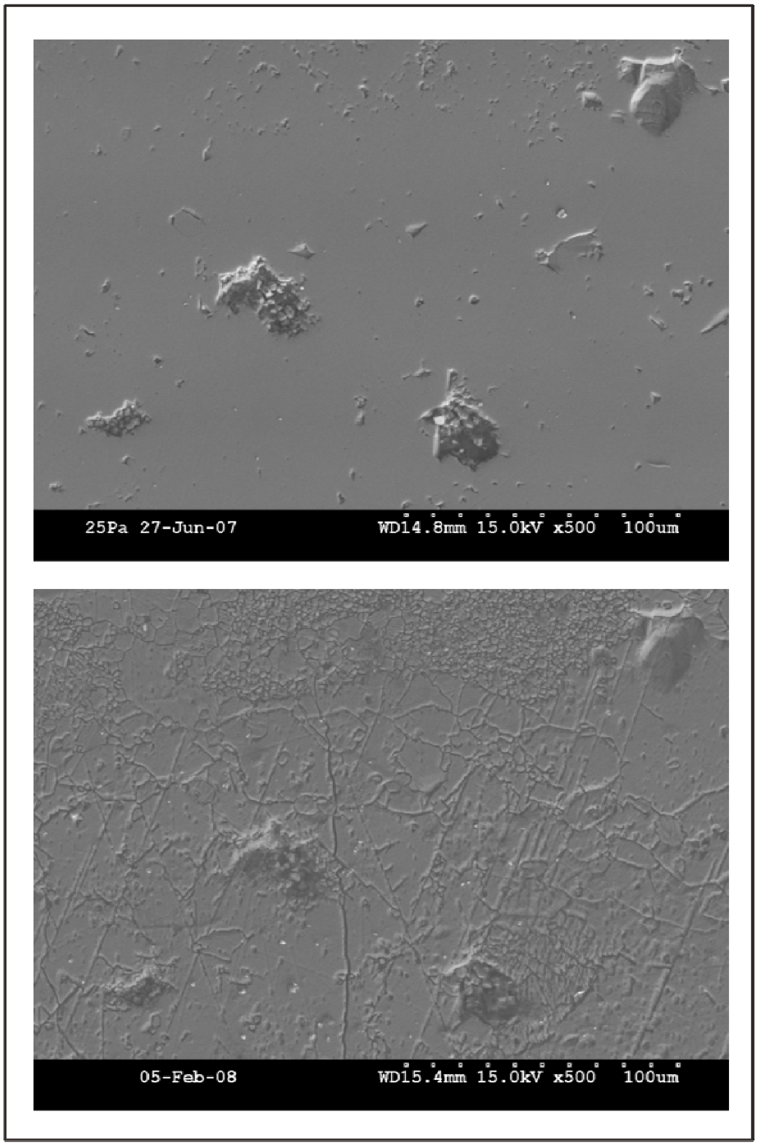
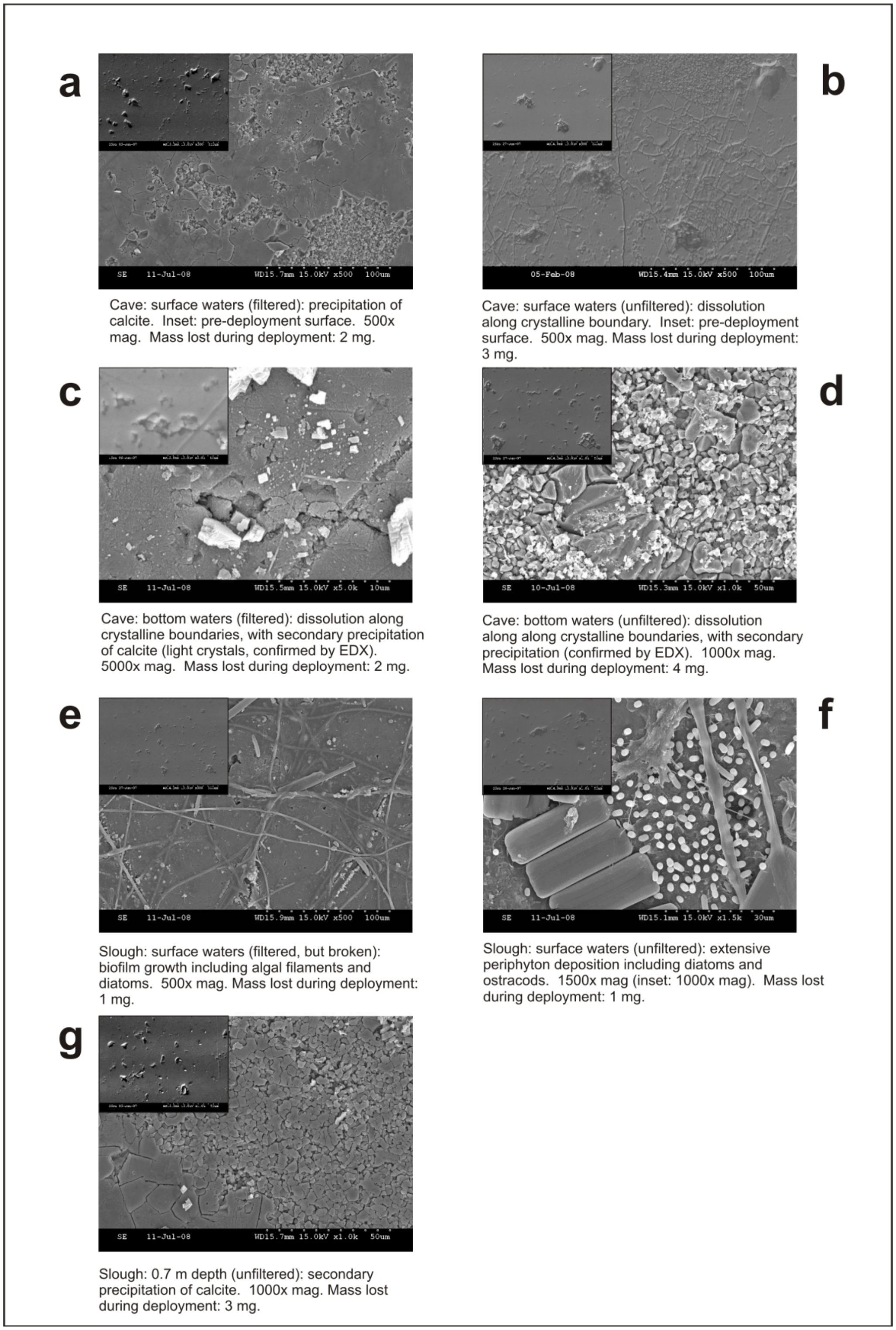


Figure 5.3. Example of limestone tablet alteration. Unfiltered tablet deployed in surface water of Palma Vista Cave and cleaned with SDS: a) micro-polished surface prior to deployment (representative of all samples pre-deployment); b) surface upon retrieval and cleaning, demonstrating etching along crystalline boundaries. 500x mag.



a: Cave: surface waters (filtered): precipitation of calcite. Inset: pre-deployment surface. 500x mag. Mass lost during deployment: 2 mg.

b: Cave: surface waters (unfiltered): dissolution along crystalline boundary. Inset: pre-deployment surface. 500x mag. Mass lost during deployment: 3 mg.

c: Cave: bottom waters (filtered): dissolution along crystalline boundaries, with secondary precipitation of calcite (light crystals, confirmed by EDX). 5000x mag. Mass lost during deployment: 2 mg.

d: Cave: bottom waters (unfiltered): dissolution along along crystalline boundaries, with secondary precipitation (confirmed by EDX). 1000x mag. Mass lost during deployment: 4 mg.

e: Slough: surface waters (filtered, but broken): biofilm growth including algal filaments and diatoms. 500x mag. Mass lost during deployment: 1 mg.

f: Slough: surface waters (unfiltered): extensive periphyton deposition including diatoms and ostracods. 1500x mag (inset: 1000x mag). Mass lost during deployment: 1 mg.

g: Slough: 0.7 m depth (unfiltered): secondary precipitation of calcite. 1000x mag. Mass lost during deployment: 3 mg.

Figure 5.4. Post-deployment SEM images of limestone tablets from Palma Vista Cave (a-d) and Taylor Slough (e-g). Pre-deployment images of identical locations on tablet insets.

All geochemical data are reported in Table 5.1 (including downsampled water-levels and rainfall for each sample date) and Figure 5.5 (illustrating raw water-level and rainfall values). Cross-correlation of raw rainfall and water-level data showed a rapid, positive response in water-levels at both sites to rainfall and that water-levels at both the well and slough strongly co-vary (Figure 5.6; values provided in Appendix VI).

Bulk PCA results are reported in Figure 5.7 (values are provided in Appendix VII) and site-specific PCA results and correlation matrices reported in Tables 5.2 and 5.3, with only those principal components complying with the Kaiser-Guttman rule given. Results of a bulk PCA for all sites showed that geochemical variation at Taylor Slough is distinct from the virtually identical Palma Vista Cave and Well (Figure 5.7). Because fluctuations in the major ions Na^+, Cl^-, and K^+ were largely unrelated to limestone dissolution processes in freshwater settings, they were omitted from further PCAs (Raddell & Katz, 1991; Panno et al., 2005; 2006). When these parameters were omitted, PCA results still showed a clear distinction between geochemical variations at Taylor Slough versus those at Palma Vista Cave and Well (Figure 5.7).

Table 5.1. Summary of geochemical data for Taylor Slough, and Palma Vista Cave Well, April 2007 through January 2008. Units for each parameter as follows: water-level (m), rainfall (cm/day), conductivity (µS/cm), alkalinity (mg/L), pCO$_2$ (atm), DO (mg/L), $\delta^{13}C_{DOC}$ (‰), $\delta^{13}C_{DIC}$ (‰), DIC concentration (µg/L) and all major ions (mg/L). Water-level and rainfall data are reported here as linear interpolations

	Date	WL	Rainfall	pH	Cond	Alk	pCO_2	DO	Calcite SI	$\delta^{13}C_{DOC}$	C/N	$\delta^{13}C_{DIC}$	DIC Conc	Ca^{2+}	Mg^{2+}	Fe	SO_4^{2-}	NO_3^-	Na^+	K^+	Cl^-
Taylor Slough	4/26/07	0.83	0.00	7.60	462	199	1.40E-04	2.30	0.37	-25.4	17.0	-5.0	24.3	75.4	4.5	172	0.18	0.014	17.8	0.9	26.1
	5/9/07	0.73	0.00	7.51	478	201	1.71E-04	2.36	0.29	-26.0	26.7	-4.9	31.6	79.5	4.7	179	0.31	0.001	18.0	0.8	26.8
	5/23/07	0.92	0.05	7.73	453	187	1.11E-04	1.72	0.49	-22.5	6.5	-4.4	31.9	71.0	4.5	231	0.39	0.001	17.6	1.1	25.9
	6/7/07	1.08	0.05	7.39	407	168	2.69E-04	2.37	0.08	-25.1	19.4	-1.7	12.8	63.4	3.7	115	1.15	0.004	13.7	0.8	21.1
	6/20/07	1.33	0.00	7.52	276	120	2.80E-04	3.55	0.01	-23.0	17.4	-0.3	5.4	48.9	2.0	51	0.82	0.015	7.0	0.4	9.8
	7/5/07	1.22	0.08	7.15	338	146	5.39E-04	4.07	-0.20	-24.4	19.9	5.2	9.7	58.9	2.5	138	0.14	0.018	10.0	0.6	14.8
	7/18/07	1.17	0.00	7.52	320	132	2.54E-04	2.67	0.06	-24.8	12.7	-1.1	13.3	47.6	3.4	151	0.07	0.004	13.6	1.1	20.4
	8/1/07	1.34	1.63	7.81	250	102	1.69E-04	4.25	0.18	-23.6	12.4	0.5	9.7	40.0	1.8	68	0.13	0.004	6.3	0.4	9.9
	8/17/07	1.22	0.00	7.71	300	123	1.76E-04	3.68	0.20	-24.1	16.2	-0.7	16.5	47.2	2.7	159	0.00	0.002	9.8	0.8	14.8
	8/29/07	0.99	0.00	7.30	454	185	3.01E-04	1.48	0.11	-25.5	15.5	-3.1	22.2	70.9	4.1	373	0.00	0.040	17.6	1.0	25.9
	9/12/07	1.07	0.25	7.42	406	167	2.53E-04	1.65	0.12	-25.2	14.0	-5.2	31.2	61.0	4.0	297	0.49	0.028	15.0	1.2	23.8
	9/26/07	1.10	4.22	7.15	352	151	5.21E-04	3.50	-0.29	-25.6	15.0	-3.5	10.5	52.6	3.2	245	0.03	0.019	12.3	1.0	18.6
	10/10/07	1.32	0.03	7.43	256	122	3.38E-04	3.05	-0.11	-23.2	15.0	0.0	5.8	45.0	1.8	58	0.70	0.004	5.5	0.5	8.0
	10/24/07	1.15	0.18	7.37	389	152	3.13E-04	2.56	-0.04	-25.4	*	-2.7	20.5	51.6	4.0	92	0.08	0.013	20.2	1.4	28.3
	11/6/07	1.21	0.25	7.45	389	157	2.52E-04	4.70	-0.01	-24.8	14.9	-1.9	12.4	51.9	3.9	60	0.12	0.011	16.1	1.2	25.2
	11/20/07	0.99	0.00	7.03	462	193	5.37E-04	1.89	-0.23	-25.2	12.6	-2.2	21.1	70.6	4.3	136	0.07	0.029	17.2	1.0	23.8
	12/6/07	0.80	0.00	7.19	463	193	3.72E-04	1.66	-0.09	-25.0	11.6	-1.8	20.0	73.7	4.3	385	0.00	0.030	15.6	0.7	22.0
	12/19/07	0.79	0.00	7.21	469	205	3.34E-04	2.90	-0.05	-25.5	21.9	-2.3	20.5	83.6	4.3	294	0.09	0.023	16.4	0.9	21.8
	1/3/08	0.65	0.00	7.59	466	203	1.41E-04	5.46	0.20	-25.6	12.3	-2.1	23.0	72.7	4.3	124	0.15	0.046	16.5	0.8	22.1
	1/17/08	0.56	0.00	7.10	472	203	4.35E-04	1.60	-0.17	-26.0	11.3	-1.1	20.7	72.9	4.7	129	0.13	0.024	18.1	1.4	24.3
	Avg	*1.02*	*0.34*	*7.41*	*393*	*165*	*2.95E-04*	*2.87*	*0.05*	*-24.8*	*15.4*	*-1.9*	*18.1*	*61.9*	*3.6*	*173*	*0.25*	*0.017*	*14.2*	*0.9*	*20.7*
	Stdev	*0.23*	*0.98*	*0.22*	*79*	*33*	*1.32E-04*	*1.14*	*0.20*	*1.0*	*4.5*	*2.4*	*8.1*	*13.1*	*1.0*	*101*	*0.31*	*0.013*	*4.3*	*0.3*	*6.1*
Palma Vista Cave	4/26/07	-0.12	0.00	7.69	381	190	1.19E-04	1.96	0.43	-27.1	12.9	-8.5	32.0	71.5	1.8	40	0.31	0.015	6.9	0.3	11.4

	Date	WL	Rainfall	pH	Cond	Alk	*p*CO_2	DO	Calcite SI	$\delta^{13}C_{DOC}$	C/N	$\delta^{13}C_{DIC}$	DIC Conc	Ca^{2+}	Mg^{2+}	Fe	SO_4^{2-}	NO_3^-	Na^+	K^+	Cl^-
Palma Vista Cave	5/9/07	-0.13	0.00	8.06	376	183	5.29E-05	1.40	0.77	-26.3	22.8	-7.3	23.7	71.4	1.8	68	0.26	0.029	6.9	0.3	11.5
cont'd	5/23/07	-0.11	0.05	8.14	385	174	4.64E-05	0.39	0.85	-26.1	*	-6.9	18.6	72.9	1.8	109	0.40	0.006	7.1	0.3	11.3
	6/7/07	-0.09	0.05	7.39	372	166	2.73E-04	0.30	0.11	-27.5	23.8	-5.6	6.9	72.1	1.2	65	1.24	0.403	7.6	0.5	14.5
	6/20/07	-0.08	0.00	7.31	367	173	3.14E-04	0.35	0.02	-27.9	22.5	-3.9	4.6	67.1	1.8	63	1.22	0.019	8.0	0.6	13.3
	7/5/07	-0.09	0.08	7.10	390	167	5.28E-04	0.33	-0.15	-27.9	20.3	-7.8	16.8	74.2	1.8	82	0.67	0.072	7.9	0.6	13.3
	7/18/07	-0.08	0.00	7.41	374	157	2.75E-04	0.72	0.11	-27.6	17.2	-7.1	15.1	67.8	1.7	52	0.71	0.001	7.2	0.6	13.1
	8/1/07	-0.08	1.63	7.55	375	163	1.92E-04	0.50	0.23	-28.0	20.3	-3.9	14.7	64.2	1.7	55	0.89	0.021	7.1	0.7	13.2
	8/17/07	-0.08	0.00	7.51	365	163	2.11E-04	0.68	0.24	-27.6	19.2	-7.5	14.6	72.3	1.7	156	0.50	0.005	7.4	0.5	13.5
	8/29/07	-0.11	0.00	7.28	408	193	3.02E-04	0.38	0.12	-22.8	27.7	-5.7	15.1	78.7	1.8	282	0.09	0.216	7.2	0.4	12.8
	9/12/07	-0.09	0.25	7.30	394	178	3.13E-04	0.58	0.07	-27.7	18.0	-7.5	15.0	72.8	1.6	83	0.39	0.014	7.1	0.5	13.3
	9/26/07	-0.08	4.22	7.24	394	181	3.53E-04	0.51	0.00	-27.7	19.5	-7.9	15.0	70.0	1.6	140	0.87	0.047	7.9	0.4	14.0
	10/10/07	-0.09	0.03	7.24	416	199	3.22E-04	0.65	0.08	-27.6	18.5	-8.0	15.3	76.9	1.7	144	0.38	0.389	7.0	0.4	12.3
	10/24/07	-0.10	0.18	7.24	425	192	3.33E-04	0.41	0.06	-27.5	26.6	-8.1	18.0	77.2	1.7	185	0.15	0.001	7.4	0.4	12.9
	11/6/07	-0.09	0.25	7.05	428	208	4.76E-04	0.30	-0.11	-26.8	*	-8.3	21.0	76.3	1.8	200	0.14	0.004	6.8	0.4	13.0
	11/20/07	-0.11	0.00	7.17	432	206	3.65E-04	0.53	-0.01	-27.3	14.8	-6.4	21.0	78.4	1.8	115	0.13	0.007	7.4	0.3	13.4
	12/6/07	-0.12	0.00	7.26	426	193	3.16E-04	0.85	0.06	-27.3	15.6	-5.0	18.2	79.9	1.8	65	0.62	0.024	7.2	0.4	13.2
	12/19/07	-0.13	0.00	7.19	423	197	3.64E-04	1.32	0.00	-27.0	22.9	-5.7	17.9	82.3	1.8	52	1.02	0.037	7.2	0.4	13.3
	1/3/08	-0.12	0.00	7.15	410	207	3.80E-04	2.07	-0.08	-27.1	15.5	-5.7	18.0	75.5	1.8	31	1.26	0.046	7.3	0.3	12.9
	1/17/08	-0.15	0.00	7.03	405	183	5.66E-04	1.82	-0.24	-26.7	17.1	-5.4	18.1	75.5	1.8	35	1.19	0.057	7.4	0.4	13.0
	Avg	*2.64*	*0.34*	*7.37*	*397*	*184*	*3.05E-04*	*0.80*	*0.13*	*-27.1*	*19.7*	*-6.6*	*17.0*	*73.9*	*1.7*	*101*	*0.62*	*0.071*	*7.3*	*0.4*	*13.0*
	Stdev	*0.02*	*0.98*	*0.30*	*23*	*16*	*1.36E-04*	*0.58*	*0.28*	*1.1*	*4.1*	*1.4*	*5.6*	*4.6*	*0.1*	*66*	*0.41*	*0.121*	*0.3*	*0.1*	*0.8*
Palma Vista Well	4/26/07	-0.12	0.00	7.47	377	176	2.14E-04	2.08	0.19	-27.1	15.1	-8.4	29.0	71.4	1.9	30	0.37	0.021	7.0	0.3	11.4
	5/9/07	-0.13	0.00	7.80	377	170	1.04E-04	1.35	0.50	-26.4	23.5	-7.9	26.2	71.4	1.8	82	0.27	0.035	7.0	0.4	11.5
	5/23/07	-0.11	0.05	7.66	347	177	1.38E-04	1.71	0.39	-26.5	*	-7.6	24.0	71.5	1.8	342	0.43	0.002	7.0	0.3	11.2
	6/7/07	-0.09	0.05	7.30	389	182	3.06E-04	0.37	0.08	-26.4	10.5	-4.4	6.5	76.9	1.8	214	0.38	0.157	7.1	0.3	11.9
	6/20/07	-0.08	0.00	7.33	345	188	2.76E-04	1.05	0.13	-26.8	21.7	-4.9	7.0	78.3	1.8	262	0.31	0.000	7.5	0.3	11.8

	Date	WL	Rainfall	pH	Cond	Alk	pCO_2	DO	Calcite SI	$\delta^{13}C_{DOC}$	C/N	$\delta^{13}C_{DIC}$	DIC Conc	Ca^{2+}	Mg^{2+}	Fe	SO_4^{2-}	NO_3^-	Na^+	K^+	Cl^-
Palma Vista Well	7/5/07	-0.09	0.08	7.07	346	193	4.91E-04	1.08	-0.10	-27.0	19.9	-5.3	16.8	78.8	1.8	248	0.21	0.202	7.1	0.3	11.8
cont'd	7/18/07	-0.08	0.00	7.54	340	191	1.68E-04	1.58	0.36	-26.8	8.4	-0.3	9.7	78.7	1.8	263	0.15	0.028	6.9	0.3	11.8
	8/1/07	-0.08	1.63	7.42	330	191	2.21E-04	1.83	0.24	-26.7	9.0	-6.0	10.7	76.5	1.8	274	0.13	0.165	7.0	0.3	12.2
	8/17/07	-0.08	0.00	7.59	309	199	1.43E-04	1.85	0.44	-26.6	9.7	-7.2	17.1	80.0	1.8	307	0.11	0.007	7.0	0.3	12.1
	8/29/07	-0.11	0.00	7.11	334	197	4.38E-04	1.98	-0.04	-26.4	9.7	-4.5	17.1	79.5	1.8	290	0.00	0.101	7.1	0.3	12.3
	9/12/07	-0.09	0.25	7.25	353	198	3.15E-04	1.36	0.09	-26.6	16.0	-7.3	19.1	77.2	1.7	355	0.09	0.019	6.7	0.3	12.3
	9/26/07	-0.08	4.22	7.15	374	197	3.99E-04	1.87	-0.02	-26.4	11.0	-7.3	21.2	77.4	1.7	323	0.03	0.004	7.2	0.3	12.1
	10/10/07	-0.09	0.03	6.88	360	199	7.36E-04	1.47	-0.28	-23.9	11.8	-6.6	15.4	77.3	1.7	311	0.21	0.004	6.7	0.3	12.2
	10/24/07	-0.10	0.18	6.98	387	204	5.70E-04	1.49	-0.17	-26.8	18.1	-8.1	18.0	76.6	1.7	322	0.08	0.023	7.2	0.4	12.8
	11/6/07	-0.09	0.25	6.89	400	208	6.88E-04	1.23	-0.27	-27.3	*	-8.6	20.3	75.7	1.8	240	0.13	0.010	6.7	0.3	13.1
	11/20/07	-0.11	0.00	6.93	437	193	6.76E-04	1.31	-0.25	*	*	-5.3	17.4	78.4	1.8	204	0.05	0.041	7.7	0.3	13.9
	12/6/07	-0.12	0.00	6.84	437	201	7.99E-04	1.36	-0.32	-26.9	15.9	-6.2	20.4	80.9	1.9	101	0.35	0.019	7.5	0.3	13.5
	12/19/07	-0.13	0.00	6.84	435	191	8.41E-04	0.87	-0.33	-26.9	18.3	-7.2	25.5	84.4	1.8	86	0.95	0.080	7.4	0.3	13.2
	1/3/08	-0.12	0.00	6.92	402	201	6.64E-04	0.84	-0.29	-26.1	15.5	-5.5	20.2	75.3	1.8	152	1.05	0.036	7.3	0.3	12.8
	1/17/08	-0.15	0.00	6.86	397	191	8.03E-04	0.76	-0.31	-26.5	18.0	-6.7	22.3	76.0	1.8	128	0.75	0.048	7.4	0.4	12.7
	Avg	*2.64*	*0.34*	*7.19*	*374*	*192*	*4.49E-04*	*1.37*	*0.00*	*-26.5*	*14.8*	*-6.3*	*18.2*	*77.1*	*1.8*	*227*	*0.30*	*0.050*	*7.1*	*0.3*	*12.3*
	Stdev	*0.02*	*0.98*	*0.31*	*37*	*10*	*2.54E-04*	*0.45*	*0.28*	*0.7*	*4.7*	*1.9*	*6.1*	*3.2*	*0.1*	*98*	*0.30*	*0.060*	*0.3*	*0.0*	*0.7*

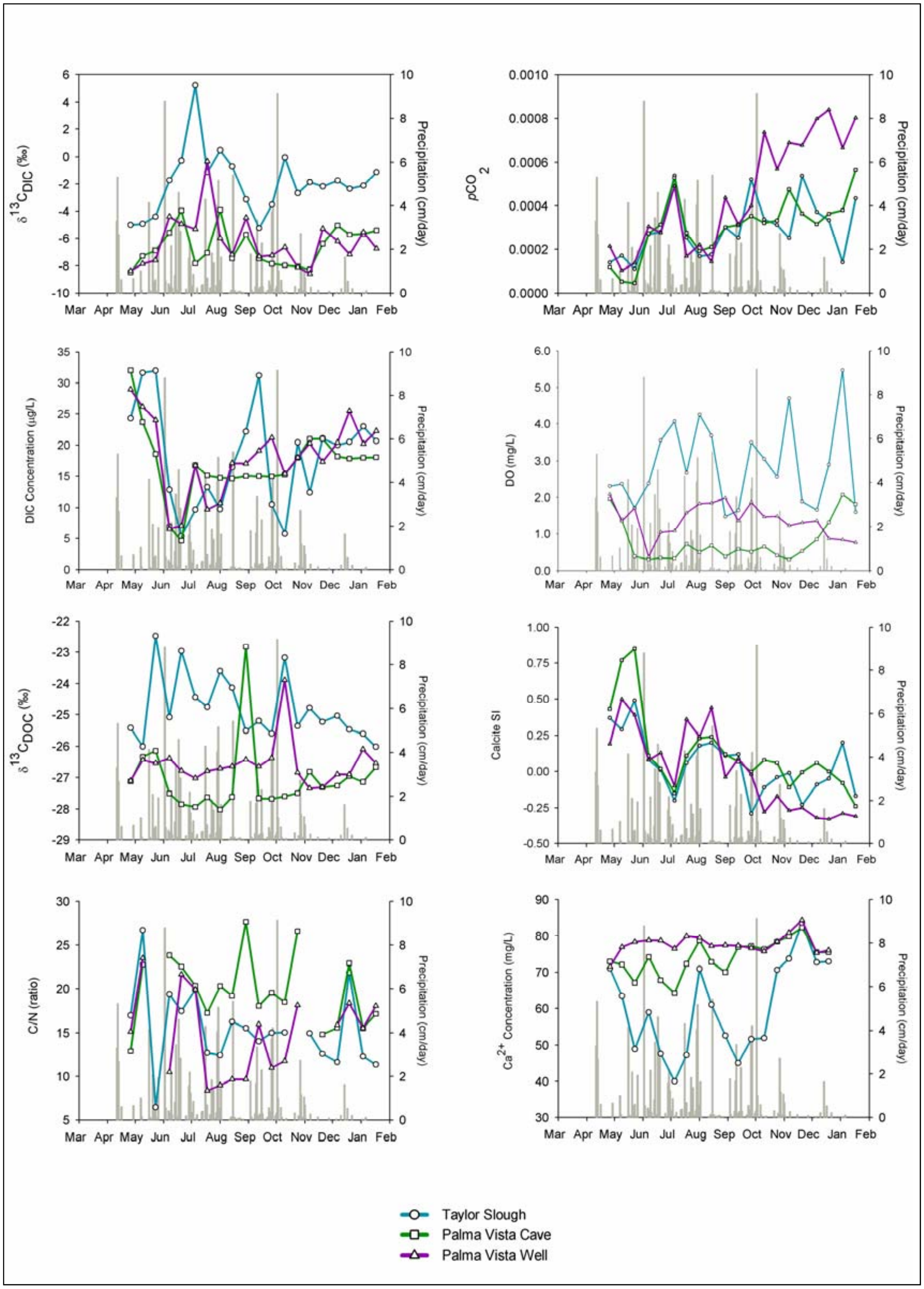


Figure 5.5. Geochemical trends for Taylor Slough, Palma Vista Cave and Palma Vista Well (*continued on following page*).

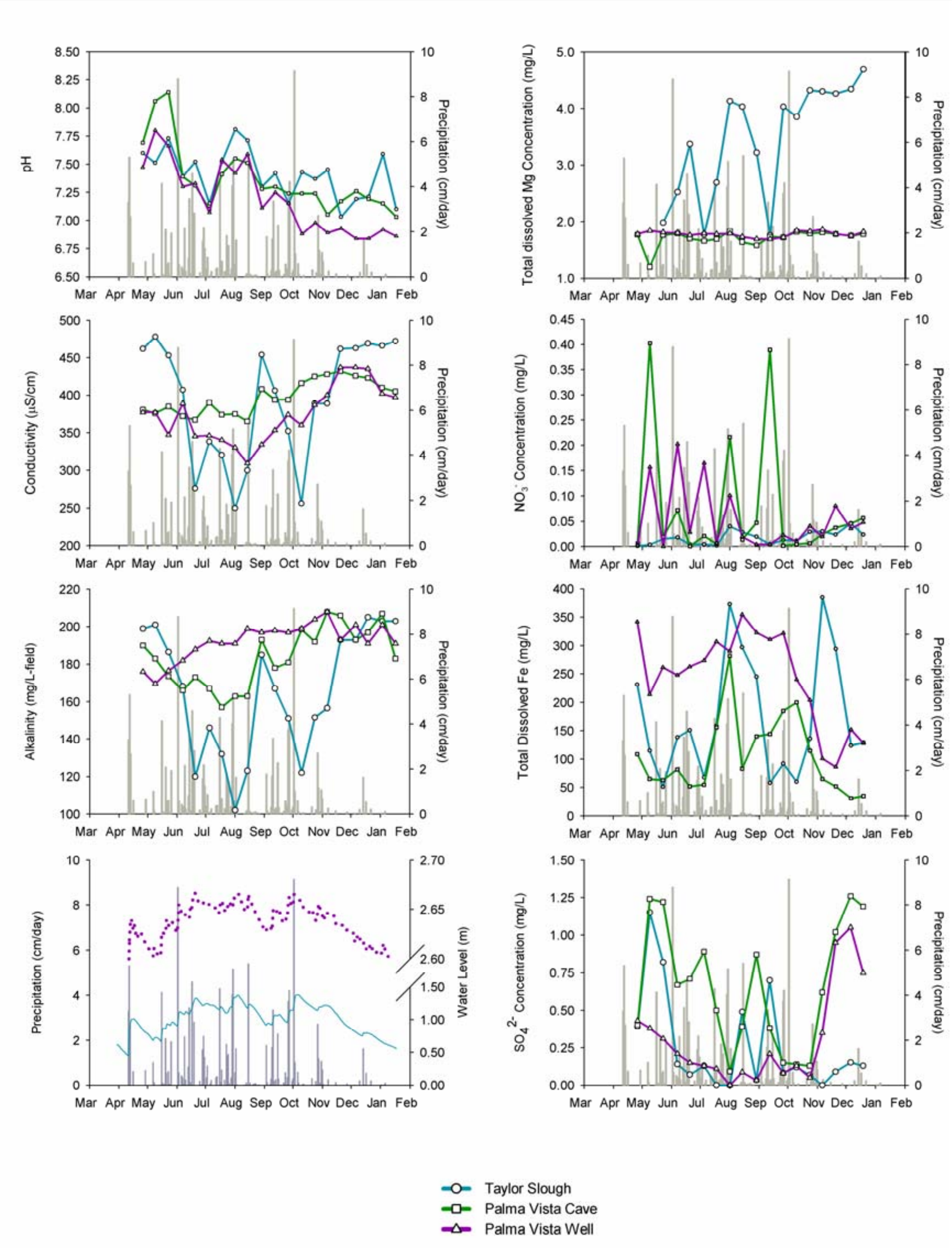


Figure 5.5. Geochemical trends for Taylor Slough, Palma Vista Cave, and Palma Vista Well (*continued from previous page*).

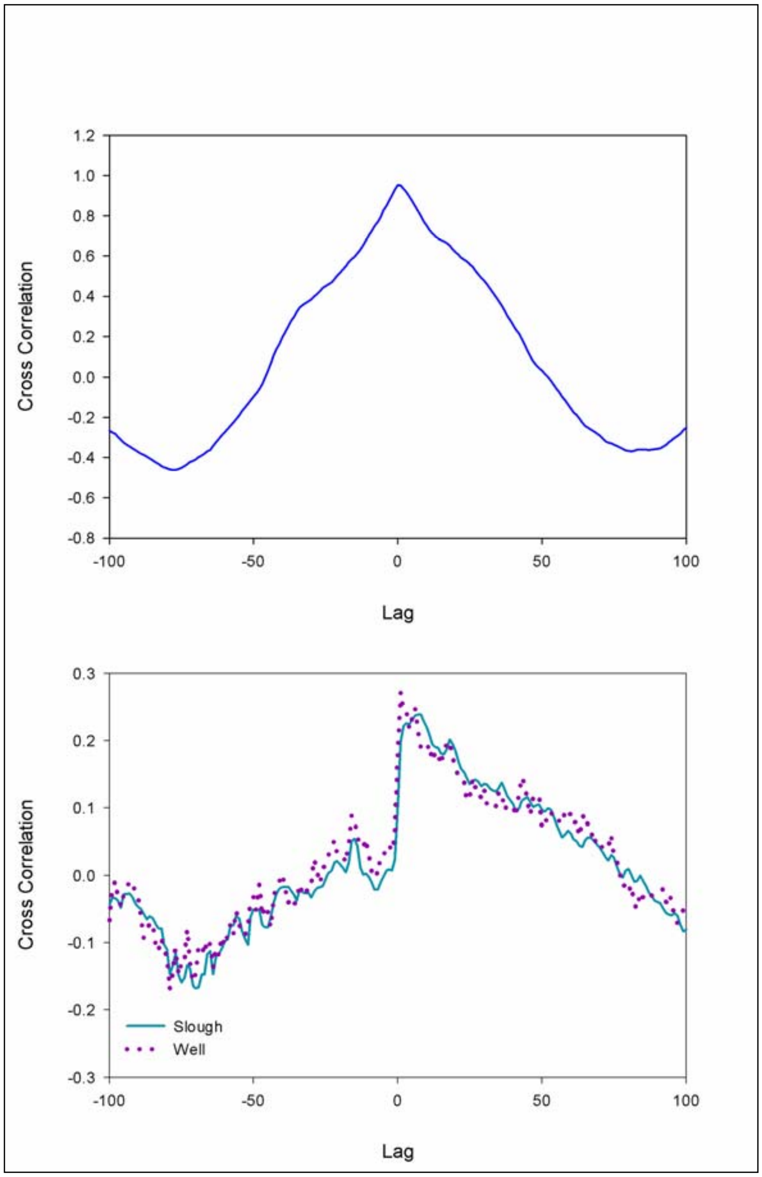


Figure 5.6. Cross correlogram of water-levels and rainfall at Taylor Slough and Palma Vista Well. Top: cross correlogram of slough and well water-levels. Bottom: cross correlogram of water-levels at each site with rainfall.

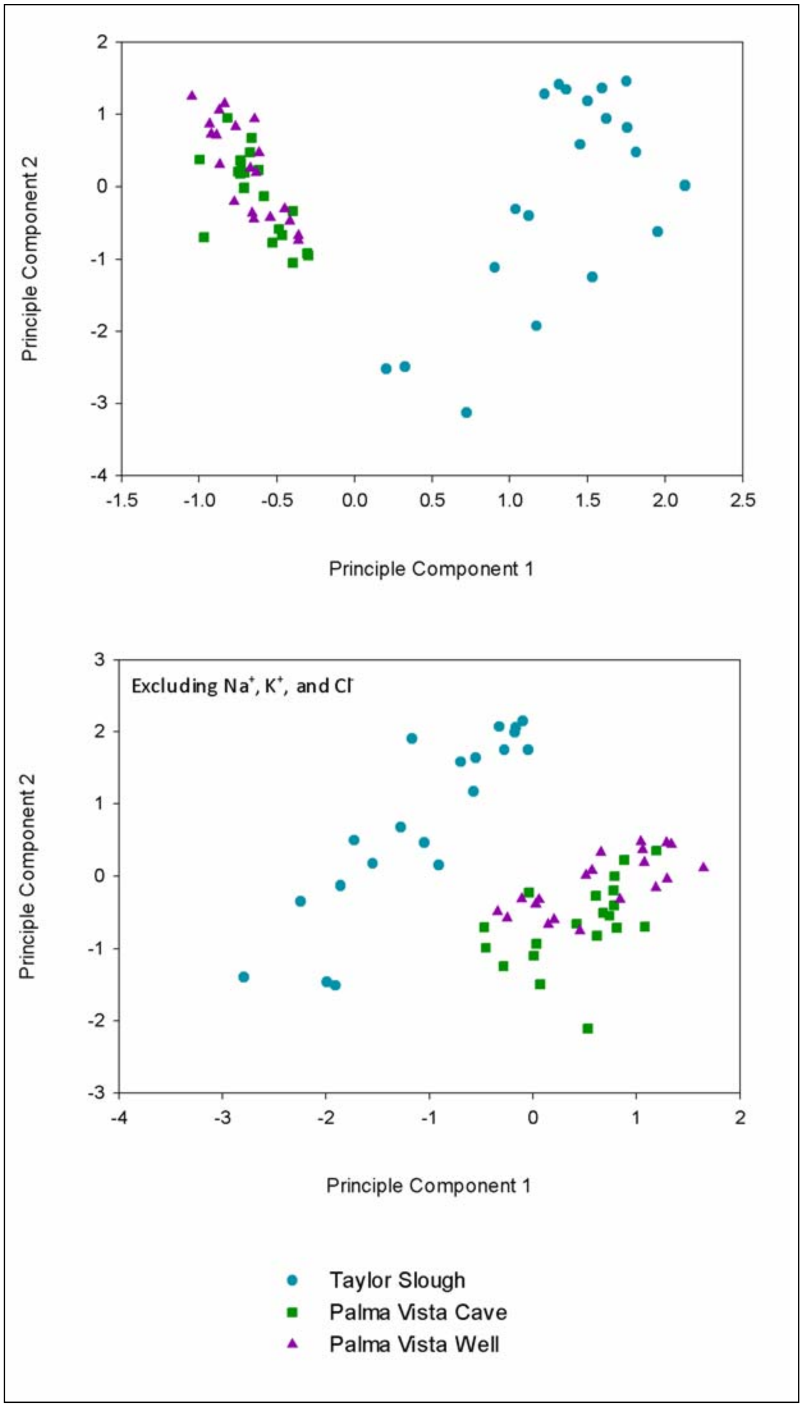


Figure 5.7. Bulk PCA results for Taylor Slough and Palma Vista Hammock. Top: PCA including all geochemical parameters. Bottom: PCA excluding Na^+, K^+ and Cl^-.

Table 5.2. PCA results for Taylor Slough, Palma Vista Cave and Palma Vista Well

Taylor Slough

	PCA 1	PCA 2	PCA 3	Component No.	Eigenvalue	Total % Var.
WL	-0.89	0.02	-0.18	1	6.75	48.22
pH	-0.31	0.92	0.20	2	3.34	23.89
Cond	0.97	-0.04	0.05	3	1.23	8.79
Alk	0.96	-0.08	0.06	4	0.99	7.08
pCO_2	-0.05	-0.96	-0.18	5	0.62	4.39
DO	-0.55	0.05	0.72	6	0.45	3.25
Calcite SI	0.22	0.94	0.08	7	0.23	1.67
$\delta^{13}C_{DIC}$	-0.65	-0.45	0.23	8	0.16	1.13
DIC Conc	0.85	0.38	-0.03	9	0.11	0.76
Ca^{2+}	0.92	-0.05	0.02	10	0.08	0.54
Mg^{2+}	0.95	0.05	0.02	11	0.03	0.18
NO_3^-	0.50	-0.49	0.39	12	0.01	0.04
Fe	0.65	-0.15	-0.10	13	0.00	0.03
SO_4^{2-}	-0.28	0.27	-0.62	14	2.55E-03	1.82E-02

Palma Vista Cave

	PCA 1	PCA 2	PCA 3	PCA 4	Component No.	Eigenvalue	Total % Var.
WL	-0.53	-0.38	-0.59	-0.32	1	4.31	30.78
pH	-0.58	0.77	-0.02	0.21	2	3.56	25.46
Cond	0.92	-0.10	-0.13	0.10	3	2.54	18.15
Alk	0.87	0.12	-0.01	0.21	4	1.29	9.24
pCO_2	0.57	-0.71	0.09	-0.27	5	0.93	6.61
DO	0.29	0.36	0.78	0.08	6	0.39	2.78
Calcite SI	-0.47	0.82	-0.10	0.26	7	0.35	2.52
$\delta^{13}C_{DIC}$	-0.23	-0.39	0.50	0.17	8	0.22	1.59
DIC Conc	0.47	0.77	0.12	-0.13	9	0.18	1.30
Ca^{2+}	0.85	-0.02	-0.08	0.36	10	0.11	0.81
Mg^{2+}	0.53	0.52	0.08	-0.40	11	0.06	0.42
NO_3^-	-0.08	-0.39	-0.23	0.78	12	0.04	0.29
Fe	0.28	-0.02	-0.85	0.07	13	0.01	0.05
SO_4^{2-}	-0.32	-0.57	0.70	0.07	14	6.97E-05	4.98E-04

Palma Vista Well

	PCA 1	PCA 2	PCA 3	Component No.	Eigenvalue	Total % Var.
WL	0.65	0.63	0.03	1	4.96	35.41
pH	0.84	-0.48	0.11	2	3.38	24.13
Cond	-0.86	-0.17	0.00	3	2.14	15.28
Alk	-0.33	0.80	-0.33	4	0.91	6.49
pCO_2	-0.92	0.32	-0.12	5	0.72	5.18
DO	0.57	-0.05	-0.56	6	0.66	4.73
Calcite SI	0.89	-0.39	0.11	7	0.42	2.97
$\delta^{13}C_{DIC}$	0.21	0.37	0.68	8	0.30	2.12
DIC Conc	-0.35	-0.63	-0.58	9	0.21	1.53
Ca^{2+}	-0.33	0.65	0.24	10	0.13	0.90
Mg^{2+}	-0.19	-0.54	0.47	11	0.09	0.64
NO_3^-	0.00	0.12	0.68	12	0.07	0.48
Fe	0.56	0.66	-0.26	13	0.02	0.13
SO_4^{2-}	-0.62	-0.35	0.22	14	3.52E-04	2.52E-03

Table 5.3. Correlation matrices for Taylor Slough, Palma Vista Cave and Palma Vista Well

Taylor Slough

	WL	pH	Cond	Alk.	pCO_2	DO	Calcite SI	$\delta^{13}C_{DIC}$	DIC Conc	Ca^{2+}	Mg^{2+}	NO_3^-	Fe	SO_4^{2-}	Na^+	K^+
WL																
pH	0.27															
Cond	-0.97	-0.34														
Alk	-0.97	-0.30	0.98													
pCO_2	0.07	-0.91	-0.01	-0.05												
DO	0.53	0.36	-0.51	-0.45	-0.15											
SI	-0.14	0.84	0.10	0.10	-0.95	-0.03										
$\delta^{13}C_{DIC}$	0.59	0.03	-0.56	-0.56	0.30	0.51	-0.34									
DIC Conc	-0.78	0.09	0.75	0.74	-0.42	-0.60	0.53	-0.79								
Ca^{2+}	-0.92	-0.28	0.95	0.95	-0.03	-0.50	0.14	-0.58	0.70							
Mg^{2+}	-0.93	-0.14	0.93	0.91	-0.20	-0.58	0.26	-0.65	0.86	0.87						
NO_3^-	-0.38	-0.57	0.37	0.39	0.46	-0.23	-0.42	-0.14	0.14	0.35	0.24					
Fe	-0.53	-0.23	0.48	0.45	0.04	-0.57	0.12	-0.59	0.57	0.57	0.43	0.29				
SO_4^{2-}	0.07	0.32	-0.07	-0.05	-0.33	0.07	0.31	0.01	-0.01	0.01	-0.05	-0.32	-0.42			
Na^+	-0.77	-0.21	0.79	0.77	-0.13	-0.56	0.19	-0.66	0.78	0.70	0.89	0.19	0.29	-0.12		
K^+	-0.37	-0.24	0.33	0.35	0.00	-0.39	-0.06	-0.55	0.49	0.19	0.49	0.14	0.20	-0.25	0.65	
Cl^-	-0.64	-0.06	0.67	0.64	-0.28	-0.54	0.33	-0.77	0.80	0.60	0.81	0.08	0.33	-0.09	0.94	0.68

Palma Vista Cave

	WL	pH	Cond	Alk	pCO_2	DO	Calcite SI	$\delta^{13}C_{DIC}$	DIC Conc	Ca^{2+}	Mg^{2+}	NO_3^-	Fe	SO_4^{2-}	Na^+	K^+
WL																
pH	0.21															
Cond	-0.47	-0.69														
Alk	-0.57	-0.57	0.87													
$pCO2$	-0.16	-0.99	0.64	0.50												
DO	-0.54	0.04	0.08	0.22	-0.02											
SI	0.10	0.95	-0.54	-0.40	-0.98	0.07										
$\delta^{13}C_{DIC}$	-0.11	0.06	-0.18	-0.20	-0.05	0.03	-0.04									
DIC Conc	-0.73	-0.14	0.54	0.58	0.11	0.40	-0.05	-0.32								
Ca^{2+}	-0.57	-0.58	0.84	0.74	0.50	0.07	-0.36	-0.05	0.40							
Mg^{2+}	-0.65	-0.12	0.36	0.51	0.09	0.20	-0.03	-0.11	0.75	0.40						
NO_3^-	-0.23	-0.26	0.01	0.12	0.22	-0.01	-0.19	0.28	-0.23	0.14	0.01					
Fe	0.32	-0.05	0.27	0.17	-0.01	-0.58	0.10	-0.47	-0.08	0.29	0.00	-0.14				
SO_4^{2-}	0.13	-0.08	-0.41	-0.38	0.14	0.15	-0.26	0.57	-0.48	-0.36	-0.49	0.34	-0.70			
Na^+	0.23	-0.32	-0.12	-0.25	0.38	-0.29	-0.45	0.34	-0.46	-0.03	-0.33	0.26	-0.01	0.44		
K^+	0.76	0.13	-0.50	-0.70	-0.07	-0.42	0.01	0.14	-0.81	-0.45	-0.60	0.04	0.05	0.36	0.29	
Cl^-	0.48	-0.22	-0.17	-0.33	0.26	-0.29	-0.36	0.23	-0.60	-0.14	-0.54	0.09	0.03	0.40	0.63	0.53

Palma Vista Well

	WL	pH	Cond	Alk	pCO_2	DO	Calcite SI	$\delta^{13}C_{DIC}$	DIC Conc.	Ca^{2+}	Mg^{2+}	NO_3^-	Fe	SO_4^{2-}	Na^+	K^+
WL																
pH	0.38															
Cond	-0.65	-0.66														
Alk	0.15	-0.57	0.20													
pCO_2	-0.38	-1.00	0.66	0.54												
DO	0.30	0.46	-0.55	0.03	-0.47											
SI	0.44	0.99	-0.71	-0.52	-0.98	0.49										
$\delta^{13}C_{DIC}$	0.25	-0.06	-0.19	-0.12	0.06	-0.26	-0.08									
DIC Conc	-0.70	-0.10	0.47	-0.12	0.11	0.10	-0.14	-0.73								
Ca^{2+}	0.25	-0.32	-0.11	0.29	0.32	0.02	-0.28	0.50	-0.36							
Mg^{2+}	-0.37	0.01	0.33	-0.35	-0.02	-0.24	0.00	0.02	0.17	-0.14						
NO_3^-	-0.28	-0.17	0.12	-0.18	0.19	-0.29	-0.20	0.42	-0.15	0.11	0.26					
Fe	0.64	0.24	-0.58	0.31	-0.24	0.43	0.29	-0.04	-0.37	0.11	-0.73	-0.41				
SO_4^{2-}	-0.52	-0.14	0.37	-0.39	0.13	-0.56	-0.23	0.02	0.30	-0.28	0.28	0.08	-0.56			
Na^+	-0.36	-0.38	0.49	-0.04	0.39	-0.43	-0.44	0.32	0.08	0.33	0.21	0.20	-0.40	0.22		
K^+	-0.66	-0.07	0.43	-0.21	0.11	-0.09	-0.12	-0.58	0.72	-0.50	0.07	0.14	-0.26	0.17	0.15	
Cl^-	-0.28	-0.82	0.62	0.69	0.82	-0.31	-0.79	0.03	0.06	0.34	-0.02	0.20	-0.15	-0.14	0.37	-0.01

5.4.1. Taylor Slough

Of the three sites, $\delta^{13}C_{DOC}$ values at the slough were significantly higher (p <0.001 when compared to the cave and well), averaging -24.8 ± 1.0‰ (Table 5.1, Figure 5.5). These values loosely tracked water-level, were highest through the summer months, and are evidence of a C_3-dominated vegetative environment. Values of C/N averaged 15.4 ± 4.5, and were significantly lower than the cave (p = 0.0025), but not significantly different from the well (p = 0.80). Like $\delta^{13}C_{DOC}$ values, greater C/N values occurred during wet summer months; however, there was little overall seasonal trend in the fluctuation of C/N over the time period analyzed (Figure 5.5).

Values of $\delta^{13}C_{DIC}$ values were also significantly higher at the slough (p <0.01, when compared to the cave and well) and were more ^{13}C-enriched by 3 to 4‰ for most of the year, averaging -1.9 ± 2.4‰ (Table 5.1, Figure 5.5). At the same time, DIC concentration was significantly different from the cave and well (p <0.01 for each) and showed a marked decrease in early summer before increasing through the fall. Unlike the cave and well, however, DIC concentrations abruptly fell and continued to fluctuate through the fall before becoming relatively more stable during the winter. Both $\delta^{13}C_{DIC}$ values and DIC concentration showed a strong, negative correlation to one another (r = -0.78; Table 5.3).

Whereas Ca^{2+} concentrations were significantly lower at the slough compared to the cave or well (p <0.01 for both comparisons), Mg^{2+} was significantly higher (p <0.001 for both; Table 5.1, Figure 5.5). Dissolved oxygen levels were significantly higher than the cave and well (p <0.001 for both; Figure 5.5). Iron and SO_4^{2-} were significantly higher and lower than the cave, respectively (p <0.01 for both), though not significantly different from the well (p = 0.20 and 0.49, respectively; Figure 5.5). Differences in NO_3^- concentrations, pH, conductivity, alkalinity, pCO_2, and calcite SI between the slough and the cave and well were not significantly different ($p \geq 0.05$; Figure 5.5).

Individual PCA of the slough show that the first three principal components accounted for just over 80% of its total geochemical variation (Table 5.2). Rotated eigenvectors (loadings) in PC1 were highest for water-level, conductivity, alkalinity, DIC concentration, Ca^{2+}, and Mg^{2+}, and to a lesser degree, $\delta^{13}C_{DIC}$, DO, NO NO_3^-, and Fe. Variation in PC2 was associated with pH, pCO_2, and calcite SI, and to a lesser degree, NO_3^- and $\delta^{13}C_{DIC}$. Few parameters dominated in PC3, with the exception of DO and SO_4^{2-}, though they were not correlated to one another ($r = 0.07$, Table 5.3). Though moderate to strong correlations existed between parameters with high loadings within PC1 and PC2, these parameters were weakly correlated to one another.

5.4.2. Palma Vista Cave

With the exception of a sharp increase on August 29, $\delta^{13}C_{DOC}$ values at Palma Vista Cave varied little during the time period analyzed, averaging -27.1 ± 1.1‰, and appear to be most negative during the wet season (Table 5.1 and Figure 5.5). Like Taylor Slough, these values are evidence of a C_3-dominated vegetative regime, though C/N values were significantly higher than the slough ($p < 0.01$), 19.75 ± 4.1. Despite the geochemical overlap between the well and cave exhibited by bulk PCA (Figure 5.7), $\delta^{13}C_{DOC}$ and C/N were significantly lower and higher at the cave than the well, respectively ($p = 0.0013$ and 0.0068, respectively).

Values of $\delta^{13}C_{DIC}$ are typical of groundwater values (Clark and Fritz, 1997), averaging -6.6 ± 1.4‰ through the year (Table 5.1, Figure 5.5), though seasonal trends are not apparent. Concentrations of DIC follow the same general trend as Taylor Slough but vary less from July through the end of the sampling period and average 17.0 ± 5.6 µg/L (Table 5.1, Figure 5.5). Like the slough, DIC concentration falls sharply at the onset of the wet season and has a strong inverse correlation to water-level (Figure 5.5,

Table 5.3). There was no significant difference between $\delta^{13}C_{DIC}$ and DIC concentration between the cave and well (p <0.1 for both).

Differences in many geochemical parameters were minimal between the cave and the well, supported by bulk PCA; however, conductivity, DO, and concentrations of Ca^{2+}, SO_4^{2-}, and Fe were significantly different. While conductivity and SO_4^{2-} concentrations were significantly higher (p = 0.032 and 0.013, respectively), DO, Ca^{2+}, and Fe were significantly lower (p = 0.0062, 0.033, and 0.00051, respectively).

Results of an individual PCA at Palma Vista Cave demonstrate that the first four principal components account for nearly 84% of the total variation (Table 5.2). In PC1, conductivity, alkalinity, and Ca^{2+} concentrations are the most important geochemical parameters, followed by water-level, pH, and pCO_2. Conductivity, alkalinity, and Ca^{2+} were positively correlated to one another, with r-values exceeding 0.70 (Table 5.3). Unlike the slough, water-level was only moderately correlated to conductivity, alkalinity, and Ca^{2+} and not at all correlated to pCO_2 or pH. In PC2, pH and pCO_2 were strongly, inversely correlated to one another (r = -0.99). Variations in calcite SI and DIC concentration and to a lesser degree, Mg^{2+} and SO_4^{2-} were also important in PC2; however, SI was poorly correlated to these parameters. DIC concentration was positively correlated to Mg^{2+} (r = 0.75) and exhibited a moderately negative correlation to SO_4^{2-} (r = -0.48), while SO_4^{2-} also showed a moderately negative correlation to Mg^{2+} (r = -0.49). Sulfate appeared again in PC3, where it seemed to play more of a role in the geochemical variation, along with Fe, and DO, followed by water-level and $\delta^{13}C_{DIC}$. Sulfate exhibited weak correlations to most other geochemical parameters, with the exception of Fe, and $\delta^{13}C_{DIC}$, to which it was somewhat strongly and moderately correlated, respectively (r = -0.70 and 0.57, respectively). Variations in NO_3^- alone were most significant in PC4, and it was only weakly correlated to the remaining geochemical parameters.

5.4.3. Palma Vista Well

As previously reported, $\delta^{13}C_{DOC}$ values at Palma Vista Well were significantly higher than the adjacent Palma Vista Cave despite similar means (p = 0.0013), and significantly lower than the slough (p <0.0001) (Table 5.1, Figure 5.5). Like the cave, these values remained relatively stable through the time period analyzed, with the exception of a brief high on October 10. Values of C/N were significantly lower than the cave as discussed above but not significantly different from the slough. Little seasonal variation was exhibited in $\delta^{13}C_{DOC}$ and C/N values.

Fluctuations in $\delta^{13}C_{DIC}$ values and DIC concentration at the well were similar to the cave with no apparent seasonal variation and had values that were not significantly different (Figure 5.5). Though DIC concentration at the well was not significantly different from the slough (p = 0.99), $\delta^{13}C_{DIC}$ values were significantly lower (p <0.0001). As discussed above, the remaining geochemical parameters (with the exception of conductivity, DO, Fe, Ca^{2+}, and SO_4^{2-}) were not significantly different from the cave; however, only DO, Ca^{2+}, and Mg^{2+} were significantly different than the slough (p <0.0001 for each).

Results from an individual PCA at the well showed that only the first three principal components were significant, accounting for slightly less than 75% of the total geochemical variation (Table 5.2). In PC1, pH, conductivity, pCO_2, and calcite SI played the largest role in geochemical variation, while only alkalinity, and to a lesser degree, water-level, DIC concentration, Ca^{2+}, and Fe were important in PC2. Variations in NO_3^-, $\delta^{13}C_{DIC}$, followed by DO and DIC concentration were dominant in PC3. Like the cave, pH, *p*CO2, and calcite SI were well-correlated and not strongly influenced by water-level, and only moderately correlated to conductivity (Table 5.3). Despite being well-correlated to conductivity, alkalinity was not a significant component in PC1, and of the remaining parameters with the highest loadings in PC2, it was best correlated to Ca^{2+}, with an *r*-

value of 0.74. Both Ca^{2+} and DIC concentration demonstrated a moderate to somewhat strong negative correlation to water-level (r = -0.57 and -0.73, respectively), though they were not well correlated to one another. Similarly, NO_3^- and $\delta^{13}C_{DIC}$ were not correlated despite their higher loadings in PC3, nor were they correlated to DO or DIC concentration.

5.5. Discussion

Results from dissolution experiments using limestone tablets in diffusion chambers document that dissolution is indeed an active process at both Taylor Slough and Palma Vista Hammock and may be facilitated by organic activity in addition to general acidity of the water, based on etching and mass loss observed for both filtered and unfiltered tablets. Nevertheless, results from statistical analyses of the data illustrate the high degree of geochemical complexity at all three sites and suggest that more than one geochemical process may be responsible for fluctuations in a given parameter. For example, since DIC is comprised of HCO_3^-, carbonate, and CO_2, $\delta^{13}C_{DIC}$ values should reflect all processes influencing these three parameters (e.g., limestone dissolution and precipitation, photosynthesis, and respiration), and while $\delta^{13}C_{DIC}$ values themselves can be used to indicate which process is most important in an open system, such as those sampled in this study, $\delta^{13}C_{DIC}$ is not likely to be influenced by any single process, as suggested by its moderate correlations to multiple geochemical parameters. While this makes a simple interpretation of dissolution mechanisms virtually impossible, utilizing a multivariate approach that combines DIC data with multiple geochemical parameters gives us a more specific understanding of how dissolution operates in this environment.

As displayed by the bulk PCA (Figure 5.7), geochemical processes varied between Taylor Slough and Palma Vista Hammock, likely as a result of differences in their exposure to surface processes (rainfall, sunlight, evaporation, etc), as well as in their respective vegetative and hydrologic regimes. Overall, water-level, calcite equilibrium reactions, and Fe and SO_4^{2-} reactions seem to be major mechanisms impacting geochemical variation at these three sites, and are discussed in more detail below. Most of these reactions, as well as other reactions that may play a minor role in the geochemical variation, are biotically mediated and fueled by the decomposition of organic matter.

5.5.1. Water-level

Water-level influences the concentration of solutes via dilution, particularly in open systems. At Taylor Slough, geochemical parameters with high loadings in PC1 demonstrated a strong negative correlation to water-level, suggesting that water-level fluctuations masked some of the solute fluctuation imparted by other geochemical processes. Water-level appeared to be less important to geochemical variation at Palma Vista Hammock based on its lower *r*-values in the correlation matrix, as well as its reduced loadings in the PCA for each site relative to the slough (Table 5.2-5.3). In PC2, loadings for SO_4^{2-} became more significant than pCO_2 and pH, though such increases in the loadings of other parameters was not observed. Similarly, at Palma Vista Well, changes in loadings were not enough to change the overall results of PC1, though loadings for Fe overtook alkalinity and SO_4^{2-} improved as well in PC2. With the exception of a slight decrease in the loading of SO_4^{2-} at the cave, water-level appeared to have a minimal impact on PC3. Collectively, these data suggest that though water-levels influence some control over the geochemistry at Palma Vista Hammock, this control is reduced compared to the slough, and that other processes influence solute concentrations, particularly values of SO_4^{2-} and Fe.

5.5.2. Calcite Equilibrium Reactions

Equilibrium reactions between calcite (and, in some limestones, dolomite as well) and the surrounding water are major components of geochemical variation in most carbonate systems (White, 1988; Ford and Williams, 2007). Precipitation and dissolution reactions influence the concentration of Ca^{2+} and HCO_3^- in natural waters and are largely determined by acidity. Carbonic-acid-driven dissolution is a common mechanism that forms the basis of most carbonate dissolution models (White, 1988; Ford and Williams, 2007). In this mechanism, pure water is charged with $CO_{2\,(g)}$ to make $CO_{2\,(aq)}$, which then hydrates to produce H_2CO_3, an acid which dissociates to dissolve limestone (Eq. 1).

$$H_2CO_3 + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad \text{(Eq. 1)}$$

In these dissolution reactions, DIC is sourced from two constituents: biogenic CO_2 and the HCO_3^- from the dissolution of the limestone. Biogenic CO_2 sourced from aerobic microbial reactions is ^{13}C-depleted due to kinetic fractionation during metabolic processes (Craig, 1953). Hence, the $\delta^{13}C$ values of biogenic CO_2 tend to be more negative (typically ~23‰ and below). In contrast, marine carbonates forming limestones such as the Miami Limestone precipitate in isotopic equilibrium with DIC in seawater, with $\delta^{13}C$ values at or near 0‰. As a result, HCO_3^- produced from the dissolution of limestone will have an intermediate $\delta^{13}C$ value reflecting HCO_3^- ions with a 1:1 ratio of ^{13}C-enriched and ^{13}C-depleted carbon atoms from limestone and biogenic CO_2, respectively; however, the degree of openness of the groundwater system will determine the relative contribution of each carbon source and ultimately its $\delta^{13}C_{DIC}$ value. In open groundwater systems, biogenic CO_2 is in infinite supply such that dissolution is continuous, yielding $\delta^{13}C_{DIC}$ values of approximately -14 to -12‰ (Clark and Fritz, 1997).

In closed groundwater systems, CO_2 is not in infinite supply, resulting in $\delta^{13}C_{DIC}$ that becomes progressively more positive, suggesting enrichment of ^{13}C from the equilibration of water with the surrounding limestone once $CO_{2(aq)}$ has been reacted (Clark and Fritz, 1997; Böttcher, 1999).

At Palma Vista Cave and Well, $\delta^{13}C_{DIC}$ values were typical of groundwater DIC produced by H_2CO_3-dissolution, and when the millequivalent concentrations of HCO_3^- and Ca^{2+} are plotted, the slope of their relationship displays the 2:1 molar ratio expected in this dissolution process (Eq. 1; Figure 5.8); however, the overall lack of a strong correlation between $\delta^{13}C_{DIC}$ and parameters of carbonic acid dissolution (e.g., calcite SI, Ca^{2+} concentration, alkalinity, and pCO_2) suggests that other processes are influencing the composition of the DIC pool. This is most evident at the cave, where DIC concentration correlates poorly to $\delta^{13}C_{DIC}$ values, suggestive of heterogeneity of DIC sources. Conversely, at the well, DIC concentration and $\delta^{13}C_{DIC}$ values are fairly and inversely, correlated. This suggests that ^{13}C-depleted carbon sources with inherently low $\delta^{13}C_{DIC}$ values, in other words, biotic sources, are major contributors to DIC concentration.

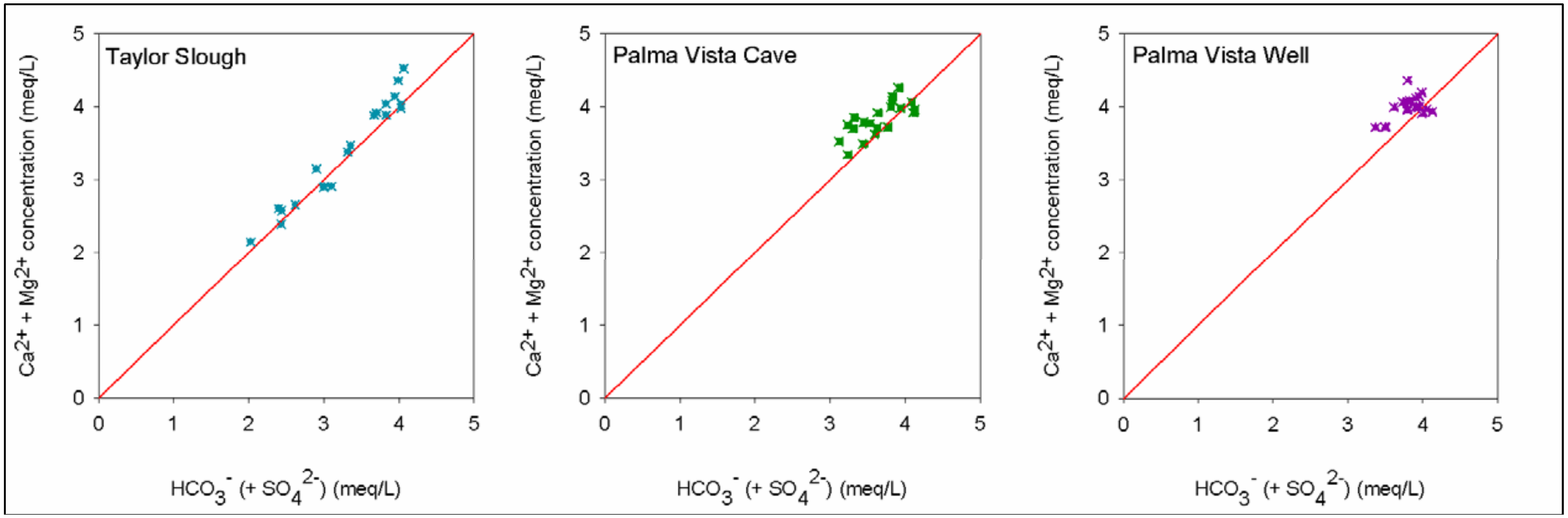


Figure 5.8. Stoichiometric ratio of Ca^{2+} + Mg^{2+} and HCO_3^- and SO_4^{2-} for Taylor Slough, Palma Vista Cave, and Palma Vista Well. Crosses: Summed millequivalent concentrations of Ca^{2+} and Mg^{2+} (*y*-axis) and HCO_3^- (*x*-axis) indicative of H_2CO_3 dissolution. Filled circles: Summed millequivalent concentrations of Ca^{2+} and Mg^{2+} (*y*-axis) and HCO_3^- and SO_4^{2-} (*x*-axis) indicative of H_2SO_4 dissolution.

At Taylor Slough, $\delta^{13}C_{DIC}$ values were significantly more positive and representative of waters in isotopic equilibrium with freshwater carbonates such as carbonate marls in the slough, rather than waters influenced by H_2CO_3-dissolution of those DIC sources. This hypothesis is supported by the cross-plot of HCO_3^- and Ca^{2+} + Mg^{2+} concentrations, which exhibited a slope of nearly 1 (Figure 5.8). Because thick deposits of peat and carbonate marls hinder surface-water limestone interactions, we can assume that marls and calcite-precipitating organisms such as calcareous periphyton are the dominant sources of Ca^{2+} and HCO_3^- in Everglades surface waters, and appear to exert a major control on $\delta^{13}C_{DIC}$ values. This relationship is particularly apparent in the summer as photosynthesizers discriminate against ^{13}C-depleted DIC (indicated by $\delta^{13}C_{DIC}$ values in excess of 2‰). $\delta^{13}C_{DIC}$ would be expected to decrease when respired CO_2 becomes more abundant as photosynthesis gives way to decomposition, as well as when groundwater discharges to the surface during the winter dry season (Harvey et al., 2004). Collectively, these data indicate that Taylor Slough waters have little direct effect upon (and/or are little affected by) dissolution in the underlying Miami Limestone. Though we might assume geochemical variation at Palma Vista Well is indicative of groundwater geochemistry underlying the slough (with relatively lower pH and higher pCO_2), similarities between the well and Palma Vista Cave shown by bulk PCA suggest that the waters at these two sites influence one another such that any correlation to groundwater at the slough may be inaccurate. Additional assessment of slough groundwaters (as opposed to surface waters only) would elucidate the degree of influence these waters have upon groundwaters at Palma Vista Hammock.

5.5.3. Iron and Sulfate Reactions

Sulfate minerals are common in carbonate rocks and, in marine/freshwater limestones, are commonly derived from the reduction of SO_4^{2-} by bacteria during anaerobic decomposition, which mineralize with other free ions to become assimilated into limestone as it forms, or become part of pre-existing limestone during diagenesis. Pyrite (FeS_2) is such a mineral and a common constituent of limestones that form in aquatic environments under anoxic conditions, wherein the bacterial reduction of SO_4^{2-} releases hydrogen sulfide (H_2S) or at pH>7, hydrosulfide ions (HS^-) that bond with elemental Fe in the presence of elemental S (Eq. 2-3):

H_2S: $2CH_2O + SO_4^{2-} + Fe^{2+} + S^0 \rightarrow 2HCO_3^- + FeS_2 + 2H^+$ (Eq. 2)

HS^-: $HS^- + Fe^{2+}\ S^0 \rightarrow FeS_2 + H^+$ (Eq. 3)

In the Everglades, pyrite is common in the Miami Limestone, and peat as well as carbonate marls support the modern formation of pyrite in surface sediments (Altschuler et al., 1983; Brown and Cohen, 1995; Randazzo and Jones, 1997). When exposed to oxidizing conditions, such as when peat deposits are drained or as oxygenated waters move through the limestone, pyrite oxidizes to sulfuric acid (H_2SO_4), which will react with the surrounding limestone to cause oxidation or dissolution (Eq. 4-5):

oxidation: $FeS_2 + 3.75O_2 + 3.5H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4$ (Eq. 4)

dissolution: $2CaCO_3 + H_2SO_4 \rightarrow 2Ca^{2+} + 2HCO_3^- + SO_4^{2-}$ (Eq. 5)

In addition, H_2S produced from the bacterial reduction of SO_4^{2-} may itself oxidize to form H_2SO_4 through a series of intermediate reactions (Palmer, 2007).

Because all carbon in HCO_3^- produced during H_2SO_4-dissolution is lithogenic, $\delta^{13}C_{DIC}$ values produced by this process are equal to the value of limestone $\delta^{13}C$, and, therefore, more positive than DIC produced during H_2CO_3-dissolution. The contribution of H_2SO_4 to dissolution can also be determined by plotting the relationship between the summed equivalent concentrations of HCO_3^-, SO_4^{2-}, and Ca^{2+} (and Mg^{2+} in dolomitic limestones), as discussed above for H_2CO_3-dissolution. Because SO_4^{2-} is an additional anion produced during H_2SO_4-dissolution, the summed millequivalent concentrations of HCO_3^- and SO_4^{2-} will produce a 3:2 stoichiometric ratio with that of Ca^{2+} and/or the sum of Ca^{2+} and Mg^{2+} (Yoshimura et al., 2001). If H_2SO_4-dissolution is occurring, it should be identified in a cross-plot if the data fall below a slope of 1.

Sulfate may also be produced in solution by dissolution of the evaporite mineral gypsum ($CaSO_4 \cdot 2H_2O$). This mineral is common to limestones produced in shallow-marine conditions, as well as modern environments where waters saturated with SO_4^{2-} and Ca^{2+} may evaporate (Hill and Forti, 1997; Palmer, 2007; Eq. 6):

$$2HCO_3^- + CaSO_4 \cdot 2H_2O \rightarrow CaCO_3 + CO_2 + SO_4^{2-} + 3H_2O \quad \text{(Eq. 6)}$$

If gypsum dissolution is actively contributing to SO_4^{2-} in the waters, the stoichiometric ratio of SO_4^{2-} to Ca^{2+} produced during dissolution should be 1. In settings where Ca^{2+} is also sourced from other processes, notably limestone dissolution, the unity line will be shifted up the *x*-axis in a cross-plot to account for the calcium excess (Jin et al., 2010). Because the source of HCO_3^- consumed to produce $CaCO_3$ in this reaction is unknown and can come from biotic or abiotic origins, the use of $\delta^{13}C_{DIC}$ values is not likely to distinguish gypsum dissolution from other processes impacting the DIC pool.

Sulfate and Fe appear to play a minor role in the geochemical variation at all three sites; however, the sources of these ions may differ. At Taylor Slough, peat and carbonate marl sediments provide a barrier to the underlying limestone such that any SO_4^{2-} in the water is likely sourced from surface processes such as the bacterial decomposition of organic matter (containing SO_4^{2-} assimilated from the environment) or from runoff from the Everglades Agricultural Area (EAA) to the north (Bates et al., 2002). At the same time, Fe may be sourced from a variety of pools, including soil/agricultural runoff and deposition of windborne Saharan dust (Prospero, 1999; Shinn et al., 2000) and decomposition of organic matter. Though $\delta^{13}C_{DIC}$ values near 0‰ might suggest that H_2SO_4-dissolution of marls is occurring, cross-plots show little excursion below the 1:1 line (Figure 5.8). Similarly, gypsum dissolution does not appear to be an important SO_4^{2-} source, as there is no identifiable 1:1 ratio between SO_4^{2-} and Ca^{2+} (Figure 5.9), further supporting limestone dissolution as the primary source of Ca^{2+} to the waters. As such, runoff and/or organic matter decomposition appear to be the primary sources of both SO_4^{2-} and Fe to Taylor Slough. Tracer studies analyzing stable isotopes of S, radioactive isotopes of C, and the speciation of Fe have been effective methods constraining inputs of these elements to Everglades water in the past, and would be useful here in determining the specific contributions of SO_4^{2-} and Fe here (Price and Casagrande, 1991; Bates et al., 2002; Wang et al., 2002; Stern et al., 2007).

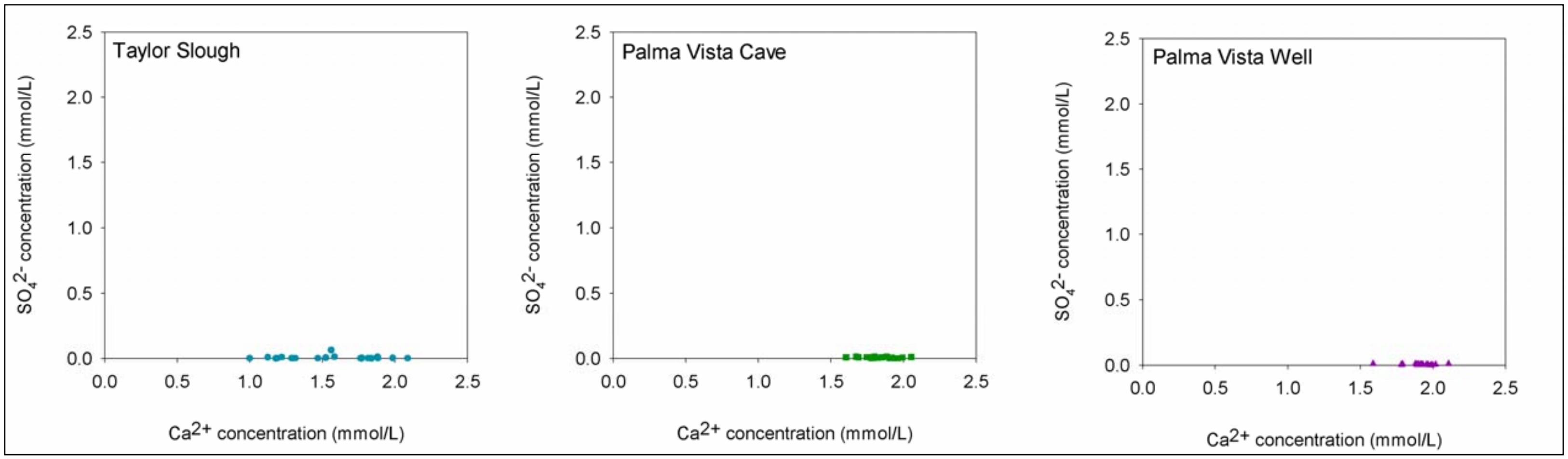


Figure 5.9. Plots of SO_4^{2-} and Ca^{2+} concentrations indicating absence of gypsum dissolution.

At Palma Vista Hammock, SO_4^{2-} and Fe appeared to have more impact on the geochemical variation of waters despite any dilution/concentration effects imparted by changing water-level (Table 5.2). Both seemed to play a minimum role in PC1, but increased in PC2 and PC3. Like the slough, SO_4^{2-} and Fe are probably sourced from the bacterial decomposition of organic matter and mineral runoff from surface soils, which is supplied directly to Palma Vista Cave from the overlying hardwood forest, before flowing into the adjacent well. In addition, direct contact of cave and well waters with the surrounding limestone combined with oxygenated conditions for at least part of the year suggests that some SO_4^{2-} and Fe may be sourced from the limestone itself. At Palma Vista Cave, SO_4^{2-} played an important role in PC2 with DIC concentration, pH, pCO_2, and calcite SI. The strongest correlation shared between SO_4^{2-} and these parameters was a mild, inverse correlation to DIC concentration (r = -0.48), an indicator that bacterial reduction of SO_4^{2-} may play a minor role in the geochemical variation here (Eq. 2), and is supported by both low DO levels and relatively high SO_4^{2-} concentrations most of the year. Because SO_4^{2-} and Fe become important contributors to geochemical variation in PC3, and because of the somewhat positive correlation between SO_4^{2-} and $\delta^{13}C_{DIC}$ (a potential indicator of H_2SO_4-dissolution, which produces both SO_4^{2-} and relatively ^{13}C-enriched HCO_3^-), it could be assumed that the oxidation of pyrite in the limestone in association with H_2SO_4-dissolution provides a significant source of SO_4^{2-} to the system, contributing to its high concentration; however, SO_4^{2-} and Fe demonstrate a relatively strong, inverse correlation, which precludes the occurrence of pyrite oxidation alone, or pyrite oxidation in association with H_2SO_4-dissolution (Eq. 4-5). Because Fe is more reactive of the two, this inverse relationship suggests the formation of other iron oxide minerals such as limonite ($FeO(OH) \cdot nH_2O$) and goethite ($FeO(OH)$), commonly found in caves and other limestone settings (Hill and Forti, 1997). Further, cross-plots do not support the occurrence of H_2SO_4-dissolution or gypsum (Figure 5.8). Therefore, both SO_4^{2-} and Fe must be sourced primarily by the runoff and decomposition of organic matter continually supplied by the hardwood forest above, with this organic matter providing the substrate on which the bacterial reduction of sulfate is occurring. To test this hypothesis, $\delta^{34}S$ analyses of SO_4^{2-} could be used to detect the degree to which sulfate reduction is occurring, due to the preferential removal of the lighter ^{32}S isotope by bacteria, enriching the remaining reservoir in ^{34}S.

At Palma Vista Well, SO_4^{2-} and Fe reactions were more obvious in PC2 (Table 5.2); however, like Palma Vista Cave, SO_4^{2-} and Fe concentrations did not appear to be driven by pyrite oxidation and/or H_2SO_4-dissolution based on the inverse correlation of SO_4^{2-} and Fe and cross-plots of the ions produced by H_2SO_4-dissolution (Figure 5.8). Iron appeared to play a more important role at the well than SO_4^{2-} based on its higher loading in PC2 and is supported by significantly higher concentrations here than the remaining sites. These results may be due to the oxidation of metal fragments observed in the well, presumably left behind from the well construction. Apart from this, Fe and SO_4^{2-} concentrations at the well appear to be driven by the same surface runoff and organic matter decomposition processes occurring at the cave. Overall, the proximity of the well and cave make it likely that any material sourced to the cave from the overlying hammock is transported to the well, along with any dissolved organic matter and ion species released during the *in situ* decomposition at the cave itself. In contrast, the relatively closed nature of the well would hinder direct surface inputs here beyond that which can infiltrate the porous limestone above. This hypothesized cave-to-well flow of material is supported by the overlap in these sites in the bulk PCA (Figure 5.7).

5.5.4. Other Microbially Driven Dissolution Mechanisms

In addition to H_2CO_3- and H_2SO_4-driven dissolution reactions, the decomposition of organic matter can promote limestone dissolution through a series of microbially mediated reactions. For example, the conversion of NH_3 (or NH_4^+) to NO_2^- and NO_3^- in the first two steps of nitrification produces acid in the form of free H^+ (Eq. 7-8).

$$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^- \quad \text{(Eq. 7)}$$

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \quad \text{(Eq. 8)}$$

These reactions are facilitated by nitrifying bacteria such as *Nitrosomonas* and *Nitrobacter*, respectively, which consume CO_2 or other forms of organic carbon as a source for growth. Acidification caused by nitrification will cause dissolution of limestone, producing lithogenic DIC that enriches the DIC pool in ^{13}C. In carbonate settings, continual nitrification will cause positive excursions in $\delta^{13}C_{DIC}$ values that could exceed that of the host limestone as NH_3 concentrations and pCO_2 decrease and NO_3^- concentrations increase. Conversely, denitrification consumes acidity as NO_3^- is converted back to N_2 and NH_4^- (Eq. 9-10).

$$CH_2O + 0.8NO_3^- + 0.8H^+ \rightarrow 0.4N_2 + CO_2 + H_2O \quad \text{(Eq. 9)}$$

$$CH_2O + 0.5NO_3^- + H^+ \rightarrow CO_2 + 0.5NH_4^+ + H_2O \quad \text{(Eq. 10)}$$

This process, as well as ammonification, provides ^{13}C-depleted CO_2 back to the DIC pool, lowering $\delta^{13}C_{DIC}$ values as NH_3 concentration and pCO_2 increase and NO_3^- concentrations decrease. With the exception of methanogenesis (which undergoes a greater kinetic fractionation to produce CH_4 with $\delta^{13}C$ values below -40‰) nitrification, denitrification, and ammonification reactions cannot be differentiated by $\delta^{13}C$ values alone, and may only be inferred in this study by including major ion analyses; however, the lack of a direct correlation between $\delta^{13}C_{DIC}$ values and geochemical parameters that should be affected by H_2CO_3-dissolution indicate that the DIC pool is also likely to be affected by these other organic processes as well. Methanogenesis does not appear to occur at any of the sites based on $\delta^{13}C$ values, though nitrogen cycling, expressed by nitrification and denitrification/ammonium reactions may play a minor role based on the appearance of NO_3^- in the site-specific PCA. At Taylor Slough, NO_3^- is a minor component of both PC1 and PC2 and is mildly correlated to pH, pCO_2, and calcite SI (r = -0.57, 0.46, and -0.42, respectively). These relationships suggest nitrification is occurring at the slough, as the increase in NO_3^- concentration corresponds to the decrease in pH and SI through the release of free H. The mild positive correlation to pCO_2 does not reflect the inverse relationship between NO_3^- and CO_2 that should occur with denitrification, although as previously discussed, numerous processes are likely contributing to the slough's CO_2 pool. Nitrate only becomes an important parameter in PC3 and PC4 at Palma Vista Hammock and is not well-correlated to any other geochemical parameters. It displays a weak correlation to $\delta^{13}C_{DIC}$ (r = 0.42) and Fe (r = 0.41) at Palma Vista Well, though a direct interpretation of this is not advisable without further study. Analyses of ions such as NH_4^+ and NO_2^-, and/or of stable isotopes such as $\delta^{15}N$, are suggested to further elucidate the role of nitrogen cycling on the dissolution of limestone at all three sites.

Some organic compounds and reduced ions are also known inhibitors of calcite precipitation by adsorption to the surface of calcite, thus blocking growth (e.g., Berner et al., 1978; Inskeep and Bloom, 1986; Hoch et al., 2000). For example, the abundance of Fe at Palma Vista Well, regardless of source, is an indicator that the inhibition of calcite crystallization is likely occurring at this site (Takasaki et al., 1994). Though not measured here, PO_4^{3-} also is known to inhibit calcite growth, and since the normally P-limited Everglades are subject to large PO_4^{3-} inputs from agricultural activity and peat decomposition in the Northern Everglades, its effects on calcium equilibrium reactions could be significant (Reddy, 1977). Finally, humic substances released during organic matter decomposition, particularly plant-derived hydrophobic acids, have been documented as strong inhibitors of calcite growth, and may indirectly promote dissolution by providing nutrients to be metabolized/oxidized by heterotrophic microorganisms (Hoch et al., 2000). These processes may be more directly assessed using bench-top experimentation that monitors calcite precipitation and dissolution rates in the presence of varying concentrations of these ions and substances.

5.5.5. Role of Organic Matter in Dissolution

Whether dissolution is caused by acidification of meteoric waters by H_2CO_3 and/or H_2SO_4 or by free H^+ released through microbially mediated oxidation reactions, or if it is supported by the presence of humic substances and other inorganic ions, it is apparent that the availability of organic matter has the potential to act as a major controlling factor. The oxidation of organic matter during decomposition fuels a variety of microbial processes that in turn, drive the availability and abundance of most major ions in solution. Though carbonate equilibrium reactions are no doubt controlled by ion exchange between the water and rock in closed systems, in open systems subject to influence by a wide variety of biogeochemical processes, it is unrealistic to expect that these processes have little effect on carbonate reactions. For example, despite the claim that H_2CO_3 production through the hydration of biogenic CO_2 is a less efficient, and therefore less common mechanism of dissolution than the addition of H^+ to $CaCO_3$ in abiotic reactions (Berner and Morse, 1974), there are no shortage of studies from a variety of karst settings consistently documenting that $\delta^{13}C_{DIC}$ of groundwaters are more depleted than host limestone values, often by at least 4-5‰ (e.g., Deines et al., 1974; Lojen et al., 2004; Doctor et al., 2008). For this and other microbially mediated reactions to occur, an energy source is vital, and in open systems, that energy source is driven by carbon derived from organic matter (Konhauser, 2006). Because organic matter is in no short supply in karst regions such as the Everglades, dissolution is most likely an active process, with rates increasing or decreasing based on the amount of organic matter available. This implies that dissolution of the Miami Limestone is likely to be more active in the few places where it is more exposed to the surface, such as the Atlantic Coastal Plain, and therefore more subject to oxidizing conditions. This is in contrast to the majority of the Everglades, where the limestone is overlain by thick deposits of peat, producing a more reducing environment; however, drainage of the Everglades for agricultural development and water resources would allow for the oxidization of the overlying peat (as has been observed in the northern Everglades), facilitating more rapid dissolution rates. To test this, a more detailed study of dissolution dynamics is necessary in the low-lying regions of the Everglades. Models of dissolution can be constructed and compared for regions impacted by drainage and peat oxidation, and regions that are relatively pristine by monitoring surface and groundwater conditions for each. Similarly, bench-top simulations allow for more direct observations of limestone responses to changes water chemistry observed in the field and/or models.

5.5.6. Broader Implications

The results of this study suggest that biologic processes appear to play an important role in the long-term evolution of carbonate and karst systems and should not be overlooked when characterizing their development. Similar studies investigating the role of microorganisms on limestone dissolution have come to the same conclusion and suggest that limestone dissolution rates can be greatly underestimated based upon incomplete dissolution models that do not account for biotic influences (Paine et al., 1933; Schwabe et al., 2008; McGee et al., 2010). Similarly, Cunningham et al. (2009), Harvey et al. (2008), and Renken et al. (2008) have demonstrated that the activity of macroorganisms such as marine invertebrates can impart substantial influences on the future evolution of carbonates as they are deposited, by determining future flow paths and conduits for water and geochemical transport, thereby controlling where and to what degree dissolution takes place once the limestone is deposited and lithified. On a human scale, this becomes important in understanding the variables affecting water and pollutant transport in carbonate aquifers and, on a broader scale, the capacity and transmissivity of modern and future oil reservoirs situated in carbonate rocks.

5.6. Conclusions

In the Everglades region of southern Florida, microbial processes fueled by ample and constant supplies of organic matter appear to exert an important control on dissolution by respiring CO_2 that combines with meteoric water to generate H_2CO_3. This process was directly observed at Palma Vista Hammock in the southern region of Everglades National Park and may also occur at Taylor Slough; however, confirmation of limestone dissolution (as opposed to dissolution of surface freshwater carbonates) at the slough could not be obtained from surface waters, illustrating the need for a direct assessment of its groundwaters. Nevertheless, from observations at Palma Vista Hammock, where the Miami Limestone crops out and is not overlain by peat and marl deposits as is the case at Taylor Slough, we can hypothesize that dissolution processes are probably more rapid due to more direct sourcing of organic material combined with relatively more oxidizing conditions. This hypothesis would suggest that the decomposition of peat from anthropogenic removal of water or natural lowering of sea-level would act to enhance dissolution rates in the sloughs, which encompass a broad area of the Everglades landscape, by providing both a greater source of nutrients and organic matter for microbial processes, as well as oxidizing conditions to make these processes more efficient. These data emphasize the importance of biota on the evolution of limestone and karst regions, and must therefore be considered when establishing dissolution models for carbonate/karst regions, particularly when these models are utilized to better understand aquifer and reservoir dynamics.

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CHAPTER 6:

LEARNING QUANTITATIVELY: ASSESSING THE ROLE OF SPREADSHEETS ACROSS THE CURRICULUM

6.1. Introduction

The dearth of graduates in STEM (Science, Technology, Engineering, and Mathematics) fields has been repeatedly targeted by educators and organizations alike as a critical issue in the American education system, one that must be remedied quickly in order to strengthen the nation's position as a leader in technology and innovation (e.g. NRC, 1996; NSF, 1996; Boyer Commission, 1998). In support of this the Obama administration launched the "Educate to Innovate" campaign in November 2009, a nationwide effort to promote STEM curricula and awareness. Budgetary constraints and lagging educational standards are considered broad causes for dwindling student participation in STEM disciplines, but on a more fundamental level, educators cite the poor preparation of students in mathematics-based courses as being particularly problematic (e.g., Cuoco et al., 1996; Battista, 1999; RAND Mathematics Study Panel, 2003). Without the capacity to transfer quantitative concepts and skills originally encountered in math courses, students struggle with the analytical and critical-thinking tasks common to most STEM disciplines, which often results in a general avoidance of these subject areas. In particular, math anxiety/avoidance is commonly encountered by STEM educators and has been addressed by education specialists and psychologists alike as early as the 1970s (Suinn and Richardson, 1972; Ashcraft, 2002). Instructor experience, motivation, and encouragement, which ultimately determine the quality of teaching and curricula development, are considered central determinants of math anxiety and overall performance (e.g., Ginsburg, 1997; Gatto, 2000;). To address these concerns, government agencies such as the National Science Foundation (NSF), as well as specialist organizations and interest groups (e.g. the National Research Council, the National Council of Teachers of Mathematics, and the Annenberg Institute) have sponsored initiatives that promote positive learning experiences through pedagogical reform.

A recent outgrowth of the mathematics field with direct pedagogical applications is *quantitative literacy* (QL), also known as *numeracy*. Specific definitions of QL vary, but it is generally deemed a “habit of mind”, or the ability to apply and utilize quantitative skills in context. Quantitative literacy is considered a critical skill for all participants in modern society (Steen, 2001; Madison and Steen, 2003). Integration of QL into the academic curriculum is becoming increasingly common, particularly at undergraduate institutions. This is carried out by the infusion of math courses with contextual applications and courses across the curricula with quantitative applications pertinent to the discipline. Spreadsheets, specifically those produced using Microsoft Excel, are a well-documented method used to promote QL in the classroom (e.g., Hsiao, 1985; Misner, 1988; Brosnan, 1989; Baker and Sugden, 2003; Goldberg and Waxman, 2003; Fratesi and Vacher, 2004; Lim, 2004). The inherent versatility of spreadsheets and their uses (which can be explored further in the journal *Spreadsheets in Education*) provides students with a hands-on tool to develop and strengthen QL skills while at the same time furthering their own technological skills.

In the early 2000s, the Department of Geology at the University of South Florida (USF) endorsed the value of QL by adopting Computational Geology (GLY4866) as a required upper-level capstone course. The course was conceived to help geology majors develop a capacity to apply quantitative reasoning skills and techniques in geological contexts. Spreadsheets were commonly used in the course to assist the students to learn and explore quantitative concepts and relationships, and ultimately they served as the platform from which the NSF project, *Spreadsheets Across the Curriculum* (SSAC), was launched as a QL initiative. The primary goal of SSAC was to promote QL computer-based teaching modules that used spreadsheets to solve a variety of discipline-specific quantitative problems. The project was prolific in its development of modules adaptable to a wide range of courses and teaching styles. Assessment of the effectiveness of these modules at teaching and improving QL skills, however, proved much more complex. The experience provided a unique insight regarding the difficulties associated with such practical approaches that, by their diverse nature, target such a diversity of subjects.

Here, we focus on the evolution of SSAC assessment in the USF Computational Geology course from 2005 to 2008 and highlight the challenges encountered which led to modifications over that time period. We also demonstrate that though assessment modification can impart its own difficulties in the interpretation of results from year to year, the changing of student subject groups from one semester to another (each with varying degrees of knowledge and skills) as well as the inability to isolate student learning gains due to module use from overall pedagogy further complicates the interpretations and comparisons of assessment data. These difficulties present a major challenge for projects such as SSAC that are designed to be applicable to a variety of learning environments and disciplines, and requires extensive planning and collaboration on the part of assessors.

6.2. History of Spreadsheets at USF

The common use of spreadsheets as teaching vehicles in the Computational Geology course was the motivator behind the Phase-1 Proof-of-Concept Course, Curriculum, and Laboratory Improvement (CCLI) proposal entitled *Spreadsheet Exercises in Geological-Mathematical Problem Solving*. This proposal was funded by NSF (DUE 0126500) in 2002 to develop a series of formal spreadsheet modules for the Computational Geology course. Each module consisted of a Microsoft PowerPoint presentation that introduced a particular geologic problem and provided step-by-step instructions for developing the spreadsheet in Microsoft Excel that allows students to calculate the necessary solutions (Figure 6.1). The Washington Center for Improving the Quality of Undergraduate Education (The Evergreen State College, Olympia, WA) disseminated the modules on their Website, and that collaboration led to *Spreadsheets Across the Curriculum* (SSAC), a Phase-2 CCLI proposal funded by NSF (DUE 0442629) in 2005. This project expanded upon the 2002 project by developing modules of a similar style covering a broader range of both disciplines and QL skills. Modules were developed during a series of three, week-long summer workshops held in Olympia, Washington, that were attended by approximately 20 educators from undergraduate institutions nationwide. Upon completion, modules underwent a review process that included editing and visual standardization by the PI and affiliated USF graduate students prior to public dissemination online via the Science Education Resource Center (SERC) at Carleton College (http://serc.carleton.edu/sp/ssac_home/index.html). A the completion of the project in March 2010, there were 55 completed modules in the SSAC

General Collection classified into 26 Library of Congress categories. These modules were developed by 40 authors from 21 educational institutions in 11 states. A more thorough discussion of the SSAC concept and its implementation is provided by the official SSAC Web address above and by Vacher and Lardner (2010).

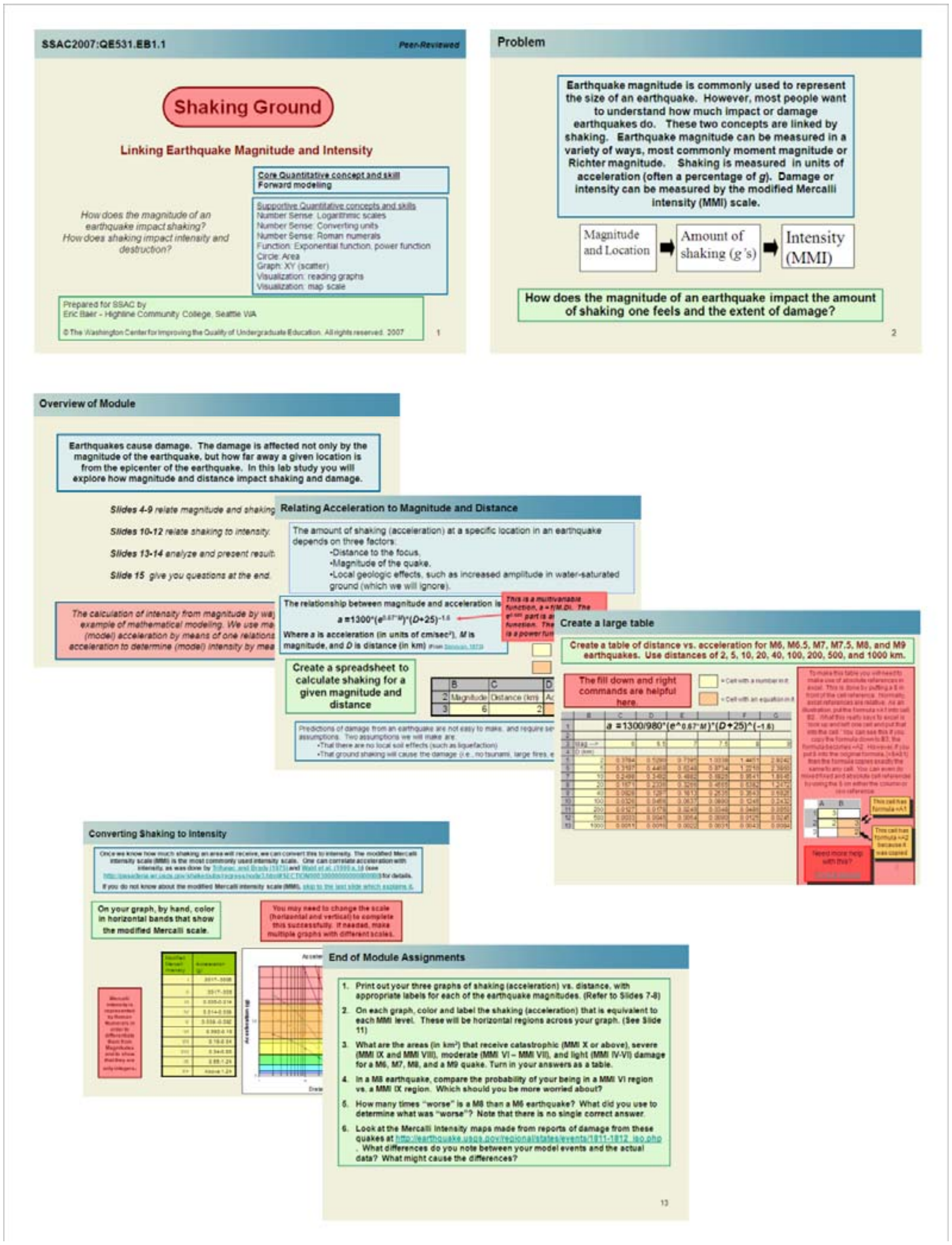

Figure 6.1. Title, introductory, instruction and end-of-module PowerPoint slides for the SSAC module *Shaking Ground: Linking Earthquake Magnitude and Intensity*, by Eric Baer (Highline Community College).

As the SSAC General Collection grew, modules covering relevant topics and QL skills were rotated through the Computational Geology course, with eight to 15 modules assigned as homework exercises each year. At the same time, USF Geology faculty came to recognize benefits of module use, and some of them adopted the concept by creating modules for their individual courses. The first of these was a series of nine modules produced by Chuck Connor and Peter LeFemina (Pennsylvania State University) that addressed quantitative concepts associated with magma and eruption dynamics for a physical volcanology (GLY4390) course. In 2007, the Department of Geology was awarded an Innovative Teaching Grant from the USF Center for 21st Century Teaching Excellence (CTE) to create additional SSAC-style modules. These modules were designed to incorporate a multimedia component, particularly videos and animations, to provide students with an enhanced conceptualization of spatial relationships and/or processes underpinning the modules' quantitative lessons. These components were designed by CTE's Media Innovation Team and applied to modules in the undergraduate Hydrogeology course (GLY4822) and the undergraduate/graduate courses, Geomechanics (GLY4930/5739) and Seismology (GLY4480/5739). One such animation entitled "Evapotranspiration" designed for the module *Evapotranspiration: Using the Penman-Montieth Equation to Calculate Daily Evapotranspiration* by Mark Rains, was awarded the 2009 Silver Telly for Best Use of Animation from the Telly Awards organization.

Expansion of SSAC modules into other USF Geology courses has also occurred through an additional CCLI-Phase 1 proposal funded by NSF entitled *Geology of National Parks: Spreadsheets, Quantitative Literacy, and Natural Resources* (DUE-0836566). In this project, SSAC modules that teach QL skills in the context of geoscience processes and natural resources occurring in U.S. national parks are being designed for use in the introductory course Geology of National Parks (GLY2160). These modules utilize data collected in the parks to explore resource preservation and management topics addressed by the U.S. National Park Service (NPS) in response to the Natural Resource Challenge, an action plan that integrates science, park management, and public outreach (NPS, 1999). Unlike modules in the SSAC General Collection, these Geology of National Parks (GNP) modules also aim to promote geoscience literacy by teaching core geoscience concepts; at the same time they aim to promote citizenship and awareness by exposing students to important issues in park preservation and management. As of June 2010, some twenty GNP modules are being completed in order to be available for rotation through the online GNP course.

Due to the continued production of SSAC and SSAC-style modules through the above-mentioned efforts, SSAC's main SERC Web site adapted to facilitate this growth by creating separate, but related, module collections. In addition to SSAC's General Collection, SERC now houses the Physical Volcanology and Geology of National Parks Collections, with future plans to include a USF Geology Collection containing modules produced for the department's courses. All modules are accessible via the SERC Web site, which provides a description for each module including teaching tips and, when available, assessment materials. Student module versions are freely available for download, with instructor versions available by request.

6.3. SSAC Assessment: Computational Geology

The efficacy of spreadsheet modules as tools for teaching QL skills is of paramount concern to the SSAC team, and since the project's inception, modules have undergone significant modifications in content, structure, and appearance in an effort to maximize learning gains. In the early days of spreadsheet use in Computational Geology, module effectiveness was assessed using a combination of summative and formative methods: student performance on modules and in the course was monitored by student grades, and student feedback regarding their attitudes and perceived learning experiences was garnered throughout the semester. When funding was obtained for module development, a more formal assessment strategy was adopted that included the use of pre- and post-assessment instruments for each module (originally developed by the SSAC team, then later required of module creators). In addition, identical pre- and post-course assessments were used to identify changes in both student attitudes towards math and levels of math proficiency over the course of the semester. Module and course assessments underwent a long evolution from 2005 to 2009 resulting from several semesters of trial and error in implementation and in response to feedback and discussions raised during collaborative discussions between the SSAC team, its partners, and affiliates. All assessments and administration strategies relative to the assessment done at USF were approved by the Internal Review Board (IRB# 103902) at the USF Office of Research and Innovation prior to course implementation. Students consented to participate on a voluntary basis.

The consistent use of modules in Computational Geology established the course as a primary SSAC assessment venue. This choice had distinct advantages and disadvantages. The primary benefit associated with this venue was the steady supply of student participants and continuous student participation from the beginning to end of each course term, eliminating the need for subject recruitment and financial incentive. Though participation in the assessment study was voluntary, no student opted out at any point during the semester, making it possible to reliably track data over time. Though student populations varied from year to year, nearly all students were geoscience majors, and variations in their skills and attitudes prior to the start of the course were considered a unique opportunity to study the effects of population on the results each year. The major disadvantage to assessing in this venue was that of the course's pedagogy. Computational Geology is a course consisting of in-class lectures and problem-solving activities, and readings and modules are assigned as homework. Each classroom session is tied to the homework activities by a common theme, typically a quantitative concept or skill. This meant that any shifts in learning gains and attitudes/perceptions observed in assessment data could not be attributed to the modules alone, and therefore served as a measure of pedagogical efficacy rather than module efficacy; however, because SSAC modules are designed to be integrated within the framework of a course, determining the success of their application within a pedagogy is appropriate. Nevertheless, an additional assessment of modules as stand-alone (i.e., outside of a structured course) tools for teaching QL skills took place at Eckerd College in St. Petersburg, Florida, and identified positive learning gains in student participants (Wetzel, 2011). This study is discussed further later in this paper.

6.4. Course Pedagogy and Assessment Methods

Computational Geology is a lecture-based course taught annually in the fall, with 15 to 25 students enrolled each year. Text material used for the course were selected columns in the Computational Geology series by Vacher in the *Journal of Geoscience Education* in 2005, a newly published quantitative literacy textbook, *Understanding our Quantitative World* (Andersen and Swanson, 2005), in 2006 and 2007, and a manuscript for a quantitative literacy textbook in preparation, *Numeracy* (Gaze, unpublished manuscript) in 2008. A typical class meeting begins with the delivery of a quantitative problem related to a QL concept/skill introduced in readings that were assigned to be read prior to the start of lecture. Students organize themselves into groups of two to four members and have 10 − 15 minutes to devise a solution or a strategy for finding the solution, based on the nature of the problem. Groups share their findings and raise questions in a class discussion, which serves as a lecture lead-in. Nearly all lectures are paired with a related SSAC module assigned as a homework exercise. Students are given a week to complete the module, and eight to 15 modules are administered per course year.

Pre- and post-module assessments were administered for most, if not all, modules assigned per course to identify changes in student knowledge following each module. Assessments were 10 − 15 minutes in length and consisted of as many as eight items pertaining to the core quantitative concepts covered in a given module. Assessment items required students to either perform a calculation or define/describe a specific quantitative concept or relationship (Appendices XI, XIII, XV, and XVII). Calculators were permitted only for assessments containing items that required the students to perform a relatively complex calculation, such as calculating weighted averages or the volume of a sphere.

For the purposes of reporting, module assessments were scored by tabulating the number of correct responses provided by students per assessment item for both pre- and post-assessments. The percent change in correct responses between assessments was calculated to identify specific items that either represented concepts with which students continued to struggle, or items that were poorly understood and in need of revision. Overall module scores were tabulated using the equation

$$\text{\textit{Assessment score}} = \frac{c}{i \times n} \qquad \text{Eq. 1}$$

where *c* is the total number of correct responses provided in each assessment, *i* is the total number of items, and *n* is the number of students participating.

Pre- and post-course assessments were administered on the first and last class meetings of Computational Geology to identify semester-long changes in student learning and attitudes (Appendices X, XII, XIV, and XVI). These assessments began with an attitude survey component designed to track changes in their perception towards both their ability to perform quantitatively and whether QL is important in the broader sense for members of modern society. This was followed by a knowledge survey consisting of quantitative items similar to those used in module assessments. Attitude surveys used Likert-style items that were scored based on increases or decreases in confidence levels and/or shifts in perception from pre- to post-assessment. This scoring was done by tabulating the number of responses representing positive and negative shifts in perception, and using the difference in these numbers to calculate a net change (%) from pre- to post-course assessment using a similar equation as above,

$$\textit{Net change in confidence/perception} = \frac{p-b}{i \times n} \times 100 \qquad \text{Eq. 2}$$

where *p* is the total number of positive shifts and *b* is the total number of negative shifts. Knowledge surveys were scored identically to module assessments using Eq. 1.

6.4.1. Module Assessments

Pre- and post-module assessments were administered in class, prior to lecture, on days modules were assigned and due, respectively. In 2005 and 2006, assessments were voluntary and administered blind (students chose a code name they utilized throughout the semester), and had no impact on course grades. The lack of incentive for students to participate led to some doubt as to whether students took the assessments seriously (e.g. putting thought and effort into their responses), increasing the likelihood that responses were not necessarily representative of student knowledge and/or ability. Time management was also considered to be a potential issue impacting assessment data and stemmed largely from assessment volume. The frequency of module assignments often led to class days in which pre- and post-tests were administered sequentially, leading to lecture constraints, particularly when students were also administered graded quizzes or exams. This led to suspicion that student attitudes toward the assessment process itself grew negative over the course of the semester, fuelling the above-mentioned lack of effort.

These assessment issues and others were raised during SSAC's Summer 2007 module workshop in Olympia, WA, and during collaborative meetings with assessment specialists from the Washington Center and other institutions. In each discussion, emphasis was placed on reducing assessment "burn-out"; improving the precision and efficiency of the module (and therefore the assessment) by being more specific in the identification of QL skills to be addressed; and raising student awareness of their own skills and learning habits. In response, SSAC revised all modules in preparation for the 2007 Computational Geology course year to improve their clarity and efficiency at teaching their specific QL skills, as well as all module assessments to improve alignment with module learning goals and ensure item clarity. Module assessment implementation methods were also revised to address issues of student response quality and time management/burn-out. Additionally, module assessments administered in the 2007 course year were made identifiable for grading purposes so students had incentive to take them seriously.

As in 2005-2006, students were administered pre-assessments on days when modules were assigned; however, post-assessments were administered as graded quizzes, with each quiz composed of two to three module post-assessments. To increase the number of modules assessed per semester without causing burn-out, some pre-assessment items were omitted from the post-assessment quiz (items that repetitively addressed the same QL skill, or addressed concepts secondary to the core QL skill). Students were required to respond only to items on the quiz that were incorrect on the pre-assessments, which were provided as copies with the quiz. Finally, for each item requiring a response on the quiz, students were asked to identify why they believed their response was originally incorrect and what they did to correct it. In addition to addressing the issues that arose during the 2005-2006 course years, these modifications to implementation also served to determine whether students were retaining information for longer time periods, and to assess whether students were cognizant of their learning gains.

Because students in the 2007 course year demonstrated they were almost always cognizant of their learning gains, this component was dropped from 2008 module assessments. Finally, because students also demonstrated the ability to retain QL skills over longer periods in 2007, post-assessments in 2008 were shifted to the two semester exams (not including the final), with each exam including items from six to seven modules.

6.4.2. Course Assessments

In 2005 and 2006, course assessments were identical and included a Likert-style confidence survey assessing student comfort levels with performing tasks identified by the National Council of Teachers of Mathematics (NCTM) in the chapter on Grades 9-12 in their Principles and Standards for School Mathematics (NCTM 2000) (Appendices X and XII). This survey included a series of “calibration” items addressing how comfortable students were at carrying out tasks common in geology, which was followed by a series of NCTM math-skills items representing QL skills commonly used in geology courses. Calibration items had little to do with quantitative skills and were used as benchmarks for comparing student confidence levels (i.e., were students more confident in their public speaking abilities than they were computing basic statistics?). The assessment concluded with a knowledge survey of ten items directly assessing students' quantitative abilities, which were derived from major quantitative concepts covered in modules assigned during the semester.

Like module assessments, course assessments underwent revision between the 2006 and 2007 Computational Geology courses. Though item clarity and participation were less of a factor, alignment of the assessment was necessary to more efficiently address how student attitudes and perceptions regarding math changed through the semester. For the 2007 course year, the calibration component of the NCTM confidence survey was replaced with 15 Likert-style items selected from the Dartmouth College *Mathematics Across the Curriculum* (MATC) survey (Appendix XIV). This survey was well aligned with SSAC in that it was designed to assess student attitudes and perceptions of math before and after completion of individual courses established as part of the Dartmouth project (Korey, 2000). The attitude and perceptions component of the assessment was also modified to focus on student reactions towards math in the geological sciences. The math confidence component of the NCTM survey was retained, as were five of the ten items from earlier knowledge surveys. These items were supplemented with 11 new items directly derived from module assessments or written by the instructor to represent QL skills as the most fundamental to geology.

For the 2008 course assessment, the SSAC team felt that including module assessment items was redundant and that a more general assessment of QL skills should be conducted. As a result, the majority of items from the knowledge component of the 2007 course assessment were replaced in the 2008 with items modeled on and/or extracted from the Wellesley College Quantitative Reasoning Assessment (Wellesley College Quantitative Reasoning Program, 2008). This assessment is a placement test administered to Wellesley's incoming freshmen, designed and vetted over several years by a faculty panel representing the college's Quantitative Reasoning Program. Because the new knowledge survey increased in size from 10 to 16 items, and because these items typically required more effort in their responses than previous years, the SSAC team chose to eliminate the math confidence component of the assessment to maintain the overall assessment length. This decision was made based on the observation that five of the 15 items in the math perception component of the attitude survey directly measured math confidence (specifically, items 1, 2, 8, 13, and 14; Appendix XVI). Though this revised course assessment was successfully administered at the start of the 2008 Computational Geology course, a clerical error occurred at the end of the course wherein the 2007 course assessment was erroneously administered as the post-course assessment. Though the math perception component was identical between the two, the knowledge survey was not. As a result, the SSAC team could infer learning gains only from comparisons of knowledge survey scores between the pre- and post-assessment.

6.5. Results and Discussion

Module assessment results are summarized in Table 6.1−6.2 and shown in Figures 6.2−6.5. Full results are provided in Appendices XI, XIII, XV, and XVII. Learning gains were found for nearly all modules assessed and were particularly high in 2008 (Table 6.2); however, we must add a few caveats prior to interpreting these results.

First and foremost, because modules were utilized in conjunction with lectures and readings covering the same quantitative concepts, it is not possible to attribute learning gains directly to SSAC module use. In addition, some students may have also learned and/or utilized similar quantitative concepts in other courses with a strong quantitative component (e.g., calculus, physics, geomechanics, volcanology. Finally, due to the issues that arose in the 2005 and 2006 course years that stemmed primarily from improper assessment alignment with module goals, student participation, and burn-out may have also impacted assessment results for those years. This is particularly relevant to results from 2005, which demonstrated the only decreases from pre- to post-module assessment observed for the four-year period. Results from the 2007 and 2008 course years are likely to be more representative of actual student learning due to the revisions of the modules and assessments (including assessment administration), made in response to those issues mentioned above. Despite these caveats, however, we can reasonably assume that learning gains identified in module assessments can be attributed primarily to the pedagogy implemented in Computational Geology. The use of SSAC modules as homework-based exercises reinforcing quantitative concepts and skills covered in readings and in-class lectures and problem-solving activities appears to be a successful strategy for improving student QL.

Table 6.1. Computational Geology pre- and post-module assessment scores, 2005-2008

	2005 (*n* = 11)		2006 (*n* = 17)		2007 (*n* = 11)		2008 (*n* = 12)	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post
How Large Is A Ton of Rock? Thinking About Rock Density	0.53	0.82	0.25	0.50	0.33	0.64	0.00	0.57
Earth's Planetary Density: Constraining What We Think About the Earth's Interior	0.45	0.77	0.38	0.71				
Earthquake Magnitude: How Do We Compare The Size of Earthquakes?	0.39	0.58						
Vertical Profile of Stream Velocity: At What Depth is the Average?	0.33	0.75						
Radioactive Decay and Popping Popcorn: Understanding the Rate Law	0.38	0.64	0.26	0.50	0.32	0.60	0.25	0.75
Understanding Radioactivity in Geology: Understanding the Decay Constant	0.83	0.33						
Understanding Radioactivity in Geology: How Did We Get to the Understanding We Have Today?	0.11	0.78						
Understanding Radioactivity in Geology: Calculating Age from the Daughter/Parent Ratio	0.50	0.29						
Is It Hot in Here? Spreadsheeting Conversions in the English and Metric Systems			0.39	0.79	0.76	0.96	0.67	1.00
How Far is Yonder Mountain? A Trig Problem			0.44	0.56			0.53	0.90
A Look at High School Dropout Rates: Average Rates of Change and Trend Lines			0.55	0.71				
How Large is the Great Pyramid of Giza? Would It Make A Wall That Would Enclose France?			0.02	0.39	0.14	0.49	0.44	0.89
Shaking Ground: Linking Earthquake Magnitude and Intensity			0.51	0.61	0.63	0.92	0.61	0.93
Earthquake Magnitude: How Can We Compare the Sizes of Earthquakes?					0.61	0.91		
Calibrating a Pipettor					0.24	0.66		
Frequency of Large Earthquakes: Introducing Some Elementary Statistical Descriptors					0.25	0.45	0.29	0.79
From Isotopes to Temperature: Working With a Temperature Equation					0.32	0.55	0.50	0.86
Carbon Sequestration in Campus Trees					0.33	0.58	0.17	0.70
Calculating the Volume of a Box: A Look at Significant Figures							0.04	0.61
How Large Is A Ton of Rock? II: Thinking About Rock Composition							0.67	0.83
Let's Take a Hike in Catoctin Mountain Park							0.67	1.00
Powers of 2: Many Grains of Wheat							0.36	0.93

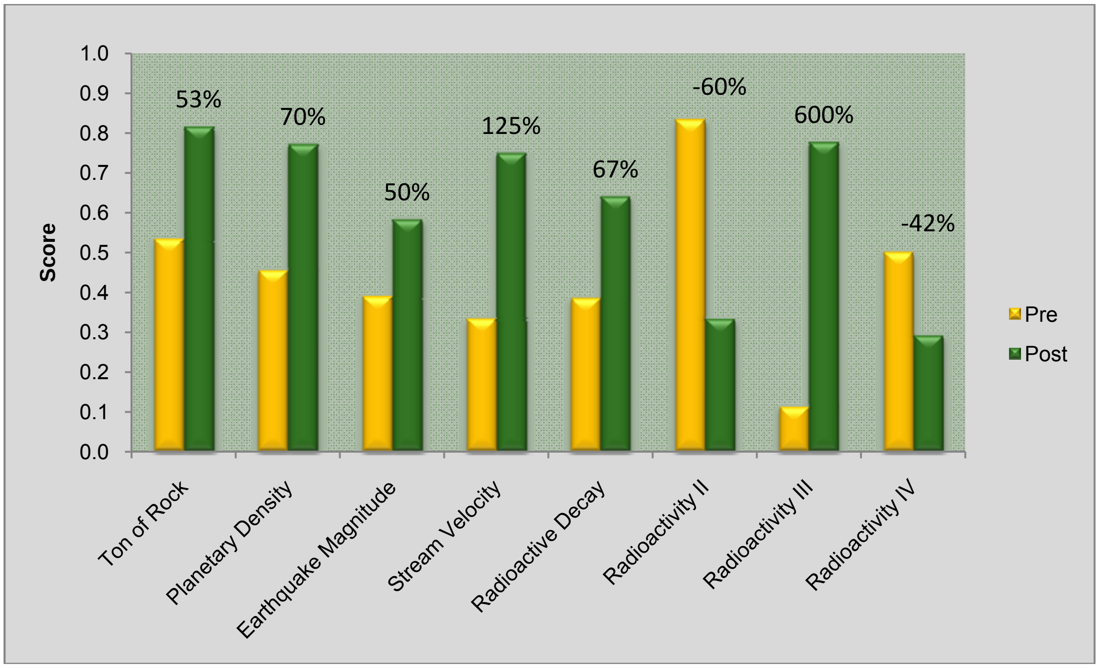

Figure 6.2. Pre- and post-assessment scores for modules administered in 2005. Percent increase and decrease in score noted for each module.

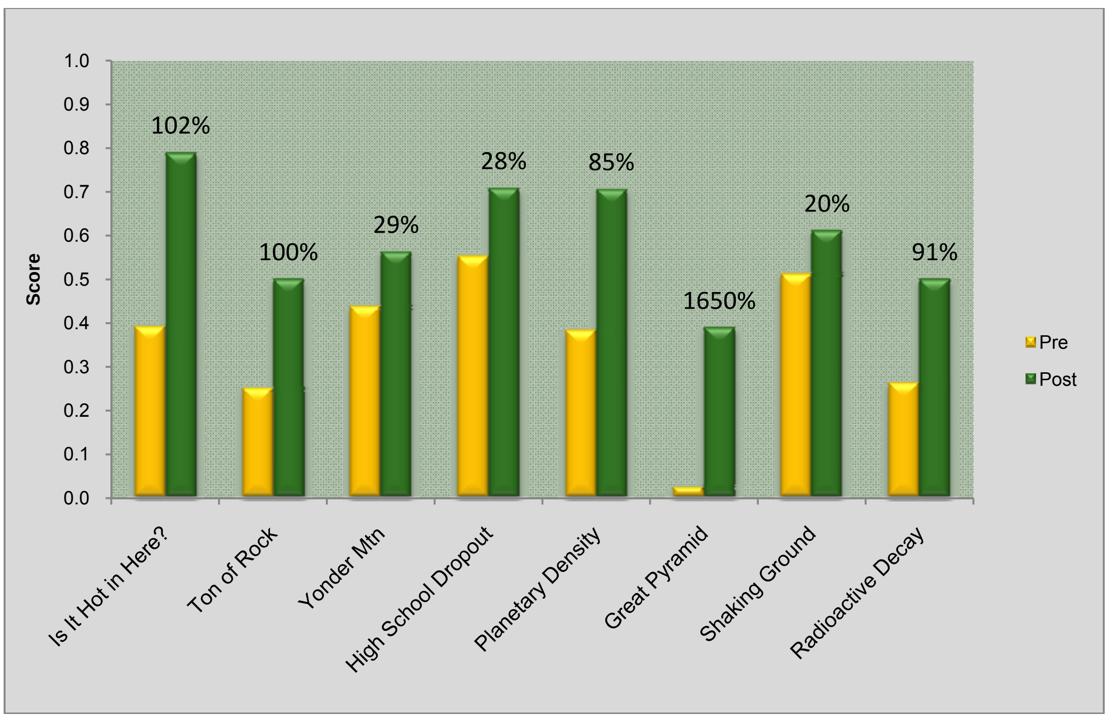

Figure 6.3. Pre- and post-assessment scores for modules administered in 2006. Percent increase in score noted for each module.

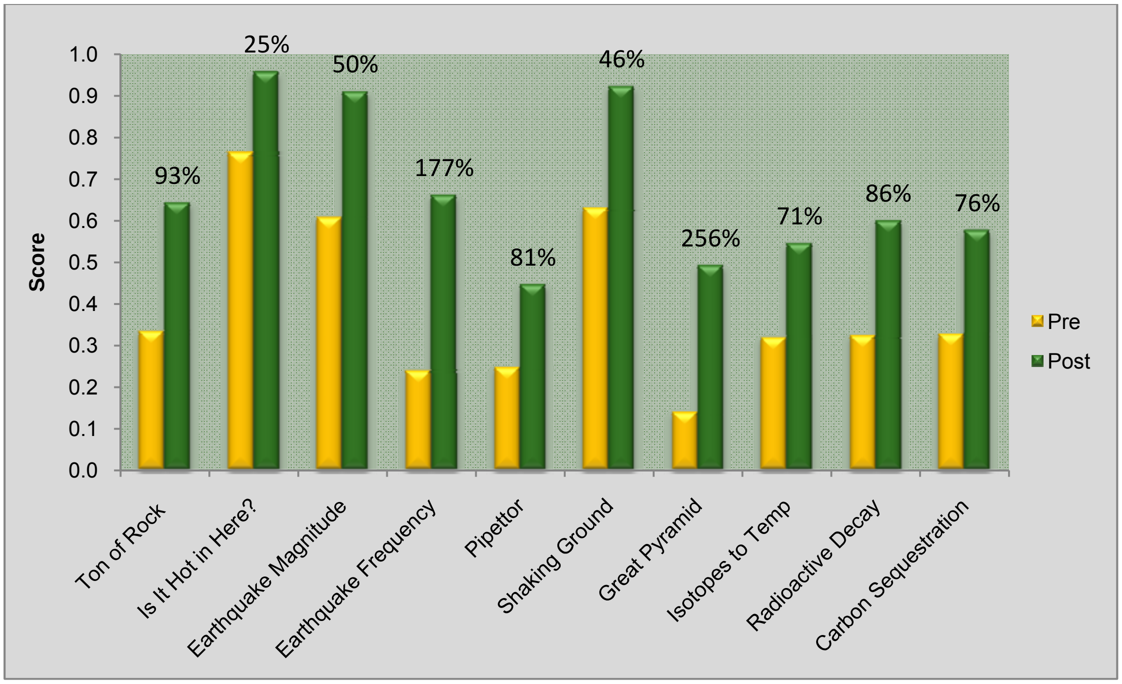

Figure 6.4. Pre- and post-assessment scores for modules administered in 2007. Percent increase in score noted for each module.

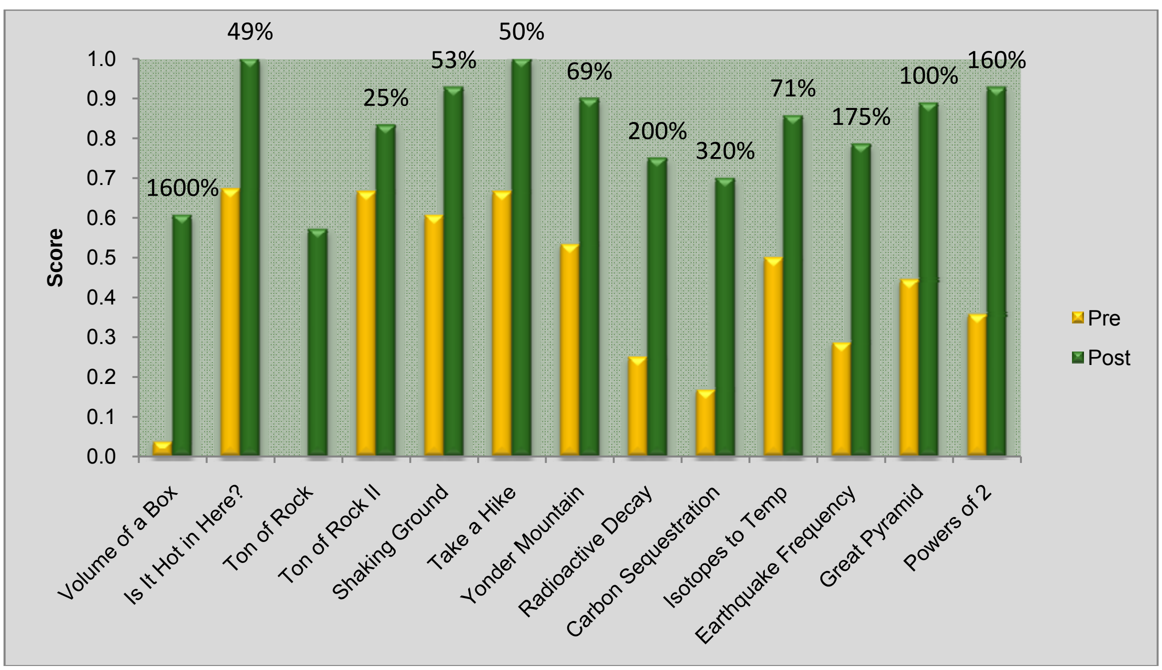

Figure 6.5. Pre- and post-assessment scores for modules administered in 2008. Percent increase in score noted for each module.

Table 6.2. Summary of average scores of pre- and post-module assessments, 2005-2008

	2005 (*n* = 11)		2006 (*n* = 17)		2007 (*n* = 11)		2008 (*n* = 12)	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post
Score	0.44	0.62	0.35	0.60	0.39	0.68	0.40	0.83
Stdev	0.20	0.21	0.17	0.13	0.20	0.19	0.24	0.14

Course assessment results are summarized in Table 6.3 and provided in full in Appendices X, XII, XIV, and XVI. Because the majority of students routinely reported high levels of confidence based on responses given for the calibration component of the course assessment, using these items as benchmarks for comparisons to gains in math confidence was not useful. Regardless, math confidence increased from pre- to post-assessment from 2005 to 2007. Similarly, knowledge survey scores nearly doubled from pre- to post-assessment in 2005 and 2006. Collectively, these data demonstrate that even though modules had not yet undergone revision in the first two assessment years, students still exhibited gains in both confidence and ability.

Student perception of their math abilities and their confidence at using math increased in 2007 (by a total of 41 and 27%, respectively), and their performance on the knowledge survey increased only by 50%. This was approximately half the learning gain measured in 2005-2006, despite the increase in math confidence from 2006 to 2007. This may be an artifact of the change in the knowledge survey between 2006 and 2007. Additionally, pre-assessment scores in 2007 were higher than 2006 (Figures 6.3-6.4, Table 6.2), indicating that students entered the course with a slightly better initial understanding of the QL skills to be addressed during the semester, which may have reduced their potential learning gains compared to previous years.

Results from the 2008 course assessments are difficult to interpret due to the error in pre- and post-assessment administration; however the math perception component of the attitude survey was identical between assessments and demonstrated a much reduced shift toward positive perception compared to 2007 (Table 6.3). The cause for this is unknown, but may also be attributable to better understanding of QL skills by that year's students at the start of the course. Despite the increase in length and the degree of complexity of items on the 2008 pre-course assessment, students scored higher on it than any of the preceding years. If this is a measure of student skills brought to the course, then it may be an indicator that little in the way of more positive perceptions toward their math abilities should be expected.

Like the module assessments, course assessments cannot be used as an indication that student learning and attitudes/perceptions towards math were directly influenced by the modules themselves. Instead, the pedagogy of Computational Geology as a whole is likely to be responsible for shifts from pre- to post-course assessment. While it is possible that some shifts may also be attributable to student experiences outside the Computational Geology course (i.e., other quantitatively-rich courses), the major emphasis placed in the Computational Geology pedagogy on improving QL and providing positive learning experiences make it more likely to exert the stronger influence on learning gains and attitudes/perceptions toward math.

Table 6.3. Results of Computational Geology pre- and post-course assessments, 2005-2008 (all numbers given as numbers of responses, except where indicated as a percent)

	2005	2006		2007	2008
	n = 11	*n* = 17		*n* = 11	*n* = 12
Calibration Confidence			***Math Perception***		
Total Confidence Increase	52	54	Total Positive Shifts	88	32
Total Confidence Decrease	24	47	Total Negative Shifts	21	30
Net Change (%)	14.14	2.29	Net Change (%)	40.61	1.11
Math Confidence			***Math Confidence***		
Total Confidence Increase	98	114	Total Confidence Increase	51	*n/a*
Total Confidence Decrease	36	50	Total Confidence Decrease	21	*n/a*
Net Change (%)	31.31	20.92	Net Change (%)	27.3	*n/a*
Knowledge Survey			***Knowledge Survey***		
Pre-Assessment Score	0.30	0.27	Pre-assessment score	0.35	0.41
Post-Assessment Score	0.59	0.53	Post-assessment score	0.53	0.65
% Change	96.97	95.65	*% Change*	50	56.96

6.6. Lessons Learned

Over the four-year history of assessment in Computational Geology at USF, the SSAC-Geology team learned several important things. First and foremost, when assessment plays such a major role in a course, it is critical that assessors devise an implementation strategy that easily integrates the assessment into the course framework. Without this forethought, assessment inevitably becomes burdensome to all involved, and it may reduce the reliability of the assessment as an accurate portrayal of student attitudes and knowledge gains. We also learned that incentive was a requirement to ensure responses were representative of actual student knowledge and ability. By abandoning the blind-assessment strategy in favor of one in which the participants were identified, module assessments became like any graded exercise (e.g., homework, quizzes, and exams) where students are motivated to perform to the best of their abilities. In addition, the reduction in the frequency of in-class assessments brought about by shifting post-assessments to graded quizzes and exams brought more information by providing a measure of semester-long retention of QL skills as well as allowing students the opportunity to recognize what and how they were learning.

Secondly, assessors need to specifically identify what they wish to learn from the assessment itself and design the assessment accordingly in order to both obtain results relevant to the questions at hand, and obtain results that may be reliably interpreted. Though this seems obvious, particularly to those experienced in the field of assessment, we found that accomplishing this task is easier said than done and requires a great deal more foresight and preparation than we originally anticipated. Through trial and error, we were able to design assessments and implementation strategies that eventually met our goals, but we may have been better served by spending more time at the outset identifying these goals and predicting how they could best be met. The revision of SSAC modules, their assessments, and their implementation strategies prior to the 2007 Computational Geology course was a major step forward in obtaining good assessment data. Particular attention was paid to ensuring that the learning goals were specific from the outset so that students clearly understood what they were learning and had a better sense of purpose and direction as they completed it. The need for enhanced communication of goals and expectations for module exercises was echoed in a report compiled by Jen Wenner (University of Wisconsin-Oshkosh), the SSAC project's evaluator for implementation of SSAC-style modules in the USF Department of Geology (Wenner, 2008). Of the 22 USF students surveyed and interviewed that had completed courses where modules were used, the majority agreed that they learned important skills from the modules; however, these students varied widely in their responses regarding why spreadsheets were valuable tools for learning quantitative skills and, therefore, why modules were used in the course curriculum. Wenner concluded that this lack of consensus represented a limited understanding by students of the purpose and benefits/goals of module use, which could ultimately impart a learning barrier, particularly in students already struggling with math avoidance and/or anxiety. She also concluded that the use of multiple modules in a given course, as opposed to only one or two, was beneficial to improving their learning gains, attitudes, and perceptions by providing repeat experiences that fostered greater comfort and ease in module use. Similar findings were reported by Wetzel (2011).

Finally, assessors need to carefully align their assessment goals with the venue best adapted for achieving them. Though the original intent of SSAC assessment was to identify how effective modules were at teaching their quantitative concepts, this was not possible when assessment was implemented in Computational Geology given the course's pedagogy. To identify whether shifts in knowledge and attitudes were directly attributable to modules themselves, the course lectures and readings must be abandoned, a dangerous strategy that becomes circular when the course is designed to improve student QL using modules whose effectiveness is yet untested. This issue is commonly encountered in the assessment community and exemplifies the effects of population, budget, and time constraints on assessment. In the case of SSAC, the best venue for assessment for isolating module effectiveness would be a low-risk environment where grades and learning are not at stake. This would require the recruitment of subject populations (which in itself may impart some bias on results) as well as the additional time, facilities, personnel, and ultimately funding, necessary to facilitate the assessment properly. Such an assessment was conducted by Wetzel (2011), wherein 21 undergraduates from varying disciplines were recruited to complete one or more modules and their associated pre- and post-module assessments. These students were also interviewed at the start and conclusion of the study to discuss their attitudes towards math and whether they felt the modules helped them learn. Wetzel found that students demonstrated positive learning gains for QL and Excel skills, and for the most part, agreed that modules were successful in helping them learn. Wetzel also conducted in-class assessments similar to those conducted in Computational Geology, and achieved similar results. This supports that the pedagogy used in Computational Geology was successful both in improving student QL and improving student attitudes/perceptions toward math. This is valuable information for any instructor looking for strategies to improve QL in their curriculum by the incorporation of SSAC modules, and can serve as a platform from which future courses are adapted and assessed.

Lessons learned in the assessment of SSAC modules in Computational Geology have already been applied to the assessment of other SSAC-style programs. To assess learning gains as a result of module use in the Geology of National Parks course, considerable time and effort was spent with assessment specialists preparing a course assessment that both targeted what assessors wanted to learn, and could be seamlessly integrated into the course itself. To date, this assessment has been administered twice, in Fall 2009 and Spring 2010. Results from the Fall 2009 GNP course indicate modest learning gains over the course of the semester prior to addition of new modules to the curriculum generated from NSF-CCLI funding (SERC, 2010). Results from the Spring 2010 course are under review. Though designed to address learning goals from module use in conjunction with course exercises, the assessment was intentionally administered prior to the addition of the module series to provide “control” data that could be compared to similar data gathered once these modules are included during the 2010−2011 academic year.

6.7. Summary:

The implementation of SSAC modules in the USF Department of Geology, specifically in the Computational Geology course, taught the SSAC-Geology team that when assessment is a vital and continuous component required to determine the efficacy of a curriculum or project, its design and implementation strategy is critical to the reliability of results. As previously stated, this should come as no surprise, particularly to those with experience in the field of assessment. What we were surprised to learn was the degree of complexity associated with designing and implementing a strategy that was simultaneously best suited to the goals of the project and best adapted to the environment in which the assessment was administered. This required much more consideration and effort than originally thought and presents a conundrum for projects, which, like SSAC, are designed to be adaptable to a wide variety of audiences and environments. If the value of a project beyond its function is its versatility, the use of an assessment standardized in both design and implementation to determine its efficacy is likely to ignore the aspects that make learning environments (e.g., instructors, pedagogies, settings, and audiences) unique. This would serve not only to skew the data and impart error in its interpretation, but also to limit the project's capacity to grow and evolve. As a result, versatile projects such as SSAC require flexibility in the assessment process, a factor that must be recognized and supported by funding agencies, and benefit greatly from close partnerships with assessment specialists.

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CHAPTER 7:

CONCLUDING REMARKS

7.1. Research Overview

This dissertation provides ample evidence to substantiate the hypothesis that microorganisms influence limestone dissolution in cave settings. Though the main objective was to determine their contribution to H_2CO_3-dissolution through the respiration of CO_2, it was clear from other geochemical observations that these organisms could influence dissolution through a variety of mechanisms including acidification during oxidation reactions, promotion of calcite inhibition through the release of humic substances and inorganic ions during the decomposition of organic matter, and mechanical weathering (as well as calcite inhibition in some cases) during substrate colonization. It is important to note that these studies were conducted at sites particularly open and susceptible to surface processes. In particular, the continuous availability of organic matter in the form of dissolved organic carbon (DOC) leached from surface soils or the direct infilling of organic matter from the surface at these sites eliminates the availability of nutrients as a limiting factor for growth. As such, the majority of organisms comprising microbial colonies here are interpreted to be heterotrophic, especially in light of experiments observing biogenic CO_2 respired from cave substrates. This must be considered before these results can be extrapolated to cave settings that are more closed and/or where organic matter is a limited; however, numerous studies conducted in such caves document the widespread growth of microbial communities dominated by chemolithotrophs, which are adapted to these conditions and utilize ions grazed from cave rock as energy resources. Because such studies from more closed cave environments are relatively more common in the karst literature, the research presented in this dissertation compliments those studies by offering a perspective from caves of a different character and a starting point from which future research can be conducted. For example, genetic studies characterizing microbial communities coupled with long-term studies of specific geochemical parameters (specifically major ions and isotopes of N, S and Fe) would more effectively target which biogenic processes (respiration, oxidation, calcite inhibition and/or mechanical weathering) are most likely to influence dissolution in a given cave. From there, laboratory studies could be conducted to quantify the effects of these processes on limestone to more effectively model their specific contributions to overall dissolution. In the end, the collective efforts of these studies provide a fascinating insight on geologic processes once considered to be largely abiotic, forcing a change in the way we think about them on an individual basis and in a broader context.

This dissertation also provided a unique perspective on the assessment of educational programs. By nature, programs such as Spreadsheets Across the Curriculum (SSAC) – designed to be adaptable to a wide range of educational settings, implementation strategies, and disciplines – are highly valued for their versatility, but incredibly difficult to assess. Even within a single course where the majority of assessments were conducted, these underwent significant modifications in both content and implementation before an effective strategy was identified. Collaboration with colleagues as well as assessment specialists was critical in this process, which benefitted SSAC greatly through the enhancement of both modules and assessments. These improvements led to more reliable data that documented clear learning gains and positive shifts in math comfort and perception, and though these gains could not be attributed directly to the modules, they were evidence of the successful incorporation of modules in the course's pedagogy. At the same time, this study brought to light the realization that determining student learning outcomes required much more foresight and planning than initially thought in order to achieve meaningful results, and requires that assessment strategies be as customizable as the modules themselves. This is a factor that is easy to underestimate and may not be feasible for many projects operating under restricted time, staffing, and budgetary restraints. Nevertheless, it is a requirement that deserves careful consideration in any education initiative where student-learning gains are an objective, and should be addressed as a collaborative effort between project PIs, the assessment community, and funding agencies.

Though both research efforts addressed in this dissertation are separate and unique, their common thread is that they are both demonstrative of gradual, yet important, shifts in thinking in both fields that are based on the collective efforts of the many rather than the few. In my mind, this signifies the recognition and acknowledgement of researchers everywhere that the modern advancement of their fields depends on collaboration and interdisciplinary approaches. Evidence of this can be found in a quick citation analysis using ISI Web of Science. For 1980, 56% of the references returned (90 of 162) using "geology" as the topical search term were authored by a single researcher (Thomson Reuters, 2010). When the same search was performed for 2009, this figure dropped to 18% (176 of 977 references).

Perhaps the shift toward collaborative research is one of the things Dr. William White had in mind when he considered the types of major breakthroughs put forth by "young minds." It certainly alters the way we view the world around us, as a series of interconnected, complex webs rather than singular, disparate ideas. Now the foundations laid down by our forbearers can be built upon with new ideas to produce a much more realistic view of how a system works—an approach that inspired the research conducted in this dissertation. If the question posed of Dr. White in 2006 regarded the future of research in general rather than karst research specifically, I feel safe in the assumption that he would acknowledge the great leaps in knowledge to be made when we venture out of our own offices, our own labs, our own fields, and even our own minds? to explore the goings on in others.

7.2. References

Thomson Reuters., 2010. ISI Web of Knowledge, Web of Science. Thomson Reuters. URL: http://apps.isiknowledge.com. Date accessed: June 2010.

APPENDICES

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
03/15/08	*	20.9	14.1	*	21.8	21.8
03/16/08	*	21.0	21.1	*	21.5	21.9
03/17/08	*	20.8	24.0	*	21.5	21.9
03/18/08	*	20.8	19.5	*	21.5	21.9
03/19/08	*	20.9	20.1	*	21.5	21.9
03/20/08	*	21.0	22.6	*	21.5	21.9
03/21/08	*	20.5	19.3	*	21.4	21.9
03/22/08	*	20.7	16.8	*	21.4	21.9
03/23/08	*	20.9	17.8	*	21.5	21.9
03/24/08	*	20.6	20.3	*	21.4	21.9
03/25/08	*	19.9	15.1	*	21.3	21.8
03/26/08	*	19.9	11.7	*	21.3	21.8
03/27/08	*	20.3	14.8	*	21.3	21.8
03/28/08	*	20.4	17.0	*	21.3	21.9
03/29/08	*	20.6	18.3	*	21.4	21.9
03/30/08	*	20.7	20.2	*	21.4	21.9
03/31/08	*	20.8	19.1	*	21.5	21.9
04/01/08	*	21.0	21.0	*	21.5	22.0
04/02/08	*	21.0	21.2	*	21.6	22.0
04/03/08	*	21.1	21.7	*	21.6	22.0
04/04/08	*	21.1	22.1	*	21.6	22.0
04/05/08	*	21.2	22.2	*	21.7	22.0
04/06/08	*	21.2	22.7	*	21.7	22.0
04/07/08	*	21.2	18.8	*	21.7	22.0
04/08/08	*	21.2	20.3	*	21.7	22.0
04/09/08	*	21.3	20.6	*	21.7	22.0
04/10/08	*	21.2	22.1	*	21.7	22.0
04/11/08	*	21.2	21.8	*	21.7	22.0
04/12/08	*	21.2	21.9	*	21.7	22.0
04/13/08	*	21.1	22.6	*	21.6	22.0
04/14/08	21.7	20.5	18.1	*	21.5	22.0
04/15/08	17.2	20.1	14.5	*	21.4	21.9
04/16/08	16.7	19.9	11.7	*	21.3	21.9
04/17/08	16.6	19.9	13.4	*	21.3	21.8
04/18/08	17.3	20.4	15.3	*	21.3	21.9
04/19/08	17.9	20.7	18.1	*	21.4	21.9
04/20/08	18.2	20.9	20.3	*	21.4	21.9
04/21/08	18.1	20.8	20.8	*	21.4	21.9
04/22/08	18.3	20.8	19.8	*	21.4	21.9
04/23/08	18.3	20.8	20.2	*	21.4	21.9
04/24/08	18.7	20.9	19.7	*	21.5	21.9
04/25/08	19.0	21.0	22.3	*	21.5	21.9
04/26/08	19.2	*	22.3	*	21.5	*
04/27/08	19.1	*	21.5	*	21.5	*
04/28/08	19.6	*	21.9	*	21.5	*
04/29/08	19.3	*	22.0	*	21.5	*
04/30/08	18.4	*	20.5	*	21.5	*
05/01/08	18.2	*	18.8	*	21.5	*
05/02/08	18.5	*	20.0	*	21.5	*

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
05/03/08	18.9	*	21.3	*	21.5	*
05/04/08	19.3	*	22.0	*	21.6	*
05/05/08	19.5	*	22.8	*	21.6	*
05/06/08	19.2	*	22.4	*	21.6	*
05/07/08	19.3	*	22.6	*	21.6	*
05/08/08	19.9	*	23.8	*	21.6	*
05/09/08	20.7	*	25.2	*	21.7	*
05/10/08	21.4	*	25.3	*	21.7	*
05/11/08	21.9	*	26.4	*	21.7	*
05/12/08	20.8	*	26.2	*	21.3	*
05/13/08	19.4	*	22.6	*	20.5	*
05/14/08	19.5	*	21.0	*	20.1	*
05/15/08	19.6	*	22.2	*	19.7	*
05/16/08	20.4	*	23.0	*	20.2	*
05/17/08	20.9	*	24.7	*	20.4	*
05/18/08	21.2	*	25.2	*	20.6	*
05/19/08	21.3	*	24.0	*	20.8	*
05/20/08	21.4	*	25.2	*	20.9	*
05/21/08	20.8	*	24.0	*	20.5	*
05/22/08	20.8	*	24.5	*	20.8	*
05/23/08	21.3	*	23.3	*	21.0	*
05/24/08	21.6	*	26.0	*	21.0	*
05/25/08	21.5	*	25.8	*	21.2	*
05/26/08	20.9	*	22.8	*	20.5	*
05/27/08	20.5	*	22.9	*	20.0	*
05/28/08	20.4	*	23.8	*	19.9	*
05/29/08	20.5	*	25.2	*	20.3	*
05/30/08	20.7	*	25.9	*	20.8	*
05/31/08	21.0	*	26.4	*	20.8	*
06/01/08	21.4	*	25.2	*	21.0	*
06/02/08	21.7	*	26.1	*	21.1	*
06/03/08	21.7	*	26.3	*	21.1	*
06/04/08	21.8	*	25.7	*	21.2	*
06/05/08	21.9	*	28.3	*	21.5	*
06/06/08	22.1	*	27.8	*	21.6	*
06/07/08	21.9	*	27.2	*	21.6	*
06/08/08	21.8	*	24.8	*	21.5	*
06/09/08	22.0	*	24.9	*	21.6	*
06/10/08	22.0	*	24.8	*	21.7	*
06/11/08	21.8	*	24.8	*	21.6	*
06/12/08	21.9	*	23.9	*	21.6	*
06/13/08	21.9	*	23.6	*	21.5	*
06/14/08	22.1	21.4	25.4	*	21.8	22.0
06/15/08	21.9	22.0	23.6	*	22.0	22.1
06/16/08	21.9	22.0	24.0	*	22.0	22.1
06/17/08	22.3	22.1	26.2	*	22.0	22.1
06/18/08	22.6	22.2	26.4	*	22.0	22.1
06/19/08	22.5	22.2	25.5	*	22.0	22.1
06/20/08	22.5	22.1	26.6	*	22.0	22.1

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
06/21/08	22.4	22.2	23.4	*	22.0	22.1
06/22/08	22.2	22.1	*	*	22.0	22.1
06/23/08	22.4	22.1	*	*	22.0	22.1
06/24/08	22.5	22.2	*	*	22.0	22.1
06/25/08	22.4	22.2	*	*	22.0	22.1
06/26/08	22.1	21.9	*	*	22.0	22.1
06/27/08	22.2	22.0	*	*	22.0	22.1
06/28/08	22.4	22.2	25.0	*	22.0	22.1
06/29/08	22.4	22.1	25.9	*	22.0	22.1
06/30/08	22.6	22.3	24.4	*	22.0	22.1
07/01/08	22.5	22.3	24.4	*	22.0	22.1
07/02/08	22.3	22.1	24.1	*	22.0	22.1
07/03/08	22.2	22.1	23.3	*	22.0	22.1
07/04/08	22.3	22.1	25.1	*	22.0	22.1
07/05/08	22.3	22.1	24.7	*	22.0	22.1
07/06/08	22.4	22.2	24.9	*	22.2	22.2
07/07/08	22.4	22.2	23.5	*	22.0	22.1
07/08/08	22.5	22.2	23.9	*	22.0	22.2
07/09/08	22.5	22.2	22.9	*	22.0	22.2
07/10/08	22.8	22.3	25.5	*	22.1	22.2
07/11/08	23.0	22.4	26.9	*	22.1	22.2
07/12/08	22.9	22.4	25.0	*	22.1	22.2
07/13/08	23.0	22.4	24.2	*	22.1	22.2
07/14/08	23.0	22.4	25.0	*	22.1	22.2
07/15/08	23.1	22.5	26.3	*	22.1	22.2
07/16/08	23.0	22.5	24.1	*	22.1	22.2
07/17/08	22.9	22.5	24.2	*	22.1	22.3
07/18/08	23.1	22.5	24.6	*	22.1	22.3
07/19/08	23.3	22.5	25.8	*	22.1	22.3
07/20/08	23.3	22.5	27.0	*	22.1	22.3
07/21/08	23.3	22.5	27.1	*	22.1	22.3
07/22/08	23.3	22.6	24.6	*	22.1	22.3
07/23/08	23.1	22.6	24.2	*	22.1	22.3
07/24/08	23.0	22.5	25.0	*	22.1	22.3
07/25/08	23.2	22.5	25.9	*	22.1	22.3
07/26/08	23.2	22.5	25.3	*	22.1	22.3
07/27/08	23.4	22.5	25.4	*	22.1	22.3
07/28/08	23.4	22.6	26.3	*	22.1	22.3
07/29/08	23.5	22.6	25.4	*	22.1	22.3
07/30/08	23.4	22.6	24.2	*	22.1	22.3
07/31/08	23.3	22.6	23.7	*	22.1	22.3
08/01/08	23.4	22.6	24.4	*	22.1	22.3
08/02/08	23.4	22.6	24.3	*	22.1	22.4
08/03/08	23.2	22.6	25.7	*	22.1	22.3
08/04/08	23.3	22.5	26.0	*	22.1	22.4
08/05/08	23.3	22.5	26.2	*	22.1	22.4
08/06/08	23.4	22.5	26.6	*	22.1	22.4
08/07/08	23.8	22.6	27.7	*	22.1	22.4
08/08/08	24.0	22.6	27.1	*	22.1	22.4

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
08/09/08	23.9	22.7	27.0	*	22.1	22.4
08/10/08	23.4	22.8	25.7	*	22.1	22.4
08/11/08	23.2	22.5	25.7	*	22.1	22.4
08/12/08	23.3	22.6	23.4	*	22.1	22.4
08/13/08	23.5	22.6	25.4	*	22.1	22.4
08/14/08	23.5	22.7	23.5	*	22.1	22.4
08/15/08	23.4	22.7	24.1	*	22.1	22.4
08/16/08	23.5	22.7	25.4	*	22.1	22.4
08/17/08	23.3	22.7	24.4	*	22.1	22.4
08/18/08	23.5	22.7	25.0	*	22.2	22.5
08/19/08	23.4	22.8	24.7	*	22.2	22.5
08/20/08	23.5	22.8	25.1	*	22.2	22.5
08/21/08	23.7	22.9	24.8	*	22.3	22.5
08/22/08	23.8	23.0	24.7	*	22.2	22.5
08/23/08	23.9	22.9	25.1	*	22.2	22.5
08/24/08	23.7	22.7	24.7	*	22.2	22.5
08/25/08	23.7	22.7	24.8	*	22.2	22.5
08/26/08	23.8	22.7	25.7	*	22.2	22.5
08/27/08	23.9	22.7	26.7	*	22.3	22.5
08/28/08	23.9	22.7	26.7	*	22.4	22.5
08/29/08	23.8	22.7	26.3	*	22.3	22.5
08/30/08	23.8	22.8	25.1	*	22.3	22.5
08/31/08	23.9	22.8	26.3	*	22.3	22.5
09/01/08	24.0	22.8	27.4	*	22.5	22.6
09/02/08	23.9	22.9	25.8	*	22.3	22.6
09/03/08	23.8	23.0	25.9	*	22.2	22.6
09/04/08	23.6	23.1	25.6	*	22.2	22.7
09/05/08	23.6	23.2	25.8	*	22.2	22.7
09/06/08	23.8	23.2	26.9	*	22.2	22.7
09/07/08	23.6	23.2	26.0	*	22.2	22.7
09/08/08	23.6	23.1	26.1	*	22.2	22.7
09/09/08	23.8	23.3	27.1	*	22.2	22.8
09/10/08	24.0	23.4	26.5	*	22.2	22.8
09/11/08	24.1	23.5	27.9	*	22.3	22.8
09/12/08	24.0	23.4	27.1	*	22.3	22.8
09/13/08	23.9	23.3	26.7	*	22.3	22.8
09/14/08	23.8	23.1	25.8	*	22.2	22.8
09/15/08	23.7	23.1	25.4	*	22.2	22.8
09/16/08	23.8	23.2	26.0	*	22.2	22.7
09/17/08	23.6	23.0	24.8	*	22.2	22.6
09/18/08	23.4	23.0	25.3	*	22.2	22.7
09/19/08	23.2	22.7	24.4	*	22.2	22.7
09/20/08	23.1	22.7	24.4	*	22.2	22.7
09/21/08	23.3	23.0	25.9	*	22.2	22.7
09/22/08	23.4	23.1	25.3	*	22.2	22.6
09/23/08	23.3	23.0	24.9	*	22.2	22.4
09/24/08	23.0	22.7	23.3	*	22.2	22.2
09/25/08	22.2	22.0	21.4	*	22.1	22.1
09/26/08	21.8	21.8	21.7	*	22.1	22.2

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
09/27/08	21.1	21.1	21.1	*	22.0	22.2
09/28/08	21.5	21.7	22.7	*	22.0	22.2
09/29/08	22.1	22.1	24.2	*	22.0	22.1
09/30/08	22.3	22.3	23.4	*	22.1	22.1
10/01/08	22.3	22.2	23.7	*	22.1	22.1
10/02/08	21.5	21.6	20.8	*	22.0	22.1
10/03/08	21.2	21.5	21.5	*	22.0	22.1
10/04/08	21.4	21.7	22.7	*	22.0	22.2
10/05/08	21.6	22.0	23.4	*	22.0	22.2
10/06/08	22.0	22.2	24.1	*	22.0	22.2
10/07/08	22.3	22.3	23.9	*	22.1	22.2
10/08/08	22.4	22.3	24.1	*	22.1	22.2
10/09/08	22.6	22.4	24.2	*	22.1	22.3
10/10/08	22.5	22.4	24.3	*	22.1	22.3
10/11/08	22.5	22.5	24.7	*	22.1	22.3
10/12/08	22.6	22.5	25.1	*	22.1	22.2
10/13/08	22.7	22.6	25.5	*	22.1	22.1
10/14/08	22.5	22.5	24.4	*	22.1	22.1
10/15/08	21.9	22.0	22.3	*	22.0	22.1
10/16/08	21.6	22.1	21.8	*	22.0	22.0
10/17/08	21.2	21.5	21.1	*	22.0	22.0
10/18/08	21.2	21.6	20.7	*	21.9	22.0
10/19/08	20.5	21.0	18.0	*	21.9	22.0
10/20/08	20.4	21.1	19.5	*	21.9	22.1
10/21/08	20.3	20.9	18.8	*	21.8	22.1
10/22/08	20.2	20.9	19.3	*	21.9	22.0
10/23/08	20.7	21.6	22.5	*	21.9	21.9
10/24/08	21.3	21.9	22.3	*	22.0	21.8
10/25/08	21.2	21.8	21.6	*	21.8	21.7
10/26/08	21.4	20.3	17.0	*	21.7	21.6
10/27/08	20.2	19.8	16.6	*	21.5	21.7
10/28/08	19.3	18.6	11.3	*	21.3	21.8
10/29/08	17.9	17.1	8.9	*	21.2	21.8
10/30/08	16.7	17.4	11.5	*	21.3	21.9
10/31/08	16.5	19.0	16.5	*	21.4	21.9
11/01/08	17.6	19.6	17.7	*	21.5	21.9
11/02/08	18.2	20.2	19.0	*	21.6	21.8
11/03/08	18.8	20.5	20.3	*	21.7	21.8
11/04/08	19.1	20.5	17.7	*	21.6	21.8
11/05/08	19.2	20.2	17.0	*	21.5	21.8
11/06/08	19.1	19.6	16.7	*	21.5	21.7
11/07/08	18.7	19.9	17.8	*	21.5	21.7
11/08/08	18.8	19.8	17.1	*	21.4	21.9
11/09/08	18.7	18.7	13.7	*	21.3	22.0
11/10/08	17.8	18.1	13.0	*	21.3	22.0
11/11/08	17.1	18.9	16.2	*	21.5	22.0
11/12/08	17.4	20.0	21.2	*	21.6	21.9
11/13/08	18.4	20.8	24.4	*	21.6	21.8
11/14/08	19.9	21.1	24.0	*	21.6	21.7

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
11/15/08	20.2	21.2	22.1	*	21.8	21.7
11/16/08	18.1	17.5	10.9	*	21.5	21.6
11/17/08	16.4	15.9	9.1	*	21.2	21.7
11/18/08	15.9	16.2	10.3	*	21.2	21.7
11/19/08	15.2	15.1	7.3	*	21.1	21.7
11/20/08	14.8	15.2	8.8	*	21.0	21.7
11/21/08	15.4	16.0	11.0	*	21.0	21.6
11/22/08	14.8	15.4	9.1	*	21.0	21.6
11/23/08	15.1	15.9	11.0	*	21.0	21.6
11/24/08	15.3	16.5	12.3	*	21.1	21.6
11/25/08	15.9	17.0	13.5	*	21.2	21.7
11/26/08	14.9	15.2	8.9	*	21.1	21.6
11/27/08	14.5	15.2	10.1	*	20.9	21.6
11/28/08	15.2	16.4	13.5	*	21.1	21.6
11/29/08	15.7	17.1	15.7	*	21.1	21.7
11/30/08	17.0	19.0	18.2	*	21.3	21.8
12/01/08	16.7	17.8	13.6	*	21.4	21.8
12/02/08	15.7	16.3	9.5	*	21.3	21.8
12/03/08	14.3	14.6	7.6	*	21.0	21.6
12/04/08	14.9	16.2	12.5	*	21.1	21.7
12/05/08	15.4	16.8	14.2	*	21.2	21.7
12/06/08	16.2	18.1	17.0	*	21.3	21.6
12/07/08	15.9	16.7	12.1	*	21.3	21.9
12/08/08	14.6	15.2	10.4	*	21.1	21.9
12/09/08	15.7	17.5	16.8	*	21.2	21.9
12/10/08	17.1	19.1	21.6	*	21.4	22.0
12/11/08	17.7	19.6	19.5	*	21.5	22.0
12/12/08	16.6	17.1	12.0	*	21.4	22.0
12/13/08	15.3	15.9	10.4	*	21.3	21.9
12/14/08	15.9	17.5	16.1	*	21.3	21.9
12/15/08	16.9	18.7	19.5	*	21.4	22.0
12/16/08	17.3	18.8	18.7	*	21.5	22.0
12/17/08	17.5	19.0	19.1	*	21.5	22.0
12/18/08	17.6	19.0	18.7	*	21.5	22.0
12/19/08	17.6	18.8	17.8	*	21.5	22.0
12/20/08	17.4	18.4	16.1	*	21.5	22.0
12/21/08	17.5	18.8	17.0	*	21.5	22.0
12/22/08	16.1	16.3	10.2	*	21.2	22.0
12/23/08	15.3	16.1	12.3	*	21.4	21.9
12/24/08	16.6	18.5	19.6	*	21.5	22.0
12/25/08	17.5	19.2	20.5	*	21.6	22.0
12/26/08	18.0	19.5	21.4	*	21.6	22.0
12/27/08	17.9	19.2	19.4	*	21.6	22.0
12/28/08	17.8	18.9	18.5	*	21.5	22.0
12/29/08	17.4	18.4	17.1	*	21.5	22.0
12/30/08	17.0	17.6	15.6	*	21.3	22.0
12/31/08	15.8	16.3	12.2	*	21.3	22.0
01/01/09	15.8	16.8	13.2	*	21.3	22.0
01/02/09	16.3	17.2	16.4	*	21.4	22.0

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
01/03/09	16.6	17.7	16.3	*	21.4	22.0
01/04/09	17.0	18.5	18.4	*	21.5	22.0
01/05/09	17.0	18.2	17.3	*	21.5	22.0
01/06/09	17.6	19.1	19.7	*	21.6	22.0
01/07/09	17.8	19.0	17.6	*	21.6	22.0
01/08/09	15.8	16.2	12.0	*	21.4	22.0
01/09/09	15.4	16.0	12.1	*	21.3	22.0
01/10/09	15.2	15.9	13.4	*	21.4	22.0
01/11/09	16.1	17.6	16.9	*	21.4	22.0
01/12/09	16.5	17.7	14.5	*	21.4	22.0
01/13/09	16.2	17.1	12.5	*	21.3	21.9
01/14/09	14.8	14.7	8.6	*	21.1	21.9
01/15/09	13.7	13.4	5.9	*	21.1	21.9
01/16/09	13.3	13.9	7.3	*	21.1	21.9
01/17/09	11.3	13.4	6.7	*	21.1	22.0
01/18/09	9.5	14.4	10.1	*	21.2	22.0
01/19/09	13.3	16.9	15.7	*	21.2	21.9
01/20/09	9.3	14.5	8.3	*	20.9	21.8
01/21/09	5.2	11.8	2.4	*	20.8	21.8
01/22/09	4.7	11.2	3.2	*	20.8	21.8
01/23/09	6.3	12.1	6.7	*	20.9	21.8
01/24/09	8.7	13.8	10.7	*	21.1	21.8
01/25/09	12.0	15.9	15.9	*	21.2	21.9
01/26/09	12.3	16.1	15.8	*	21.3	21.9
01/27/09	13.9	17.1	18.1	*	21.4	21.9
01/28/09	16.0	18.3	21.0	*	21.5	22.0
01/29/09	16.7	18.8	18.9	*	21.4	22.0
01/30/09	14.9	17.2	12.6	*	21.2	22.0
01/31/09	13.7	16.9	7.7	*	21.1	22.0
02/01/09	12.9	14.0	8.4	*	21.1	22.0
02/02/09	14.0	14.0	13.3	*	21.2	22.0
02/03/09	13.9	16.2	10.6	*	21.1	22.0
02/04/09	12.3	15.2	5.7	*	20.9	21.9
02/05/09	11.0	13.0	2.2	*	20.9	21.9
02/06/09	10.6	11.4	5.1	*	20.9	21.9
02/07/09	11.5	11.7	9.5	*	21.0	22.0
02/08/09	12.4	13.2	11.9	*	21.1	22.0
02/09/09	12.9	14.3	13.1	*	21.2	22.0
02/10/09	13.7	15.9	15.7	*	21.2	22.0
02/11/09	14.8	17.2	19.1	*	21.3	22.0
02/12/09	16.2	18.4	21.2	*	21.3	22.0
02/13/09	15.4	17.0	16.8	16.0	21.3	22.0
02/14/09	15.3	17.2	17.1	15.3	21.4	22.0
02/15/09	16.0	18.1	19.0	16.2	21.4	22.0
02/16/09	15.7	17.5	16.5	15.7	21.2	22.0
02/17/09	14.4	15.5	12.0	14.4	21.4	22.0
02/18/09	14.7	17.0	16.2	14.8	21.3	22.0
02/19/09	16.0	18.5	19.2	16.1	21.0	21.9
02/20/09	14.5	15.5	11.1	14.3	21.1	22.0

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
02/21/09	13.0	14.0	9.3	13.1	21.2	22.0
02/22/09	13.6	15.5	13.9	13.9	21.1	21.9
02/23/09	13.5	15.2	12.6	13.6	21.1	22.0
02/24/09	13.1	14.7	11.6	13.2	21.2	22.0
02/25/09	13.8	15.9	15.0	14.0	21.2	22.0
02/26/09	14.3	16.2	15.5	14.4	21.3	22.0
02/27/09	14.5	17.4	16.6	14.8	21.3	22.0
02/28/09	15.2	16.9	18.7	15.5	21.1	21.9
03/01/09	14.7	14.1	14.2	15.2	21.0	21.9
03/02/09	12.7	13.3	8.0	13.1	21.0	22.0
03/03/09	11.9	13.9	7.8	12.2	21.1	22.0
03/04/09	12.1	15.2	10.8	12.4	21.2	22.0
03/05/09	13.1	15.6	14.6	13.4	21.2	22.0
03/06/09	13.6	16.1	15.5	13.9	21.2	22.0
03/07/09	14.0	16.5	16.4	14.5	21.2	22.0
03/08/09	14.5	16.7	17.4	15.0	21.3	22.0
03/09/09	14.7	17.1	17.7	15.4	21.3	22.0
03/10/09	15.0	17.4	19.2	15.9	21.3	22.0
03/11/09	15.3	17.7	19.4	16.3	21.4	22.0
03/12/09	15.6	18.2	19.9	16.6	21.4	22.1
03/13/09	16.0	18.5	20.7	17.1	21.5	22.1
03/14/09	16.5	18.7	21.9	17.6	21.5	22.1
03/15/09	16.8	19.2	22.0	17.9	21.5	22.1
03/16/09	17.4	18.8	22.9	18.6	21.5	22.0
03/17/09	17.1	18.6	19.7	18.2	21.5	22.0
03/18/09	16.8	18.3	20.1	17.9	21.4	22.0
03/19/09	16.6	18.1	19.3	17.8	21.2	22.0
03/20/09	16.6	17.8	19.0	17.6	21.3	22.0
03/21/09	16.2	17.4	17.8	17.1	21.5	22.0
03/22/09	16.0	17.8	16.9	16.8	21.5	22.0
03/23/09	16.2	17.6	16.6	16.9	21.5	22.0
03/24/09	16.2	17.4	17.9	16.8	21.5	22.0
03/25/09	16.0	18.1	18.2	16.8	21.5	22.0
03/26/09	16.3	18.7	20.6	17.3	21.5	22.0
03/27/09	17.0	19.6	22.3	18.0	21.6	22.0
03/28/09	18.2	19.4	24.7	19.0	21.6	22.0
03/29/09	18.4	17.4	20.7	19.5	21.6	22.0
03/30/09	16.6	18.5	16.5	17.8	21.6	22.0
03/31/09	17.2	19.3	21.1	18.5	21.6	22.0
04/01/09	18.0	19.7	22.0	19.6	21.6	22.0
04/02/09	18.4	19.9	22.9	19.7	21.7	22.0
04/03/09	18.9	18.4	22.1	20.4	21.6	22.0
04/04/09	17.4	19.0	19.4	19.0	21.6	21.8
04/05/09	17.9	19.6	22.4	19.5	21.7	21.7
04/06/09	18.7	14.7	21.0	20.0	21.6	21.8
04/07/09	15.6	16.1	11.9	17.0	21.5	21.8
04/08/09	14.1	16.4	11.6	15.9	21.6	21.8
04/09/09	14.9	17.2	16.7	16.5	21.8	21.8
04/10/09	14.9	17.7	22.3	17.5	21.8	21.8

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
04/11/09	15.9	18.8	23.4	18.8	21.9	21.8
04/12/09	17.6	19.1	23.8	19.4	21.9	21.7
04/13/09	17.8	19.3	18.4	19.7	21.9	21.7
04/14/09	18.1	19.1	17.9	18.9	21.9	21.6
04/15/09	18.0	18.3	18.3	18.5	21.9	21.6
04/16/09	17.2	17.5	19.4	18.1	21.9	21.6
04/17/09	16.5	18.4	19.0	18.5	21.9	21.5
04/18/09	17.0	17.9	19.3	18.2	21.9	21.5
04/19/09	16.8	17.8	20.4	18.2	21.9	21.5
04/20/09	16.8	18.8	19.6	19.0	21.9	21.4
04/21/09	17.7	18.6	19.9	18.9	21.9	21.4
04/22/09	17.4	18.1	20.7	18.5	21.9	21.5
04/23/09	16.8	18.1	22.1	18.7	22.0	21.5
04/24/09	16.9	18.2	21.7	19.1	22.0	21.5
04/25/09	17.2	18.6	21.5	19.3	22.0	21.5
04/26/09	17.5	18.7	21.9	19.3	22.0	21.5
04/27/09	17.6	18.8	21.9	19.5	22.0	21.5
04/28/09	17.7	18.9	22.2	19.6	22.0	21.5
04/29/09	17.8	19.0	22.3	19.7	22.0	21.5
04/30/09	17.9	18.9	23.0	19.7	22.0	21.5
05/01/09	17.9	19.1	22.8	20.1	22.0	21.5
05/02/09	18.1	19.2	23.8	20.2	22.0	21.6
05/03/09	18.3	19.5	24.2	20.5	22.0	21.6
05/04/09	18.9	19.7	22.7	20.9	22.0	21.6
05/05/09	19.0	19.7	24.4	20.9	22.0	21.6
05/06/09	19.3	20.1	24.1	21.3	22.0	21.6
05/07/09	19.3	20.0	24.8	21.3	22.0	21.6
05/08/09	19.4	20.1	25.1	21.4	22.0	21.6
05/09/09	19.4	20.2	25.1	21.6	22.0	21.6
05/10/09	19.4	20.2	25.3	21.6	22.0	21.7
05/11/09	19.6	20.4	23.1	21.9	22.0	21.7
05/12/09	19.6	20.4	23.7	21.7	22.0	21.7
05/13/09	19.9	20.6	22.7	22.0	22.0	21.7
05/14/09	20.0	20.7	24.1	22.0	22.0	21.7
05/15/09	20.0	20.9	24.9	22.2	22.0	21.7
05/16/09	20.1	20.9	23.4	22.5	22.0	21.7
05/17/09	20.3	20.7	19.6	22.1	22.0	21.7
05/18/09	20.0	20.3	17.4	21.2	22.0	21.7
05/19/09	19.4	20.5	19.4	19.6	22.0	21.8
05/20/09	19.6	20.6	21.0	20.1	22.0	21.9
05/21/09	19.7	21.0	21.7	20.6	22.0	21.9
05/22/09	20.1	21.1	21.9	21.4	22.0	21.9
05/23/09	20.3	21.2	21.5	21.6	22.0	21.9
05/24/09	20.3	21.1	21.8	21.7	22.0	21.9
05/25/09	20.3	21.4	21.7	21.7	22.0	21.9
05/26/09	20.5	21.4	23.6	21.9	22.0	21.9
05/27/09	20.8	21.7	23.6	22.0	22.0	21.9
05/28/09	21.0	21.5	25.1	22.5	22.0	21.9
05/29/09	21.5	21.6	24.9	22.9	22.0	21.9

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
05/30/09	21.4	21.8	23.1	23.0	22.0	21.9
05/31/09	20.7	21.7	24.7	22.3	22.0	22.0
06/01/09	20.8	21.2	24.3	22.6	22.0	22.0
06/02/09	20.9	21.5	23.1	22.8	22.0	22.0
06/03/09	21.0	21.7	22.9	22.6	22.0	22.0
06/04/09	21.2	21.7	23.2	22.7	22.0	22.0
06/05/09	21.3	21.9	22.8	22.8	22.0	22.0
06/06/09	21.3	22.0	24.2	22.7	22.0	22.0
06/07/09	21.4	21.9	24.4	23.0	22.0	22.0
06/08/09	21.4	22.0	25.5	23.0	22.0	22.0
06/09/09	21.5	21.9	27.0	23.3	22.0	22.0
06/10/09	21.8	22.2	26.7	24.0	22.0	22.0
06/11/09	21.9	22.2	26.2	24.0	22.0	22.0
06/12/09	22.0	22.2	25.5	24.0	22.0	22.0
06/13/09	22.1	22.1	26.1	23.9	22.0	22.0
06/14/09	22.2	22.2	26.9	24.1	22.0	22.0
06/15/09	22.3	22.3	27.6	24.4	22.0	22.0
06/16/09	22.5	22.3	25.8	24.7	22.0	22.0
06/17/09	22.3	*	23.8	24.4	22.0	*
06/18/09	22.3	*	25.6	24.1	22.0	*
06/19/09	22.3	*	27.9	24.2	22.0	*
06/20/09	22.8	*	29.7	24.9	22.0	*
06/21/09	23.4	*	30.3	25.8	22.0	*
06/22/09	23.9	*	26.9	26.1	22.0	*
06/23/09	23.6	*	25.7	25.1	22.0	*
06/24/09	22.9	*	26.5	24.4	22.0	*
06/25/09	23.1	*	25.7	25.1	22.0	*
06/26/09	23.2	*	25.4	25.1	22.0	*
06/27/09	23.2	*	25.8	25.1	22.0	*
06/28/09	23.4	*	27.2	25.3	22.0	*
06/29/09	23.7	*	24.9	25.6	22.0	*
06/30/09	23.6	*	23.9	25.3	22.0	*
07/01/09	23.3	*	25.5	24.9	22.0	*
07/02/09	23.3	*	27.5	25.0	22.0	*
07/03/09	23.7	*	27.8	25.5	22.0	*
07/04/09	23.8	*	27.0	25.8	22.0	*
07/05/09	23.5	*	25.8	25.6	22.0	*
07/06/09	23.6	*	25.3	25.5	22.0	*
07/07/09	23.7	*	24.0	25.4	22.0	*
07/08/09	23.5	*	23.9	24.8	22.0	*
07/09/09	23.3	*	23.2	24.7	22.0	*
07/10/09	23.2	*	24.2	24.5	22.2	*
07/11/09	22.9	*	24.7	24.3	25.6	*
07/12/09	23.0	*	25.7	24.6	26.7	*
07/13/09	23.5	*	26.2	25.0	27.1	*
07/14/09	24.2	*	27.0	25.3	27.3	*
07/15/09	24.8	*	27.6	25.6	27.2	*
07/16/09	25.1	*	27.4	25.8	26.6	*
07/17/09	25.2	*	25.3	25.8	26.1	*

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
07/18/09	25.1	*	24.6	25.6	26.1	*
07/19/09	24.7	*	23.7	25.3	26.6	*
07/20/09	24.7	*	25.5	24.4	26.8	*
07/21/09	24.9	*	25.9	24.9	26.9	*
07/22/09	25.1	*	26.7	25.2	26.5	*
07/23/09	25.1	*	26.8	25.4	26.2	*
07/24/09	25.2	*	26.8	25.5	26.4	*
07/25/09	25.1	*	24.4	25.5	26.1	*
07/26/09	25.0	*	25.2	25.1	26.2	*
07/27/09	25.1	*	25.6	25.3	26.3	*
07/28/09	25.0	*	25.4	25.4	26.2	*
07/29/09	25.1	*	26.0	25.3	26.5	*
07/30/09	25.3	*	25.1	25.5	26.5	*
07/31/09	25.3	*	26.4	25.4	26.7	*
08/01/09	25.5	*	26.4	25.7	26.6	*
08/02/09	25.5	*	26.7	25.8	26.4	*
08/03/09	25.5	*	26.0	25.9	26.2	*
08/04/09	25.5	*	26.1	25.8	26.5	*
08/05/09	25.3	*	24.8	25.7	26.7	*
08/06/09	25.3	*	26.2	25.4	26.8	*
08/07/09	25.6	*	27.4	25.6	26.9	*
08/08/09	25.7	*	27.4	25.9	27.0	*
08/09/09	25.8	*	27.6	26.0	26.7	*
08/10/09	26.0	*	28.1	26.1	26.0	*
08/11/09	26.2	*	26.7	26.3	25.8	*
08/12/09	25.9	*	24.9	26.3	25.8	*
08/13/09	25.6	*	24.4	25.7	25.7	*
08/14/09	25.6	*	25.1	25.4	25.9	*
08/15/09	25.5	*	25.0	25.5	25.8	*
08/16/09	25.6	*	26.0	25.5	25.8	*
08/17/09	25.6	*	25.7	25.7	25.8	*
08/18/09	25.6	*	25.8	25.9	25.8	*
08/19/09	25.6	*	26.8	25.8	25.8	*
08/20/09	25.7	*	25.9	26.1	25.8	*
08/21/09	25.4	*	23.9	26.2	25.8	*
08/22/09	25.3	*	24.9	25.5	25.7	*
08/23/09	25.0	*	25.2	25.5	25.6	*
08/24/09	25.2	*	25.4	25.3	25.4	*
08/25/09	25.1	*	24.6	25.6	25.3	*
08/26/09	25.1	*	24.3	25.1	25.3	*
08/27/09	25.3	*	25.5	25.1	25.2	*
08/28/09	25.3	*	26.1	25.6	25.2	*
08/29/09	25.0	*	25.9	25.9	25.5	*
08/30/09	25.2	*	26.1	25.7	25.6	*
08/31/09	25.3	*	24.8	25.8	25.8	*
09/01/09	25.2	*	23.5	25.7	25.5	*
09/02/09	24.9	*	24.1	25.2	25.1	*
09/03/09	25.0	*	25.1	25.0	25.3	*
09/04/09	25.2	*	25.3	25.3	25.8	*

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
09/05/09	25.1	*	25.3	25.6	25.9	*
09/06/09	25.2	*	25.6	25.5	26.1	*
09/07/09	25.0	*	25.1	25.6	26.0	*
09/08/09	24.8	*	24.9	25.4	25.8	*
09/09/09	24.9	*	25.8	25.1	25.8	*
09/10/09	25.1	*	25.6	25.3	25.9	*
09/11/09	25.2	*	24.3	25.4	25.8	*
09/12/09	25.2	*	25.3	25.3	25.8	*
09/13/09	25.4	*	25.7	25.5	26.0	*
09/14/09	25.3	*	25.4	25.7	26.1	*
09/15/09	25.3	*	26.0	25.7	26.2	*
09/16/09	25.5	*	26.3	25.8	26.5	*
09/17/09	25.6	*	26.0	26.0	26.6	*
09/18/09	25.6	*	26.2	26.0	26.6	*
09/19/09	25.5	*	26.6	26.0	26.5	*
09/20/09	25.7	*	26.4	26.0	26.6	*
09/21/09	25.7	*	26.7	26.1	26.5	*
09/22/09	25.9	*	26.4	26.2	26.6	*
09/23/09	25.7	*	25.8	26.2	26.4	*
09/24/09	25.8	*	26.6	25.9	26.2	*
09/25/09	25.7	*	26.0	26.1	26.2	*
09/26/09	25.6	*	25.5	26.0	26.1	*
09/27/09	25.1	*	24.6	25.9	25.9	*
09/28/09	24.8	*	24.8	25.3	25.8	*
09/29/09	23.6	*	19.6	25.2	25.6	*
09/30/09	22.5	*	19.1	23.4	25.4	*
10/01/09	22.8	*	21.6	22.5	25.3	*
10/02/09	23.4	*	23.1	22.7	25.3	*
10/03/09	24.0	*	24.4	23.2	25.3	*
10/04/09	24.4	*	25.0	23.8	25.3	*
10/05/09	24.7	*	26.0	24.3	25.3	*
10/06/09	24.9	*	26.4	25.0	25.3	*
10/07/09	24.9	*	26.8	25.3	25.2	*
10/08/09	25.0	*	27.4	25.5	25.2	*
10/09/09	25.1	*	26.8	25.9	25.2	*
10/10/09	25.0	*	26.3	25.9	25.2	*
10/11/09	25.1	*	26.5	25.8	25.1	*
10/12/09	24.9	*	26.2	25.9	25.1	*
10/13/09	24.9	*	25.7	25.7	25.1	*
10/14/09	24.9	*	24.7	25.6	25.0	*
10/15/09	25.0	*	24.0	25.5	24.9	*
10/16/09	23.3	*	16.1	25.4	24.6	*
10/17/09	20.9	*	12.1	22.7	24.5	*
10/18/09	20.4	*	14.2	19.8	24.4	*
10/19/09	20.9	*	18.1	19.1	24.4	*
10/20/09	21.6	*	20.7	19.8	24.4	*
10/21/09	22.4	*	22.5	20.8	24.4	*
10/22/09	22.7	*	23.3	21.9	24.4	*
10/23/09	22.8	*	21.5	22.4	24.3	*

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
10/24/09	22.0	*	18.4	22.5	24.3	*
10/25/09	22.2	*	22.2	21.2	24.3	*
10/26/09	23.0	*	24.4	21.8	24.3	*
10/27/09	23.4	*	24.5	23.1	24.3	*
10/28/09	23.5	*	25.4	23.8	24.3	*
10/29/09	23.7	*	25.5	24.2	24.3	*
10/30/09	23.4	*	24.3	24.5	24.3	*
10/31/09	23.4	*	21.9	24.0	24.2	*
11/01/09	22.3	*	19.8	23.6	24.1	*
11/02/09	22.1	*	18.6	22.0	24.1	*
11/03/09	21.8	*	20.5	21.5	24.0	*
11/04/09	21.6	*	18.5	21.3	23.9	*
11/05/09	20.5	*	17.0	21.0	23.9	*
11/06/09	20.7	*	18.4	19.8	23.9	*
11/07/09	20.9	*	20.2	20.0	23.9	*
11/08/09	21.6	*	23.2	20.3	23.9	*
11/09/09	22.1	*	23.8	21.3	23.9	*
11/10/09	22.3	*	20.7	22.1	23.8	*
11/11/09	21.1	*	14.8	22.1	23.7	*
11/12/09	19.9	*	15.2	19.8	23.7	*
11/13/09	19.9	*	16.5	18.8	23.7	*
11/14/09	19.6	*	15.4	18.9	23.7	*
11/15/09	19.5	*	16.0	18.5	23.6	*
11/16/09	19.8	*	17.2	18.4	23.6	*
11/17/09	20.0	*	18.4	18.8	23.6	*
11/18/09	20.2	*	18.0	19.2	23.6	*
11/19/09	20.3	*	18.6	19.4	23.6	*
11/20/09	20.3	*	18.7	19.5	23.6	*
11/21/09	20.7	*	20.4	19.6	23.6	*
11/22/09	21.1	*	20.7	20.2	23.6	*
11/23/09	21.0	*	19.8	20.9	23.5	*
11/24/09	21.0	*	17.5	20.6	23.4	*
11/25/09	20.0	*	14.3	20.2	23.4	*
11/26/09	18.2	*	10.1	18.6	23.4	*
11/27/09	17.2	*	9.5	16.5	23.4	*
11/28/09	17.6	*	12.8	15.4	23.4	*
11/29/09	17.9	*	15.6	15.8	23.4	*
11/30/09	18.9	*	18.1	16.4	23.4	*
12/01/09	19.8	*	21.6	17.8	23.3	*
12/02/09	20.2	*	18.8	19.2	23.3	*
12/03/09	19.0	*	12.2	19.7	23.2	*
12/04/09	18.6	*	11.7	16.8	23.2	*
12/05/09	17.5	*	10.6	15.9	23.2	*
12/06/09	18.5	*	17.8	15.1	23.2	*
12/07/09	19.5	*	21.0	17.0	23.1	*
12/08/09	20.3	*	23.9	18.7	23.0	*
12/09/09	20.3	*	17.7	19.9	23.1	*
12/10/09	18.4	*	11.2	19.6	23.1	*
12/11/09	18.8	*	19.0	16.5	23.1	*

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
12/12/09	19.9	*	22.6	17.6	23.1	*
12/13/09	20.2	*	21.8	19.7	23.1	*
12/14/09	20.3	*	21.3	20.2	23.0	*
12/15/09	20.0	*	17.8	20.3	23.0	*
12/16/09	19.6	*	18.0	19.5	23.0	*
12/17/09	20.0	*	19.1	18.7	22.9	*
12/18/09	18.4	*	11.7	19.5	22.9	*
12/19/09	17.1	*	8.7	17.2	22.8	*
12/20/09	16.1	*	7.9	15.3	22.8	*
12/21/09	16.0	*	9.3	14.2	22.7	*
12/22/09	16.4	*	12.7	14.0	22.6	*
12/23/09	17.4	*	17.3	14.5	22.5	*
12/24/09	18.5	*	19.0	15.8	22.5	*
12/25/09	17.6	*	10.8	17.6	22.4	*
12/26/09	16.7	*	10.1	15.5	22.4	*
12/27/09	16.2	*	9.4	14.3	22.4	*
12/28/09	15.3	*	6.7	13.9	22.4	*
12/29/09	15.2	*	11.0	12.5	22.3	*
12/30/09	16.7	*	16.5	13.0	22.2	*
12/31/09	17.3	*	14.0	15.0	22.2	*
01/01/10	15.8	*	7.3	16.0	22.2	*
01/02/10	14.5	*	3.8	13.1	22.2	*
01/03/10	13.5	*	3.1	11.5	22.2	*
01/04/10	13.1	*	3.2	10.3	22.2	*
01/05/10	12.4	*	1.8	9.8	22.2	*
01/06/10	12.3	*	3.8	8.9	22.2	*
01/07/10	13.1	*	6.0	8.8	22.2	*
01/08/10	12.8	*	1.0	9.6	22.2	*
01/09/10	11.5	*	-0.2	8.3	22.2	*
01/10/10	11.3	*	1.2	7.1	22.2	*
01/11/10	11.4	*	3.4	7.0	22.2	*
01/12/10	12.0	*	5.7	7.3	22.2	*
01/13/10	12.5	*	9.0	8.0	22.2	*
01/14/10	13.8	*	14.9	8.9	22.2	*
01/15/10	15.2	*	20.3	10.9	22.2	*
01/16/10	16.4	*	19.8	13.4	22.2	*
01/17/10	16.0	*	13.8	15.5	22.2	*
01/18/10	15.1	*	12.2	14.0	22.2	*
01/19/10	15.0	*	13.8	12.9	22.2	*
01/20/10	16.5	*	20.8	13.0	22.2	*
01/21/10	17.4	*	20.9	14.9	22.2	*
01/22/10	16.9	*	19.4	16.6	22.2	*
01/23/10	17.6	*	23.8	15.8	22.2	*
01/24/10	17.7	*	18.3	17.0	22.2	*
01/25/10	15.9	*	12.6	16.8	22.2	*
01/26/10	15.0	*	11.3	14.3	22.2	*
01/27/10	14.7	*	12.7	13.2	22.2	*
01/28/10	15.3	*	16.7	12.9	22.2	*
01/29/10	16.4	*	19.0	13.7	22.2	*

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
01/30/10	16.0	*	12.2	15.2	22.2	*
01/31/10	15.5	*	14.9	13.9	22.2	*
02/01/10	16.4	*	18.0	13.3	22.2	*
02/02/10	16.1	*	14.9	15.1	22.2	*
02/03/10	16.0	*	18.2	14.0	22.2	*
02/04/10	17.1	*	16.5	14.3	22.2	*
02/05/10	16.9	*	11.8	16.2	22.2	*
02/06/10	15.6	*	11.7	15.4	22.2	*
02/07/10	14.6	*	14.3	13.4	22.2	*
02/08/10	15.2	*	11.5	12.7	22.2	*
02/09/10	15.1	*	9.7	13.2	22.2	*
02/10/10	14.0	*	10.0	12.8	22.2	*
02/11/10	14.3	*	9.9	11.3	22.2	*
02/12/10	14.0	*	9.6	10.8	22.2	*
02/13/10	13.2	*	12.7	10.5	22.2	*
02/14/10	13.4	*	10.2	10.4	22.1	*
02/15/10	13.9	*	9.7	10.9	22.1	*
02/16/10	13.2	*	10.6	11.1	22.1	*
02/17/10	13.3	*	12.8	10.4	22.1	*
02/18/10	13.5	*	16.2	10.4	22.1	*
02/19/10	14.4	*	17.6	10.8	22.1	*
02/20/10	14.8	*	20.0	11.9	22.1	*
02/21/10	15.9	*	21.0	12.8	22.1	*
02/22/10	16.5	*	15.5	14.1	22.1	*
02/23/10	16.1	*	10.5	15.4	22.1	*
02/24/10	14.8	*	9.7	14.2	22.1	*
02/25/10	13.4	*	10.6	12.4	22.1	*
02/26/10	13.9	*	12.0	11.4	22.1	*
02/27/10	13.8	*	14.0	11.2	22.1	*
02/28/10	13.9	*	16.4	11.3	22.1	*
03/01/10	15.0	*	12.3	11.7	22.1	*
03/02/10	14.7	*	10.5	12.6	22.1	*
03/03/10	13.9	*	11.1	11.9	22.1	*
03/04/10	13.3	*	12.2	11.1	22.1	*
03/05/10	13.4	*	13.1	10.9	22.1	*
03/06/10	13.3	*	15.4	11.0	22.1	*
03/07/10	13.9	*	17.6	11.2	22.1	*
03/08/10	14.8	*	19.7	11.9	22.1	*
03/09/10	15.3	*	21.4	12.7	22.1	*
03/10/10	16.5	*	20.1	13.5	22.1	*
03/11/10	17.2	*	19.1	15.8	22.1	*
03/12/10	17.0	*	18.7	16.5	22.1	*
03/13/10	16.8	*	17.9	15.6	22.1	*
03/14/10	16.6	*	16.0	15.1	22.1	*
03/15/10	16.2	*	16.5	14.9	22.1	*
03/16/10	16.2	*	15.7	14.4	22.1	*
03/17/10	16.3	*	17.2	14.3	22.1	*
03/18/10	15.9	*	17.8	14.3	22.1	*
03/19/10	15.8	*	17.5	14.3	22.1	*

APPENDIX I Daily average air and water temperatures (°C) within Thornton's Cave and at the surface (continued)

Date	Catfish Entrance Air	The Deep Air	Surface Temp	Soil Temp	Tangerine Entrance Water	The Deep Water
03/20/10	16.8	*	16.1	14.4	22.1	*
03/21/10	16.2	*	17.2	15.0	22.1	*
03/22/10	16.3	*	17.6	14.4	22.1	*
03/23/10	16.0	*	20.0	14.6	22.1	*
03/24/10	16.7	*	19.2	14.6	22.1	*
03/25/10	17.5	*	18.9	15.6	22.1	*
03/26/10	17.0	*	18.5	16.7	22.1	*
03/27/10	17.5	*	17.4	16.2	22.1	*
03/28/10	17.6	*	15.2	16.8	22.1	*
03/29/10	16.5	*	16.2	17.0	22.1	*
03/30/10	16.0	*	17.6	15.8	22.1	*
03/31/10	16.3	*	19.3	15.6	22.1	*
04/01/10	16.6	*	18.7	16.0	22.1	*
04/02/10	16.3	*	18.3	16.5	22.1	*

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
3/15/2008	0.02	1.07	12.21
3/16/2008	0	1.12	12.21
3/17/2008	0	1.19	12.21
3/18/2008	0	1.16	12.21
3/19/2008	0	1.09	12.21
3/20/2008	0	1.11	12.22
3/21/2008	1.12	1.16	12.22
3/22/2008	1	1.11	12.21
3/23/2008	0	1.09	12.21
3/24/2008	0	1.13	12.21
3/25/2008	0	1.2	12.2
3/26/2008	0	1.18	12.2
3/27/2008	0	1.13	12.19
3/28/2008	0	1.09	12.18
3/29/2008	0	1.09	12.18
3/30/2008	0	1.1	12.17
3/31/2008	0.04	1.09	12.16
4/1/2008	0.08	1.07	12.16
4/2/2008	0.04	1.07	12.15
4/3/2008	1.04	1.06	12.16
4/4/2008	0.06	1.02	12.15
4/5/2008	1.38	0.99	12.14
4/6/2008	4.24	1	12.16
4/7/2008	0	1.04	12.18
4/8/2008	0	1.07	12.17
4/9/2008	0	1.07	12.17
4/10/2008	0	1.06	12.16
4/11/2008	0	1.03	12.16
4/12/2008	0	1.01	12.16
4/13/2008	0.04	1.02	12.16
4/14/2008	0	1.02	12.16
4/15/2008	0	1.04	12.16
4/16/2008	0	1.06	12.17
4/17/2008	0	1.05	12.17
4/18/2008	0	1.03	12.17
4/19/2008	0	0.99	12.18
4/20/2008	0	0.96	12.18
4/21/2008	0	0.94	12.19
4/22/2008	0	0.93	12.19
4/23/2008	0	0.94	12.2
4/24/2008	0	0.95	12.2
4/25/2008	0	0.95	12.2
4/26/2008	0	0.95	12.2
4/27/2008	0	0.93	12.2
4/28/2008	0.06	0.9	12.2
4/29/2008	0.04	0.9	12.19
4/30/2008	0.02	0.92	12.18
5/1/2008	0	0.91	12.17
5/2/2008	0	0.89	12.16
5/3/2008	0	0.87	12.15
5/4/2008	0	0.85	12.13

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Precipitation	Tangerine Entrance Water-level	Withlacoochee River Water-level
5/5/2008	0	0.83	12.12
5/6/2008	0.02	0.82	12.11
5/7/2008	0.02	0.8	12.1
5/8/2008	0	0.77	12.08
5/9/2008	0.02	0.75	12.07
5/10/2008	0	0.74	12.06
5/11/2008	0	0.71	12.05
5/12/2008	0	0.7	12.03
5/13/2008	0	0.74	12.02
5/14/2008	0	0.75	12.01
5/15/2008	0	0.72	12
5/16/2008	0	0.68	11.98
5/17/2008	0	0.66	11.98
5/18/2008	0.06	0.63	11.97
5/19/2008	0.02	0.63	11.96
5/20/2008	0.04	0.61	11.95
5/21/2008	0	0.59	11.95
5/22/2008	1.46	0.61	11.94
5/23/2008	0.08	0.63	11.95
5/24/2008	0	0.61	11.95
5/25/2008	0	0.62	11.94
5/26/2008	0	0.63	11.93
5/27/2008	0	0.62	11.92
5/28/2008	0	0.63	11.91
5/29/2008	0	0.64	11.9
5/30/2008	0	0.65	11.89
5/31/2008	1	0.63	11.88
6/1/2008	1.14	0.62	11.88
6/2/2008	0	0.61	11.87
6/3/2008	0.08	0.61	11.86
6/4/2008	0.02	0.61	11.86
6/5/2008	0	0.63	11.85
6/6/2008	1	0.66	11.84
6/7/2008	0	0.67	11.83
6/8/2008	1.14	0.65	11.82
6/9/2008	0.02	0.63	11.84
6/10/2008	0.06	0.64	11.82
6/11/2008	0.02	0.63	11.81
6/12/2008	2.56	0.65	11.81
6/13/2008	0.08	0.66	11.83
6/14/2008	0.02	0.63	11.83
6/15/2008	1.64	0.61	11.84
6/16/2008	1.46	0.63	11.87
6/17/2008	0.06	0.64	11.87
6/18/2008	0.04	0.61	11.86
6/19/2008	1.88	0.62	11.87
6/20/2008	0.02	0.64	11.86
6/21/2008	4.26	0.66	11.86
6/22/2008	2.02	0.66	11.88
6/23/2008	0.02	0.69	11.89
6/24/2008	0.02	0.72	11.88

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
6/25/2008	3.7	0.73	11.88
6/26/2008	4.42	0.72	11.92
6/27/2008	0.02	0.74	11.95
6/28/2008	0.02	0.76	11.95
6/29/2008	0	0.76	11.96
6/30/2008	1.34	0.74	11.96
7/1/2008	0.06	0.75	11.96
7/2/2008	0.62	0.76	11.96
7/3/2008	0	0.77	11.97
7/4/2008	0	0.77	11.97
7/5/2008	0.32	0.75	11.96
7/6/2008	0.52	0.74	11.96
7/7/2008	0.58	0.76	11.96
7/8/2008	1.16	0.77	11.97
7/9/2008	0	0.77	11.98
7/10/2008	0	0.77	11.97
7/11/2008	1.04	0.77	11.96
7/12/2008	0.64	0.76	11.97
7/13/2008	0	0.71	11.98
7/14/2008	0	0.69	11.98
7/15/2008	0.8	0.72	11.98
7/16/2008	0.32	0.74	11.98
7/17/2008	0.1	0.74	11.98
7/18/2008	0	0.74	11.98
7/19/2008	0	0.76	11.98
7/20/2008	0	0.77	11.98
7/21/2008	0	0.75	11.98
7/22/2008	0.26	0.75	11.97
7/23/2008	0.08	0.75	11.98
7/24/2008	0.02	0.75	11.97
7/25/2008	0	0.75	11.97
7/26/2008	0	0.74	11.97
7/27/2008	0.8	0.73	11.98
7/28/2008	0	0.73	11.98
7/29/2008	0.12	0.74	11.98
7/30/2008	0.74	0.75	11.98
7/31/2008	1.72	0.75	12
8/1/2008	0.52	0.77	12.02
8/2/2008	0.34	0.78	12.03
8/3/2008	0	0.78	12.04
8/4/2008	0	0.8	12.03
8/5/2008	0.1	0.8	12.02
8/6/2008	0	0.78	12.01
8/7/2008	0	0.75	12
8/8/2008	0	0.71	11.99
8/9/2008	0	0.69	11.99
8/10/2008	0	0.69	11.98
8/11/2008	0	0.68	11.98
8/12/2008	2.26	0.68	11.98
8/13/2008	0.5	0.69	11.99
8/14/2008	2.38	0.76	12.03

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
8/15/2008	0.36	0.86	12.05
8/16/2008	0.04	0.87	12.05
8/17/2008	1.42	0.86	12.05
8/18/2008	0	0.86	12.05
8/19/2008	0.38	0.84	12.05
8/20/2008	0.28	0.83	12.05
8/21/2008	2.62	0.83	12.06
8/22/2008	7.34	0.93	12.15
8/23/2008	0.3	1.16	12.19
8/24/2008	0.42	1.24	12.2
8/25/2008	2.32	1.28	12.21
8/26/2008	0.04	1.32	12.22
8/27/2008	0	1.35	12.22
8/28/2008	0	1.35	12.21
8/29/2008	0	1.36	12.2
8/30/2008	0.84	1.37	12.2
8/31/2008	0.02	1.38	12.19
9/1/2008	0	1.4	12.18
9/2/2008	0.08	1.4	12.17
9/3/2008	0	1.38	12.16
9/4/2008	0	1.36	12.15
9/5/2008	0	1.32	12.14
9/6/2008	0	1.37	12.13
9/7/2008	0	1.38	12.12
9/8/2008	0.32	1.37	12.12
9/9/2008	0	1.34	12.12
9/10/2008	0.18	1.32	12.12
9/11/2008	0	1.34	12.12
9/12/2008	0	1.34	12.11
9/13/2008	0	1.31	12.1
9/14/2008	0	1.29	12.09
9/15/2008	0	1.29	12.09
9/16/2008	0	1.28	12.09
9/17/2008	0.02	1.27	12.09
9/18/2008	0	1.26	12.09
9/19/2008	0	1.26	12.09
9/20/2008	0	1.24	12.08
9/21/2008	0	1.24	12.07
9/22/2008	0	1.24	12.07
9/23/2008	0.06	1.23	12.07
9/24/2008	0	1.2	12.07
9/25/2008	0	1.16	12.06
9/26/2008	0	1.14	12.05
9/27/2008	0	1.14	12.05
9/28/2008	0	1.14	12.04
9/29/2008	0.64	1.13	12.05
9/30/2008	0	1.12	12.05
10/1/2008	0.08	1.1	12.06
10/2/2008	0	1.1	12.06
10/3/2008	0	1.13	12.05
10/4/2008	0	1.15	12.05

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
10/5/2008	0	1.15	12.04
10/6/2008	0.38	1.13	12.04
10/7/2008	0	1.14	12.07
10/8/2008	0	1.12	12.06
10/9/2008	0	1.09	12.06
10/10/2008	0	1.1	12.07
10/11/2008	0	1.1	12.07
10/12/2008	0	1.12	12.06
10/13/2008	0	1.13	12.06
10/14/2008	0	1.12	12.05
10/15/2008	0	1.11	12.05
10/16/2008	0	1.1	12.05
10/17/2008	0	1.08	12.04
10/18/2008	0	1.05	12.03
10/19/2008	0	1.08	12.03
10/20/2008	0	1.1	12.02
10/21/2008	0	1.08	12.02
10/22/2008	0	1.06	12.02
10/23/2008	0.06	1.06	12.01
10/24/2008	1.14	1.03	12.04
10/25/2008	0	1.03	12.04
10/26/2008	0	1.06	12.04
10/27/2008	0	1.07	12.03
10/28/2008	0	1.11	12.02
10/29/2008	0	1.13	12.02
10/30/2008	0	1.14	12.01
10/31/2008	0	1.14	12.01
11/1/2008	0	1.1	12.01
11/2/2008	0.02	1.06	12.01
11/3/2008	0	1.04	12.01
11/4/2008	0	1.02	12.01
11/5/2008	0	1.01	12.01
11/6/2008	0	1.01	12.01
11/7/2008	0	0.99	12
11/8/2008	0	0.97	12
11/9/2008	0	0.98	12
11/10/2008	0	1	11.99
11/11/2008	0	1	11.99
11/12/2008	0	0.91	11.99
11/13/2008	0	0.81	11.99
11/14/2008	0	0.79	11.99
11/15/2008	0	0.77	11.98
11/16/2008	0	0.85	11.98
11/17/2008	0	0.87	11.97
11/18/2008	0	0.86	11.97
11/19/2008	0	0.88	11.97
11/20/2008	0	0.84	11.96
11/21/2008	0	0.86	11.96
11/22/2008	0	0.92	11.96
11/23/2008	0	0.9	11.96
11/24/2008	0	0.85	11.96

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
11/25/2008	0	0.8	11.96
11/26/2008	0.02	0.81	11.96
11/27/2008	0	0.81	11.95
11/28/2008	0	0.77	11.95
11/29/2008	0	0.71	11.95
11/30/2008	0.64	0.64	11.95
12/1/2008	0.06	0.74	11.96
12/2/2008	0.6	0.83	11.97
12/3/2008	0	0.85	11.96
12/4/2008	0	0.82	11.96
12/5/2008	0	0.8	11.96
12/6/2008	0.16	0.77	11.96
12/7/2008	0	0.8	11.96
12/8/2008	0	0.82	11.96
12/9/2008	0	0.79	11.96
12/10/2008	0	0.74	11.96
12/11/2008	0.82	0.68	11.97
12/12/2008	0.06	0.77	11.98
12/13/2008	0	0.85	11.98
12/14/2008	0	0.85	11.98
12/15/2008	0.04	0.85	11.98
12/16/2008	0	0.83	11.98
12/17/2008	0	0.83	11.98
12/18/2008	0	0.84	11.98
12/19/2008	0	0.82	11.97
12/20/2008	0	0.78	11.97
12/21/2008	0.14	0.75	11.97
12/22/2008	0	0.83	11.97
12/23/2008	0	0.86	11.96
12/24/2008	0.06	0.83	11.96
12/25/2008	0.04	0.82	11.96
12/26/2008	0	0.82	11.95
12/27/2008	0	0.8	11.95
12/28/2008	0	0.78	11.95
12/29/2008	0	0.77	11.95
12/30/2008	0.02	0.75	11.94
12/31/2008	0	0.71	11.94
1/1/2009	0	0.74	11.94
1/2/2009	0.04	0.72	11.94
1/3/2009	0	0.71	11.94
1/4/2009	0.1	0.72	11.94
1/5/2009	0	0.71	11.94
1/6/2009	0	0.65	11.93
1/7/2009	0.18	0.62	11.93
1/8/2009	0.02	0.66	11.93
1/9/2009	0.02	0.71	11.93
1/10/2009	0	0.72	11.92
1/11/2009	0.12	0.68	11.92
1/12/2009	0.18	0.68	11.92
1/13/2009	0.52	0.66	11.92
1/14/2009	0	0.73	11.93

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
1/15/2009	0.04	0.77	11.92
1/16/2009	0	0.81	11.92
1/17/2009	0	0.79	11.91
1/18/2009	0.02	0.7	11.93
1/19/2009	0.48	0.59	11.96
1/20/2009	0.04	0.6	11.96
1/21/2009	0	0.71	11.96
1/22/2009	0	0.74	11.95
1/23/2009	0	0.73	11.95
1/24/2009	0	0.7	11.95
1/25/2009	0.02	0.69	11.94
1/26/2009	0	0.72	11.94
1/27/2009	0	0.71	11.87
1/28/2009	0	0.65	11.87
1/29/2009	0	0.62	11.87
1/30/2009	0	0.65	11.87
1/31/2009	0	0.72	11.87
2/1/2009	0	0.7	11.86
2/2/2009	0	0.61	11.86
2/3/2009	0	0.66	11.87
2/4/2009	0	0.74	11.85
2/5/2009	0	0.81	11.84
2/6/2009	0	0.8	11.83
2/7/2009	0	0.79	11.82
2/8/2009	0	0.76	11.8
2/9/2009	0	0.72	11.78
2/10/2009	0	0.69	11.76
2/11/2009	0	0.66	11.74
2/12/2009	0.04	0.65	11.73
2/13/2009	0	0.63	11.74
2/14/2009	0	0.59	11.74
2/15/2009	0.04	0.58	11.75
2/16/2009	0	0.62	11.76
2/17/2009	0	0.65	11.76
2/18/2009	0	0.59	11.76
2/19/2009	0.1	0.54	11.76
2/20/2009	0	0.62	11.77
2/21/2009	0	0.63	11.77
2/22/2009	0	0.63	11.77
2/23/2009	0	0.65	11.77
2/24/2009	0	0.64	11.77
2/25/2009	0	0.63	11.77
2/26/2009	0	0.62	11.77
2/27/2009	0	0.57	11.76
2/28/2009	0	0.53	11.75
3/1/2009	0.42	0.49	11.74
3/2/2009	0	0.55	11.74
3/3/2009	0	0.6	11.73
3/4/2009	0	0.62	11.73
3/5/2009	0	0.63	11.73
3/6/2009	0	0.62	11.72

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
3/7/2009	0	0.59	11.71
3/8/2009	0	0.56	11.71
3/9/2009	0	0.55	11.7
3/10/2009	0	0.53	11.69
3/11/2009	0	0.52	11.68
3/12/2009	0	0.52	11.67
3/13/2009	0	0.5	11.66
3/14/2009	0	0.48	11.65
3/15/2009	0	0.49	11.64
3/16/2009	0	0.49	11.63
3/17/2009	0	0.47	11.62
3/18/2009	0	0.46	11.61
3/19/2009	0	0.43	11.59
3/20/2009	0	0.43	11.58
3/21/2009	0	0.48	11.56
3/22/2009	0	0.49	11.55
3/23/2009	0.18	0.46	11.54
3/24/2009	0	0.45	11.53
3/25/2009	0	0.42	11.52
3/26/2009	0	0.38	11.5
3/27/2009	0	0.32	11.48
3/28/2009	0	0.29	11.47
3/29/2009	1.54	0.31	11.48
3/30/2009	0	0.36	11.48
3/31/2009	0	0.33	11.47
4/1/2009	0.36	0.31	11.45
4/2/2009	0	0.27	11.44
4/3/2009	0.72	0.26	11.44
4/4/2009	0	0.32	11.43
4/5/2009	0	0.3	11.41
4/6/2009	0.02	0.26	11.4
4/7/2009	0	0.32	11.39
4/8/2009	0	0.35	11.38
4/9/2009	0	0.32	11.37
4/10/2009	0	0.33	11.37
4/11/2009	0	0.33	11.36
4/12/2009	0	0.32	11.36
4/13/2009	0.92	0.29	11.36
4/14/2009	2.6	0.27	11.36
4/15/2009	0	0.31	11.36
4/16/2009	0	0.34	11.36
4/17/2009	0	0.37	11.36
4/18/2009	0	0.35	11.36
4/19/2009	0	0.3	11.36
4/20/2009	0.54	0.25	11.35
4/21/2009	0	0.26	11.35
4/22/2009	0	0.29	11.35
4/23/2009	0	0.31	11.35
4/24/2009	0	0.31	11.35
4/25/2009	0	0.31	11.34
4/26/2009	0	0.3	11.34

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
4/27/2009	0	0.29	11.34
4/28/2009	0	0.27	11.34
4/29/2009	0	0.25	11.33
4/30/2009	0	0.23	11.33
5/1/2009	0	0.21	11.33
5/2/2009	0	0.17	11.33
5/3/2009	0	0.14	11.32
5/4/2009	0	0.13	11.32
5/5/2009	0.28	0.13	11.32
5/6/2009	0	0.11	11.31
5/7/2009	0	0.1	11.31
5/8/2009	0	0.08	11.31
5/9/2009	0	0.09	11.31
5/10/2009	0	0.08	11.3
5/11/2009	0	0.05	11.3
5/12/2009	1.42	0.04	11.3
5/13/2009	2.22	0.06	11.3
5/14/2009	0.3	0.08	11.3
5/15/2009	0	0.06	11.3
5/16/2009	0	0.04	11.29
5/17/2009	5.42	0.01	11.29
5/18/2009	2.2	0.04	11.29
5/19/2009	5.33	0.08	11.29
5/20/2009	4.04	0.2	11.3
5/21/2009	1.38	0.32	11.34
5/22/2009	0.72	0.4	11.36
5/23/2009	4.74	0.46	11.38
5/24/2009	0.38	0.56	11.43
5/25/2009	1.94	0.6	11.46
5/26/2009	0.3	0.63	11.48
5/27/2009	0.02	0.65	11.47
5/28/2009	1.46	0.67	11.47
5/29/2009	0	0.69	11.46
5/30/2009	0	0.69	11.45
5/31/2009	0	0.71	11.44
6/1/2009	0	0.72	11.43
6/2/2009	0.02	0.72	11.41
6/3/2009	2.04	0.72	11.41
6/4/2009	2.34	0.72	11.42
6/5/2009	0.5	0.72	11.45
6/6/2009	0.2	0.74	11.47
6/7/2009	0	0.78	11.47
6/8/2009	0	0.78	11.47
6/9/2009	0	0.77	11.49
6/10/2009	0	0.76	11.52
6/11/2009	0	0.75	11.55
6/12/2009	0	0.75	11.59
6/13/2009	0	0.76	11.63
6/14/2009	0	0.76	11.66
6/15/2009	0	0.76	11.68
6/16/2009	0	0.76	11.71

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
6/17/2009	0.28	0.77	11.73
6/18/2009	1.34	0.76	11.75
6/19/2009	0	0.76	11.78
6/20/2009	0	0.75	11.8
6/21/2009	0	0.72	11.81
6/22/2009	0	0.69	11.81
6/23/2009	8.28	0.67	11.83
6/24/2009	0	0.75	11.89
6/25/2009	1.06	0.79	11.89
6/26/2009	0.1	0.81	11.9
6/27/2009	0.3	0.84	11.9
6/28/2009	1.44	0.83	11.91
6/29/2009	0.02	0.81	11.92
6/30/2009	4.02	0.84	11.95
7/1/2009	0.48	0.92	11.97
7/2/2009	0	0.99	11.98
7/3/2009	0	1.03	11.98
7/4/2009	0	1.03	11.99
7/5/2009	0	1.02	11.99
7/6/2009	0.32	1.01	11.99
7/7/2009	0.44	1.02	12.01
7/8/2009	4.3	1.06	12.05
7/9/2009	0.48	1.15	12.09
7/10/2009	1.3	1.22	12.11
7/11/2009	0.02	1.28	12.15
7/12/2009	0.08	1.3	12.18
7/13/2009	1.38	1.34	12.24
7/14/2009	0	1.43	12.29
7/15/2009	0	1.5	12.33
7/16/2009	0	1.5	12.35
7/17/2009	0	1.5	12.36
7/18/2009	0.5	1.52	12.38
7/19/2009	0.54	1.57	12.4
7/20/2009	2.22	1.59	12.42
7/21/2009	0.16	1.6	12.44
7/22/2009	0	1.62	12.44
7/23/2009	0	1.64	12.45
7/24/2009	0	1.66	12.46
7/25/2009	0	1.67	12.47
7/26/2009	0.32	1.68	12.48
7/27/2009	0.52	1.68	12.49
7/28/2009	0	1.66	12.48
7/29/2009	0.38	1.65	12.48
7/30/2009	1.02	1.65	12.48
7/31/2009	0.02	1.7	12.49
8/1/2009	0.02	1.7	12.48
8/2/2009	0	1.69	12.48
8/3/2009	0	1.69	12.47
8/4/2009	0.04	1.7	12.48
8/5/2009	0	1.7	12.49
8/6/2009	0.64	1.69	12.49

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
8/7/2009	0	1.7	12.48
8/8/2009	0	1.71	12.47
8/9/2009	0	1.7	12.45
8/10/2009	0	1.67	12.44
8/11/2009	0	1.63	12.42
8/12/2009	1.48	1.6	12.42
8/13/2009	2.08	1.62	12.41
8/14/2009	0	1.65	12.41
8/15/2009	0.92	1.65	12.41
8/16/2009	0.3	1.65	12.4
8/17/2009	0.02	1.66	12.4
8/18/2009	0.02	1.65	12.39
8/19/2009	0.54	1.63	12.39
8/20/2009	0	1.63	12.39
8/21/2009	0.66	1.61	12.38
8/22/2009	1.06	1.59	12.37
8/23/2009	0	1.6	12.37
8/24/2009	0	1.61	12.37
8/25/2009	0	1.61	12.36
8/26/2009	3.58	1.62	12.37
8/27/2009	0.96	1.65	12.39
8/28/2009	0.02	1.64	12.41
8/29/2009	0	1.65	12.42
8/30/2009	0.02	1.67	12.41
8/31/2009	0.02	1.68	12.41
9/1/2009	1.02	1.68	12.41
9/2/2009	3.4	1.68	12.41
9/3/2009	0.04	1.69	12.42
9/4/2009	0.02	1.74	12.45
9/5/2009	0.04	1.78	12.46
9/6/2009	0	1.81	12.46
9/7/2009	0	1.82	12.46
9/8/2009	0	1.83	12.47
9/9/2009	0	1.84	12.48
9/10/2009	0.04	1.84	12.48
9/11/2009	0	1.84	12.49
9/12/2009	3.8	1.82	12.49
9/13/2009	0.06	1.87	12.49
9/14/2009	0.02	1.9	12.5
9/15/2009	0.06	1.9	12.5
9/16/2009	0	1.9	12.51
9/17/2009	0.02	1.9	12.51
9/18/2009	0.02	1.91	12.52
9/19/2009	0	1.9	12.52
9/20/2009	0.02	1.88	12.53
9/21/2009	0.02	1.86	12.53
9/22/2009	0	1.84	12.53
9/23/2009	0	1.82	12.52
9/24/2009	0.02	1.81	12.49
9/25/2009	0.02	1.8	12.47
9/26/2009	0.04	1.77	12.45

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
9/27/2009	0.02	1.74	12.43
9/28/2009	0	1.74	12.41
9/29/2009	0	1.74	12.39
9/30/2009	0	1.74	12.37
10/1/2009	0	1.73	12.34
10/2/2009	0	1.7	12.32
10/3/2009	0	1.7	12.3
10/4/2009	0	1.71	12.28
10/5/2009	0.06	1.7	12.27
10/6/2009	0.04	1.7	12.25
10/7/2009	0	1.71	12.23
10/8/2009	0	1.71	12.22
10/9/2009	0	1.69	12.2
10/10/2009	0	1.67	12.19
10/11/2009	0.06	1.68	12.18
10/12/2009	0.02	1.67	12.17
10/13/2009	0	1.65	12.16
10/14/2009	0	1.62	12.14
10/15/2009	0.78	1.58	12.13
10/16/2009	0.96	1.58	12.12
10/17/2009	0	1.64	12.12
10/18/2009	0	1.68	12.12
10/19/2009	0	1.69	12.11
10/20/2009	0	1.67	12.1
10/21/2009	0	1.65	12.09
10/22/2009	0	1.61	12.08
10/23/2009	0	1.57	12.07
10/24/2009	0	1.54	12.05
10/25/2009	0	1.56	12.04
10/26/2009	0.02	1.57	12.03
10/27/2009	0.22	1.55	12.02
10/28/2009	0.24	1.55	12.01
10/29/2009	0	1.56	12
10/30/2009	0	1.54	11.98
10/31/2009	0	1.52	11.97
11/1/2009	0	1.52	11.95
11/2/2009	0	1.52	11.94
11/3/2009	0	1.53	11.93
11/4/2009	0	1.55	11.91
11/5/2009	0	1.56	11.9
11/6/2009	0	1.55	11.88
11/7/2009	0	1.53	11.87
11/8/2009	0	1.5	11.86
11/9/2009	0.02	1.47	11.85
11/10/2009	1.5	1.42	11.84
11/11/2009	0.1	1.37	11.83
11/12/2009	0.02	1.38	11.85
11/13/2009	0	1.39	11.85
11/14/2009	0	1.41	11.84
11/15/2009	0	1.43	11.84
11/16/2009	0	1.42	11.84

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
11/17/2009	0	1.4	11.84
11/18/2009	0	1.41	11.84
11/19/2009	0	1.41	11.84
11/20/2009	0	1.4	11.84
11/21/2009	0	1.38	11.85
11/22/2009	0.76	1.37	11.86
11/23/2009	0	1.4	11.87
11/24/2009	0.34	1.4	11.89
11/25/2009	0.66	1.4	11.89
11/26/2009	0	1.4	11.91
11/27/2009	0	1.43	11.91
11/28/2009	0	1.42	11.91
11/29/2009	0	1.41	11.9
11/30/2009	0	1.38	11.89
12/1/2009	0	1.35	11.88
12/2/2009	1.26	1.3	11.88
12/3/2009	0	1.36	11.88
12/4/2009	4.24	1.4	11.89
12/5/2009	0.64	1.46	11.9
12/6/2009	0	1.52	11.95
12/7/2009	0.16	1.51	11.95
12/8/2009	0	1.49	11.95
12/9/2009	0	1.44	11.95
12/10/2009	0.28	1.49	11.94
12/11/2009	0	1.57	11.94
12/12/2009	0	1.55	11.93
12/13/2009	0	1.52	11.92
12/14/2009	0	1.51	11.91
12/15/2009	0	1.5	11.91
12/16/2009	0	1.52	11.9
12/17/2009	0	1.49	11.89
12/18/2009	0.6	1.37	11.89
12/19/2009	0	1.42	11.89
12/20/2009	0	1.5	11.89
12/21/2009	0	1.53	11.89
12/22/2009	0	1.51	11.88
12/23/2009	0	1.48	11.87
12/24/2009	0	1.42	11.86
12/25/2009	0.14	1.39	11.86
12/26/2009	0	1.45	11.86
12/27/2009	0	1.46	11.85
12/28/2009	0	1.46	11.85
12/29/2009	0	1.5	11.85
12/30/2009	0	1.49	11.84
12/31/2009	0.18	1.44	11.83
1/1/2010	2.42	1.44	11.82
1/2/2010	0	1.52	11.82
1/3/2010	0	1.52	11.85
1/4/2010	0	1.51	11.87
1/5/2010	0	1.53	11.87
1/6/2010	0	1.53	11.87

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
1/7/2010	0	1.51	11.86
1/8/2010	0.08	1.48	11.86
1/9/2010	0	1.52	11.85
1/10/2010	0	1.57	11.84
1/11/2010	0	1.58	11.84
1/12/2010	0	1.54	11.83
1/13/2010	0	1.54	11.82
1/14/2010	0	1.52	11.81
1/15/2010	0	1.49	11.81
1/16/2010	0.76	1.43	11.8
1/17/2010	0.66	1.42	11.8
1/18/2010	0	1.46	11.8
1/19/2010	0	1.47	11.83
1/21/2010	0	1.45	11.82
1/22/2010	0.02	1.39	11.82
1/23/2010	0.26	1.39	11.82
1/24/2010	0	1.42	11.82
1/25/2010	0	1.38	11.83
1/26/2010	1.14	1.4	11.84
1/27/2010	0	1.49	11.84
1/28/2010	0	1.53	11.85
1/29/2010	0	1.51	11.86
1/30/2010	0	1.46	11.87
1/31/2010	0.84	1.4	11.87
2/1/2010	0	1.48	11.87
2/2/2010	1.38	1.49	11.89
2/3/2010	0.52	1.47	11.91
2/4/2010	0	1.52	11.93
2/5/2010	0	1.52	11.97
2/5/2010	2.04	1.45	11.99
2/6/2010	0	1.46	12.02
2/7/2010	0	1.52	12.04
2/8/2010	0	1.55	12.07
2/9/2010	2.08	1.51	12.09
2/10/2010	0	1.57	12.1
2/11/2010	0	1.58	12.12
2/12/2010	2.34	1.52	12.15
2/13/2010	0	1.6	12.16
2/14/2010	0	1.64	12.18
2/15/2010	0	1.62	12.2
2/16/2010	0	1.64	12.21
2/17/2010	0	1.65	12.22
2/18/2010	0	1.68	12.22
2/19/2010	0	1.69	12.23
2/20/2010	0	1.68	12.23
2/21/2010	0	1.65	12.23
2/22/2010	0.16	1.57	12.24
2/23/2010	0	1.56	12.24
2/24/2010	0.6	1.58	12.24
2/25/2010	0	1.66	12.25
2/26/2010	0	1.66	12.25

APPENDIX II Daily rainfall (cm/day), and water-levels (m) for Thornton's Cave at the Tangerine Entrance, and the Withlacoochee River (continued)

Date	Rainfall	Tangerine Entrance Water-level	Withlacoochee River Water-level
2/27/2010	0.32	1.62	12.25
2/28/2010	0	1.65	12.25
3/1/2010	0	1.64	12.26
3/2/2010	1.12	1.55	12.26
3/3/2010	0	1.62	12.25
3/4/2010	0	1.67	12.26
3/5/2010	0	1.69	12.26
3/6/2010	0	1.71	12.24
3/7/2010	0	1.72	12.23
3/8/2010	0	1.68	12.22
3/9/2010	0	1.65	12.2
3/10/2010	0	1.62	12.18
3/11/2010	4.54	1.57	12.17
3/12/2010	2.32	1.61	12.15
3/13/2010	0	1.66	12.17
3/14/2010	0	1.71	12.23
3/15/2010	0	1.75	12.24
3/16/2010	0	1.79	12.25
3/17/2010	0.06	1.78	12.26
3/18/2010	0.18	1.78	12.27
3/19/2010	0	1.82	12.29
3/20/2010	0	1.84	12.31
3/21/2010	1.52	1.82	12.32
3/22/2010	0	1.84	12.34
3/23/2010	0	1.88	12.37
3/24/2010	0	1.91	12.4
3/25/2010	2.16	1.89	12.42
3/26/2010	0	1.93	12.44
3/27/2010	0	2.01	12.48
3/28/2010	2.04	2.01	12.52
3/29/2010	0.62	2.01	12.54
3/30/2010	0	2.09	12.55
3/31/2010	0	2.15	12.58
4/1/2010	0	2.18	12.58
4/2/2010	0	2.19	12.59

APPENDIX III Lag and correlation values for cross correlation analyses of water-levels (WL) at Tangerine Entrance (TE) of Thornton's Cave and Withlacoochee River (WR), and rainfall and water-level values at TE and WR

WL Lag	WL Correlation	TE Precip/WL Lag	TE Precip/WL Correlation	WR Precip/WL Lag	WR Precip/WL Correlation
-200	-0.073	-200	0.060	-200	0.041
-199	-0.073	-199	0.060	-199	0.040
-198	-0.073	-198	0.066	-198	0.039
-197	-0.073	-197	0.067	-197	0.039
-196	-0.074	-196	0.060	-196	0.039
-195	-0.074	-195	0.056	-195	0.041
-194	-0.074	-194	0.055	-194	0.041
-193	-0.075	-193	0.059	-193	0.041
-192	-0.076	-192	0.056	-192	0.041
-191	-0.077	-191	0.053	-191	0.040
-190	-0.078	-190	0.053	-190	0.039
-189	-0.079	-189	0.049	-189	0.038
-188	-0.081	-188	0.046	-188	0.038
-187	-0.082	-187	0.043	-187	0.036
-186	-0.084	-186	0.034	-186	0.032
-185	-0.086	-185	0.030	-185	0.030
-184	-0.088	-184	0.032	-184	0.027
-183	-0.091	-183	0.035	-183	0.025
-182	-0.094	-182	0.035	-182	0.023
-181	-0.097	-181	0.029	-181	0.022
-180	-0.099	-180	0.025	-180	0.019
-179	-0.102	-179	0.021	-179	0.016
-178	-0.105	-178	0.019	-178	0.015
-177	-0.108	-177	0.019	-177	0.014
-176	-0.110	-176	0.015	-176	0.013
-175	-0.113	-175	0.011	-175	0.012
-174	-0.115	-174	0.007	-174	0.011
-173	-0.117	-173	0.010	-173	0.010
-172	-0.120	-172	0.007	-172	0.011
-171	-0.123	-171	0.002	-171	0.011
-170	-0.125	-170	-0.004	-170	0.012
-169	-0.128	-169	-0.006	-169	0.011
-168	-0.130	-168	-0.009	-168	0.010
-167	-0.132	-167	-0.007	-167	0.008
-166	-0.133	-166	-0.005	-166	0.005
-165	-0.134	-165	-0.009	-165	0.002
-164	-0.134	-164	-0.012	-164	-0.001

APPENDIX III Lag and correlation values for cross correlation analyses of water-levels (WL) at Tangerine Entrance (TE) of Thornton's Cave and Withlacoochee River (WR), and rainfall and water-level values at TE and WR (continued)

WL Lag	WL Correlation	TE Precip/WL Lag	TE Precip/WL Correlation	WR Precip/WL Lag	WR Precip/WL Correlation
-163	-0.135	-163	-0.013	-163	0.002
-162	-0.136	-162	-0.013	-162	-0.001
-161	-0.137	-161	-0.013	-161	-0.001
-160	-0.139	-160	-0.007	-160	0.008
-159	-0.140	-159	-0.006	-159	0.009
-158	-0.142	-158	-0.001	-158	0.008
-157	-0.144	-157	-0.001	-157	0.008
-156	-0.145	-156	-0.006	-156	0.008
-155	-0.147	-155	-0.006	-155	0.010
-154	-0.148	-154	-0.002	-154	0.006
-153	-0.149	-153	-0.003	-153	0.003
-152	-0.151	-152	-0.007	-152	0.003
-151	-0.152	-151	-0.008	-151	0.001
-150	-0.154	-150	-0.006	-150	0.003
-149	-0.155	-149	-0.006	-149	0.000
-148	-0.156	-148	-0.007	-148	-0.003
-147	-0.158	-147	-0.008	-147	-0.008
-146	-0.159	-146	-0.008	-146	-0.010
-145	-0.161	-145	-0.007	-145	-0.011
-144	-0.163	-144	-0.005	-144	-0.011
-143	-0.166	-143	-0.005	-143	-0.012
-142	-0.168	-142	-0.008	-142	-0.015
-141	-0.171	-141	-0.016	-141	-0.017
-140	-0.173	-140	-0.018	-140	-0.019
-139	-0.175	-139	-0.019	-139	-0.022
-138	-0.177	-138	-0.017	-138	-0.023
-137	-0.179	-137	-0.020	-137	-0.022
-136	-0.180	-136	-0.026	-136	-0.023
-135	-0.181	-135	-0.033	-135	-0.026
-134	-0.182	-134	-0.034	-134	-0.028
-133	-0.184	-133	-0.033	-133	-0.030
-132	-0.185	-132	-0.038	-132	-0.033
-131	-0.186	-131	-0.041	-131	-0.037
-130	-0.186	-130	-0.044	-130	-0.038
-129	-0.187	-129	-0.046	-129	-0.041
-128	-0.187	-128	-0.044	-128	-0.044
-127	-0.187	-127	-0.042	-127	-0.047

APPENDIX III Lag and correlation values for cross correlation analyses of water-levels (WL) at Tangerine Entrance (TE) of Thornton's Cave and Withlacoochee River (WR), and rainfall and water-level values at TE and WR (continued)

WL Lag	WL Correlation	TE Precip/WL Lag	TE Precip/WL Correlation	WR Precip/WL Lag	WR Precip/WL Correlation
-126	-0.186	-126	-0.046	-126	-0.048
-125	-0.185	-125	-0.052	-125	-0.049
-124	-0.184	-124	-0.057	-124	-0.050
-123	-0.183	-123	-0.056	-123	-0.051
-122	-0.182	-122	-0.058	-122	-0.051
-121	-0.180	-121	-0.064	-121	-0.052
-120	-0.178	-120	-0.068	-120	-0.052
-119	-0.176	-119	-0.069	-119	-0.051
-118	-0.173	-118	-0.067	-118	-0.052
-117	-0.170	-117	-0.066	-117	-0.056
-116	-0.166	-116	-0.073	-116	-0.063
-115	-0.162	-115	-0.081	-115	-0.066
-114	-0.158	-114	-0.085	-114	-0.069
-113	-0.154	-113	-0.083	-113	-0.073
-112	-0.149	-112	-0.080	-112	-0.077
-111	-0.144	-111	-0.082	-111	-0.080
-110	-0.139	-110	-0.086	-110	-0.085
-109	-0.134	-109	-0.087	-109	-0.088
-108	-0.130	-108	-0.089	-108	-0.093
-107	-0.125	-107	-0.089	-107	-0.094
-106	-0.120	-106	-0.092	-106	-0.100
-105	-0.116	-105	-0.094	-105	-0.106
-104	-0.111	-104	-0.094	-104	-0.112
-103	-0.106	-103	-0.093	-103	-0.109
-102	-0.099	-102	-0.093	-102	-0.108
-101	-0.093	-101	-0.093	-101	-0.114
-100	-0.087	-100	-0.094	-100	-0.119
-99	-0.082	-99	-0.098	-99	-0.119
-98	-0.076	-98	-0.097	-98	-0.115
-97	-0.070	-97	-0.097	-97	-0.120
-96	-0.064	-96	-0.097	-96	-0.120
-95	-0.057	-95	-0.100	-95	-0.123
-94	-0.050	-94	-0.101	-94	-0.126
-93	-0.043	-93	-0.103	-93	-0.125
-92	-0.036	-92	-0.099	-92	-0.124
-91	-0.029	-91	-0.100	-91	-0.127
-90	-0.021	-90	-0.102	-90	-0.129

APPENDIX III Lag and correlation values for cross correlation analyses of water-levels (WL) at Tangerine Entrance (TE) of Thornton's Cave and Withlacoochee River (WR), and rainfall and water-level values at TE and WR (continued)

WL Lag	WL Correlation	TE Precip/WL Lag	TE Precip/WL Correlation	WR Precip/WL Lag	WR Precip/WL Correlation
-89	-0.013	-89	-0.101	-89	-0.127
-88	-0.004	-88	-0.104	-88	-0.130
-87	0.005	-87	-0.105	-87	-0.134
-86	0.014	-86	-0.107	-86	-0.136
-85	0.024	-85	-0.108	-85	-0.136
-84	0.033	-84	-0.111	-84	-0.137
-83	0.043	-83	-0.113	-83	-0.138
-82	0.053	-82	-0.113	-82	-0.140
-81	0.064	-81	-0.113	-81	-0.139
-80	0.075	-80	-0.112	-80	-0.139
-79	0.085	-79	-0.114	-79	-0.142
-78	0.096	-78	-0.116	-78	-0.143
-77	0.107	-77	-0.116	-77	-0.144
-76	0.118	-76	-0.114	-76	-0.147
-75	0.129	-75	-0.115	-75	-0.148
-74	0.140	-74	-0.116	-74	-0.148
-73	0.152	-73	-0.119	-73	-0.150
-72	0.164	-72	-0.124	-72	-0.154
-71	0.175	-71	-0.130	-71	-0.157
-70	0.187	-70	-0.133	-70	-0.156
-69	0.199	-69	-0.134	-69	-0.157
-68	0.211	-68	-0.134	-68	-0.155
-67	0.223	-67	-0.134	-67	-0.155
-66	0.236	-66	-0.137	-66	-0.155
-65	0.249	-65	-0.143	-65	-0.157
-64	0.263	-64	-0.148	-64	-0.158
-63	0.276	-63	-0.146	-63	-0.158
-62	0.288	-62	-0.144	-62	-0.159
-61	0.300	-61	-0.143	-61	-0.161
-60	0.313	-60	-0.141	-60	-0.160
-59	0.325	-59	-0.141	-59	-0.161
-58	0.338	-58	-0.142	-58	-0.164
-57	0.350	-57	-0.142	-57	-0.164
-56	0.362	-56	-0.143	-56	-0.163
-55	0.374	-55	-0.146	-55	-0.164
-54	0.386	-54	-0.150	-54	-0.165
-53	0.398	-53	-0.151	-53	-0.168

APPENDIX III Lag and correlation values for cross correlation analyses of water-levels (WL) at Tangerine Entrance (TE) of Thornton's Cave and Withlacoochee River (WR), and rainfall and water-level values at TE and WR (continued)

WL Lag	WL Correlation	TE Precip/WL Lag	TE Precip/WL Correlation	WR Precip/WL Lag	WR Precip/WL Correlation
-52	0.410	-52	-0.154	-52	-0.169
-51	0.422	-51	-0.156	-51	-0.169
-50	0.433	-50	-0.155	-50	-0.168
-49	0.444	-49	-0.152	-49	-0.167
-48	0.455	-48	-0.150	-48	-0.167
-47	0.466	-47	-0.151	-47	-0.168
-46	0.476	-46	-0.151	-46	-0.168
-45	0.486	-45	-0.149	-45	-0.167
-44	0.496	-44	-0.148	-44	-0.166
-43	0.506	-43	-0.142	-43	-0.166
-42	0.516	-42	-0.139	-42	-0.168
-41	0.526	-41	-0.139	-41	-0.169
-40	0.536	-40	-0.138	-40	-0.169
-39	0.545	-39	-0.137	-39	-0.169
-38	0.554	-38	-0.134	-38	-0.168
-37	0.563	-37	-0.132	-37	-0.165
-36	0.572	-36	-0.128	-36	-0.163
-35	0.580	-35	-0.127	-35	-0.162
-34	0.589	-34	-0.123	-34	-0.160
-33	0.597	-33	-0.118	-33	-0.157
-32	0.606	-32	-0.115	-32	-0.155
-31	0.614	-31	-0.114	-31	-0.155
-30	0.622	-30	-0.111	-30	-0.153
-29	0.630	-29	-0.110	-29	-0.151
-28	0.638	-28	-0.109	-28	-0.149
-27	0.646	-27	-0.109	-27	-0.149
-26	0.655	-26	-0.107	-26	-0.147
-25	0.662	-25	-0.105	-25	-0.146
-24	0.670	-24	-0.106	-24	-0.146
-23	0.677	-23	-0.109	-23	-0.147
-22	0.684	-22	-0.108	-22	-0.139
-21	0.690	-21	-0.106	-21	-0.137
-20	0.697	-20	-0.106	-20	-0.136
-19	0.704	-19	-0.110	-19	-0.134
-18	0.710	-18	-0.115	-18	-0.134
-17	0.717	-17	-0.118	-17	-0.133
-16	0.723	-16	-0.118	-16	-0.133

APPENDIX III Lag and correlation values for cross correlation analyses of water-levels (WL) at Tangerine Entrance (TE) of Thornton's Cave and Withlacoochee River (WR), and rainfall and water-level values at TE and WR (continued)

WL Lag	WL Correlation	TE Precip/WL Lag	TE Precip/WL Correlation	WR Precip/WL Lag	WR Precip/WL Correlation
-15	0.729	-15	-0.119	-15	-0.132
-14	0.735	-14	-0.119	-14	-0.129
-13	0.741	-13	-0.117	-13	-0.126
-12	0.746	-12	-0.115	-12	-0.122
-11	0.751	-11	-0.114	-11	-0.117
-10	0.756	-10	-0.114	-10	-0.113
-9	0.760	-9	-0.112	-9	-0.110
-8	0.764	-8	-0.109	-8	-0.104
-7	0.768	-7	-0.103	-7	-0.097
-6	0.771	-6	-0.096	-6	-0.091
-5	0.774	-5	-0.091	-5	-0.088
-4	0.777	-4	-0.090	-4	-0.085
-3	0.779	-3	-0.089	-3	-0.081
-2	0.781	-2	-0.086	-2	-0.078
-1	0.782	-1	-0.084	-1	-0.075
0	0.783	0	-0.078	0	-0.062
1	0.781	1	-0.047	1	-0.043
2	0.778	2	-0.022	2	-0.028
3	0.774	3	-0.006	3	-0.017
4	0.770	4	0.007	4	-0.009
5	0.765	5	0.013	5	-0.002
6	0.760	6	0.013	6	0.000
7	0.754	7	0.021	7	0.008
8	0.749	8	0.032	8	0.017
9	0.742	9	0.035	9	0.015
10	0.736	10	0.042	10	0.020
11	0.729	11	0.050	11	0.025
12	0.722	12	0.057	12	0.030
13	0.715	13	0.054	13	0.031
14	0.708	14	0.055	14	0.036
15	0.701	15	0.062	15	0.043
16	0.693	16	0.069	16	0.051
17	0.685	17	0.073	17	0.058
18	0.677	18	0.075	18	0.065
19	0.669	19	0.079	19	0.071
20	0.661	20	0.081	20	0.079
21	0.654	21	0.084	21	0.087

APPENDIX III Lag and correlation values for cross correlation analyses of water-levels (WL) at Tangerine Entrance (TE) of Thornton's Cave and Withlacoochee River (WR), and rainfall and water-level values at TE and WR (continued)

WL Lag	WL Correlation	TE Precip/WL Lag	TE Precip/WL Correlation	WR Precip/WL Lag	WR Precip/WL Correlation
22	0.646	22	0.079	22	0.086
23	0.638	23	0.065	23	0.079
24	0.630	24	0.069	24	0.084
25	0.621	25	0.072	25	0.090
26	0.612	26	0.074	26	0.097
27	0.603	27	0.074	27	0.104
28	0.593	28	0.073	28	0.107
29	0.583	29	0.073	29	0.110
30	0.573	30	0.074	30	0.114
31	0.563	31	0.075	31	0.118
32	0.553	32	0.070	32	0.118
33	0.542	33	0.068	33	0.120
34	0.531	34	0.068	34	0.121
35	0.520	35	0.067	35	0.124
36	0.509	36	0.070	36	0.127
37	0.498	37	0.076	37	0.132
38	0.487	38	0.081	38	0.137
39	0.475	39	0.086	39	0.139
40	0.464	40	0.088	40	0.142
41	0.452	41	0.090	41	0.146
42	0.439	42	0.092	42	0.149
43	0.427	43	0.095	43	0.152
44	0.415	44	0.096	44	0.153
45	0.402	45	0.101	45	0.155
46	0.390	46	0.110	46	0.160
47	0.377	47	0.114	47	0.163
48	0.364	48	0.114	48	0.166
49	0.351	49	0.119	49	0.170
50	0.338	50	0.119	50	0.169
51	0.326	51	0.126	51	0.176
52	0.313	52	0.135	52	0.182
53	0.300	53	0.137	53	0.181
54	0.287	54	0.144	54	0.187
55	0.274	55	0.149	55	0.192
56	0.262	56	0.153	56	0.198
57	0.250	57	0.150	57	0.200
58	0.239	58	0.160	58	0.208

APPENDIX III Lag and correlation values for cross correlation analyses of water-levels (WL) at Tangerine Entrance (TE) of Thornton's Cave and Withlacoochee River (WR), and rainfall and water-level values at TE and WR (continued)

WL Lag	WL Correlation	TE Precip/WL Lag	TE Precip/WL Correlation	WR Precip/WL Lag	WR Precip/WL Correlation
59	0.227	59	0.167	59	0.212
60	0.216	60	0.168	60	0.214
61	0.205	61	0.169	61	0.214
62	0.194	62	0.176	62	0.221
63	0.183	63	0.179	63	0.223
64	0.172	64	0.184	64	0.227
65	0.162	65	0.190	65	0.229
66	0.152	66	0.193	66	0.231
67	0.141	67	0.197	67	0.231
68	0.131	68	0.197	68	0.228
69	0.122	69	0.197	69	0.228
70	0.112	70	0.195	70	0.228
71	0.102	71	0.195	71	0.231
72	0.092	72	0.199	72	0.234
73	0.082	73	0.202	73	0.235
74	0.073	74	0.203	74	0.234
75	0.064	75	0.204	75	0.234
76	0.055	76	0.201	76	0.230
77	0.046	77	0.199	77	0.225
78	0.037	78	0.200	78	0.224
79	0.028	79	0.197	79	0.222
80	0.019	80	0.193	80	0.219
81	0.010	81	0.189	81	0.217
82	0.002	82	0.189	82	0.216
83	-0.007	83	0.188	83	0.215
84	-0.016	84	0.188	84	0.214
85	-0.025	85	0.185	85	0.214
86	-0.034	86	0.186	86	0.213
87	-0.042	87	0.185	87	0.211
88	-0.051	88	0.183	88	0.208
89	-0.060	89	0.185	89	0.206
90	-0.068	90	0.181	90	0.203
91	-0.076	91	0.178	91	0.201
92	-0.084	92	0.170	92	0.191
93	-0.091	93	0.169	93	0.187
94	-0.099	94	0.167	94	0.184
95	-0.107	95	0.164	95	0.180

APPENDIX III Lag and correlation values for cross correlation analyses of water-levels (WL) at Tangerine Entrance (TE) of Thornton's Cave and Withlacoochee River (WR), and rainfall and water-level values at TE and WR (continued)

WL Lag	WL Correlation	TE Precip/WL Lag	TE Precip/WL Correlation	WR Precip/WL Lag	WR Precip/WL Correlation
96	-0.114	96	0.161	96	0.177
97	-0.121	97	0.154	97	0.175
98	-0.128	98	0.152	98	0.172
99	-0.135	99	0.154	99	0.170
100	-0.142	100	0.156	100	0.170
101	-0.148	101	0.159	101	0.170
102	-0.155	102	0.165	102	0.171
103	-0.161	103	0.166	103	0.171
104	-0.167	104	0.164	104	0.170
105	-0.173	105	0.162	105	0.168
106	-0.178	106	0.158	106	0.165
107	-0.183	107	0.158	107	0.165
108	-0.187	108	0.160	108	0.167
109	-0.192	109	0.163	109	0.167
110	-0.196	110	0.164	110	0.167
111	-0.200	111	0.163	111	0.166
112	-0.204	112	0.166	112	0.166
113	-0.208	113	0.168	113	0.166
114	-0.211	114	0.164	114	0.166
115	-0.215	115	0.165	115	0.166
116	-0.219	116	0.168	116	0.166
117	-0.222	117	0.170	117	0.165
118	-0.225	118	0.169	118	0.163
119	-0.227	119	0.164	119	0.157
120	-0.228	120	0.147	120	0.142
121	-0.229	121	0.143	121	0.139
122	-0.230	122	0.140	122	0.132
123	-0.231	123	0.139	123	0.129
124	-0.232	124	0.136	124	0.126
125	-0.233	125	0.132	125	0.122
126	-0.234	126	0.127	126	0.117
127	-0.234	127	0.123	127	0.112
128	-0.235	128	0.120	128	0.107
129	-0.236	129	0.117	129	0.100
130	-0.236	130	0.113	130	0.095
131	-0.236	131	0.109	131	0.090

APPENDIX III Lag and correlation values for cross correlation analyses of water-levels (WL) at Tangerine Entrance (TE) of Thornton's Cave and Withlacoochee River (WR), and rainfall and water-level values at TE and WR (continued)

WL Lag	WL Correlation	TE Precip/WL Lag	TE Precip/WL Correlation	WR Precip/WL Lag	WR Precip/WL Correlation
132	-0.235	132	0.104	132	0.082
133	-0.235	133	0.101	133	0.076
134	-0.234	134	0.096	134	0.071
135	-0.232	135	0.093	135	0.066
136	-0.231	136	0.092	136	0.061
137	-0.230	137	0.092	137	0.057
138	-0.228	138	0.091	138	0.055
139	-0.227	139	0.091	139	0.053
140	-0.225	140	0.087	140	0.049
141	-0.223	141	0.082	141	0.046
142	-0.221	142	0.081	142	0.044
143	-0.219	143	0.081	143	0.040
144	-0.216	144	0.076	144	0.032
145	-0.214	145	0.074	145	0.030
146	-0.211	146	0.072	146	0.028
147	-0.209	147	0.070	147	0.026
148	-0.206	148	0.071	148	0.024
149	-0.204	149	0.071	149	0.024
150	-0.201	150	0.067	150	0.024
151	-0.199	151	0.065	151	0.024
152	-0.196	152	0.063	152	0.023
153	-0.193	153	0.066	153	0.022
154	-0.191	154	0.070	154	0.021
155	-0.189	155	0.066	155	0.019
156	-0.186	156	0.059	156	0.018
157	-0.183	157	0.054	157	0.017
158	-0.180	158	0.053	158	0.012
159	-0.177	159	0.055	159	0.012
160	-0.174	160	0.050	160	0.010
161	-0.172	161	0.047	161	0.008
162	-0.170	162	0.046	162	0.008
163	-0.169	163	0.046	163	0.005
164	-0.167	164	0.048	164	0.004
165	-0.166	165	0.054	165	0.002
166	-0.165	166	0.059	166	0.002
167	-0.165	167	0.058	167	-0.001

APPENDIX III Lag and correlation values for cross correlation analyses of water-levels (WL) at Tangerine Entrance (TE) of Thornton's Cave and Withlacoochee River (WR), and rainfall and water-level values at TE and WR (continued)

WL Lag	WL Correlation	TE Precip/WL Lag	TE Precip/WL Correlation	WR Precip/WL Lag	WR Precip/WL Correlation
168	-0.164	168	0.055	168	-0.005
169	-0.163	169	0.053	169	-0.011
170	-0.162	170	0.049	170	-0.017
171	-0.161	171	0.047	171	-0.020
172	-0.160	172	0.044	172	-0.022
173	-0.159	173	0.041	173	-0.023
174	-0.158	174	0.041	174	-0.025
175	-0.158	175	0.041	175	-0.026
176	-0.157	176	0.040	176	-0.026
177	-0.157	177	0.035	177	-0.027
178	-0.157	178	0.027	178	-0.028
179	-0.156	179	0.032	179	-0.028
180	-0.156	180	0.032	180	-0.029
181	-0.156	181	0.028	181	-0.031
182	-0.156	182	0.028	182	-0.031
183	-0.157	183	0.030	183	-0.029
184	-0.158	184	0.033	184	-0.028
185	-0.159	185	0.034	185	-0.026
186	-0.160	186	0.036	186	-0.025
187	-0.162	187	0.034	187	-0.022
188	-0.163	188	0.031	188	-0.021
189	-0.165	189	0.033	189	-0.022
190	-0.167	190	0.032	190	-0.022
191	-0.169	191	0.028	191	-0.022
192	-0.171	192	0.027	192	-0.022
193	-0.174	193	0.032	193	-0.021
194	-0.177	194	0.032	194	-0.020
195	-0.180	195	0.030	195	-0.018
196	-0.183	196	0.029	196	-0.020
197	-0.186	197	0.029	197	-0.019
198	-0.189	198	0.029	198	-0.020
199	-0.192	199	0.029	199	-0.019
200	-0.195	200	0.031	200	-0.016

APPENDIX IV Bulk PCA-A values for Thornton's Cave and surface waters: Tangerine Entrance (TE), Catfish Entrance (CE), Thornton's Slough (TS) and the Withlacoochee River (WR)

Date	TE PC1	TE PC2	CE PC1	CE PC2	TS PC1	TS PC2	WR PC1	WR PC2
04/14/08	0.572	-0.728	0.581	-0.658	-0.186	0.497	-0.497	-0.097
04/26/08	0.589	0.638	0.596	0.400	-0.186	0.498	-0.497	-0.097
06/14/08	0.668	-0.478	0.671	-1.547	-0.190	-0.427	-0.497	-0.102
06/27/08	0.723	0.132	0.670	-0.193	-0.211	-0.925	-0.533	-0.269
07/06/08	0.621	0.283	0.600	1.105	0.019	-1.195	-0.374	-1.017
07/19/08	0.692	-0.837	0.668	-0.411	-0.260	0.703	-0.124	2.256
07/26/08	0.713	-0.114	0.748	-0.051	-0.186	0.495	-0.497	-0.100
08/14/08	0.788	-0.535	0.384	-0.704	-1.042	3.649	-0.056	5.128
09/03/08	0.772	-0.226	0.582	-0.596	-0.654	-0.306	-0.534	-0.521
09/28/08	0.730	-0.084	0.752	-0.978	-0.470	0.191	-1.053	-0.006
10/25/08	0.816	-0.090	0.841	-0.264	-0.098	-0.594	-0.602	-0.571
11/12/08	0.839	-0.460	0.840	-0.295	0.004	-0.781	0.941	-1.705
12/06/08	0.840	-0.369	0.860	0.195	0.057	-0.614	0.160	-0.519
12/17/08	0.865	-0.563	0.857	-0.375	0.340	-0.308	0.118	-0.475
01/17/09	0.868	0.035	0.909	-0.189	0.190	0.338	0.014	-0.545
01/30/09	0.864	0.918	0.864	0.904	0.653	0.339	-0.027	-0.287
02/13/09	0.906	0.688	0.899	-0.582	1.204	-0.817	0.039	-0.786
02/24/09	0.912	0.191	0.910	1.343	-0.186	0.492	1.212	-2.288
03/20/09	1.003	-0.404	1.015	0.306	-0.186	0.489	0.408	-0.588
04/10/09	1.071	-0.453	0.999	0.555	-0.186	0.486	-0.021	-0.689
04/27/09	1.060	-0.938	1.060	0.575	-0.185	0.486	-0.214	-1.779
05/20/09	0.971	0.097	0.922	0.516	2.172	2.405	-0.510	-0.929
06/05/09	0.898	0.763	0.903	0.105	1.210	3.435	0.550	0.233
06/17/09	0.916	-0.485	0.896	0.377	0.575	1.634	-0.298	0.189
07/06/09	0.799	-0.155	0.870	0.430	0.082	2.379	-1.214	0.330
07/22/09	-1.587	-0.817	-1.544	-0.840	-1.306	-0.823	-2.004	0.148
08/12/09	-2.148	-0.067	-2.148	-0.127	-2.103	0.837	-2.065	-0.066
08/27/09	-1.611	-0.546	-1.346	-0.723	-1.436	0.537	-1.995	0.096
09/17/09	-2.157	-0.100	-2.174	-0.166	-2.010	0.616	-2.268	0.522
10/01/09	-1.604	-0.826	-2.089	-0.436	-2.181	0.596	-1.954	-0.241
10/29/09	-0.659	-0.337	-0.802	0.135	-0.462	0.091	-0.997	-0.842
11/14/09	0.314	-0.919	0.083	-0.873	-0.033	1.630	-0.654	0.950
12/07/09	0.912	-1.223	0.771	-2.003	1.098	0.289	-0.411	1.420

APPENDIX V Bulk PCA-B values for Thornton's Cave and surface waters: Tangerine Entrance (TE), Catfish Entrance (CE), Thornton's Slough (TS) and the Withlacoochee River (WR)

Date	TE PC1	TE PC2	CE PC1	CE PC2	TS PC1	TS PC2	WR PC1	WR PC2
05/20/09	1.1496	-1.0659	1.1423	-1.0955	2.1451	1.02	0.0215	0.362
06/05/09	1.2796	-0.9105	1.2472	-0.8845	2.0107	4.3574	0.8817	0.3945
06/17/09	1.3503	-1.1566	1.2871	-1.0195	1.1007	0.3974	0.2805	0.5565
07/06/09	1.2492	-0.5939	1.3298	-1.4181	0.6857	0.0113	-0.4124	-0.097
07/22/09	-0.6382	0.0877	-0.6591	-0.3956	-0.2775	0.7161	-1.0802	-0.3719
08/12/09	-0.7799	0.6329	-0.5537	1.9897	-0.6625	9.64E-03	-0.9688	0.6485
08/27/09	-0.7973	-0.4523	-0.4849	-0.2983	-0.537	-0.0146	-0.9501	-0.35
09/17/09	-1.0586	0.2826	-0.9994	0.5416	-1.1303	-0.3835	-1.2199	0.0314
10/01/09	-0.6993	0.0892	-0.7483	0.8225	-0.9884	0.4433	-1.0638	-0.2959
10/29/09	0.0516	-0.8212	-0.0594	-0.2255	0.2433	-0.5462	-0.6867	-0.9978

APPENDIX VI Lag and correlation values for cross correlation analyses of water-levels (WL) at Taylor Slough (TS) and Palma Vista Well (PVW) and rainfall and water-level values at TS and PVW

WL Lag	WL Correlation	TS Precip/WL Lag	TS Precip/WL Correlation	PVW Precip/WL Lag	PVW Precip/WL Correlation
-100	-0.266	-100	-0.043	-100	-0.067
-99	-0.275	-99	-0.034	-99	-0.024
-98	-0.283	-98	-0.034	-98	-0.008
-97	-0.297	-97	-0.037	-97	-0.029
-96	-0.311	-96	-0.048	-96	-0.047
-95	-0.326	-95	-0.027	-95	-0.032
-94	-0.336	-94	-0.028	-94	-0.017
-93	-0.345	-93	-0.026	-93	-0.011
-92	-0.354	-92	-0.032	-92	-0.008
-91	-0.363	-91	-0.042	-91	-0.028
-90	-0.372	-90	-0.047	-90	-0.031
-89	-0.381	-89	-0.050	-89	-0.065
-88	-0.389	-88	-0.058	-88	-0.093
-87	-0.396	-87	-0.065	-87	-0.082
-86	-0.404	-86	-0.061	-86	-0.072
-85	-0.415	-85	-0.063	-85	-0.070
-84	-0.424	-84	-0.072	-84	-0.101
-83	-0.431	-83	-0.079	-83	-0.113
-82	-0.444	-82	-0.079	-82	-0.093
-81	-0.450	-81	-0.103	-81	-0.112
-80	-0.454	-80	-0.110	-80	-0.119
-79	-0.459	-79	-0.147	-79	-0.170
-78	-0.461	-78	-0.134	-78	-0.149
-77	-0.463	-77	-0.115	-77	-0.109
-76	-0.458	-76	-0.149	-76	-0.148
-75	-0.451	-75	-0.159	-75	-0.132
-74	-0.443	-74	-0.153	-74	-0.132
-73	-0.433	-73	-0.134	-73	-0.080
-72	-0.423	-72	-0.138	-72	-0.128
-71	-0.417	-71	-0.164	-71	-0.158
-70	-0.410	-70	-0.168	-70	-0.147
-69	-0.398	-69	-0.166	-69	-0.107
-68	-0.390	-68	-0.147	-68	-0.102
-67	-0.381	-67	-0.148	-67	-0.118
-66	-0.368	-66	-0.117	-66	-0.095
-65	-0.362	-65	-0.112	-65	-0.102
-64	-0.341	-64	-0.147	-64	-0.137
-63	-0.324	-63	-0.121	-63	-0.108
-62	-0.307	-62	-0.117	-62	-0.119
-61	-0.290	-61	-0.109	-61	-0.091
-60	-0.274	-60	-0.098	-60	-0.105
-59	-0.258	-59	-0.095	-59	-0.089
-58	-0.242	-58	-0.075	-58	-0.073
-57	-0.225	-57	-0.074	-57	-0.089
-56	-0.210	-56	-0.061	-56	-0.053
-55	-0.190	-55	-0.064	-55	-0.071
-54	-0.169	-54	-0.082	-54	-0.086
-53	-0.153	-53	-0.094	-53	-0.090
-52	-0.131	-52	-0.103	-52	-0.078

APPENDIX VI Lag and correlation values for cross correlation analyses of water-levels (WL) at Taylor Slough (TS) and Palma Vista Well (PVW) and rainfall and water-level values at TS and PVW (continued)

WL Lag	WL Correlation	TS Precip/WL Lag	TS Precip/WL Correlation	PVW Precip/WL Lag	PVW Precip/WL Correlation
-51	-0.117	-51	-0.062	-51	-0.037
-50	-0.098	-50	-0.051	-50	-0.032
-49	-0.081	-49	-0.052	-49	-0.051
-48	-0.060	-48	-0.051	-48	-0.013
-47	-0.035	-47	-0.073	-47	-0.060
-46	-0.002	-46	-0.077	-46	-0.045
-45	0.033	-45	-0.077	-45	-0.055
-44	0.070	-44	-0.061	-44	-0.077
-43	0.107	-43	-0.040	-43	-0.033
-42	0.138	-42	-0.026	-42	-0.017
-41	0.165	-41	-0.020	-41	-0.008
-40	0.193	-40	-0.017	-40	0.003
-39	0.223	-39	-0.017	-39	-0.017
-38	0.251	-38	-0.017	-38	-0.042
-37	0.274	-37	-0.022	-37	-0.033
-36	0.297	-36	-0.029	-36	-0.043
-35	0.322	-35	-0.038	-35	-0.038
-34	0.342	-34	-0.021	-34	-0.013
-33	0.354	-33	-0.025	-33	-0.027
-32	0.367	-32	-0.027	-32	-0.030
-31	0.375	-31	-0.025	-31	-0.016
-30	0.384	-30	-0.033	-30	-0.016
-29	0.398	-29	-0.024	-29	0.024
-28	0.411	-28	-0.019	-28	0.007
-27	0.425	-27	-0.018	-27	-0.012
-26	0.442	-26	-0.016	-26	0.008
-25	0.451	-25	-0.005	-25	0.019
-24	0.458	-24	0.004	-24	0.030
-23	0.469	-23	0.007	-23	0.042
-22	0.486	-22	0.019	-22	0.052
-21	0.502	-21	0.021	-21	0.034
-20	0.518	-20	0.016	-20	0.031
-19	0.532	-19	0.012	-19	0.031
-18	0.549	-18	0.005	-18	0.019
-17	0.570	-17	0.019	-17	0.047
-16	0.585	-16	0.051	-16	0.089
-15	0.596	-15	0.055	-15	0.081
-14	0.611	-14	0.044	-14	0.058
-13	0.630	-13	0.012	-13	0.046
-12	0.654	-12	0.001	-12	0.041
-11	0.678	-11	0.003	-11	0.055
-10	0.704	-10	-0.003	-10	0.031
-9	0.726	-9	-0.011	-9	0.006
-8	0.748	-8	-0.021	-8	0.014
-7	0.768	-7	-0.022	-7	0.002
-6	0.795	-6	-0.010	-6	0.027
-5	0.824	-5	-0.003	-5	0.028
-4	0.848	-4	0.008	-4	0.042
-3	0.874	-3	0.009	-3	0.047

APPENDIX VI Lag and correlation values for cross correlation analyses of water-levels (WL) at Taylor Slough (TS) and Palma Vista Well (PVW) and rainfall and water-level values at TS and PVW (continued)

WL Lag	WL Correlation	TS Precip/WL Lag	TS Precip/WL Correlation	PVW Precip/WL Lag	PVW Precip/WL Correlation
-2	0.901	-2	0.007	-2	0.036
-1	0.928	-1	0.024	-1	0.057
0	0.953	0	0.101	0	0.182
1	0.950	1	0.198	1	0.272
2	0.934	2	0.222	2	0.245
3	0.916	3	0.226	3	0.243
4	0.896	4	0.225	4	0.217
5	0.873	5	0.231	5	0.233
6	0.847	6	0.238	6	0.249
7	0.823	7	0.239	7	0.216
8	0.798	8	0.239	8	0.190
9	0.773	9	0.230	9	0.182
10	0.750	10	0.220	10	0.186
11	0.730	11	0.209	11	0.195
12	0.714	12	0.196	12	0.170
13	0.700	13	0.191	13	0.182
14	0.687	14	0.190	14	0.184
15	0.679	15	0.181	15	0.164
16	0.673	16	0.180	16	0.183
17	0.665	17	0.188	17	0.197
18	0.651	18	0.202	18	0.200
19	0.634	19	0.195	19	0.175
20	0.619	20	0.185	20	0.165
21	0.605	21	0.170	21	0.145
22	0.592	22	0.159	22	0.142
23	0.582	23	0.152	23	0.140
24	0.571	24	0.143	24	0.110
25	0.559	25	0.135	25	0.116
26	0.545	26	0.141	26	0.144
27	0.527	27	0.142	27	0.130
28	0.508	28	0.139	28	0.129
29	0.492	29	0.132	29	0.114
30	0.476	30	0.136	30	0.127
31	0.458	31	0.134	31	0.103
32	0.438	32	0.128	32	0.103
33	0.417	33	0.126	33	0.103
34	0.397	34	0.124	34	0.101
35	0.376	35	0.129	35	0.124
36	0.352	36	0.138	36	0.122
37	0.329	37	0.128	37	0.097
38	0.304	38	0.118	38	0.103
39	0.279	39	0.111	39	0.107
40	0.255	40	0.105	40	0.104
41	0.234	41	0.095	41	0.087
42	0.214	42	0.099	42	0.118
43	0.189	43	0.111	43	0.146
44	0.160	44	0.114	44	0.134
45	0.129	45	0.116	45	0.111
46	0.100	46	0.108	46	0.090

APPENDIX VI Lag and correlation values for cross correlation analyses of water-levels (WL) at Taylor Slough (TS) and Palma Vista Well (PVW) and rainfall and water-level values at TS and PVW (continued)

WL Lag	WL Correlation	TS Precip/WL Lag	TS Precip/WL Correlation	PVW Precip/WL Lag	PVW Precip/WL Correlation
47	0.078	47	0.101	47	0.116
48	0.059	48	0.104	48	0.121
49	0.046	49	0.105	49	0.118
50	0.031	50	0.097	50	0.073
51	0.017	51	0.094	51	0.070
52	0.001	52	0.099	52	0.093
53	-0.017	53	0.097	53	0.094
54	-0.038	54	0.087	54	0.085
55	-0.058	55	0.076	55	0.089
56	-0.077	56	0.065	56	0.080
57	-0.097	57	0.056	57	0.076
58	-0.117	58	0.061	58	0.095
59	-0.135	59	0.067	59	0.099
60	-0.155	60	0.063	60	0.088
61	-0.175	61	0.054	61	0.075
62	-0.187	62	0.051	62	0.082
63	-0.207	63	0.044	63	0.058
64	-0.227	64	0.043	64	0.085
65	-0.243	65	0.053	65	0.091
66	-0.252	66	0.057	66	0.074
67	-0.261	67	0.056	67	0.072
68	-0.271	68	0.052	68	0.047
69	-0.280	69	0.046	69	0.056
70	-0.291	70	0.041	70	0.052
71	-0.305	71	0.035	71	0.040
72	-0.320	72	0.027	72	0.039
73	-0.326	73	0.022	73	0.041
74	-0.330	74	0.031	74	0.061
75	-0.335	75	0.026	75	0.025
76	-0.341	76	0.013	76	0.021
77	-0.350	77	0.001	77	0.004
78	-0.357	78	-0.003	78	-0.016
79	-0.364	79	0.007	79	-0.014
80	-0.367	80	0.010	80	-0.025
81	-0.368	81	0.000	81	-0.014
82	-0.368	82	-0.009	82	-0.041
83	-0.362	83	-0.008	83	-0.050
84	-0.360	84	0.000	84	-0.025
85	-0.360	85	-0.008	85	-0.032
86	-0.361	86	-0.016	86	-0.037
87	-0.363	87	-0.025	87	-0.040
88	-0.361	88	-0.031	88	-0.030
89	-0.358	89	-0.037	89	-0.027
90	-0.358	90	-0.040	90	-0.021
91	-0.355	91	-0.041	91	-0.017
92	-0.346	92	-0.049	92	-0.022
93	-0.335	93	-0.056	93	-0.039
94	-0.324	94	-0.058	94	-0.027
95	-0.312	95	-0.059	95	-0.038

APPENDIX VI Lag and correlation values for cross correlation analyses of water-levels (WL) at Taylor Slough (TS) and Palma Vista Well (PVW) and rainfall and water-level values at TS and PVW (continued)

WL Lag	WL Correlation	TS Precip/WL Lag	TS Precip/WL Correlation	PVW Precip/WL Lag	PVW Precip/WL Correlation
96	-0.301	96	-0.055	96	-0.063
97	-0.292	97	-0.061	97	-0.071
98	-0.280	98	-0.074	98	-0.064
99	-0.264	99	-0.084	99	-0.051
100	-0.252	100	-0.080	100	-0.041

APPENDIX VII Bulk PCA values for Taylor Slough (TS), Palma Vista Cave (PVC) and Palma Vista Well (PVW)

Date	TS-PC1	TS-PC2	PVC-PC1	PVC-PC2	PVW-PC2	PVW-PC2
04/26/07	1.620	0.941	-0.397	-0.331	-0.451	-0.302
05/09/07	1.594	1.360	-0.304	-0.919	-0.362	-0.675
05/23/07	1.757	0.809	-0.396	-1.052	-0.418	-0.476
06/07/07	1.036	-0.308	-0.969	-0.696	-0.775	-0.206
06/20/07	0.325	-2.493	-0.530	-0.773	-0.659	-0.362
07/05/07	0.903	-1.114	-0.706	0.192	-0.868	0.299
07/18/07	1.531	-1.249	-0.464	-0.666	-0.362	-0.740
08/01/07	0.719	-3.132	-0.295	-0.947	-0.649	-0.442
08/17/07	1.171	-1.926	-0.488	-0.580	-0.543	-0.421
08/29/07	1.500	1.183	-0.736	0.364	-0.634	0.188
09/12/07	1.452	0.580	-0.583	-0.127	-0.672	0.252
09/26/07	1.122	-0.401	-0.710	-0.019	-0.617	0.464
10/10/07	0.206	-2.529	-0.997	0.370	-0.889	0.709
10/24/07	2.130	0.017	-0.672	0.469	-0.768	0.826
11/06/07	1.953	-0.622	-0.818	0.950	-0.873	1.059
11/20/07	1.363	1.342	-0.661	0.675	-0.644	0.935
12/06/07	1.223	1.280	-0.618	0.229	-0.838	1.146
12/19/07	1.316	1.411	-0.730	0.313	-1.049	1.245
01/03/08	1.813	0.475	-0.733	0.172	-0.925	0.723
01/17/08	1.751	1.459	-0.749	0.207	-0.934	0.864

APPENDIX VIII Bulk PCA values for Taylor Slough (TS), Palma Vista Cave (PVC) and Palma Vista Well (PVW). Values exclude Na^+, K^+ and Cl^-

Date	TS-PC1	TS-PC2	PVC-PC1	PVC-PC2	PVW-PC2	PVW-PC2
04/26/07	-0.556	1.638	-0.038	-0.222	0.055	-0.323
05/09/07	-0.328	2.069	-0.472	-0.704	-0.252	-0.576
05/23/07	-0.701	1.582	-0.455	-0.986	-0.111	-0.309
06/07/07	-0.911	0.149	0.528	-2.101	0.450	-0.756
06/20/07	-1.994	-1.460	0.070	-1.491	0.202	-0.601
07/05/07	-1.551	0.169	0.810	-0.710	0.837	-0.315
07/18/07	-1.859	-0.133	0.008	-1.099	-0.343	-0.484
08/01/07	-2.794	-1.396	-0.286	-1.243	0.145	-0.668
08/17/07	-2.245	-0.342	0.034	-0.927	0.026	-0.383
08/29/07	-0.277	1.750	0.780	-0.192	0.508	0.010
09/12/07	-0.575	1.173	0.422	-0.652	0.569	0.073
09/26/07	-1.051	0.461	0.619	-0.822	0.656	0.326
10/10/07	-1.910	-1.510	1.081	-0.695	1.073	0.186
10/24/07	-1.279	0.677	0.790	-0.003	1.059	0.365
11/06/07	-1.731	0.492	1.191	0.351	1.288	0.457
11/20/07	-0.049	1.746	0.880	0.226	1.038	0.472
12/06/07	-0.167	2.060	0.604	-0.262	1.335	0.435
12/19/07	-0.101	2.147	0.782	-0.399	1.645	0.106
01/03/08	-1.172	1.899	0.678	-0.505	1.186	-0.157
01/17/08	-0.177	1.991	0.738	-0.541	1.295	-0.041

APPENDIX IX R Codes

Note: All data saved as .txt files, then imported to R for analysis. All cross correlation, correlation, and PCA data cross-checked in PAST

Cross Correlation:
Object, file and header names, and lag.max values vary by analysis.

Read text file:
```
>ObjectName <- read.table (file="FileName.txt", header=TRUE)
```

Report correlation values by lag number:
```
>ccf(ObjectName[,"HeaderName1"],ObjectName[,"HeaderName2"], lag.max = 100, type = "correlation", plot = "FALSE")
```

View cross correlogram:
```
>ccf(ObjectName[,"HeaderName1"],ObjectName[,"Headername2"], lag.max = 100, type = "correlation", ylab="CCF", main="Lag")
```

Correlation Matrices:

Read text file:
```
>ObjectName <- read.table (file="FileName.txt", header=TRUE)
```

Report correlation table:
```
>cor(ObjectName, y = NULL, use = "all.obs", method = c("spearman"))
```

Principle Component Analyses:
All data rotated, centered and scaled during analysis.

Read text file:
```
>ObjectName <- read.table (file="FileName.txt", header=TRUE)
```

Report loadings/eigenvectors by parameter:
```
>prcomp(ObjectName, rtx = TRUE, center = TRUE, scale = TRUE)
```

Load and report eigenvalues
```
>pr.r = prcomp(ObjectName, rtx = TRUE, center = TRUE, scale = TRUE)
>summary(prcomp(ObjectName, rtx = TRUE, center = TRUE, scale = TRUE))
```

APPENDIX X 2005 Course assessment and results (n = 11)

CALIBRATION COMPONENT			
Item #	**Item**	**Confidence Increase**	**Confidence Decrease**
1	Balance a check book.	1	0
2	Find the distance between two points on a USGS topographic map.	3	0
3	Use a GPS.	1	1
4	Construct a sentence consisting of more than 15 words without committing a grammatical error.	1	2
5	Drive a stick-shift car or truck.	0	3
6	Public speaking.	5	3
7	Make a case for evolution	4	0
8	Identify common rocks and minerals.	5	1
9	Mix with professional geologists in a social setting.	3	0
10	Plan and carry out a trip by car across the country.	2	0
11	Know the geologic time scale.	3	2
12	Explain why the geologic time scale is important.	2	2
13	Identify the states of the US on a map showing only their outlines.	1	0
14	Identify the countries of Europe (including eastern Europe) on a map showing only their outlines.	4	1
15	Identify the countries of Africa on a map showing only their outlines	4	3
16	Identify the countries of South America on a map showing only their outlines.	4	2
17	List the names of US Presidents in correct sequence for the 20th century.	4	4
18	Use metric and English units interchangeably.	5	0
	Total	*52*	*24*
	Net Change		*14.14%*

APPENDIX X 2005 Course assessment and results (n = 11) (continued)

MATH COMPONENT			
Item #	**Item**	**Confidence Increase**	**Confidence Decrease**
1	Understand very large and very small numbers and various representations of them.	1	5
2	Understand properties of, and representations for, the addition and multiplication of vectors.	5	3
3	Perform operations with real numbers and vectors, using mental computation or paper-and-pencil calculations for simple cases and technology for more-complicated cases.	5	3
4	Understand the properties of functions, including exponential, polynomial, rational, logarithmic, and periodic functions.	2	1
5	Interpret representations of functions of two variables.	7	1
6	Write equivalent forms of equations, inequalities and systems of equations and solve them fluently -- mentally or with paper and pencil in simple cases and using technology in all cases.	4	3
7	Approximate and interpret rates of change from graphical and numerical data.	6	0
8	Use trigonometric relationships to determine lengths and angle measurements.	5	0
9	Use Cartesian and polar coordinates to analyze geometric situations.	6	3
10	Understand and represent translations, reflections, rotations, and dilations of objects in the plane by using sketches, coordinates, vectors and function notation.	7	1
11	Visualize three-dimensional objects from different perspectives and analyze their cross sections.	3	3
12	Make decisions about units and scales that are appropriate for problem situations involving measurements.	4	1
13	Analyze precision, accuracy, and approximate error in measurement situations.	2	3
14	Know the characteristics of well-designed studies, including the role of randomization in surveys and experiments.	3	2
15	Understand histograms, parallel box plots, and scatterplots and use them to display data.	4	1
16	Compute basic statistics and understand the distinction between a statistic and a parameter.	6	2
17	For univariate measurement data, be able to display the distribution, describe its shape, and select and calculate summary statistics.	5	1
18	For bivariate measurement data, be able to display a scatterplot, describe its shape, and determine regression coefficients, regression equations, and correlation coefficients using technological tools.	7	2
19	Understand how sample statistics reflect the values of population parameters and use sampling distributions as the basis for informal inference.	5	1
20	Understand the concepts of conditional probability and independent events.	5	0
21	Understand how to compute the probability of a compound event.	6	0
	Total	*98*	*36*
	Net Change		*31.31%*

APPENDIX X 2005 Course assessment and results (n = 11) (continued)

KNOWLEDGE SURVEY			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	You measure a rectangular box as follows: length= 7.0 cm, width = 2.1 cm, height = 1.3 cm. What is the volume of the box?	2	3
2	What is the logarithm of 100,000?	3	7
3	The scale of your map is 1:60,000. You measure the distance between two points on the map as 3.0 cm. How many km are the points apart on the ground?	2	4
4	You know that radioactive decay of an isotope has a constant half-life. Does this mean that it has a constant third-life as well?	4	8
5	What is a function?	1	3
6	What does *dx* mean?	8	10
7	What is a derivative?	2	8
8	What is the ratio of a circle's circumference to its diameter?	4	8
9	What is the formula for a sine?	3	8
10	How many feet are in a meter?	4	6
	Assessment Score	*0.30*	*0.59*
	% Change		*96.97%*

APPENDIX XI 2005 Module assessments and results

How Large Is A Ton of Rock? Thinking About Rock Density			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	What is density? What are its units?	5	11
2	What is the equation for the volume of a cube?	11	12
3	What is the equation for the volume of a sphere?	4	10
4	Which is larger: a cube of ice weighing a ton or a cube of quartz weighing a ton?	11	10
5	What is a weighted average?	1	6
	Assessment Score	*0.53*	*0.82*
	% Change		*53.13%*
	n = 12		

Earth's Planetary Density: Constraining What We Think About the Earth's Interior			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	What is weighted average?	3	9
2	Imagine you work at a concession stand selling sodas, bottled water, and orange juice. In one day you sell 75 sodas, 50 bottles of water, and 32 bottles of orange juice. The price of a soda is $0.50, water is $1.00, and orange juice is 1.50. What is the average amount of money you made per beverage sold in that one day?	7	8
	Assessment Score	*0.45*	*0.77*
	% Change		*70%*
	n = 11		

Earthquake Magnitude: How Do We Compare The Size of Earthquakes?			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	What is the rage of the Richter Scale? On what is the Richter Scale based?	4	4
2	A magnitude 8 earthquake produces waves with a seismic amplitude __________ times larger than a magnitude 5 earthquake.	6	5
3	The two graphs below show the same data plotted with two different scales on the y-axis. Which graph is plotted with a linear scale? Which graph is plotted with a logarithmic scale?	5	12
	Assessment Score	*0.39*	*0.58*
	% Change		*50%*
	n = 12		

Vertical Profile of Stream Velocity: At What Depth is the Average?			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	What is the rule of thumb for the average stream velocity in a vertical section of a channel?	4	9
	Assessment Score	*0.33*	*0.75*
	% Change		*125%*
	n = 12		

APPENDIX XI 2005 Module assessments and results (continued)

Radioactive Decay and Popping Popcorn: Understanding the Rate Law			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	What is a decay chain?	3	6
2	What is a decay constant?	5	9
3	If you had a population of 50 pet frogs and there was 20% probability that any individual frog would escape in the period of one day, how many frogs would be left in the tank after 3 days?	7	10
	Assessment Score	*0.38*	*0.64*
	% Change		*66.67%*
	n = 13		

Understanding Radioactivity in Geology: Understanding the Decay Constant			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Imagine you have designed an experiment to determine the decay constant for 226Ra. You have invented a new instrument that measures the amount of atoms that decay over a given time increment. You can adjust this increment simply by entering a new value into your machine. Your experimental design allows for 1 month of samples to be taken. Which of the following measurement intervals will give you the best estimate of the decay constant for 226Ra?	10	4
	Assessment Score	*0.83*	*0.33*
	% Change		*-60%*
	n = 12		

Understanding Radioactivity in Geology: How Did We Get to the Understanding We Have Today?			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	In one sentence, explain the underlying concept that Rutherford's equation describes mathematically.	0	2
2	What is the "intensity of activity" for any radioactive population?	5	9
	Assessment Score	*0.11*	*0.78*
	% Change		*600%*
	n = 9		

Understanding Radioactivity in Geology: Calculating Age from the Daughter/Parent Ratio			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Which is longer: at third-life or a fourth-life?	6	5
2	What is the daughter-parent ratio after 4 half-lives?	2	0
3	Which of the following is an appropriate graph of D/P ratio vs. time?	4	2
	Assessment Score	*0.50*	*0.29*
	% Change		*-41.67%*
	n = 8		

APPENDIX XII 2006 Course assessment and results (n = 17)

CALIBRATION COMPONENT			
Item #	**Item**	**Confidence Increase**	**Confidence Decrease**
1	Balance a check book.	2	2
2	Find the distance between two points on a USGS topographic map.	3	2
3	Use a GPS.	5	3
4	Construct a sentence consisting of more than 15 words without committing a grammatical error.	5	1
5	Drive a stick-shift car or truck.	1	2
6	Public speaking.	3	4
7	Make a case for evolution	2	3
8	Identify common rocks and minerals.	6	2
9	Mix with professional geologists in a social setting.	4	2
10	Plan and carry out a trip by car across the country.	1	1
11	Know the geologic time scale.	1	2
12	Explain why the geologic time scale is important.	4	2
13	Identify the states of the US on a map showing only their outlines.	2	1
14	Identify the countries of Europe (including eastern Europe) on a map showing only their outlines.	2	7
15	Identify the countries of Africa on a map showing only their outlines	3	3
16	Identify the countries of South America on a map showing only their outlines.	4	4
17	List the names of US Presidents in correct sequence for the 20th century.	2	4
18	Use metric and English units interchangeably.	4	2
	Total	*54*	*47*
	Net Change		*2.30%*

APPENDIX XII 2006 Course assessment and results (n = 17) (continued)

MATH COMPONENT			
Item #	**Item**	**Confidence Increase**	**Confidence Decrease**
1	Understand very large and very small numbers and various representations of them.	2	0
2	Understand properties of, and representations for, the addition and multiplication of vectors.	4	2
3	Perform operations with real numbers and vectors, using mental computation or paper-and-pencil calculations for simple cases and technology for more-complicated cases.	3	3
4	Understand the properties of functions, including exponential, polynomial, rational, logarithmic, and periodic functions.	5	1
5	Interpret representations of functions of two variables.	3	3
6	Write equivalent forms of equations, inequalities and systems of equations and solve them fluently -- mentally or with paper and pencil in simple cases and using technology in all cases.	4	4
7	Approximate and interpret rates of change from graphical and numerical data.	5	2
8	Use trigonometric relationships to determine lengths and angle measurements.	6	2
9	Use Cartesian and polar coordinates to analyze geometric situations.	2	3
10	Understand and represent translations, reflections, rotations, and dilations of objects in the plane by using sketches, coordinates, vectors and function notation.	5	5
11	Visualize three-dimensional objects from different perspectives and analyze their cross sections.	5	1
12	Make decisions about units and scales that are appropriate for problem situations involving measurements.	5	4
13	Analyze precision, accuracy, and approximate error in measurement situations.	4	4
14	Know the characteristics of well-designed studies, including the role of randomization in surveys and experiments.	6	2
15	Understand histograms, parallel box plots, and scatterplots and use them to display data.	9	1
16	Compute basic statistics and understand the distinction between a statistic and a parameter.	8	1
17	For univariate measurement data, be able to display the distribution, describe its shape, and select and calculate summary statistics.	9	2
18	For bivariate measurement data, be able to display a scatterplot, describe its shape, and determine regression coefficients, regression equations, and correlation coefficients using technological tools.	8	2
19	Understand how sample statistics reflect the values of population parameters and use sampling distributions as the basis for informal inference.	7	2
20	Understand the concepts of conditional probability and independent events.	8	4
21	Understand how to compute the probability of a compound event.	6	2
	Total	*114*	*50*
	Net Change		*20.92%*

APPENDIX XII 2006 Course assessment and results (n = 17) (continued)

KNOWLEDGE SURVEY			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	You measure a rectangular box as follows: length= 7.0 cm, width = 2.1 cm, height = 1.3 cm. What is the volume of the box?	1	2
2	What is the logarithm of 100,000?	2	7
3	The scale of your map is 1:60,000. You measure the distance between two points on the map as 3.0 cm. How many km are the points apart on the ground?	6	8
4	You know that radioactive decay of an isotope has a constant half-life. Does this mean that it has a constant third-life as well?	6	12
5	What is a function?	2	10
6	What does *dx* mean?	13	16
7	What is a derivative?	3	9
8	What is the ratio of a circle's circumference to its diameter?	2	11
9	What is the formula for a sine?	3	6
10	How many feet are in a meter?	7	9
	Assessment Score	*0.27*	*0.53*
	% Change		*95.65%*

APPENDIX XIII 2006 Module assessments and results

Is It Hot in Here? Spreadsheeting Conversions in the English and Metric Systems			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Convert the following numbers to decimal notation and Excel: 6.345×10^5	4	16
2	Convert the following numbers to decimal notation and Excel: 8.5×10^{-4}	4	18
3	What is the relationship between: a kilogram and a gram?	17	18
4	What is the relationship between: a liter and a milliliter?	17	18
5	Convert 55 millimeters to kilometers.	6	11
6	How would you write the following mathematic formulae as Excel equations: 7.3 multiplied by the contents of call column A, Row 6?	2	12
7	How would you write the following mathematic formulae as Excel equations: 5.2 + 4 + (10 divided by 7)?	2	12
	Assessment Score	*0.39*	*0.79*
	% Change		*101.92%*
	n = 19		

How Large Is A Ton of Rock? Thinking About Rock Density			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Convert these grades to a weighted GPA. PRE: Class 1 (Hours: 3, Grade: A), Class 2 (Hours: 4, Grade: C), Class 3 (Hours: 5, Grade: B), Class 4 (Hours: 2, Grade: D)---POST: Class 1 (Hours: 2, Grade: C), Class 2 (Hours: 5, Grade: A), Class 3 (Hours: 4, Grade: B), Class 4 (Hours: 3, Grade: D)	4	8
	Assessment Score	*0.25*	*0.50*
	% Change		*100%*
	n = 16		

How Far is Yonder Mountain? A Trig Problem			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Suppose you want to know the height of a tree. You stand at the tree and measure a distance 100 ft out from the tree. You turn around and measure the angle from you to the top of the tree. What trigonometric ratio do you use to find the height of the tree from those two numbers? Please don't guess. If you don't know, say so. *Assume ground is horizontal.*	9	11
2	Suppose you want to know the height of that tree, but you can't walk up to the tree. There's a big, mean dog chained to it. You're standing 200 ft from the tree, and you can measure angles to the top of the tree, and you have a tape measure. How can you determine the height of the tree? If you can't figure this out in 5 minutes, say so. Don't guess. Answer only if you're confident of your answer. *Assume ground is horizontal.*	9	9
3	What number does Excel return for =cos(20)?	3	7
	Assessment Score	*0.44*	*0.56*
	% Change		*28.57%*
	n = 16		

APPENDIX XIII 2006 Module assessments and results (continued)

A Look at High School Dropout Rates: Average Rates of Change and Trend Lines			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	What is an average rate of change?	6	9
2	What is a scatter plot?	16	19
3	What is a trend line?	15	13
4	Given the following data points, calculate the average rate of change of the dataset: (2,4)(5,7)(13,14)(20,12)	0	4
5	A classmate claims that the fact that the average rate of change in product sales was positive between 1995 and 2005 means that the product sales have increased every year between 1995 and 2005. Do you agree or disagree? Explain.	14	13
6	Does calculating the average rate of change over an entire dataset give you the slope of the trend line? Explain.	2	10
	Assessment Score	*0.55*	*0.71*
	% Change		*28.30%*
	n = 16		

Earth's Planetary Density - Constraining What We Think of the Earth's Interior			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	What is the formula for the volume of a spherical shell with the inside radius R1 and outside radius R2?	2	12
2	Explain how you would calculate the overall density of a planet that consisted of two shells: crust and core.	4	9
3	Name the four shells composing the earth?	14	16
4	Which of the four shells is the thinnest?	15	16
5	Which of the four shells has the smallest volume?	3	9
6	What is the Gutenberg Discontinuity?	1	10
	Assessment Score	0.38	0.71
	% Change		84.62%
	n = 17		

How Large is the Great Pyramid of Giza? Would It Make A Wall That Would Enclose France?			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	How many acres are in a square mile?	0	11
2	What is the volume of a pyramid that has a base of 30 acres and a height of 300 ft? Give answer in acre-ft.	1	7
3	What is the volume of a cone that has a base of 30 acres and a height of 300 ft? Give answer in acre-ft?	0	0
4	A snake has a volume of 30 cm^3. It's cross-sectional area is 1 square cm. How long is the snake? Give the answer in inches.	0	3
5	How long would it take you to walk from campus to the intersection of Kennedy and Westshore? Give the answer in minutes, and explain how you got it.	0	6
6	Suppose the Geoclub wanted to fill this lecture room with balloons. How many balloons would it take? Explain your answer.	1	8
	Assessment Score	0.02	0.39
	% Change		1650%
	n = 15		

Shaking Ground: Linking Earthquake Magnitude and Intensity			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	From the graph, what is the recurrence interval of a flood with discharge of 30,000 ft^3/s?	3	9
2	From the graph, what is the discharge of a flood with a 3-year recurrence interval?	12	9
3	What is the area of a circle with a radius of 3 meters?	12	14
4	If you are 10 km from the epicenter of a magnitude 7 earthquake, what acceleration (a) do you feel?	6	7
5	What is IX-VI?	13	16
	Assessment Score	0.51	0.61
	% Change		19.57%
	n = 18		

Radioactive Decay and Popping Popcorn: Understanding the Rate Law			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Given that the half-life is constant in radioactive decay, is the third-life constant too?	9	11
2	Which is longer, the half-life or the third-life?	7	6
3	How does the rate of reaction (radioactivity) vary with time in radioactive decay?	2	7
4	^{14}C decays to ^{14}N by beta decay. ^{40}K decays to ^{40}Ar by beta decay. Which isotope is more radioactive, ^{14}C or ^{40}Ar? Or are they equally radioactive?	1	6
5	What does the equation $dN/dt = -kN$ mean?	0	3
6	In the equation $N = N_0e^{-kt}$, what are the dimensions of k?	3	4
7	What is the Law of Large Numbers?	0	5
	Assessment Score	0.26	0.50
	% Change		90.91%
	n = 12		

APPENDIX XIV 2007 Course assessment and results (n = 11)

MATH PERCEPTION			
Item #	**Item**	**# Positive Shifts**	**# Negative Shifts**
1	I am good at math.	5	0
2	If I work at it, I can do well in math.	5	0
3	Good math teachers show students the exact way to answer the questions they'll be tested on.	6	3
4	Using a computer makes learning math more complicated than it needs to be.	7	1
5	Math helps me understand the world around me.	4	1
6	Mathematics has been an important tool to help me learn other subjects.	5	4
7	I rarely encounter situations that are mathematical in nature outside school.	7	1
8	I try to avoid courses that involve mathematics.	7	2
9	Becoming more proficient in math prepares you for the next math class, but that's about all.	7	0
10	In mathematics you can be creative and discover things for yourself.	6	0
11	After I've forgotten all the formulas, I'll still be able to use ideas I've learned in math.	9	0
12	I often see familiar mathematical concepts in courses outside of math.	6	2
13	Doing math helps me think clearly and logically.	4	4
14	Expressing scientific concepts in mathematical equations just makes them more confusing.	3	3
15	I don't need a good understanding of math to achieve my career goals.	7	0
	Total	*88*	*21*
	Net Change		*40.60%*

APPENDIX XIV 2007 Course assessment and results (n = 11) (continued)

MATH CONFIDENCE			
		Confidence Increase	**Confidence Decrease**
1	Understand very large and very small numbers and various representations of them.	7	2
2	Perform operations with real numbers using mental computation or paper-and-pencil calculations for simple cases and technology for more complicated cases.	8	1
3	Understand the properties of functions, including linear, exponential, logarithmic, power, and periodic functions.	5	3
4	Interpret representations of functions of two variables.	4	2
5	Approximate and interpret rates of change from graphical and numerical data.	5	1
6	Use trigonometric relationships to determine lengths and angle measurements.	5	0
7	Visualize three-dimensional objects from different perspectives and analyze their cross sections.	5	2
8	Make decisions about units and scales that are appropriate for problem situations involving measurements.	5	2
9	Analyze precision, accuracy, and approximate error in measurement situations.	3	3
10	Define basic descriptive statistics such as mean, standard deviation, and correlation coefficient.	4	5
	Total	*51*	*21*
	Net Change		*27.27%*

APPENDIX XIV 2007 Course assessment and results (n = 11) (continued)

KNOWLEDGE SURVEY			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	What is the volume of a rectangular box that is 15 cm by 12 cm by 2.1 cm?	0	2
2	Suppose you decided to fill a 20 ft x 50 ft classroom with balloons. How many balloons would it take? Explain your answer.	3	8
3	Can you describe in words, or with an equation, a *power function*? How might you apply the use of this function to a geological situation?	3	4
4	What is the formula for sine?	5	7
5	What is a weighted average?	2	7
6	Given that the half-life is constant in radioactive decay, is the third-life constant too? *Yes or no*.	5	7
7	Convert 55 millimeters to kilometers.	8	9
8	Write a cell equation in Excel to convert 55 mm to km.	2	6
9	What is a function?	2	4
10	From the graph, what is the recurrence interval of a flood with a discharge of 15,000 ft^3/s? (see graph below)	8	8
11	Put in correct scientific notation: 25,000,000,000,000. How many significant figures does it have?	7	7
12	Put in correct scientific notation: 0.00000000608. How many significant figures does it have?	6	7
13	What is the range of the earthquake frequencies shown in the table below?	2	5
14	Write a cell equation in Excel to find the range of the earthquake frequencies shown in the table below. (see table below)	3	3

Graph for item 10:

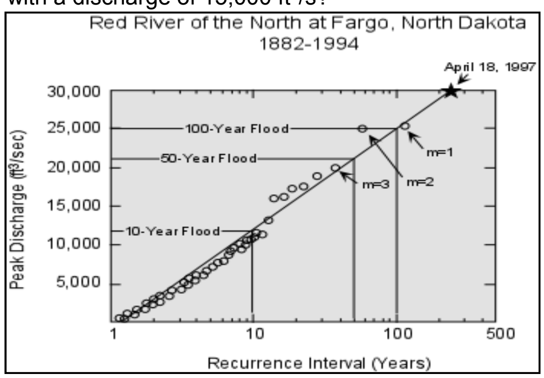


Table for items 13 and 14:

	B	C
2	Year	Number
3	1970	29
4	1971	23
5	1972	20
6	1973	16
7	1974	21
8	1975	21
9	1976	25
10	1977	16
11	1978	18
12	1979	19

KNOWLEDGE SURVEY (cont'd)			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
15	A sphere of iron ore has a diameter of 1 foot. Its density is 5.5 g/cm^3. What is its mass in kg?	0	0
16	What does *dx* mean in the expression $\int f(x)\,dx$?	6	9
	Assessment Score	*0.35*	*0.53*
	% Change		*50%*

APPENDIX XV 2007 Module assessments and results

How Large Is A Ton of Rock? Thinking About Rock Density			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Joe's grades last semester were as follows: Minerology (4 credits), B. Calculus (4 credits), A. Sociology (3 credits), C. Golf (2 credits), C. English (3 credits), B. What was Joe's grade point average for the semester?	4	8
4	A sphere of iron ore has a diameter of 1 foot. Its density is 5.5 g/cm^3. What is its mass in kg?	3	5
5	A kg weighs how many pounds?	7	14
	Assessment Score	0.33	0.64
	% Change		92.86%
	n = 14		

Is It Hot in Here? Spreadsheeting Conversions in the English and Metric Systems			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Convert the following numbers to decimal notation and Excel: 6.345×10^5	9	11
2	Convert the following numbers to decimal notation and Excel: 8.5×10^{-4}	9	11
5	Convert 55 millimeters to kilometers.	10	11
8	The table here shows the conversion of ounces to grams. How many ounces is equivalent to 15 grams? Grams / Ounces 10 / 0.352 20 / 0.705 30 / 1.057 40 / 1.410 50 / 1.762	9	12
9	How would you write the following mathematic formulae as Excel equations: 7.3 multiplied by the contents of call column A, Row 6?	9	12
10	How would you write the following mathematic formulae as Excel equations: 5.2 + 4 + (10 divided by 7)?	9	12
	Assessment Score	0.76	0.96
	% Change		25.45%
	n = 12		

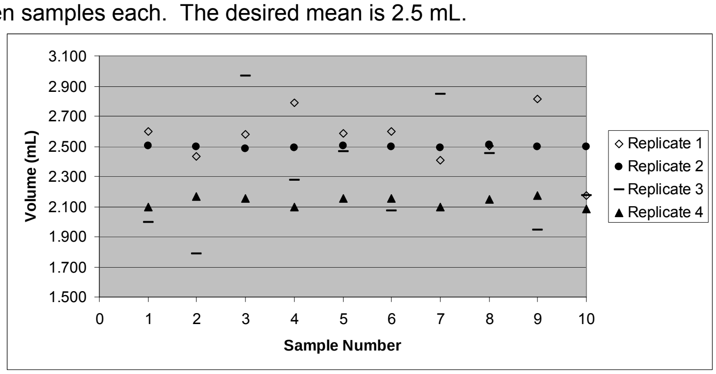
APPENDIX XV 2007 Module assessments and results (continued)

Earthquake Magnitude: How Can We Compare the Sizes of Earthquakes?			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Solve the following equation for x: 32 = 4* log(x) + 28	10	11
4	Put in correct scientific notation: 25,000,000,000,000. How many significant figures does it have?	9	13
5	Put in correct scientific notation: 0.00000000608. How many significant figures does it have?	10	14
6	You have been studying the growth of a bacteria culture in biology class. After learning that bacteria growth is an exponential function, you create the plot on the right showing how large you expect your bacteria population to be after 50 days. Describe how your plot would look if you changed your y-axis to a logarithmic scale.	5	13
	Assessment Score	0.61	0.91
	% Change		50%
	n = 14		

Calibrating a Pipettor			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Distinguish between accuracy and precision by describing the difference between an inaccurate and an imprecise piece of laboratory equipment.	1	11
2	If you have a sample of liquid with a mass of 6 grams and a density of 0.95 g/cm3, what is its volume?	2	6
3	What do the mean and standard deviation measure?	5	13
	This spreadsheet shows the cumulative weights of ten successive samples of powder added one by one to a weighing pan. The orange cells are intended to show the weights of the individual samples, the mean weight, and the standard deviation of the sample weights.		

	B	C	D
2	Sample	Cumulative Wt (g)	Weight of sample (g)
3	1	0.501	
4	2	1.003	
5	3	1.498	
6	4	1.998	
7	5	2.49	
8	6	2.988	
9	7	3.495	
10	8	3.996	
11	9	4.486	
12	10	4.991	
13			
14	Mean		
15	Standard Deviation		

4	To complete the spreadsheet, what cell equations do you need to place in Cell D10?	5	11
5	To complete the spreadsheet, what cell equations do you need to place in Cell D14?	2	6
6	To complete the spreadsheet, what cell equations do you need to place in D15?	1	8
	The scatter plot shows information from four replicate sets of volume measurements of ten samples each. The desired mean is 2.5 mL.		



7	Which datasets have the highest accuracy?	2	8
8	Which ones have the highest precision?	12	13
9	Which dataset best reflects the desired results?	0	2
10	How does relative/percent error differ from standard deviation?	0.24	0.66
	Assessment Score		177.42%
	% Change		
	n = 13		

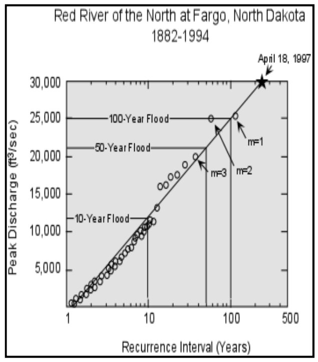
Frequency of Large Earthquakes: Introducing Some Elementary Statistical Descriptors

Use the spreadsheet to answer the following questions.

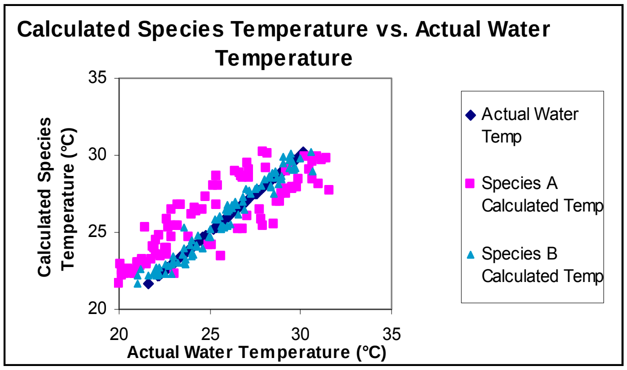
	B	C
2	Year	Number
3	1970	29
4	1971	23
5	1972	20
6	1973	16
7	1974	21
8	1975	21
9	1976	25
10	1977	16
11	1978	18
12	1979	19

Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	What is the mean number of earthquakes per year?	8	9
2	What is the median?	1	4
3	What is Q1, the first quartile?	2	5
4	What is the 90th percentile?	5	6
5	Write out the cell equation that finds the range in the number of earthquakes per year.	0	3
	Assessment Score	0.25	0.45
	% Change		81.25%
	n = 13		

APPENDIX XV 2007 Module assessments and results (continued)

Shaking Ground: Linking Earthquake Magnitude and Intensity			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
			
1	From the graph, what is the recurrence interval of a flood with discharge of 30,000 ft^3/s?	9	13
2	From the graph, what is the discharge of a flood with a 3 year recurrence interval?	10	11
3	What is the area of a circle with radius 3 meters?	9	13
4	If you are 10 km from the epicenter of a magnitude 7 earthquake, what acceleration (*a*) do you feel? The relationship between magnitude and shaking (acceleration) is $a = 1300*(e^{0.67*M})*(D+25)^{-1.6}$, where *a* is acceleration (in units of cm/sec^2) , *M* is magnitude, and *D* is distance (in km) (from Donovan, 1973).	2	10
5	What is IX minus VI ?	11	13
	Assessment Score	0.63	0.92
	% Change		46.34%
	n = 13		

How Large is the Great Pyramid of Giza? Would It Make A Wall That Would Enclose France?			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	How many acres are in a square mile?	1	10
2	What is the volume of a pyramid that has a base of 30 acres and a height of 300 ft? Give answer in acre-ft.	2	6
3	What is the volume of a cone that has a base of 30 acres and a height of 300 ft? Give answer in acre-ft.	0	1
4	A snake has a volume of 30 cm^3. Its cross-sectional area is 1 square cm. How long is the snake? Give answer in inches.	4	7
6	Suppose you decided to fill a 20 ft x 50 ft classroom with balloons. How many balloons would it take? Explain your answer.	2	8
	Assessment Score	0.14	0.49
	% Change		255.56%
	n = 13		

From Isotopes to Temperature: Working With a Temperature Equation			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	What is $\delta^{18}O$ and how is it related to ^{18}O and ^{16}O?	3	6
2	Describe the difference between R^2 and R.	1	2
3	For which correlation of calculated temperature to actual temperature is R^2 the greatest for the two species in the given figure? 	4	9
4	You are using the equation below to calculate the temperature based on two variables, *a* and *b*, using Excel. The values for *a* occupy the range A3 to A32, and the values for *b* occupy the range B3 to B32. Write out the Excel formula for the equation below, as you would enter it into cell C3 (prior to dragging and copying the equation down to C32). $\mathrm{T(°C)} = \frac{(a-b)-7.55}{-0.34}$	6	7
	Assessment Score	0.32	0.55
	% Change		71.43%
	n = 11		

Radioactive Decay and Popping Popcorn: Understanding the Rate Law			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Given that the half-life is constant in radioactive decay, is the third-life constant too?	7	13
2	Which is longer, the half-life or the third life?	7	7
3	How does the rate of reaction (radioactivity) vary with time in radioactive decay?	1	6
4	^{14}C decays to ^{14}N by beta decay. ^{40}K decays to ^{40}Ar by beta decay. Which isotope is more radioactive, ^{14}C or ^{40}Ar? Or are they equally radioactive?	2	7
5	What does the equation $dN/dt = -kN$ mean?	4	6
	Assessment Score	0.323076923	0.6
	% Change		85.71%
	n = 13		

APPENDIX XV 2007 Module assessments and results (continued)

Carbon Sequestration in Campus Trees			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Can you describe in words, or with an equation, a *power function*?	4	6
2	Can you define an *allometric relationship*?	2	8
3	Why might scientists be interested in finding relationships between the growth and size of a whole organism and the growth and size of a portion of that same organism?	10	11
4	If we find a straight line on a graph where both vertical and horizontal axes are logarithmic scales, what kind of a curve would that straight line become when plotted on a graph where each axis has a linear scale.	1	5
	Assessment Score	0.33	0.58
	% Change		76.47%
	n = 13		

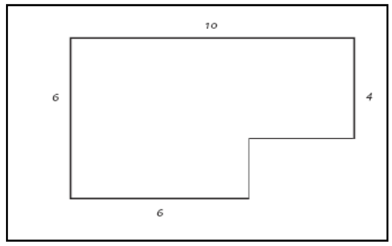
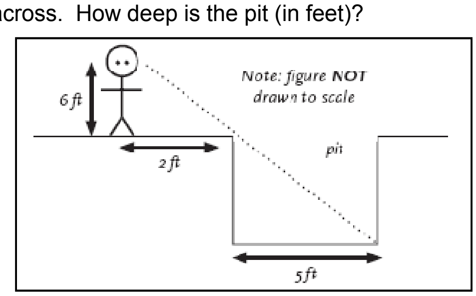
APPENDIX XVI 2008 Course assessment and results (n = 12) (continued)

Note: Post-course results to knowledge survey refer to items from knowledge survey from 2007 course assessment

MATH PERCEPTION			
Item #	**Item**	# Positive Shifts	# Negative Shifts
1	I am good at math.	1	1
2	If I work at it, I can do well in math.	1	2
3	Good math teachers show students the exact way to answer the questions they'll be tested on.	4	2
4	Using a computer makes learning math more complicated than it needs to be.	4	2
5	Math helps me understand the world around me.	1	4
6	Mathematics has been an important tool to help me learn other subjects.	3	3
7	I rarely encounter situations that are mathematical in nature outside school.	0	2
8	I try to avoid courses that involve mathematics.	4	1
9	Becoming more proficient in math prepares you for the next math class, but that's about all.	1	2
10	In mathematics you can be creative and discover things for yourself.	3	2
11	After I've forgotten all the formulas, I'll still be able to use ideas I've learned in math.	1	2
12	I often see familiar mathematical concepts in courses outside of math.	2	1
13	Doing math helps me think clearly and logically.	2	2
14	Expressing scientific concepts in mathematical equations just makes them more confusing.	4	0
15	I don't need a good understanding of math to achieve my career goals.	1	4
	Total	32	30
	Net Change		1.11%

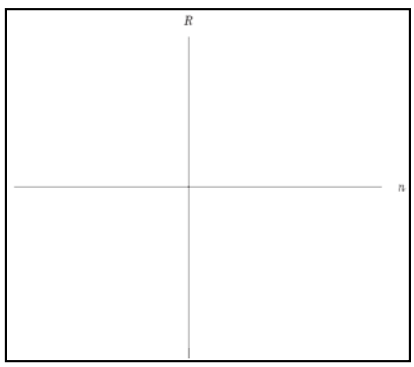
APPENDIX XVI 2008 Course assessment and results (n = 12) (continued)

Note: Post-course results to knowledge survey refer to items from knowledge survey from 2007 course assessment (continued)

KNOWLEDGE SURVEY			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	What is the area of this figure? If it has a uniform height of 4, what would be its volume?  	9	5
2	You are saving money for field camp and decide to invest in the stock market rather than rely on the interest rate from a savings account. In the six months since you began investing, the market increases 15%. In the seventh month, it loses 15%. Are you left with more, less, or the same amount of money you originally invested after this time period (ignore brokerage fees and other investment costs)? Explain your answer.	5	10
3	A certain sinkhole covers an area of 100 square meters and expands its area by 10% per year. What area is it after 6 years?	1	9
4	What is the value of the derivative of $x^2 + 3x + 7$ at $x = 2$?	10	10
5	Write an Excel-formatted equation that will convert 55 mm to km.	4	7
6	The expression y = mx + b (where m and b are constants) states a linear function. Give an expression than states a power function.	6	11
7	Eight geology students were sent into the field to bring back samples of granite. By the time they all got back to camp, they had brought back 12 samples of granite and 16 samples of arkose. How many samples of granite were brought in by the first four students?	5	9
8	As shown in the following figure, a man whose eyes are six feet above the ground stands next to a round pit dug into the ground. The pit measures five feet across. How deep is the pit (in feet)?  	4	8

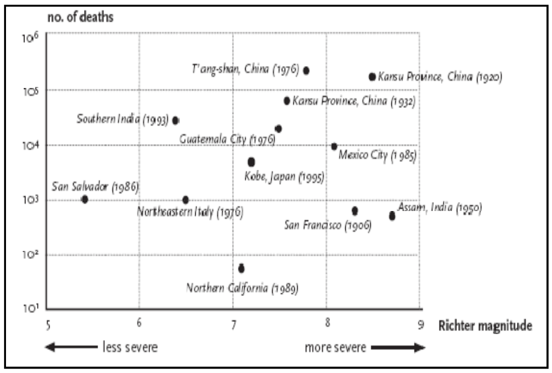
APPENDIX XVI 2008 Course assessment and results (n = 12) (continued)

Note: Post-course results to knowledge survey refer to items from knowledge survey from 2007 course assessment (continued)

KNOWLEDGE SURVEY (cont'd)			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
9	The Richter Magnitude scale is logarithmic. A RM-6 earthquake for example releases about 30× the amount of energy as a RM-5 earthquake, and a RM-7 earthquake releases about 30× the amount of energy as a RM-6 earthquake. That being the case, an 8.6-Richter Magnitude earthquake releases how many times the energy of a 6.6-Richter Magnitude earthquake?	2	8
10	Put the number in correct scientific notation: 25,000,000,000,000. How many significant figures does it have?	12	8
11	Put the number in correct scientific notation: 0.00000000608. How many significant figures does it have?	9	12
12	Sketch a graph of the equation $5R - 12n = 60$ on the set of axes given. Label the coordinates of the n- and R- intercepts. 	5	12
13	A hectare is a metric unit of area and an acre is a U.S. unit of area. Both are often used to measure the sizes of large plots of land. An acre is 1/640 of a square mile. One hectare is approximately two and a half acres. A certain piece of land measures 5 miles by 5 miles. What is its area in hectares?	0	8

APPENDIX XVI 2008 Course assessment and results (n = 12) (continued)

Note: Post-course results to knowledge survey refer to items from knowledge survey from 2007 course assessment (continued)

KNOWLEDGE SURVEY (cont'd)			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
14	This figure describes 12 earthquakes that occurred in different parts of the world. The horizontal axis gives the magnitude of the earthquake using the Richter scale. The vertical axis gives the number of people killed by the quake. How many of the earthquakes killed at least 100 times as many people as the San Salvador earthquake in 1986? 	7	7
15	Calories as reported on nutritional labels are actually kilocalories (abbreviated as Cal or kcal), and are capitalized to differentiate them from calories (non-capitalized, abbreviated as cal), which are 1/1000 of a Calorie. For example, a 580-Calorie Big Mac from McDonalds is actually 580,000 calories. While doing field work, you burn calories at the rate of 100 cal/kg/min. What is that rate in cal/lbs/hour?	2	6
16	If 2^{10} is approximately the same as 10^3 (a thousand, or kilo-), then 2^{40} is approximately what?	5	10
	Assessment Score	*0.41*	*0.65*
	% Change		*56.96%*

APPENDIX XVII 2008 Module assessments and results

Calculating the Volume of a Box: A Look at Significant Figures			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	You measure a rectangular box as follows: length= 7.0 cm, width = 2.1 cm, height = 1.3 cm. What is the volume of the box?	1	13
4	Let a = 140 ± 5 and b = 5 ± 1. What is $a \div b$?	0	4
	Assessment Score	0.04	0.61
	% Change		1600%
	n = 14		

Is It Hot in Here? Spreadsheeting Conversions in the English and Metric Systems			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Convert the following numbers to decimal notation and Excel: 6.345×10^5	7	13
2	Convert the following numbers to decimal notation and Excel: 8.5×10^{-4}	7	13
5	Convert 55 millimeters to kilometers.	11	13
8	The table here shows the conversion of ounces to grams. How many ounces is equivalent to 15 grams? Grams / Ounces: 10 / 0.352; 20 / 0.705; 30 / 1.057; 40 / 1.410; 50 / 1.762	10	13
	Assessment Score	0.67	1.00
	% Change		48.57%
	n = 13		

How Large Is A Ton of Rock? Thinking About Rock Density			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
2	A sphere of iron ore has a diameter of 1 foot. Its density is 5.5 g/cm^3. What is its mass in kg?	0	8
	Assessment Score	0.00	0.57
	% Change		*
	n = 14		

How Large Is A Ton of Rock? II: Thinking About Rock Composition			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
3	What is a weighted average?	8	10
	Assessment Score	0.67	0.83
	% Change		25%
	n = 12		

APPENDIX XVII 2008 Module assessments and results (continued)

Shaking Ground: Linking Earthquake Magnitude and Intensity			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
2	A magnitude 8 earthquake produces waves with a seismic amplitude of _____ times larger than a magnitude 5 earthquake.	8	13
3	The entering freshman class at a local university has 4000 female students and 2000 male students. What is the ratio of female to male students in the freshman class?	5	11
4	Put in correct scientific notation: 25,000,000,000,000. How many significant figures does it have?	11	14
5	You have been studying the growth of a bacteria culture in biology class. After learning that bacteria growth is an exponential function, you create the plot below showing how large you expect your bacteria population to be after 50 days. Describe how your plot would look if you changed your *y*-axis to a logarithmic scale.	10	14
	Assessment Score	0.61	0.93
	% Change		52.94%
	n = 14		

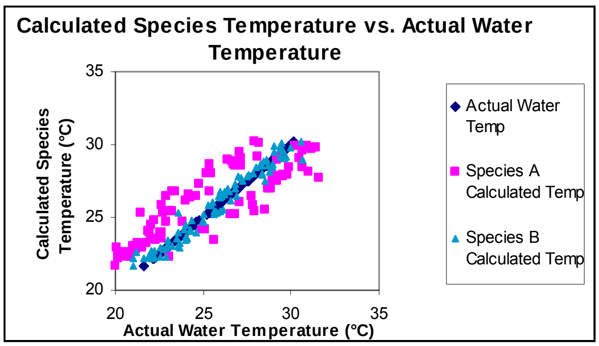
Let's Take a Hike in Catoctin Mountain Park			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
2	What is grade and how is it calculated?	7	15
3	What trigonometric function can you use to find the angle of a slope?	12	15
4	Which of the following is correct: a McDonald's Big Mac has 560 calories or 560,000 calories? Explain your answer.	11	15
	Assessment Score	0.67	1.00
	% Change		50%
	n = 15		

How Far is Yonder Mountain? A Trig Problem			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Convert azimuth 217 to a bearing.	12	14
2	Convert bearing S15E to an azimuth.	11	15
5	Where do the following lines cross? $25x + 5y = 45$ and $5x - 10y = -20$	7	14
6	Geometrically, what is the following equation? $4x + 5y - 4z = 20$	2	11
	Assessment Score	0.53	0.90
	% Change		68.75%
	n = 15		

Radioactive Decay and Popping Popcorn: Understanding the Rate Law			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
5	In the equation $N = N_0e^{-kt}$, what are the dimensions of *k*?	3	9
	Assessment Score	0.25	0.75
	% Change		200%
	n = 15		

APPENDIX XVII 2008 Module assessments and results (continued)

Carbon Sequestration in Campus Trees			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	Can you describe in words, or with an equation, a *power function*?	3	14
2	Can you define an *allometric relationship*?	2	7
	Assessment Score	0.17	0.70
	% Change		320%
	n = 15		

From Isotopes to Temperature: Working With a Temperature Equation			
Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	What is $\delta^{18}O$ and how is it related to ^{18}O and ^{16}O?	1	8
3	For which correlation of calculated temperature to actual temperature is R^2 the greatest for the two species in the given figure? 	12	14
4	You are using the equation below to calculate the temperature based on two variables, *a* and *b*, using Excel. The values for *a* occupy the range A3 to A32, and the values for b occupy the range B3 to B32. Write out the Excel formula for the equation below, as you would enter it into cell C3 (prior to dragging and copying the equation down to C32). $T(°C) = \frac{(a-b)-7.55}{-0.34}$	8	14
	Assessment Score	0.50	0.86
	% Change		71.43%
	n = 14		

Frequency of Large Earthquakes: Introducing Some Elementary Statistical Descriptors

Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
	Use the spreadsheet to answer the following questions.		

	B	C
2	Year	Number
3	1970	29
4	1971	23
5	1972	20
6	1973	16
7	1974	21
8	1975	21
9	1976	25
10	1977	16
11	1978	18
12	1979	19

Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
2	What is the median?	7	14
3	What is Q1, the first quartile?	4	12
4	What is the 90th percentile?	1	7
	Assessment Score	0.29	0.79
	% Change		175%
	n = 14		

How Large is the Great Pyramid of Giza? Would It Make A Wall That Would Enclose France?

Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	How many acres are in a square mile?	8	12
2	What is the volume of a pyramid that has a base of 30 acres and a height of 300 ft? Give answer in acre-ft.	2	10
4	A snake has a volume of 30 cm^3. Its cross-sectional area is 1 square cm. How long is the snake? Give answer in inches.	6	10
	Assessment Score	0.44	0.89
	% Change		100%
	n = 12		

Powers of 2: Many Grains of Wheat

Item #	**Item**	**# Correct (Pre)**	**# Correct (Post)**
1	The number 100 can be "described" as 1 followed by 2 zeroes. How many zeroes must follow 1 to approximate 2^{20}?	5	13
	Assessment Score	0.36	0.93
	% Change		160%
	n = 14		

ABOUT THE AUTHOR

Dorien K. McGee is from Charleston, South Carolina and received a B.S. in Environmental Studies from Emory University in 2003. In 2005, she received a M.S. in Geology from the University of North Carolina-Wilmington, which earned her the Department of Geology's Outstanding Research Award. Her experience as a teaching assistant at UNCW led to her secondary interest in education, which she actively pursued alongside her doctoral research at the University of South Florida. While at USF, she was the recipient of several student research grants and was awarded the Richard A. Davis Fellowship by the Department of Geology, as well as the Outstanding Service and Outstanding Teaching Assistant Awards. Her publishing record includes several peer-reviewed articles in addition to numerous modules, resource guides, and assessment instruments for the *Spreadsheets Across the Curriculum* and *Geology of National Parks: Spreadsheets, Quantitative Literacy, and Natural Resources* projects.