12-2013

Sources of CO_2 Controlling the Carbonate Chemistry of the Logsdon River, Mammoth Cave, Kentucky

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Recommended Citation

Hatcher, Bruce Elliott, "Sources of CO_2 Controlling the Carbonate Chemistry of the Logsdon River, Mammoth Cave, Kentucky" (2013). *Masters Theses & Specialist Projects.* Paper 1311.
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SOURCES OF CO_2 CONTROLLING THE CARBONATE CHEMISTRY OF THE LOGSDON RIVER, MAMMOTH CAVE, KENTUCKY

A Thesis
Presented to
The Faculty of the Department of Geography and Geology
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
Of the Requirements for the Degree of
Master of Science

By
Bruce Elliott Hatcher

December 2013

SOURCES OF CO_2 CONTROLLING THE CARBONATE CHEMISTRY OF THE LOGSDON RIVER, MAMMOTH CAVE, KENTUCKY

Date Recommended 11/22/13

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12-13-13

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ACKNOWLEDGEMENTS

There are so many people that have supported me throughout this project. Without the help of all of these individuals I likely would have never accomplished the task of finishing this project.

First, I must thank my family for never letting me give up. To my wonderful wife Amy: Thank you for your encouragement and understanding while I would have to head to the caveland and disappear underground throughout our engagement. It wasn’t easy being away from you, but you loved me through it all. It was your encouragement and good example that gave me the fortitude to complete my writing. You are my perfect complement, and I can accomplish anything with your support. To my parents Johnny and Laura: Without your support and encouragement I would not be the man that I am. Thank you for directing me and setting an example that I strive to emulate as a parent. You never complained once about dirty cave clothes and regularly fed anyone that I could convince to come along and help me on my sampling trips. I couldn’t have done this without both of you. To my grandmother Marian England: You never let me give up, and for that I can’t thank you enough. You supported me in so many ways, and you were always committed to seeing me succeed. To my daughter Brooklyn: I apologize for all of the times that I had to leave you to go into the cave. Always remember that the best part of those trips for me was when I would get home and hear you yell, “Daddy!!!” while flying into my arms for a big hug. To everyone above and the rest of my family (especially Mandy, Boyd, and Clark): Thank you for your encouragement, and for always being there to watch over and entertain Brooklyn while I was underground.

So many people at Western Kentucky University helped me throughout this process. I want to thank the entire staff of the Geography and Geology Department for teaching me and allowing me to have such great memories of my time at WKU. To my advisor Dr. Chris Groves: Thank you for never giving up on me. I know that you went through extra effort to make sure I got back on track. I appreciate your guidance and for being willing to work with me even after I had been away for so long. It feels so appropriate that I am completing this project with you as my advisor after you were the one who introduced me to my love of caves so long ago. Who would have guessed that one of the second graders that you introduced to caves at WKU's Super Saturday Seminars in 1990 would eventually be completing a thesis under your guidance. Also, I want to thank Dr. Michael May, Dr. Jason Polk, and Dr. David Keeling for being willing to go through this process with me. Your willingness to work with me after so many years of my absence is a testament to your character and care for the students you educate. A big thank you, as well, to Wendy DeCroix for always being helpful by keeping me connected and on Chris' mind when I wasn't around.

I want to extend an extra big thanks to Dave Weller for allowing this project to occur. I always enjoyed our conversations, and I learned so much about the history of Roppel Cave from you. Without your cooperation and permission to access your land this project would have never been possible. Thank you Pauline Norris for always being willing to coordinate and help me with my lab analysis. Thank you Jim Borden for your help with providing access to maps of Roppel while writing my thesis. A big thank you to Bob Scott, Bob Jones, Ryan Howell, and Bill Overman at Kentucky's Division of Abandoned Mine Lands for support and allowing me time off whenever I needed to work on this project. To Johnny Merideth: You always stood as a bastion of hope that I would be able to complete this project. I vowed to not follow the same path as you. Yet, in the end, your footsteps aren’t too bad to follow.

I want to say a special thanks to Jeremy Reedy. There is no way that I would have been able to collect all of these samples if it weren’t for your help. You were always available and would rearrange your schedule to help me out. When no one else was available I could always count on you. Finally I want to thank everyone who spent countless hours in the cave with me taking samples: Jeremy Reedy(x10), John Davis(x3), Kevin Carney(x2), Michael Goodman(x2), Nick Blair(x2), Alvin Campbell(x2), Bryan Nichols(x2), Spencer Kerley, Marcus Key, Brian Ham, James Townsend, Tudor Bowers, Jackie Wheet, Ben Miller, Clint Barber, Kayla New, Jessica Love, Jason King, Jenny King, Rose Clark, David Kem, Weldon Hawkins, Aaron Clark, and Calvin Wiley. You all volunteered to come along for nothing more than the opportunity to see some parts of the cave that were new to you…or maybe for the promise of dinner at my parents’ house. For whatever reason you came along, you always kept things entertaining for me even when I’d traveled the same route countless times. I loved the opportunity to share the cave with each of you. Judging by some of the muddy exhausted figures that eventually dragged themselves back up the ladders to the surface; I might have gotten more enjoyment out of the experience than anyone.

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Bruce Hatcher December 2013 55 Pages

Directed by: Chris Groves, Michael May, and Jason Polk

Department of Geography and Geology Western Kentucky University

Logsdon River is a major, base-level stream within the Turnhole Bend Drainage basin of the Mammoth Cave System. The Logsdon River system has provided a unique opportunity to examine the geochemical evolution of a stream flowing through a major karst conduit that can be traversed for 10 km. This study examines CO_2 inputs at the upstream portion of the river, which provide major control for the river's hydrochemistry.

Samples were collected from the upstream portion of Logsdon River at what is referred to as the S-188 sump and also nearby at Crowbar Dome over the course of 44 weeks from May 2012 through April 2013. The concentrations of CO_2 for samples were calculated from field and laboratory analysis. The CO_2 concentrations were examined during the study period to assess potential sources of CO_2 input to the karst system in the context of seasonal variation. Seasonal fluctuations were found to be greatest in the near surface sample site, Crowbar Dome. Attenuation of seasonal variation of CO_2 pressures in the upstream Logsdon River S-188 Sump suggests both surface inputs plus additional inputs of CO_2 entering the system, perhaps from the decay of organic material in the saturated passages upstream beyond the accessible portion of the Logsdon River S-188 Sump. This in-cave source of CO_2 has some control on hydrochemistry, and thus water-rock interaction and speleogenesis of the karst landscapes in south-central Kentucky.

I. Introduction

Throughout human history caves have generated interest. This inherent curiosity of the unknown naturally sparked a drive for a greater scientific investigation. Questions about the origins of caves, the processes that shape them, and their continuing development have brought to light a broader understanding of their environments by focusing research efforts. Some of the earliest scientific research conducted in karst environments focused on the origins of caves. Following those original studies, it is well-known that the most common caves are the result of dissolution of limestone bedrock by carbonic acid solutions (e.g. Plummer and Wigley, 1976; Plummer et al., 1978; White, 1988; Palmer, 1991; Palmer, 2007). While many details of these processes have been established through field and laboratory studies, application of geochemical principles and the development of conceptual and mathematical models, there is still much that can be learned from these inhospitable and often inaccessible environments.

For several reasons, in recent years karst systems throughout the world have been the focus of an increased number of basic and applied studies, partly in response to increasing population pressures on water resources. Estimates suggest that as much as 25% of the world's population relies directly or indirectly on karst water resources (Doerfliger et al., 1999; Mahler et al., 2000; Goldscheider, 2005; Ford and Williams, 2007). There is also interest in biological diversity (e.g. Hamilton-Smith, 2001; Culver et al., 2006) and as potential for carbonate mineral weathering as an atmospheric carbon sink (e.g. Liu and Zhao, 2000; Groves and Meiman, 2001; Cao et al., 2012). Yet, few karst areas in the world are studied as intensely as the Mammoth Cave region (Hess, 1974; Palmer, 1981; Hess and White, 1988; White and White, 1989; Ray and Currens, 1998a; Ray and Currens, 1998b). Studies in the Mammoth Cave region have provided a background on the hydrology and geochemistry of the karst systems in this area, and more broadly the understanding of a number of more generally applicable principles of karst hydrology have evolved from work here (White and White, 1989). In the south-central Kentucky area, there is an abundance of limestone that is readily soluble to allow the formation of caves (Palmer, 1981; White and White, 1989).

The karst aquifer/landscape system in and around the Mammoth Cave area has long been viewed as a classic example of a well-developed karst landscape. The nature of karst landscapes can make them difficult to examine in depth. Water commonly disappears into the ground through sinkholes or sinking streams and is not accessible again for great distances. In some cases, the water will only appear aboveground again at its final resurgence when it reaches an associated base-level stream. This can result in only having two endpoints of the karst system to examine. Even establishing clear connections between such points using groundwater tracing tests can be challenging, and often provides the starting point of research in karst areas throughout the world.

Interactions between soluble bedrock and chemically undersaturated waters are the foundation upon which karst systems are developed. In the case of the Mammoth Cave area, the soluble rock that is present is largely limestone with small amounts of dolostone. The main solvent responsible for the dissolution of these carbonate rocks in the Mammoth Cave area is carbonic acid (H_2CO_3). Water samples collected in karst environments can give insight into the extent that this carbonic acid solution interacted with the surrounding rock. Analyses and calculations can be performed to determine the extent to which water samples are in various states of disequilibrium with respect to the major minerals present in the rock.

The Mammoth Cave region provides a distinct advantage that allows more in-depth research of these water-rock interactions. In this region, both the surface and caves below have been extensively studied and explored for many decades (e.g. Pohl, 1936; Quinlan and Ewers, 1989; White and White, 1989; Palmer, 1991; Ryan and Meiman, 1996; Groves and Meiman, 2005). Mapping and exploration of the cave system has provided detailed understanding of the open conduits that carry the groundwater throughout the system. As a result of this exploration, more than 645 kilometers of cave passages have been mapped and surveyed in the Mammoth Cave system alone, with hundreds of kilometers of additional cave passages explored in the area that are currently not physically connected to Mammoth Cave. This expansive network of known and surveyed cave passages in the area provides many potential opportunities to examine the water that is passing through the subsurface drainage of the Mammoth Cave area.

II. Research Area Overview

The Mammoth Cave region sits on the western flank of a large-scale, regional geologic feature where rocks of the Cincinnati Arch dip toward the Illinois Basin. The Cincinnati Arch is a large anticlinal feature that passes through central Kentucky and extends from beyond Cincinnati, Ohio to the north through Nashville, Tennessee to the south. As a result of this large scale fold, rocks around the Mammoth Cave area exhibit a monoclinal structure, dipping gently to the northwest at dips from zero to about three degrees (Palmer, 1981). Principal karst-forming host rocks in the area consist of the Mississippian-aged St. Louis, Ste. Genevieve, and Girkin limestones, in ascending stratigraphic order. The landscape is also impacted by clastic rocks of the Mississippian Big Clifty Member and Hardinsburg Sandstone, and the Pennsylvanian Caseyville Formation (and other minor units), which overly the carbonate rocks. The sandstone and shale of the overlying clastic formations provide resistant “caprocks” that form the dissected Mammoth Cave Plateau and protect the more soluble limestones from erosion, thus influencing the surface and groundwater hydrology (Figure 1). The southern edge of the Mammoth Cave Plateau forms the Dripping Springs Escarpment; south of this boundary lies the Pennyroyal Plateau, forming an extensive sinkhole plain on a lower surface about 100 m below.

This structural framework provided by the Cincinnati Arch is very important to groundwater flow and the development of the cave systems in the Mammoth Cave area. As a result of the bedrock dip, older rocks of Mississippian age are exposed to the southeast in an area of the Pennyroyal Plateau sinkhole plain. To the southeast of the

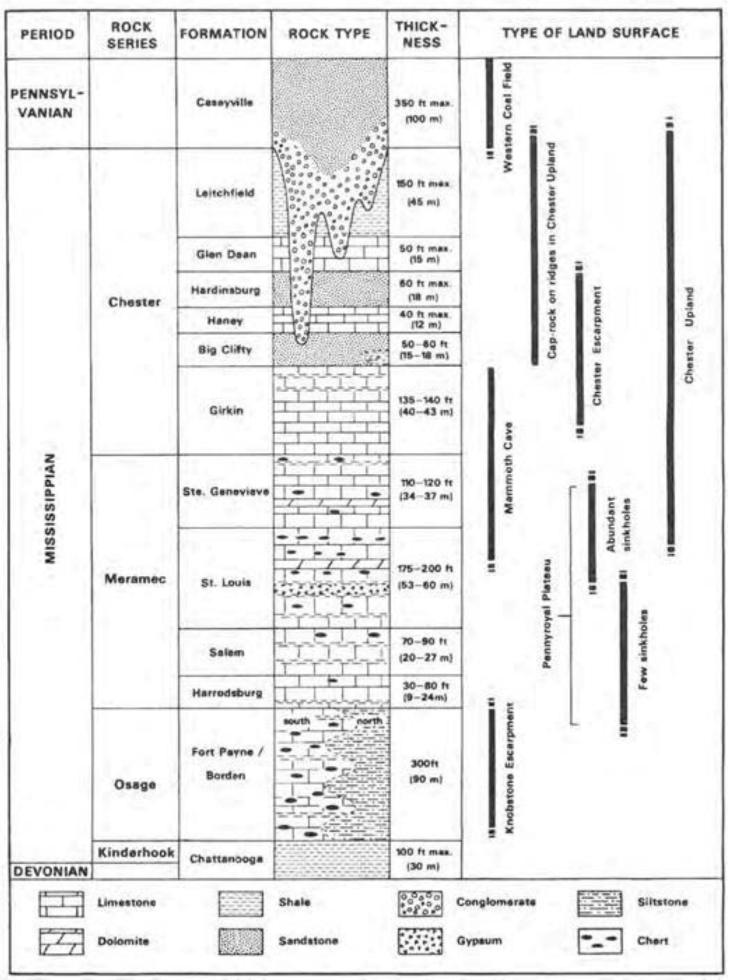

Figure 1: Stratigraphic Section of the Mammoth Cave Region from Palmer (1981).

sinkhole plain is an area known as the Glasgow Upland that is developed on an area of less soluble rock of the lower St. Louis Limestone Limestone. In this area, surface streams flow northward along the dip of the rock until they reach the more soluble middle portions of the upper parts of the St. Louis Limestone. At this point, the water is pirated underground through sink points into the conduit drainage below the sinkhole plain (Figure 2).

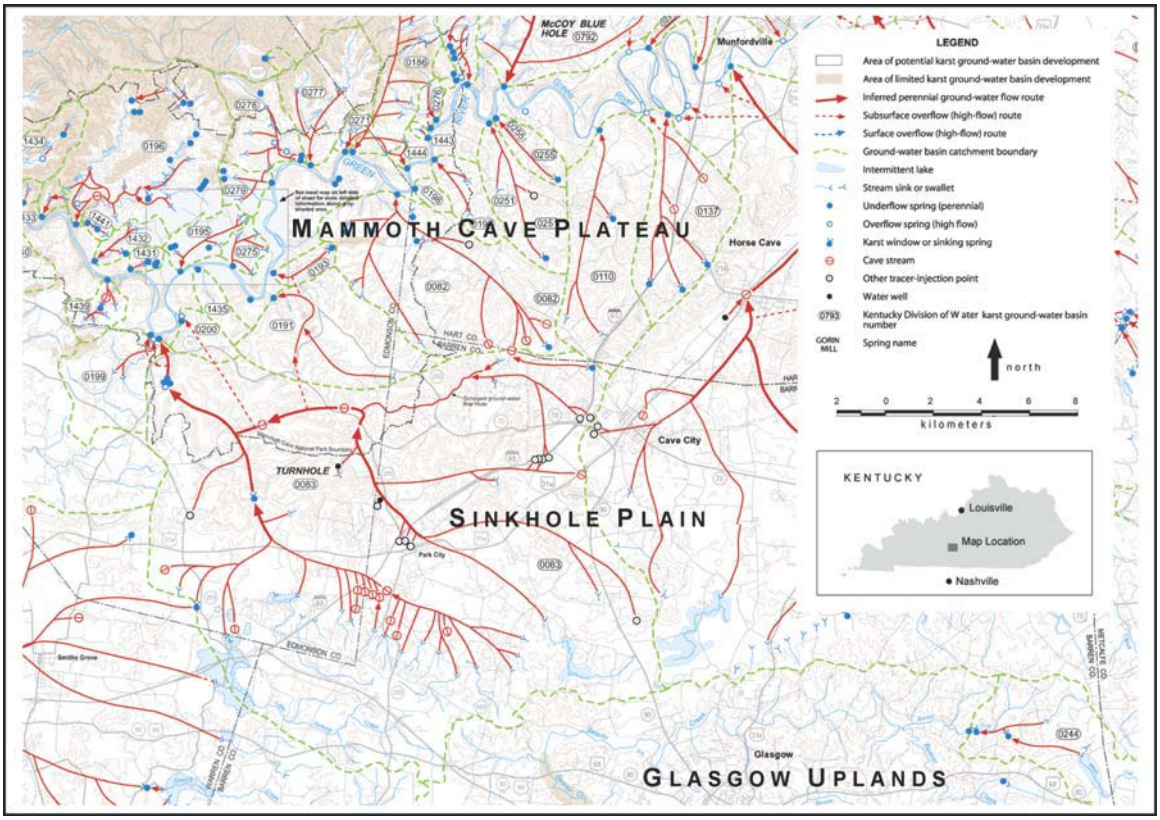

Figure 2: Location of Turnhole Bend Groundwater Basin from Glennon and Groves (2002, modified from Ray and Currens 1998a, 1998b).

Throughout the sinkhole plain the rocks of the St. Genevieve Limestone and the upper St. Louis Limestone are exposed at the surface. The location of these very soluble rock units at the surface create a situation of autogenic drainage, where water falls directly onto the karst surface. This autogenic drainage is responsible for the development of a multitude of sinkholes whose internal drainage feeds to the base-level conduits flowing beneath the sinkhole plain. These conduits typically follow the bedrock dip to the northwest where they pass under the Dripping Springs Escarpment and flow beneath the Mammoth Cave Plateau. The regional northwest dip of the rocks also aids in conveying water from the sinkhole plain, located to the southeast, into the major base-level cave streams of the Mammoth Cave System.

The Mammoth Cave Plateau is the area to the northwest of the sinkhole plain. It is an upland area that is capped by ridges made of less soluble upper Mississippian Rocks (namely the Big Clifty Sandstone Member and Hardinsburg Sandstone with other minor interspersed clastic units) and lower Pennsylvanian (Caseyville Formation sandstones and conglomerates). These less soluble rocks have protected the limestones below by resisting chemical weathering. This has allowed the preservation of multiple levels of cave passages beneath the plateau. Allogenic drainage is the predominant means of conveying water into the karst system under the Mammoth Cave Plateau. In an allogenic drainage situation, rainwater falls on a surface of insoluble rock, and must make its way to the edge of these resistant rock layers to be conveyed into the underground conduit systems through sinking streams or developed karst valleys and sinkholes.

Much of the Mammoth Cave System is formed beneath the Big Clifty Sandstone Member, though significant parts lie underneath karst valleys within the plateau where the sandstone has been breached and removed by erosion. The cave system is contained within a 160-meter thick section of limestone composed of the Girkin, St. Genevieve, and St. Louis Limestones. As water flows along the dip of these rocks beneath the Mammoth Cave Plateau it eventually reaches the Green River to the northwest. Ultimately, all of the water flowing through the Mammoth Cave System reaches the Green River, which flows east-west through Mammoth Cave National Park. This surface river is the major regional base-level river in this area, and dictates the regional water table potentiometric surface for the Mammoth Cave area. The current normal pool elevation for the Green River at the Mammoth Cave Ferry is approximately 128 meters above mean sea level.

III. Previous Investigations and Research Questions

The formation of carbonic acid takes place when carbon dioxide (CO_2) is diffused into water. This process can occur from a variety of CO_2 sources. The most commonly considered CO_2 inputs into a typical, natural karst system come from atmospheric CO_2 and soil CO_2. Research has shown that CO_2 produced from decaying organic material in the soil and plant root respiration of CO_2 are the main controlling factors in determining soil CO_2 levels (e.g. Lundegårdh, 1927; Raich and Schlesinger, 1992). In the studies focusing on the decay of organic material, conclusions have been drawn to show bacterial processes in the soil play a significant role in the amount of CO_2 in a system. It has also been found that plant root respiration, likewise plays a role in the production of CO_2 in the soil (e.g. Raich and Schlesinger, 1992; Atkin, 2000). In the summer months, when there are warmer temperatures, plants and microbial organisms in the soil are more active. As a result, both plant roots and microbial organisms, by quickening the decay process of organic material, expel more CO_2. This, in turn, creates a larger volume of CO_2 in the soil system. Conversely, the winter months, with lower temperatures, typically show much lower levels of soil CO_2 (Lloyd and Taylor, 1994; Raich and Tufekciogul, 2000). Research focusing on this correlation has gone as far as to not only show an increase in soil water CO_2 levels during summer months, but has also shown elevated levels of soil water CO_2 during the daylight hours compared to CO_2 levels at nighttime in some settings due to plant roots expelling CO_2 during photosynthesis (Atkin et al., 2000; Liu et al., 2006; Liu et al., 2007).

Research on correlating soil CO_2 levels to waters found in cave systems has also shown an increase in soil and cave water CO_2 levels during summer months (Atkinson, 1977; Wood, 1985; Yoshimura et al., 2001; Baldini et al., 2008). As a result of the studies that have been done involving the correlation between soil CO_2 concentrations versus the concentration of CO_2 in cave streams, it has become commonly accepted that the main determinant in the CO_2 levels of cave water is the input from the soil zone.

In the Mammoth Cave area, work by Hess (1974) and Hess and White (1993) showed a decrease in dissolved solids and CO_2 levels in water as it moved from the sinkhole plain, passed under the Mammoth Cave Plateau, and ultimately reached the spring resurgences along the Green River. They describe this as a dilution of the water originating from the sinkhole plain. They attribute the high CO_2 and Specific Conductance (SpC) values of the water originating from the sinkhole plain to the thicker soils in that area. The lower CO_2 and SpC values observed at the springs were considered to be a product of dilution from the inputs of allogenic water originating on the plateau area, which was not as high in CO_2 concentrations and SpC as the water from the sinkhole plain. This was attributed to the much thinner soils of the plateau, and as a result, a shorter residence time of the water passing through these soils. This conclusion was later supported in research by Merideth (2009) that compared water samples from two locations within very close proximity to one another, but with different flowpaths within the cave beneath the plateau. One location sampled water that was entering the cave near the soil bedrock interface under the Mammoth Cave Plateau and was free falling approximately 30 meters to the sample point through a tall vertical shaft. The other sample location contained water at the same elevation, but was assumed to be in constant contact with limestone throughout its descent. The comparison of these samples showed that throughout the year the free falling water had much lower SpC. This was determined to be a result of the impact of rainwater entering the system through the thin plateau soils, whereas the water that has had contact with the limestone for a longer period of time, as expected, displayed higher SpC values from increased limestone dissolution.

A direct correlation between soil CO_2 concentrations and cave water CO_2 values might generally be the case in many settings. Yet, it must not be assumed that the soil CO_2 concentration is the only driving force behind the levels of CO_2 found in cave streams in south-central Kentucky karst. Studies within the Mammoth Cave system (Anthony, 1998; Vaughan, 1998) and elsewhere (Atkinson, 1977; Wood, 1985; Wilhartitz, 2009) found evidence that decaying organic material brought into the karst aquifer and degraded there can add CO_2 to the system as a deeper source. The principal purpose of this research is to discriminate between these sources (surface vs. within aquifer CO_2 sources) within a major underground river of the Mammoth Cave System, the Logsdon River at its upstream accessible terminus, the S-188 Sump.

Within the Mammoth Cave area one of the more intensely studied drainage basins is the Turnhole Bend Drainage Basin, originally delineated through years of dye tracing work in the 1970s (Quinlan and Ray, 1989). Important early studies in this region were undertaken by Hess (1974) and Hess and White (1993). They used easily accessible surface features such as sinking streams, karst windows, and springs within the established groundwater basin to obtain geochemical information about the groundwater system. These studies collected samples on a monthly or twice monthly scale and determined that water through this system fluctuated in slight amounts of undersaturation with respect to calcite. It was also noted in these early studies that CO_2 concentrations and SpC values would increase during summer months and decrease during the winter, presumably as a result of surface biological activity.

In 1979, the discovery of new passages in the Mammoth Cave System within the Turnhole Bend Basin, namely the passageway containing Logsdon River (Coons and Engler, 1980; Brucker and Borden, 2000), provided more opportunity to focus on the details of hydrochemistry within the Turnhole Bend Drainage. Logsdon River is one of the two principle trunk underground rivers within the Turnhole Bend Groundwater Basin. This river is accessible for direct exploration and sampling without SCUBA gear for over 10 kilometers between the upstream end at the S-188 sump and its confluence with the Hawkins River at the downstream end. This makes it among the longest continually traversable underground river passages in the United States, and perhaps the world.

Work within Logsdon River in the 1990s (Groves and Meiman, 2001, 2005; Raeisi et al. 2007) utilized monitoring wells that were installed into the underground conduits containing the Logsdon and Hawkins Rivers in between the accessible surface sites that were studied by Hess and White (1993). This work utilized data loggers to collect high-resolution data for stage, temperature, and SpC. The results of the high-resolution data provided them with a different view of the aquifer than reported by Hess and White (1993). Groves and Meiman (2005) found that this portion of the Turnhole Bend Drainage system was, in fact, oversaturated with respect to calcite for a significant portion of the year. Their high-resolution data showed that when storm pulses passed through the cave system, a change would occur in the water chemistry that led to undersaturated conditions. The high-resolution data also showed seasonal variations in Logsdon River’s saturation state with respect to calcite. This showed that the geochemical behavior of the river system, and in turn carbon transport and water-rock interactions, were highly variable and more complex than previously thought, and followed from variations in carbon dioxide concentrations.

To better understand the reasons behind carbonate chemistry variations at the study site near the downstream end of the river, a subsequent study was undertaken in which samples were taken along the longitudinal profile of the roughly ten kilometers of accessible cave stream within Logsdon River, with sample stations spaced about every kilometer (Anthony, 1998; Anthony et al., 2003). Logsdon River provides a unique study area in the Turnhole Bend Drainage Basin because it remains perched in a passage on top of chert layers in this section of the cave. It is assumed that many parts of the other undiscovered major cave streams of the Turnhole Bend Basin are in the phreatic (completely water-filled) zone, but the resistant chert layers of this area have kept the Logsdon River passages in the vadose (unsaturated) zone. The entire traversable length of Logsdon River was accessed and geochemical analysis was performed at select locations along the river during the warm season. During the warm season, dissolved CO_2 levels at the S-188 Sump were about 35 times atmospheric background (0.013 atm), and steadily decreased in the samples that were taken in the downstream direction over the next six kilometers in the Logsdon River to about five times atmospheric background level (0.002 atm). This was ascribed to outgassing of CO_2 as the river travels through the air-filled passages of the vadose zone, of which the atmosphere has lower CO_2 concentrations. For the next two kilometers, however, the concentrations went up, which was assumed to be a result of the degradation of organic debris within the sediment that was ultimately washed into this area and was visibly accumulating in pools in the downstream portion of the river.

Upstream from the S-188 Sump, divers have continued upstream in Logsdon River and found that the passage continues upstream, water-filled for more than 100 meters until eventually reaching more sections of air-filled passage.

The results of the study by Anthony (1998) then led to the research questions that drive the current research:

1) What controls the high CO_2 concentrations at the S-188 Sump, which have such significant influence on the next ten kilometers of river, and thus on the hydrochemistry of the Turnhole Bend Basin?

2) What are the relative impacts of various CO_2 sources, including those which are primarily from surface soil sources or sources from internal aquifer generation of CO_2 (for example, from degradation of interstitial organic material within conduit sediments)?

One hypothesis about the high levels of dissolved CO_2 at this upstream water-filled passage is that decaying organic matter within the sediment in the flooded passage upstream from the S-188 Sump is contributing CO_2 into the system, which cannot escape because there is no air surface into which CO_2 can diffuse. In eogenetic karst environments, such as coastal carbonate areas, much of the primary depositional matrix permeability and porosity of the limestone has been retained (Vacher and Mylroie, 2002), and opportunities for CO_2 exchange through the rock matrix can greatly influence water chemistry (Gulley et al., 2011, 2013). The Mammoth Cave area, however, is a telogenetic karst environment, with highly compact limestone that has lost most of its primary permeability due to burial, compaction and cementation. In this environment there very is limited opportunity for CO_2 to degas from the saturated passages through fractures and primary porosity (Vacher and Mylroie, 2002).

As indicated previously there is evidence for CO_2 production within the cave flow system. If CO_2 is significantly being produced along the phreatic conduit flowpath, and the opportunity for CO_2 to degas is minimal, it may speak to the importance of this process within phreatic passages of the system.

The approach to answering the questions herein relied on two interrelated observations: (1) seasonal evaluation of CO_2 (and associated geochemistry parameters) behavior over 44 weeks capturing complete warm and cool seasons at the S-188 Sump, and (2) comparing these data to CO_2 over the same period at Crowbar Dome, an epikarst water drain in the same eastern (Roppel) section of the cave. Water at Crowbar Dome is presumably closely coupled to seasonal surface conditions (including soil CO_2 production). The S-188 Sump, located at base-level along Logsdon River, and thus deeper along the flow path into the cave, may or may not be as closely coupled to surface conditions. Comparing the behavior at the two sites should help clarify this question. Also, if the warm season high CO_2 levels at the S-188 Sump identified by Anthony (1988) are predominantly derived from surface CO_2, it would be expected for them to drop significantly as the cold season progresses and soil CO_2 production drops off. If instead the CO_2 is strongly influenced by in-cave sources of sediment-produced CO_2 in the river, then one might expect these levels to remain more constant across seasonal atmospheric changes outside.

IV. Detailed Study Site Description

This research is focused on a major trunk river of the Turnhole Bend Drainage Basin. The Turnhole Bend Drainage Basin, which drains approximately 244 square kilometers of surface area, is the largest drainage basin that intersects with the passages of the Mammoth Cave System. This basin drains water from the sinkhole plain to the south and southeast of the Mammoth Cave Plateau. The resurgence of this drainage is located at the Turnhole Bend Spring, which emerges as a Blue Hole in the south bank of the Green River within Mammoth Cave National Park.

The earliest studies of the Turnhole Bend Basin were limited in scope. During these early studies, the only places where water from this system could be encountered were at recharge points on the sinkhole plain, at two karst windows (Mill Hole and Cedar Sink), and at the resurgence of Turnhole Bend Spring (Hess, 1974; Hess and White, 1988; Hess and White, 1989). The eventual discovery of the Logsdon and Hawkins Rivers provided the opportunity to view the flow path of this system in greater detail.

From these discoveries, the Turnhole Bend Drainage Basin was further defined as containing the Mill Hole sub-basin and the Proctor sub-basin. The Proctor basin was then further subdivided to include the Cave City and Patoka Creek sub-basins (Quinlan and Ray, 1989). The entirety of the traversable length of Logsdon River within the Mammoth Cave System is contained within the Cave City sub-basin. Logsdon River is an important flow path in the Turnhole Bend Drainage Basin because it is the only place within the Mammoth Cave System where an underground stream can be followed for such length, approximately 10 kilometers.

The main focus of this research was to evaluate the geochemical parameters of water in the farthest upstream portion of the Logsdon River system, and compare it to the parameters of water obtained from a nearby vertical shaft which is receiving water that had much less residence time within the cave system, and therefore more closely coupled to surface conditions and the influence of surface derived CO_2. The Logsdon River sample site for this study was located at the S188 Sump of Logsdon River (Figure 3). This is the farthest upstream point that can be accessed in Logsdon River without diving. The baseflow water level at the S-188 sump is approximately 170 meters above sea level. This site was chosen as the focus of this study because of the relevance it has to previous studies in the area, and because it has been shown to exhibit high values of CO_2 concentration (Anthony, 1998) as opposed to other portions of the drainage system.

The other sample site for this research was located in Crowbar Dome (Figure 4). This site was chosen because it provides an opportunity to sample water that has had a relatively short residence time within the cave system, and should provide a signature of water that has direct influence from rainfall and the influences of the overlying soils. Soil surveys of the area show that the approximate drainage area for Crowbar Dome encompasses less than ten different mapped soil units (Mitchell, 1993; USDA-NRCS, 2013). While the drainage area for the upstream Logsdon River site is fed by an area encompassing greater than 40 mapped soil units (Latham et al., 1969; USDA-NRCS, 2013). Thus, the soil variability influencing the Crowbar Dome samples is less than that of the Logsdon River samples.

Water emerges into Crowbar Dome from approximately 18 meters above the bottom of the dome and free falls to the sample collection point. The base of Crowbar

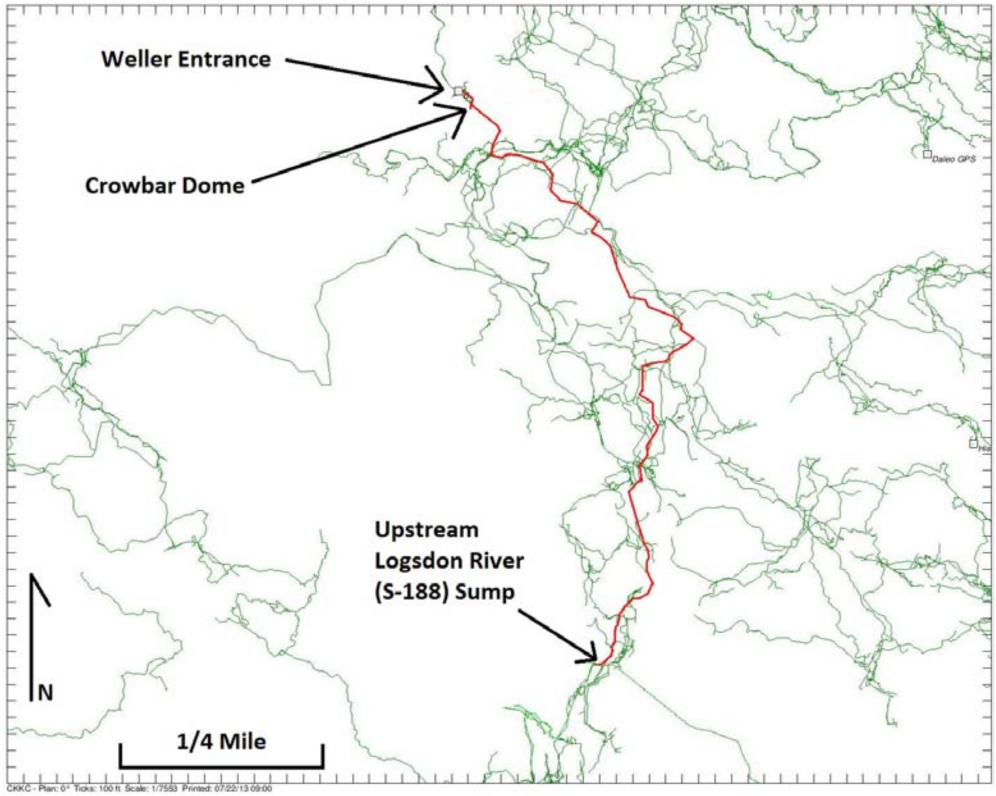

Figure 3: Sampling Route Highlighted in Red. Base map courtesy of James Borden.

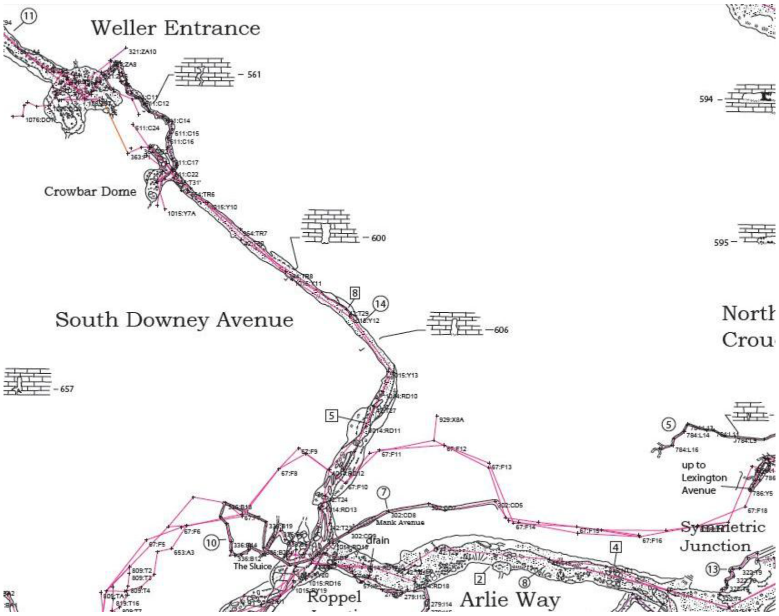

Figure 4: Detailed Map of Weller Entrance and Crowbar Dome Area (Courtesy of James Borden).

Dome is surveyed at an elevation of 176 meters above sea level. Water emerges into Crowbar Dome at roughly 194 meters above sea level, and the land surface above this area is approximately 223 meters above sea level. By the time water emerges into Crowbar Dome it has traveled just under 30 vertical meters into the cave system. This site is convenient because it is a vertical shaft with a consistent, year-round supply of water that is located along the route to the S188 Sump.

Samples were taken every two weeks throughout the warm and cold seasons of 2012 and 2013, for 44 weeks starting on May 15, 2012. Attention was paid to collect samples only at times exhibiting flow levels around the normal base flow for the particular time of year the sampling was taking place. As the purpose of the study was to understand seasonal variations on hydrochemistry rather than storm-scale fluctuation, this helped to insure that the samples are comparable, representative of typical baseflow conditions, and not anomalous storm events.

Access was gained to the sampling areas of Crowbar Dome and the upstream sump of Logsdon River through the Roppel Cave portion of the Mammoth Cave System (Figure 5). Sampling trips entered the Weller (Downey Avenue) Entrance on Toohey Ridge. Upon entering this portion of the cave one immediately descends through a shaft complex via a series of ladders, quickly dropping about 35 meters vertically into the cave system (Figure 6). This entry descent leads through the Girkin Limestone and into the St. Genevieve Limestone. After reaching the bottom of this shaft complex, progress is made through a canyon / shaft drain which leads into Crowbar Dome. This is the location of the Crowbar Dome sample site (Figure 7). From this point, the route continues up a sediment bank into South Downey Avenue. This passage leads

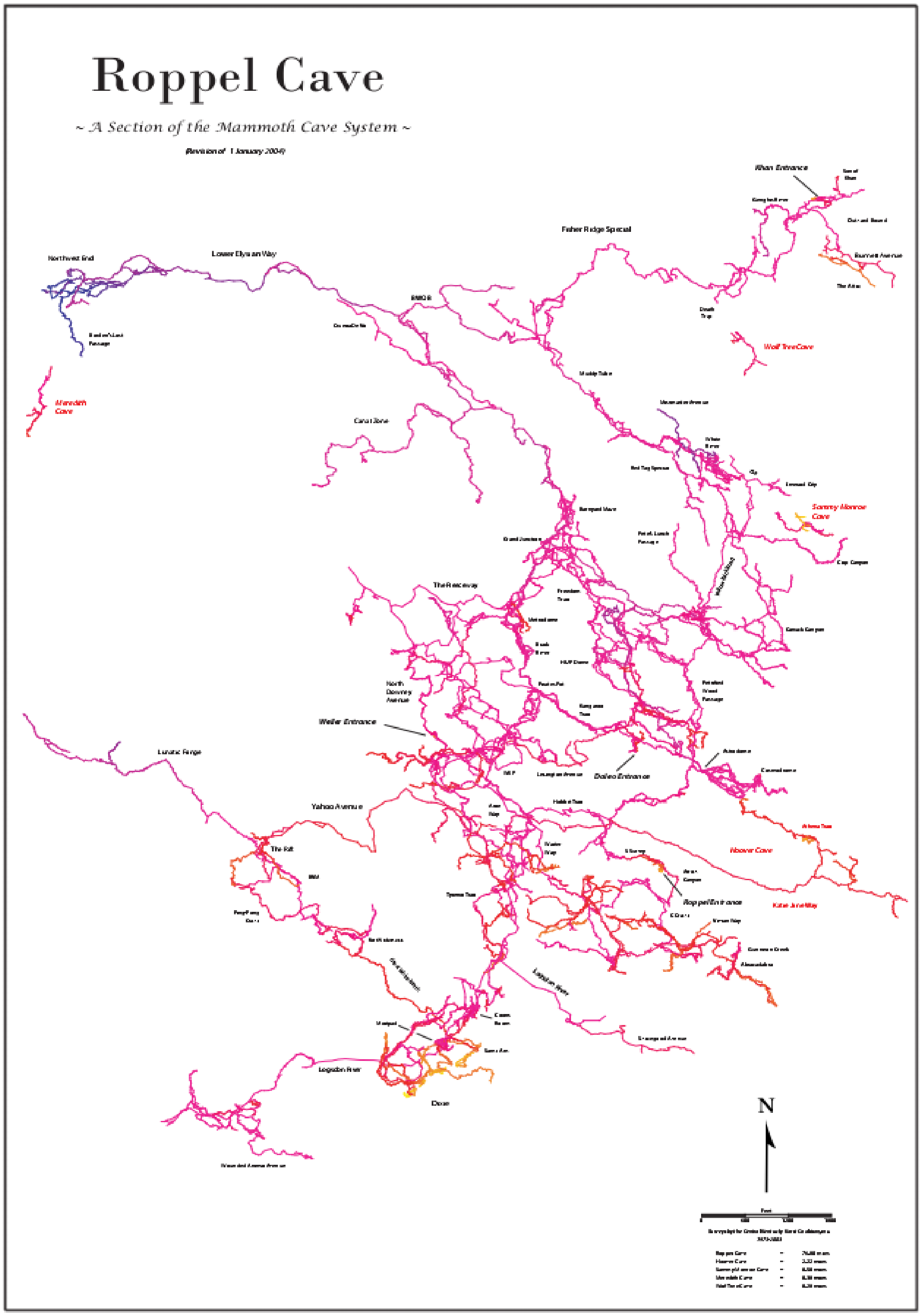

Figure 5: Map of the Roppel Section of Mammoth Cave (courtesy of James Borden).

to a junction where Arlie Way intersects as a tubular shaped passage on the left. Following Arlie Way leads to the water crawls of the Cumquat Causeway (Figure 8). From the Cumquat Causeway you eventually reach a muddy climb-down that leads directly to the S188 Logsdon River sump. This is the location of the upstream Logsdon River sump sample site (Figure 9). Exiting the cave requires backtracking along the exact same route that was used to access these areas.

Any researchers accessing this area should be extremely cautious of weather conditions. This area is particularly flood prone, and the water can rise quickly!

Figure 6: Weller Entrance

Figure 7: Crowbar Dome

Figure 8: Cumquat Causeway.

Figure 9: Upstream Logsdon River S-188 Sump

V. Methodology

Samples were analyzed in the cave for pH, SpC, and temperature at the time of collection using a Hanna Model HI 991301 Multimeter. This meter was calibrated prior to each trip with pH and SpC standard solutions. The accuracy of this meter is ±0.01 units for pH, ±2% F.S. for SpC, and ±0.5°C for temperature. Values for pH, SpC, and temperature were recorded in a field book for each sample site during each trip. The other parameter analyzed while in the cave was alkalinity. This was measured using a Hach Field Alkalinity Test Kit. A 15 mL sample was obtained after being triple rinsed at each sample location. A pillow packet of bromocresol-green / methyl-red indicator was placed in the sample. Drops of 0.03 N sulfuric acid solution were slowly added while swirling the bottle to ensure proper mixing. When a color change took place in the solution and persisted for more than 30 seconds the end point had been reached. The number of drops required to create that change was noted in the field book at the time of collection. After the sampling trip, the true value for alkalinity in milligrams/liter (mg/L) of calcium carbonate was calculated by multiplying the number of drops of sulfuric acid by 6.84. This provides the alkalinity of the sample in mg/L of calcium carbonate. For this study, measurements focused on alkalinity in the form of bicarbonate alkalinity, because samples ranged between pH values of 6.4 and 10.33. At that range of pH bicarbonate alkalinity is the dominant species (Drever, 1997). In order to convert the alkalinity from mg/L of calcium carbonate to mg/L of bicarbonate the following reaction must be considered:

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2 \ . \qquad (1)$$

For this conversion, the molecular weights of each compound must be considered. $CaCO_3$ has a molecular weight of approximately 100 grams per mole and bicarbonate (HCO_3^-) has a molecular weight of approximately 61 grams per mole. Each mole of $Ca(HCO_3)_2$ corresponds to one mole of $CaCO_3$. Therefore, each mole of $CaCO_3$ corresponds with two bicarbonate ions. By using the molecular weight of each compound, the alkalinity values obtained in mg/L of calcium carbonate can be multiplied by (122 g/mol / 100 g/mol). This simplifies to show that the alkalinity value with respect to calcium carbonate is multiplied by 1.22 to give the alkalinity value with respect to bicarbonate.

A 500 mL HDPE bottle was triple rinsed at each sample site, and filled with a water sample. To obtain this sample in Crowbar Dome, access along the ledges at the bottom of the dome allowed the sample collector to place the sample bottle on a ledge to collect drip water, without disturbing the pooled water below. Water samples at the upstream Logsdon River sump were obtained by advancing upstream as close to the sump as possible. This allowed samples bottles to be rinsed and capped below water to remove any air bubbles in the sample bottle, while also not disturbing the sample.

After returning to the surface, the samples were immediately acidified with 4 mL of concentrated nitric acid. Samples were later analyzed for cations via Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis at the Western Kentucky University (WKU) Advanced Materials Institute Lab within the 180 day holding time for cation analysis (Barcelona et al., 1987).

The pressures of CO_2 in this study were determined by the following equations, which were programmed as a series of transforms into the computer program Sigma Plot. This allowed input of raw data from field sampling and laboratory analysis into a spreadsheet, and used the computer program to make calculations for many samples at the same time. The first step in calculating the CO_2 pressure was calculating the molar concentration (moles/L) of each ion of interest from the laboratory reported concentration (mg/L). This is calculated by dividing the concentration of a particular ion in mg/L by 1000 to give a concentration in g/L. The concentration in g/L is then divided by the atomic mass of the particular ion. The ionic strength (*I*) of each sample was then calculated with the following formula (Stumm and Morgan, 1981):

$$I = \frac{1}{2} \sum m_i z_i^2 \qquad (2)$$

where m_i is the concentration of the *i*th ion and z_i is the charge of that ion.
The ionic strength was then used in the Debye-Hückel Equation to determine the activity of each species in the reaction:

$$\log \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + B a_0 \sqrt{I}} \qquad (3)$$

where γ_i is the activity of the *i*th ion, z_i is the charge of the *i*th ion, A and B are constants depending on temperature, and a_0 is a parameter for the hydrated radius of the *i*th ion.

Following this step, one must consider the chemical reaction that is being evaluated in order to determine the values of CO_2 partial pressures for samples. The carbonate system is dominated by the uptake of carbon dioxide into water, which produces carbonic acid:

$$CO_{2(g)} + H_2O = H_2CO_3^* \qquad (4)$$

where $H_2CO_3^*$ is the sum of H_2CO_3 and aqueous CO_2. Some of the carbonic acid ($H_2CO_3^*$) then dissociates into hydrogen and bicarbonate ions:

$$H_2CO_3^* = H^+ + HCO_3^- . \qquad (5)$$

Some of the bicarbonate present will also dissociate into hydrogen and a carbonate ion:

$$HCO_3^- = H^+ + CO_3^{2-} . \qquad (6)$$

Each of the dissociation reactions above has a corresponding temperature dependent equilibrium constant (K value). These can be used to assess the activities of the different species in the equation. The K values are equal to the activities of the products divided by the activities of the reactants. So, for these reactions:

$$K_{CO_2} = \frac{aH_2CO_3^*}{P_{CO_2}}, \qquad (7)$$

$$K_1 = \frac{(aH^+)(aHCO_3^-)}{aH_2CO_3^*}, \qquad (8)$$

and

$$K_2 = \frac{(aH^+)(aCO_3^{2-})}{aHCO_3^-}\,. \qquad (9)$$

Since field data collected during this study included pH (-log(aH$^+$)), bicarbonate alkalinity (HCO_3^-), and temperature, it becomes possible to calculate the partial pressure of CO_2 for the collected samples. By manipulating the equations above it is possible to obtain an activity value for carbonic acid from bicarbonate and pH values:

$$aH_2CO_3 = \frac{(aH^+)(aHCO_3^-)}{K_1}\,. \qquad (10)$$

After obtaining a value for the activity of carbonic acid the partial pressure of CO_2 can be calculated, where

$$P_{CO_2} = \frac{aH_2CO_3}{K_{CO_2}}\,. \qquad (11)$$

This value represents the carbon dioxide partial pressure of a hypothetical atmosphere within which the water samples are in equilibrium at the time of sample collection. These values are given in atmospheres of pressure. In order to make CO_2 values easier to interpret, the values of CO_2 in this study were normalized to the current standard CO_2 in earth's atmosphere at the time of this study, approximately 395 ppm (Tans and Keeling, 2013). This was accomplished by dividing the calculated value of

P_{CO_2} by 0.000395. A value of one means the sample has the same CO_2 pressure as the atmospheric background, 10 is ten times atmospheric background, etc.

A calcite Saturation Index (SI*c*) was calculated for each sample taken. This provides a value of the degree to which the sample is either saturated or undersaturated with respect to the mineral calcite. This is calculated by first determining the Ion Activity Product (IAP), which is equal to the activities of the products over the reactants. Then the SI*c* is calculated by the following equation:

$$SIc = \log\left(\frac{IAP}{K_{cal}}\right), \qquad (12)$$

where : $IAP = aCa^{2+} \times aCO_3^{2-}$, and K_{cal} = a temperature dependent solubility constant for the mineral calcite.

Soil temperature and rainfall data were obtained from the closest proximity Kentucky Mesonet Site. Rainfall, in inches, and soil temperature, in degrees Celsius, were recorded every 30 minutes throughout the study period at this site. This closest Kentucky Mesonet Site is located approximately 12 miles away in Barren County, KY.

VI. Results and Discussion

Throughout the course of the study field samples were analyzed for pH, SpC, temperature, and bicarbonate alkalinity. The pH values observed at the Crowbar Dome sampling site ranged from 6.79 to 7.72, while the Logsdon River site's values ranged from 6.94 to 7.72. The pH values at the Crowbar Dome sampling site showed a wider variation than the Losgdon River site (Figure 10). This can be expected due to the seasonal changes and surface variables having a more direct influence on the Crowbar Dome samples. The Logsdon River samples were variable, but less so, throughout the study period.

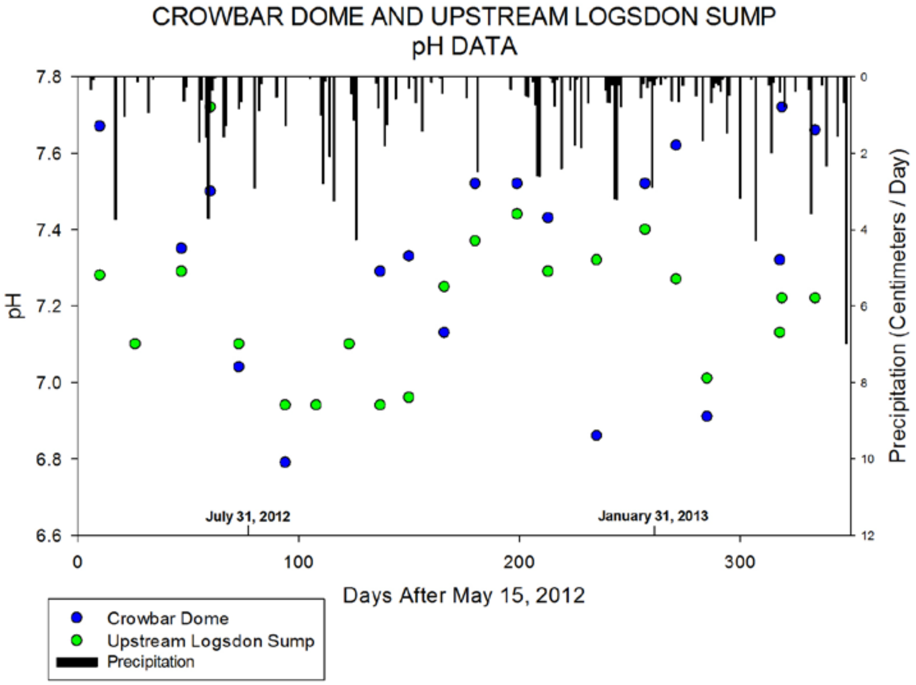

Figure 10: pH Values

The SpC values between the two sites differ in their behavior throughout the study (Figure 11), while bicarbonate concentrations exhibit a similar trend (Figure 12). Both of these parameters exhibited higher values during the warmer weather portions of the study, and showed a decrease in values throughout the colder portion of the year. The bicarbonate concentrations showed a similar decline in both sample sites, although the bicarbonate concentrations for the upstream Logsdon River sump remained roughly twice as high throughout. The SpC values showed somewhat dissimilar trends. Throughout the course of the year the Crowbar Dome samples appeared to respond to the fluctuation in outside temperature by a decrease in SpC values during colder weather. The SpC values of the upstream Logsdon River samples remained fairly consistent during the year and did not show much variation due to changes in outside temperature.

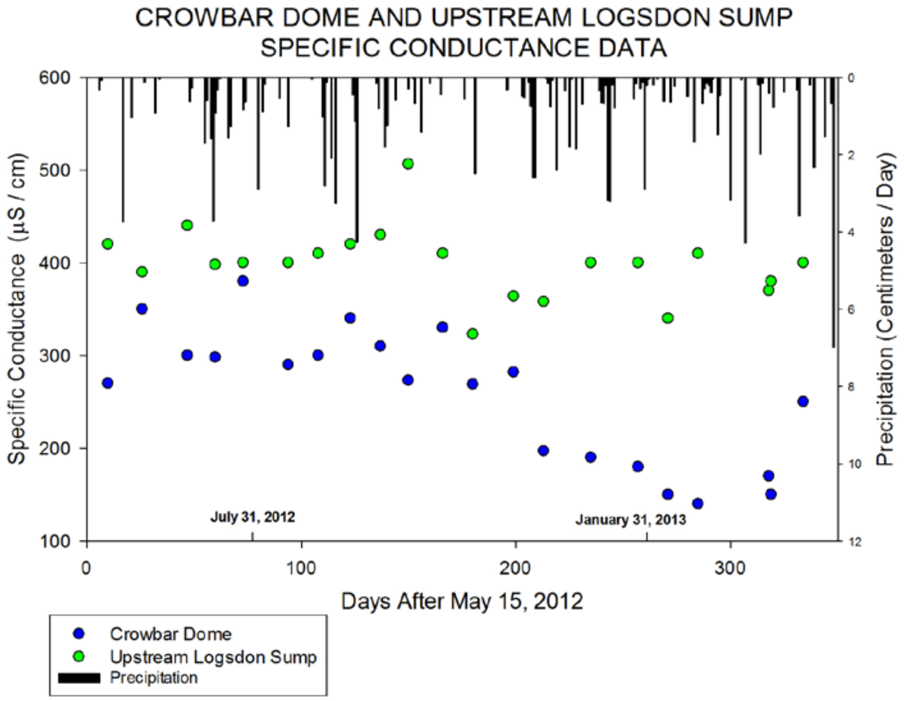

Figure 11: Specific Conductance Values

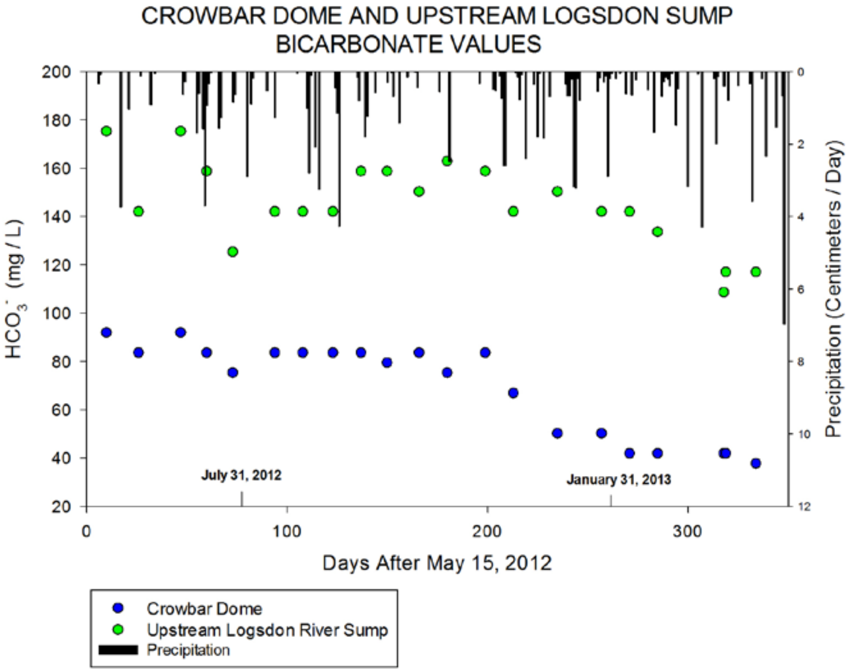

Figure 12: Bicarbonate Concentrations

Temperatures from the two sample sites showed similar trends throughout the study (Figure 13). Both sample sites showed a decrease in temperature throughout the study period. Although the Crowbar Dome sample represents a near surface cave water sample, it did not fluctuate significantly more than the upstream Logsdon River sample. In fact, during the summer months one might expect the temperature to be higher at Crowbar Dome due to direct influence from surface temperatures. This was not the case during the course of the study, as the water had apparently had a chance to thermally equilibrate with the rock of the aquifer framework, explained by the conveyance of the water through “thermally effective” rather than “thermally ineffective” pathways (Luhmann et al., 2011; Covington et al. 2011) that allow transfer of more or less thermal energy from the rock matrix to the throughflowing water depending on the rate at which the water passes through more or less hydrologically efficient flowpaths.

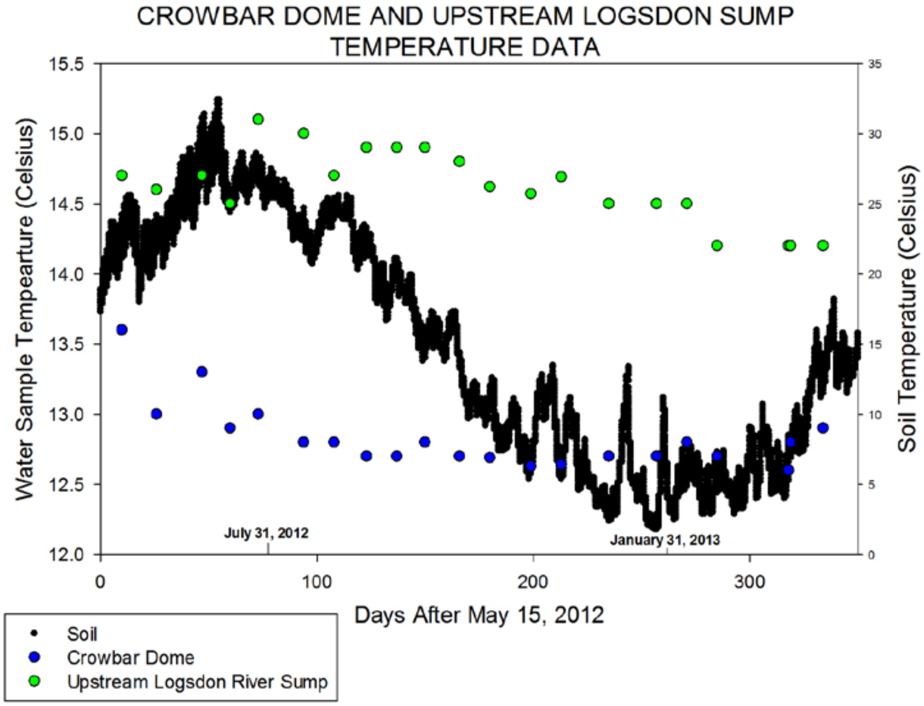

Figure 13: Water Sample and Soil Temperatures

Throughout the entire study period temperatures at the upstream Logsdon River sump were higher than those at Crowbar Dome. The fact that the seasonal variations at both sites are relatively small compared to outside air temperature variations suggests that water at both sites has been thermally equilibrated to the rock matrix, and the fact that the Logsdon River is significantly lower in the rock section than the epikarstic zone rock influencing temperatures at Crowbar Dome is consistent with the geothermal gradient, with average values for the Illinois Basin of about 5^{o}C/100 meters (Profitt et al., 2013).

Samples that were collected during this study were analyzed for an array of cations by ICP-OES analysis. The most influential of these cations, in regard to ionic strength and calcite saturation conditions, was calcium. This is the main cation that is involved in geochemical reactions in the karst of the Mammoth Cave area. Laboratory analysis was not able to be completed for a few of the sampling events, though field measurements were taken in these instances. In order to obtain estimates for the calcium concentration in these instances, the relationship between calcium and SpC was examined in the samples that were analyzed at the laboratory (Figures 14 and 15). A linear relationship exists in many cases for karst settings, including Mammoth Cave aquifers, between SpC and calcium concentrations (e.g. Groves and Meiman, 2005). Upon linearly regressing those values, an equation showing the relationship between the two parameters was developed for each the upstream Logsdon sump and the Crowbar Dome areas using least squares regression (Draper and Smith, 1981). Caution must be exercised when using a small sample size, as in this study. Yet, previous investigations in the Logsdon River (Groves and Meiman, 2001, 2005) with large data sets have proved least squares regression to be an effective method for comparing Ca^{2+} and SpC in this watershed.

The following equations were used to estimate a value of the calcium concentration for the samples that lack laboratory analysis. The Crowbar Dome equation was found to be:

$$Ca^{2+} = 0.1881(SpC) - 6.6403 , \qquad (13)$$

with an R-squared value of 0.9078 (Figure 14) .

The relationship for the upstream Logsdon sump was found to be represented by the equation:

$$Ca^{2+} = 0.1179(SpC) + 21.8623\,, \qquad (14)$$

and an R-squared value of 0.4678 (Figure 15).

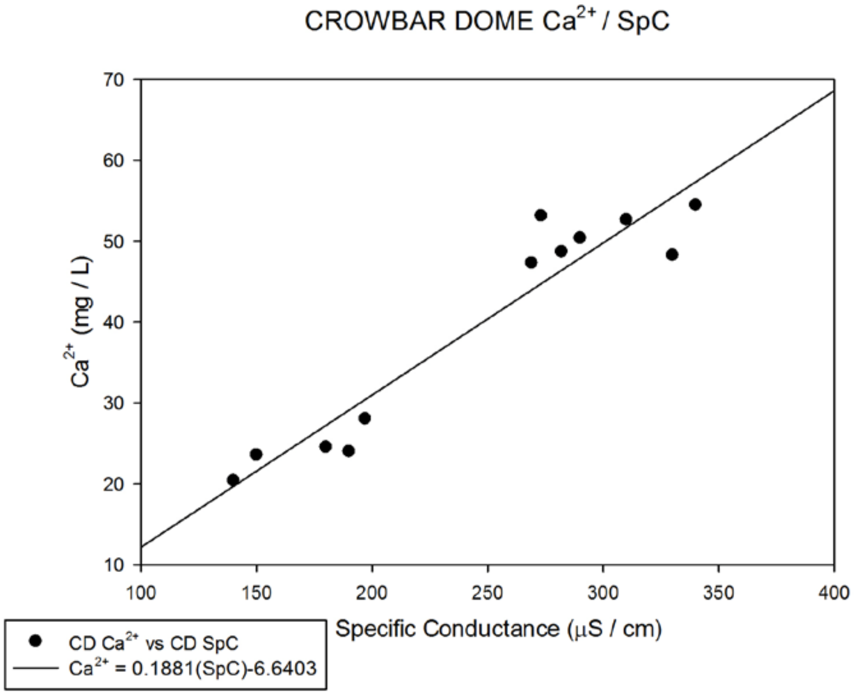

Figure 14: Crowbar Dome Calcium vs. SpC Regression

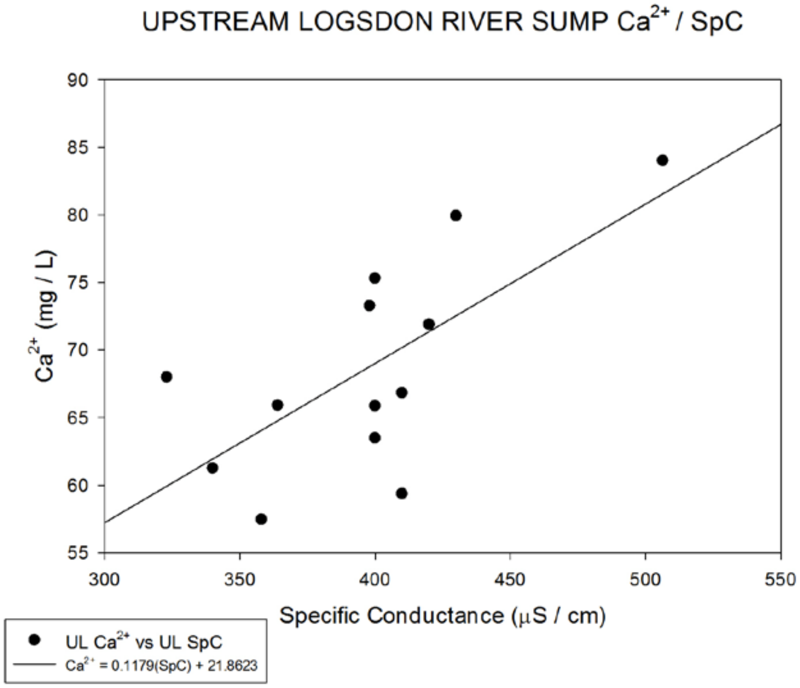

Figure 15: Upstream Logsdon River S-188 Sump Calcium vs. SpC Regression.

This method shows a strong correlation between SpC and calcium values for the Crowbar Dome Samples. This is not surprising because in this location the water that is being sampled is entering the cave from a surface drainage that is a predominantly forested area. This steady and homogenous surface land use provides, during any given season, a consistent geochemical input, and by the time the water reaches the sample site limestone dissolution has been the dominant control on its ionic strength. The samples that were taken at the upstream Logsdon River sump show a weaker correlation. This is a likely result due to the fact that the source for this sample point comes from a wide variety of land uses outside of Mammoth Cave National Park. Upstream Logsdon River drains an area containing residential, agricultural, commercial, and forested lands. SpC samples collected at this point can be influenced by many anthropogenic surface activities due to the drainage area feeding into this sample location (e.g. crop fertilization, road salting, etc.). This can lead to varying degrees of uncertainty in the causes of SpC fluctuation and chemical concentrations in these samples over the course of this study.

While looking at all of the data in this project, it must be reiterated that samples were collected roughly every two weeks, and taken as long as practicable after a rain event. This was done in an effort to obtain samples as near as possible to the seasonal baseflow at the sample sites, and also had a practical limitation as this area of the cave is flood-prone and thus potentially dangerous during wet conditions.

Calcium concentrations throughout the study period for each site displayed similar trends (Figure 16). The range in calcium concentrations for the Crowbar Dome samples showed more variation through the year, ranging from 64.84 mg/L in July to 20.40 mg/L in February. The Logsdon River samples showed a seasonal change in calcium concentrations as well, 84.00 mg/L in October to 57.54 mg/L in December, but displayed a more subtle change overall. Though with the relatively poor correlation of Logsdon River samples we can make inferences with respect to the directions of changes, but less so with regard to the magnitudes. In the winter months the calcium concentrations decreased for each sample site. This was seen more dramatically in the Crowbar Dome samples. This is expected as a result of the decrease in biological activity in the soil during the winter months. During the winter months the microbes in the soil become less active. This decrease in activity causes them to release less carbon dioxide into the soil. As a result of this decrease in soil CO_2 there becomes less CO_2 dissolved in the water that passes through the soil, and due to the decreased CO_2 in the water there is less calcite dissolved as water travels into Crowbar Dome. The samples taken from the

Logsdon River site do not show as dramatic of a seasonal change because water at this site has had a much longer residence time within the cave. This has allowed it to dissolve more calcite, and gain more inputs of CO_2 from decaying organic material in the cave system. In order to determine if the temperature difference between the two sites had a significant impact on CO_2 pressures and SI*c*, all CO_2 and SI*c* calculations were repeated with the temperature values from the two sites switched. This resulted in an average change of 0.37 normalized units of CO_2 concentrations, and an average change of 0.03 units of calcite saturation indices. As a result of this, the temperature difference between the two sites is considered negligible in the overall changes that are observed in CO_2 concentration and saturation state during this study.

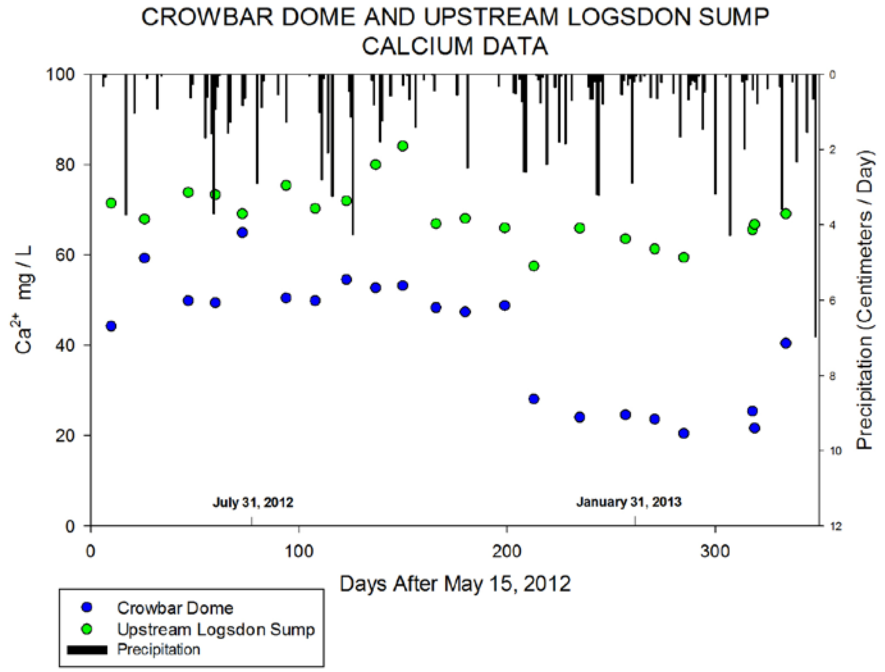

Figure 16: Calcium Concentrations

Explanations of the calcium concentrations at the sites are inferred from the data collected in this study because of the change in the calculated values of the partial pressures of CO_2. After performing these calculations, P_{CO_2} values can be compared between the upstream Logsdon River site and the Crowbar Dome site (Figure 17). It was found that during the course of this study, the P_{CO_2} values observed at the upstream Logsdon River site were more than double the values of the Crowbar Dome samples during most sampling events. This would seem to go against the conventional wisdom related to CO_2 sources in karst systems. Instead of finding higher CO_2 pressures at the near surface location, this study has shown significantly higher pressures of CO_2 in the deeper sample location.

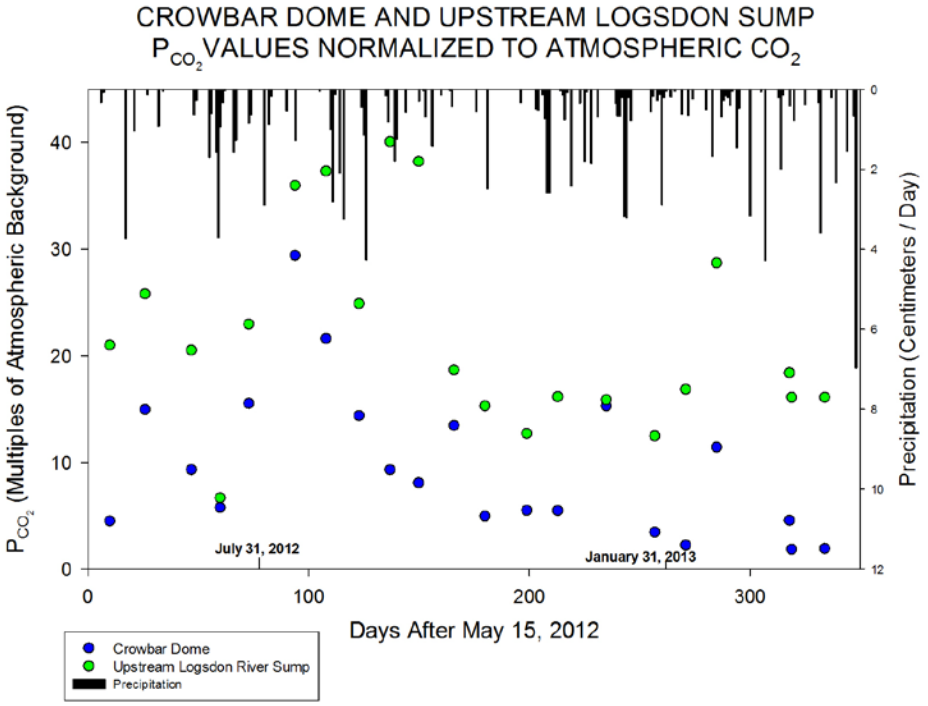

Figure 17: CO_2 Concentrations

Most past research has presented the assumption that the main source of CO_2 comes from the soil and epikarstic zone. In situations where this is assumed to be the case, it is observed that as water progresses through a karst system the CO_2 degasses as a result of turbulent flow, and is also taken up by dissolution of the limestone. In the previous study by Anthony (1998) the general trend in water as it passes through the system was a decrease in P_{CO_2} values. The sample collected at the base of Crowbar Dome does allow potential for CO_2 degassing, but it must also be noted that upstream of the S-188 sump in Logsdon River divers reached an area of the Logsdon River conduit that was not completely water filled. This section of passage displayed turbulent flow that would similarly allow degassing of CO_2 as water passed through this section. The P_{CO_2} results of this study support the assumption that there is an additional source of CO_2 being introduced into the system deeper into the cave.

The study started off during the spring in south-central Kentucky and as it progressed into the summer months there was a general increase in CO_2 concentration. During the summer months, the CO_2 values were consistently higher at the Logsdon River site. Both Crowbar Dome and Logsdon River displayed some variation, but the general trend of the data shows that there was an increase in CO_2 concentrations through the summer months. Crowbar Dome displayed a sharp decrease in CO_2 concentrations during the fall that continued gradually diminishing during the winter. The Logsdon River samples also showed a decrease in CO_2 concentrations, but that decrease did not occur until roughly two months after the CO_2 concentrations began to decrease at Crowbar Dome.

The SI*c* was calculated for each sample taken, where values were obtained that could either be positive numbers, negative numbers, or zero. If the SI*c* of a sample equals 0 then that sample is in equilibrium with respect to calcite. If the SI*c* of a sample is negative then that sample is undersaturated with respect to calcite. Likewise, if the SI*c* is a positive number that sample is oversaturated with respect to calcite. Saturation Indices calculated for Crowbar Dome and the upstream Logsdon River sump showed that during almost all sampling events both sites were undersaturated with respect to calcite.

Throughout the entire course of sampling only one sample taken at the upstream Logsdon River sump was oversaturated with respect to calcite (Figure 18). This contrasts the findings of the Groves and Meiman (2001; 2005) study in the downstream portion of Logsdon River that showed the river downstream was oversaturated with respect to calcite throughout the majority of the year, which is consistent with outgassing along the river between the two locations. In their study, the water in the downstream portion of Logsdon River was undersaturated mainly following rain events.

SI*c* values at the Upstream Logsdon Sump in this study remain fairly consistent throughout the study period. There does not appear to be a significant seasonal variation in the SI*c* at the upstream Logsdon River site. The Crowbar Dome samples show some variability throughout the study, but they display their lowest values during the coldest portions of the year. The two Crowbar Dome samples that display the most undersaturated values are the same samples that display the higher P_{CO2} values compared with the lower values for the surrounding winter samples. These samples do not, however, show any marked difference in calcium concentrations.

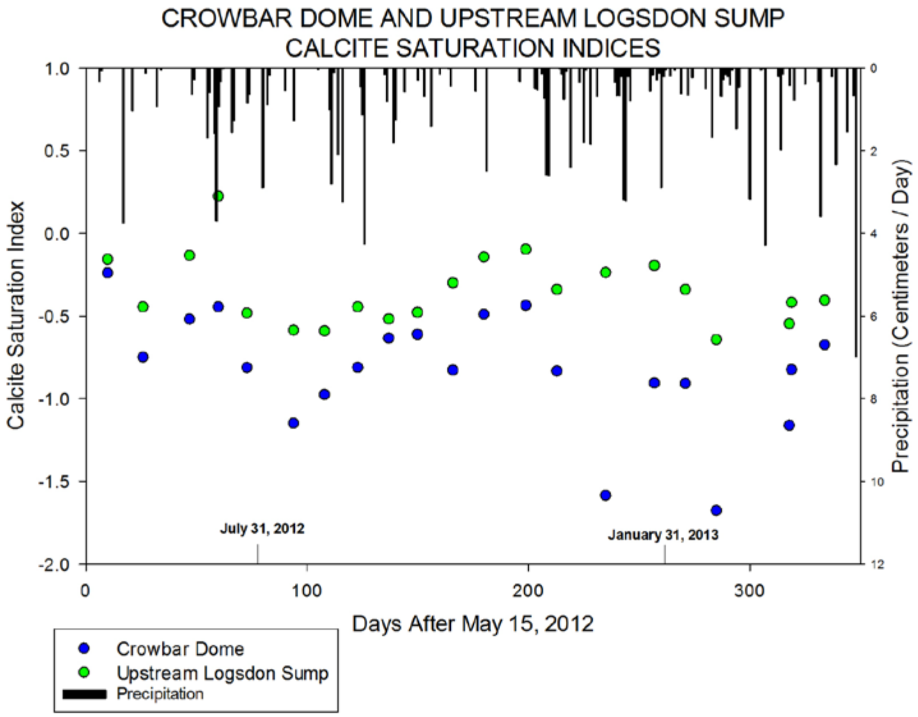

Figure 18: Calcite Saturation Indices

Similarly, the July 14, 2012 sample event showed an upstream Logsdon River sample P_{CO2} value lower than the other samples taken. The calcium concentrations for this sample were similar to other surrounding samples. This is the sampling event that corresponds to the only oversaturated SI*c* calculated. Since this was the only sample that took place soon after a rain event the over-saturated sample potentially could be attributed to aquifer water, which had a longer residence time within the fractures of the limestone, being pushed out of these fractures during the initial storm pulse.

VII. CONCLUSIONS

The temperature of water samples throughout the study exhibit relatively little seasonal variation. There was, however, an unexpected difference between the sampling sites. It was assumed that due to Crowbar Dome's closer proximity to the surface that the temperature values at that sampling site would fluctuate more greatly than the upstream Logsdon River Site. It was also assumed, prior to conducting this study, that the samples at Crowbar Dome would be warmer than the Logsdon River samples during the summer and colder during the winter. This was not the case, and the Crowbar Dome samples were, in fact, colder throughout the study period. It must be concluded that they were both to some degree thermally equilibrated to the rock, but the Logsdon River site, about 2^{o}C warmer, was exposed to deeper rock, warmer due to the regional geothermal gradient. Through visual observation, it is evident that the water falling at Crowbar Dome exhibits a discharge that is orders of magnitude less than the discharge at the Logsdon River site. This lower flow is accumulated from water that is seeping through the soil and infiltrating off of the caprock in this area. This water has a greater residence time within the soil zone, and as a result reaches temperature equilibrium with the rock in the shallow epikarstic zone. During the winter months, the Logsdon River site still displays warmer temperatures, even though the flow remains at much higher levels than the Crowbar Dome site. It does not appear that the larger drainage area for Logsdon River is affecting the temperature by bringing in larger quantities of cold water in the winter than the Crowbar Dome site.

Calcium concentrations throughout the study show a decline at both sites from the warm to cool season. The Logsdon River samples show a very slight decline, while the

Crowbar Dome samples display a more steep decrease in concentration. This can be expected throughout the winter months because the amount of available CO_2 produced in the soil zone is decreasing. As a result of this, there is less limestone being dissolved and through the epikarst and upper portions of each flow path. The Logsdon River samples remain higher in calcium concentrations because of a longer upstream flowpath, and additional CO_2 inputs along this flowpath.

It can also be noted that the calcium concentrations in Crowbar Dome show a sharp drop around day 212 (December 15, 2012). The decrease in concentration at this time is also evident in the SpC and bicarbonate values at Crowbar Dome. This may represent the beginning of the coldest portion of the winter that, in turn, greatly slows down soil microbial activity.

Observing the values and changes in the concentration of CO_2 was the main focus of this study. It can be observed that throughout this study the concentration of CO_2 at the Logsdon River site was generally double or greater the CO_2 concentration at Crowbar Dome. As the study progressed from the spring into the summer months there was a general increase in CO_2 concentration. During the summer months, the CO_2 values were consistently higher at Logsdon River. Both Crowbar Dome and Logsdon River displayed some variation, but the data shows a general trend which displays an increase in CO_2 concentrations through the summer months. The sample taken at Crowbar Dome around the onset of autumn displayed a sharp decrease in CO_2 concentration. From this point the Crowbar Dome CO_2 values continued gradually diminishing during the winter. The Logsdon River samples also showed a decrease in CO_2 concentrations, but the decrease at this site did not occur until roughly two months after the CO_2 concentrations began to decrease at the Crowbar Dome site. This can presumably be attributed to the accumulation of a fresh source of organic debris being washed into the system. As the amount of vegetative mass on the surface begins to decrease the microbial communities in the near surface environment begin to slow down. Yet, at that time, fresh sources of dying organic material are swept into the cave to renew the organic material in the bedload of cave streams.

Previous studies produced data displaying CO_2 concentrations averaging in a range from 5 to 10 times atmospheric CO_2 concentrations at the downstream end of Logsdon River (Groves and Meiman, 2001), and one warm season sample of 35 times atmospheric background at the upstream end (Anthony 1998). The Crowbar Dome data from this study shows similar concentrations. The water samples at the upstream Logsdon River sump display much higher concentrations of CO_2. Concentrations throughout this study, on average, range from 15 to 40 times the atmospheric concentration of CO_2. This site typically displays CO_2 concentrations 3 to 4 times greater than the surrounding surface inputs and the downstream portions of Logsdon River.

The relatively high concentrations of CO_2 at this location, in consideration with some seasonal variation, particularly highest levels in late summer and fall, suggest that both externally produced CO_2 and an internal source of CO_2 that is being produced along the flowpath in the cave influence the high levels at the upstream sump. This in-cave source is most likely a result of microbial breakdown of organic material in the bedload of Logsdon River. At many places in the cave this material may break down in the bedload of a cave stream and be able to degas into the cave atmosphere. This situation was found by Vaughan (1998) when he observed that greater CO_2 pressures were present in cave stream sediments at depth than the surface stream flowing above them in Mammoth Cave's River Styx. At the upstream Logsdon River sump there is a mapped area of completely water filled passageway upstream of the sample site for approximately 100 meters. Beyond that, there are likely more completely water filled passageways. Due to the fact that this distance of the flowpath upstream of our sampling site is completely filled with water, organic material that is broken down may accumulate CO_2 into solution because the CO_2 has no atmosphere in contact into which the CO_2 can degas.

All of the samples taken during this study, except for one, were undersaturated with respect to calcite. The one oversaturated sample was taken the most quickly after a rain event of any other sample. This sample displayed the lowest CO_2 concentration of all of the Logsdon River samples and conversely the highest pH value. The remaining parameters remained roughly the same. This sample was presumably part of the tailing end of a storm pulse which had resulted in an increased residence time within the system, while the increased flow potentially diluted CO_2 inputs.

Throughout the rest of the study period all of the samples were undersaturated with respect to calcite. The Crowbar Dome samples were the most undersaturated. This is understandable due to the short residence time the water has had within the system at this point. The Logsdon River samples remained consistently undersaturated throughout the year. This is in contrast to the observed Saturation Indices in the downstream portion of Logsdon River by Groves and Meiman (2001). These results can be coordinated by the work of Anthony (1998). In that study, it is observed that throughout the longitudinal profile of Logsdon River the CO_2 concentrations dropped. The upstream portion of

Logsdon River remains undersaturated throughout the year. As the water progresses downstream, it degasses CO_2 while continuing to dissolve limestone. By the time the water reaches the downstream portions of Logsdon River is has become oversaturated. The major driver in the dissolution processes in Logsdon River at base flow appears to be the upstream portion of the river.

Since the majority of these samples were taken at base flow conditions, the sample taken in the days after the storm event shows a different trend. It is not known if this oversaturated sample is solely influenced by a change in geochemistry during the tailing end of the storm pulse, or if there was a potential sampling error resulting in the high pH value.

The Crowbar Dome samples throughout the study period were more undersaturated with respect to calcite relative to the upstream Logsdon River samples. This can be expected due to the short residence time the water has within the system before reaching the sample point. They displayed a fairly steady level of undersaturation with the most undersaturated conditions occurring at two points during the winter months. These samples displayed higher CO_2 values than the surrounding samples in that season and lower pH values. These samples each were taken after rain events of roughly 0.5 inch of rain. It could be likely that atmospheric CO_2 played a role in the increase in these winter samples resulting in their increased CO_2 pressures, lower pH, and higher degree of undersaturation.

Overall, it appears that the water emerging from the S-188 sump in the upstream portion of Logsdon River is influenced by surface CO_2 sources as well sources other than those produced in the soil zone. This portion of the river does not mimic the geochemical trends that the water in nearby Crowbar Dome displays. There must be an additional influx of CO_2 into the system in this area. The most logical explanation would be the input of CO_2 from decaying organic material in the system.

Future studies in this area could gain a better understanding of the geochemical reaction of these sites to rain events by utilizing data loggers to collect high resolution data. This will come with significant challenges due to the extremely flood-prone nature of the sample sites. Additionally, examination of the bedload of the Logsdon River and interstitial CO_2 concentrations of the sediments in Logsdon River during future studies could lead to a better understanding of the sources of CO_2 in the Logsdon River system.

APPENDIX 1

FIELD MEASUREMENTS AND LAB / CALCULATED VALUES FROM CROWBAR DOME SAMPLING SITE

FIELD MEASUREMENTS AND LAB / CALCULATED VALUES FROM CROWBAR DOME SAMPLING SITE

Date	Days from May 15th, 2012	Time	pH	SpC (micro-siemens)	Temp. (°C)	Ca (mg/L)	Alkalinity (HCO$_3$ mg/L)	Pco$_2$	Pco$_2$ Normalized to Atmosphere	Calcite Saturation Index
5/25/2012	10	10:00:00	7.67	270	13.6	44.15	91.744	0.001766	4.470962	-0.2406
6/10/2012	26	13:16:00	7.10	350	13.0	59.20	83.448	0.005894	14.92246	-0.7508
7/1/2012	47	08:30:00	7.35	300	13.3	49.79	91.744	0.003667	9.282629	-0.5203
7/14/2012	60	18:29:00	7.50	298	12.9	49.35	83.448	0.002268	5.742909	-0.44684
7/27/2012	73	17:35:00	7.04	380	13.0	64.84	75.152	0.006126	15.50932	-0.8143
8/17/2012	94	17:05:00	6.79	290	12.8	50.38	83.448	0.011612	29.3981	-1.15082
8/31/2012	108	16:20:00	6.94	300	12.8	49.79	83.448	0.008531	21.59629	-0.9777
9/15/2012	123	12:52:00	7.10	340	12.7	54.46	83.448	0.005669	14.35199	-0.81297
9/30/2012	137	20:38:00	7.29	310	12.7	52.63	83.448	0.003663	9.273725	-0.63608
10/12/2012	150	18:30:00	7.33	273	12.8	53.13	79.300	0.003179	8.047268	-0.61255
10/26/2012	166	18:11:00	7.13	330	12.7	48.27	83.448	0.005305	13.43027	-0.82943
11/11/2012	180	09:45:00	7.52	269	12.69	47.31	75.152	0.001948	4.931172	-0.49179
11/30/2012	199	15:27:00	7.52	282	12.63	48.70	83.448	0.002159	5.464748	-0.43738
12/14/2012	213	09:20:00	7.43	197	12.64	28.03	66.734	0.002153	5.450398	-0.83451
1/5/2013	235	09:40:00	6.86	190	12.7	24.00	50.020	0.006025	15.25393	-1.58693
1/27/2013	257	13:00:00	7.52	180	12.7	24.53	50.020	0.001352	3.422025	-0.90748
2/10/2013	271	11:03:00	7.62	150	12.8	23.58	41.724	0.000875	2.2161	-0.9096
2/24/2013	285	18:40:00	6.91	140	12.7	20.40	41.724	0.004495	11.38074	-1.67847
3/29/2013	318	11:15:00	7.32	170	12.6	25.34	41.724	0.001788	4.52694	-1.1639
3/30/2013	319	20:30:00	7.72	150	12.8	21.58	41.724	0.000714	1.806684	-0.82627
4/14/2013	334	08:20:00	7.66	250	12.9	40.39	37.576	0.000740	1.872356	-0.67586

APPENDIX 2

FIELD MEASUREMENTS AND LAB / CALCULATED VALUES FROM UPSTREAM LOGSDON RIVER S-188 SUMP SAMPLING SITE

FIELD MEASUREMENTS AND LAB / CALCULATED VALUES FROM UPSTREAM LOGSDON RIVER S-188 SUMP SAMPLING SITE

Date	Days from May 15th, 2012	Time	pH	SpC (micro-siemens)	Temp. (°C)	Ca (mg/L)	Alkalinity (HCO$_3$ mg/L)	Pco$_2$	Pco$_2$ Normalized to Atmosphere	Calcite Saturation Index
5/25/2012	10	11:00:00	7.28	420	14.7	71.38	175.192	0.008284	20.97152	-0.1587
6/10/2012	26	14:30:00	7.10	390	14.6	67.84	141.886	0.010181	25.77361	-0.4469
7/1/2012	47	09:15:00	7.29	440	14.7	73.74	175.192	0.008095	20.49415	-0.1359
7/14/2012	60	19:35:00	7.72	398	14.5	73.26	158.600	0.002618	6.629001	0.221532
7/27/2012	73	20:55:00	7.10	400	15.1	69.02	125.172	0.009058	22.93266	-0.4844
8/17/2012	94	18:08:00	6.94	400	15.0	75.29	141.886	0.014204	35.96003	-0.5875
8/31/2012	108	17:09:00	6.94	410	14.7	70.20	141.886	0.014734	37.30188	-0.592
9/15/2012	123	13:55:00	7.10	420	14.9	71.88	141.886	0.009823	24.86777	-0.44726
9/30/2012	137	21:31:00	6.94	430	14.9	79.91	158.600	0.015820	40.05123	-0.51993
10/12/2012	150	19:33:00	6.96	506	14.9	84.00	158.600	0.015093	38.20915	-0.48053
10/26/2012	166	19:32:00	7.25	410	14.8	66.81	150.182	0.007364	18.64375	-0.30196
11/11/2012	180	10:30:00	7.37	323	14.62	67.98	162.748	0.006033	15.27261	-0.14491
11/30/2012	199	16:45:00	7.44	364	14.57	65.89	158.600	0.005005	12.67009	-0.09865
12/14/2012	213	10:10:00	7.29	358	14.69	57.45	141.886	0.006371	16.1292	-0.34188
1/5/2013	235	11:08:00	7.32	400	14.5	65.85	150.182	0.006255	15.83557	-0.23898
1/27/2013	257	14:00:00	7.40	400	14.5	63.47	141.886	0.004921	12.45853	-0.19705
2/10/2013	271	09:40:00	7.27	340	14.5	61.24	141.886	0.006642	16.8157	-0.3413
2/24/2013	285	19:53:00	7.01	410	14.2	59.35	133.468	0.011334	28.69303	-0.64471
3/29/2013	318	12:20:00	7.13	370	14.2	65.49	108.458	0.007258	18.37394	-0.54833
3/30/2013	319	18:30:00	7.22	380	14.2	66.66	116.876	0.006350	16.07516	-0.42029
4/14/2013	334	09:35:00	7.22	400	14.2	69.02	116.876	0.006350	16.07516	-0.40663

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