Atmosphere/Landscape CO2 Interactions in Mammoth Cave National Park: Hydrochemistry of Cascade River, Great Onyx Cave

Jessica Williams
Western Kentucky University, jessica.williams897@topper.wku.edu

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ATMOSPHERE/LANDSCAPE CO₂ INTERACTIONS IN MAMMOTH CAVE
NATIONAL PARK: HYDROCHEMISTRY OF CASCADE RIVER, GREAT ONYX CAVE

A Capstone Experience/Thesis Project Presented in Partial Fulfillment
of the Requirements for the Degree Bachelor of Arts
with Mahurin Honors College Graduate Distinction
at Western Kentucky University

By

Jessica M. Williams

December 2021

CE/T Committee:
Dr. Chris Groves, Chair
Dr. Albert Meier
Ms. Susann Davis
ABSTRACT

High-resolution analysis of water/CO$_2$/carbonate rock geochemistry was conducted at the Great Onyx Groundwater Basin in Mammoth Cave National Park. The purpose of this work has been to undertake hydrochemical characterization of the karst groundwater in Cascade River, the largest cave stream in the upper level of Great Onyx Cave, which is below a relatively pristine karst landscape.

Hydrochemical monitoring of Cascade River at Biz Falls using field, laboratory, and high-resolution electronic data-sonde measurements has provided a detailed picture of the stream’s behavior with respect to the transport and influence of carbon dioxide in the surface and groundwater system as well as quantifying water/rock interactions. Comparison of cool and warm season hydrochemical dynamics shows waters of Cascade River are influenced only by atmospheric CO$_2$ in winter while the warming of the seasons adds additional CO$_2$ from a surface source, presumably soil respiration influenced by degradation of soil organic material and root respiration. The waters of Cascade River stay undersaturated with respect to the limestone bedrock so that the aquifer framework is continuously dissolving, though more rapidly in winter. In all seasons, storms have a rapid impact on the groundwater showing a relatively direct hydrologic connection from the surface through a significant conduit that most likely stays water filled.

These results advance the understanding of hydrology and geochemistry of the Great Onyx Groundwater Basin, representing an important first step towards long-term study.
I dedicate this thesis to all my friends, professors and family who have supported and encouraged me during my writing of this thesis – without them I wouldn’t have gotten as far as I have.
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VITA

EDUCATION

Western Kentucky University, Bowling Green, KY Dec. 2021
  B.A. in Critical Zone Science (Honors Self-Designed Studies)
  Minors in Chemistry and Mathematics
  Certificate in Geographic Information Science
  B.A in Chinese – Mahurin Honors College Graduate
  Honors CE/T: Atmosphere/Landscape CO2 Interactions in Mammoth Cave National Park: Hydrochemistry of Cascade River, Great Onyx Cave

Gatton Academy of Mathematics and Science, Bowling Green, KY May 2017

Randall K. Cooper High School May 2017

PROFESSIONAL EXPERIENCE

Wild Health Aug. 2021 - Present
  Location Manager/Covid Screener

Kentuckians for the Commonwealth Aug. – Nov. 2020
  Voter Empowerment Staff

  Lab Technician

The Learning Center Jan. – May 2019
  Math and Reading Tutor

WKU Department of Math Aug. 2018 – May 2019
  Math Tutor

PRESENTATIONS

WKU Research Conference, April 2021
UNESCO Karst Conference, May 2020
WKU Research Conference, March 2020
AWARDS & HONORS

Gatton Academy and Craft Academy Graduates Research and Experiential Learning Award, Summer 2021
Critical Language Scholarship Semifinalist 2020
Faculty-Undergraduate Student Experience (FUSE) Grant, 2019-2020
Gatton Academy and Craft Academy Graduates Research and Experiential Learning Award, Summer 2019
World Topper Scholarship, Summer 2019
Chinese Flagship Funding, Summer 2019

INTERNATIONAL EXPERIENCE

Beijing Normal University, Beijing, China
Princeton in Beijing

Jun. – Aug. 2019

Harlaxton College, England

English 200

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1. INTRODUCTION

This research is on the carbonate rock geochemistry of Great Onyx Groundwater Basin in Mammoth Cave National Park. By understanding relevant processes, we can get closer to understanding karst landscapes and their relationship with global climate change. In limestone karst regions like those so spectacularly developed at Kentucky’s Mammoth Cave National Park (Figure 1), the limestone bedrock, water in the form of rainwater and groundwater, and carbon dioxide (CO$_2$) gas chemically interact to remove CO$_2$ from the atmosphere (e.g., Lu and Zhao, 2000; Groves and Meiman, 2005; Cao et al., 2012, 2018; Martin, 2017). This results in an impact on the concentration of atmospheric CO$_2$ of which changes are closely tied to global climate change (e.g., Fakowskey et al., 2000). In this work we studied the hydrogeochemistry of an essentially pristine karst aquifer located in Mammoth Cave National Park by conducting high-resolution hydrochemical monitoring to help characterize one of Great Onyx’s most important streams, Cascade River, at its upstream end where it enters the cave at Biz Falls.

Figure 1. Karst landscapes of Kentucky, in blue, showing the location of Mammoth Cave National Park (Paylor and Currens, 2001).
2. BACKGROUND

2.1 Karst

Karst is defined as any landform that was created by the dissolving of rock (White, 1988). Karst landscapes mostly occur where there are carbonate rocks, most commonly limestone ($\text{CaCO}_3$), dolomite ($\text{(Ca, Mg)(CO}_3\text{)}_2$) or non-carbonate soluble rock like gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$). Features are created by the slow dissolving of these highly soluble rocks, which differs from other landscapes in which mechanical erosion of rock primarily shapes the landscapes. This dissolution creates caves, sinkholes, underground streams, sinking streams, swallets, and springs (Veni et al., 2001).

Typically, karst landscapes have few above ground streams and lack surface water except during times of intense rainfall. Rainwater is absorbed by soil and the rainwater travels through the soluble rock below. Karst features are created by water dissolving rock as it passes through the underground. Rainwater can either enter bedrock through established conduits and fractures at a specific spot or seep into the ground through the soil over a wide area. It can enter through the soil, a sinkhole, or a swallet (sinking stream). The water then drains through a path of least resistance, typically through already established conduits as well as porous and permeable rock, dissolving rock on its way through to underground streams (Veni et al., 2001).

The process of water entering the bedrock in a karst area is called recharge. The water reemerges on the surface, typically at the level of the water table, through springs, seeps, and wells. Many important springs are found in karst landscapes (Veni et al., 2001) including some of the world's largest (Auler and Stevanović, 2021). The reemergence of water is called discharge. This discharged water travels on the surface to streams, lakes,
wetlands, and eventually the ocean (Veni et al., 2001).

Many of the water flow and substantial landscape changes occur at or just below the water table. The water table fluctuates over time and in response to rainfall inputs, which is what has led to the formation of extensive cave systems. The water table delineates the undersaturated and saturated regions of bedrock with respect to water content, with the saturated being below. In karst aquifers, the saturated zone is referred to as the phreatic zone and the unsaturated zone is called the vadose zone. The vadose zone has air within the pore spaces of the rocks while the phreatic zone stores water in its pore spaces and is thus saturated.

When there are substantial storm events, the water table will rise. This can cause sinkholes to become springs and above ground streams to form. When there is significant drought, the water table will lower. This can cause springs to become points of recharge. Features that change from discharge to recharge points are called estavelles (Veni et al., 2001).

The formation of caves allows water to quickly travel through the underground, creating more cave systems and networks. Because of the creation of more area to store water, the water table will slowly lower over time as water is drained to lower areas. As the water table lowers, older cave passages are left drained and dry. Corridors and narrow and tall pits form in response to the lowering water table as water rushes through caves, eventually reaching the water table. At the water table, more horizontal cave passages are formed. Newer cave passages are formed at lower elevations. In drier areas, the dripping of water as it passes through can deposit minerals and create speleothems, or stalactites, stalagmites, columns and other interesting cave structures (Veni et al., 2001).
Karst systems are typically heterogeneous and anisotropic (Auler and Stevanović, 2021). This poses problems with modeling and studying their features. Characterizing their hydrology, geochemistry and biological processes requires extensive collection of data, sometimes over long periods of time, to capture not only information to describe the basic processes but also the diversity of events that could impact karst landscapes. In addition to studying karst involving a significant time commitment, it can also be a substantial financial commitment to acquire the technology that could accurately characterize all desired aspects of karst systems. Auler and Stevanović (2021) noted that to explain karst and its groundwater, one would need to study many things like the "mechanisms of recharge and their intensity, the role of epikarst and soil cover, the prevalence of turbulent regime rather than laminar flow in large channels and cavities, complex variations of karst dissolution rates depending on geochemical zoning, deep water recharge and circulation." Each characteristic would also have to be evaluated for water flow through the rock, fractures, and conduits of karst. This complexity is why there is a lack of information on karst impacts to communities and how karst interacts with global change (Xu et al., 2018).

However, karst landscapes impact a large proportion of people. Researchers have proposed that karst landscapes cover 11-15% of ice-free land surface (Ford and Williams, 2007). Others have proposed that 15% of the ice-free land surface could be carbonate karst (Goldscheider et al., 2020). Karst is home to 1.18 billion people or 16.5% of the global population. Europe has the largest percentage of land area covered by karst at 21.8% while Asia has the largest absolute area at 8.35 million km² (Goldscheider et al., 2020). Karst is concentrated in Asia, Europe and North America, with over 60% of
carbonate rock found between 20-50°N latitude (Cao et al., 2012). Over a fifth of the United States consists of karst (Veni et al., 2001). Due to the growing recognition of the importance of karst landscapes, over the past couple decades there have been improvements in modeling and observational technology that will enable future researchers to rapidly expand our understanding of karst terrain and its impacts on humanity.

One challenge for modeling karst is that watersheds are not discernible by analyzing the topography of the landscape due to the variable dissolution of carbonate rock underneath the soil and therefore must be mapped from the inside. A common method to delineating the watershed of karst terrains is performing groundwater tracer tests. These are used to determine underground flow paths, transport processes and water-rock interactions. Many substances can be used for tracer tests, most commonly certain types of fluorescent dyes (Benischke, 2021) Tracers can occur naturally in the water, or they can be artificially added.

Dye tracing is a common method for delineating surface/subsurface watersheds known as groundwater basins with karst terrains. An initial investigation of the above ground landscape and known underground cave streams in a given area leads to identification of potential entry and exit points for a watershed. Dye receptors made of activated charcoal are placed throughout the identified locations where water might flow. Different types of nontoxic, fluorescent dye are then injected into potential entry points or points on the potential flow path. The dye receptors will pick up trace amounts of the fluorescent dye as the dye travels through the watershed. The charcoal is then analyzed to identify the dye and map the water flow of the watershed. This is an iterative process that
can take multiple trials but is one of the simplest ways to complete the identification of a watershed in karst terrain and is employed globally (Benischke, 2021).

To understand our study site, fluorescent dye traces were performed to determine the boundaries of the Great Onyx aquifer and determine the source for our study locations. Our team has also connected two different underground streams in the cave to establish that they are in fact one river, which was named Cascade River. This is the most important stream in the cave’s upper level and the focus of this research project.

2.2 The Global Carbon Cycle

The carbon cycle is a natural process that involves the transfer of carbon atoms through its various organic and inorganic states via chemical, physical, geological, and biological processes in and between the hydrosphere, lithosphere, and atmosphere (Figure 2). The exchanges exist in either a fast domain or a slow domain. The fast domain exchanges carbon relatively rapidly, with reservoir turnover times in the units of years, decades or millennia (Ciais et al., 2013). Reservoir turnover times take into account the rate of outflow from the reservoir and the size of the reservoir to define the amount of time it takes for the total size of the reservoir to be exchanged (Cao et al., 2012). The fast domain is typically what is focused on in climate change modelling. It consists of the exchanges between the atmosphere, the ocean, near surface ocean sediments, soils, freshwater, and plants. The slow domain contains any processes acting on timescales greater than 10,000 years. Transfer exists between the slow and fast domain through processes such as volcanic emissions of CO₂, chemical weathering, erosion, and ocean sediment formation, although the exchange is typically still a slow process and is considered constant in time when looking at carbon exchange in the range of a few
centuries; however, the burning of fossil fuels has accelerated this exchange (Ciais et al., 2013).

The observed global carbon fluxes (transfer rates between various carbon storage reservoirs) and modeled carbon fluxes do not match up. The cause for approximately 2.5 PgC/a of the annual global carbon flux has not been discovered (Cao et al., 2018). Coupled carbonate weathering has been proposed as part of this missing flux (Cao et al., 2012; Martin et al., 2013; Martin, 2017; Liu et al., 2018; Zeng et al., 2019). Coupled carbonate weathering is a term to

Figure 2. Elements of the global carbon cycle (Cais et al., 2013).
describe the relationship between carbonate rock dissolution and hydrophyte photosynthesis (Larson, 2011; Cao et al., 2012; Martin, 2017). Previously, it was believed that the carbon sink caused by carbonate mineral dissolution was balanced by the carbon source caused by mineral precipitation in the oceans, and so silicate rock weathering rates were used to make estimates for the geologic flux (Liu et al., 2018). However, even if the balance between terrestrial dissolution and oceanic precipitation balances out on a time scale of centuries to tens of millions of years (Berner, 1989) it has been shown that the carbon sink effect due to carbonate dissolution can have an effect on atmospheric carbon in the short term, with some estimates saying the flux could alter atmospheric carbon dioxide levels on time scales of less than a century (Martin, 2017). This is in part due to the carbon cycle being tied to the hydrologic cycle (Larson, 2011), which has a turnover time of 2,000 years, and the terrestrial carbon cycle (Cao et al., 2012), which has a turnover time of 50 years (Schlesinger, 1997).

Coupled carbonate weathering occurs as the dissolved inorganic carbon, mostly in the form of bicarbonate, from the dissolution of carbonate rock is taken up by primary productivity. It is converted to organic carbon and is buried in the plants and soil of carbonate terrains (Cao et al., 2012; Martin, 2017). The karst carbon cycle can be described as follows: carbonic acid is created from CO₂ produced in the soil or from the atmosphere; the acid dissolves carbonate rock; the dissolved inorganic carbon is taken up by aquatic plant photosynthesis and converted to organic carbon; finally, the organic carbon is deposited in sediment at the bottom of bodies of water (Cao et al., 2018).

Lakes have been proposed to contribute to coupled carbonate weathering (Liu et al., 2018). Streams from karst areas that drain into lakes increase the DIC concentration
of the lakes, increasing primary productivity and reducing CO$_2$ released from carbonate precipitation (Lerman and Mackenzie, 2005). It is estimated that lakes bury 0.07 PgC/a which is equal to a fourth of carbon burial attributed to oceans, while lakes take up 0.8% of the space that oceans do (Einsele et al., 2001). The increase in agriculture and thus fertilizer run-off has also increased lake carbon burial. It is predicted that lakes may have an ever-increasing impact on global carbon flux (Pacheco et al., 2014). However, while the lakes store more carbon, this causes them to go through eutrophication due to increased rates of primary productivity and can lead to destruction of freshwater habitats (Heathcote and Downing, 2012; Liu et al., 2018).

Carbonate rock stores about 99.55% of the Earth’s total carbon, with estimates up to 61 x 10$^{15}$ tons (Falkowski et al., 2000). It is three orders of magnitude more than that stored in the oceans, which is the largest reservoir that is currently included as part of the active global carbon cycle. It holds 3.8 x 10$^4$ PgC while carbonate rock holds 4 x 10$^7$ PgC (Martin et al., 2013). Estimates of annual carbon sink attributed to coupled carbonate rock weathering (CCW) range from 0.32 PgC/a (Zeng et al., 2019), 0.5 PgC/a (Liu et al., 2018), 0.53-0.58 PgC/a (Cao et al., 2018) to 0.7052 PgC/a (Liu et al., 2010). At the middle estimate around 0.5 PgC/a, CCW would account for 22.08% to 24.17% of the missing carbon sink and is equal to about a third of the global forest carbon sink and two-thirds of the soil carbon flux (Cao et al., 2018).

It is predicted that that this flux will increase as the Earth warms because of anthropogenic emissions of CO$_2$. Increasing atmospheric CO$_2$ levels increase dissolution rates. Changing temperature and precipitation rates will also impact dissolution rates.
Land use changes and agriculture practices are also predicted to impact CCW (Liu et al., 2010; Zeng et al., 2019).

A study predicting impacts of climate change on the global carbon sink flux due to carbonate rock weathering found that from 1950-2100, there was a 9.8-17.1% increase in the predicted flux (Zeng et al., 2019), indicating the dissolution reactions are sensitive to climate change impacts. It has been extensively shown that the rate of dissolution is closely correlated with rainfall events, and as models predict an increase in precipitation as the Earth warms, it is safe to assume that dissolution rates will also increase because of increasing precipitation (Liu et al., 2010; Cao et al., 2012; Martin, 2017; Zeng et al., 2019). Temperature is shown to have a negative impact on dissolution rates (Martin, 2017), with maximum dissolution rates found between 10-15 degrees Celsius, which includes the impact of vegetation. Low and high temperatures limit carbonate weathering due to controls on the thermodynamics of dissolution reactions and effects on soil microbe carbon dioxide production (Gaillardet et al., 2019; Romero-Mujalli et al., 2019). However, increasing atmospheric CO$_2$ concentrations may lead to an increase in soil microbe activity that may create more carbon dioxide and accelerate rates of soil acidification which leads to an increase in carbonate rock dissolution.

Changing agricultural practices have already shown impacts on karst. Specifically, because of run-off, excess fertilizer use increases aquatic primary productivity and leads to a decrease in dissolved carbon dioxide (measured as pCO$_2$) levels (Liu et al., 2018). As a result, less carbon dioxide is outgassed from the water back into the atmosphere and thus water sources can act as a larger carbon sink (Liu et al., 2010). In carbonate rock terrains, this is expected to lead to an increase in carbonate rock
dissolution rates. This is because bicarbonate concentrations decrease due to uptake by photoautotrophs which bury bicarbonate as organic carbon in the water sediments. Contrastingly, nitrogen from fertilizer can be oxidized to form nitric acid. In areas with high fertilizer usage, carbonate rock is dissolved by nitric acid and releases carbon dioxide, acting as a small but notable carbon source that could become more important as humans continue to alter the nitrogen cycle (Martin, 2017; Zeng et al., 2019).

Changes in vegetation type and coverage also play a role in carbonate dissolution rates (Liu and Zhao, 2000; Liu et al., 2010; Zeng et al., 2019). Afforestation, or the conversion of old agricultural lands to forests, has been shown to increase soil pCO$_2$ levels, thus leading to greater dissolution rates (Liu et al., 2010).

3. FIELD SITE – THE GREAT ONYX GROUNDWATER BASIN

Mammoth Cave National Park (abbreviated by its official US government acronym MACA), located in southcentral Kentucky, protects the world’s most extensive known cave system. It has been designated by the United Nations as both a World Heritage Site and International Biosphere Reserve. This research adds to 60+ years of investigation into the hydrogeology of MACA (e.g. Brown, 1966; Quinlan, 1981; Granger et al., 2001; Groves and Meiman, 2005, p. 205; Worthington, 2009; White and White, 2017). Explorers and scientists have explored and mapped nearly 1,000 km of cave passages in and around the park (Guilden, 2021), including more than 670 km of passages just in the Mammoth Cave System itself. Hundreds of dye traces have also mapped more than 100 km of active flow paths of the MACA drainage system (Glennon and Groves, 2002)
Great Onyx (GO) Spring, the main discharge point of the study area, has a recharge area of about 4 km² (Figures 3 and 4) and flows into the south side of the Green River. The boundaries of the GO recharge area are still being fine-tuned with on-going groundwater tracing and cave exploration. These studies also help map the flow paths within the recharge area. Understanding the sub-surface patterns of flow informs design of a long-term monitoring system to quantify drivers and processes influencing the fate and transport of carbon, nutrients, and sediment.

To understand these processes, having a control to understand background processes helps delineate natural and anthropogenic influences on karst processes. The GO Groundwater Basin, deep within MACA, offers an essentially pristine landscape that has not been affected by contaminants from direct land use since at least 1961 when the Park assumed responsibility for the area and began record keeping. Prior to that, there were only two small tourist hotels and scattered farmsteads. The site is also secure--access to the cave requires an NPS permit, and keys must be acquired to open a gated gravel road that leads about three km to the cave entrance.

Great Onyx Cave (Figures 3, 4, and 5) offers access to about at least 7.4 kilometers of passages into the karst aquifer of the groundwater basin, and additional 15.6 kilometers of passages within the basin are accessible through the Austin Entrance of the Flint Ridge section of the Mammoth Cave System. Great Onyx Cave has two main, largely horizontal levels separated vertically by about 25 meters. In the main upper level of the cave, Edwards and Cox Avenues (Figure 5) are developed in the Girkin limestone. The principal stream in the upper level starts in the cave at the bottom of a small, cascading waterfall that sinks into gravel and cave wall a few meters away. A few
hundred meters downstream, northwest along the passage heading back towards the entrance, down a slam climb on the north side of the passage another similar-sized stream emerges from beneath a wall, flows about 30 meters and then over the edge of Cascade Falls (Figure 6) where it then falls about 25 meters to the lower lever on the cave. Here, Cascade River joins the stream flowing from Halloween Crawl to form the Lucykovah River. This has been dye traced to Blindfish River in the Flint Ridge section of the Mammoth Cave System and from there onwards to emerge at Great Onyx Spring and on to the Green River.
This stream is the main flow for the upper level of the cave and is the focus of this research. Previously unnamed, here we propose to call this stream Cascade River, based on the historic name of the large waterfall (Figure 6) over which it falls on its way to the cave’s lower levels. For naming standardization, we propose to call the waterfall at its upstream end *Biz Falls*, the short segment of stream below that *Upstream Cascade River*, and the next short segment of stream above Cascade Falls *Downstream Cascade River*. 
4. MATERIALS AND METHODS

4.1 Field Methods

4.1.1 ISCO Water Sampler

An ISCO Automatic Water Sampler 3000 was utilized at Downstream Cascade River for storm sampling and tracer experiments. This is an instrument that contains 24 one-liter bottles that are filled by a computer-controlled pump at pre-set intervals. The water sampler (Figure 7) was placed in the Downstream Cascade River in Great Onyx Cave where it was set at various time intervals for different projects for collecting samples.
Figure 6. 1922 photograph of the bottom of Cascade Fall by an unnamed photographer (Library of Congress). The current focus of this work is on the stream just upstream of this waterfall, the section between Biz Falls and Cascade Falls. This picture is the only known historical record for a name for the stream we are studying and based on this we propose to call this stream system Cascade River.

Figure 7. This project is a collaboration among a variety of partners. Right: Bowling Green High School Chemistry Teacher Cristen Olson deploys an automatic water sampler at Downstream Cascade River. Left: The bottles in the bottom of the sampler can be seen as Crawford Hydrology Lab Assistant Director Lee Anne Bledsoe collects samples after a tracer test (photos by Chris Groves).
4.1.2 MS5 Data Sonde

A Hydrolab MS5 Water Quality Multiprobe was used to take timed measurements of the water of Biz Falls (Figure 8). The instrument had pH, temperature, and specific conductance (SpC) probes. The factory recommended procedures were followed for calibration and deployment using the recommended software, *Hydras 3 LT*, installed on a Windows PC.

For calibrating the data sonde, it is recommended to calibrate it in the field in ambient conditions due to temperature changes impacting pH and SpC. The first calibration for us, however, was done in the lab. Subsequent calibrations were performed every month in field at Biz Falls or in the lab if the sonde had to be taken out of the field. All calibrations were done via Hydras 3 LT. A three-point calibration was used for the pH probe, starting with a buffer solution of pH 7 and then moving to a buffer solution of pH 10 and ending with a buffer solution of pH 4. A two-point calibration was used for the SpC probe. The first point was deionized water with an assumed SpC of 0 μS/cm. The second point or the buffer solution used was 1000 μS/cm.

Using Hydras 3 LT, the resolution for the data sonde was set at 20 minutes. It was deployed into the field using zip ties to secure the sonde’s sensor guard to a plastic bin that was placed under the stream of water coming from Biz Falls (Figure 8). Data were usually downloaded from the sonde either once a week or once every other week, although there were other gaps under various circumstances. Data were downloaded via Hydras 3 LT and turned into an excel document. Batteries had to be changed once every two weeks or once a month.
4.1.3 Water Grab Samples

Grab samples were taken of the water from Biz Falls and Lower Cascade River to perform alkalinity titrations and cation and anion analysis.

Plastic bottles were prepared before going into the field by rinsing with deionized water. These bottles ranged in sizes, but for the alkalinity titrations, water samples were obtained that would add up to 250 mL and for the cation and anion analysis two 125 mL bottles were used.

Sample bottles were also stored in an ice chest after retrieving in the field and then transferred to a refrigerator. These cool temperatures minimize microbial degradation of any organic material that may be present, which can produce CO$_2$ gas and thus impact bicarbonate concentrations.

4.1.4 YSI Handheld pH and SpC meter

A YSI Pro1030 was used to take field measurements of SpC, temperature and pH whenever collecting data from the data sonde and taking grab samples.

The calibration of the YSI sonde was done in the lab. It involved a three-point calibration for the pH and a one-point calibration for the SpC. The temperature did not need to be calibrated, much like the MS5 data sonde. The measurements of SpC and temperature automatically accounted for temperature.

After prerinsing the probe with the water at the testing locations three times, the conductivity and pH sensors were completely submerged in sample bottles collected from Biz Falls and Upper Cascade River. Results were recorded and utilized in calculations.
4.2 Laboratory Methods

4.2.1 Alkalinity Titrations

A two-point Gran titration was used to measure alkalinity of the grab samples. Using a sulfuric acid solution of normality 0.02, 50-100 mL of sample was titrated slowly using a stir bar to mix. The first target pH was 4.45-4.55. The second was 4.15-4.25. Before beginning, the initial pH and temperature of the sample were recorded. First, a 100-microliter pipet was used to dispense acid until about a pH of 5. As a titration nears the inflection point, it becomes much more sensitive to the addition of acid and thus much easier to overshoot the target pH range by the addition of too much acid, so a 10-microliter pipet was used for the rest of the titration. The amount of titrant added to get to each pH range was recorded as well as the exact pH. More information on the chemistry and calculations used to determine the alkalinity are in section 5.1.

4.2.2 Cation and Anion Analysis

Water grab samples were analyzed for cations lithium, sodium, ammonium, potassium, magnesium and calcium and the anions fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate using ion chromatography at the WKU Applied Materials Institute Laboratory. A Dionex ICS-1000 Ion Chromatography System was used with the computer program Chromeleon. Water samples were placed into an auto sampler. Quality control samples were included every five samples. The ion concentrations were then calculated with the computer program. Samples had been filtered and cation solutions had to be acidified shortly after collection from the field. The hold time for anion analysis was two weeks, while cations, once acidified, could be held for six months before analysis.
Figure 8. The lowest section of Biz Falls, and the deployed Hydrolab water quality meter that takes water measurements every 20 minutes (photo by Chris Groves).
5 THEORY/CALCULATIONS

5.1 Alkalinity

Alkalinity is defined as the acid-neutralizing capacity of water, and in the settings of carbonate rock systems, bicarbonate is assumed to be the dominant species contributing to alkalinity, and other contributing ions are assumed to be negligible. For carbonate waters, it is defined as follows:

\[
\text{Alk} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{1}
\]

where brackets denote species activities.

To determine the bicarbonate concentrations, we used the two pH ranges and titrant added from the alkalinity titrations, using formulas from the Gran titration method below:

\[
\psi_1 = (V_s + V_1)(10^{-pH_1}) \tag{2}
\]

\[
\psi_2 = (V_s + V_2)(10^{-pH_2}) \tag{3}
\]

\[
\frac{d\psi}{dV} = \frac{\psi_2 - \psi_1}{V_2 - V_1} \tag{4}
\]

\[
\Delta V = \frac{\psi_2}{d\psi/dV} \tag{5}
\]

\[
V_e = V_2 - \Delta V \tag{6}
\]

\[
\text{moles of } H^+ = (V_e \text{ mL}) \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \left( \frac{0.005 \text{ mol}}{L} \right) \tag{7}
\]

\[
\text{moles of } H^+ = \text{moles of } HCO_3^- \tag{8}
\]
\[
mg \ HCO_3^- = (\text{moles of } HCO_3^-) \left( \frac{61,000 \ mg}{1 \ mol} \right)
\]

\[
\frac{mg}{L} \ HCO_3^- = \frac{mg \ HCO_3^-}{V_s (L)}
\]

where \( V_s \) is the starting sample volume; \( V_1 \) and \( pH_1 \) are the volume and \( pH \) measured at the first point of inflection in the \( pH \) range 4.45-4.55; \( V_2 \) and \( pH_2 \) are for the second point in the range 4.15-4.25. The result of the equations gives the bicarbonate content in milligrams/liter.

### 5.2 Partial Pressure of Carbon Dioxide (PCO₂)

The partial pressure of carbon dioxide (PCO₂) is a useful metric for understanding carbonate water chemistry. It is defined as “the \( CO_2 \) concentration of a hypothetical gas atmosphere in which the water is in equilibrium, typically expressed in units of atmosphere (atm), or the proportion of that gas to the total gas present in a sample” (Weissinger et al., 2020). PCO₂ is calculated as follows:

\[
PCO_2 = \frac{\alpha_{H^+} \alpha_{HCO_3^-}}{K_H K_1}
\]

Where \( K_H \) and \( K_1 \) are equilibrium constants associated with carbonate chemical reactions and \( \alpha_{H^+} \) is the activity of hydrogen ion in solution. It is therefore defined as

\[
\alpha_{H^+} = [H^+] = 10^{-pH}
\]

We can define \( \alpha_{HCO_3^-} \) as the activity of bicarbonate in solution. The activity of an ion is the effective ion concentration. It is used instead of concentration of the ions because ion strength is affected by ion interactions in solution. It is defined as:
\[ \alpha_i = \gamma_i c_i \] (13)

Where \( \gamma \) is the activity coefficient and \( c \) is the molar concentration of the ion \( i \). The activity coefficient, \( \gamma \), is calculated using a modified Debye-Hückel equation:

\[ \log(\gamma_i) = \frac{A Z_i^2 \sqrt{I}}{1 + \bar{a}_i B \sqrt{I}} \] (14)

where \( I \) is the ionic strength, \( A \) and \( B \) are constants determined by the temperature and solvent, which is water in our case. \( Z_i \) is the formal charge on the ion, \( i \), and \( \bar{a}_i \) is the effective hydrated diameter of the ion and is specific to each ion. It effectively measures the ionic diameter in solution. Ionic strength is the sum of all charges exhibited by ions in solution, given by the following equation:

\[ I = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2 \] (15)

Where \( c \) is the molar concentration of the ion, \( z \) is the charge of the ion and \( n \) is the number of ions.

### 5.2.1 Equilibrium Constants and Chemical Reactions for Calcium Carbonate

\( K_C \) is the solubility product constant for the calcite dissociation chemical reaction. At 10°C, \( pK_C \) is 8.41. This implies it is rather difficult to dissolve calcium carbonate in solution. However, as carbonate ions react with hydrogen ions in water, the carbonate...
content will decrease, so more calcium carbonate must be dissolved to move back towards equilibrium.

\[ CaCO_3(s) \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \]  

(16)

KCO₂ and is the equilibrium constant for the exchange of CO₂ between a gas and aqueous phase and the formation of carbonic acid. It is defined by the following reactions:

\[ CO_2(g) \rightleftharpoons CO_2(aq) \]  

(17)

\[ CO_3^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^-_{(aq)} + OH^-_{(aq)} \]  

(18)

\[ CO_2(aq) + H_2O_{(l)} \rightleftharpoons H_2CO_3(aq) \]  

(19)

pK_{1H} is the greatest of the carbonate equilibrium constants but is still quite small at 1.27 for 10°C. This implies that carbonic acid is not very stable, so not much of it is made when at equilibrium. However, as the amount of carbon dioxide in the surrounding atmosphere increases, more carbon dioxide will be dissolved, and more carbonic acid will be formed as a result.

K₁ is the first acid dissociation constant for carbonic acid. The acid dissociation reactions are as follows:

\[ H_2CO_3(aq) \rightleftharpoons HCO_3^-_{(aq)} + H^+_{(aq)} \]  

(20)

\[ HCO_3^-_{(aq)} \rightleftharpoons CO_3^{2-}_{(aq)} + H^+_{(aq)} \]  

(21)
The dissociation of carbonic acid is also associated with low K values. At 10°C, pK$_1$ is 6.46 and pK$_2$ is 10.49. Because the pK$_2$ is lower than pK$_1$, the reverse reaction for K$_2$ will be most likely to occur. That means any carbonate in solution will be more likely to pick up spare hydrogen ions to form bicarbonate than bicarbonate will be to produce carbonic acid. Because the dissociation of carbonic acid produces hydrogen ions, the solution becomes mildly acidic as more is dissociated.

Carbonic acid is a weak acid, as is evidenced by its very small acid dissociation constants. Because of this, its conjugate base, carbonate, is a strong base. As more calcium carbonate is dissolved, the pH will rise as carbonate ions react with water to form bicarbonate ions, resulting in a basic solution. The K value for this reaction would be very great as it is the opposite of the K$_2$ reaction above. At typical cave stream pH and temperature, bicarbonate is the dominant inorganic carbon species in solution, which is important for our alkalinity determination. The equation below is essentially the reverse reaction of K$_2$. It is the strongest of the carbonate equations shown.

$$CO_3^{2-} (aq) + H_2O (l) \rightleftharpoons HCO_3^- (aq) + OH^- (aq)$$  \hspace{1cm} (22)

Basically, the more carbonate is utilized to create bicarbonate, the more that calcium carbonate can dissolve.

**5.3 Saturation Index**

The saturation index tells us if the waters are supersaturated, at equilibrium, or undersaturated with respect to the mineral calcite (calcium carbonate) that makes up the limestone bedrock. Supersaturated waters are predicted to precipitate calcite, leading to
the creation of speleothems. Undersaturated waters will dissolve the rock. At equilibrium, there is neither net additional dissolution nor precipitation of calcite. A saturation index value of zero indicates equilibrium. A negative value indicates undersaturated and a positive value indicates supersaturation. The rate of deposition or dissolution is related to the magnitude of the saturation index but in a complex way (Plummer et al., 1978). This is calculated from:

\[ SI_{\text{CAL}} = \log \left( \frac{(\alpha_{Ca^{2+}})(\alpha_{HCO_3^-})K_2}{(\alpha_{H^+})K_w} \right) \]  

(23)

5.4 Regression Analyses

Specific Conductance (SpC) is a measurement of how well water can conduct an electrical current and is affected by the number of ions; therefore, it gives an estimate of the number of ions in solution. Because determining alkalinity, cations and anions is a much more laborious and time sensitive process than continuous measurements of pH and SpC, being able to determine ion concentrations from SpC measurements enables long-term, continuous study of Great Onyx to be much simpler.

To calculate SI\textsubscript{CAL} and PCO\textsubscript{2} for our data sonde data, we created linear regressions to use the measured SpC from our sonde data to estimate ion concentrations. The cation, anion and alkalinity data from the water samples were combined with their SpC measurements to create linear regressions in excel. The equations created were applied to the data sonde data and SI and PCO\textsubscript{2} values were estimated for each measurement from the data sonde.
6 RESULTS

6.1 Regressions Relating Continuous SpC to Calcium and Bicarbonate

The linear regressions shown in figures 9 and 10 show a linear relationship between measured SpC of Biz River and the calcium ion concentration and bicarbonate ion concentration, respectively. They both show strong correlations for a linear relationship so that these ions can be predicted from the high-resolution SpC data logger measurements.

6.2 High Resolution Hydrolab Sonde Data

To evaluate seasonal and storm scale influences on the hydrochemistry and carbon dioxide dynamics at Biz Falls, high resolution data have been plotted, including SpC and temperature (Figure 12), pH (Figure 13), PCO$_2$ (Figure 14), and calcite saturation index, SI$_{\text{CAL}}$ (Figure 15). Seasonal impacts are shown by comparing the left (cool season, March 14-31) and right (warm season, June 26-July 21) graphs in Figures 12-15, as the y-axes in each is scaled the same. Within each graph impacts are shown by the system behavior in response to rainfall, (measured from the Barren County station of the Kentucky Mesonet system and represented by the bars coming down from the top, with the length of the bar indicating how much rain had fallen during that day). For example, for most of the rainfall events in Figures 11-14, rainfall coincides with a drop in SpC as the dilute rainwater comes through the system.

6.3 Summary Observations of Cascade River (Biz Falls) Conditions

Table 1 lists the range (maximum and minimum) of values for measured parameters at Biz Falls including water temperature, pH, SpC, PCO$_2$ and SI$_{\text{CAL}}$ for the
Figure 9. Regression of measured SpC and calcium ions for Biz Falls, Great Onyx Cave.

Figure 10. Linear Regression of measured SpC and bicarbonate ion concentrations for Biz Falls, Great Onyx Cave.
Figure 11. Seasonal and storm-scale behavior of temperature and SpC at Biz Falls, Great Onyx Cave during cool season (March 14-31) and warm season (June 26-July 21) conditions.
Figure 12. Seasonal and storm-scale behavior of pH and SpC at Biz Falls, Great Onyx Cave during cool season (March 14-31) and warm season (June 26-July 21) conditions.
Figure 13. Seasonal and storm-scale behavior of carbon dioxide pressure and SpC at Biz Falls, Great Onyx Cave during cool season (March 14-31) and warm season (June 26-July 21) conditions.
Figure 14. Seasonal and storm-scale behavior of the calcite saturation index and SpC at Biz Falls, Great Onyx Cave during cool season (March 14-31) and warm season (June 26-July 21) conditions.
entire period of testing at Biz Falls. Table 2 lists the summary observations based on interpretation of cool and warm season conditions (Figure 11-14) at Biz Falls.

Table 2. Minimum and maximum values of the measured parameters over the study period.

<table>
<thead>
<tr>
<th></th>
<th>Temp</th>
<th>pH</th>
<th>SpC</th>
<th>PCO₂</th>
<th>SICAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>16.37</td>
<td>7.97</td>
<td>207</td>
<td>2.1</td>
<td>-0.7</td>
</tr>
<tr>
<td>Min</td>
<td>7.94</td>
<td>6.92</td>
<td>32</td>
<td>0.4</td>
<td>-2.8</td>
</tr>
</tbody>
</table>

7. DISCUSSION

This work represents the first hydrochemical characterization of karst groundwater and an evaluation of the processes that influence its behavior for the Great Onyx Groundwater Basin in a remote and pristine area of Mammoth Cave National Park. In collaboration with other hydrologic efforts to evaluate the geographic extent of the basin and its internal plumbing (Paylor and Currens, 2001; Groves and Meiman, 2005), this work advances the opportunity for the Great Onyx Basin to serve as an outstanding demonstration site to measure baseline (relatively unimpacted) conditions of geochemistry, water quality, and other physical, chemical, and biological processes at work in a very well-developed karst groundwater flow system. The observations of a variety of directly measured and calculated parameters from Biz Falls (Figures 11-14, Tables 1 and 2) tell a clear and consistent story. Most obvious is that conditions at Biz Falls generally respond rapidly to rainfall events. This is clear for a variety of parameters. For example, the specific conductance (SpC), which in this case reflects how concentrated the water is with ions produced from dissolved limestone, typically drops rapidly with rainfall. This occurs as the relatively dilute rainfall infiltrates the ground and
Table 2. Summary observations based on interpretation of cool and warm season responses at Biz Falls.

<table>
<thead>
<tr>
<th>Cool season</th>
<th>Warm season</th>
<th>Comparisons</th>
</tr>
</thead>
<tbody>
<tr>
<td>SpC (Figures 11-14)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rapid response to rainfall, SpC drops from rainfall events</td>
<td>Typically, rapid response to rainfall, SpC drops from rainfall events. No response for small storms or during dry conditions</td>
<td>Cool season baseflow SpC about 100 μS</td>
</tr>
<tr>
<td>In between rains, increasing asymptotically towards cool season baseflow condition</td>
<td>In between rains, increasing asymptotically towards warm season baseflow condition</td>
<td>Warm season baseflow SpC about 200 μS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>All cool season storms produce SpC signal, a threshold rainfall amount is required to produce a signal in the warm season.</td>
</tr>
<tr>
<td>Water Temperature (Figure 11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rapid response to rainfall, Temp drops from rainfall events due to outside air temps being cooler than cave temperature</td>
<td>Rapid response to rainfall, Temp rises from rainfall events when it is warmer outside than cave temperature. No response for small storms or during dry conditions</td>
<td>Inverted responses depending on outside air temperature</td>
</tr>
<tr>
<td>In between rains, increasing asymptotically from below towards cave temperature of about 12.4°C</td>
<td>In between rains, decreasing asymptotically from above towards cave temperature of about 12.4°C</td>
<td>All cool season storms produce SpC signal while a threshold rainfall amount is required to produce a signal in the warm season.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<tr>
<td>pH (Figure 12)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rapid response to rainfall, typically drops from rainfall events</td>
<td>Rapid response to rainfall, typically drops from rainfall events. No response for small storms or during dry conditions</td>
<td>Noisier signal between storms in warm season than in cool season, similar pH range</td>
</tr>
<tr>
<td>Relatively high pH values, small pH range</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCO₂ (Figure 13)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rapid response to rainfall, values mostly at or below atmospheric background</td>
<td>Rapid response to rainfall, typically drops from rainfall events. No response for small storms or during dry conditions</td>
<td>Generally higher PCO₂ in warm than in cool season</td>
</tr>
<tr>
<td>Typically rises in response to storms</td>
<td></td>
<td>Noisier signal between storms in warm season than in cool season, generally higher PCO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si&lt;sub&gt;CAL&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Values stay below zero</td>
<td>Rapid response to rainfall, typically drops from rainfall events. No response for small storms or during dry conditions</td>
<td>Generally higher (less negative) in warm than in cool season, but continually undersaturated</td>
</tr>
<tr>
<td>Rapid response to rainfall, becomes more negative during rainfall events</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
flows through the system. The rapidity with which this happens suggests that this infiltration occurs at one or more discrete sinking streams on the surface (allogenic recharge), rather than a more diffuse pathway through the soil and fractures within the bedrock (autogenic recharge).

A different situation sometimes happens during the warm season. On the left-hand side of the right-hand graph of Figure 11 (days 135-150 on the x-axis) despite there being several rain events, the SpC did not change at Biz Falls unlike during other storms. During this time, water temperatures also stayed around cave temperature at 12.4° degrees. One explanation for this phenomenon is that the water from those storms was absorbed and consumed by the soil and plant roots and so did not reach Biz Falls. When leaves begin to grow during the warm season, transpiration consumes much of the water moving through the soil root zone. The soil is also often drier, so it can hold more water than during the cool season.

During the cool season, CO₂ concentrations at Biz Falls drop to mostly at or below atmospheric levels. One explanation for this could be that soil microbes are less active in lower temperatures, so less CO₂ is produced from the degradation of organic material within the soil. This suggests that the atmosphere is the principal source of pCO₂ during the cool season. As limestone dissolution in this setting consumes CO₂, the levels falling below suggest the conduit(s) connecting the surface to Biz Falls is(are) completely filled with water—if it was a stream flowing across the floor of an air-filled passage, as the CO₂ was depleted by dissolving the limestone, it would be replaced by CO₂ from the cave atmosphere and the levels would stay closer to atmospheric.
The higher PCO$_2$ in the waters of Biz Falls in the warm season reflect an additional source of CO$_2$ coming down from above, presumably from increased CO$_2$ production in the soils above the cave. This is also consistent with the inverse relationship between PCO$_2$ and pH (Figures 12 and 13), that is, as CO$_2$ goes up, more carbonic acid is formed (see Section 5.2 equation (19)) and so the pH drops. The impact of the warm season storms on days 152-153 (Figures 12 and 13) in which both pH and pCO$_2$ drop is not clear, though this may reflect dilution from a thorough “rinsing” of the flow system by two relatively large storms with a few days.

These examples provide a sense of how this kind of high-resolution monitoring can serve as a sensitive “instrument” to understand the dynamics of karst flow systems. There is much yet to do at Great Onyx, and this work represents a significant contribution to establish a potentially important site to better understand not only karst hydrogeology and hydrochemistry but the impact on the world’s karst landscapes on the global carbon cycle.

8. CONCLUSION

High-resolution analysis of water/CO$_2$/carbonate rock geochemistry of the Great Onyx Groundwater Basin in Mammoth Cave National Park informs understanding of karst landscapes and their relationship with global climate change. The purpose of this work has been to undertake hydrochemical characterization of karst groundwater in Great Onyx Cave beneath relatively pristine karst landscape above, with a focus on Cascade River, the largest cave stream in the cave’s upper level. Fluorescent dye tracing has tied
together the upstream end of the stream at Biz Falls to lower Cascade River, which reaches the surface at Great Onyx Spring.

Hydrochemical monitoring of Cascade River at Biz Falls using field, laboratory, and high-resolution electronic data-sonde measurements has provided a detailed picture of the stream’s behavior with respect to the transport and influence of carbon dioxide in the surface and groundwater system, as well as quantifying water/rock interactions. Comparison of cool and warm season hydrochemical dynamics shows waters of Cascade River are influenced only by atmospheric CO$_2$ in winter, while warming adds additional CO$_2$ from a surface source, presumably soil respiration influenced by degradation of soil organic material root respiration. The waters of Cascade River are undersaturated with respect to, and thus continuously dissolving, the limestone bedrock of the aquifer framework, though more rapidly in winter. In all seasons, storms have a rapid impact on the groundwater showing a relatively direct hydrologic connection from the surface through a significant conduit that probably stays water filled.

These results advance the understanding of hydrology and geochemistry of the Great Onyx Ground Groundwater Basin, representing an important first step towards long-term study.
9. REFERENCES CITED


Liu, Z., Dreybrodt, W., and Wang, H., 2010, A new direction in effective accounting for the atmospheric CO2 budget: Considering the combined action of carbonate dissolution, the global water cycle and photosynthetic uptake of DIC by aquatic


