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A Trace Metal Content Database Of Cave Sediments Of Midcontinent U.S.A.

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A TRACE METAL CONTENT DATABASE OF CAVE SEDIMENTS OF MIDCONTINENT U.S.A.

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Matthew D. Smith

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ABSTRACT

The midcontinent of the United States has thousands of documented caves. These caves contain cave sediments, which are the accumulation of biological, geological, and anthropological debris. At this time there is no known database for trace metals of cave sediments of the midcontinent United States. Considering that caves host a wide variety of life, it is important to create a database to examine potential effects of trace metals on cave systems. In order to develop this baseline, 14 caves were sampled from across the midcontinent. Caves were selected based on geologic and hydrologic attributes. The sediments were analyzed for the following suite of metals: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, La, Mg, Mn, Ni, P, Pb, S, Sr, V, and Zn. As documented in this study, metal variation among caves is dictated by land use history, surficial watersheds, and geology. The preliminary results indicated that mineralization and anthropogenic impacts amplified trace metal concentrations in two caves, which were omitted to further evaluate the remaining 12 caves based on geologic and hydrologic factors. When geologic factors were examined, the geochemical variation between evaporites and carbonates resulted in B, Mg, S, and Sr concentrations being clearly associated with evaporites, while the differences between limestone and dolostone are primarily related to the mineralogy. When hydrologic attributes were analyzed, urban areas were more enriched with Cd, Cu, La, Mn, and Zn because of the multitude of potential sources available in urban areas over rural areas.

KEYWORDS: karst, cave sediments, trace metals, geochemistry, midcontinent

This abstract is approved as to form and content

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CHAPTER 1. INTRODUCTION

1.0 Purpose and Objective

The purpose of this study is to establish a trace metals baseline database of cave sediments of the midcontinent by analyzing for the following suite of trace metals: Al (Aluminum), As (Arsenic), B (Boron), Ba (Barium), Ca (Calcium), Cd (Cadmium), Co (Cobalt), Cr (Chromium), Cu (Copper), Fe (Iron), La (Lanthanum), Mg (Magnesium), Mn (Manganese), Ni (Nickel), P (Phosphorous), Pb (Lead), S (Sulfur), Sr (Strontium), V (Vanadium), and Zn (Zinc). All of these trace metals are naturally occurring and therefore will have varying quantities across earth's surface. The question is, to what extent do natural and unnatural trace metal sources affect cave sediments? Considering that caves host a wide variety of life, it is important to create a database of trace metals that can be utilized to examine possible links between biota and geochemistry. However, at this time there is no known database for trace metals of midcontinent cave sediments. Thus the objective of this study is to interpret the geochemical data to achieve a greater understanding of midcontinent caves and metal variability by considering the following factors:

1. Geologic factors, like lithology and geologic age.
2. Hydrologic attributes connected to the surficial land use watershed.
3. Geochemical properties that can affect metal accumulation in sediments.
4. Other factors, like the historical uses of the cave.

1.1 Karst Landscapes

Roughly 20% of the United States is covered by karst landscapes (Veni and DuChene, 2001), which form by the dissolution of soluble rock (i.e. limestone, dolostone, and gypsum). Due to the extensive physical and chemical weathering of soluble rock, karst landscapes are defined by caves, sinkholes, sinking streams, red clay residuum, and pinnacles and cutters (Palmer, 2007). Caves are natural sediment traps (Matmon et al., 2012), as such, the sediments in these caves represent the accumulation of insoluble components of biological, geological, and anthropological origin. These sediments offer clues to the past and present of the local environment (White, 2007).

The use of cave sediment for research has far reaching implications for many aspects of karst science. Forbes and Bestland (2007) were able to determine sediment provenance from clastic cave sediments in the Naracoorte cave system of Southern Australia, while Zhou et al. (2000) used cave sediments for paleoclimate reconstruction in China. Research by Muri et al. (2013) and Munteanu et al. (2012) documented the effects of land use on the geochemistry of cave sediments in karstic regions of southern Europe. Doughty and Johnson (2012) documented a possible link between cave sediment geochemistry and the abundance of aquatic cave biota.

Missouri alone, has over 6000 documented caves, as well as 927 species documented in the Missouri cave life database (Elliot, 2007). This includes several species classified as endangered or threatened by the U.S. Fish and Wildlife Service. By studying cave sediments, greater insights may be gained into the unique world of karst environments.

1.2 Cave Sediments

White (2007) classifies cave sediments into two categories, chemical and clastic sediments. Chemical sediments are derived in place, like speleothems (White, 2007), which have a documented history for paleoclimate reconstruction due to annual growth lamina (Fairchild et al., 2006). Clastic sediments are composed of varying grain sizes that originate from the movement of material to another location via suspended load and bedload (Bosch and White, 2004). This study will only focus on clastic sediments, which account for a large portion of cave sediments.

Suspended load consists of medium to fine grained sediment that is transported by stream flow. The deposition of material is typically related to stream velocity and cross sectional area. Bedload material is derived from the scouring of flowing water over loose sediment, which can transport coarse to very fine material depending on stream velocity (Farrant and Smart, 2011).

Clastic Sediments. Clastic sediments are further subdivided based on source area into autochthonous and allochthonous sediments (White, 2007). Autochthonous sources are derived in the cave and are composed of weathered detritus, breakdown, and biological sediments. Weathered detritus consists of insoluble components that are left over after bedrock dissolution, this includes sand, silicified fossils, and chert (White, 2007). Breakdown material is derived from the structural collapse of the overlying sediment or ceiling and results in the deposition of various clast sizes (Klimchouk and Andrejchuk, 2002). Biological sediments are material generally derived from animal waste. The most common source in caves is bat guano.

Allochthonous sediments have been reported for a majority of cave sediments (Mahler and Lynch, 1999) and are derived from external sources influenced by physical and chemical erosion. These sources include entrance talus, infiltrates, and aeolian deposits (White, 2007). The entrance talus is made of biological and anthropological material that form a thin layer of sediments at the entrance of the cave (White, 2007). Infiltrates (e.g. sinkholes, sinking streams, runoff, and recharge area) are sources of sediment that percolate downward into the cave through solutionally-widened fractures and hydrological conduits (White 2007). Lastly, aeolian sediment deposits originate from sand and loess being blown into the cave (White, 2007).

Trace Elements in Sediment. Trace elements are the accumulation of metals in minute quantities, generally occurring at the part per million (ppm) to part per billion (ppb) level. Trace metal concentrations can be affected by biologic, geologic, and chemical properties. As documented by Gadd (2010), microbes play a key role in the biosphere, which affects trace metal variability, particularly in biogeochemical cycles, metal and mineral transformations, and soil and sediment formation. Geologic properties such as grain size have been shown to increase trace element concentrations as grain size decreases (Horowitz and Elrick, 1987). Cave sediments contain significant fine grained material and should contain ample amounts of trace metals. Cation exchange, a chemical property, is the ability of sediments and soils to hold positively charged ions (cations). Fine grained sediments, like clays, which hold a strong negative charge have the ability to attract and capture the positively charged cations (Drever, 1988).

Trace elements can also be weathered out from the cave host rock. Drever (1988) reported the following trace metal concentrations in limestone: Ba (10 ppm), Cr (11 ppm), Cu (4 ppm), Mn (1100 ppm), Ni (20 ppm), Sr (600 ppm), Pb (9 ppm), V (20 ppm), and Zn (20 ppm). This commonly only accounts for minor amounts of trace metals with the exception of Sr and Mn. Strontium is the 15th most abundant element on Earth with an estimated average of 360 ppm in earth's crust (Turekian and Wedepohl, 1961). Manganese is likely related to chemical absorption, as hydrous manganese has an affinity for trace metals, which results in high absorption capabilities in non-reducing environments like caves (Drever, 1988). White et al. (2009) found that stream cobbles coated in Fe-Mn oxides were enriched with Ba, Co, Cr, Cu, Mo, Ni, V, and Zn from the expected background in a karst stream.

1.3 Previous Studies

Many studies on trace elements in sediments are focused on metals contamination relative to surficial land use. Many of the metals may even overlap, depending on the land use activity. Karst landscapes are more prone to metals contamination because of dynamic hydrological processes which allow for direct and rapid transfer of metals downstream (Vesper, 2005). Metals contamination directly affects water quality, since karst aquifers can transport large quantities of sediment via suspended bedload (Wong et al., 2012).

Trace Metals and Rural Landscapes. In rural settings, the most likely sources for metals are from agricultural practices, e.g. fertilizers, pesticides, and bio-waste. Fertilizers and pesticides can contribute Co, Cu, Fe, Mn, Mo, Ni, and Zn to supplement necessary nutrients for flora or for the use in pest extermination (Wuana and Okieimen, 2011). While bio-waste can accumulate the following metals: As, Cd, Cr, Cu, Ni, Pb, Zn, and others (Basta et al., 2005). Any of these metals can be spread by the actions of wind and water and can result in contamination miles away from the original source in karst landscapes. Mining activities can also contribute metals, as Loska et al. (2004) documented farming soil contamination by As, Cd, Hg, Sb, and Pb from a local smelter and coal mine. Those metals accounted for 90% of soil contamination which, if left unchecked, the metals could contaminate the local drinking water (Loska et al., 2004). Other non-conventional sources likely exist, like the burning or dumping of waste, leaky septic tanks, and the oxidation of sheet metal structures and automobiles. Additionally, in karst landscapes, a common practice is the use of sinkholes for dumping grounds. This practice, creates direct access for metals contamination into the subsurface.

Trace Metals and Urban Landscapes. In urban settings, trace metals have a multitude of potential sources. Many metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Sn, V, and Zn) in urban settings are related to anthropogenic sources like smelters, heavy construction, and daily urban activities (Albanese and Cicchella, 2012). One general activity in urban settings is the daily commute to and from work. Automobile byproducts like gasoline, motor oil, and tires release metals like Cd, Ni, Pb, and Zn (Lagerwerff and Specht, 1970). This daily activity is recorded in sediments and soils beside the road, where concentrations of Cd, Ni, Pb, and Zn have been shown to decrease with distance from traffic (Lagerwerff and Specht, 1970).

In one study, topsoil samples around urban St. Louis, Missouri had Cu and Zn concentrations over 10,000 ppm and Pb close to 2,000 ppm (Kaminski and Landsberger, 2000). In the same study at a separate site, Kaminski and Landsberger (2000) recorded 81 ppm Cd, 340 ppm Cu, 700 ppm Pb, and 6,000 ppm Zn, half a mile downwind of a zinc and copper smelter in clay soils. Vermillion et al. (2005) used Pb isotopes to document the prolonged effects of lead smelters in the St. Louis urban area recorded in lake sediment cores, with results showing that Pb concentrations steadily increased from 5 ppm in the early 1800's to 100-300 ppm in the early 2000's.

Trace Metals and Mineralization. Missouri has a long history of mining going back to the 1700's during French colonial times (Lippmann et al., 2010). Presently there are four identifiable Mississippi Valley Type (MVT) deposits in Missouri. Figure 1 provides a map showing the following four districts: Tri-State Lead/Zinc District, Old Lead Belt, Central Mining District, and New Lead Belt. Mississippi Valley Type deposits are known to contain Pb-Zn-Cu-Fe ores and the following secondary metals: Ag, As, Ba, Cd, Co, and Ni hosted in carbonate rocks (Leach et al., 1995).

Many of the mines in the Old Lead Belt and Tri State Lead/Zinc mining districts have since shuttered. Some of these mines have left behind tailings enriched with trace metals, which can end up in the local watershed by runoff or wind. A study by Gale et al. (2004) documented elevated concentrations of Cd, Pb, and Zn in fish in watersheds associated with the Old Lead Belt. A similar study was conducted on the Pearson Creek watershed, an area associated with the Tri-State mining district in the early 1900's in Springfield, Missouri. The study found Zn stream sediment concentrations from 85-1441 ppm based on stream geomorphology along the Pearson Creek watershed (Womble, 2009).

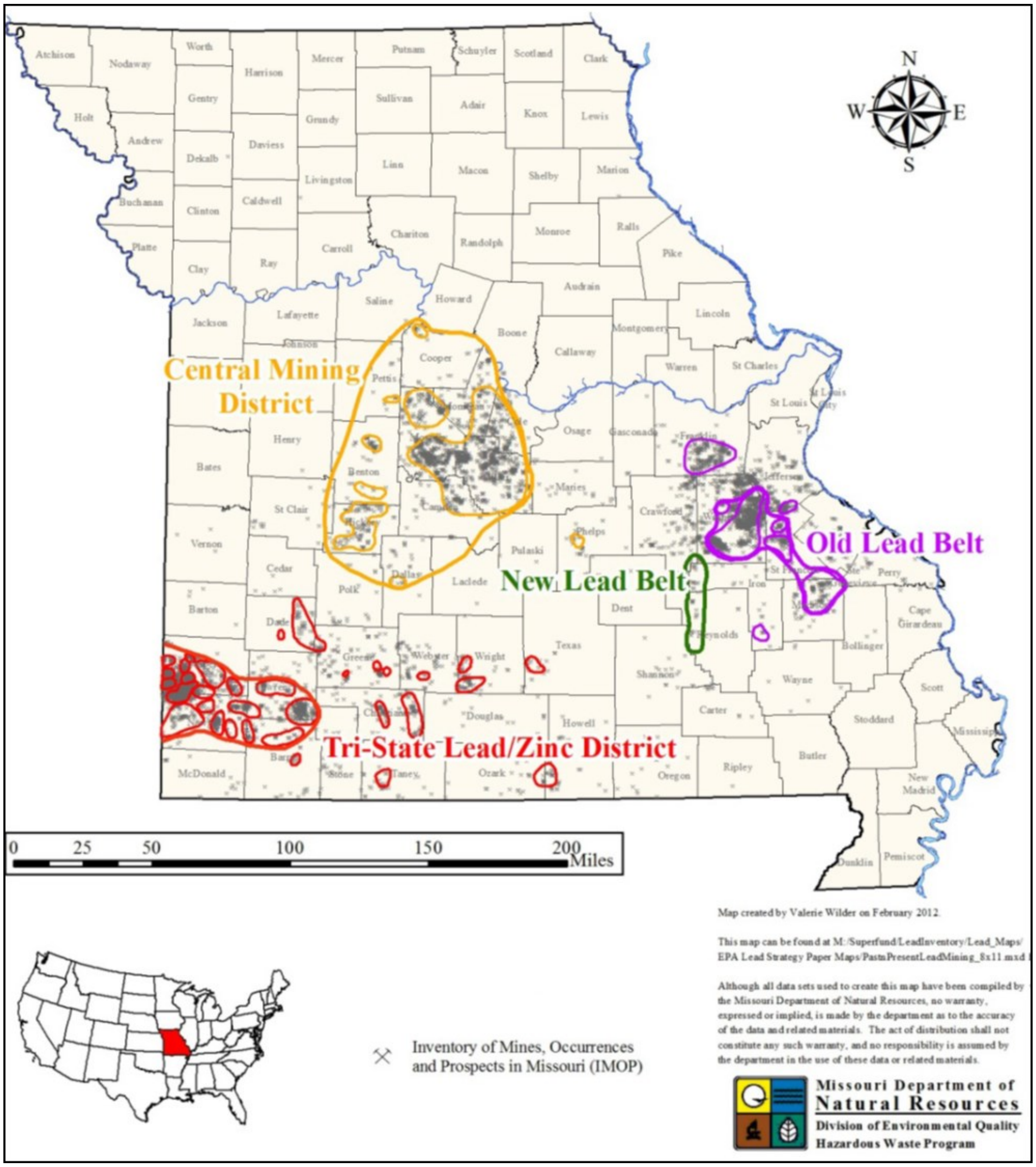

Figure 1. Map of Missouri Mississippi Valley Type Mining Districts, (MoDNR, 2015).

Cave Sediments and Trace Metals. The metals trapped in cave sediments reflect the impacts made by both natural and unnatural causes on the local environment. A study conducted by Munteanu et al. (2012), found that cave sediments in Romanian karst recorded higher concentrations of metals in cave sediments compared to surface soils. Cave sediments contained 26-55 ppm Pb, 18-63 ppm Cu, and 54-96 ppm Cr, while surface soils contained 4-16 ppm Pb, 2.89-60 ppm Cu, and 22-121 ppm Cr (Munteanu et al., 2012). Miko et al. (2001) recorded high concentrations of Cu (2,869 ppm), Zn (951 ppm), Cd (28 ppm), and light rare earth elements (REE's) from bat guano. The original purpose of Miko and others (2001) study was to determine the geochemical baseline for the cave sediment, but the natural contributions exceeded possible anthropogenic impacts.

A study by Muri et al. (2013) examined dust deposits from a Slovenian show cave (Postojnska Jama) with a double-track railway, high concentrations of Cu (217 ppm), Pb (4,940 ppm), and Zn (1,060 ppm) were documented and linked to the rail system. The metals observed in the study were higher than their natural abundance, which could harm the cave ecosystem with continued exposure (Muri et al., 2013). Doughty and Johnson (2012) analyzed land use impacts on cave sediments from three caves hosted in the Springfield Plateau around Springfield, Missouri. The results showed that the highest metal concentrations (Pb, Mn, and Zn) came from Giboney (urban) cave, while the lowest concentrations came from the Smallin (control) cave. The results potentially correlated to the presence or absence of cave biota, as Smallin cave had the most diverse aquatic cave biota and lowest metals concentration, while Giboney with the highest metals concentrations was devoid of aquatic biota.

CHAPTER 2. GEOLOGIC SETTING OF THE STUDY AREA

The midcontinent of the United States is a broad area bound by the Rocky Mountains on the west and Appalachian Mountains on the east. Between the Rockies and Appalachians almost 300 million years (542 million years ago (mya) to 251mya) of geologic history is recorded by Paleozoic era rock outcrops. This study only focused on three distinct geographic karst regions that span multiple geologic periods. Palmer (2007) defined these three regions as the Low Plateau (Kentucky), the Ozark Plateau (Missouri), and the Southern Great Plains (Oklahoma). The Ozark Plateau has been further divided into the Salem and Springfield Plateaus (Peterson et al., 1995). The Low Plateau is covered with Mississippian age (360-325 mya) host rock. The Ozark Plateau includes Cambrian age (581-485 mya), Ordovician age (485-444 mya) and Mississippian age outcrops. Caves from the Southern Great Plains are hosted in Permian age rocks (299-252 mya). Figure 2 provides a karst map of the United States (Veni, 2002) and outlines the study area within the midcontinent. However, because the caves in this study are privately held, the exact locations are generalized for privacy. Table 1 summarizes the caves sampled by name, county, state, and geologic age of host rock.

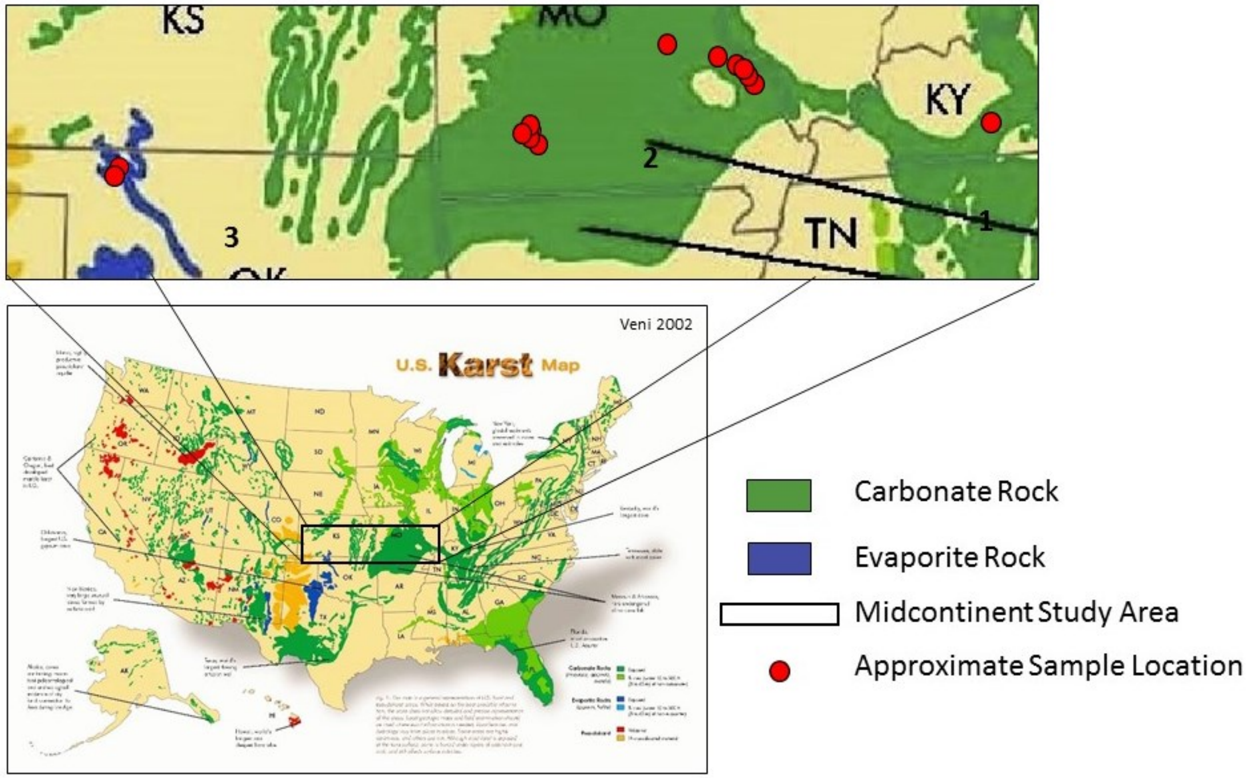

Figure 2. Karst map of United States with approximate sampling sites. Samples were collected from the (1) Low Plateau, (2) Ozark Plateau, and (3) Southern Great Plains. Modified from Veni 2002.

Table 1. Listing of Caves Sampled.

List of caves Sampled			
Cave Name	County	State	Host Rock Geologic Age
Pierson Creek	Greene	Missouri	Mississippian
Fitzpatrick	Christian	Missouri	Mississippian
Fieldin	Christian	Missouri	Mississippian
Breakdown	Christian	Missouri	Mississippian
Giboney	Greene	Missouri	Mississippian
Onondaga	Crawford	Missouri	Ordovician
Black Fathom	Ste Genevieve	Missouri	Mississippian
Crevice	Perry	Missouri	Ordovician
Lloyds	Ste Genevieve	Missouri	Ordovician
Gegg	Ste Genevieve	Missouri	Ordovician
Crankshft pit	Jefferson	Missouri	Ordovician
Alabaster caverns	Woodward	Oklahoma	Permian
Owl	Woodward	Oklahoma	Permian
Lone Star	Hart	Kentucky	Mississippian

2.0 The Low Plateau

The caves of the Low Plateau underlie a broad karst landscape covered by sinkholes and thick red soils (Grabowski, 1986). The area is often referred to as the Pennyroyal Plateau, Pennyrile Plateau, or the Mississippian Plateau because the rock units are of Mississippian age (360-325 mya). The bedrock for the caves of the Low Plateau originate from a period of intensive upwarping in the Devonian period (410-360 mya) that deposited unlithified sediments along a carbonate shelf in widespread shallow seas during the Mississippian period (Grabowski, 1986). These sediments lithified into the present day Mississippian rock outcrops shown in Figure 3. By the end of the Pennsylvanian period (325-290 mya), sedimentation had ceased (Grabowski, 1986).

The caves in the Low Plateau are hosted in the Mississippian aged Ste. Genevieve, St. Louis, and Girken limestones (White and White, 2003). The St. Louis limestone is characterized as a fine-grained, moderately cherty, argillaceous and dolomitic limestone with fossilized corals (Grabowski, 1986). The overlying Ste. Genevieve limestone is characterized as an oolitic to skeletal limestone with some sandstone occurrence (Grabowski, 1986). Overlying the Ste. Genevieve limestone is the Girken limestone, which consists of fine to medium grained, skeletal and argillaceous limestones with minor occurrences of oolitic limestone (Grabowski, 1986). Figure 4 provides a generalized stratigraphy of the Mississippian Plateau. Only one sample was collected from the Low Plateau, Lone Star cave, which is hosted in St. Louis limestone. The sample was provided by the Louisville Grotto of the National Speleological Society and contained an abundance of clay with minor amounts of chert.

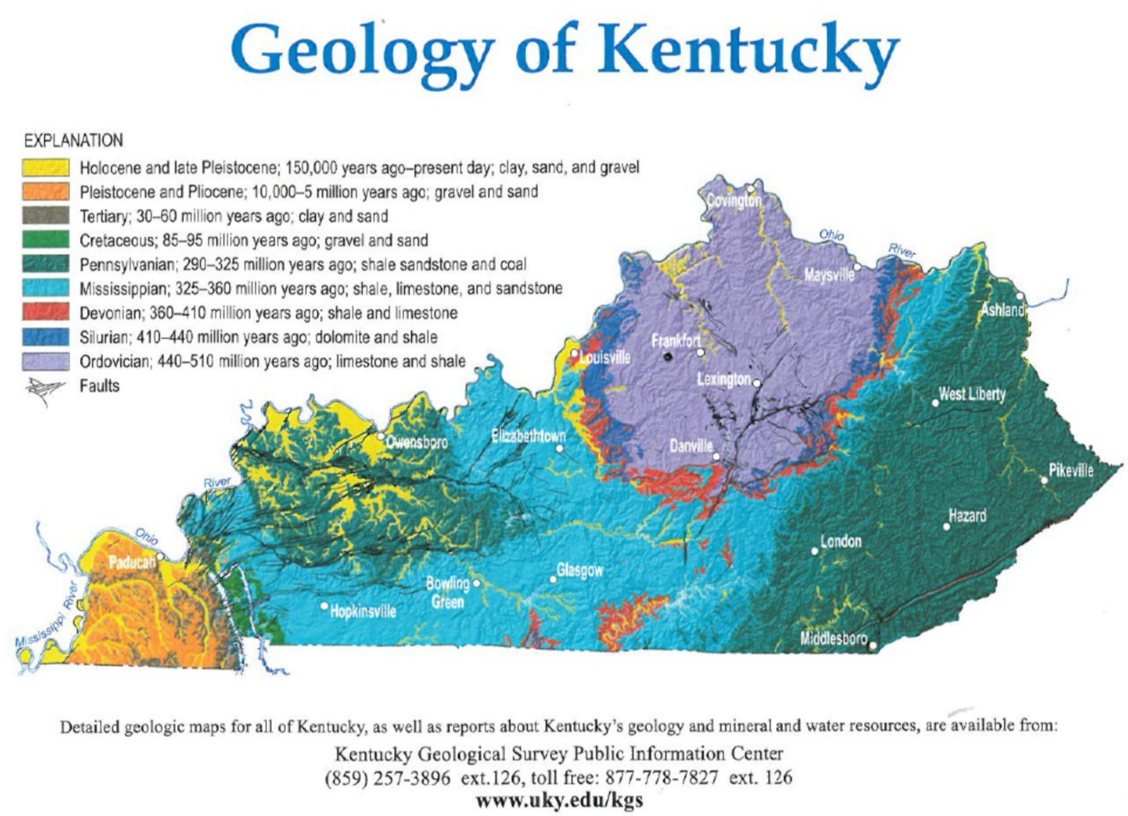

Figure 3. Generalized Geology of Kentucky. Cave bearing strata is hosted in Mississippian aged limestone in light blue. From Kentucky Geologic Survey, 2015

System	Series	Formation Name	Thickness (Ft)	Lithology
Mississippian	Valmeyeran-Chesterian	Girken	130	Fine to medium grained fossiliferous limestone
		Ste. Genevieve	200-300	Oolitic to fossiliferous limestone with occasional sandstone/shale layers
		St. Louis	500	Fine grained argillaceous dolomitic limestone with abundant chert layers and pockets of fossiliferous limestone

Figure 4. Generalized Mississippian stratigraphic column of the Low Plateau. (After Grabowski, 1986)

2.1 Ozark Plateau

The Ozark Plateau is an expansive area of the midcontinent, covering portions of Arkansas, Kansas, Missouri, and Oklahoma and includes the Springfield Plateau, Salem Plateau, and the Boston Mountains (Peterson et al., 1995). At the center of the Ozark Plateau in southeast Missouri are the Precambrian aged St. Francois Mountains (Bickford and Mose, 1975). The St. Francois Mountains are a structural dome made of felsic (silica rich) igneous rocks, which are known sources for Fe, Mn, Pb, Ag, and REE's (Kisvarsanyi, 1990). Surrounding the St. Francois Mountains are Paleozoic aged sedimentary rocks of Cambrian, Ordovician, and Mississippian age (Bretz, 1953).

Ozark Plateau Geologic History. Within Missouri, during the Cambrian, there was continual deposition of carbonate sediments in shallow marine waters, with periods of erosion and clastic sedimentation through the mid-Ordovician (Frezon and Glick, 1959). From the mid-Ordovician to the Mississippian the Ozark Plateau was uplifted multiple times, limiting sedimentation (McCracken, 1971). Carbonate sedimentation resumed in the Mississippian, resulting in the deposition of limestone in warm shallow waters (McCracken, 1971). After the Mississippian, the Ozark Plateau experienced more uplift and erosion that exposed the underlying Ordovician rocks and formed the present day topography of hills and valleys (McCracken, 1971).

Ozarks Plateau Sampling. This study sampled 14 caves, of which only three were collected from outside Missouri. Samples were collected from three different areas within Missouri, each with different lithologic settings and formations. In order to differentiate the areas, they have been labeled A, B, and C on Figure 5. Samples from area A were collected from caves within strata of the Mississippian Osagean and

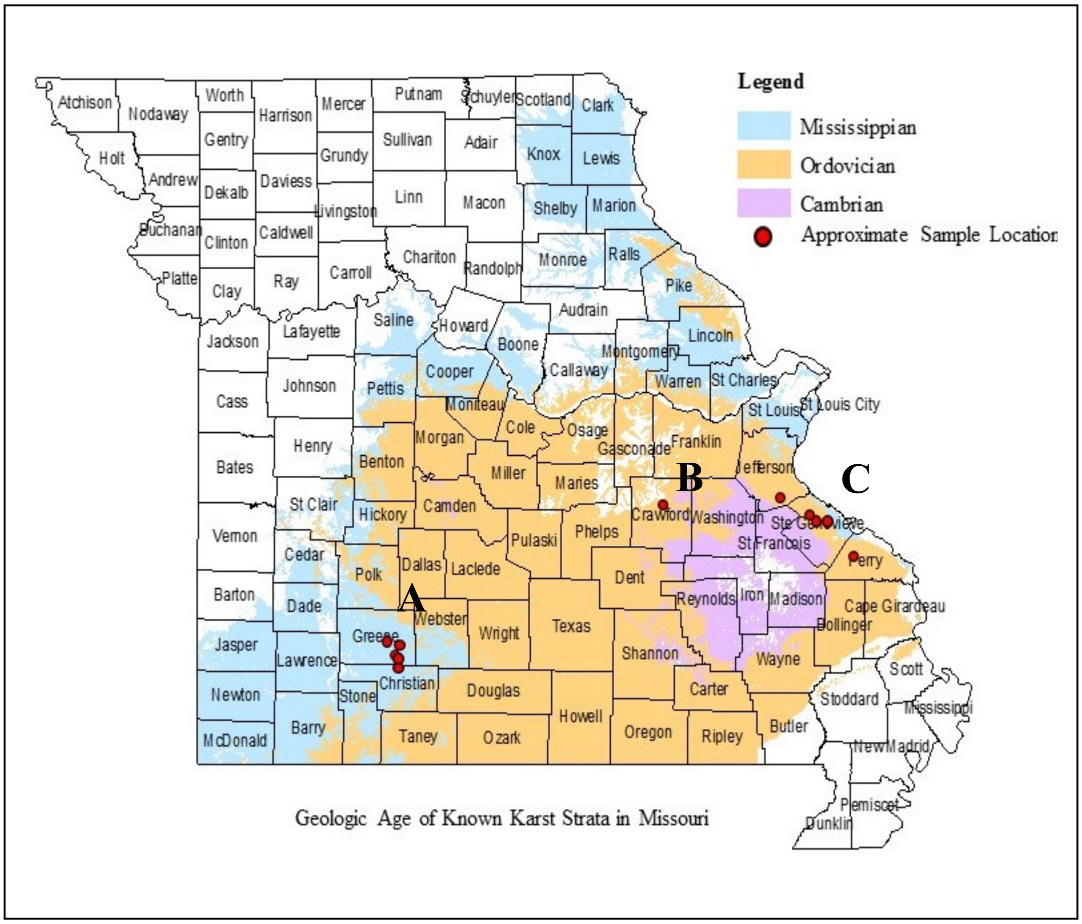

Figure 5. Geologic Age of the Known Karst Hosting Strata of Missouri. Map created off Data from MoDNR (2015)

Kinderhookian series. These caves are generally characterized by crystalline fossiliferous limestone (host rock) with abundant chert and clay residuum. Figure 6 provides the generalized stratigraphy of area A. Samples were collected from caves in the Burlington-Keokuk, Pierson, and Compton limestones.

Samples from areas B and C were collected from strata of the Ordovician Ibexian (area B) and Mohawkian (area C) series. These caves are generally characterized by abundant clay residuum hosted in fine to medium grained dolostones with minor limestone. Figure 7 provides the generalized stratigraphy of areas B and C. For area B, samples were collected from the Gasconade dolomite. These samples consisted of abundant clay with minor amounts of chert. For area C, samples were collected by the Southeast Missouri grotto from the Plattin group and Joachim dolomite, with one sample being from the Mississippian St. Louis limestone (previously described in the section titled “Low Plateau”). These samples were fat clays, with little to no chert.

System	Series	Formation	Thickness (Ft)	Lithology
Mississippian	Osagean	Burlington-Keokuk	0-200	Medium to thick beds crystalline fossiliferous limestone. Occasionally cherty, weathers grey
		Elsey-Reeds Spring	variable	Crystalline light gray limestone with abundant chert beds
		Pierson	20	Gray-brown fossiliferous limestone, some chert
	Kinderhookian	Northview Shale	< 10	Greenish siltstone-shale
		Compton	10-20	Gray-green thin bedded fossiliferous limestone

Figure 6. Mississippian Stratigraphy of area A in Ozarks Plateau. Abbreviated from *The Stratigraphic Succession in Missouri* by Thompson 1995

System	Series	Formation	Thickness (Ft)	Lithology
Ordovician	Ibexian	Roubidoux	100-200	Fine grained cherty dolomite to sandy dolomite with occasional sandstone layers
		Gasconade	250-300	Light brownish-grey cherty dolomite
Cambrian	Upper Cambrian	Eminence	150-290	Coarse light grey massive bedded dolomite with chert
		Potosi	75-300	Finely crystalline dolomite, brownish grey, weathers to light grey, abundant Barite

System	Series	Formation	Thickness (Ft)	Lithology
Mississippian	Meramecian - Chesterian	St. Genevieve	50-100	Oolitic to fossiliferous limestone with occasional sandstone/shale layers
		St. Louis	50-100	Fine grained argillaceous dolomitic limestone with abundant chert layers and pockets of fossiliferous limestone
		Salem	100-160	Sandy limestone with abundant chert near the top of the formation
Ordovician	Mohawkian	Plattin Group	Variable	Evenly bedded light to dark grey to light tan, finely crystalline limestone
		Joachim	50-175	Yellowish brown argillaceous dolomite with interbedded limestone
		Dutchtown	20-150	Medium to thinly bedded dark blue to grey dolomite with occasional hydrocarbons
		St. Peter Sandstone	60-80	Well sorted, friable quartz sandstone with rounded, spherical grains, white when fresh, grey to brown weathered

Figure 7. Cambrian, Ordovician, and Mississippian Stratigraphy of areas B (top) and C (Bottom) of the Ozarks Plateau. Abbreviated from *The Stratigraphic Succession in Missouri* by Thompson 1995

2.2 Southern Great Plains

The Southern Great Plains is an expansive area that covers parts of four states, however, this study only focuses on the Permian-aged Nippewalla Group in western Oklahoma. During the late Paleozoic, the Nippewalla Group was deposited in a series of basins (Benison and Goldstein, 2001) that were surrounded by multiple orogenic belts, including the ancestral Rockies, Ouachitas, and Ozarks (Foster et al., 2014). The sediments that filled these basins were of a felsic-mafic mixture transported by eolian dust from the weathering of orogenic belts (Foster et al., 2014; Sweet et al., 2013). Felsic sources are silica rich, while mafic sources are iron and magnesium rich. The caves in this area are hosted in the Blaine Formation that formed in shallow tidal waters (Benison and Goldstein, 1999). The Blaine Formation is about 80 feet of interbedded rock gypsum and shale, with the Dog Creek Shale above it and the Flower Point Shale below (Gibson et al., 1969). Figure 8 provides a generalized stratigraphy of the Nippewalla Group.

Samples were collected from the Blaine Formation at Alabaster Cavern State Park near Freedom, Oklahoma. The dominant karst features at Alabaster Cavern are solution valleys, sinkholes, and caves. These caves are generally characterized by massive selenite gypsum breakdown and red to grey clay residuum with coarse to silt sized insoluble detritus.

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System	Series	Group	Formation	Lithology
Permian	Leonardian	Nippewalla Group	Dog Creek	Red mudstones, siltstones, and anhydrite
			Blaine	Anhydrite and gypsum
			Flowerpoint Shale	Red mudstones, siltstones, and anhydrite
			Cedar Hills Sandstone	Red siltstones and sandstones
			Salt Plain	Red mudstones, sandstones, and anhydrite
			Harper Sandstone	Red siltstones and sandstones

Figure 8. Generalized Stratigraphy of the Nippewalla Group. Oldest on bottom and youngest on top.

CHAPTER 3. METHODOLOGY

3.0 Site Selection

The greatest challenge in this study was securing cave access for sample collection. As a result, site selection was dependent on cave owner permission (i.e. individual, city, or state). The process to gain access could range from a simple hand shake to submitting research/sample collection forms for approval. Cave access was also gained by working with National Speleogical Society (NSS) grottos. These grottos manage or own many caves across the study area.

3.1 Sample Collection

Sample collection could consist of a combination of air, water, host rock, surface soils, and cave sediments within a set interval around a cave. Given the limited time and funding of this study, only cave sediment samples were collected. However, the process of building a database has to account for multiple variables. This study considered the effects of surficial watersheds and rock type in creating the database. However, future researchers should consider a more comprehensive approach to sample collection to better understand metal variability.

During the course of this study, some samples were generously collected by members of the Southeast Missouri (SEMO) Grotto and the Louisville (Kentucky) Grotto. The members of these organizations were provided with sampling instruction and guidance via electronic mail. Samples collected by the SEMO grotto were collected using a random sampling technique, as this study had not yet adopted the stratified sampling technique used for the remainder of the study. The stratified sampling technique was adopted in April 2015 to create a more consistent methodology. This methodology adoption coincides with the start of summer field work when a majority of samples were collected. Appendix A denotes how access was granted and sampling method employed.

3.2 Field Methods

The primary field method was to collect shallow sediment samples proportional to total cave passage length. For every 200-250 feet along the primary cave passage, one sample was collected. A range of three to twelve samples was collected from any one cave, with an average of 6 samples per cave. As noted, some caves were sampled by a random method. The collection method described below was still followed, however there was no set interval between sample collection sites.

This study also utilizes bulk sampling of cave sediment. The justification for bulk sampling is based off a study by Peterson and Wicks (2003). Their study documented hydraulic conductivity values from sediments in two karst aquifers that span the range of carbonate rock. The hydraulic conductivity values indicate that sediment could be represented as one mathematical unit in flow models for karst aquifers. This allows the researcher the ability to perform bulk sampling over core sampling.

Sampling Guidelines. The sediment sampling procedures used in this study are based off techniques used by Smith et al. 2013. However, to accommodate for sampling in caves, minor alterations were made for collection techniques. Sample collection in caves is dependent on the occurrence of sediment. The following methodology was developed and employed during field work:

1) Sediment sampling occurs in the primary cave passage

   a. A feasible effort was made to follow a primary passage that generally coincides with the entrance(s) of any one cave or one of the following:

      i. The longest measured passage for any one cave

      ii. The traverse of a cave/subsurface stream

2) All samples were taken within the first six inches of the sediment horizon.

3) Using a plastic measuring cup, one cup of sediment was collected using a stainless steel scoop to collect sediment at each sampling site within the cave.

   a. The number of scoops needed varied at each location depending the on grain size, moisture content, and distribution.

4) At each cave, all samples were deposited into one large Ziploc bag throughout the collection process.

5) Following completion of sampling, all equipment and clothing was decontaminated following U.S. Fish and Wildlife Service national white nose syndrome decontamination protocol Version 06.25.2012.

While at each cave, a simple form was filled out to document pertinent information about the cave. The form included the following information: cave name, relative location, geologic age, cave passage length, number of samples collected, surficial land use, cave description, cave history, and acknowledgments. All field notes are summarized in Appendix B.

3.3 Pearson Creek Cave Laboratory Methodology

Pearson Creek Cave was the preliminary test cave to help establish a lab methodology. The sampling of this cave exposed flaws that led to the creation of the methodology described in the next section, which is more consistent, as it accounts for the drying nature of clays and abundance of chert. Pearson Creek Cave was processed using the following methods:

1) Air dry sample in an aluminum foil pan for a minimum of 48 hours to a maximum of 30 days
2) Sieve sample using a 5/16 sieve over an aluminum foil pan to remove chert.
    a. Cleanse the sieve by rinsing with tap water, washing with deionized water, and leave to dry for 24 hours.
3) Homogenize the sample using the cone and quarter technique on sterile flat surface. Start by pouring the sample into a cone shape. Flatten the sample out using a spatula and divide into four equal quarters. Mix the two opposite quarters and recombine entire sample.
4) Using a Humboldt soil crusher, pour sample into the crusher using a disposable plastic cup. The crusher turned the sample into powder smaller than 16 mm.
5) Re-homogenize sample using the cone and quarter method.
6) Divided sample into two separate labeled Ziploc bags.
7) Cleanse all non-disposable equipment by rinsing with tap water, washing with deionized water, and leaving to dry for 24 hours. Sterilize all lab surfaces using an antibacterial wipe.

3.4 Laboratory Methodology

The Pearson Creek sample exposed flaws in the laboratory preparation that led to the following methodology. After laboratory preparation, samples were sent out to commercial laboratories for geochemical analysis. Geochemical analysis services were performed under contract by the University of Arkansas Stable Isotope Lab and ALS Global. Samples were prepared at Missouri State University using the following laboratory methodology:

1) Air dry sample for a minimum of 48 hours to a maximum of 30 days in an aluminum foil pan.
    a. Disaggregate clay masses so they can pass through a 10cm x 8cm rough opening on the top of the Humboldt soil crusher.
        i. Wash hands before and after breaking clay masses to prevent cross contamination.
2) Using a Humboldt soil crusher, pour sample into the crusher using a disposable plastic cup. The crusher turned the sample into a powder less than 16 mm.
    a. Samples that contain an abundance of chert (SiO_2) caused the crushers exit screen to become blocked, which required the chert to be manually emptied before samples are sent for analysis.
    b. The remaining chert is placed into a separate labeled Ziploc bag for storage in the event it becomes relevant in interpreting the results.
3) Place a labeled Ziploc bag under the exit screen to collect newly powdered sand-silt sized sample.

4) Hand mix the powdered sample in a Ziploc bag by hand for a minimum of 1 minute to homogenize the sample.
    a. Agitation consist of tossing, turning, flipping, shaking, and rotating bag.
5) Divide sample into two separate labeled Ziploc bags. Each bag does not have to contain the same amount of sample.
    a. Most trace metal analytical equipment requires only a few grams (1-10g) of material. Utilizing the field methodology described above, generates a surplus (100+ grams) of sample that exceeds most minimal requirements.
        i. The University of Arkansas received one of the two bags for each sample.
        ii. ALS Global received 3 grams of weighed material in a labeled Ziploc bag out of the remaining samples.
        iii. MSU retained the remaining sample from step ii.
6) Once processing is complete, sterilize all lab surfaces with an antibacterial wipe. Cleanse all non-disposable equipment by rinsing with tap water, washing with deionized water and leaving to dry for a minimum of 24 hours.
    a. Sterilization is done to prevent cross contamination, as the trace elements are chemically bound to each sediment sample and vary with each sample.

CHAPTER 4. RESULTS

The following section reports the data received from ALS Global services for the 14 cave sediment samples. ALS Global analyzed the samples by inductively coupled plasma - optical emission spectroscopy (ICP-OES) for a purchased suite of 35 elements. This project reports the findings of the following 20 elements: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, La, Mg, Mn, Ni, P, Pb, S, Sr, V, and Zn. A comprehensive report from ALS Global for all 35 elements is reported in Appendix C. All caves listed in the comprehensive dataset can be further grouped based on physical attributes, like geologic and hydrologic properties to further examine metal variability.

A preliminary set of samples was sent to the University of Arkansas Stable Isotope Lab. These samples were analyzed by inductively coupled plasma - mass spectroscopy (ICP-MS). However, these results were preliminary and do not reflect the entire dataset. All geochemical data received from University of Arkansas is recorded in the Appendix D.

As stated, the 14 caves can be grouped based on geologic properties. This study sampled caves hosted in Ordovician-aged, Mississippian-aged, and Permian-aged rock. The five caves sampled in Ordovician-aged rock were: Onondaga cave, Crevice cave, Lloyds cave, Gegg cave, and Crankshaft Pit. The seven caves sampled from Mississippian- aged rock were: Pearson Creek cave, Fitzpatrick cave, Fieldin cave, Black Fathom cave, Lone Star cave, Giboney cave, and Breakdown cave. Alabaster Cavern and Owl cave represent the two Permian aged caves.

When grouped by hydrologic properties, the caves sampled are broken up into urban (5 caves), rural (6 caves), and state park (3 caves) watersheds. The following five caves sampled were considered urban: Pearson Creek cave, Fitzpatrick cave, Fieldin cave, Giboney cave, and Breakdown cave. The following six caves sampled were considered rural: Black Fathom cave, Crevice cave, Lloyds cave, Gegg cave, Crankshaft Pit, and Lone Star cave. The following state parks were sampled: Onondaga cave, Alabaster Cavern, and Owl cave, which is located on the property of Alabaster Cavern.

Table 2 summarizes the 20 elements of interest for each of 14 caves sampled. The mean, median, and standard deviation of each element are reported within Table 2. Metals with a less than symbol are considered below detection limit, for statistical analysis these metals were evaluated using the detection limit reported by ALS Global. Due to time and cave access limitations it was not feasible to sample enough caves to utilize the median as the baseline. Therefore, the mean is primarily used for all dataset baselines because it generates an overall average score for the 14 caves sampled in this study and in many instances is similar to the median. However, it is important to acknowledge that mean takes into account high or low anomalies that skew the data. Hopefully, future researchers will expand the database to improve the statistical data.

Preliminary examination of Table 2 shows Pearson Creek cave and Crankshaft Pit are clearly more enriched in metals in comparison to the other caves. Figures 9 and 10 show the enrichment of metals in comparison to the elemental medians presented in Table 2. These two caves, along with the rest, are fully examined in the next chapter to assess geologic factors, hydrologic factors, and other factors that might affect trace metal concentrations.

Table 2. Comprehensive trace metal dataset. In total 14 caves were sampled and analyzed for 20 metals of interest. Dataset includes mean, median, and standard deviation.

Comprehensive Trace Metal Dataset										
Cave Name	Element Concentrations in PPM									
	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe
Fitzpatrick	15000	4.0	10.0	180.0	63000	0.9	8.0	63.0	69.0	14000
Pearson Creek	30000	14.0	10.0	190.0	62000	5.7	9.0	78.0	36.0	29000
Fieldin	23000	6.0	10.0	160.0	172000	1.4	10.0	70.0	22.0	19000
Onondaga	16000	6.0	10.0	120.0	34000	0.7	9.0	81.0	60.0	18000
Black Fathom	11000	4.0	<10	110.0	7000	<0.5	10.0	47.0	16.0	16000
Crevice	9000	2.0	<10	150.0	3000	<0.5	5.0	58.0	12.0	11000
Lloyds	9000	5.0	10.0	310.0	44000	0.8	6.0	47.0	29.0	12000
Gegg	8000	3.0	<10	100.0	2000	<0.5	6.0	58.0	12.0	11000
Crankshaft Pit	34000	19.0	10.0	200.0	19000	0.5	20.0	39.0	40.0	48000
Alabaster	17000	3.0	30.0	120.0	37000	<0.5	6.0	62.0	15.0	16000
Owl	13000	2.0	40.0	50.0	120000	<0.5	4.0	26.0	7.0	13000
Lone Star	17000	5.0	10.0	190.0	15000	0.5	8.0	52.0	14.0	17000
Giboney	8000	4.0	<10	180.0	178000	6.0	13.0	70.0	35.0	21000
Breakdown	15000	4.0	10.0	120.0	34000	0.7	7.0	42.0	19.0	14000
Mean (N = 14)	16071.4	5.8	15.0	155.7	56429	1.9	8.6	56.6	27.6	18500
Median (N = 14)	15000.0	4.0	10.0	155.0	35500	0.8	8.0	58.0	20.5	16000
Stdev (N = 14)	7456.6	4.5	9.9	57.5	55123	2.0	3.8	14.5	17.5	9068
	La	Mg	Mn	Ni	P	Pb	S	Sr	V	Zn
Fitzpatrick	30.0	1000	1155.0	18.0	1690	31.0	800	34.0	28.0	95.0
Pearson Creek	70.0	3000	1250.0	51.0	6000	348.0	300	48.0	48.0	994.0
Fieldin	40.0	2000	953.0	35.0	520	26.0	300	31.0	38.0	164.0
Onondaga	20.0	14000	374.0	30.0	2780	30.0	200	60.0	35.0	114.0
Black Fathom	20.0	1000	782.0	17.0	420	18.0	100	14.0	30.0	57.0
Crevice	20.0	2000	665.0	14.0	320	8.0	200	119.0	23.0	34.0
Lloyds	20.0	2000	1270.0	31.0	6720	9.0	1000	63.0	22.0	129.0
Gegg	20.0	1000	565.0	12.0	280	13.0	200	10.0	22.0	30.0
Crankshaft Pit	30.0	5000	1930.0	90.0	1210	51.0	200	41.0	59.0	571.0
Alabaster	10.0	14000	302.0	18.0	610	9.0	23000	256.0	26.0	61.0
Owl	10.0	14000	187.0	13.0	560	3.0	10000	695.0	18.0	30.0
Lone Star	20.0	2000	1060.0	16.0	640	17.0	600	55.0	29.0	63.0
Giboney	40.0	1000	4760.0	62.0	600	45.0	600	50.0	23.0	951.0
Breakdown	30.0	1000	790.0	17.0	2760	17.0	200	20.0	26.0	87.0
Mean (N = 14)	27.1	4500.0	1145.9	30.3	1794	44.6	2693	106.9	30.5	241.4
Median (N = 14)	20.0	2000.0	871.5	18.0	625	17.5	300	49.0	27.0	91.0
Stdev (N = 14)	14.5	4935.3	1060.6	21.5	1986	82.6	5975	180.3	11.3	338.5

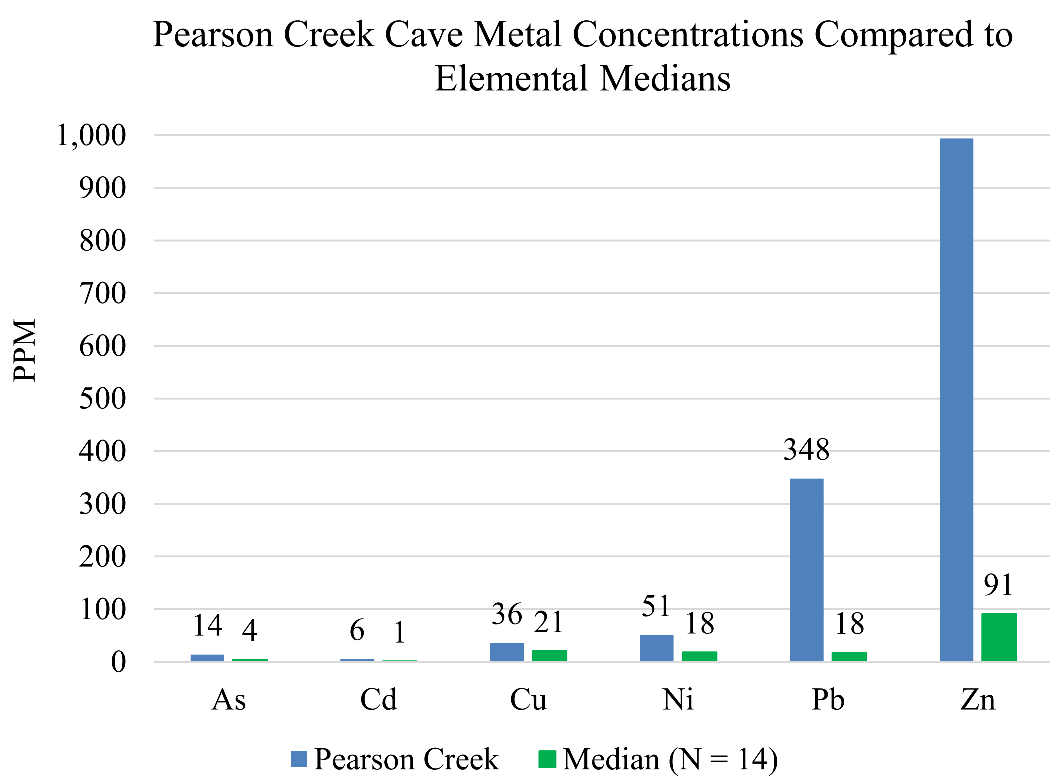

Figure 9. Pearson Creek cave trace metal concentrations. Cave is compared to study elemental median concentrations.

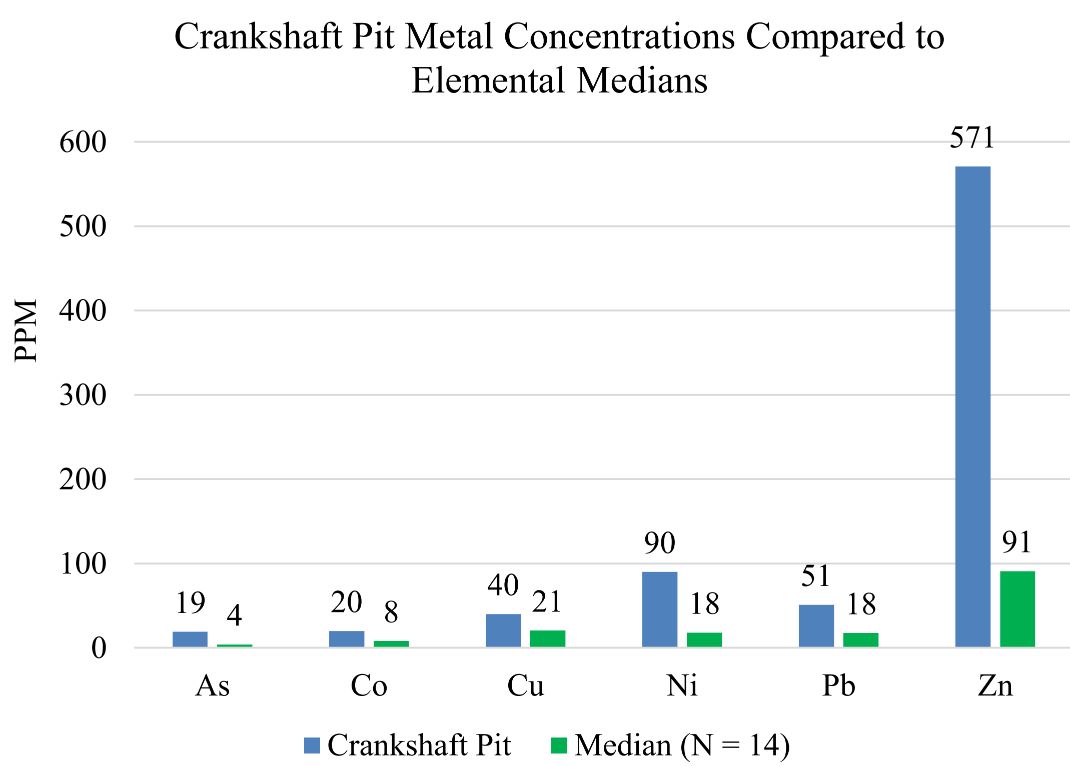

Figure 10. Crankshaft Pit metal trace metal concentrations. Cave is compared to study elemental median concentrations.

CHAPTER 5. DISCUSSION

The initial review of data indicates that two caves can be classified as anomalies. These caves continually recorded high metal concentrations in the top quartile for any single trace metal of the 20 metals reported in the comprehensive dataset. The two caves are Pearson Creek cave and Crankshaft Pit, which are examined in the first section of this chapter using the data recorded in Table 2. The second section of this chapter analyzes trace metal variation across the remaining caves after removing Pearson Creek cave and Crankshaft Pit to create a new baseline. Interpretation of all trace metal concentrations in each cave is based off field notes, history, and geochemical properties that could affect metal accumulation. The third section examines the effects of geologic attributes, while the final section examines the effects of hydrologic attributes on trace metal variability.

5.0 Pearson Creek Cave and Crankshaft Pit

Pearson Creek Cave is located in southeast Greene County within the city limits of Springfield, Missouri in an urban watershed. This area, as documented by Womble (2009), is associated with the Tri-State lead/zinc mining district. The cave is hosted in Mississippian aged limestone that has been mineralized by Mississippi Valley Type (MVT) associated metals. The primary metals for MVT deposits are Pb, Zn, Cu, and Fe with Ag, As, Ba, Cd, Co, and Ni occurring as secondary metals (Leach et al., 1995). The results indicate that Tri-State lead/zinc mineralization has affected the rocks in Pearson Creek Cave and therefore the sediments in the cave. Lead was recorded at 348 ppm, four standard deviations above the project median of 17.5 ppm. Samples from Paleozoic carbonate rock considered as non-mineralized generally have a mean of about 25 ppm lead, whereas samples from areas of active mining and milling have an average of 393 ppm lead (Leach et al., 1995). The data from Pearson Creek cave almost mirrors the findings of Leach et al. (1995). Womble (2009) documented zinc concentrations from 85-1441 ppm in the Pearson Creek watershed that were related to mine tailings. This study recorded zinc at 994 ppm, within the range reported by Womble (2009). Lead and zinc are commonly found in the Tri-State mining district and fit documented levels indicative of mineable deposits. Therefore the sediments in Pearson Creek cave are considered atypical and will be removed from further discussion or comparison datasets in this project.

Crankshaft Pit is hosted in Ordovician aged dolostone in a rural watershed of Jefferson County, Missouri. This cave, as the name might suggest, has something to do with automobiles. At the bottom of this pit entrance are several Model T era car parts. Jaradat et al. (2005), found that an automobile scrapyard contained higher concentrations of metals (Al, Cd, Cu, Fe, Mn, Pb, and Zn) compared to the surrounding areas. Crankshaft Pit in essence is a scrapyard, where auto parts have had roughly a century to oxidize in a damp environment. The oxidation of car parts has released many metals into the environment. Theses metals include Al, As, Co, Fe, Ni, Pb, V, and Zn, which are common for automobiles, past or present. Because of the presence of auto parts and the occurrence of these metals in the findings of Jaradat et al. (2005), Crankshaft Pit is considered atypical and will be removed from further discussion or comparison datasets in this project.

5.1 Revised Cave Dataset

In order to create a natural baseline for cave sediments of the midcontinent, Pearson Creek cave and Crankshaft Pit have been removed from the dataset due to reasons described in the previous section. Removing these anomalies results in Table 3, a revised baseline for cave sediments. A graphical representation of the revised comprehensive dataset can be found in Appendix E. However, many of the remaining 12 caves have individual anomalies that can be discussed relative to geologic and hydrologic factors. These anomalies are highlighted in red (high anomaly) and green (low anomaly) on Table 3. Only Black Fathom cave, Crevice cave, Lone Star cave, and Breakdown cave had all of their metal concentrations fall within one standard deviation above or below the median. Therefore this section explores the metal variation among the remaining caves.

Gegg Cave. Gegg cave is a narrow rubble filled cave hosted in Ordovician dolostone in a very rural watershed that was depleted in Al, P, Sr, and Zn. Gegg cave contains coarser sediment, which as documented by Horowitz and Elrick (1987) results in lower metals accumulation. Gegg cave also floods often and Van Gundy and White (2009) documented complete sediment flushing of cave sediments by flood waters. Therefore, it is possible that any given storm event could flush Gegg cave with runoff from the surrounding rural area. Due to the isolated location of the cave, the metals common in rural runoff (Co, Cu, Fe, Mn, Mo, Ni, P, and Zn - from Wuana and Okieimen, 2011) are less prevalent. Combined, the flooding and rubble make metal accumulation difficult, which could also explain why Gegg cave is depleted in P, Sr, Zn and has generally low metal concentrations overall.

Table 3. Revised comprehensive trace metal concentration dataset. Only includes remaining 12 caves.

Revised Cave Dataset

Cave Name	Trace Metal Concentrations in PPM[1]									
	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe
Fitzpatrick	15000	4.0	10.0	180.0	63000	0.9	8.0	63.0	69.0	14000
Fieldin	23000	6.0	10.0	160.0	172000	1.4	10.0	70.0	22.0	19000
Onondaga	16000	6.0	10.0	120.0	34000	0.7	9.0	81.0	60.0	18000
Black Fathom	11000	4.0	<10	110.0	7000	<0.5	10.0	47.0	16.0	16000
Crevice	9000	2.0	<10	150.0	3000	<0.5	5.0	58.0	12.0	11000
Lloyds	9000	5.0	10.0	310.0	44000	0.8	6.0	47.0	29.0	12000
Gegg	8000	3.0	<10	100.0	2000	<0.5	6.0	58.0	12.0	11000
Alabaster	17000	3.0	30.0	120.0	37000	<0.5	6.0	62.0	15.0	16000
Owl	13000	2.0	40.0	50.0	120000	<0.5	4.0	26.0	7.0	13000
Lone Star	17000	5.0	10.0	190.0	15000	0.5	8.0	52.0	14.0	17000
Giboney	8000	4.0	<10	180.0	178000	6.0	13.0	70.0	35.0	21000
Breakdown	15000	4.0	10.0	120.0	34000	0.7	7.0	42.0	19.0	14000
Mean (N = 12)	13417	4.0	16.3	149.2	59083	1.6	7.7	56.3	25.8	15167
Median (N = 12)	14000	4.0	10.0	135.0	35500	0.8	7.5	58.0	17.5	15000
Stdev (N = 12)	4236	1.2	10.7	59.5	58288	1.7	2.3	13.5	18.3	2957

Cave Name	La	Mg	Mn	Ni	P	Pb	S	Sr	V	Zn
Fitzpatrick	30.0	1000	1155	18.0	1690	31.0	800	34.0	28.0	95.0
Fieldin	40.0	2000	953	35.0	520	26.0	300	31.0	38.0	164.0
Onondaga	20.0	14000	374	30.0	2780	30.0	200	60.0	35.0	114.0
Black Fathom	20.0	1000	782	17.0	420	18.0	100	14.0	30.0	57.0
Crevice	20.0	2000	665	14.0	320	8.0	200	119.0	23.0	34.0
Lloyds	20.0	2000	1270	31.0	6720	9.0	1000	63.0	22.0	129.0
Gegg	20.0	1000	565	12.0	280	13.0	200	10.0	22.0	30.0
Alabaster	10.0	14000	302	18.0	610	9.0	23000	256.0	26.0	61.0
Owl	10.0	14000	187	13.0	560	3.0	10000	695.0	18.0	30.0
Lone Star	20.0	2000	1060	16.0	640	17.0	600	55.0	29.0	63.0
Giboney	40.0	1000	4760	62.0	600	45.0	600	50.0	23.0	951.0
Breakdown	30.0	1000	790	17.0	2760	17.0	200	20.0	26.0	87.0
Mean (N = 12)	23.3	4583	1072	23.6	1492	18.8	3100	106.9	30.5	241.4
Median (N = 12)	20.0	2000	786	17.5	605	17.0	450	49.0	27.0	91.0
Stdev (N = 12)	9.1	5285	1116	13.2	1743	11.1	6342	193.9	5.7	255.3

1: Red indicates high anomaly, green indicates low anomaly

Lloyds Cave. Lloyds Cave is hosted in Ordovician aged dolostone in a rural watershed in Ste. Genevieve County, Missouri. This was the only cave to record high levels of P and Ba, as seen in Table 3. Phosphorous was recorded at 6720 ppm, which is 10 times higher than the median of 605 ppm. As noted by Miko et al. (2001), bat guano can increase metal concentrations for P, Cd, Cu and Zn. Coincidentally, of the remaining 12 caves, Lloyds cave recorded the fourth and third highest concentration of Cu and Zn respectively. Figure 11 ranks the caves in terms of Cu and Zn concentrations to show the elevated levels in Lloyds cave. Copper was at 29 ppm, above the median of 17.5 ppm. Zinc was 129 ppm, above the median of 91 ppm. The cave also receives some agricultural runoff, which is known to contain P, Cu, and Zn as documented by Wuana and Okieimen (2011). Either of these sources, bat guano, runoff, or both could explain why P levels are so high in Lloyds cave compared to the other caves.

Barium was recorded at 310 ppm, about three standard deviations above the median of 135 ppm. The Ba might be related to the cave's proximity to the Washington County (Missouri) Barite District (Leach et al., 1995), one county to the west. Figure 12 shows the district in proximity to Ste. Genevieve County, marked with a star, where Lloyds cave is located. There are many abandoned mines, tailings, and smelters, which can transport metals miles away by wind or water, as shown by Kaminski and Landsberger (2000) and Gale et al. (2004). Barium could also be scavenged by the cation exchange capacity of clays. The samples from Lloyds cave were fat clays. Clays have a high cation exchange capacity, which has been proven to increase metals concentrations by Carroll (1959).

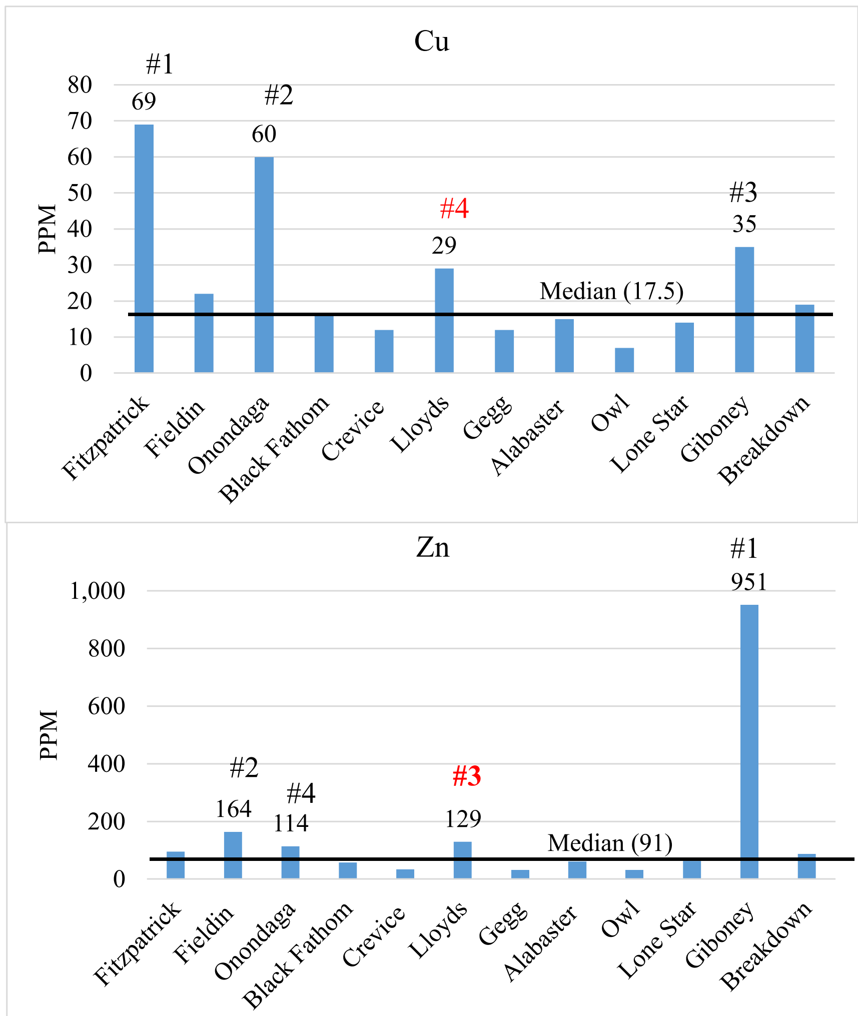

Figure 11. Ranking of Llyods cave Cu and Zn metal concentrations. Lloyds cave is 4th in Cu and 3rd in Zn, in terms of highest concentrations of the remaining 12 caves.

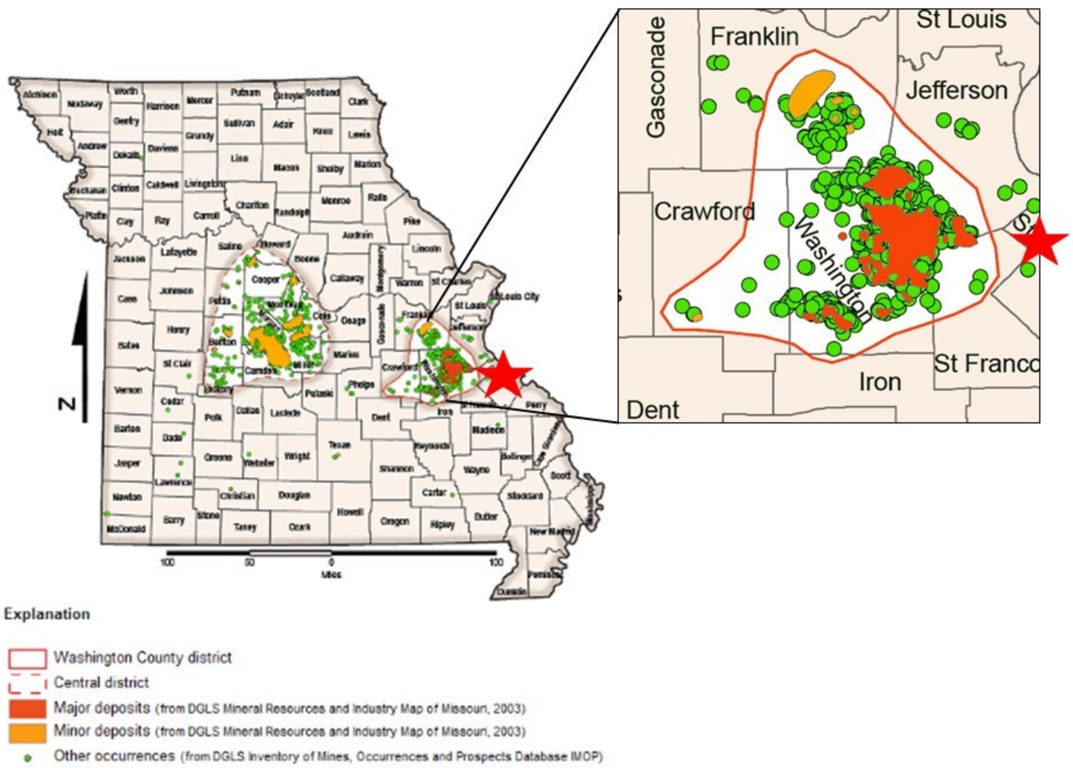

Figure 12. Map of Missouri Barite District in Proximity to Ste. Genevieve County (marked with red star) where Llyods cave is located (map from MoDNR, 2015).

Fitzpatrick Cave. Fitzpatrick cave is located in south Springfield, Missouri. The cave is along the banks of the James River and prone to frequent flooding. Fitzpatrick cave recorded the highest Cu concentration of the study at 69 ppm compared to the median of 17.5 ppm. The James River receives urban runoff from multiple tributaries within Greene county Missouri that originate from commercial, residential, and industrial neighborhoods (Fredrick, 2001). This also includes runoff from a power plant, which are known sources for trace metals, including Cu (Mandal and Sengupta, 2006). Considering that the James River floods often, the Cu could be backwashed into the cave with any flood event.

However, it is interesting that Breakdown cave had a Cu concentration of 19 ppm. Breakdown cave is around 100 feet upstream of Fitzpatrick cave and about 40 feet uphill from the James River. Breakdown cave is also less prone to flooding compared to Fitzpatrick cave because of the elevation difference. Fitzpatrick cave is more likely to flood on regular basis which could accumulate more Cu in comparison to Breakdown.

It is also possible that paleo-hydrology contributes to different metal results. Breakdown cave at one point was fully connected to Fitzpatrick cave. In the past water would flow from breakdown to Fitzpatrick to the James River. That process is now reversed. Due to the current hydrology of Fitzpatrick, it likely receives more Cu from flooding of the James River because Fitzpatrick floods before Breakdown. But it is also possible that Breakdown cave could have similar Cu concentrations if substantial flooding occurs, like a 100 year flood event.

Giboney Cave. Giboney cave was the most enriched of the remaining 12 caves, with 10 elements more than one standard deviation above the respective median. Giboney cave is hosted in Mississippian Burlington-Keokuk limestone and located in Doling Park in Springfield, Missouri in an urban watershed. This cave, as reported by Doughty and Johnson (2012), was used as an open sewer by the city of Springfield and as a show cave. The cave is also less than a mile from major roadways to the north (I-44) and south (Route 66). Lagerwerff and Specht (1970) documented a direct correlation between distance from roads and metal concentrations for Cd, Ni, Pb, and Zn. Giboney cave recorded very high concentrations of Cd, Ni, Pb, and Zn in comparison to the other caves, as seen in Figure 13.

Because Giboney cave is in an urban watershed, the urban runoff could potentially contribute to the metals accumulation in the cave. During storm events, surficial runoff bolsters trace metal concentrations (Liebens, 2001). Giboney cave is prone to flooding and could explain why Co was enriched in Giboney cave compared to the other caves. Albanese and Cicchella (2012) noted that Co is by-product of glass and ceramics, which were found in the sediment samples from Giboney cave. This was also the only cave where Mn coatings were well pronounced over extensive portions of the cave. The pronounced Mn staining on passages of Giboney cave likely explain why Mn was recorded at 4760 ppm, the highest concentration recorded for the study and about four standard deviations above the median. However, Manganese coatings also have the potential to amplify trace metal concentrations (Cd, Co, Ni, Pb, and Zn) as documented by White et al. (2009), which could also explain some of the metal concentrations for Giboney cave.

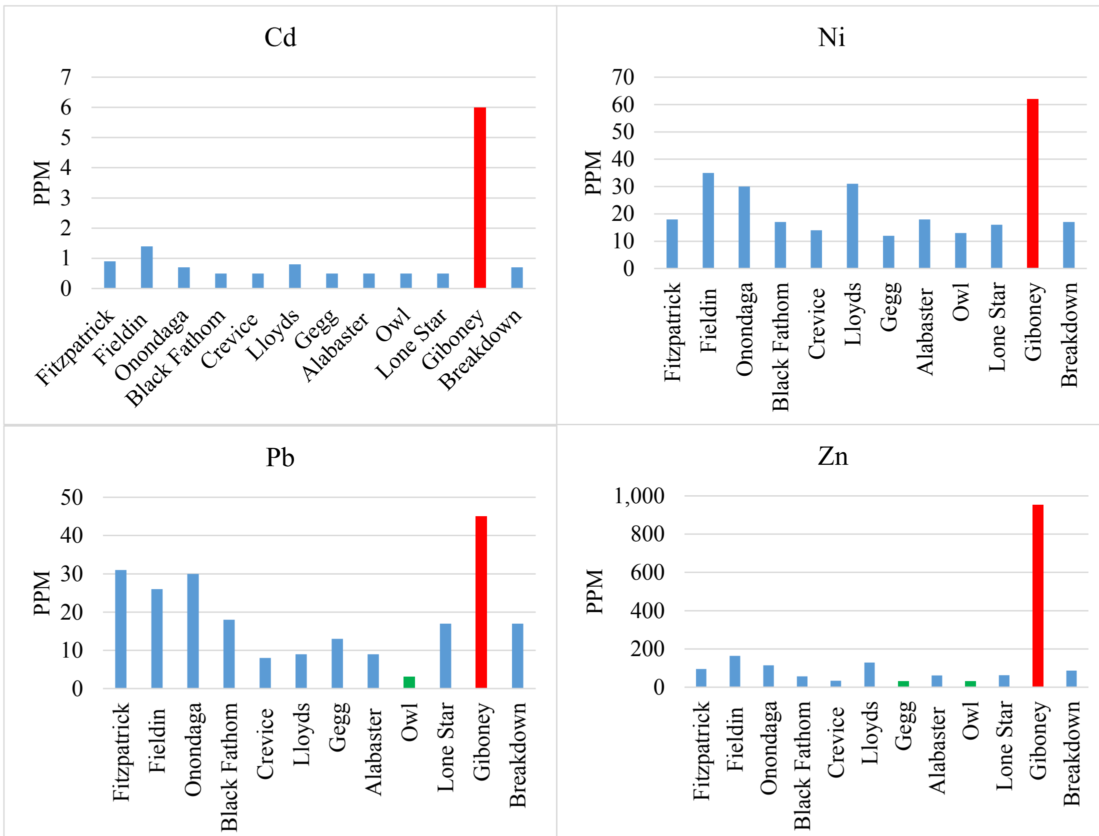

Figure 13. Graph of the enrichment of Cd, Ni, Pb, and Zn in Giboney Cave.

Fieldin Cave. Giboney cave and Fieldin cave are both hosted in the Mississippian aged Burlington-Keokuk limestone and both had oddities of Al and Ca. Aluminum, is one of the most abundant element in earth's crust (Erickson, 1973). Fieldin cave located in Ozark, Missouri (satellite city of Springfield, Missouri) in Burlington-Keokuk limestone on the property of Smallin cave had an Al concentration at 23,000 ppm, about two standard deviations above the median (14,000 ppm). However, Giboney cave was depleted in Al (8000 ppm) and is also in the Burlington-Keokuk limestone. This discrepancy is interesting considering the caves are only separated by 20 miles and they share similar geologic and hydrological attributes. Hydrologically, they both receive urban runoff, but Fieldin cave receives some rural runoff.

The Al anomaly could be explained by the aluminum guard rail leading into the Fieldin cave. The Al could have been deposited in the sediments by soldering or grinding during installation or maintenance work associated with property upkeep. However, both samples could be affected by grain size differences, which are known to affect metal concentrations. Giboney cave had coarser sediments in comparison to Fieldin cave, which tends to result in lower concentrations. It could also be because Al is one of the most abundant elements on earth.

It is also interesting that Giboney cave and Fieldin cave recorded Ca concentrations over 170,000 ppm. The median for the study was 35,500 ppm. Both of these caves are hosted in the Burlington-Keokuk limestone. Limestone is a Ca rich rock, which makes it hard to explain why these two caves have such high readings compared to all other caves.

State Park Tourism Caves. Onondaga cave and Alabaster cavern are both state park tourism caves. Onondaga recorded a high Cu concentration about half a standard deviation above the mean. It should also be noted that Ni, Pb, and Zn had elevated concentrations, but were within one standard deviation of the median. This is interesting because Muri et al. (2013) documented a tourism cave enriched with Cu, Pb, and Zn. Coincidentally Alabaster cavern, another tourism cave recorded higher metal concentrations of Cr, Mn, Pb, and Zn in comparison to Owl cave (non-tourism cave), which is located on the same property. Figure 14, compares tourism caves to non-tourism caves and the difference between them. Even though Onondaga and Alabaster cavern are hosted in different rock types, Figure 14 supports the conclusion of Muri et al. (2013) that tourism caves have higher metal readings. These caves also recorded other elemental oddities that are likely related to other factors that are further discussed at length below.

Onondaga Cave. Onondaga Cave State Park is located in the Ordovician Gasconade dolomite in Crawford County, Missouri along the Meramec River. The cave is open to the public for tours and has a history dating back to the late 1800's. The cave has been used for many purposes, including onyx mining, private show cave, and even a dance hall. Onondaga cave recorded the highest Cr content in the study at 81 ppm, which is about two standard deviations above the median of 58 ppm. It is hard to explain why the Cr content is so high compared to all other caves. However, with a hundred plus years of human usage, it very plausible that Cr has increased overtime due to anthropogenic impacts related to the history of the cave.

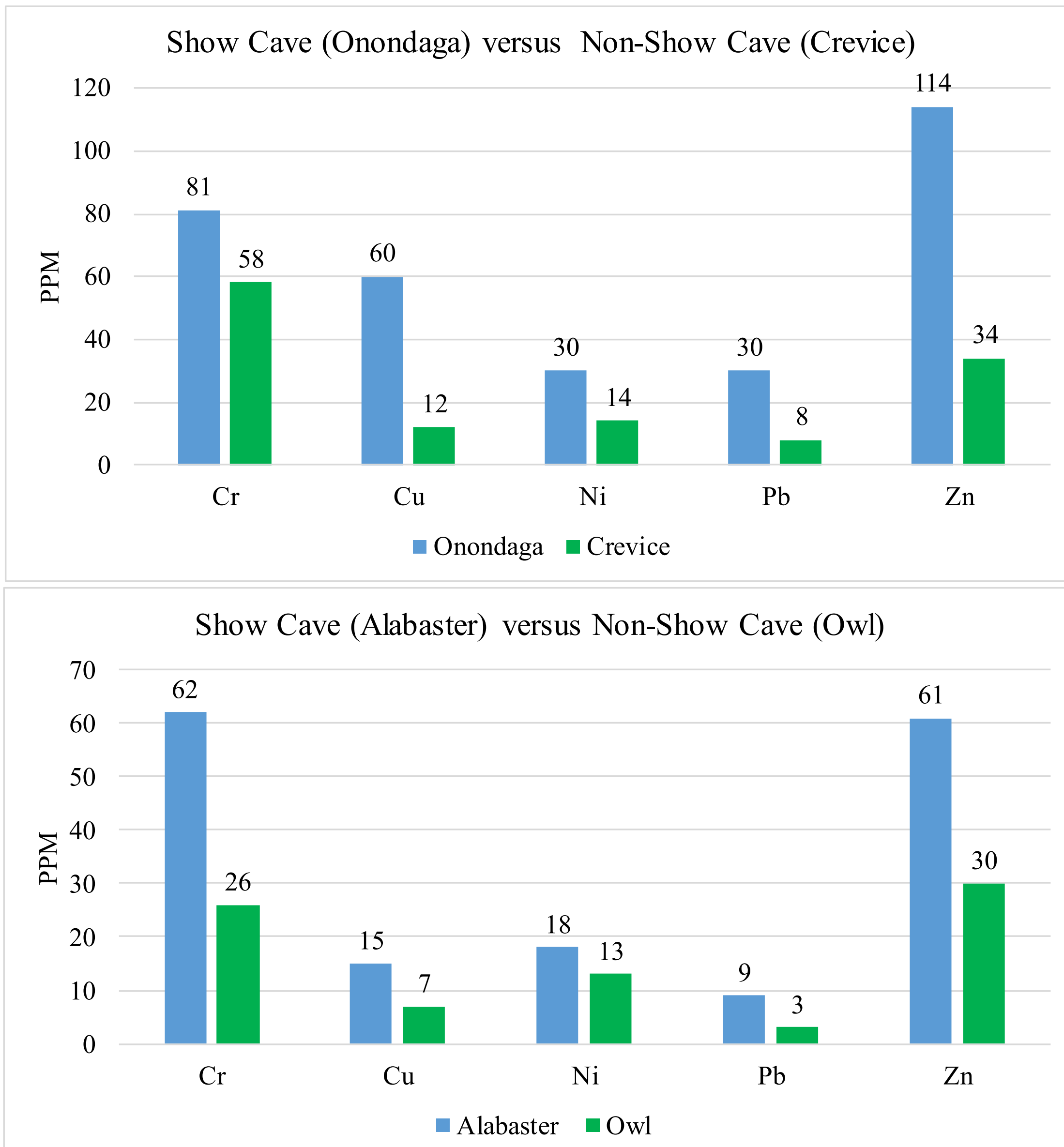

Figure 14. Comparison of tourism versus non-tourism cave metal concentrations. The non-tourism caves selected for comparison were chosen due to similar geologic age and rock type.

Onondaga cave also recorded the highest Mg concentration (14,000 ppm). When compared to the other caves in Ordovician rock the Mg content is excessively high, but this might be explained by lithologic differences. Onondaga is in the Gasconade dolomite, while Gegg, Lloyds, and Crevice cave are primarily in the Joachim dolomite. The Joachim dolomite contains interbedded limestone and this lithological variation indicates two environments of deposition. Any geochemical variation in the environment of deposition at the time of formation could have resulted in higher Mg concentrations for the Gasconade dolomite. Magnesium was also found at 14,000 ppm in caves hosted in Permian strata, but these concentrations are discussed in the next section on Alabaster cavern and Owl cave.

Alabaster Cavern and Owl Cave. Alabaster cavern and Owl cave are both hosted in Permian aged rock gypsum ($CaSO_4 \cdot 2H_2O$) near Freedom, Oklahoma. Both of these caves share the same high anomalies of B, Mg, S, Sr. These metals were marked with red bars on the comprehensive dataset (Figure 7) and are likely related to the geologic setting. The sulfur content is likely from the fact that gypsum is a sulfate mineral, which makes it a natural sulfur source. Boron tends to be found in arid to semi-arid environments (Kistler and Helvaci, 1994), like conditions that were present at the time of bedrock formation in the Permian (Foster et al., 2014). Magnesium, at first glance does not make sense because the cave is hosted in rock gypsum. However, the sediments that make the bedrock of the cave originate from a felsic-mafic mixture (Foster et al., 2014). Mafic material is high in Mg and would have originated from the weathering of the ancestral Rockies (Sweet et al., 2013). Strontium is an alkali earth metal, number 38 on the periodic table. Calcium is number 20 on the periodic table, which means that strontium can mimic the chemical properties of calcium. Strontium is also the 15th most abundant element on Earth, with an estimated average of 360 ppm (Turekian and Wedepohl, 1961). The discrepancy between Alabaster (256 ppm) and Owl (695 ppm) in Sr could be related to construction that removed sediment from Alabaster Cavern to install a new lighting system. Owl Cave could also have an abundance of Celestite ($SrSO_4$), a sulfate mineral in the sediment that is common with evaporite deposits.

Both caves also recorded some of the lowest concentrations of the study, in particular Owl cave, which was depleted in Ba, Co, Cr, Mn, Pb, and Zn. These metals were at least one standard deviation below the median for each element. The depletion could be related to numerous factors. First, the bedrock of the cave is derived from the weathering of orogenic belts (Sweet et al., 2013), which might have been depleted in metals from weathering. Second, Owl cave is not a tourism cave, which have been shown to have higher metal concentrations, as noted by Muri et al. (2013). Last, Owl cave has a lot of breakdown (large grain size), which has been documented to reduce metal concentrations (Horowitz and Elrick, 1987).

Summary. This section explored the revised cave dataset by looking at caves with only a few anomalies, which made identifying a possible contamination source difficult. As the section progressed, it started to become more evident that geologic and hydrologic factors were affecting these caves. For example, the metals in Alabaster cavern and Owl cave appeared to be affected by the geologic setting, while it appeared that land use watershed affected Giboney cave. The following two sections further explore metals variability based on the geologic and hydrologic attributes.

5.2 Geologic Attributes

It is important to assess the potential effects of geologic properties (e.g. lithology, host rock age, and geochemistry) on the trace metal concentrations. The data in this section is analyzed into two subsets. First, a comparison of evaporite rock (Permian) versus carbonate rock (Ordovician and Mississippian). Second, a comparison of Ordovician dolostone against Mississippian limestone. In order to assess any effects, the remaining 12 caves are grouped based on host rock age and shown Table 4. A graphical representation of Table 4 is provided in Appendix F.

Evaporite versus Carbonate. The mineralogy between evaporites and carbonates is vastly different between the two groups, which affects trace metals accumulation. The difference between the two is recorded by B, Mg, S, and Sr. Figure 15 shows the recorded variation of B, Mg, S, and Sr between evaporites and carbonates. These same metals were identified and interpreted in the Alabaster cavern and Owl cave section, which are both evaporite hosted caves. To recap the Alabaster cavern and Owl cave section, Boron accumulation occurs in arid to semi-arid environments (Kistler and Helvaci, 1994). At the time of host rock formation, the Southern Great Plains were in an arid environment (Foster et al., 2014). The evaporites in this study are made of rock gypsum, which is a sulfur rich mineral. Strontium has the ability to mimic Ca chemical attributes, which allows for Sr to be scavenged by cation exchange. Magnesium is from the sediments that make the bedrock of the caves Southern Great Plains. The sediments were derived from a felsic-mafic mixture that originates from the weathering of orogenic belts (Sweet et al., 2013). Mafic material is high in Mg and likely originated from the ancestral Rockies (Sweet et al., 2013), which explains the high Mg levels.

Table 4. Comprehensive geologic attribute database. Caves grouped by geologic age and rock type into Mississippian limestones, Ordovician dolostone, or Permian gypsum.

Comprehensive Geologic Trace Metal Baseline										
Geologic Attribute[1]	Mean Concentration									
	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe
Ordovician	10500	4.0	10	170.0	21000	0.8	6.5	61.0	28.3	13000
Mississippian	14833	4.5	10	156.7	78167	1.9	9.3	57.3	29.2	16833
Permian	15000	2.5	35	85.0	78500	<0.5	5.0	44.0	11.0	14500
	La	Mg	Mn	Ni	P	Pb	S	Sr	V	Zn
Ordovician	20.0	5000	718.5	21.8	2525	15.0	400	63.0	25.5	76.8
Mississippian	30.0	1333	1583.3	27.5	1105	25.7	433	34.0	29.0	236.2
Permian	10.0	14000	244.5	15.5	585	6.0	61500	475.5	22.0	45.5
	Median Concentration									
	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe
Ordovician	9000	4.0	10	135.0	19000	0.8	6.0	58.0	20.5	11500
Mississippian	15000	4.0	10	170.0	48500	0.9	9.0	57.5	20.5	16500
Permian	15000	2.5	35	85.0	78500	0.5	5.0	44.0	11.0	14500
	La	Mg	Mn	Ni	P	Pb	S	Sr	V	Zn
Ordovician	20.0	2000	615.0	22.0	1550	11.0	200	61.5	22.5	74.0
Mississippian	30.0	1000	1006.5	17.5	620	22.0	450	32.5	28.5	91.0
Permian	10.0	14000	244.5	15.5	585	6.0	61500	475.5	22.0	45.5

1: Geologic Attributes Comprised of Ordovican Dolostone (N = 5), Mississippian Limestone (N = 6), and Permain Gypsum (N = 2)

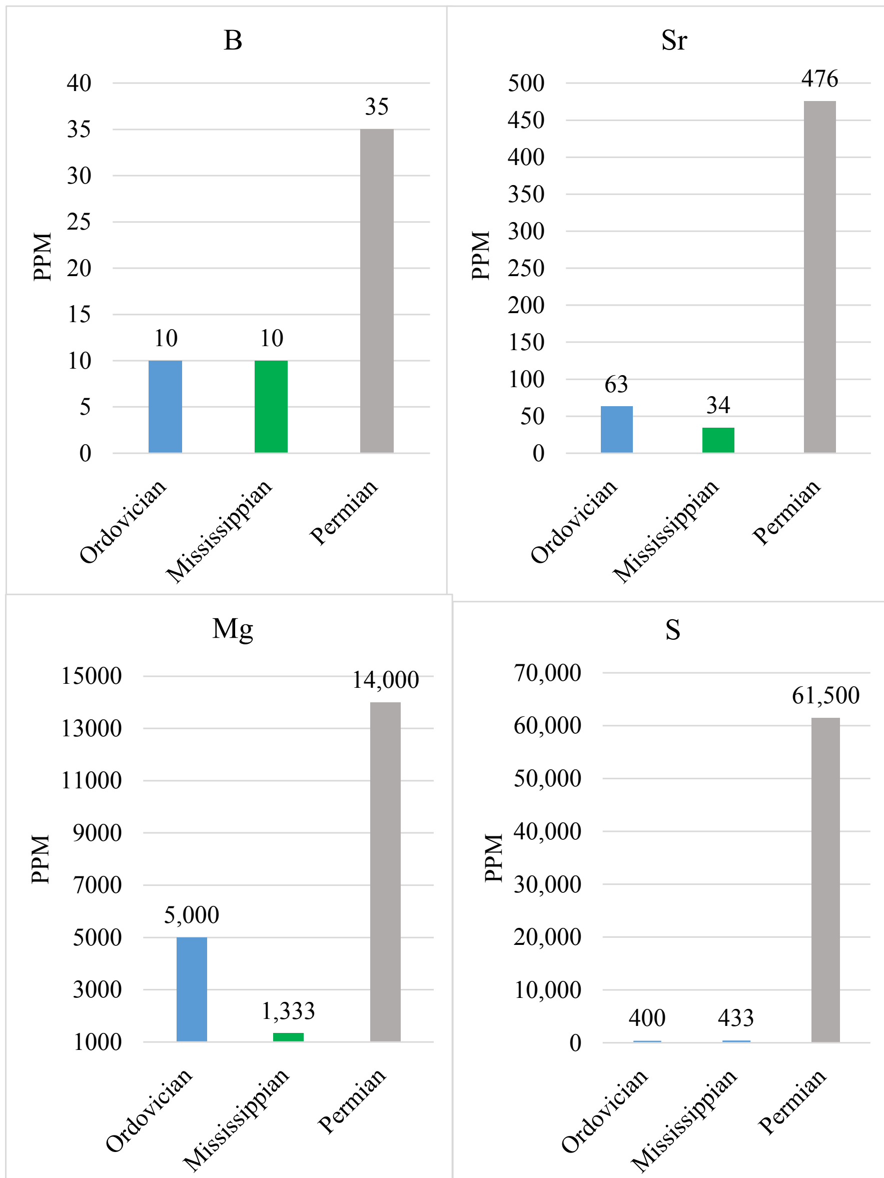

Figure 15. Comparison of B, Mg, S, and Sr concentrations in evaporites and carbonates.

Ordovician and Mississippian carbonates, on the other hand, recorded higher mean concentrations of Ba, Cd, Cr, Cu, Fe, P, Pb, and Zn, as seen throughout the comprehensive geologic dataset (Table 4). As noted in geologic setting for the Ozark Plateau in chapter 2, there are many areas of Mississippi Valley Type (MVT) mineralization. Many caves sampled in this study are in proximity to the Tri-State Pb-Zn district or Old Lead Belt, which are generally considered as primary sources for Pb-Zn-Fe and secondary sources of Ba-Cd-Cr-Cu (Leach et al., 1995). Mining activities like ore transportation or smelting can increase trace metal concentrations in soils and sediments as noted by Loska et al. (2004) and Kaminski and Landsberger (2000). Surface watershed could also contribute Ba, Cd, Cr, Cu, Fe, P, Pb, and Zn or any of the other metals. However, hydrologic factors will be explored in depth in chapter 5.4.

Mississippian Limestone versus Ordovician Dolostone. The primary mineralogical differences between limestone (calcium carbonate) and dolostone (calcium-magnesium carbonate) resulted in limestone being enriched with Ca and dolostone in Mg, as seen in Figure 16. Barium was also enriched in the Ordovician, which could be due to the proximity to the Washington County Barite District (refer to Figure 12) in relation to the caves sampled. Three of the four Ordovician caves were sampled in watersheds downstream of this area. Samples from Ordovician rock caves also recorded higher concentrations of P, as shown in Figure 16. The caves in the Ordovician were primarily located in rural areas with sizable bat communities present. As noted by Miko et al. (2001) and Wuana and Okieimen (2011), bat guano or agricultural practices have been shown to increase P concentrations.

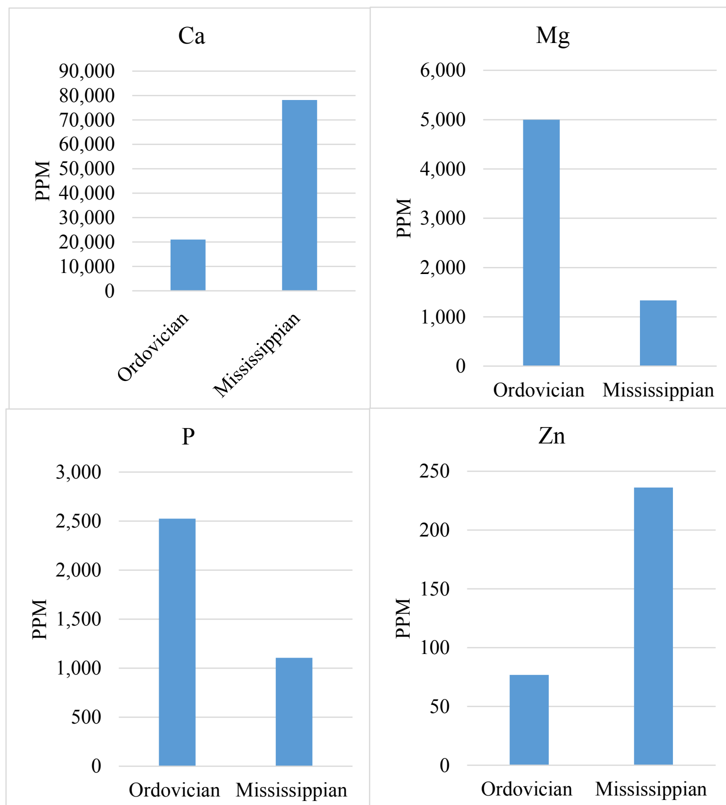

Figure 16. Metal variability in Mississippian limestone and Ordovician dolostone.

Strontium, however, is the hardest to explain because the Ordovician mean was double the Mississippian mean and there is no identifiable source for Sr. The most likely explanation is related to geochemical properties because Sr, Mg, Ca, and Ba are alkaline earth metals, which means they mimic each other chemically. Alkaline earth metals have the same number of electrons in their outer shell, which when shed, creates a cation charge of plus two. Weathering of the rock then releases Sr into the environment until Sr is potentially captured by cation exchange. The greater the cation charge, the more likely it is to be captured by cation exchange (Carroll, 1959). Clays have a high cation exchange capacity (Drever, 1988). The samples from the Ordovician were fat clays in comparison to the cherty to sandy clay from the Mississippian samples. Slight grain size differences can affect trace metal accumulation, as noted by Horowitz and Elrick (1987) and this might explain the differences between the limestones and dolostones.

The Mississippian limestone hosted caves had higher concentrations of Fe and Mn compared to the Ordovician caves, likely because of Fe and Mn oxides. These oxides were most notably seen in the Mississippian hosted Giboney cave. White et al. (2009) noted that Mn oxides can amplify trace metals in karst settings. This could also explain why the Mississippian was enriched with a mean of 236 ppm Zn, compared to 76.8 ppm for the Ordovician, as shown in Figure 16 previously. The concentrations for Zn in this study hint that other factors amplify trace metals, as Drever (1988) reported an average background concentration of 20 ppm for Zn in limestone.

5.3 Hydrologic Attributes

This last section assesses the potential impacts of urban and rural watersheds on metal variability. State park watersheds were planned to be assessed along with urban and rural watersheds. However, preliminary analysis indicated that state park watersheds were enriched with B, Mg, S, and Sr and depleted in Ba, La, Mn and P. These are the same metals documented for the Permian aged evaporite caves of Alabaster cavern and Owl cave. Because the data is skewed towards the evaporites, Alabaster Cavern and Owl cave are omitted to accurately assess watershed metal variation. The remaining state park, Onondaga cave is best grouped to the rural watersheds. Table 5 shows the baseline for the remaining 10 caves based on surficial urban or rural watershed land use. A graphical representation of Table 5 is provided in Appendix G.

Urban. This study found that Ca, Cd, Cu, La, Mn, and Zn recorded higher concentrations of metals in urban caves compared to rural caves. Figure 17 shows the trace metal accumulation of urban watersheds in comparison to rural watersheds. Lagerwerff and Specht (1970) related Cd, Cu, and Zn to automobile sources, which is likely the main source of these metals. Lanthanum is a rare earth element that is commonly used in electronics and as an additive to glass (Albanese and Cicchella, 2012). Glass was found in the sediment samples from Giboney cave and Fitzpatrick cave. Manganese is common in heavy manufacturing, ceramics and glass, and automobiles as noted by Albanese and Cicchella (2012). All the caves sampled in urban areas were located near roadways or other anthropogenic structures. The presence of anthropogenic structures/sources is an unavoidable reality when sampling in urban areas and likely contributes to metal enrichment. Considering that rural areas generally have less

Table 5. Comprehensive hydrologic attribute database. Caves grouped by surficial land use watershed into either urban or rural watershed continued. Alabaster caverns and Owl cave omitted due to data skewing.

Comprehensive Hydrologic Attribute Database										
Landuse watershed[1]	Mean Concentration									
	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe
urban	15250	4.5	10.0	160.0	111750	2.3	9.5	61.3	36.3	17000
rural	11667	4.2	10.0	163.3	17500	0.7	7.3	57.2	23.8	14167
	La	Mg	Mn	Ni	P	Pb	S	Sr	V	Zn
urban	35.0	1250	1914.5	33.0	1392.5	29.8	475.0	33.8	28.8	324.3
rural	20.0	3667	786.0	20.0	1860.0	15.8	383.3	53.5	26.8	71.2
	Median Concentration									
	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe
urban	15000	4.0	10.0	170.0	117500	1.2	9.0	66.5	28.5	16500
rural	10000	4.5	10	135	11000	0.7	7	55	15	14000
	La	Mg	Mn	Ni	P	Pb	S	Sr	V	Zn
urban	35.0	1000	1054.0	26.5	1145.0	28.5	450.0	32.5	27.0	129.5
rural	20	2000	723.5	16.5	530	15	200	57.5	26	60

1: Based on Surficial watershed, dataset is comprised of Urban (N = 4) and Rural (N = 6) watersheds

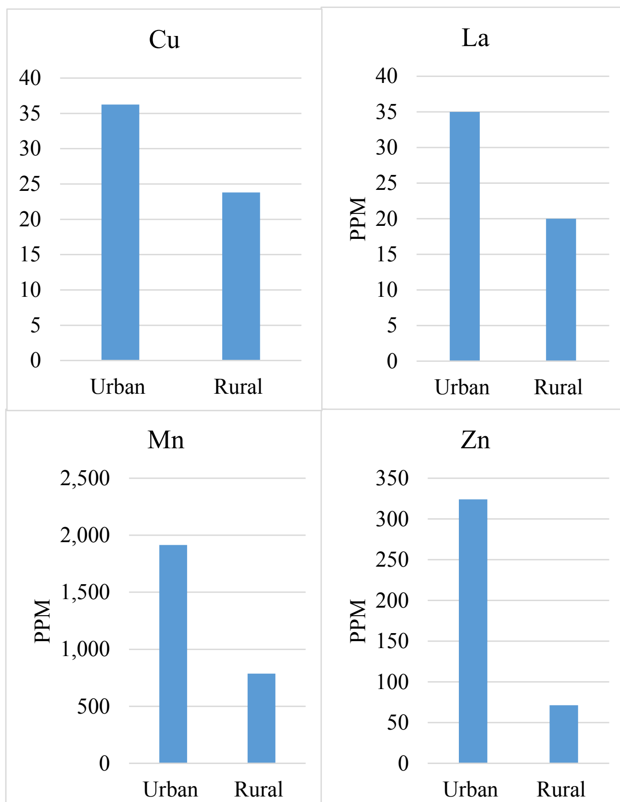

Figure 17. Comparison of urban versus rural concentrations of Cu, La, Mn, and Zn.

anthropogenic influence, it likely explains why rural areas were depleted in Cd, La, Mn, and Zn compared to urban areas. Urban caves were hosted in Ca rich limestone, which could explain why Ca levels were so high. It is also possible that Ca could be from the de-icing agent calcium chloride, which has been shown to increase Ca in groundwater by Pollock and Toler (1973).

Rural. Rural landscapes were enriched with Mg, P and Sr compared to urban land uses. The rural caves were mostly hosted in dolostone, which is likely why rural caves were enriched with Mg. As noted in the geologic attributes section 5.3, Sr could originate from the geochemical properties of alkaline earth elements. In rural watersheds Sr was double the concentration of the urban caves, just like the results noted in the geologic attributes section. Phosphorous is likely related to agricultural practices or bat guano, both known sources for P (Wuana and Okieimen, 2011 and Miko et al., 2001). As seen in Table 5, rural areas had lower metal concentrations overall. This is likely because there were fewer anthropogenic sources present in comparison to urban areas.

CHAPTER 6. SUMMARY AND CONCLUSIONS

6.0 Summary

The purpose of this study was to build a trace metal baseline of cave sediments of the midcontinent United States. Cave sediments are the insoluble detritus of biologic, geologic, and anthropologic origin. Caves were selected using multiple factors which included: urban or rural cave drainage basins, host rock formation age, rock type, and other characteristics. This study was primarily anchored in the Mississippian aged and Ordovician aged carbonate rocks of Missouri. However, to establish a larger baseline database of the midcontinent, some samples were collected from Mississippian aged limestone of Kentucky and the Permian aged selenite of Oklahoma.

Samples from 14 caves were analyzed for the following suite of metals: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, La, Mg, Mn, Ni, P, Pb, S, Sr, V, and Zn. The results indicated that a variety of factors affect cave sediments. The comprehensive data set (table 2) documented two caves, Pearson Creek cave and Crankshaft Pit with high concentrations for many metals. These metals were related back to environmental factors that included Pb-Zn mineralization for Pearson Creek Cave and anthropologic impacts from Model T era car parts for Crankshaft Pit. These caves were removed from the comprehensive dataset to construct a revised baseline (Table 3). Using the new dataset, the remaining caves were analyzed based on geologic and hydrologic attributes. Through the interpretation of the data, the following results were documented:

1. Tourist caves contain higher levels of Cr, Cu, Ni, Pb, and Zn. These metals are commonly associated with urban sources (Jaradat et al. 2005 and Lagerwerff and Specht 1970).

2. Trace metals in cave sediments are affected by geologic attributes of the karst region or host rock mineralogy.

   a. Samples from Ozarks Plateau carbonates were enriched in Ba, Cd, Cr, Cu, Fe, Pb, and Zn. These metals have been associated with Mississippi Valley Type mineralization (Leach et al., 1995)
   b. Samples from Mississippian limestone and Ordovician dolostone are geochemically different, which results in Ca enrichment of Mississippian limestone and Mg enrichment of Ordovician dolostone.
   c. Samples from Mississippian limestone were enriched in Fe, Mn, and Zn. The exact source of enrichment is unknown but could be from Fe-Mn oxides which were more abundant in Mississippian caves or local watershed as the Mississippian caves were primarily sampled from an urban setting, which can amplify metal levels.
   d. Samples from the Ordovician dolostone were enriched with Ba and P. The exact source of enrichment is unknown but could be from local environmental factors like runoff or bat guano.

3. Urban caves were enriched with Cd, Cu, La, Mn, and Zn. Cadmium, Cu, and Zn have been related to urban sources like glass production, electronics, vehicles, and other daily urban activities by Albanese and Cicchella (2012).

4. Rural areas are enriched with Ba and P. Barium is likely because of the Washington County Barite District. Phosphorous enrichment might be related to agricultural practices or bat guano, as both can supply high amounts of P (Miko et al., 2001 and Wuana and Okieimen, 2011).

6.1 Future Work

Science is about continual discovery and the improvement of pre-existing knowledge. This study created a database of trace metal concentrations of midcontinent caves and in the process, generated many new questions that merit attention, as well as technical aspects that could improve the dataset. Future research should consider the following unresolved facets:

1. Expansion of the dataset to create better parity of samples.
2. The effects of seasonality on trace metal concentrations in cave sediments.
3. The effect of metal concentrations on cave species.
4. The potential effect of microbes on trace metal accumulation.

6.2 Conclusions

Overall, this study sampled 14 caves out of 10,000 plus caves that span the United States' extensive karst landscapes. Hopefully this study has led to a better understanding of the value of cave sediments to karst science. Future researchers must consider the findings of this study along with similar studies of cave sediments if a better understanding is to be achieved. Caves are home to many unique species, many of which are classified as threated or endangered by the U.S. Fish and Wildlife Service. If left unchecked, metals contamination could potentially destroy the karst ecosystem. As Doughty and Johnson (2012) noted, the presence or absence of aquatic biota might be dependent on metals accumulation. By establishing a baseline, future researchers may use the baseline to monitor environmental change, which will hopefully be used to preserve this truly unique ecosystem.

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APPENDICES

Appendix A: Chart of How Access was Gained and Sampling Methodology.

List of Owners and Sampling Methods Employed

Cave Name	Access Granted By	Sampling Method Used
Pearson Creek	Springfield Plateau Grotto	Random
Fitzpatrick	Springfield Plateau Grotto	Stratified
Fieldin	Smallin Cave	Stratified
Breakdown	Springfield Plateau Grotto	Stratified
Giboney	Springfield-Greene County Parks Board	Stratified
Onondaga	Missouri Department of Natural Resources	Stratified
Black Fathom	SEMO Grotto	Random
Crevice	SEMO Grotto	Random
Lloyds	SEMO Grotto	Random
Gegg	SEMO Grotto	Random
Crankshft pit	SEMO Grotto	Random
Lone Star	Louisville Grotto	Stratified
Alabaster Caverns and Owl	Oklahoma Tourism and Recreation Department	Stratified

Appendix B: Summation of Field Notes.

Note: All passage lengths rounded for simplicity

<u>Pearson Creek Cave</u>
Location: Greene County, Missouri
Host Rock Age: Mississippian
Watershed: Urban
Passage Length: 800 ft.
Notes: Tri-State Pb-Zn mining area in 1900's. Used by homeless/college students until gating.

<u>Fitzpatrick Cave</u>
Location: Christian County, Missouri
Host Rock Age: Mississippian
Watershed: Urban
Passage Length: 650 ft.
Notes: Along James River, prone to flooding, Endangered Species present and Paleo-Indian site.

<u>Fieldin Cave</u>
Location: Christian County, Missouri
Host Rock Age: Mississippian
Watershed: Urban
Passage Length: 400 ft.
Notes: Show cave, Paleo-Indian Site, used during Civil War, located in dense vegetation stream valley.

<u>Breakdown Cave</u>
Location: Christian County, Missouri
Host Rock Age: Mississippian
Watershed: Urban
Passage Length: 2000 ft.
Notes: Along James River, Occasional flooding, Loess Deposit within, belly-crawl entrance.

<u>Giboney Cave</u>
Location: Greene County, Missouri
Host Rock Age: Mississippian
Watershed: Urban
Passage Length: 1000 ft.
Notes: was an open sewer for city of Springfield, show cave, beside I-44 to north and Route 66 to the south, salvage yard to east.

<u>Onondaga Cave</u>
Location: Crawford County, Missouri

Host Rock Age: Ordovician
Watershed: State Park
Passage Length: 9100 ft.
Notes: Lighted show cave, sizeable bat community, onyx mining in past, along Meramec River, 100 plus years of known history

<u>Crevice Cave</u>
Location: Perry County, Missouri
Host Rock Age: Ordovician
Watershed: Rural
Passage Length: 31 mi. (only portion sampled)
Notes: Longest in state of Missouri, prehistoric campsite.

<u>Black Fathom Cave</u>
Location: Ste. Genevieve County, Missouri
Host Rock Age: Mississippian
Watershed: Rural
Passage Length: 7 mi. (only portion sampled)
Notes: sinkhole lake entrance, easily floods, relatively new discovery.

<u>Lloyd's Cave</u>
Location: Ste. Genevieve County, Missouri
Host Rock Age: Ordovician
Watershed: Rural
Passage Length: 1900 ft.
Notes: High Canyon cave, very rural

<u>Gegg Cave</u>
Location: Ste. Genevieve County, Missouri
Host Rock Age: Ordovician
Watershed: Rural
Passage Length: 1900 ft.
Notes: sinkhole entrance, floods easily, sizeable bat community

<u>Crankshaft Pit</u>
Location: Jefferson County, Missouri
Host Rock Age: Ordovician
Watershed: Rural
Passage Length: 1900 ft.
Notes: sink entrance, Model T era car part dump

Alabaster Cavern
Location: Woodward County, Oklahoma
Host Rock Age: Permian
Watershed: State Park
Passage Length: 3500 ft.
Notes: lighted show cave, surrounded by cattle grazing land.

Owl Cave
Location: Woodward County, Oklahoma
Host Rock Age: Permian
Watershed: State Park
Passage Length: 700 ft.
Notes: sink entrance, abundant breakdown, surrounded by dense vegetation

Lone Star Cave
Location: Hart County, Kentucky
Host Rock Age: Mississippian
Watershed: Rural
Passage Length: 1000 ft.
Notes: mushroom farming and saltpeter mining in past, road passes over portion of cave

Appendix C: ALS Global Geochemical Analysis Results

	Ag	Al	As	B	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Pierson Creek	<0.2	23000	14	10	190	1.6	<2	62000	5.7	9	78	36
Fitzpatrick	<0.2	15000	4	10	180	0.8	<2	63000	0.9	8	63	69
Fieldin	<0.2	16000	6	10	160	1	<2	172000	1.4	10	70	22
Onondoga	<0.2	11000	6	10	120	0.8	<2	34000	0.7	9	81	60
Black Fathom	0.7	9000	4	<10	110	0.7	<2	7000	<0.5	10	47	16
Crevice	<0.2	9000	2	<10	150	<0.5	<2	3000	<0.5	5	58	12
Lloyds	0.2	8000	5	10	310	0.5	<2	44000	0.8	6	47	29
Gegg	<0.2	17000	3	<10	100	<0.5	<2	2000	<0.5	6	58	12
Crankshaft Pit	<0.2	13000	19	10	200	2.3	<2	19000	0.5	20	39	40
Alabaster	<0.2	17000	3	30	120	0.7	2	37000	<0.5	6	62	15
Owl	<0.2	8000	2	40	50	0.5	2	120000	<0.5	4	26	7
Lone Star	<0.2	15000	5	10	190	0.8	2	15000	0.5	8	52	14
Giboney	<0.2	15000	4	<10	180	0.8	2	178000	6	13	70	35
Breakdown	<0.2	1.47	4	10	120	0.8	<2	34000	0.7	7	42	19

	Fe	Ga	Hg	K	La	Mg	Mn	Mo	Na	Ni	P	Pb
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Pierson Creek	29000	10	<1	2500	70	2500	1250	3	200	51	6000	348
Fitzpatrick	14000	<10	<1	2100	30	1000	1155	1	100	18	1690	31
Fieldin	19000	10	<1	2400	40	2000	953	1	100	35	520	26
Onondoga	18000	<10	<1	1700	20	14000	374	1	100	30	2780	30
Black Fathom	16000	<10	<1	1000	20	1000	782	1	100	17	420	18
Crevice	11000	<10	<1	1700	20	2000	665	1	300	14	320	8
Lloyds	12000	<10	<1	2400	20	2000	1270	2	2200	31	6720	9
Gegg	11000	<10	<1	1100	20	1000	565	1	100	12	280	13
Crankshaft Pit	48000	10	1	4600	30	5000	1930	4	200	90	1210	51
Alabaster	16000	<10	<1	3900	10	14000	302	1	800	18	610	9
Owl	13000	<10	<1	2800	10	14000	187	1	300	13	560	3
Lone Star	17000	<10	<1	2100	20	2000	1060	1	100	16	640	17
Giboney	21000	<10	<1	500	40	1000	4760	2	100	62	600	45
Breakdown	14000	<10	<1	2300	30	1000	790	1	100	17	2760	17

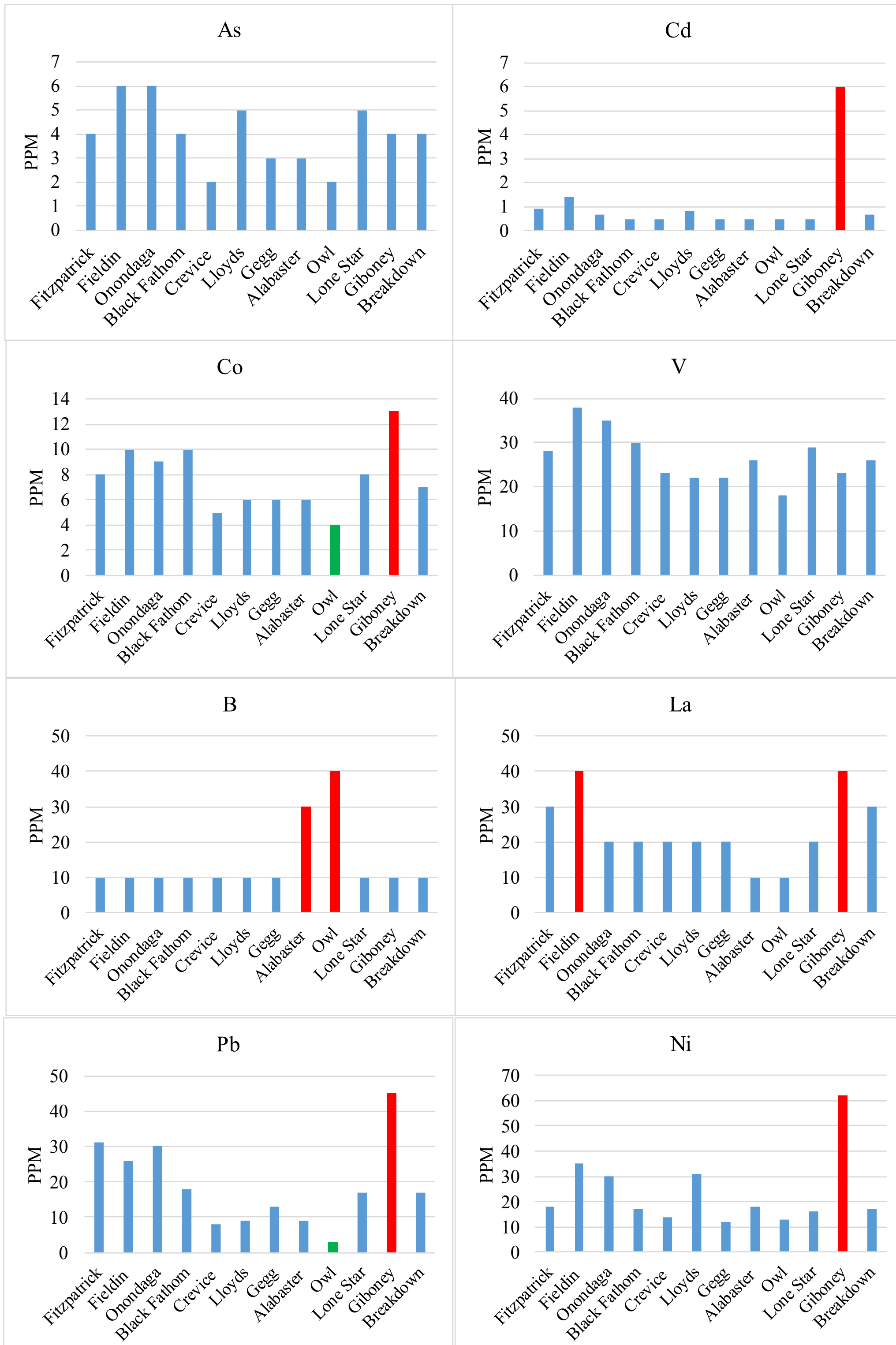
	S	Sb	Sc	Sr	Th	Ti	Tl	U	V	W	Zn
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Pierson Creek	300.0	2	8	48	<20	200	<10	<10	48	<10	994
Fitzpatrick	800.0	<2	3	34	<20	200	<10	<10	28	<10	95
Fieldin	300.0	<2	4	31	<20	200	<10	<10	38	<10	164
Onondoga	200.0	<2	4	60	<20	200	<10	<10	35	<10	114
Black Fathom	100.0	<2	3	14	<20	200	<10	<10	30	<10	57
Crevice	200.0	<2	2	119	<20	400	<10	<10	23	<10	34
Lloyds	1000.0	<2	2	63	<20	200	<10	<10	22	<10	129
Gegg	200.0	<2	2	10	<20	200	<10	<10	22	<10	30
Crankshaft Pit	200.0	<2	9	41	<20	100	<10	<10	59	<10	571
Alabaster	23000.0	<2	3	256	<20	200	<10	<10	26	<10	61
Owl	10000.0	<2	2	695	<20	100	<10	<10	18	<10	30
Lone Star	600.0	<2	3	55	<20	100	<10	<10	29	<10	63
Giboney	600.0	<2	2	50	<20	100	<10	<10	23	<10	951
Breakdown	200.0	<2	3	20	<20	200	<10	<10	26	<10	87

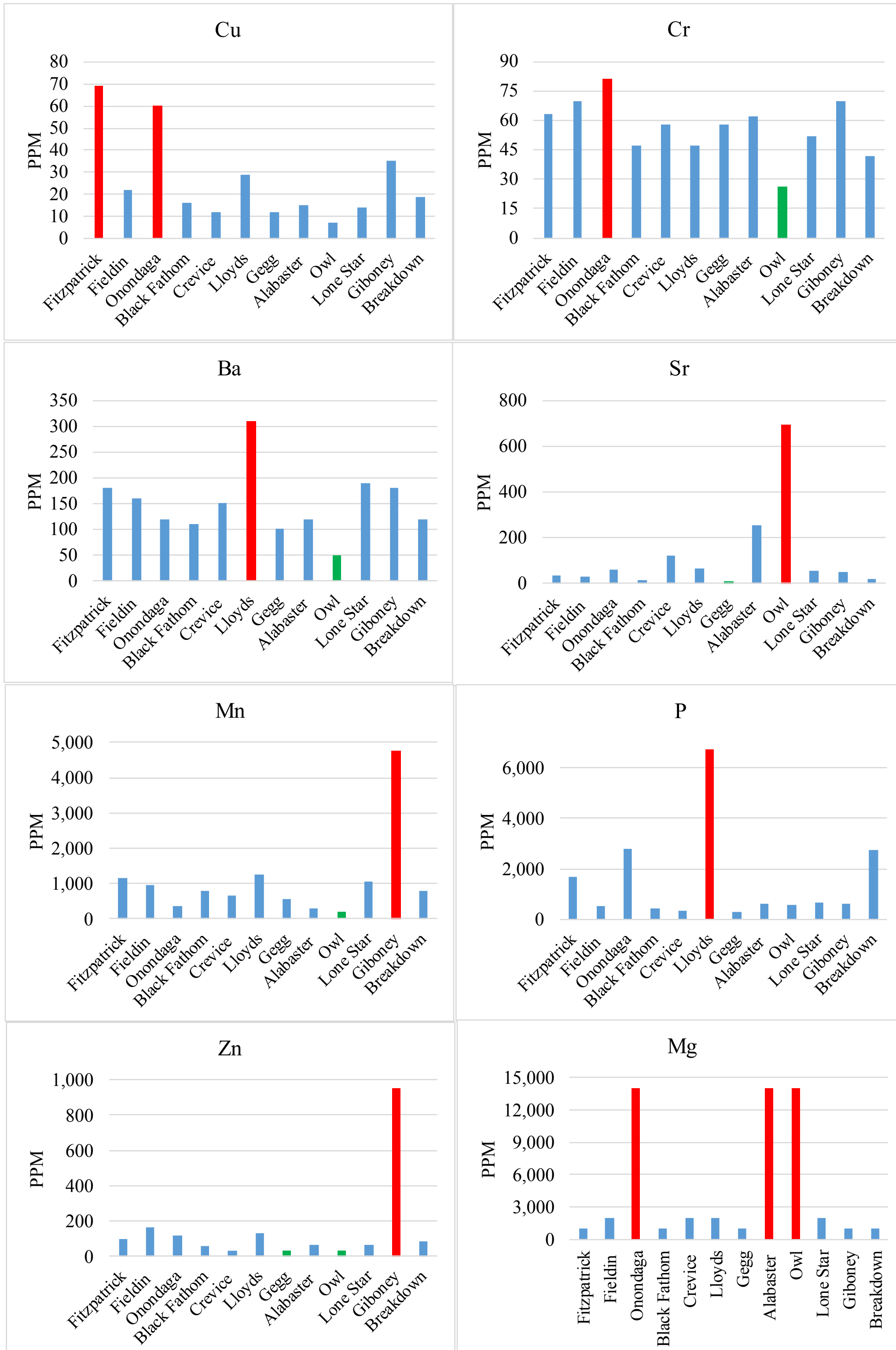
Appendix D: University of Arkansas Geochemical Analysis Results.

	Ag	As	Ba	Be	Cd	Ce	Co	Cr	Cu	Ga
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Black Fathom	0.8	2.8	109.1	1.5	1.0	38.8	10.7	9.9	7.5	2.9
Lone Star	0.8	3.8	191.1	1.6	1.1	36.5	8.9	9.3	9.5	3.2
Onondaga	0.9	3.1	93.9	1.3	1.3	31.5	7.3	8.7	36.0	3.0
Owl	0.8	3.0	33.3	1.2	0.7	11.5	4.5	7.1	5.0	2.8
Alabaster Cavern	0.8	3.2	51.7	1.2	0.8	17.1	5.0	7.6	7.9	3.0
Crankshaft Pit	0.8	5.6	141.4	2.3	0.9	66.3	11.7	8.5	15.3	3.6
Gegg	0.8	2.8	81.5	1.3	0.8	25.2	7.1	6.6	6.9	2.4
Lloyds	1.0	4.1	332.7	1.2	1.4	27.3	7.5	8.2	20.4	2.5
Crevice	0.8	2.6	121.0	1.1	0.8	25.7	6.6	6.3	7.6	2.5
Fieldin	1.5	4.5	106.8	1.5	2.0	30.1	8.9	11.8	5.5	3.4
Pearson Creek	0.8	5.9	162.4	1.9	6.3	70.0	9.0	15.3	25.4	4.5
Fitzpatrick	0.8	3.4	145.5	1.5	1.3	37.5	9.3	8.8	12.4	2.9

	La	Ni	Pb	Rb	Se	Th	Tl	U	V	Zn
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Black Fathom	18.9	11.7	13.2	7.8	0.8	5.4	0.7	1.2	17.3	37.2
Lone Star	18.2	9.0	15.7	9.9	0.9	4.8	0.8	1.6	13.7	43.9
Onondaga	20.9	10.3	25.5	6.3	0.9	4.6	0.8	1.2	14.0	105.3
Owl	5.0	9.2	2.9	5.8	0.8	2.9	0.7	1.8	9.2	21.0
Alabaster Cavern	7.5	9.8	6.2	5.8	1.5	3.6	0.7	1.4	10.9	33.7
Crankshaft Pit	21.4	47.1	36.6	10.8	1.1	11.1	1.2	1.6	18.8	305.7
Gegg	10.8	7.5	11.9	5.0	0.7	3.8	0.7	1.2	12.0	20.6
Lloyds	14.6	26.3	8.3	9.1	1.2	4.3	0.8	3.5	12.9	121.0
Crevice	11.7	10.2	8.5	5.6	0.8	4.2	0.8	1.1	11.0	29.4
Fieldin	36.1	18.8	16.1	9.7	1.0	4.8	0.9	1.0	17.9	109.9
Pearson Creek	69.8	26.9	295.9	11.1	2.1	8.2	0.9	1.7	17.6	827.9
Fitzpatrick	21.5	11.2	27.4	8.5	1.2	4.3	0.7	1.1	13.4	67.0

Appendix E. Graphical Representation of Revised Comprehensive Cave Dataset. Metals arranged by increasing PPM concentrations. Red is a high anomaly and green a low anomaly.

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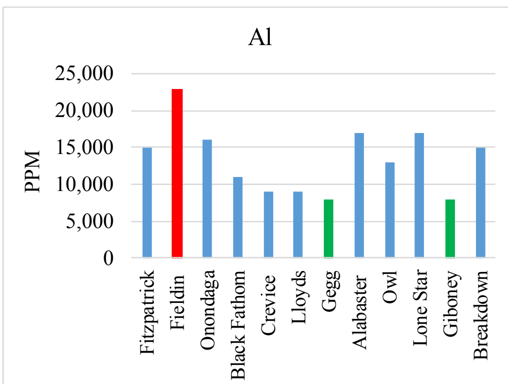
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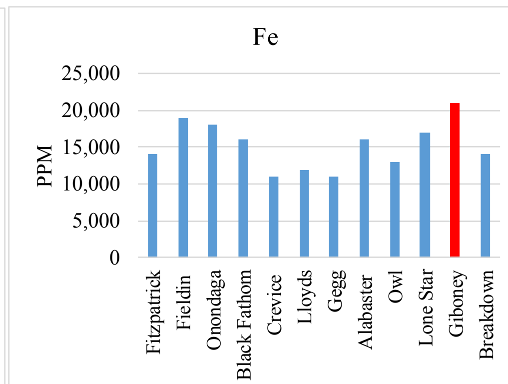
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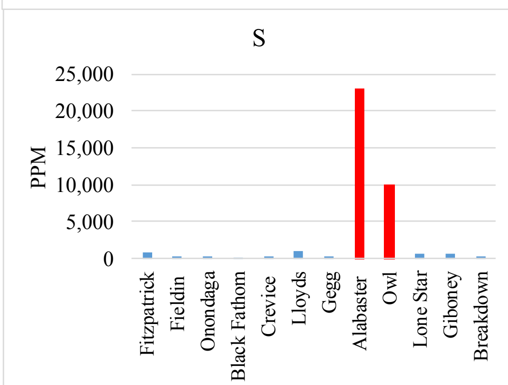
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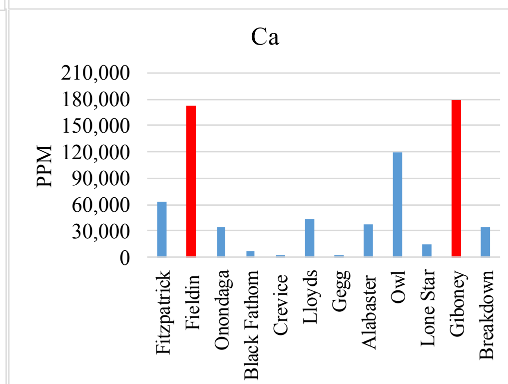
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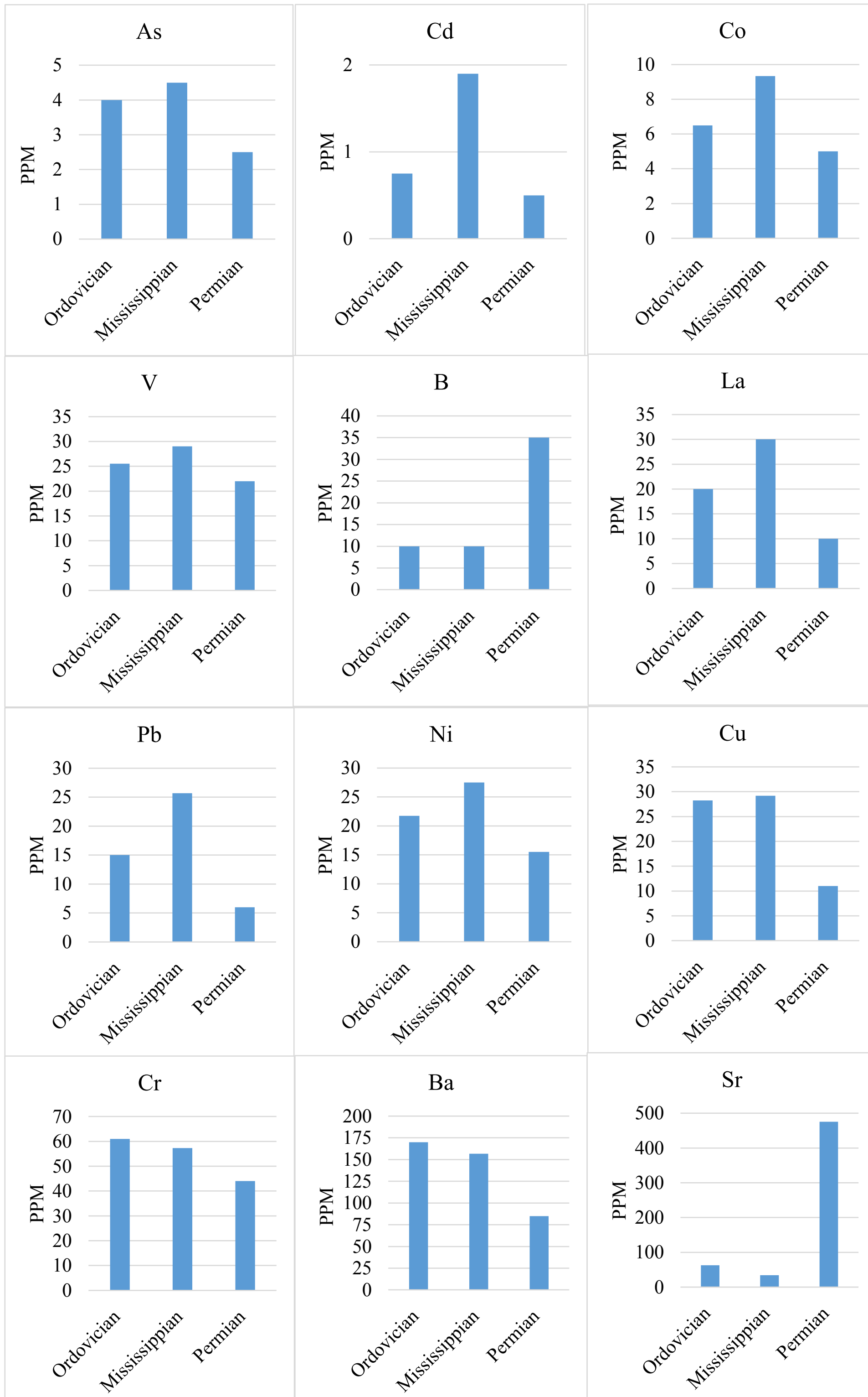
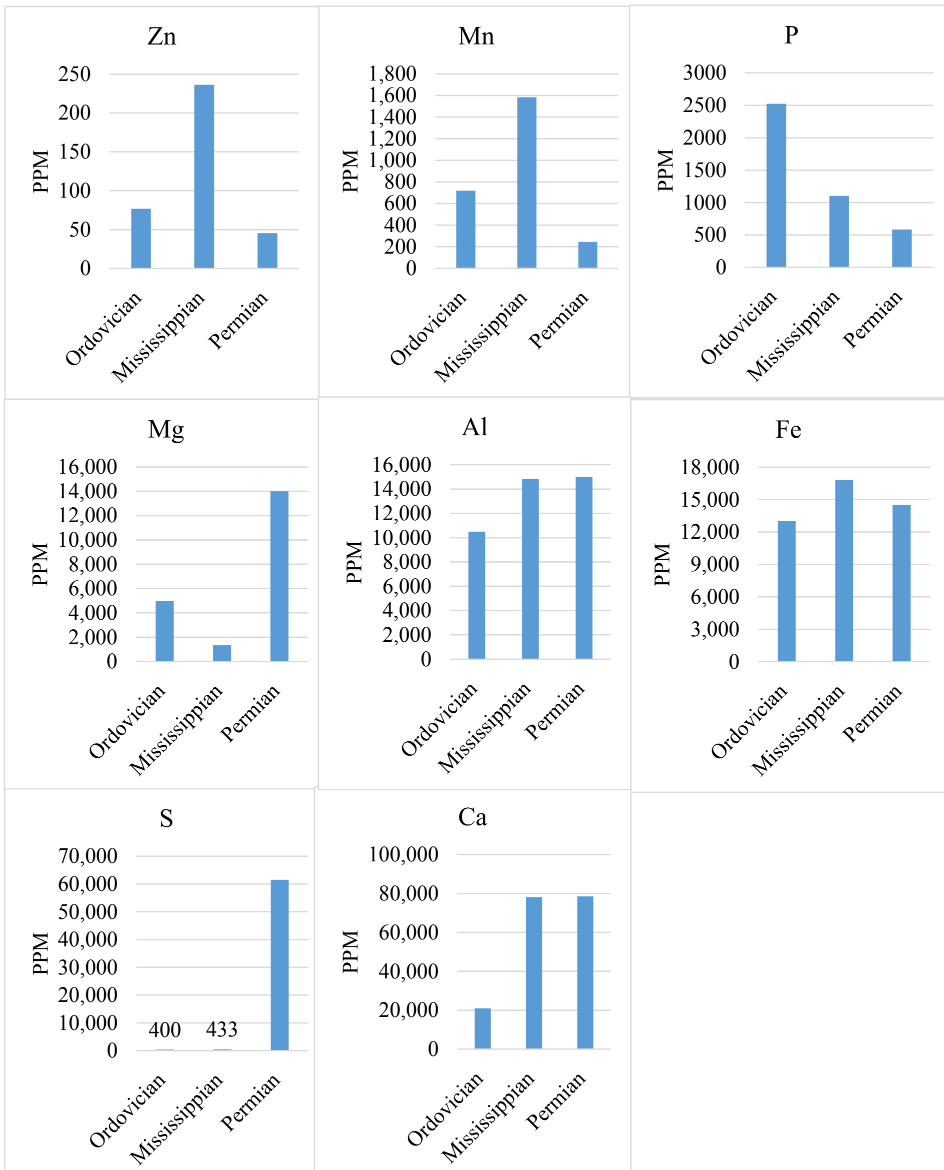
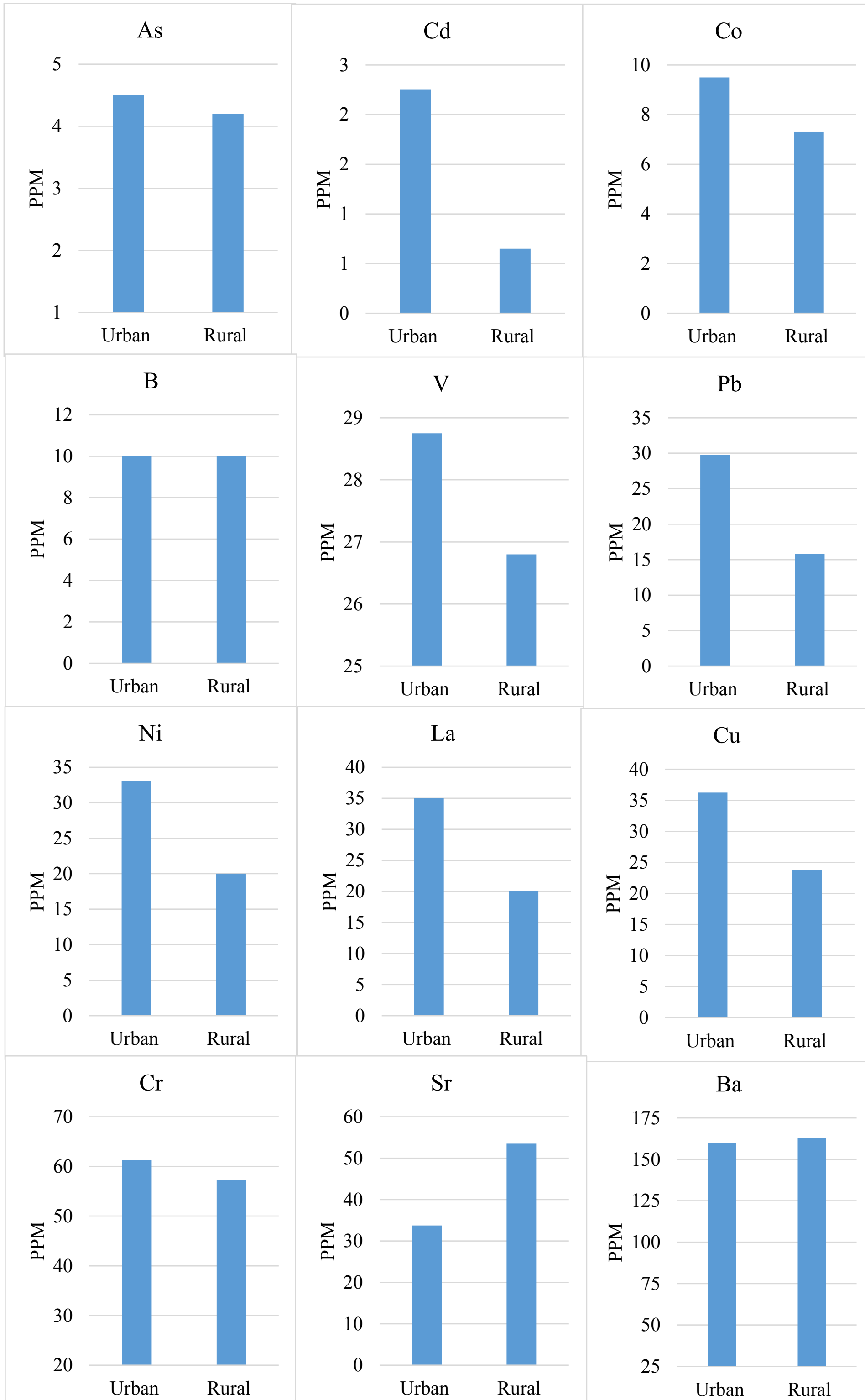
90,000
60,000
30,000
0
Fitzpatrick
Fieldin
Onondaga
Black Fathom
Crevice
Lloyds
Gegg
Alabaster
Owl
Lone Star
Giboney
Breakdown

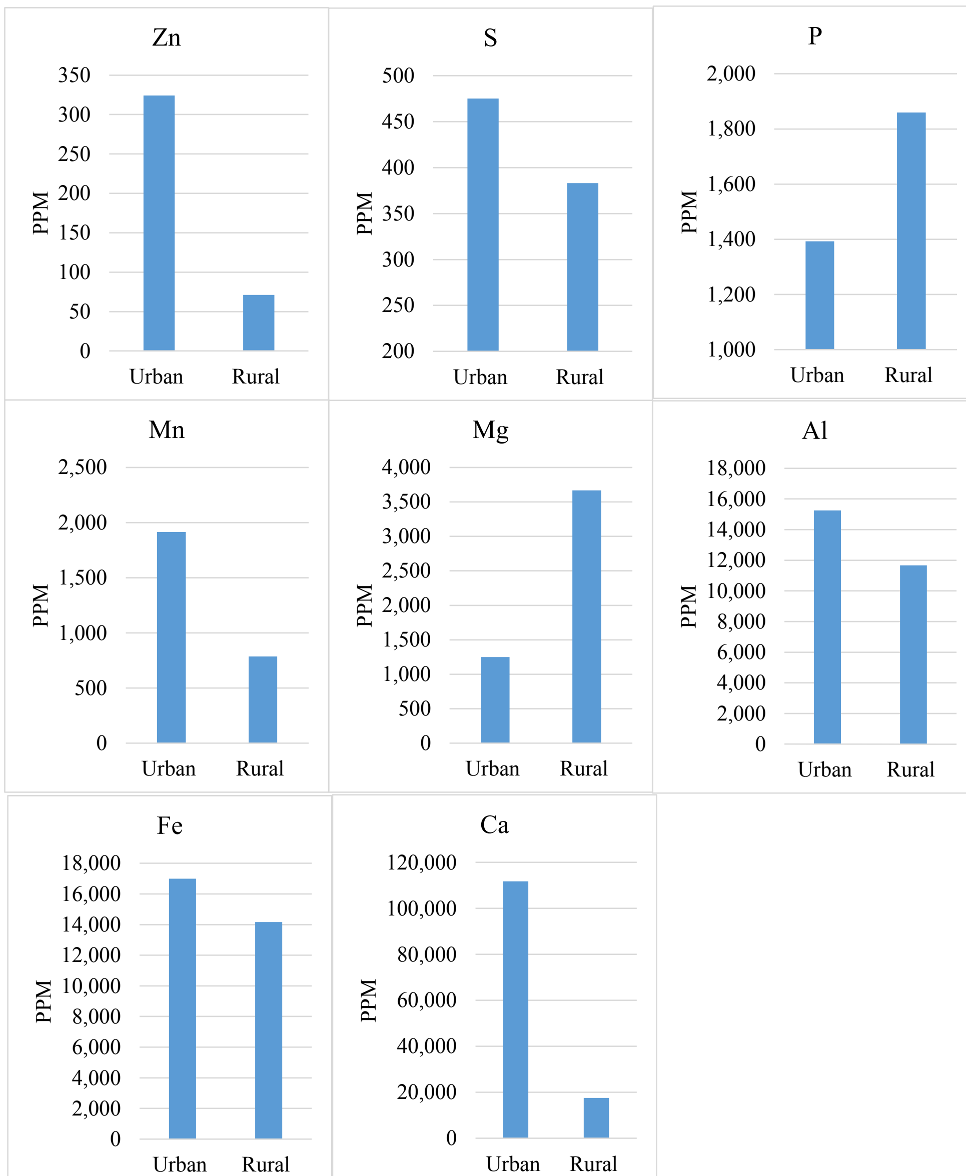
Appendix F. Graphical Representation of Comprehensive Geologic Attribute Dataset. Metals arranged by increasing PPM concentrations.




Zn
PPM
250
200
150
100
50
0
Ordovician
Mississippian
Permian
Mn
PPM
1,800
1,600
1,400
1,200
1,000
800
600
400
200
0
Ordovician
Mississippian
Permian
P
PPM
3000
2500
2000
1500
1000
500
0
Ordovician
Mississippian
Permian
Mg
PPM
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
Ordovician
Mississippian
Permian
Al
PPM
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
Ordovician
Mississippian
Permian
Fe
PPM
18,000
15,000
12,000
9,000
6,000
3,000
0
Ordovician
Mississippian
Permian
S
PPM
70,000
60,000
50,000
40,000
30,000
20,000
10,000
0
400
433
Ordovician
Mississippian
Permian
Ca
PPM
100,000
80,000
60,000
40,000
20,000
0
Ordovician
Mississippian
Permian

Appendix G. Graphical Representation of Comprehensive Hydrologic Attribute Dataset. Metals arranged by increasing PPM concentrations.




Zn
PPM
350
300
250
200
150
100
50
0
Urban
Rural
S
PPM
500
450
400
350
300
250
200
Urban
Rural
P
PPM
2,000
1,800
1,600
1,400
1,200
1,000
Urban
Rural
Mn
PPM
2,500
2,000
1,500
1,000
500
0
Urban
Rural
Mg
PPM
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
0
Urban
Rural
Al
PPM
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
Urban
Rural
Fe
PPM
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
Urban
Rural
Ca
PPM
120,000
100,000
80,000
60,000
40,000
20,000
0
Urban
Rural