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Heavy Metal Chemistry of Sediments in Caves of the Springfield Plateau, Missouri-Arkansas-Oklahoma: A Link to Subterranean Biodiversity

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HEAVY METAL CHEMISTRY OF SEDIMENTS IN CAVES OF THE SPRINGFIELD PLATEAU, MISSOURI-ARKANSAS-OKLAHOMA: A LINK TO SUBTERRANEAN BIODIVERSITY?

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ABSTRACT

We used X-ray fluorescence (XRF) to compare the heavy metal chemistry of sediments in caves in rural and urban areas to the chemistry of sediments from a control cave in a relatively undisturbed watershed in the Springfield (MO) Plateau. Sediment from Smallin Cave near Ozark, MO, the control cave, has the smallest peak sizes for Zn and Mn and a moderately-sized Pb peak. Sediment from the rural cave exhibited larger peaks of Zn and Mn and a smaller Pb peak. Sediment from the urban cave had the largest Zn, Mn and Pb peaks. Interestingly, smaller peak sizes appear to correlate to the presence of aquatic troglobites. The control cave hosts the most diverse troglobitic fauna and has sediment with smaller peak sizes. Ruark caves are rural caves, and are barren of troglobites and have sediment with larger peak sizes. Giboney Cave**,** an urban cave in Doling Park in Springfield, MO, provides the most interesting evidence. Giboney Cave splits into two branches, each of which has a unique chemical fingerprint. One channel is barren of cave life and has sediment that exhibits large metal peaks. The second channel hosts aquatic troglobites and has sediment that has small metal peaks. These findings are of particular importance because the caves of the Springfield Plateau host abundant troglobitic species, including the endangered Ozarks cavefish (*Amblyopsis rosae*). Sediment metal concentrations may indicate which cave systems are capable of supporting life, with XRF analysis providing a non-destructive, rapid way to identify such systems.

KEY WORDS: Springfield Plateau, Ozark caves, troglobites, Smallin Cave, Ruark Cave, Giboney Cave, Ozark cavefish, *Amblyopsis rosae,* heavy metal pollution

INTRODUCTION

This study compares the heavy metal chemistry of sediments in caves in rural and urban areas to the chemistry of sediments from a control cave in a relatively undisturbed watershed. The study is designed to investigate the link between variations in heavy metal chemistry of cave sediments and surface land use, and to determine if that variation can provide a unique chemical fingerprint. Similar studies of surface stream systems often are used as indicators of human impacts on environmental quality (e.g. Mantei and Sappington, 1994; Desenfant *et al.*, 2004; Gutierrez *et al.*, 2004). Because caves are uniquely sensitive to disturbance, it is possible that any heavy metal contamination that enters the cave system can have a destructive impact on cave life. The Springfield Plateau is of particular interest because it hosts abundant troglobitic macrofauna, including the endangered

Ozarks Cavefish (*Amblyopsis rosea*) (Woods and Inger, 1957).

GEOLOGIC SETTING

The Ozark Plateaus extend across the southern half of Missouri, into northern Arkansas, and extreme northeastern Oklahoma (Peterson, 1998). The Plateaus can be subdivided into the Springfield Plateau in the south and southwest, the Boston Mountains in the extreme south, the Salem Plateau, encompassing the eastern two-thirds, and the St. Francois Mountains within the Salem Plateau (Fig. 1). The Springfield and Salem Plateaus are underlain by vast quantities of limestone and dolostone bedrock that hosts an extensive network of cave systems (Unklesbay and Vineyard, 1992).

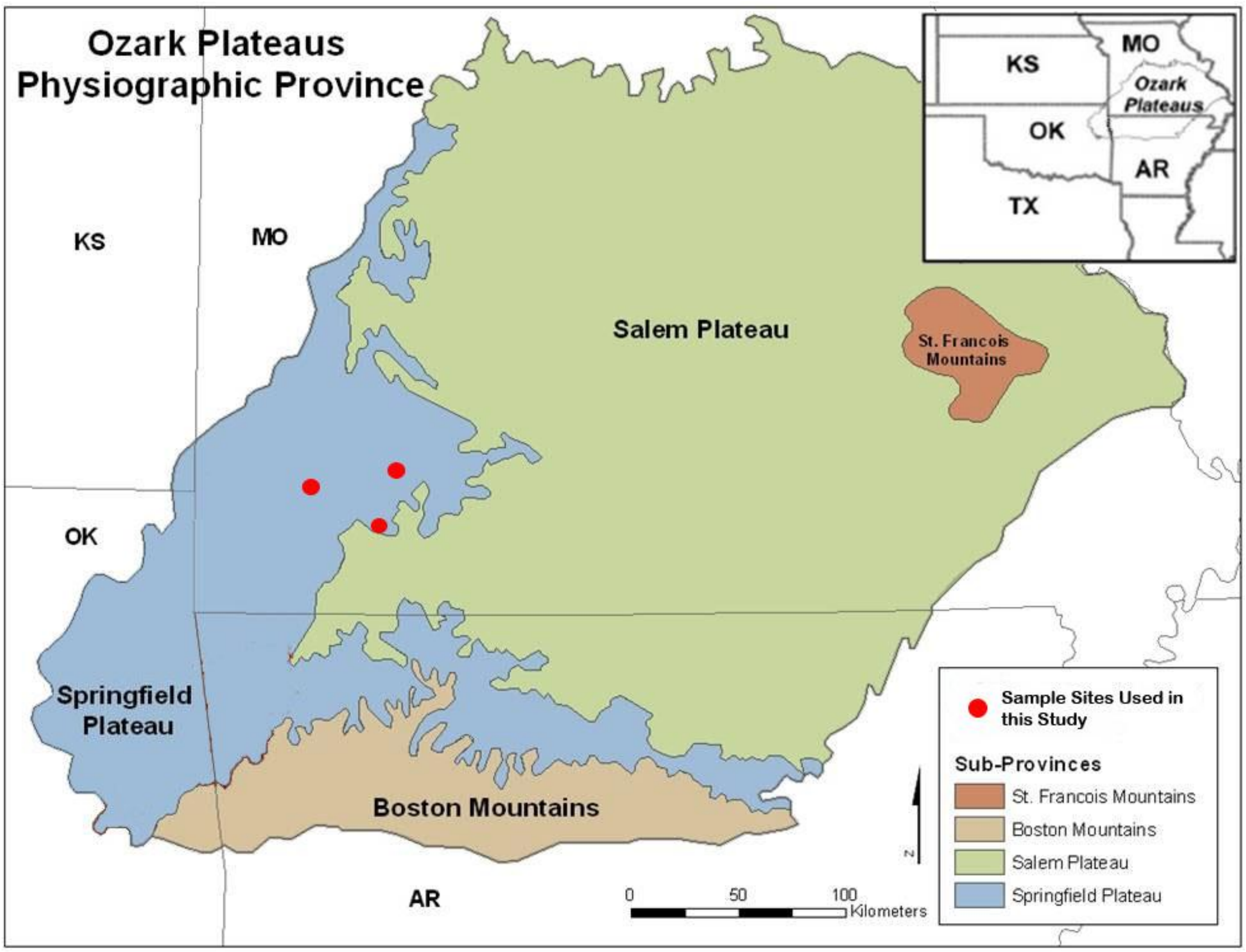

Figure 1. Map showing the physiography of the Ozark Plateaus. This study focuses on the Springfield Plateau. Sample sites are denoted with a red dot (after Keen-Zebert and Shepherd, 2011).

Stratigraphic Setting

The Paleozoic stratigraphy of the Springfield Plateau encompasses parts of two cratonic sequences resting on Precambrian basement rocks (Table 1). Sedimentary rocks of the Sauk (Cambrian to mid-Ordovician) sequence lie nonconformably upon the Precambrian basement. The LaMotte Sandstone marks the base of the Paleozoic sequence in the region, and is conformably overlain by the Bonneterre Dolomite. The Davis Formation and Derby-Doerun Dolomite lie upon the Bonneterre Dolomite. These units are overlain by the Potosi and Eminence Dolomites, the youngest of the Cambrian rocks in the Springfield Plateau region (Thompson, 1995). The Ordovician Gasconade Formation lies upon the Cambrian rocks. The Gasconade Formation includes the Gunter Sandstone Member at the base, with the rest of the formation consisting of dolostone. The Roubidoux Formation, which consists of a mixture of dolostone, dolomitic sandstone, and sandstone, rests conformably upon the Gasconade Formation. The Roubidoux Formation is overlain by the Jefferson City, Cotter, and Powell Dolomites, which reach a total thickness of more than 200 meters near the Arkansas border, thinning substantially to the north (Thompson, 1995).

Rocks of the Kaskaskia Sequence (Early Devonian to Latest Mississippian) unconformably overlie the Ordovician sedimentary units. Rocks of the Tippecanoe Sequence are notably absent. Throughout most of the Springfield Plateau the Mississippian Compton Formation lies unconformably upon the Cotter Formation. However, in the far southwestern part of Missouri, some 30 feet of Devonian Chattanooga Shale lies upon the Cotter Formation and is unconformably overlain by the Compton Formation. The Northview Shale, primarily a green shale and siltstone ranging from a few centimeters to a couple of meters in thickness, overlies the Compton Formation. The remainder of the Paleozoic stratigraphic section is predominantly limestone, much of which includes significant percentages of chert in the form of nodules, primarily along bedding planes. The section includes the Pierson Limestone, the Reeds Spring Formation, the Elsey Formation and the Burlington-Keokuk Limestone. The Burlington-Keokuk Limestone is the most widespread and thickest Mississippian unit, forming the bedrock surface throughout most of the Springfield Plateau. In the far northwest reaches, the Burlington-Keokuk Limestone is overlain by the Warsaw Formation (Thompson, 1995).

The majority of caves in the Springfield Plateau Missouri are hosted in the Burlington-Keokuk and Pierson Limestones (Noltie and Wicks, 2001). The caves tend to be very shallow; often plant roots are seen intruding into cave passages. Cave passage morphologies include branch-work (tree-like), network and rudimentary patterns (Dom and Wicks, 2003).

Butscher and Huggenberger (2009) noted that cave systems are more vulnerable to changes both in the quantity and quality of groundwater, and are very sensitive to disturbances in recharge areas. In addition, because karst hydrologic systems include both a conduit like flow system and a diffuse flow system, proximity to the surface may make caves in the Springfield Plateau more sensitive to land use changes than are the deeper caves of the Ozark Plateau (Noltie and Wicks, 2001).

Table 1 (below). Summary of the Paleozoic stratigraphy of the Springfield Plateau province of the Ozark Plateaus. Cratonic sequence boundaries are denoted with double lines. Not to scale.

System	Formation Name	Thickness (m)	Lithology
Mississippian	Warsaw Limestone	0-40	granular limestone, interbedded with dolomite and chert
	Burlington-Keokuk Limestone	0-50	Light gray, medium- to thick-bedded crinoidal limestone
	Elsey-Reeds Spring Formation	25-40	medium gray, finally crystalline limestone with large chert nodules
	Pierson Formation	7.5	grayish-brown crinoidal limestone
	Northview Shale	0.5-1.5	bluish-green siltstone and shale
	Compton Formation	3.5-4	grayish green thin-bedded crinoidal limestone
Devonian	Chattanooga Shale	0-10	black, fissile, carbonaceaous shales
Ordovician	Powell Dolomite	0-25	dolomite with thin beds of sandstone and shale
	Jefferson City-Cotter Dolomite	110-210	oolitic dolomite with thin beds of sandstone and shale
	Roubidoux Formation	40-60	Dolomite, fine-grained and cherty, sandstone near base
	Gasconade Dolomite	75-90	light gray to buff dolomite with chert
Cambrian	Eminence Dolomite	45-90	light- gray, medium- to coarse-grained, massively bedded, cherty
	Potosi Dolomite	75-90	brown to gray dolomite, fine- to medium-grained, quartz druse
	Derby Doe-Run Dolomite	30-60-	tan to buff fine- to medium-grained argillaceous dolomite
	Davis Formation	40-70	dolomitic, shale, thin-bedded with edgewise conglomerate layers
	Bonneterre Dolomite	60-120	light-gray to dark-brown, fine- to medium-grained dolomite
	LaMotte Sandstone	0-150	Sandstone and conglomerate, quartzose to arkosic

SUBTERRANEAN BIODIVERSITY OF THE OZARKS PLATEAUS

The biodiversity of ecosystems in karst regions of the Ozarks Plateaus is remarkable, with some 927 species known to occur in Missouri caves (Elliott, 2007). About 17% (1082) of the 6200 Missouri caves are known to host species with 8% (491) hosting 5 or more species (Fig. 2). Of these species 82 are considered to be troglobites, spending all of their life cycle within cave systems. About 9% (597) of Missouri caves are known to harbor cave troglobites. Missouri has relatively low total biodiversity in cave systems, ranking 7th nationally in terms of troglobite species richness. However, the region is among the richest areas for biodiversity of aquatic species in North America (Elliott, 2007). Of the federally recognized endangered and threatened species native to Missouri, more than 25% are found in caves of the Ozarks Plateaus and 10% are aquatic troglobites (USFWS, 2012).

The region is widely recognized for the unique biodiversity of amblyopsid cave fish (Noltie and Wicks, 2001). Within the plateau three regions host various species: 1) the Bootheel region (*Chlorogaster agassiz*); 2) the Salem Plateau (*Amblyopsis spelaea*); and, 3) the Springfield Plateau (*Amblyopsis rosae*) (Willis and Brown, 1985). This distribution makes the Ozark Plateaus the only region in the United States to host three species of amblyopsid cave fish. Of the three amblyopsid species native to Missouri, the Ozarks cavefish (*Amblyopsis rosae*) is listed by the United States Fish and Wildlife Service as threatened, and is considered endangered in Missouri (Elliott, 2003; USFWS, 2012).

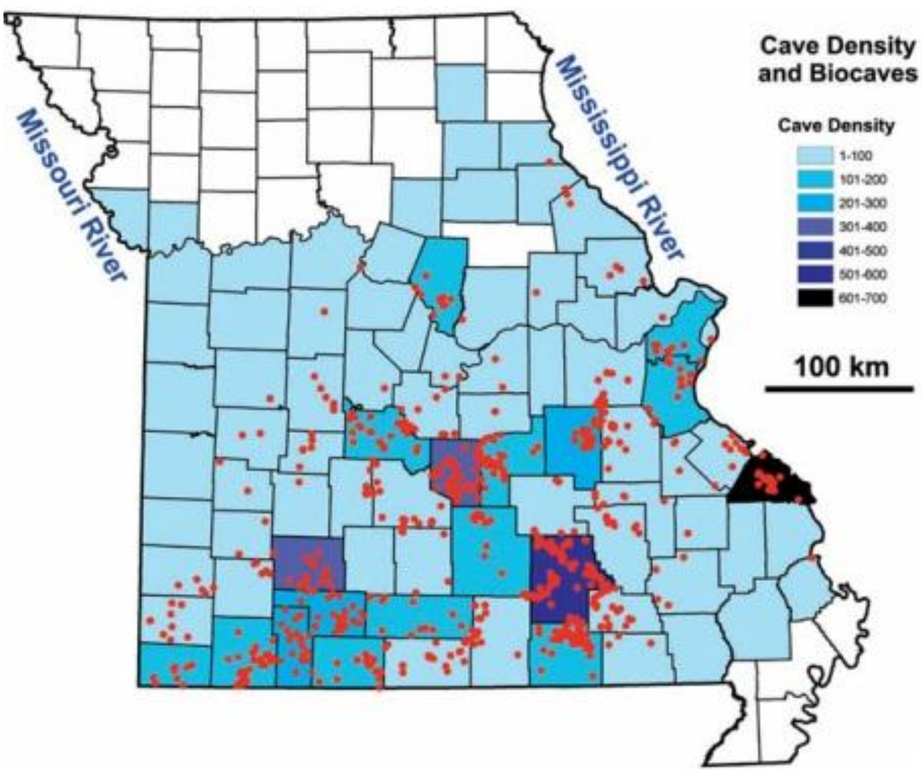

Figure 2. Map showing the cave density by county in Missouri (shaded) and the distribution of caves hosting species that spend some or all of their lifespan in the subsurface (biocaves), denoted by red dots. (From Elliott, 2007).

The Ozarks Cavefish-*Amblyopsis rosae*

The Ozarks Cavefish is small, generally less than 7 cm in total length (Means and Johnson, 1995). The species is de-pigmented, with vestigial eyes, and exhibits brain morphology consistent with de-emphasized visual input and enhanced use and interpretation of olfactory systems (Woods and Inger, 1957; Poulson, 1963). The fish is long-lived and slow-growing, with maturation likely to take many years. Captive populations of the Southern Cavefish (*A. spelaea*) have been maintained for a decade with no smaller fish approaching larger sizes; mortality appears to be independent of size (Noltie and Wicks, 2001). It is likely that the lifespan of the Southern Cavefish and its Ozark cousin could be decades. Primary food sources for the Ozark cavefish include copepods, salamander larvae, crayfish, isopods, and amphipods, along with young cavefish (Poulson, 1963). Each of these food sources spends some or all of its life cycle in sediment or near the sediment-water interface.

METHODS

Selecting Suitable Caves

Caves selected for this study include those whose watersheds have been impacted by farming or urbanization and a control cave whose watershed is relatively unimpacted. All caves are hosted in the Burlington Limestone. We selected the three Ruark caves as prime candidates for study due to their location on Ruark Farm, a Missouri Century Farm that has seen uninterrupted use as a cattle farm since the late 1800's (Fig. 3). These caves, identified as Ruark A, B, and C, have been widely accessed by the public, and display abundant evidence of human impacts. Cave openings are fenced to prohibit injury to cattle, but the entrances are open to runoff from areas associated with cattle farming. No troglobitic species are known from any of the Ruark Caves. The caves are variously littered with trash, lined with the stubs of recently utilized candles, and host numerous etchings dating from the early 1900's to the present.

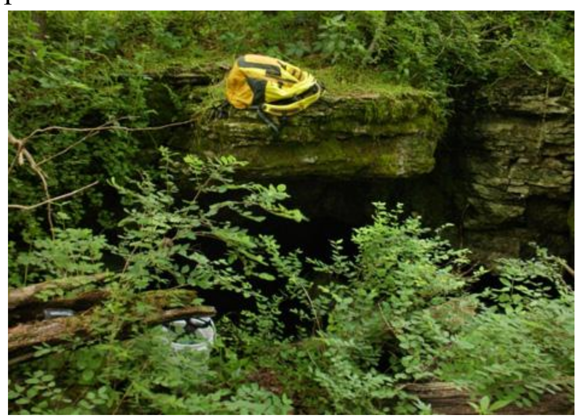

Figure 3. Sinkhole entrance to Ruark Cave A. Area around entrance is fenced to prevent injury to cattle.

Giboney Cave, located in Doling Park in Springfield, MO, provided an ideal urban cave (Fig. 4). The cave has a long history of use, ranging from once serving as an open sewer for the city Springfield, MO, to occasional development as a show cave (Doug Gouzie, personal communication). The cave currently is gated, and utilized primarily for underground education. The main channel of the cave is not known to host cave biota, but a side passage known as the 'Duck Walk' is known to house crayfish and cave fish. Once a year, generally during January, the cave discharges milky white water and develops a thin white crust.

Chemical analysis reveals that this crust is calcium carbonate. The sequence of events leading to this deposition is unknown.

Figure 4. Entrance to Giboney Cave, in Doling Park, Springfield, MO.

Smallin Cave, near Ozark, MO, was chosen as the control cave, due to the relatively unimpacted nature of the surface watershed (Fig. 5). While the entire watershed is not unimpacted, surface development is neither heavily agricultural nor urban, water quality in the cave is excellent, and the system hosts a remarkable diversity of cave species, including cave isopods and amphipods, crickets, salamanders, multiple species of crayfish, and cavefish. The cave is now very closely monitored and used primarily as a show cave.

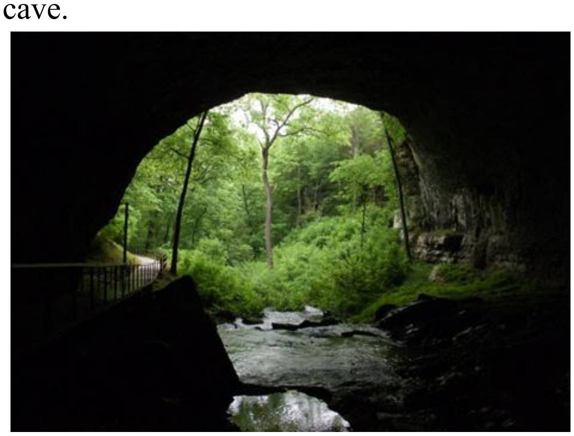

Figure 5. View out the entrance to Smallin Civil War Cave.

Sample Collection and Preparation

Field Methods

Sediment samples were collected from five caves during the period from May 22-25, 2011. Samples were collected using a sediment sampling procedure developed by the Wisconsin Department of Natural Resources (2003) for heavy metal assessment. Samples were collected using a plastic gardening trowel and placed into labeled plastic bags (Fig. 6). We used latex gloves to reduce the possibility of contaminating the samples during collection. Between samples, the trowel was sanitized using doubly deionized water and sterile wipes. Sample collection started at the cave entrance and continued at set increments such that a minimum of 10 and maximum of 14 samples were collected along the primary cave passage. At Giboney Cave the sample procedure was reversed due to the threat of rain causing a rapid rise in water levels. Sampling at Smallin cave was interrupted by rapidly rising water levels due to spring storm activity, resulting in a truncated sampling section.

Figure 6. Sample bagged on site in Ruark Cave B.

Laboratory Methods

Upon returning to the lab, supernatant liquid was decanted, and the sample was then deposited on a paper towel and placed in a 50°C drying oven to remove residual fluid. Dried samples were crushed via mortar and pestle and sieved to 180 micrometers. The mortar and pestle were washed and rinsed with doubly-deionized water between samples. The final sample product was placed in plastic bags for analysis.

Sample Analysis

Samples were analyzed using a Bruker hand-held XRF converted to a bench top analytical system. Each sample was analyzed for 180 seconds at three energy settings recommended by the manufacturer to analyze for a range of metals. The first range included the elements from magnesium to iron, the second included elements from titanium to silver, and the third included elements from molybdenum to lead.

RESULTS

We compared peak size of metals in sediment samples from each of the five caves. A summary of qualitative data from the XRF spectrographs (Figures 7, 8, and 9) reveals that sediment from the control cave (Fig. 7) has the lowest concentrations of Zn and Mn and a moderately-sized spike in Pb. Sediment from the rural cave (Fig. 8) has higher peaks of Zn and Mn and a smaller spike of Pb. Sediment from the urban cave (Fig. 9) had the highest amounts of Zn, Mn and Pb. Peak variation was consistent for each metals across all analytical energy levels. Sediment concentrations of other metals varied widely. In some samples large calcium peaks, indicate a significant fraction of sediment derived from carbonate debris. In others, iron peaks are large, likely a result of the iron-rich red clays that continually are weathered from the Burlington Limestone.

DISCUSSION

Qualitative analysis reveals a complex relationship that is understood poorly. First, Zn, Mn, and, to some extent, Pb concentrations in cave sediments appear to vary based on surface land use. Higher metal concentrations (large peaks) appear to be associated with urbanization, lower concentrations (smaller peaks) with animal husbandry, with the lowest concentrations (smallest peaks) found in the relatively undisturbed watershed (Figs. 7-9).

Secondly, and perhaps more intriguingly, low Zn, Mn (and perhaps Pb) values appear to correlate to the presence of aquatic cave biota. Sediment from Smallin Cave exhibits the lowest concentrations of metals and hosts the most diverse aquatic cave biota (Fig. 7). Sediments from the Ruark Caves have high concentrations of metals and are barren of benthic cave life (Fig. 8). However, it is Giboney Cave that provides the most intriguing evidence of the relationship of sediment metal concentrations to the presence of benthic cave fauna. This cave splits into two branches, each of which appears to have an independent water source and associated surface watershed. Sediment collected from the larger channel that runs through the central portion of the cave exhibits large Zn and Mn peaks corresponding to higher

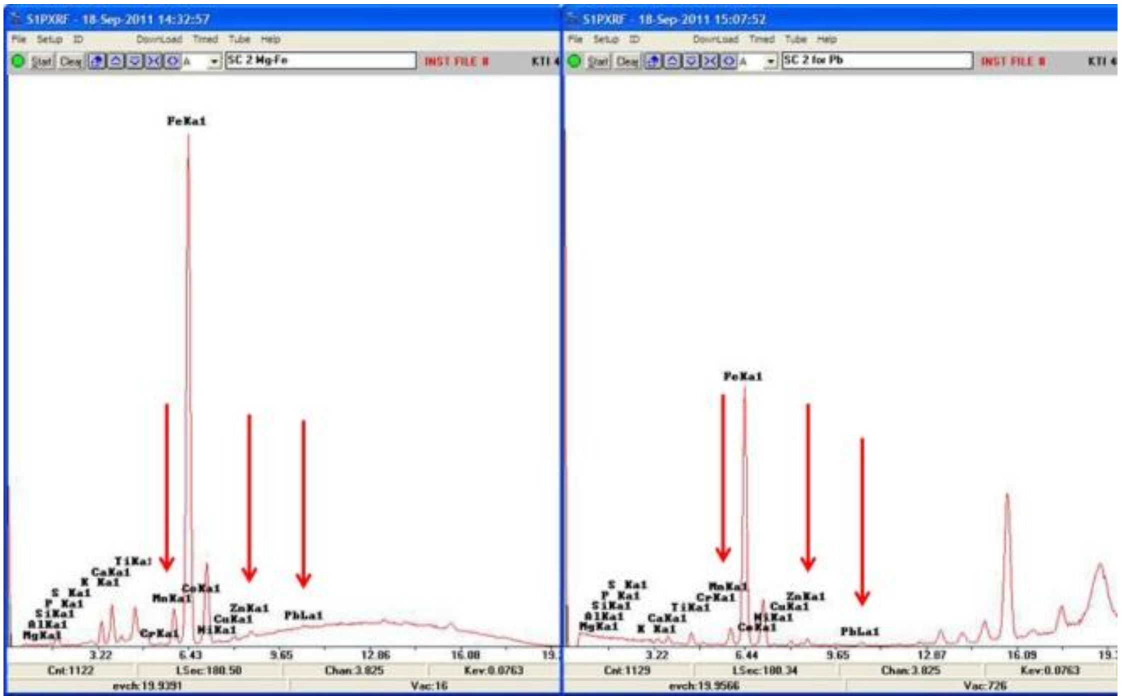

Figure 7. X-ray fluorescence spectra from Smallin Cave (control) showing the relative sizes of Mn, Zn, and Pb peaks, denoted by the location of red arrows. Spectrum on left is output for analysis at energy levels for Mg to Fe analysis. Spectrum on right is output for analysis at energy levels for Pb analysis.

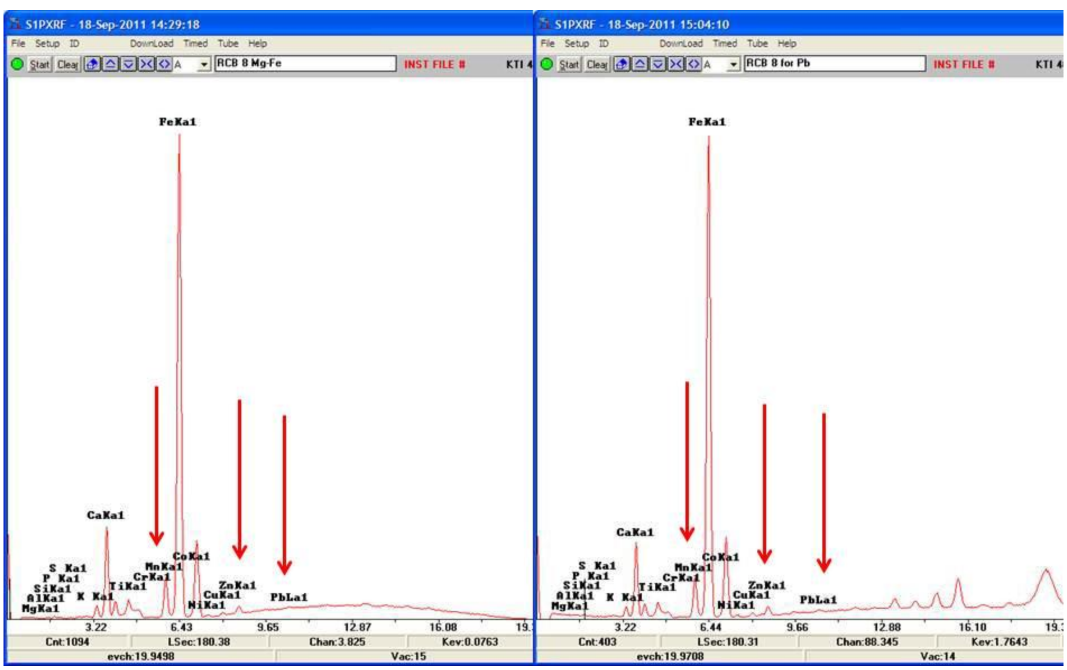

Figure 8. X-ray fluorescence spectra from Ruark Cave A (rural) showing the relative sizes of Mn, Zn, and Pb peaks, denoted by the location of red arrows. Spectrum on left is output for analysis at energy levels for Mg to Fe analysis. Spectrum on right is output for analysis at energy levels for Pb analysis.

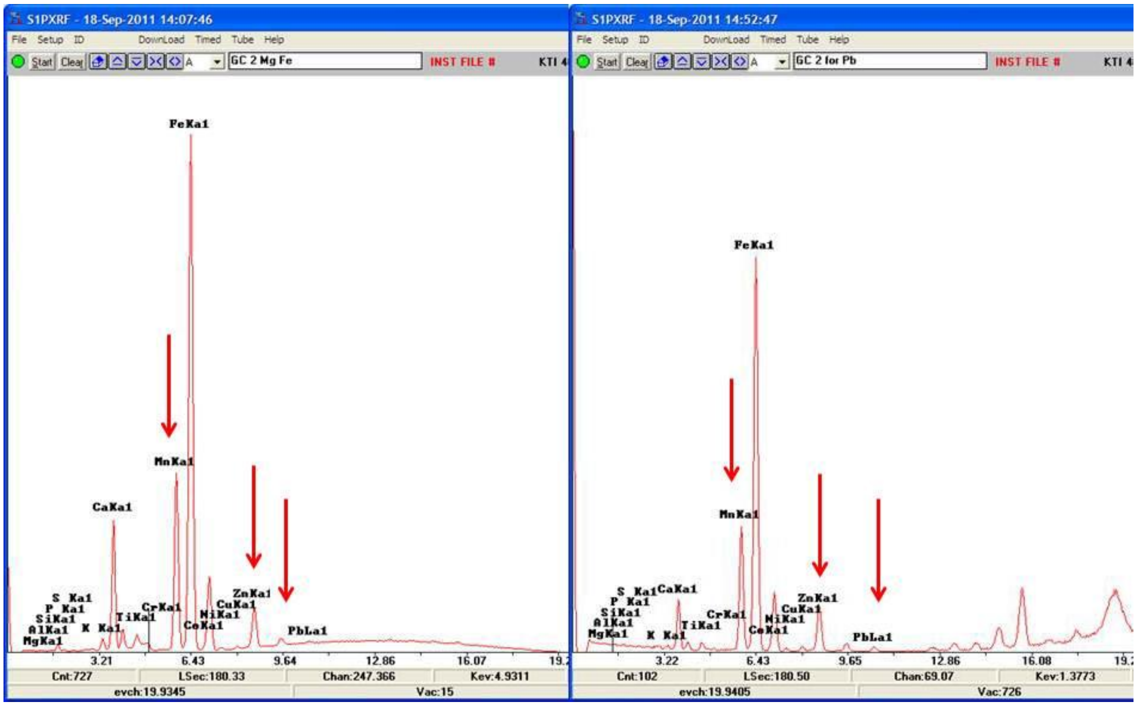

Figure 9. X-ray fluorescence spectra from Giboney Cave (urban) showing the relative sizes of Mn, Zn, and Pb peaks, denoted by the location of red arrows. Spectrum on left is output for analysis at energy levels for Mg to Fe analysis. Spectrum on right is output for analysis at energy levels for Pb analysis.

sediment metal concentrations. This large channel is bereft of cave life and has a history of pollution entering from the surface. However, sediment in a side passage of Giboney Cave has low total metal concentrations, similar to those at Smallin Cave, and hosts aquatic troglobitic cave organisms, including both crayfish and cave fish (Fig. 10).

Canli and Atli (2003) found that in Mediterranean fish species, higher tissue levels of Zn corresponded to smaller, less fecund fish. This data suggests that the presence of higher levels of Zn in sediment could result in decreases in fish populations in cave systems, as metals proliferate through the food chain. In addition, specific adaptations to low-energy cave environments (e.g. low metabolic rates, lower production of metallothionein which removes metals from tissue) make bioaccumulation of heavy metals an area of special concern in subterranean ecosystems (Dickson *et al.*, 1979). The potential for negative impacts from metal contamination is magnified by the longer lifespan associated with specific adaptations to the low energy cave environment (Dickson et al., 1979).

Potential explanations for variations in sediment metal concentrations include: 1) Metals derived from trace amounts of base metal sulfides associated with the Tri-States Mississippi Valley-Type (MVT) Zn-Pb district; 2) metals originating in sewage from human or animal impacts; 3) metals from the removal of metals from sediments.

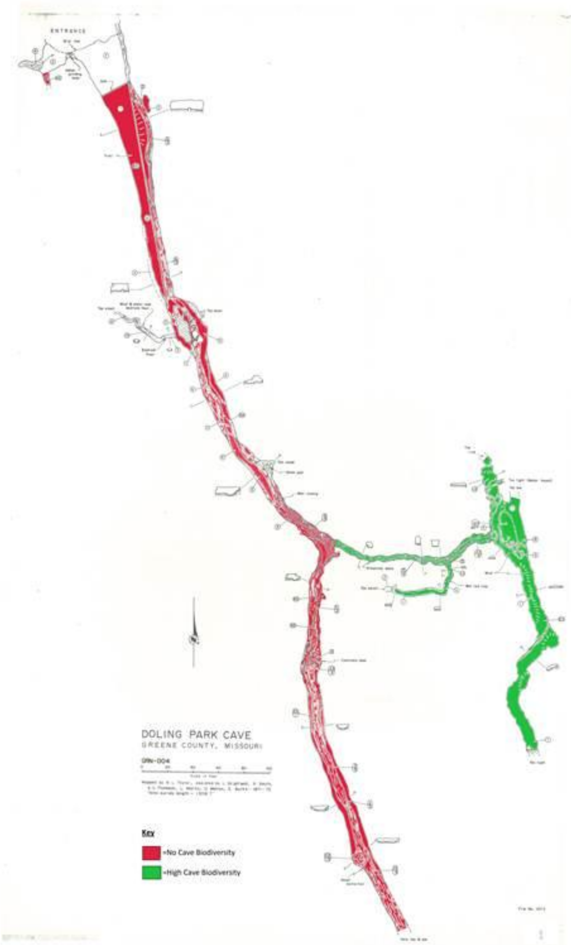

Figure 10. Map of Giboney Cave, also called Doling Park Cave, color coded for sediment chemistry. Sediment from passages coded green are low in Zn, Mn, and Pb and are in areas known to host benthic troglobitic fauna. Sediment from passages coded in green are high in Zn, Mn, and Pb, and are barren of benthic troglobitic fauna.

1. Metals from Sulfide Minerals of the Tri-States District

The Tri-States mineral district extends from near Ash Grove, Missouri west

introduced by industrial processes including fuels and fuel spills; or 4) variation resulting to Baxter Springs, KS, and south to Picher, OK (Fig. 11). Mineralization in the district primarily included sphalerite, galena, and chalcopyrite associated with dolomite and quartz (Brockie *et al.*, 1968). It is possible that non-economic concentrations of base metal sulfides are hosted in the Burlington Limestone. However, no mineralization was visible in any of the caves, and no sulfide minerals were visible upon inspection of sediments under binocular microscope.

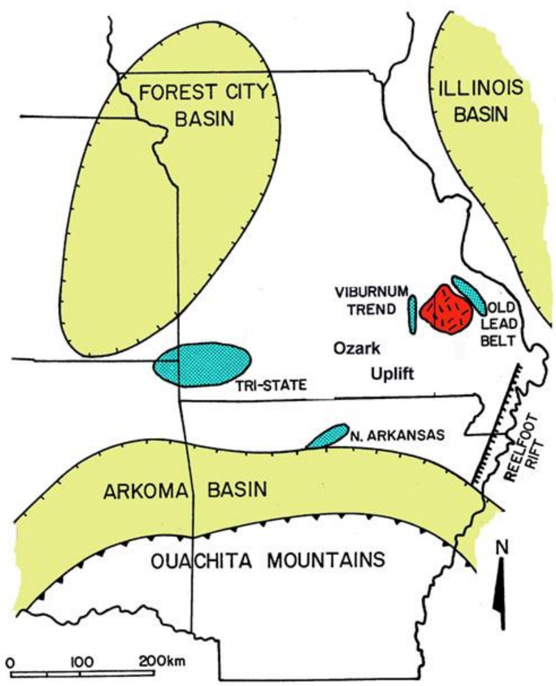

Figure 11. Map showing the location of major mineral districts in the southern half of Missouri. The Tri-States district is in the far southeastern portion of the map area (after Gregg et al., 1992).

2. Metals from raw waste

Both Giboney Cave and the Ruark Caves have been impacted by untreated animal waste. Giboney Cave once acted as an open sewer for portions of Springfield, MOS (Gouzie, personal communication). The Ruark Caves are on property that has been continuously used as a beef cattle operation for more than a century. It is well known that heavy metal contamination is a primary concern associated with sewage (e.g. Lagerwerff *et al.*, 1976; Chang *et al.*, 1983). It is possible that Zn and Pb originate with sewage sludge or in animal waste. However, other metals commonly associated with sewage sludge (e.g. Cd, Cu) either were not present or were present at concentrations below the detection limit of the instrument.

3. Metals from industrial processes

Neither Giboney Cave nor the Ruark Caves are situated in heavily industrialized watersheds. Light industrial use is common in north Springfield, and includes a larger industrial dairy operation and numerous retail outlets. No industry has ever been present in the area associated with the Ruark Caves. Graney *et al.* (1995) showed that lead from gasoline sources can be detected in lake sediments. It is possible that Pb in the rural and urban caves is a result of agricultural and automotive use of leaded gasoline. The presence of Pb from gasoline would imply long residence times and very slow sedimentation rates in cave systems. However, sedimentation rates vary widely depending on the characteristics of the surface watershed (e.g. Fichez, 1990; Granger *et al*., 2001).

4. Variation Resulting from Removal of Metals

It is possible that the variation of metal concentrations in sediment results from the removal of metals. Simon *et al.* (2007), showed that organic matter fluxes in cave systems include both particulate organic matter (POC) and dissolved organic matter (DOC) that are generated at the surface. Saiz-Jiminez and Hermosin (1999) found that DOC in dripping waters in Altamira Cave included components derived from lignin. In addition, humic and fulvic acids account for up to 60% of dissolved organic carbon in aquatic environments (Frimmel *et al.*, 2008). Einseidl *et al.* (2007), showed that it is possible for these organic acids to persist for decades in karst systems. Organic acids are well known as chelating agents and commonly are used to remove heavy metals from contaminated soils (e.g. Wasay *et al.*, 1998). It is possible that the organic acids in karst systems act as chelating agents, stripping metals from cave sediment as water flows through the cave system. When more organic acids are present, metal concentrations in sediment will be lower. With acids making up at most 60% of organic carbon, it is possible that the remaining carbon provides nutrients to the cave ecosystem. If this is the case, metal concentrations in sediment can be an indicator of those cave systems which are capable of supporting life, making XRF analysis a safe, rapid, and inexpensive mechanism by which to identify these systems.

DIRECTION OF FUTURE RESEARCH

The results of this study present several interesting avenues for research. Analysis of the mineral composition of cave sediment could provide insight into the sources of Zn, Mn, and Pb in cave sediments. The apparent correlation between Zn and Mn concentrations and troglobitic fauna bears closer scrutiny. It is possible this apparent relationship is an artifact of sample size. Investigating this relationship in other caves may provide a statistically robust data set. If this relationship holds, it may be possible to utilize this non-invasive technique as a first estimate of the health of cave ecosystems. In this case, the technique could help cave biologists focus biodiversity surveys on those caves or portions of caves that would be more likely to host cave fauna. The link between the geospatial distribution of surface land use to subsurface sediment chemistry remains unclear. Regionally extensive studies of the chemistry of subsurface sediment could provide important clues as to the extent and impact of surface land use changes on subterranean ecosystems.

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