Fall 2020

Micro-analysis of contaminants in suspended load and bank deposits from the Mineral Fork Creek Watershed in Potosi, Missouri, 2019-2020

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Recommended Citation

Miller, William Joseph, "Micro-analysis of contaminants in suspended load and bank deposits from the Mineral Fork Creek Watershed in Potosi, Missouri, 2019-2020" (2020). *Masters Theses*. 7968.
https://scholarsmine.mst.edu/masters_theses/7968

MICRO-ANALYSIS OF CONTAMINANTS IN SUSPENDED LOAD AND BANK DEPOSITS FROM THE MINERAL FORK CREEK WATERSHED IN POTOSI, MISSOURI, 2019-2020

by

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A THESIS

Presented to the Graduate Faculty of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

in

GEOLOGICAL ENGINEERING

2020

Approved by:

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ABSTRACT

There are rising concerns pertaining to water contamination produced by toxic heavy metal contaminants such as lead and zinc. For this study, lead, zinc, and barite are three identified contaminants currently threatening Missouri water supplies. A micro-analysis of the amounts of lead, zinc, and barite in the water of Mineral Fork Creek was conducted, involving both field and laboratory work. The purpose of the study was to determine the levels of lead, zinc, and barite contaminants, contributing to Big River, by Mineral Fork Creek, in Potosi Missouri, Washington County.

This research study uses a quantitative micro-analysis approach to determine the levels of contamination of lead, zinc, and barite found in the Mineral Fork Creek watershed. A total of 95 suspended sediment samples were collected and analyzed using X-ray fluorescence (XRF) to identify the amounts of lead, zinc, and barite minerals. A total of 72 sediment samples were collected from streambanks. Over the duration of the study, water levels were recorded at 20 minute intervals. A total of 167 soil samples were collected July 7, 2020 to September 26, 2020.

The results of this study indicate that there are no direct relationships between rainfall events and the amounts of metal and clay minerals present in Mineral Fork Creek. The results also suggest that there is no relationship between the water discharge and amounts of metal and clay minerals present in Mineral Fork Creek. The analysis suggests a possible relationship between the amounts of metal and clay minerals present, the pH level of the water, and the water discharge.

ACKNOWLEDGMENTS

First and foremost, thank-you GOD for providing me an opportunity to complete this project. I would like to personally and sincerely thank my advisor, Dr. Katherine Grote, for helping and guiding me through this tremendous, yet daunting journey. I would also like to thank my advisory committee, Dr. David J. Rogers, and Dr. David J. Wronkiewicz for their support. A note of thanks goes to Ms. Lyndsey Bennett, Mr. John Schmacher, and Mr. Austin Kochis of the U.S. Geological Survey (USGS) Office, at Rolla, Missouri for helping with this research study. A special note of thanks to Ms. Claire Croley, Ms. Ashton Vonnahme, and Mr. Merrick Ackert for helping collect samples.

Finally, I would like to thank my family, to my Dad, Mr. Billy D. Miller, Jr., who always had my back, as we trampled through the Missouri streambeds, and to my Mom, Dr. Michelle A. Miller who never lost faith in me or in my ability to finish this project. Without the love and support of my entire family, including my Grandmother and my sister, Olivia, I would never have made it. Thanks again, for all the love, hugs, encouragement, and support.

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1. INTRODUCTION

1.1. GENERAL INTRODUCTION

In September 2019, the U.S. Geological Survey Office, Rolla, Missouri, proposed a joint research project to determine levels of barite, and other contaminants contributing to Big River, specifically by Mineral Fork Creek, in Potosi, Washington County, Missouri. There are concerns pertaining to water contamination produced by toxic heavy metal contaminants such as lead and zinc. For this study, lead, zinc, and barite are three identified contaminants currently threatening Missouri water supplies. A micro-analysis of the amounts of lead, zinc, and barite in the water of Mineral Fork Creek was conducted. This study included both field and laboratory investigation.

1.2. PURPOSE AND SCOPE

The purpose of this study was to determine levels of lead, zinc, barite and other contaminants contributing to Big River, by Mineral Fork Creek, in Potosi, Washington County, Missouri. The hypothesis of this study is that the amount of lead, zinc, and barite present in the water increases as water travels further downstream and increases after a rain event. Lead and zinc are heavy metals and toxic to wildlife and humans. Likewise, as hazardous, barite (barium sulfate), when falling out of suspension in the water, fills beds of rivers, dams, and lakes damaging wildlife habitats.

1.3. THESIS ORGANIZATION

This thesis consists of five sections. Section 1 contains the general introduction and overarching purpose of this study. Section 2 contains the literature review purposefully related to historical mining activity in the Barite District region, an examination of rainfall and contaminant correlations, and finally, a review of the specific contaminants of lead, zinc and barite and related impacts. Section 3 outlines the research methodology used to perform a quantitative micro-analysis to include site selection, installation of the samplers, sampling methods, lab analysis, data collection and data summary. Section 4 provides the results and findings of the study; a sampling overview; a statistical analysis of the study; the sampling schedule; the passive sampling data; a comparison of different watersheds; a comparison of sediment samples before and after rainfall events; a depth comparison; the relationship between contaminant load and discharge; and a section summary. Finally, Section 5 describes all conclusions and future recommendations from this research study.

2. LITERATURE REVIEW

2.1. GENERAL INTRODUCTION

Mining continues to be commonplace in some parts of Missouri and as a result, the earth's surface is left exposed to elevated levels of contaminants. These contaminants are most spread via rainfall, surface runoff, and groundwater flow. For the purpose of this literature review, the specific contaminants of lead, zinc, and barite will be presented, discussed, and analyzed. Heavy metals, lead and zinc are both toxic to humans and wildlife alike[1], while barite is a clay mineral[2] that damages water bodies[3].

This literature review is detailed by three major sections; first, Missouri mining, followed by Rainfall and Contaminant Correlations, and finally, Contaminants and the Impacts. Missouri mining is further broken into subsections of 1.) Historical mining activity in the Barite District of Missouri, 2.) The contribution of waterborne contaminants, and finally 3.) A review of tailings and contaminant containment. The second major section contains Missouri Rainfall and Contaminant Correlations. The final major section of Contaminants and the Impacts, provides an overview of specific heavy metals of 1.) Lead, and 2.) Zinc and 3.) Barite, the focus of this study.

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[1] Environmental Protection Agency (EPA). Rules of Department of Natural Resources: Division 20-Chapter 7 -10 CSR 20-7.010 -10 CSR 20-7.050. July 28, 2020. Website: https://www.epa.gov/sites/production/files/2015-09/documents/mowqs.pdf#page=26.

[2] González-Sánchez, Francisco, et al. "Geological Setting and Genesis of Stratabound Barite Deposits at Múzquiz, Coahuila in Northeastern Mexico." *Ore Geology Reviews*, vol. 81, 2017, pp. 1184-1192.

[3] Crook, A. R. "Missouri Lead and Zinc Regions Visited by the Geological Society of America." *Science*, vol. 19, no. 474, 1904, pp. 197-198.

2.2. MISSOURI MINING RESEARCH AND CONTAMINANT MIGRATION

The presence of lead was first documented in Missouri as early as 1700 by French Missionaries. Fr. Jacques (James) Gravier, a French Jesuit missionary, wrote of his travels, about the potential of lead mining along the famous Meramec River. One of, if not the first, documented mines in Missouri, *Mine La Motte*, was established in 1715 along Old Mines Creek[4] and continued production until closure in the mid-1950s. Originally, mines were established wherever ore was easily and conveniently accessed, thus mining activity quickly spread throughout the state of Missouri beginning from, what would later become Washington County. Washington County is the seat of this research study.

2.2.1. Historical Mining Activity in the Barite District. Lead mining activity in Missouri began in the Barite District in 1715[5]. The oldest, recorded barite mine in Missouri was founded in 1872. Barite mines were not frequently documented, so it is possible many mines were founded prior to 1872. Zinc mining activity in Missouri began soon after the American Civil War, most notably from the Valles Mines[6] in the Southern Barite District. Before the war, Zinc extracted from mines was disposed of using a variety of methods, to include tailings piles and tailings ponds. These unwanted materials became a source of contamination for Missouri waterways[7].

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[4] Mugel, Douglas N., Geology and Mining History of the Southeast Missouri Barite District and the Valles Mines, Washington, Jefferson, and St. Francois Counties, Missouri. *U.S. Geological Survey Scientific Investigations Report* 2016–5173. Reston, Virginia : U.S. Department of the Interior, U.S. Geological Survey, 2016.

[5] Ibid.

[6] Ibid.

[7] *The Ozarks in Missouri History : Discoveries in an American Region*, edited by Lynn Morrow, University of Missouri Press, 2013. ProQuest Ebook Central, https://ebookcentral-proquest-com.libproxy.mst.edu/lib/umr-ebooks/detail.action?docID=3440842.

2.2.2. Contribution of Waterborne Contaminants. While lead, zinc, and barite are naturally present in Missouri waterways[8], each the concentrations of these contaminants are generally below regulatory levels. When lead and zinc are introduced in larger amounts, potentially from tailings piles typically transported by rain runoff, the contaminants create toxic and dangerous circumstances[9]. To one extreme, where there are extremely high concentrations of contaminants, the water will be toxic to all lifeforms that consume and reside within the water. Likewise, if only slightly elevated concentrations of aforementioned heavy metals, the toxicity may kill off the microorganisms residing in the water. The death of microorganisms creates a vacuum in the food chain, therefore starving off the creatures that would normally feed on the microorganisms. This disruption of the food chain can potentially, cause severe damage to the ecosystem, the environment, and the animals that live there.

Like lead and zinc, barite is also a hazard to waterways. Normally, if barite remains in suspension of the water, it is not an issue. But, if the water slows, the barite will fall out of suspension and settle on the bed of the body of water. In Missouri, there are many locations where water can naturally slow, such as the widening of a stream, a river feeding into lake, or the approach towards a dam[10]. The presence of a large amount of barite or any combination of clay minerals on the bed of any body of water, is a major

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[8] Besser, John M., et al. "Ecological Impacts of Lead Mining on Ozark Streams: Toxicity of Sediment and Pore Water." *Ecotoxicology and Environmental Safety*, vol. 72, no. 2, 2008, pp. 516-526.

[9] Besser, John M., et al. "Toxicity of Sediments from lead–zinc Mining Areas to Juvenile Freshwater Mussels (Lampsilis Siliquoidea) Compared to Standard Test Organisms." *Environmental Toxicology and Chemistry*, vol. 34, no. 3, 2015, pp. 626-639.

[10] Besser, John M., et al. "Biomonitoring of Lead, Zinc, and Cadmium in Streams Draining Lead-Mining and Non-Mining Areas, Southeast Missouri, USA." *Environmental Monitoring and Assessment*, vol. 129, no. 1, 2007, pp. 227-241.

flooding concern[11], as the barite occupies volume that would otherwise contain water, as such, this leads to an increase of area flooded during floods[12].

Barite can also cause problems with manmade structures in the water, such as canals and dams. In canals, barite causes similar problems to that which occur in natural water bodies, however in dams, barite differs. Large amounts of barite and other clay minerals can cause dams to structurally fail, leading to a catastrophe. The contaminants, lead, zinc, and barite, potentially derived from unwanted tailings piles and subsequently transported by rain runoff, form lethal[13] and unsafe conditions.

2.2.2.1. Contaminants: Release and storage. Missouri soil and groundwater have become contaminated by the mining industry. Heavy metal contaminants provide a substantial chemical risk and hazard for being released back into environment[14]. There are various ways that contaminants are released and stored into the soil, air and groundwater. Historically, unregulated mining greatly contributed to a harmful release of contaminants into Missouri soils and groundwater. For the purpose of this study, open pit mining, underground mining, in situ leach mining, heap leaching, brine mining, radionuclides, and dust and metal mining exposure are some of the ways that mining contaminants were released and stored in the soils and waters.

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[11] Poulton, B.C., Allert, A.L., Besser, J.M. *et al.* A macroinvertebrate assessment of Ozark streams located in lead–zinc mining areas of the Viburnum Trend in southeastern Missouri, USA. *Environ Monit Assess* 163, 619–641 (2010). https://doi-org.libproxy.mst.edu/10.1007/s10661-009-0864-2.

[12] Pal, Sandip, Temple R. Lee, and Nicholas E Clark. "The 2019 Mississippi and Missouri River Flooding and its Impact on Atmospheric Boundary Layer Dynamics." *Geophysical Research Letters*, vol. 47, no. 6, 2020, pp. n/a.

[13] National Academies of Sciences, Engineering, and Medicine, et al. *Investigative Strategies for Lead-Source Attribution at Superfund Sites Associated with Mining Activities.* National Academies Press, Washington, 2017, doi:10.17226/24898.

[14] Wuana, Raymond A., and Okieimen, Felix E.,"Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation", *International Scholarly Research Notices*, vol. 2011, Article ID 402647, 20 pages, 2011. https://doi.org/10.5402/2011/402647.

According to the Missouri Department of Natural Resources[15], mining of lead and barite was predominantly accomplished using small pits, hand mining, and later mechanized mining. Both lead and barite were originally removed from the rock host by hand mining and cleaning with tools such as picks, shovels, and sledge hammers and later mechanized mining shovels and front-end loaders by drilling and blasting. Lead was released back into the environment when galena fines remained with the barite and the waste was used to fill small pits or shafts. Lead was then unintentionally reintroduced back into the environment through runoff and precipitated back into the earth via the water cycle. Lead is found as a suspended sediment because of the infiltration of water across the earth's soil. Barite naturally exists as a component of clay. Barite was commonly used in oil drilling mud. As with the production of barite, galena was a by-product. It is important to note, Washington County, once held the highest barite production record for the nation and the world. Barite is released into the environment through the water cycle. Barite is frequently found as a suspended sediment due to its natural proximity to the water as clay.

Mining of zinc was accomplished using drilling and blasting methods. Using these methods, zinc was removed from the rock host and brought to the surface for crushing, grinding, and floatation to produce a concentrate. Zinc was released into the environment and into the water in the same manner as lead and barite. Zinc is found as a suspended sediment because of the infiltration of water across the earth's soil.

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[15] Missouri Department of Natural Resources, *Missouri Lead Mining History by County*, Washington County Barite District. Website: https://dnr.mo.gov/env/hwp/sfund/lead-mo-history-more.htm.

Soil acts as a “basin” for heavy metals to be released back into the environment, where heavy metal contaminants remain present for long periods of time[16] or until released back into the ecosystem. Heavy metals are stored within the basins and may be chemically altered when reintroduced back into the environment through the transport of water. Impacts of mining on surface and groundwater can be directly attributed to “spill erosion, sedimentation, and disturbance on hydrological cycle and rainfall[17].”

Lead and zinc can both be dissolved and transported in water. Once dissolved in the water, there are two key components controlling when the lead and zinc will sorp out of the water; flow velocity and the acidity. Lower flow rates allow for the dissolved metal to sorp more readily. When water has a higher acidity, zinc will sorp preferentially before lead. In turn, when water has a lower acidity, lead will sorp preferentially before zinc.

2.2.2.2. Contaminants: Altered geochemically. Changes or alterations of heavy metal contaminants from their original chemical forms (speciation) and bioavailability (the ability to be absorbed) are potential and probable[18]. The bioavailability of a contaminant is dependent upon the characteristics of the soil, the site, and the water. Specific to this study, galena (PbS) and its oxidization product, anglesite ($PbSO_4$) are the typical forms of lead associated with mining waste found in Washington County.

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[16] Wuana, Raymond A., and Okieimen, Felix E.,"Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation", *International Scholarly Research Notices*, vol. 2011, Article ID 402647, 20 pages, 2011. https://doi.org/10.5402/2011/402647.

[17] Ay, Ugya & Ajibade, Fidelis & Ajibade, Temitope. (2018). Water Pollution Resulting From Mining Activity: An Overview. https://www.researchgate.net/publication/326925600_Water_Pollution_Resulting_From_Mining_Activity_An_Overview.

[18] Wuana, Raymond A., and Okieimen, Felix E.,"Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation", *International Scholarly Research Notices*, vol. 2011, Article ID 402647, 20 pages, 2011. https://doi.org/10.5402/2011/402647.

The existence of heavy toxic metals may further be affected by the biodegradation process[19]. Heavy metal contamination of lead and zinc pose high risks and hazards to humans and wildlife and when geochemical alteration occurs there are many other factors to be considered such as rate of generation, oxidation, biological degradation, direct exposure, concentrations, erosion, corrosion, bioavailability of the metal, atmospheric deposition, weathering, permeability of the rock fabric, acid rock drainage or leaching that all must be considered[20]. Most heavy metal mines, located near open water sources, are predicted to have contaminated chemically altered water. This water will likely be acidic with large amounts of dissolved metals present. If the contaminated water escapes into the environment, it can eventually reach an underground aquifer or some other source of drinking water. In this event, it may be years before the aquifer is safe to drink from again, even if treated.

2.2.2.3. Contaminants: Transport through water. Mining activity is known to contribute to ground water contamination. Water sources located near a source of contamination increases the risk of contamination of the water source. Typically, based on the specific physical, chemical, and biological properties of a contaminant, when released into an ecosystem, the contaminant may be transported through an aquifer similar to the movement and direction of groundwater. Due to slow movement of groundwater, contaminants generally, remain concentrated and are transported along the same path.

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[19] Ibid.

[20] Tchounwou, Paul B et al. "Heavy metal toxicity and the environment." *Experientia supplementum (2012)* vol. 101 (2012): 133-64. doi:10.1007/978-3-7643-8340-4_6

Contamination also occurs when rainfall leaches soluble minerals from mine tailings into the groundwater below. Heavy metal contaminants are commonly introduced into water systems by unregulated acid mine drainage systems in contact with soil, rocks, and groundwater. Transportation, of contaminants through water, is dependent on many factors, such as the contaminant properties, the amount or size, the solubility, the density and velocity of the water. Contaminants of this study, lead, zinc and barite are easily transported through water and fractures in rock formations.

Once heavy metal contaminant comes in contact with the water, both lead and zinc are generally soluble in soft, slightly acidic water. According the Missouri Department of Natural Resources, the groundwater of Washington County, Missouri, has an average pH value of 8.1 and is thus slightly basic. As rainwater infiltrates the through the ground and into the subsurface it will likely travel through carbonate rock, as it does so, some of the rock will dissolve. The dissolution of carbonate rock into water will cause it to become slightly acidic, this new acidity is how the water is able to dissolve any subterranean lead and zinc it encounters.

Somewhat different, barite, neither absorbs nor dissolves, but remains in suspension and is carried along in the water. However, when the water slows, barite may fall out of suspension and remain in the floor of the basin. Missouri tailings may contain heavy metals, such as lead and zinc. Some abandoned mines were used as waste pits or have been filled with water. To maintain these mines, the mines were sometimes pumped, and this pumping may cause an upward migration of contaminated groundwater, posing an additional threat to all nearby water sources.

2.2.2.4. Relationship between discharge and sediment transport. Sediment discharge, sometimes referred to as the “sediment-transport rate”, can be defined as the amount of sediment that is moved by a stream in a prescribed amount of time that can be measured by quantity; such as volume or weight. Stream discharge can be determined by the “quantity (volume) of water passing by a given point in a certain amount of time.” Water flow, often referred to as water discharge, is an important element of sediment transport. Stream discharge can be calculated as $Q = V * A$, where V is equal to the stream velocity and A is equal to the cross-sectional area of the stream. Units of discharge are volume per time (e.g., m^3/sec or million gallons per day, mgpd). Sediment transport is generically defined as the transport of granular particles by fluids.

Sediment transport, sometimes called “sediment load,” does not remain constant and can be influenced by weather, water (both levels and flows) and of course, human intervention. The three ways that contaminants can be transported in streams include in-solution or dissolved load (dissolved ions), in suspension (suspended load, such as fine clay or silt particles), or in the bed load (such as sand and gravel)[21].

2.2.3. Tailings and Contaminant Containment. Tailings are waste material from mining activity. Such waste material can contain trace elements of possibly toxic materials such as heavy metals[22] including lead and zinc. Due to the high mining activity in the Mineral Fork Creek watershed, Washington County, Missouri, there are numerous sources of tailings and subsequently many possible sources of contaminants[23].

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[21] Yuce, Mehmet & Eşit, Musa & Ercan, Burcu. (2018). A Relationship between Flow Discharge, Sediment Discharge and Sub-Basin Areas in Ceyhan Catchment.

[22] Beattie, Rachelle E., et al. "Quantitative Analysis of the Extent of Heavy-Metal Contamination in Soils Near Picher, Oklahoma, within the Tar Creek Superfund Site." *Chemosphere*, vol. 172, 2017, pp. 89-95.

[23] Gutiérrez, Mélida, et al. "Metal Content of Stream Sediments as a Tool to Assess Remediation in an Area Recovering from Historic Mining Contamination." *Minerals (Basel)*, vol. 10, no. 3, 2020, pp. 247.

There are multiple ways to store tailings once extracted from a mine. The two most common storage methods, in Missouri, are tailings ponds and dry stacking. Tailings ponds are usually a manmade area of containment. The manmade containment areas are often comprised of materials indigenous to the local area and are designed to contain the tailings and the slurry. The containment must feature a barrier able to retain water and to prevent any dissolved contaminant from escaping into the ground water.

Another method used to store tailings is dry stacking. Dry stacking involves stacking or assembling the tailings into large piles. If the tailings are extracted from the mine using a slurry, the tailings must first be dewatered. Tailings are most often dewatered using a vacuum or pressure filter. Similar to the tailings pond, the dry stack method must also have employed a containment barrier. The barrier is used to prevent any dissolved contaminants from escaping into the ground, in the event of rain. Rainfall will cause the erosion and corrosion of the present contaminants.

The Mineral Fork Watershed study area has numerous documented and undocumented tailing piles/ponds. The Missouri 2019 Inventory of Mines, Occurrences and Prospects (IMOP) database, found on the Missouri Spatial Data Information Service Open Data Site, contains a partial inventory of mines, occurrences and prospects in Missouri with a published record of 17 documented number of tailings pile/ponds throughout the study area of Potosi, Missouri.

2.3. RAINFALL AND CONTAMINANT CORRELATIONS

Located approximately seventy miles, southeast of St. Louis. Missouri, Washington County is home to two cities: Potosi and Irondale. The larger of the two cities, Potosi was first founded between the years of 1760 to 1780 as a lead mining settlement[24]. According to U.S. Climate Data, the average precipitation for Potosi, Missouri ranges from a low of 2.55 inches in January to a high of 4.82 inches in May. Large amounts of precipitation result in increases to river and streams, and the flow of contaminants in the waterways. One body of water located in Washington County is Mineral Fork Creek in Figure 2.1.

Figure 2.1 Mineral Fork Creek, Potosi, Missouri

Mineral Fork Creek, named for its deposits of lead ore, is a tributary of Big River. Big River, originating at approximately 232 meters in elevation[25], is a tributary of the Meramac River located throughout east-central Missouri. Specific data for the

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[24] Eaton, D., *The Missouri Historical Review*. Vol. 10, No. 3, How Missouri Counties, Towns and Streams Were Named, April, 1916.

[25] Samuel, D.E., Stauffer, J, R., Hocutt, C. H., and Mason, W. T. Jr., 1978. Surface Mining and Fish/Wildlife Needs in the Eastern United States. Proceedings of a Symposium, *U. S. Fish and Wildlife Service,* December 1978. FWS/OBS-78/81, Morgantown, WV. 386.

contamination levels of Mineral Fork Creek and its tributaries does not presently exist. This gap in data supports the need for this research. Mineral Fork Creek, sometimes referred to as *Fourche a Renault* Creek, is a major contributor of not only lead and zinc, but also barite, to Big River[26].

2.4. CONTAMINANTS AND IMPACTS

Missouri watersheds contain a huge variety of contaminating entities and foreign bodies related to mining outputs. Underground rocks and soils contain heavy metals such as lead, arsenic, cadmium, zinc, and a variety of others. Because Missouri mining was so prolific beginning in the early 1800's, the Missouri soils and waterways are fertile with contaminants[27]. The focus of this research study involves a detailed examination of the heavy metals of lead and zinc and barite in Missouri waterways, thereby examining the future impacts on the ecosystem.

2.4.1. Heavy Metals (Lead and Zinc). The heavy metal, lead, most commonly exists in Missouri in its mineral form, Galena (PbS), and is often sought after for industrial uses such as batteries, protective coatings, paints, and weights. As the result of high amounts of mining throughout southern Missouri, particularly in Washington County, there are large amounts of Galena readily available at the surface and in the shallow subsurface of the ground. The resulting elevated presence of lead is also evident

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[26] Pavlowsky, Robert T., et al. "Legacy Sediment, Lead, and Zinc Storage in Channel and Floodplain Deposits of the Big River, Old Lead Belt Mining District, Missouri, USA." *Geomorphology*, vol. 299, 2017, pp. 54-75.

[27] Mugel, Douglas N., Geology and Mining History of the Southeast Missouri Barite District and the Valles Mines, Washington, Jefferson, and St. Francois Counties, Missouri. *U.S. Geological Survey Scientific Investigations Report* 2016–5173. Reston, Virginia : U.S. Department of the Interior, U.S. Geological Survey, 2016.

in the wildlife and waterways in the effected regions[28]. In regions where there are high concentrations on lead present in the ground and water, there will be reduced populations of wildlife.

The primary concern involving the elevated presence of Galena and thus lead, is lead poisoning[29]. Lead poisoning can be derived from a variety of sources including inhalation, ingestion, and extended physical contact[30]. The symptoms of lead poisoning vary between children and adults, but some of the most concerning, are the delayed mental and physical development, seizures, premature birth, high blood pressure, miscarriage, and, in some extreme cases, death[31].

Zinc is another heavy metal, commonly found throughout Missouri, in its mineral form sphalerite (ZnS). Like galena, sphalerite is also extensively mined throughout Missouri for uses in industrial and manufacturing settings. Unlike galena, zinc is a common vitamin in supplements for human health, though extreme amounts can cause nausea, indigestion, and headaches[32]. Definitively, both lead and zinc, when found in high doses, present high risk, but these two heavy metals are not the only contaminants filling Missouri waterways. Barite is another mineral which can damage the ecosystem.

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[28] Beyer, WN; Dalgarn, J; Dudding, S; French, JB; Mateo, R; Miesner, J; Sileo, L; Spann J; "Zinc and Lead Poisoning in Wild Birds in the Tri-State Mining District (Oklahoma, Kansas, and Missouri)." *Archives of Environmental Contamination and Toxicology*, U.S. National Library of Medicine, 2005, pubmed.ncbi.nlm.nih.gov/15657812/.

[29] National Academies of Sciences, Engineering, and Medicine, et al. *Investigative Strategies for Lead-Source Attribution at Superfund Sites Associated with Mining Activities.* National Academies Press, Washington, 2017, doi:10.17226/24898.

[30] Zhang, Xiuwu, et al. "Impacts of Lead/Zinc Mining and Smelting on the Environment and Human Health in China." *Environmental Monitoring and Assessment*, vol. 184, no. 4, 2011, pp. 2261–2273. doi:10.1007/s10661-011-2115-6.

[31] Ibid.

[32] Ghorbel, Manel, et al. "Health Risk Assessment for Human Exposure by Direct Ingestion of Pb, Cd, Zn Bearing Dust in the Former Miners' Village of Jebel Ressas (NE Tunisia)." *European Journal of Mineralogy*, vol. 22, no. 5, 2010, pp. 639–649., doi:10.1127/0935-1221/2010/0022-2037.

2.4.2. Barite. Barite ($BaSO_4$)[33], which is extremely common and widely mined throughout Missouri, is a clay mineral. The Big River Basin, and thus the Mineral Fork Creek Watershed, contains numerous barite mines[34]. Missouri barite mines were typically strip-pit mines as opposed to deep-shaft mines[35]. Reports of large areas of soil exposed to erosion, the presence of barite strip-pit mines, and the abundance of tailing piles contribute to barite siltation throughout Missouri.

Barite has been used for drilling fluid, ceramics, glass, explosives, medicine, and numerous other applications. Barite has many industrial uses as well including, but not limited to, the production of paints, concrete, drilling mud, and X-Ray and Gamma Ray shielding. In a natural state, barite is harmless to people and wildlife. Despite containing the heavy metal Barium, barite is not considered toxic under Section 313 of the Emergency Planning and Community Right-to-Know Act of 1986. Barite can be ingested with no bodily harm. However, if barite is inhaled as a powder, it can cause Silicosis[36]. If left untreated, the disease causes scarring of the lung tissue and symptoms such as bronchitis. Silicosis can develop into life threatening illnesses of tuberculosis, lung cancer, and potentially death[37].

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[33] González-Sánchez, Francisco, et al. "Geological Setting and Genesis of Stratabound Barite Deposits at Múzquiz, Coahuila in Northeastern Mexico." *Ore Geology Reviews*, vol. 81, 2017, pp. 1184-1192.
[34] Samuel, D.E., Stauffer, J, R., Hocutt, C. H., and Mason, W. T. Jr., 1978. Surface Mining and Fish/Wildlife Needs in the Eastern United States. Proceedings of a Symposium, U. S. Fish and Wildlife Service, December 1978. FWS/OBS-78/81, Morgantown, WV. 386.
[35] Ibid.
[36] Shahab, B., Bashir, E., Kaleem, M. *et al.* Assessment of barite of Lasbela, Balochistan, Pakistan, as drilling mud and environmental impact of associated Pb, As, Hg, Cd and Sr. *Environ Earth Sci* **75,** 1115 (2016). https://doi.org/10.1007/s12665-016-5916-7.
[37] "Silicosis Symptoms, Causes, and Risk Factors." *American Lung Association*, www.lung.org/lung-health-diseases/lung-disease-lookup/silicosis/symptoms-diagnosis.

3. QUANTITATIVE RESEARCH METHODOLOGY

3.1. DATA ACQUISITION

Data was compiled through the accumulated measurement of the presence of lead, zinc, and barite. Given data was subsequently processed using X-Ray Fluorescence (XRF) technology and analyzed for numerical and statistical inferences. Quantitative research was selected to specifically identify and micro-analyze contaminant levels found in Mineral Fork Creek. This section is outlined by an analysis of the site selection, sampler construction and installation, sampler locations, sediment collection, laboratory analysis, XRF processing, and concludes with a data acquisition summary.

3.2. MICRO-ANALYSIS

This environmental study uses a quantitative micro-analysis approach. A microanalysis involves a physical or chemical analysis on a small scale or small volume of data resulting in highly focused results. Microanalysis is most appropriate for this study due to time constraints and other specific limitations. This study will determine levels of contamination of lead, zinc, and barite found in Mineral Fork Creek, Potosi, Missouri. A total of 95 suspended sediment samples were collected and analyzed using X-ray fluorescence (XRF) to identify lead, zinc, and barite minerals. XRF, as the name implies, uses X-rays to cause different elements to fluoresce, and this fluorescence is thenceforth measured to determine the amounts of different materials present.

3.2.1. Site Selection. The sampling site locations were chosen based on 1.) The location of tributary confluence, 2.) Ease of access, and 3.) Mining activity. This research study was prepared in coordination and cooperation with the U.S. Geological Survey (USGS), Rolla, Missouri. The map provided below in Figure 3.1 shows the locations of each sampler and mine.

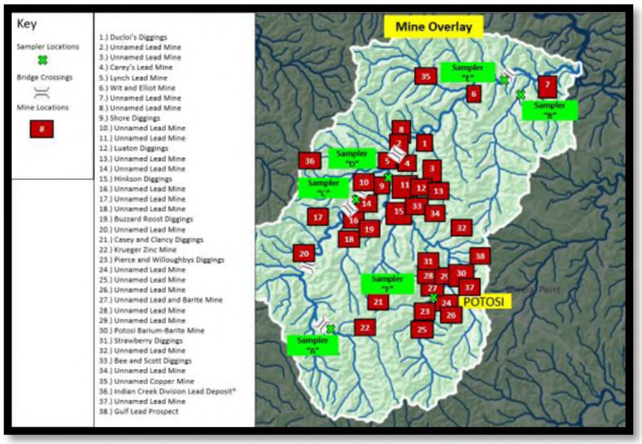
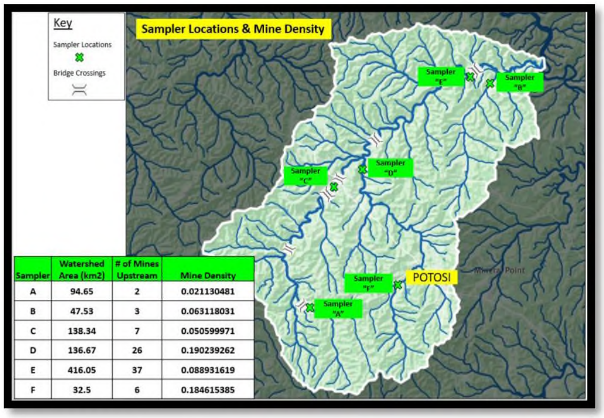


Figure 3.1 Map of Mineral Fork Watershed Mines and Sampler Overlay

The next map, in Figure 3.2, depicts the location of the samplers and the mine density. Site locations were chosen to represent a range of mining densities.



Sampler	Watershed Area (km2)	# of Mines Upstream	Mine Density
A	94.65	2	0.021130481
B	47.53	3	0.063118031
C	138.34	7	0.050599971
D	136.67	26	0.190239262
E	416.05	37	0.088931619
F	32.5	6	0.184615385

Figure 3.2 Map of Sampler Locations and Mine Density

The next map, in Figure 3.3, depicts the location of the samplers in relationship to documented tailing ponds.

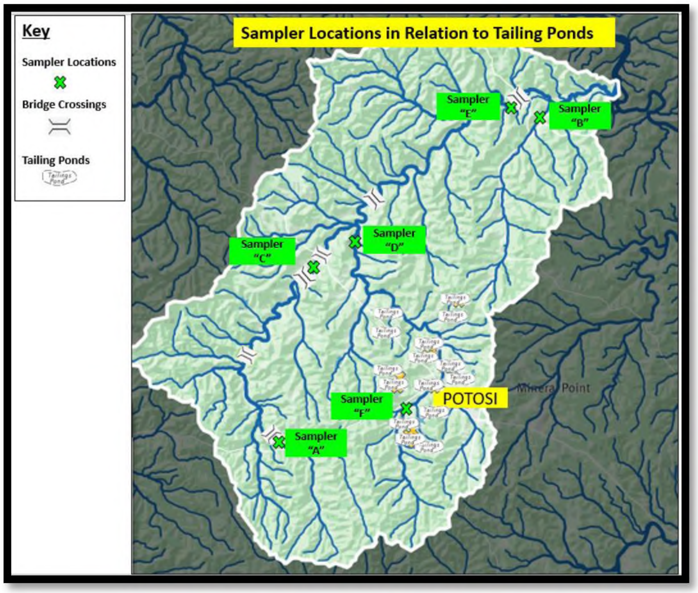


Figure 3.3 Map of Sampler Locations and Tailing Ponds

3.2.2. Sample Collection. Site visits were based on travel to Potosi, Missouri on a bi-monthly basis, or following significant rainfall events. Eight dates of travel and data sampling collection occurred on July 7 and 18; August 1, 15, and 29; September 5, 12, and 26. Due to limitations of the study, samples were installed beginning in June 2020.

3.2.3. Sampler Construction and Installation. Sampler construction included the following items; one-fourth inch (¼") gauge polyvinyl chloride (PVC) pipes of forty-six inches (46") in length, nozzle cones, removable, threaded end caps, hose clamps, 5/6" hex-head screws, PVC cleaner, PVC cement and (galvanized pipe hanging struts) metal poles. The tubes and cones were special ordered by USGS and Missouri S&T. Materials were commercially obtained from Lowe's and Menard's Home and Garden Stores. Figures 3.4 and 3.5 show examples of samplers once installed.

Figure 3.4 Sampler Installation

Figure 3.5 Sampler Identification Markings

The construction of the samplers began with the sample collection tube. Step 1.) Holes were drilled through the tip of the nozzle cone and the center of the removable portion of the end cap. Step 2.) Thread the nozzle cone onto the threaded end of the PVC pipe. Step 3.) Using PVC cleaner, clean the open end of the PVC pipe and the inside of the end cap. Step 4.) Apply cement to the cleaned areas and attach the removable, threaded end cap to the opposite end of the pipe. Step 5.) Once dry, apply markers for identification, write in permanent marker or apply USGS sticker. Each sampling station required two sample collection tubes, these steps were repeated twice for each potential station. Additionally, each station required four pipe clamps and two metal poles as shown in Figure 3.6.

Figure 3.6 Sampler Construction

Once all of the sample collection tubes were assembled, specific locations for sampling were chosen, general locations were predetermined. Ease of access, protection, and detectability were considerations. Sample station location must be reasonably easy to access, considering the terrain, water depth, and distance from available parking. The sampler, while rigid, does require protection from large debris that may flow downstream. Location considerations should be toward one side of the stream and tucked in a small alcove, if possible. Finally, samplers were placed in locations to not be tampered with, not easily seen from the road to avoid any unnecessary attention as demonstrated in Figure 3.7.

Figure 3.7 Sampler Stability Testing

After ideal locations were found, the support structures for the sampling station were assembled on site. Using a post driver, metal poles were driven into the streambed. Two metal poles were required to build the support structure, installed approximately 1.5 feet apart and oriented with the open side toward the closest bank as shown in Figure 3.8. Poles stability was ensured by attempting to rock the pole from side to side.

Figure 3.8 Metal Pole Installation

Sampling collection tubes were then attached to the metal poles using the pipe clamps. The top sampler was attached approximately 4” inches above the surface of the water and the bottom was attached 2” inches below the surface of the water. Pipe clamps were ran through the holes in the metal poles, to horizontally secure the sample collection tube. Clamp screws were adjusted for easy access and maintenance. Both upper and lower sample collection tubes were oriented with the nozzle cone pointed upstream as shown in Figure 3.9.

Figure 3.9 Samplers Oriented Upstream

3.2.4. Sampler Location. The sampler equipment was first prepared and assembled for installation then installed at the prescribed locations listed below. The latitude and longitude for all samplers are depicted in Table 3.1.

Table 3.1 Sampler Latitude/Longitude

SAMPLER	LATITUDE/LONGITUDE
SAMPLER A	37°58’01” N 90°55’20” W
SAMPLER B	38°04’32” N 90°44’22” W
SAMPLER C	38°00’29” N 90°52’50” W
SAMPLER D	38°02’17” N 90°50’24” W
SAMPLER E	38°05’44” N 90°44’52” W
SAMPLER F	37°56’50” N 90°47’58” W

Installation involved a lengthy four-day process. Day 1: Four samplers (A, C, E, & F) were installed using metal poles. Day 2: One sampler (B) was installed using diagonally driven poles. On Day 2, three additional locations for a sixth sampler were scouted, but all sites were ruled unfeasible. Day 3: Sampler (D) was installed using vertical metal poles. Day 4: An additional sampling device was installed at each of the following locations (A, B, C, D, E, and F) for collecting samples of baseline sediment amounts in the water.

Additionally, five crest gages (Water Leveloggers) were installed at Samplers A, B, D, E and F to monitor water levels for water level datalogging. During normally scheduled data collections, two of the Leveloggers were identified as missing from Samplers B and D. At Sampler E, a barometer (Barometric Pressure Logger) was installed to record barometric pressure. During data collection, on September 5, 2020, the barometer at Sampler E was found vandalized, and no data was able to be recovered. During this study, sampling station equipment that was vandalized, lost, or destroyed was reinstalled using a similar process, if possible. A total of 72 bank sediment samples were collected from streambanks. Over the duration of the study, water levels were recorded every 20 minutes.

3.2.5. Sediment Collection. Passive sample collection procedures included the following steps; 1.) Removing the sampler from the stand; 2.) Spraying water into the forward-facing nozzle; 3.) Agitating the sampler, ensuring to coat all inside surfaces with water, while holding both tube holes sealed; 4.) Draining the contents of the tube into a marked and dated, gallon-sized zip-lock plastic bag and sealing the bag; 5.) Replacing and securing the sampler tube onto the stand for future collection; 6.) Transporting the samples to the Missouri S&T University Laboratory for further analysis addressed below and to air dry; 7.) Once enough individual samples were collected, samples were processed, prepared, and presented to the USGS lab for an XRF analysis of the sediments, and finally; 8.) Upon conclusion of this specific research study, Sampler E will remain in-place to facilitate future longer-term studies. All other samplers were removed.

Streambank sampling procedures included a three step process; Step 1.) Using a trowel, samples were collected from the stream banks at each location. Two (2) samples were taken from upstream of the sampler on opposite sides of the bank. Two (2) samples were taken from downstream of the sampler on opposite sides of the bank. Two (2) samples were taken at the sampler on each side of the bank. Step 2.) Samples were stored in a marked, quart size, plastic bag, filling approximately fifty percent (50%) of the bag. The samples were collected to contain as much fine grain particulate as possible. Gravel-sized rocks were avoided. Step 3.) Samples were returned to the University Lab for drying and sieving similar to passive samples.

3.2.6. Laboratory Analysis. After the samples were collected from the sampling stations in the field, the samples were taken to the University Hydrogeology Laboratory located in McNutt Hall. All samples were transported in plastic zip locked bags, in sealed water-tight totes. At the lab, samples were removed and sorted to determine, whether or not, decanting was required. If samples did not require decanting, the samples were spread out on plates to begin a natural drying process.

Samples, that required decanting, were hung above a sink, in the plastic bag first collected in, with contiguous slits cut down the side of the bag to allow water to drain off. The bag slits were perforated where the water above that point was visibly clear of any particulate. Once the sample was mostly free of water, the contents of the bag were carefully transferred to a plate or bowl, depending on the volume. Large volumes of decanted sediments were transferred onto a plate to allow for drying at an adequate rate. Samples with only a small volume of sediments were transferred into a bowl to air dry. A bowl was used for smaller samples to help concentrate the sediments as the drying process occurred.

After samples had fully dried, the samples were prepared to sieve to less than 63 microns. Dried samples were transferred from the bowl or plate to a mortar and pestle. The mortar and pestle were used to break the large clumps of sediment. Extreme care was taken to avoid grinding particulate into an unusable size and to avoid misrepresenting the amounts of fine-grained materials.

Finally, after having been fully dried and processed using a mortar and pestle, the samples were ready to be sieved. The sieves were two-layered, to save time and ensure a large enough sample afterwards. The layers of the sieve consist of Sieve No. 230 and the pan. After the sample was loaded into the sieve, the lid was placed onto the sieve and the sieve was locked into a sieve shaker. The sieve shaker was then powered and allowed to run for no less than two minutes. Once the sieve shaker finished, the sieve was removed and the contents from the pan were transferred into a labeled zip-lock bag. Samples required no further processing and were ready to be transferred to the USGS Office for X-Ray Fluorescence (XRF) analysis.

3.2.7. XRF Processing. Located at the U.S. Geological Survey (USGS), Rolla, Missouri Office, a Delta X-Ray Fluorescence (XRF) Spectrometry Analyzer was used for processing all sediment samples as shown in Figure 3.10. XRF Model number, DPO-4050-C was used for sample processing.

Figure 3.10 XRF Model DPO-4050-C

A USGS representative analyzed all samples in the “soil-environmental mode” and in triplicate. According to the XRF User’s Manual, XRF Spectrometry provides a quantitative analysis of sediments of rapid identification and quantifications of elements over an extensive concentration range. This range includes parts per million (PPM) levels up to 100% by weight. The scan does not damage the sample. Extreme care and caution must be used when operating the XRF system, due to the production of ionizing radiation. The sample processing time is complete in seconds.

Sample were collected, dried, and sieved, prior to submission to the USGS Office. The prepared sample was then placed into a clear plastic bag for analysis. Samples were submitted to the USGS in clear, plastic, marked bags for future processing and identification. The National Institute of Standards & Technology (NIST) Certificate of Analysis Standard Reference Material 2710a and National Institute of Standards & Technology (NIST) Certificate of Analysis Standard Reference Material 2711a were provided as documentation for certification of the XRF equipment.

A trained USGS representative, initially scanned all samples, then between each scan, samples were removed from the test stand, the sediment was moved around, and a scan of a different area of the bag was performed, so as to be more representative of the entire contents of the sample. As recommended by the XRF User’s Manual, sediment samples were scanned in clear plastic bags, therefore the Ba recovery was possibly (-10-20%) of an expected interference.

The XRF is a lightweight, hand-held device that can rapidly identify and quantify elements present in soil sample testing. Prepared samples were prepared as uniform and similar in size for best results. The device was pointed at the sample and scanned for identification. The data information from the scan was then exported for further analysis and interpretations. According to the User's Manual, XRF technology uses "the principle that individual atoms, when excited by an external energy source, emit X-ray photons of a characteristic energy or wavelength". The number of photons of each energy emitted from a sample was then counted for each element present and identified and quantitated.

3.2.8. Data Acquisition Summary. Limitations of this study included the loss of access to U.S. Geological Survey (USGS) equipment from the months of March to June 2020. Due to the COVID pandemic, USGS personnel were placed on telework status with mandatory stay-at-home orders. Additionally, University campus closure and loss of access to buildings, labs, equipment, and personnel were impacted. Initially, in the Fall Semester 2019, an arrangement to emplace samplers in the Spring 2020 was agreed upon with the USGS. Mandatory shelter-in-place Missouri state orders impeded the timely installation of samplers. Additionally, USGS restrictions required approximately 25 samples to gain access to X-Ray Fluorescence (XRF) for processing samples. Limitations of vandalism, theft, and tampering proved to be problematic with the installation and maintenance of sampler stations.

In this section, Quantitative research was selected to collect and analyze numerical data, thereby providing a systematic investigation of particular to contaminants found in the water sampled from Mineral Fork Creek Watershed in Potosi, Missouri. This section was outlined by a discussion of micro-analysis, followed by an analysis of the site selection, sample collection, sampler construction and installation, sampler locations, sediment collection, laboratory analysis, and XRF processing.

4. STATISTICAL MICRO-ANALYSIS RESULTS AND FINDING

4.1. GENERAL INTRODUCTION

This section provides the results and findings, a sampling overview, the statistical analysis of the study, the sampling schedule, the passive sampling data, a comparison of different watersheds, a comparison of sediment samples before and after rainfall events, a depth comparison, and the relationship between contaminant load and discharge. The section concludes with a section summary.

4.2. GENERAL RESULTS AND FINDINGS

The Environmental Protection Agency (EPA), Rules of Department of Natural Resources, Division 20, Clean Water Commission, Chapter 7, Water Quality (10 CSR 20-7) dated July 28, 2020 was used as a baseline for acceptable levels of lead, zinc, and barite found in Missouri waters. According to the EPA, Missouri groundwater regulations stipulates that "Water contaminants shall not cause or contribute to exceedance of Table A1, groundwater limits in aquifers and caves.[38]" Furthermore, "values listed as health advisory levels shall be used in establishing management strategies and groundwater cleanup criteria, until additional data becomes available to support alternative criteria or other standards are established.[39]" Table A1, page 22, establishes the following criteria for lead and barium.

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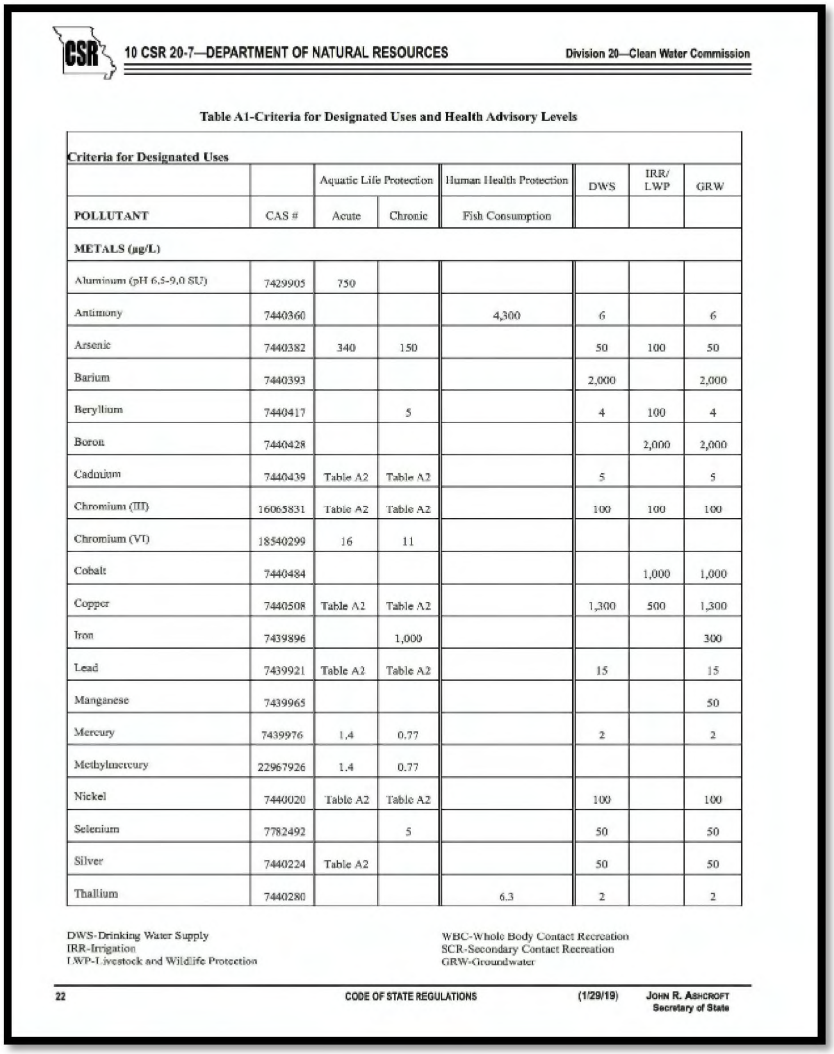
[38] Environmental Protection Agency (EPA). Rules of Department of Natural Resources: Division 20-Chapter 7 -10 CSR 20-7.010 -10 CSR 20-7.050. July 28, 2020. https://www.epa.gov/sites/production/files/2015-09/documents/mowqs.pdf#page=19.

[39] Ibid.

Table 4.1 10 CSR 20-7.050. July 28, 2020[40]



10 CSR 20-7—DEPARTMENT OF NATURAL RESOURCES — Division 20—Clean Water Commission

Table A1-Criteria for Designated Uses and Health Advisory Levels

Criteria for Designated Uses

		Aquatic Life Protection		Human Health Protection	DWS	IRR/ LWP	GRW
POLLUTANT	CAS #	Acute	Chronic	Fish Consumption			
METALS (µg/L)							
Aluminum (pH 6.5-9.0 SU)	7429905	750					
Antimony	7440360			4,300	6		6
Arsenic	7440382	340	150		50	100	50
Barium	7440393				2,000		2,000
Beryllium	7440417		5		4	100	4
Boron	7440428					2,000	2,000
Cadmium	7440439	Table A2	Table A2		5		5
Chromium (III)	16065831	Table A2	Table A2		100	100	100
Chromium (VI)	18540299	16	11				
Cobalt	7440484					1,000	1,000
Copper	7440508	Table A2	Table A2		1,300	500	1,300
Iron	7439896		1,000				300
Lead	7439921	Table A2	Table A2		15		15
Manganese	7439965						50
Mercury	7439976	1.4	0.77		2		2
Methylmercury	22967926	1.4	0.77				
Nickel	7440020	Table A2	Table A2		100		100
Selenium	7782492		5		50		50
Silver	7440224	Table A2			50		50
Thallium	7440280			6.3	2		2

DWS-Drinking Water Supply
IRR-Irrigation
LWP-Livestock and Wildlife Protection

WBC-Whole Body Contact Recreation
SCR-Secondary Contact Recreation
GRW-Groundwater

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Both the Drinking Water Supply (DWS) and Groundwater acceptable level for lead is 15 µg/L or 0.015 PPM. Both the Drinking Water Supply (DWS) and Groundwater acceptable level for Barium is 2000 µg/L or 2 PPM. Table 4.1 also establishes the criteria for Zinc as following.

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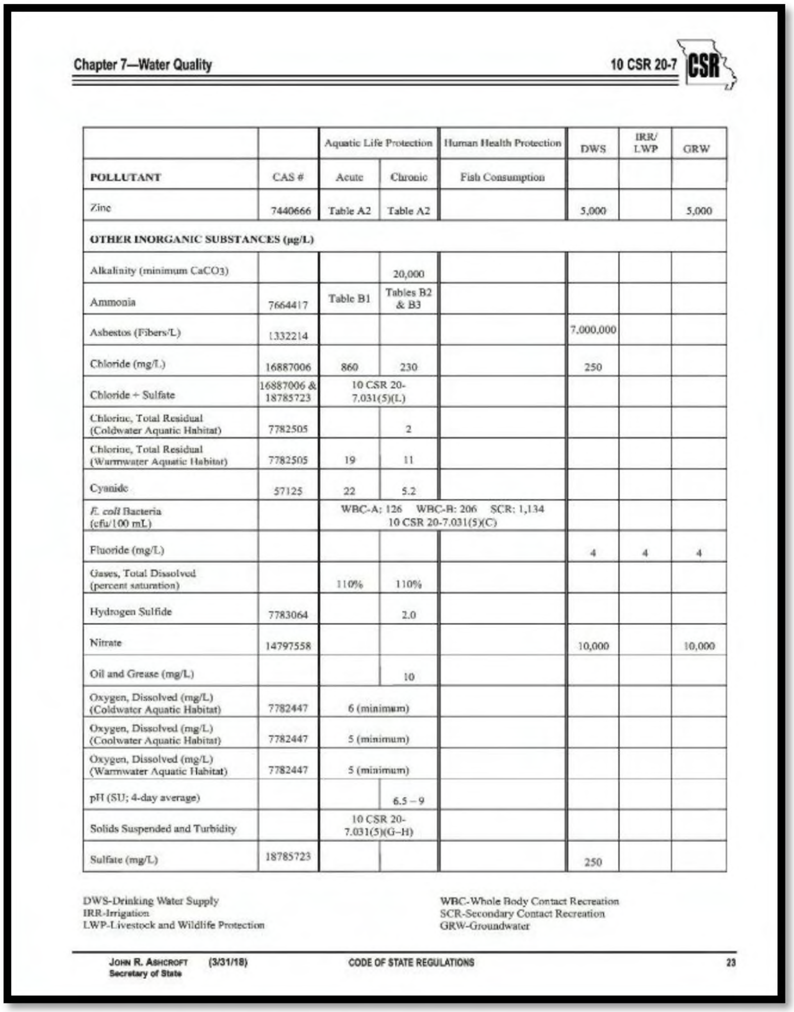
[40] Ibid.

Table 4.2 10 CSR 20-7.050. July 28, 2020[41]



Chapter 7—Water Quality **10 CSR 20-7**

		Aquatic Life Protection		Human Health Protection	DWS	IRR/ LWP	GRW
POLLUTANT	CAS #	Acute	Chronic	Fish Consumption			
Zinc	7440666	Table A2	Table A2		5,000		5,000
OTHER INORGANIC SUBSTANCES (µg/L)							
Alkalinity (minimum CaCO3)			20,000				
Ammonia	7664417	Table B1	Tables B2 & B3				
Asbestos (Fibers/L)	1332214				7,000,000		
Chloride (mg/L)	16887006	860	230		250		
Chloride + Sulfate	16887006 & 18785723	10 CSR 20-7.031(5)(L)					
Chlorine, Total Residual (Coldwater Aquatic Habitat)	7782505		2				
Chlorine, Total Residual (Warmwater Aquatic Habitat)	7782505	19	11				
Cyanide	57125	22	5.2				
E. coli Bacteria (cfu/100 mL)		WBC-A: 126 WBC-B: 206 SCR: 1,134 10 CSR 20-7.031(5)(C)					
Fluoride (mg/L)					4	4	4
Gases, Total Dissolved (percent saturation)		110%	110%				
Hydrogen Sulfide	7783064		2.0				
Nitrate	14797558				10,000		10,000
Oil and Grease (mg/L)			10				
Oxygen, Dissolved (mg/L) (Coldwater Aquatic Habitat)	7782447	6 (minimum)					
Oxygen, Dissolved (mg/L) (Coolwater Aquatic Habitat)	7782447	5 (minimum)					
Oxygen, Dissolved (mg/L) (Warmwater Aquatic Habitat)	7782447	5 (minimum)					
pH (SU; 4-day average)			6.5 – 9				
Solids Suspended and Turbidity		10 CSR 20-7.031(5)(G–H)					
Sulfate (mg/L)	18785723				250		

DWS-Drinking Water Supply
IRR-Irrigation
LWP-Livestock and Wildlife Protection

WBC-Whole Body Contact Recreation
SCR-Secondary Contact Recreation
GRW-Groundwater

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Secretary of State

Both the Drinking Water Supply (DWS) and Groundwater acceptable level for Zinc is 5000 µg/L or 5 PPM.

4.2.1. Streambank Sampling Overview. Various sampling methods were used to collect data. The data is presented in the following manner, first, a statistical analysis of the amounts of lead, zinc, and barite present in the water and the relationship to each

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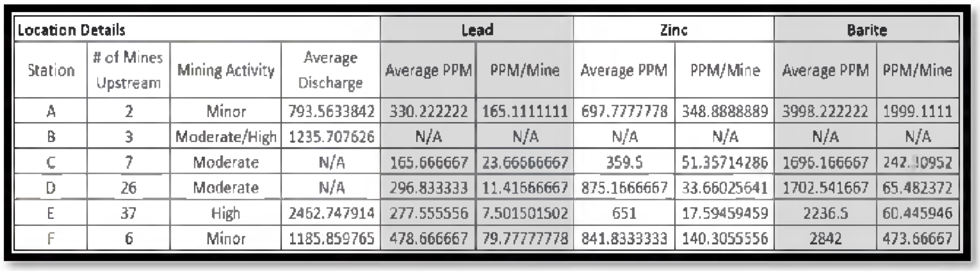
[41] Ibid.

respective number of mines. Then, the sampling schedule, passive sampling, a comparison of watersheds, a comparison of sediment samples before and after rainfall events, a depth comparison, and the relationship between water load and discharge are micro-analyzed.

4.2.1.1. Sampling statistical analysis of sediment. The following analysis table depicts the average amounts of lead, zinc and barite present in the water and the relationship to the respective number of mines. The data suggests that there is no direct correlation between the mining activity upstream of the sampler and the amount of contaminants present in the water. Sample XRF analysis was conducted by the USGS.

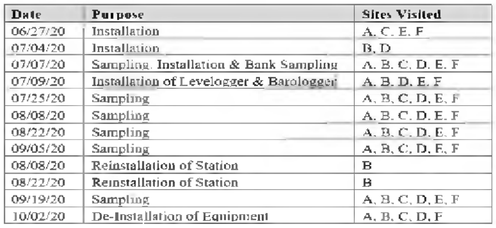
Table 4.3 Sampling Statistics by Sampler



Location Details				Lead		Zinc		Barite	
Station	# of Mines Upstream	Mining Activity	Average Discharge	Average PPM	PPM/Mine	Average PPM	PPM/Mine	Average PPM	PPM/Mine
A	2	Minor	793.5633842	330.222222	165.1111111	697.7777778	348.8888889	3998.222222	1999.1111
B	3	Moderate/High	1235.707626	N/A	N/A	N/A	N/A	N/A	N/A
C	7	Moderate	N/A	165.666667	23.66666667	359.5	51.35714286	1696.166667	242.30952
D	26	Moderate	N/A	296.833333	11.41666667	875.1666667	33.66025641	1702.541667	65.482372
E	37	High	2462.747914	277.555556	7.501501502	651	17.59459459	2236.5	60.445946
F	6	Minor	1185.859765	478.666667	79.77777778	841.8333333	140.3055556	2842	473.66667

4.2.1.2. Sampling schedule. The following table depicts the date of the visits, the purpose of the visits and the site locations visited. Visits included installation, sampling, reinstallation, and de-installation.

Table 4.4 Sampling Schedule



Date	Purpose	Sites Visited
06/27/20	Installation	A, C, E, F
07/04/20	Installation	B, D
07/07/20	Sampling, Installation & Bank Sampling	A, B, C, D, E, F
07/09/20	Installation of Levelogger & Barologger	A, B, D, E, F
07/25/20	Sampling	A, B, C, D, E, F
08/08/20	Sampling	A, B, C, D, E, F
08/22/20	Sampling	A, B, C, D, E, F
09/05/20	Sampling	A, B, C, D, E, F
08/08/20	Reinstallation of Station	B
08/22/20	Reinstallation of Station	B
09/19/20	Sampling	A, B, C, D, E, F
10/02/20	De-Installation of Equipment	A, B, C, D, F

4.2.1.3. Passive sampling. The following graph depicts the average contaminant levels of zinc, barite, and lead were plotted against the recorded water levels over time. This graph indicates that as the water level decreases the amount of zinc increases, the amount of barite decreases, and the amount of lead remains nearly constant. The decrease in barite is related to the decrease in water level and thus discharge, with less water available to move the barite, there is less barite suspended in the water. The increase in zinc and the decrease in barite are potentially related.

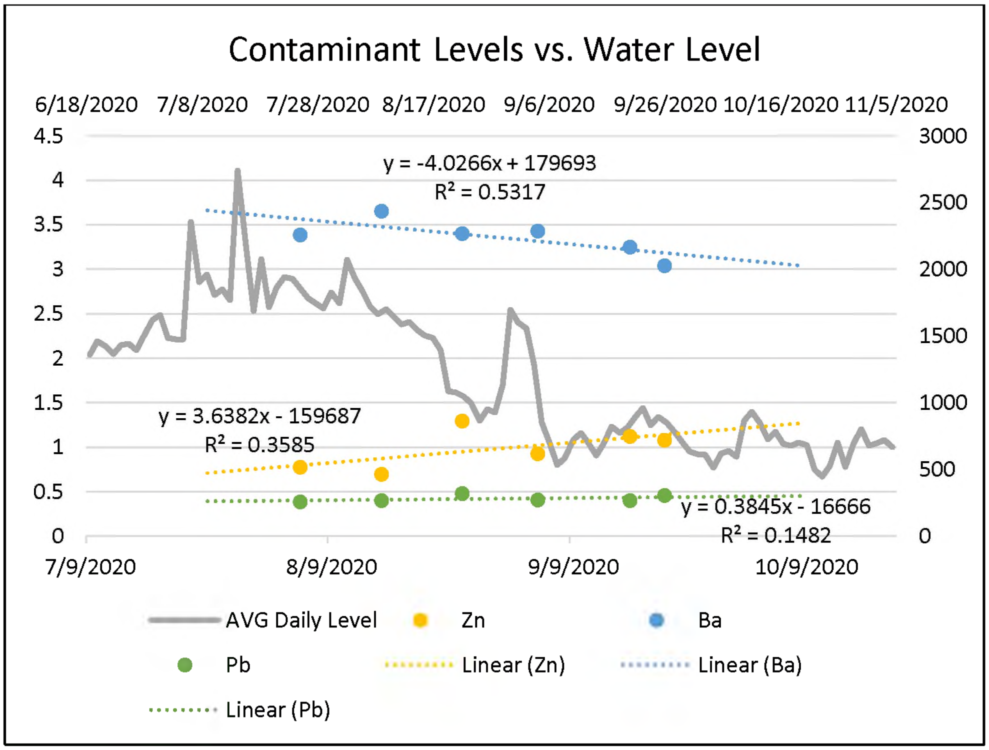


Figure 4.1 Passive Sampling Data

Similar to Figure 4.1, Figure 4.2 – Figure 4.5 show the average concentration of contaminants over time plotted against the average daily discharge at a given location. Figures 4.2 and 4.4 present the samples collected from the upper samplers of locations E and F, respectively. Figures 4.3 and 4.5 present the samples collected from the lower samplers of locations E and F respectively.

The comparison of upper and lower samplers shows the difference in suspended sediment concentrations during normal and flood conditions. The purpose of plotting the concentration against average daily discharge is to identify if there are changes in the concentration after a significant rainfall event. Over the duration of this study there were two major rainfall events, after which there were no notable increases or decreases in contaminants collected.

Also similar to Figure 4.1, all four of these graphs depict a general trend of barite decreasing, zinc increasing, and lead remaining relatively constant.

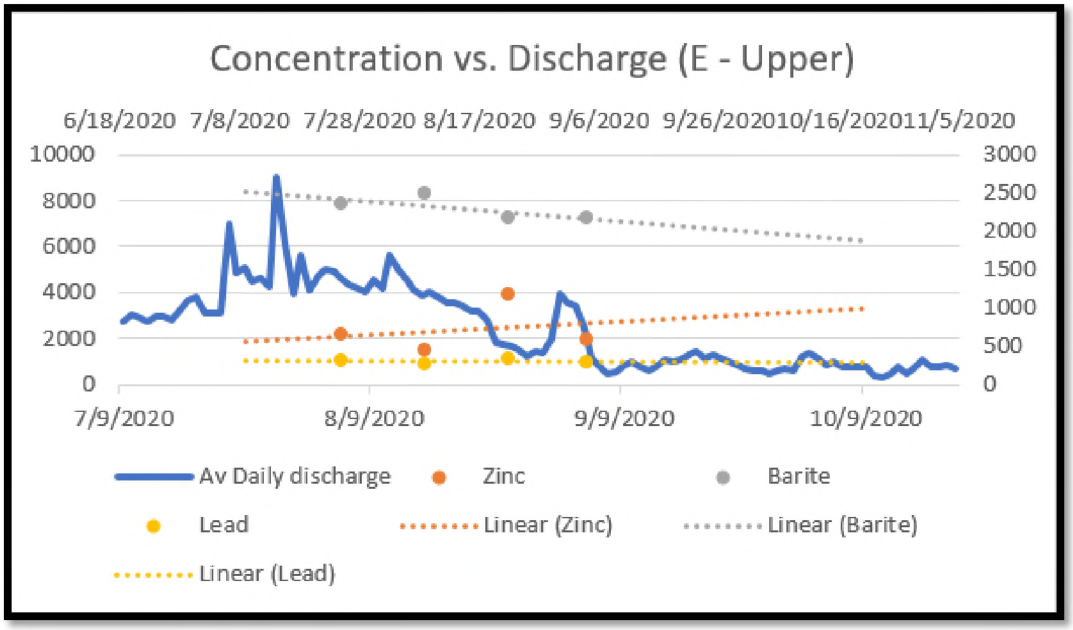


Figure 4.2 Concentration vs. Discharge (Sampler E Upper)

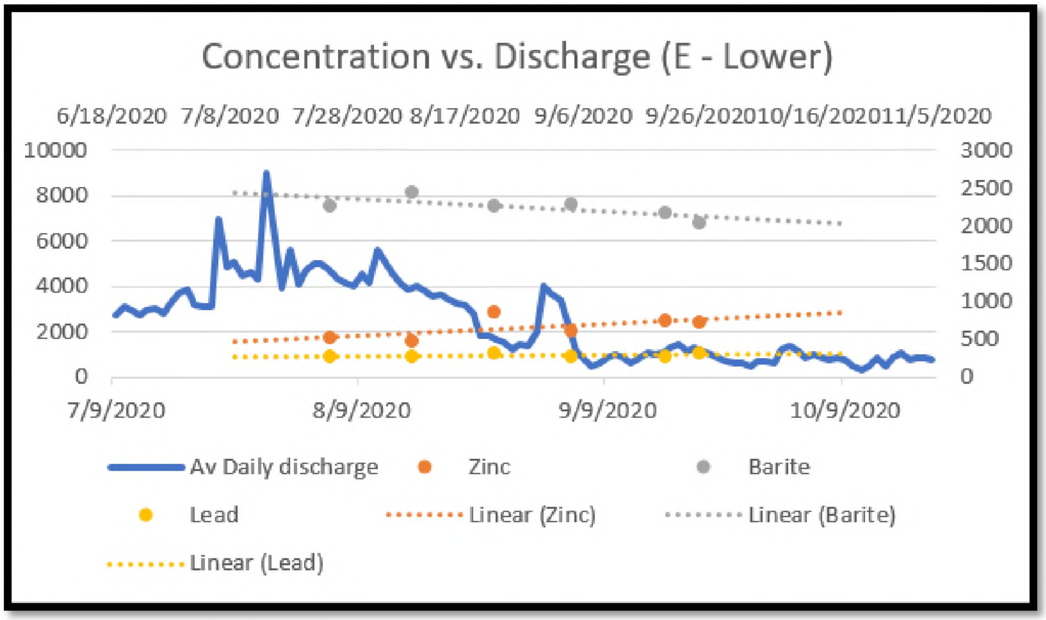


Figure 4.3 Concentration vs. Discharge (Sampler E Lower)

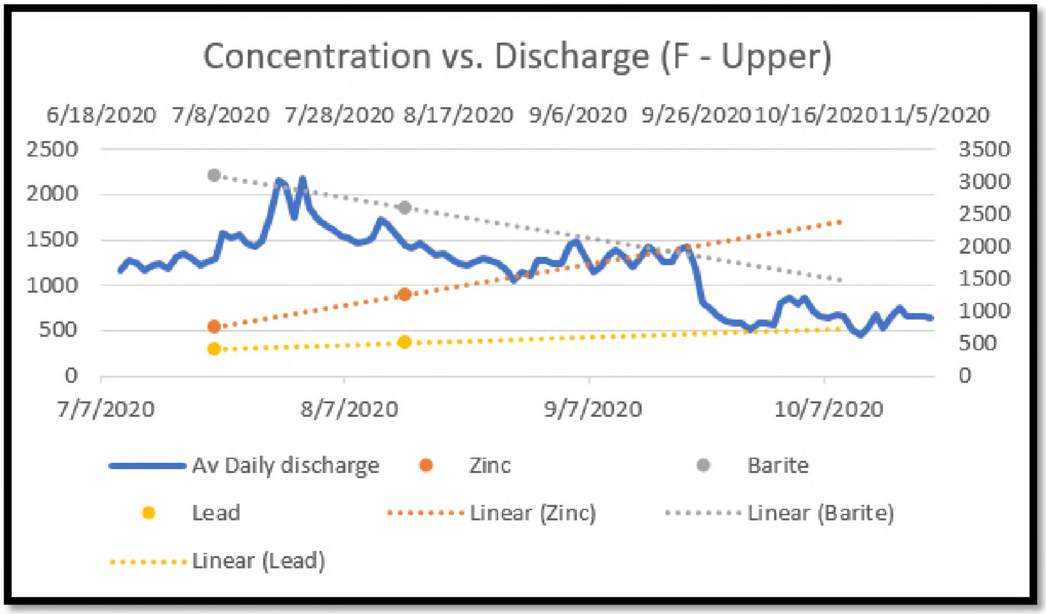


Figure 4.4 Concentration vs. Discharge (Sampler F Upper)

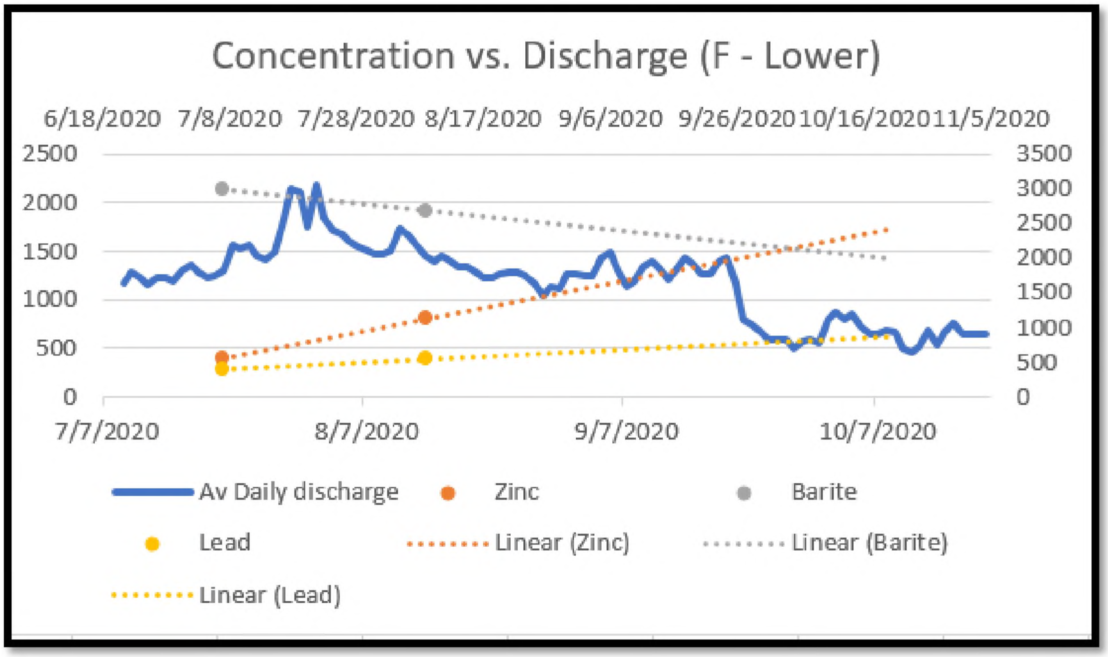


Figure 4.5 Concentration vs. Discharge (Sampler F Lower)

4.2.1.4. Comparison of different watersheds. Figure 4.6 shows the concentrations for all samples collected with respect to the size of the watershed the concentrations were collected. This graph establishes a trend between the size of the watershed and the amounts of contaminants collected, barring the second smallest watershed, the number of contaminants collected increase as the size of the watershed increases. A potential reason, for the second smallest watershed being an outlier, is that for a significant portion of the study, an earthen dam was constructed approximately 100 feet upstream. This dam was built using earthen fill from a nearby site. The fill was likely composed mostly of barite and other clay minerals, explaining the increase in barite content, it also explains the normal amounts of lead and zinc found since neither are found abundantly

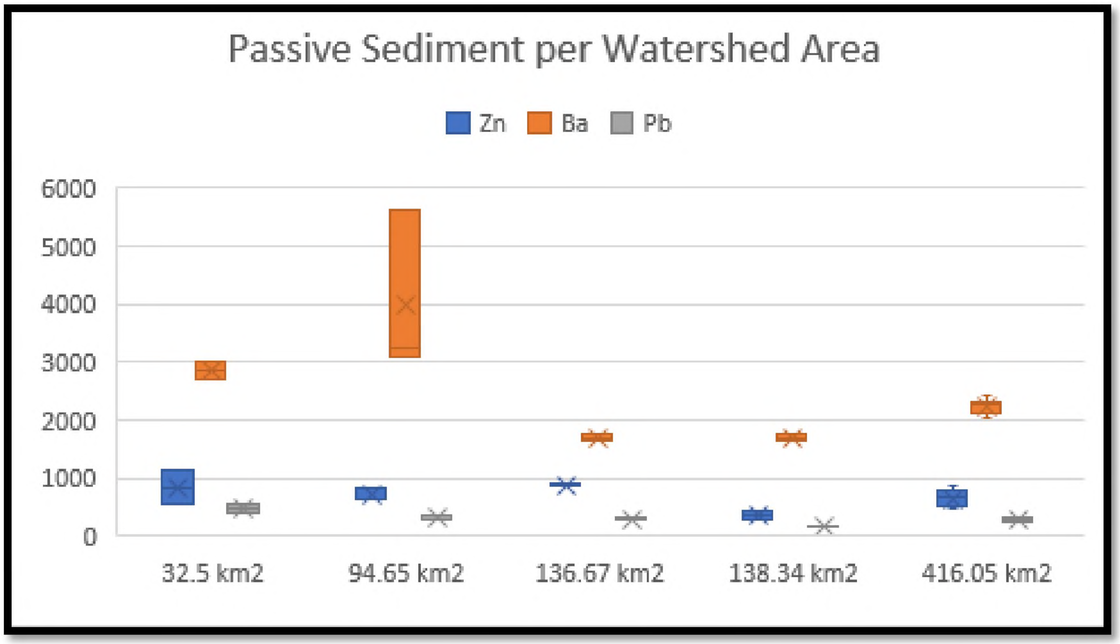


Figure 4.6 Passive Sediment per Watershed Area

Figures 4.7 – 4.9 displays the amounts of lead, zinc, and barite passively collected with respect to the area of the sampler's watershed. The tightly clustered data, in Figure 4.7, indicates little variation in the lead content of the banks further supporting the theory that the amount of lead present remains relatively constant. Figure 4.8 depicts a larger variation in the amounts of zinc collected from each watershed.

Figure 4.9 displays little variation in the amounts of barite collected, excluding the second smallest watershed. The second smallest watershed belonged to sampler A. The aforementioned sampler was located approximately 100 feet downstream of a temporary earthen dam for a significant time. The dam was constructed from dirt fill and likely contained large amounts of barite and other clay minerals, it could have also potentially contained amounts of lead and zinc, but if it did it was not reflected in the contents of the sampler.

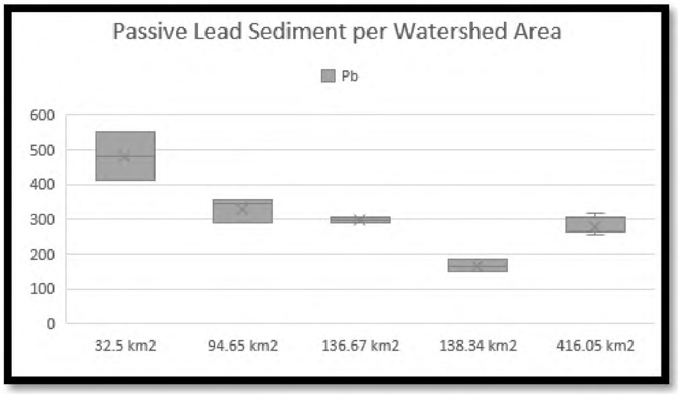


Figure 4.7 Passive Lead Sediment per Watershed Area

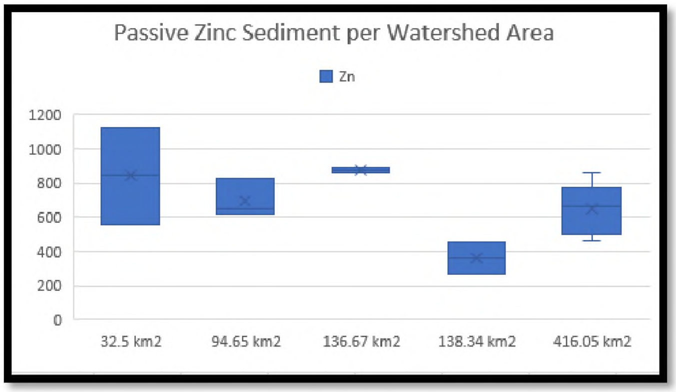


Figure 4.8 Passive Zinc Sediment per Watershed Area

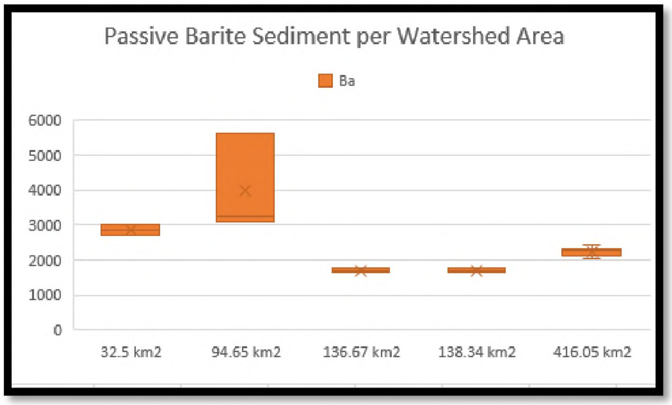


Figure 4.9 Passive Barite Sediment per Watershed

Figures 4.10 – 4.18 show the bank contaminant content with respect to the watershed area. Specifically, Figures 4.10 – 4.12 show this for the sampling on July 7, and Figures 4.13 – 4.15 show this for the sampling on August 22. Figures 4.16 – 4.18 show variation in bank contaminants for July and August combined. Figure 4.10 and 4.13 demonstrate little variation in the amounts of lead. Similarly, Figures 4.11 and 4.14 show little variation in the content of zinc. However, Figures 4.12 and 4.15 show a notable decrease in the amount of barite present in the bank samples.

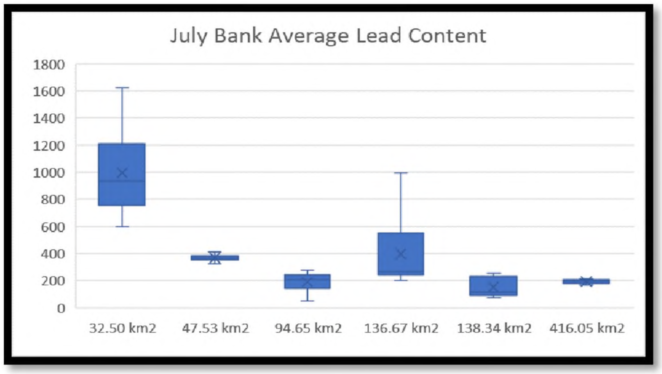


Figure 4.10 Watershed Comparison for July (Lead)

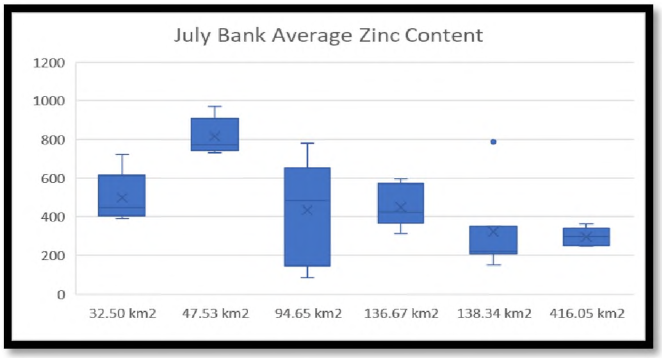


Figure 4.11 Watershed Comparison for July (Zinc)

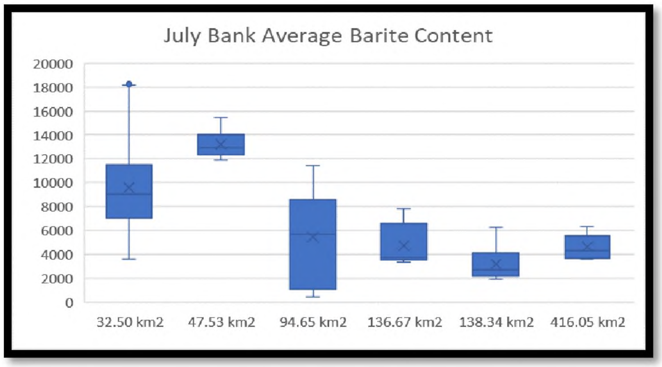


Figure 4.12 Watershed Comparison for July (Barite)

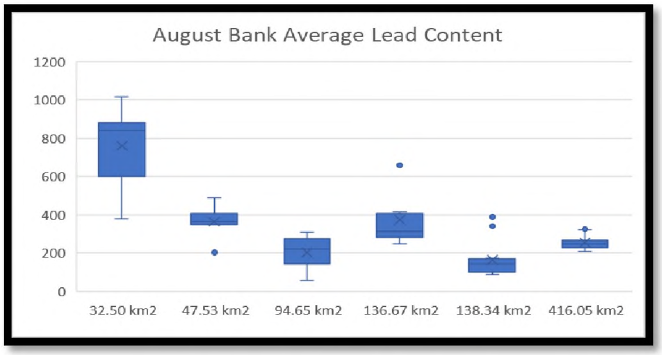


Figure 4.13 Watershed Comparison August (Lead)

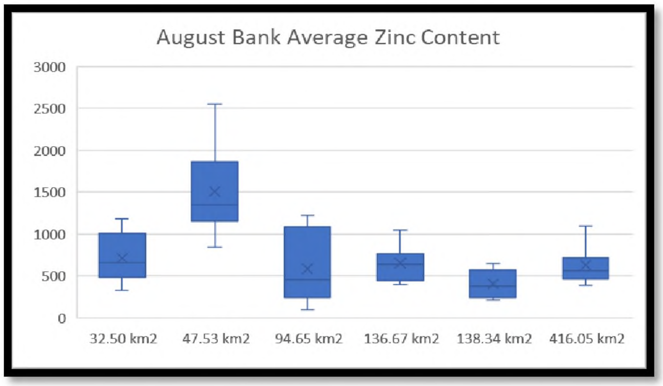


Figure 4.14 Watershed Comparison August (Zinc)

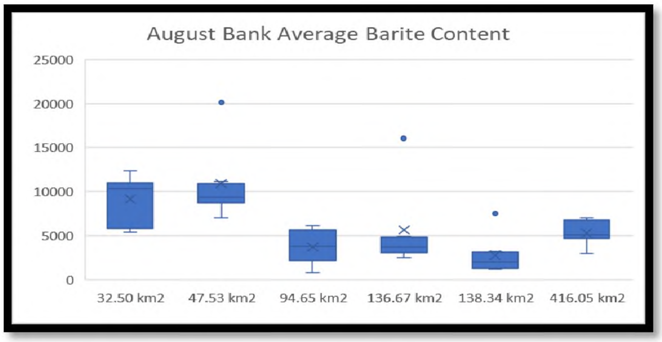


Figure 4.15 Watershed Comparison August (Barite)

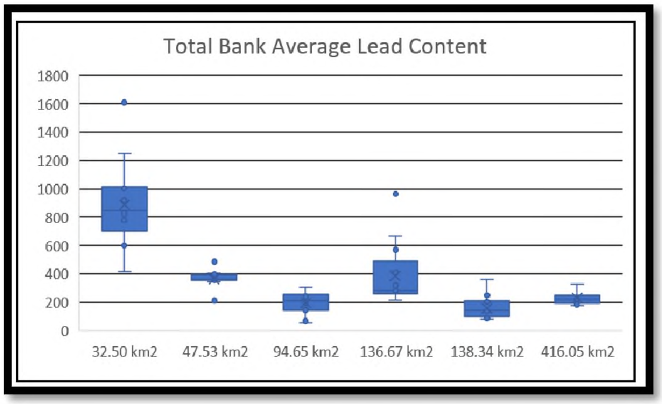


Figure 4.16 Watershed Comparison Total Combined (Lead)

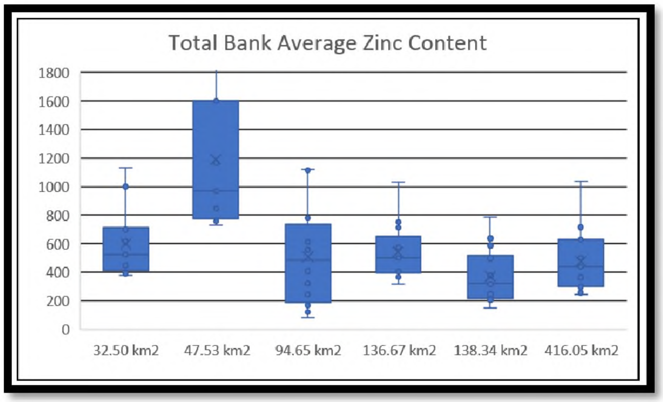


Figure 4.17 Watershed Comparison Total Combined (Zinc)

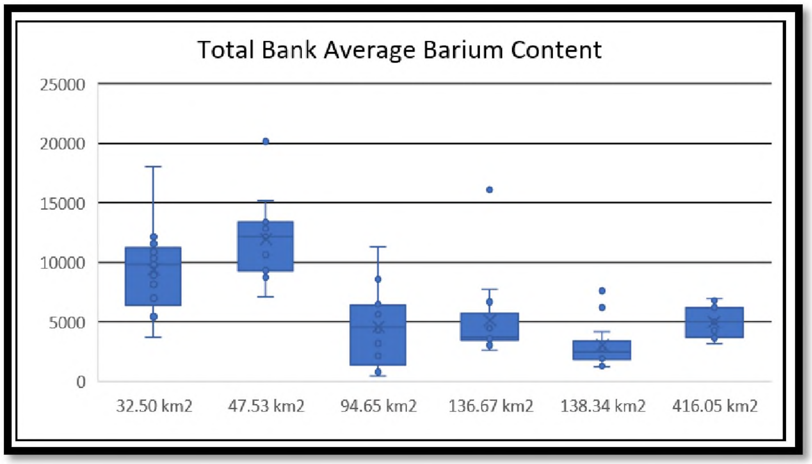


Figure 4.18 Watershed Comparison Total Combined (Barite)

Figures 4.19 – 4.21 show the variation in the concentrations of the contaminants collected from each sampler in regard to the amount of mining activity, both active and historical, upstream of the sampler. These graphs demonstrate there is little relationship between lead and the other two contaminants, however, the data does show a weak relationship between the amounts of zinc and barite present.

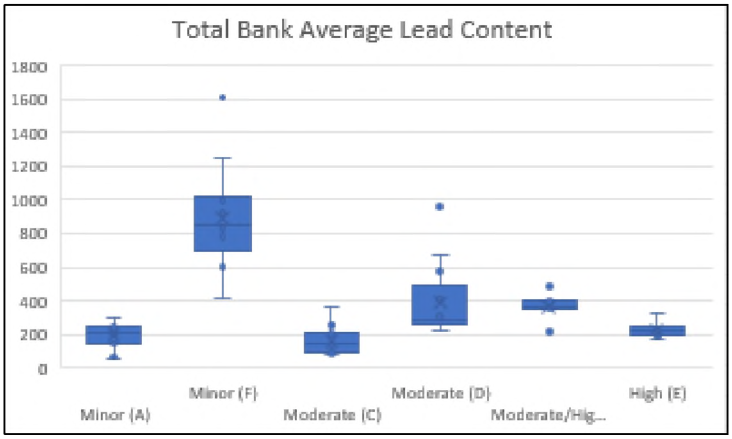


Figure 4.19 Total Bank Average Lead Content per Mining Activity

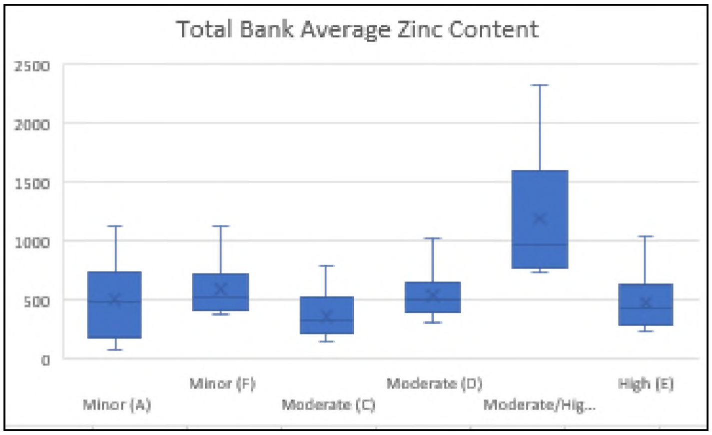


Figure 4.20 Total Bank Average Zinc Content per Mining Activity

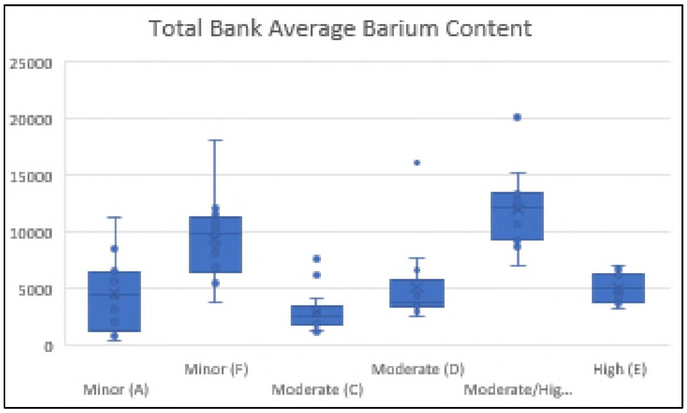


Figure 4.21 Total Bank Average Barium Content per Mining Activity

Figures 4.22 – 4.24 show a comparison of two of the contaminants each. This creates a visual representation of all data points without regard to time or location. Figure 4.22 demonstrates that zinc is more often found in higher concentrations than lead. Figure 4.23 and Figure 4.24 demonstrate that when compared to lead or zinc, barite is found in staggeringly higher concentrations.

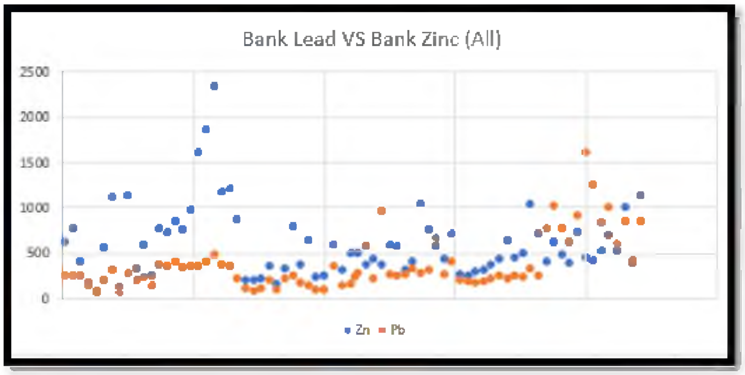


Figure 4.22 Bank Lead vs Bank Zinc

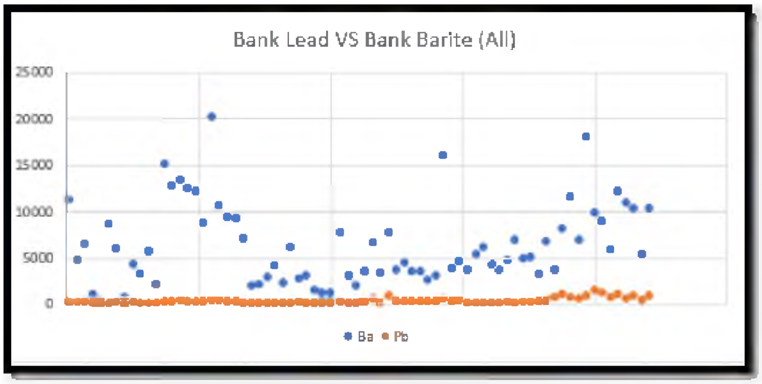


Figure 4.23 Bank Lead vs Bank Barite

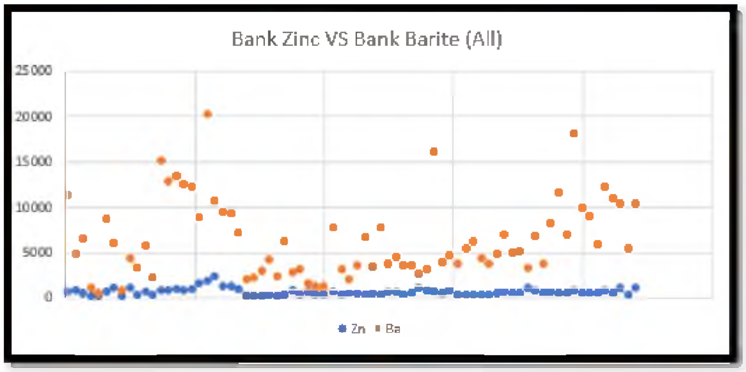


Figure 4.24 Bank Zinc vs Bank Barite

Similar to Figures 4.22 – 4.24, Figures 4.25 – 4.27 show a comparison of the two of each contaminant, except the graphs are broken down by their respective samplers. This provides a finer investigation of the data provided previously in Figures 4.22 – 4.24.

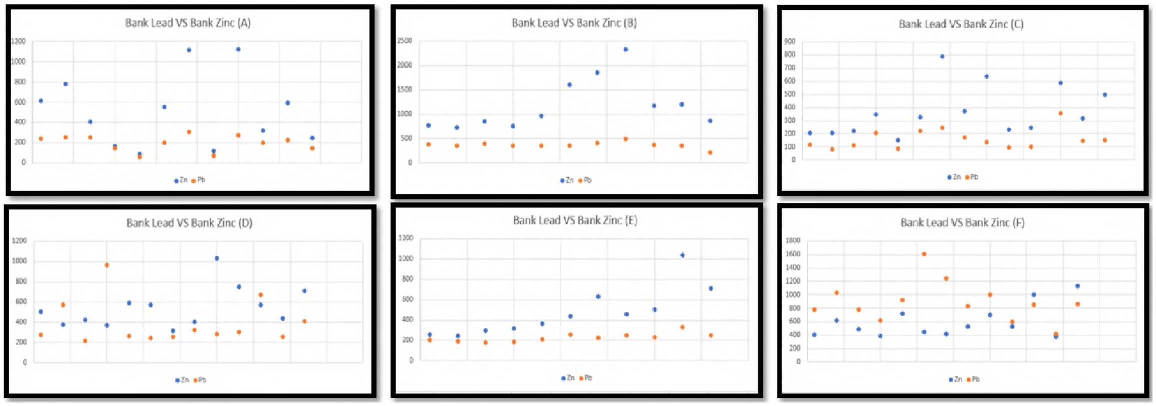


Figure 4.25 Bank Samples: Lead vs. Zinc

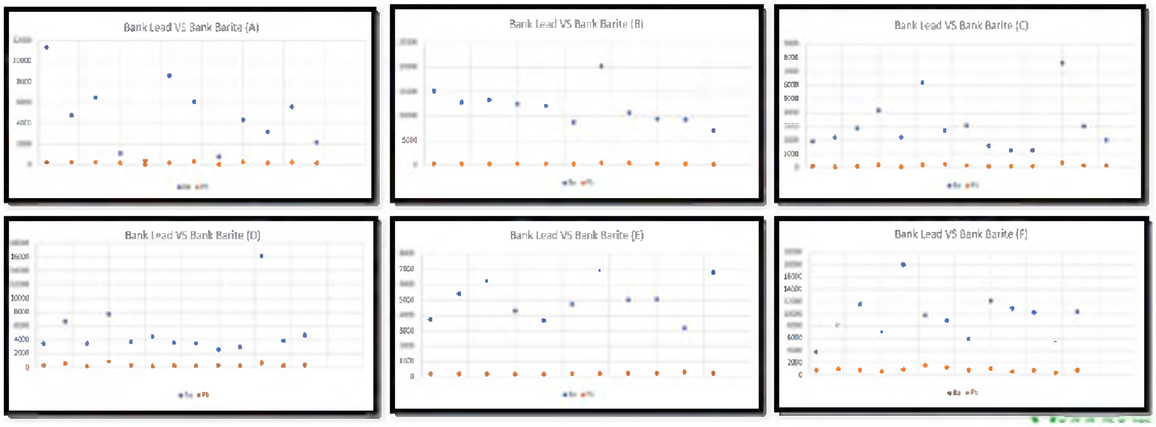


Figure 4.26 Bank Samples: Lead vs. Barite

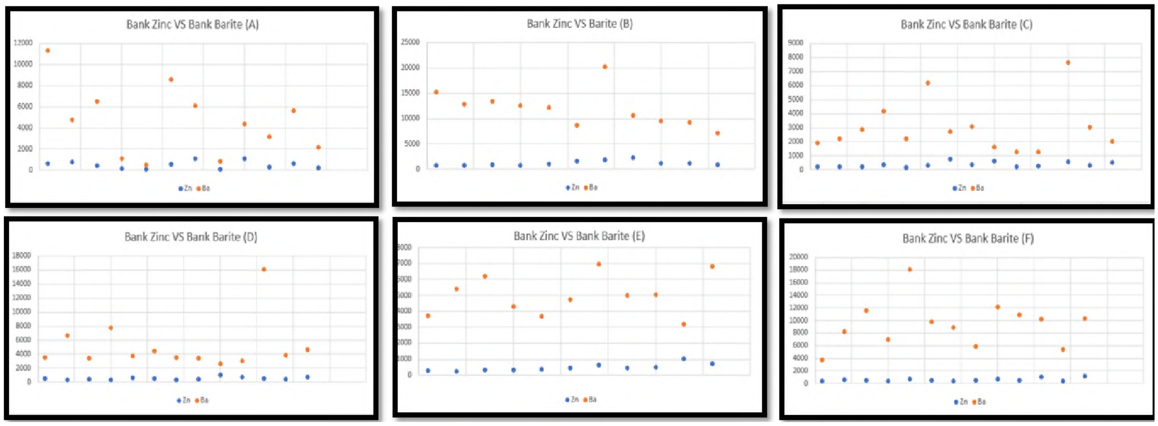

Bank Zinc VS Bank Barite (A)
Bank Zinc VS Barite (B)
Bank Zinc VS Bank Barite (C)
Bank Zinc VS Bank Barite (D)
Bank Zinc VS Bank Barite (E)
Bank Zinc VS Bank Barite (F)

Figure 4.27 Bank Samples: Zinc vs. Barite

4.2.1.5. Comparison of samples before and after rainfall events. Figures 4.29 and 4.30 depict the discharge and the levels of lead, zinc, and barite recorded before and after a flood event at Samplers E and F respectively. The figures illustrate the direct relationship between the water depths and discharge; as the water level increases, so too will the discharge. The levels of lead, zinc, and barite are measured in PPM.

For this study, a flood event is defined as an increase in water level for a limited duration related to rainfall. Both graphs show that the levels of lead, zinc, and barite are minimally affected by flood events. The variations between the levels of zinc, barite, and lead over time are slight and not significant enough to be directly tied to the flood event.

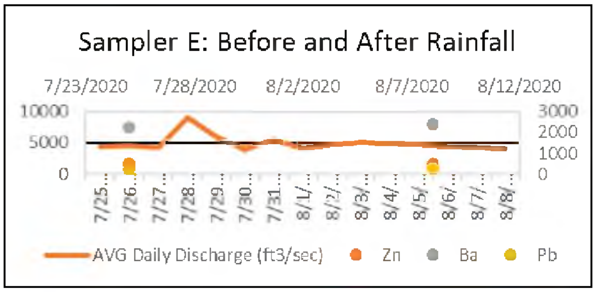

Sampler E: Before and After Rainfall

Figure 4.28 Sampler E: Before and After Rainfall

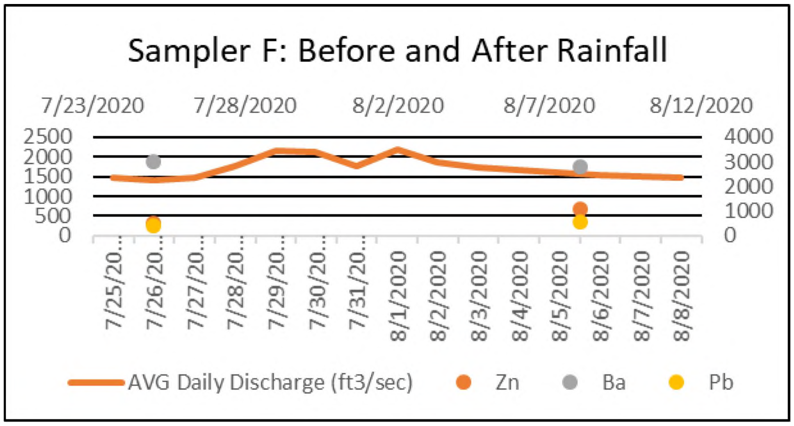


Figure 4.29 Sampler F: Before and After Rainfall

Figures 4.30 and 4.31 show the levels of contaminants present, plotted against the change in water level, over time. These figures establish the same trend as Figures 4.2 – 4.5; as the water level drops, the amounts of barite decrease, zinc increases, and lead remains relatively constant. Figure 4.31 has exaggerations in its trend line, largely due to the lack of data, resulting from Sampler F's inability to produce usable samples.

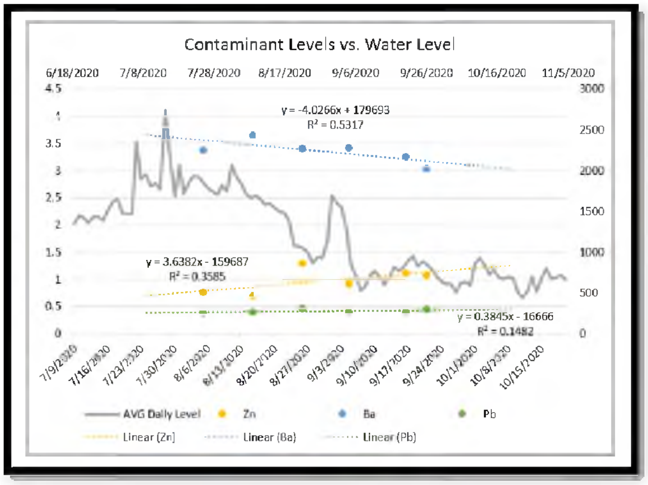


Figure 4.30 Contaminant Levels vs. Water Level (Sampler E)

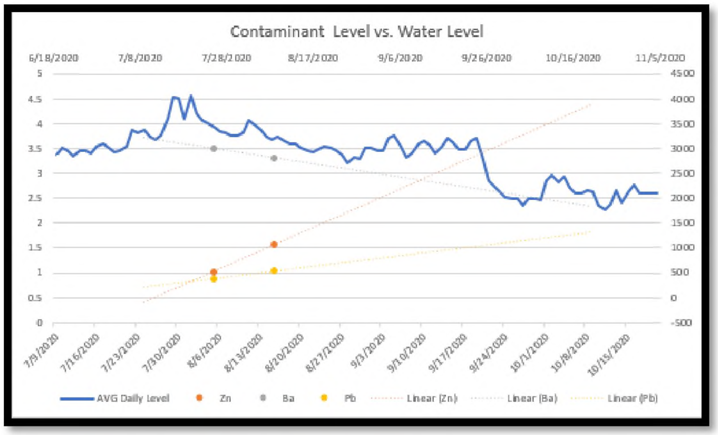


Figure 4.31 Contaminant Levels vs. Water Level (Sampler F)

Figure 4.32 shows the contaminant levels per sampling for each location. This reinforces the previously established theory, that over time, the amounts of barite decrease, zinc increases, and lead remain relatively constant.

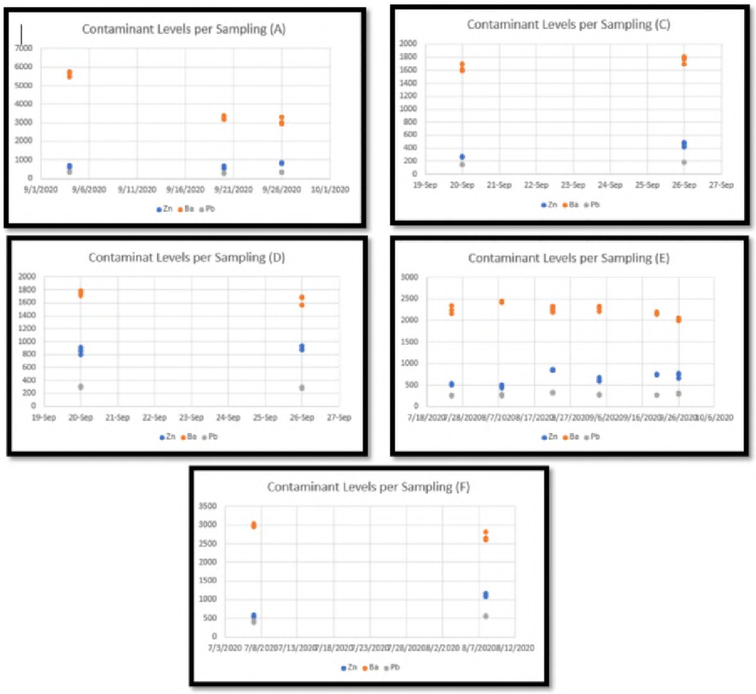


Figure 4.32 Contaminant Concentration for each Campaign/Time

Figures 4.33 – 4.35 all use sediment load. Sediment load is equal to the discharge at a given time, multiplied by the contaminant load at a given time, showing the amount of lead, zinc, and barite contaminants travelling downstream at a given time. Similar to Figure 4.1, Figure 4.33 shows barite decreasing and lead remaining nearly constant. However, Figure 4.33 also shows zinc initially increasing and then decreasing. Figures 4.34 and 4.35 show the Sediment load per location and watershed size for the upper and lower samplers respectively. Most notably, this shows the massive amount of barite that travels past Sampler E during a flood event, however, the concentration remains unchanged.

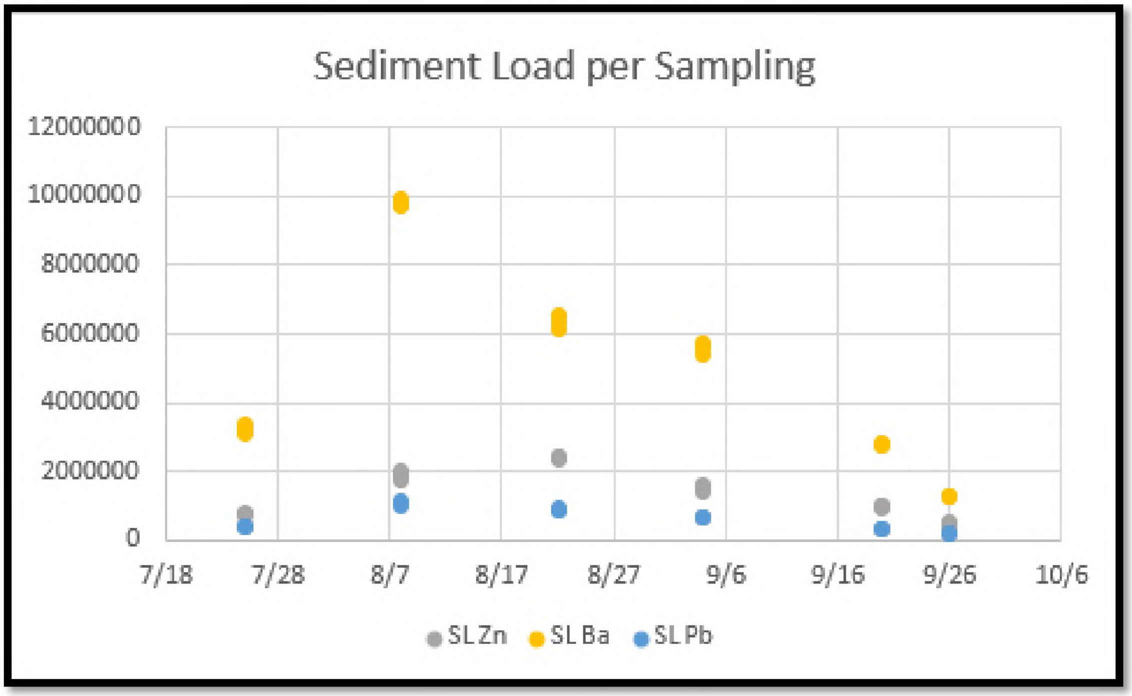


Figure 4.33 Sediment Load for each Campaign/Time

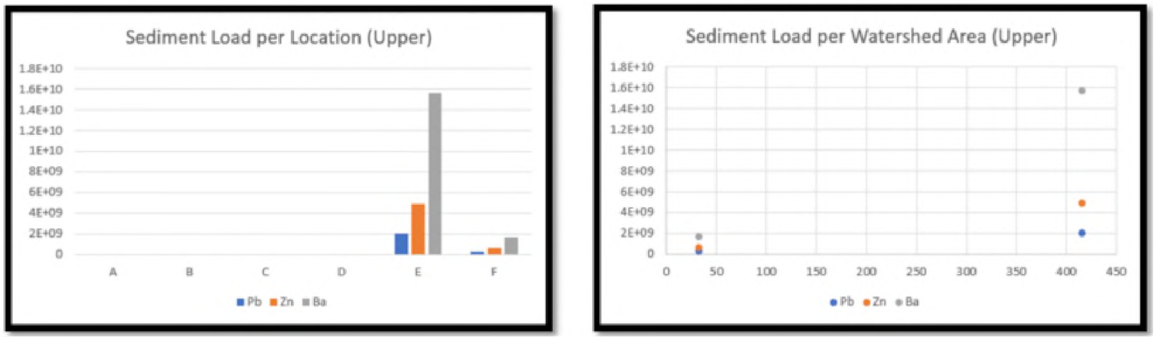


Figure 4.34 Sediment Load (Upper Sampler)

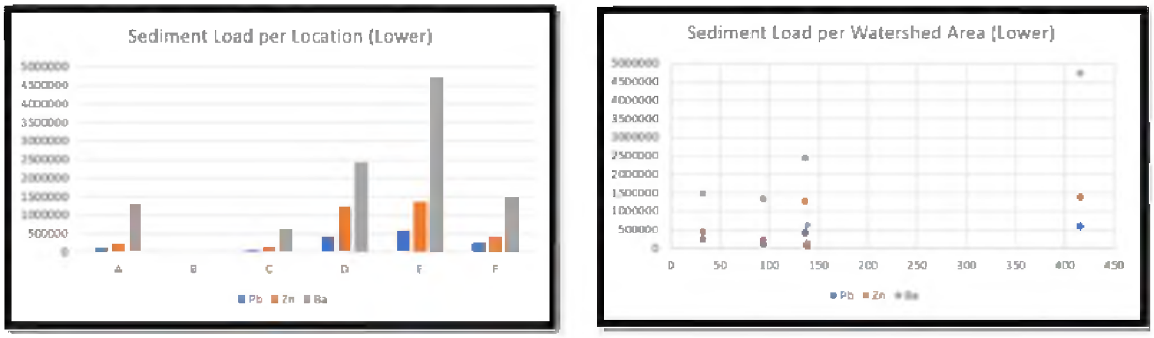


Figure 4.35 Sediment Load (Lower Sampler)

4.2.1.6. Depth comparison. Figures 4.38 and 4.39 show the amounts of lead, zinc, and barite present in the upper and lower samplers respectively with respective to time. Despite the upper sampler not directly showing the trend, both graphs depict the same trend as Figure 4.1; as the amount of barite decreases, the amount of zinc increases, and the amount of lead remains relatively constant. The reason the upper sampler shows a constant amount of barite and an increasing amount of zinc is because the upper samplers only collect during flood events. Therefore, with the increase in water level, there will be an increase in the amount of barite. Due to the limited duration of flood events, there is not sufficient time for the zinc to sorb onto the barite.

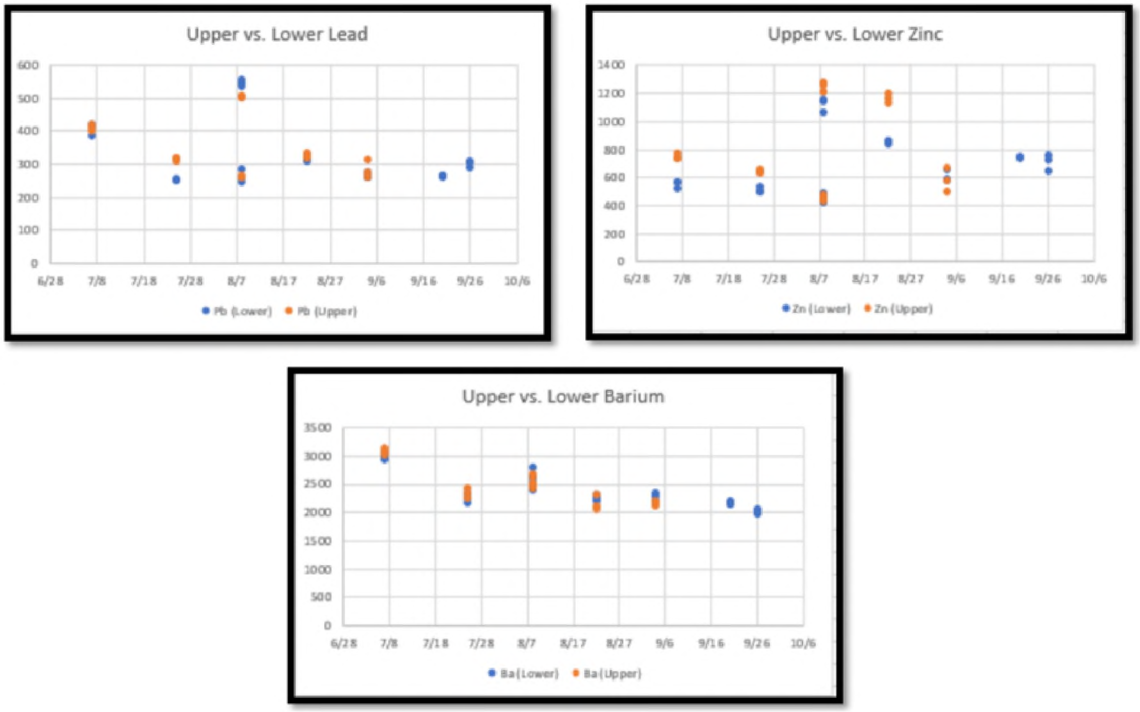


Figure 4.36 Upper and Lower Sampler Comparison

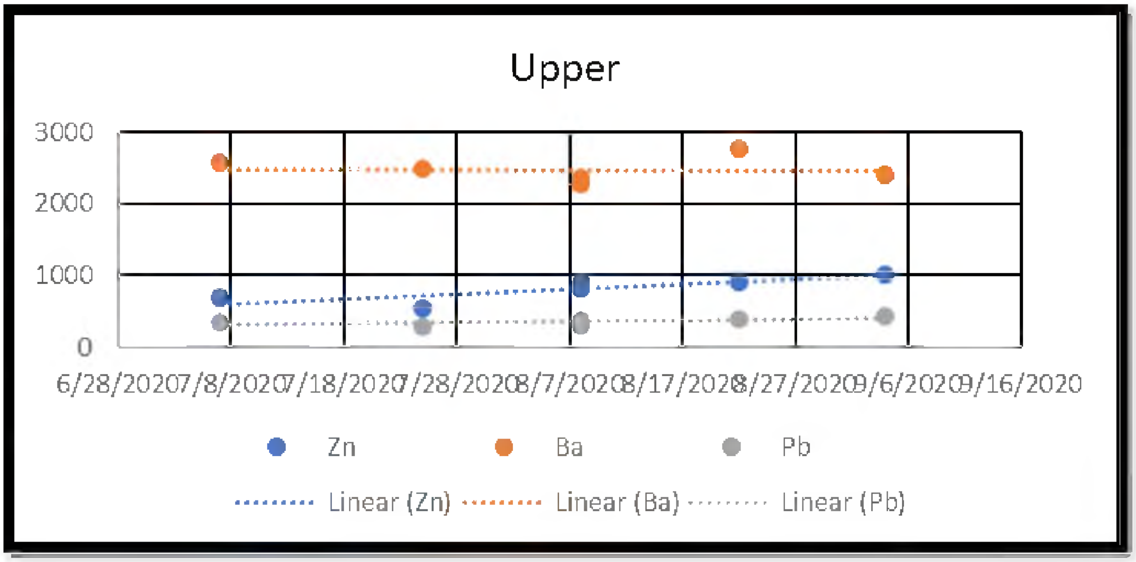


Figure 4.37 Depth Comparison (Upper)

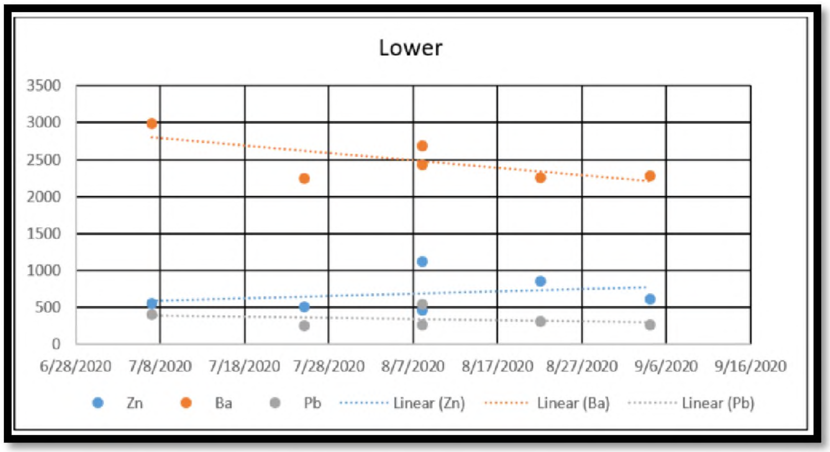


Figure 4.38 Depth Comparison (Lower)

4.2.1.7. Relationship between contaminant load and discharge. Figures 4.40 and 4.41 depict levels of lead, zinc, and barite present in the water and the discharge with respect to time at Samplers E and F respectively. These graphs display the same trend as Figures 4.1, 4.37, and 4.38; as the water level decreases, the amount of barite decreases, the amount of zinc increases, and the amount of lead remains relatively constant. Figure 4.41 exaggerates this trend due to Sampler F's inability to produce useful samples.

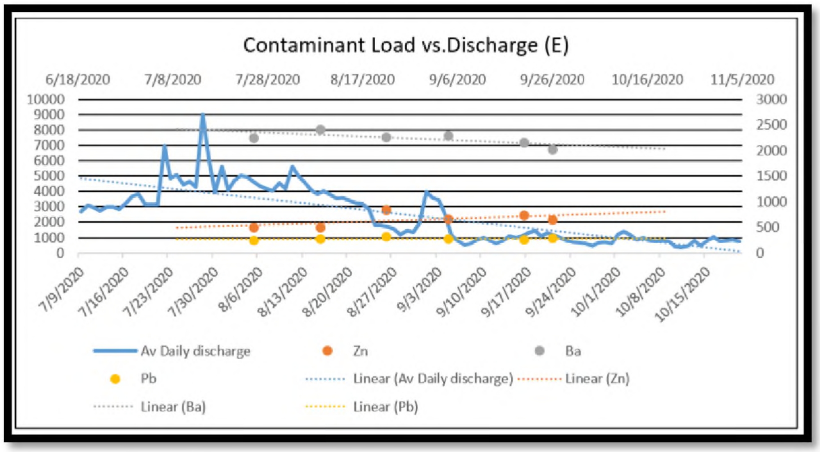


Figure 4.39 Water Load and Discharge Comparison (Sampler E)

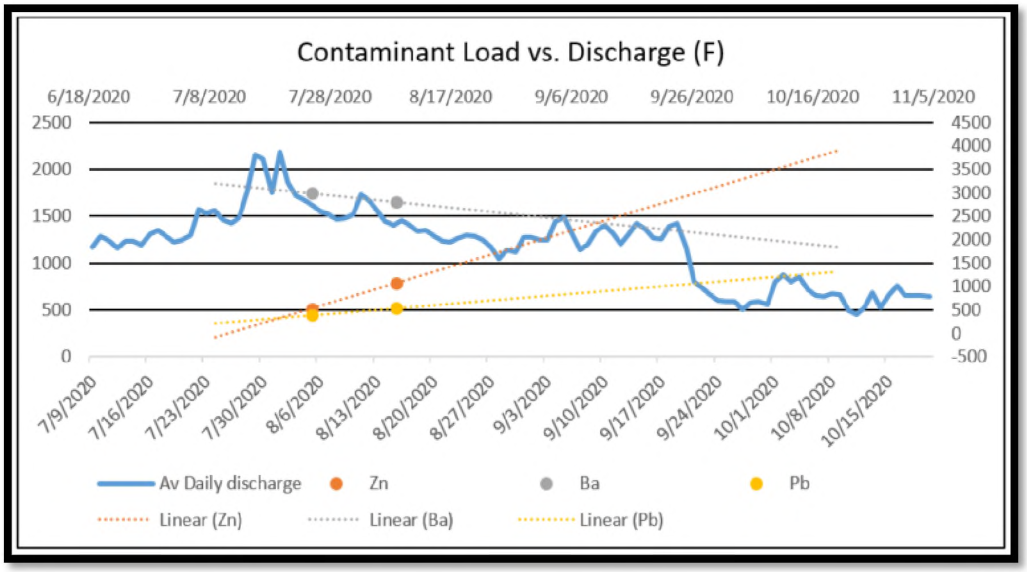


Figure 4.40 Contaminant Load and Discharge Comparison (Sampler F)

4.2.2. Summary. This section provided results and findings, a sampling overview, the statistical analysis of the study. Next the sampling schedule, passive sampling results, a comparison of different watersheds, a comparison of sediment samples before and after rainfall events, and a depth comparison was provided. Finally, the relationship between contaminant load and discharge was analyzed and presented.

5. CONCLUSIONS AND RECOMMENDATIONS

The results and finding, of this research study, provide a snapshot in time of the contaminant levels of lead, zinc, and barite, contributing to Big River, by Mineral Fork Creek, in Potosi, Missouri, Washington County. Based on the EPA guidelines for acceptable levels in groundwater, the identified levels of lead, zinc, and barite are within acceptable ranges and require no further investigation in regard to a health risk.

As specifically designed, this study also determined and recorded the current levels of lead, zinc, and barite contributing to Big River, by Mineral Fork Creek. The data demonstrates that there is no direct correlation between the amount of lead, zinc, and barite in the water as it travels further downstream nor with the amounts after a rain event, thus rendering the original hypothesis null.

The study did however uncover a potential relationship between the amounts of lead, zinc, and barite present in the water. The results indicate that as the water level and discharge decrease, the amount of barite decreases, the amount of zinc increases, and the amount of lead remains nearly constant. This relationship could potentially be the result of the pH level of the water. The average pH level of the groundwater in Washington County are 8.1, creating a slightly basic environment. This could establish favorable conditions for zinc to preferentially sorb onto the surface of barite particles before lead. Thus, with less barite present in the water, there is more dissolved zinc in the water. It is also important to note that while remaining nearly constant, the amounts of lead marginally increase over time, which is also indicative of the potential preferential sorption[42] theory.

Future study recommendations involve a replication of this study conducted over the predicted rainy season (March - August) for Potosi, Missouri. New studies and data collection should occur in this timeframe. COVID-19 greatly impacted this research study. Originally scheduled to begin in the spring months (March - May) the study was postponed until COVID-19 restrictions were lessened. Greater study, conducted after rainfall events, would assist in solidifying the data results and findings. Further longitudinal studies would also assist in determining greater levels of accuracy for lead, zinc, and barite. All future studies should record the pH levels of the water similar to how the water level was recorded in this study.

This micro-analysis research study of the contaminants in suspended load and bank deposits from the Mineral Fork Creek Watershed, consisted of five sections. Section 1 established the overarching purpose of this study. Section 2 contained an extensive review of literature related to historical mining activity in the Barite District region, the rainfall and contaminant correlations, and a review of the contaminants lead, zinc, and barite. Section 3 outlined the research methodology used in performing this quantitative micro-analysis, including site selection, the installation of the samplers, the sampling methods, the lab analysis, the data collection, and a data summary. Section 4 provided the results and findings, a sampling overview, the statistical analysis, the sampling

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[42] Smith, Kathleen S., *Reviews in Economic Geology, Volumes 6A and 6B, the Environmental Geochemistry of Mineral Deposits, Society of Economic Geologists (SEG), Inc.*, Chapter 7, Metal Sorption on Mineral Surfaces: An Overview with Examples Relating to Mineral Deposits. 1999. https://clu-in.org/conf/tio/r10hardrock3_030513/Ch7Smith_SEG1999.pdf., Accessed October 25, 2020.

schedule, the passive sampling data, a comparison of different watersheds, a comparison of sediment samples before and after rainfall events, a sampler depth comparison, and finally establishing the relationship between contaminant load and discharge.

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