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Study of contamination resulting from historical mining within the Old Lead Belt: Mineral Fork Watershed, 2021-2022

Tessa Nicole Mortensen

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STUDY OF CONTAMINATION RESULTING FROM HISTORICAL MINING WITHIN THE OLD LEAD BELT: MINERAL FORK WATERSHED, 2021-2022

by

TESSA NICOLE MORTENSEN

A THESIS

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Approved by:

Katherine Grote, Advisor
David Rogers
Jeffery D. Cawlfield

ABSTRACT

The Old Lead Belt in Missouri has been mined extensively over the past two hundred years, and with historical mining practices often not meeting modern environmental protection standards many areas have significant soil and water contamination as a result. This study focuses on the Mineral Fork River's watershed in Washington County, Missouri, which includes portions of four separate Superfund sites. In this study, we exam the impact of historical mining on the health of alluvial systems, as evaluated by lead, zinc, and barium (barite) concentrations in the suspended and sediments within tributaries of the Mineral Fork River system. To relate this to historic mining, the concentrations of lead, zinc, and barium (barite) will be compared to the density of recorded mining operations in the sub-watershed of each sampled tributary. Six pre-established sub-watersheds were evaluated using ten sampling locations within the Mineral Fork River's watershed. This study builds on similar previous work performed within this watershed, with an objective to expand upon it by increasing the sample resolution, extending the study for a longer time period, and using more advanced methods of soil analysis to determine the extent of contamination within the Mineral Fork River watershed. Within this study, a positive correlation was found between the density of mining activity and the elevated concentrations of lead and zinc on suspended sediments, while no correlation was found between barium (barite) and the density of mining activity. These correlations were attributed to the contaminant properties. It is suggested that further research be conducted in the area to further refine and verify the results.

ACKNOWLEDGMENTS

Throughout the duration of this research, I have received substantial support and would like to thank all of those who believed in my abilities and encouraged me to continue in my studies when I struggled.

To Joe, thank you for doing such a great job at recording your data and findings. Without your records, I don’t think I would have even had a project to begin with.

To my roommate, Sam, who helped me install the first samplers, I want to say thank you for donating one of your few days off to helping me get started with this project and for the care you showed to my dog while I spent long days out in the field.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Page

1. INTRODUCTION

1.1. SITE BACKGROUND AND PROJECT MOTIVATION

On the border of Washington County, Missouri, just north of Washington State Park and Route 21, the Mineral Fork River joins the Big River as it winds through the rolling hills on the fringes of the Ozark Highlands. Many local anglers spend afternoons fishing in the Big River, as well as the Mineral Fork. It is advised, however, that anglers use a catch and release method when fishing in the Big River, as several of the fish species that populate the waters are not safe to eat. According to the Missouri Department of Health and Senior Services (DHSS) in their 2020 Missouri Fish Advisory, several species of Sunfish, Carp, and sucker fish of any size should not be eaten from the Big River and several of its tributaries, as the fish have dangerously elevated levels of lead in their meat.

Contaminated fish within an ecosystem is a clear indication of environmental contamination, and it's no surprise that the Big River has been contaminated. Southeastern Missouri was once known as the Old Lead Belt, as lead mining through the area began in the early 1700's and barite production in the area began in the 1860's (Mugel et al., 2017). It has since been determined, by the United States Environmental Protection Agency, that there is pervasive contamination thought the area, particularly and including Washington County (WC), Missouri, where elevated levels lead, barium, and other metals have been recorded (Mugel et al., 2017).

1.1.1. Motivation and Government Interest. Contamination within Washington County (WC) is quite extensive, and the Environmental Protection Agency (EPA) has since stepped in. After evaluation of many areas of WC, the EPA approved four separate sites to be put on the National Priorities List (NPL) for remediation, deeming them Superfund Sites (Environmental Protection Agency (EPA), 2021). Figure 1.1 below illustrates the extent of these Superfund Sites.

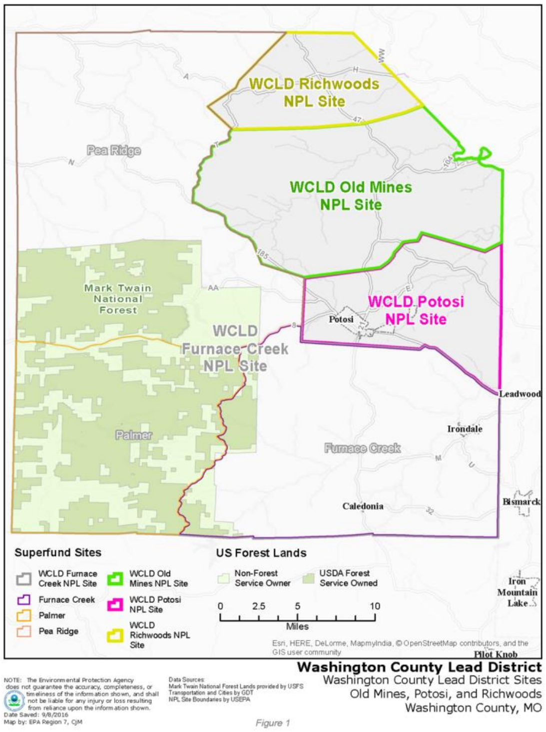


Figure 1.1 Map of the Washington County Lead District. (Environmental Protection Agency (EPA), 2021).

The entire area of WC is enveloped in Superfund Sites. Contamination within the area is mainly in the form of contaminated water and soil, where old strip mines, mine dumps, tailings ponds, etc. have served as point and nonpoint contamination sources. (Environmental Protection Agency (EPA), n.d.-c) Poor environmental stewardship, lack of regulations, and insufficient public education regarding environmental contamination has also resulted in the sale of contaminated mining waste as cheap fill for construction projects, gravel roads and driveways, and as sand for playgrounds, and the sale of properties with old mining features, such as tailings ponds or piles, to unknowing citizens (Environmental Protection Agency (EPA), n.d.-c). Cleanup projects have been ongoing in the area since 2006 and continue to this day (Environmental Protection Agency (EPA), n.d.-c).

Other than the risk to human health that these areas pose, Superfund Sites are contributors to downstream contamination. Contaminants from the point and nonpoint sources that still exist due to historic mining activity can be transported from their original location to new locations, such as bodies of water, during meteorologic precipitation events (rain, storms, snowmelt, etc.). Contaminants can be transported as contaminated sediments where the contaminant has latched (sorbed) onto a soil particle, as a dissolved constituent in surface or groundwater, and sometimes as a pure contaminant. This study is concerned with the transportation of contamination as soil and sediment particles.

As previously discussed, the Big River has a contamination issue, particularly with lead, and it passes through and along the edges of the northeastern parts of WC. Also, in the northeastern part of WC, a tributary called the Mineral Fork discharges into the Big River. The Mineral Fork is a river that stretches across a large portion of WC and has a watershed that covers portions of all four Superfund Sites. This watershed, regarded as the Mineral Fork River System (MFRS) within this body of work, is the chosen area of study for this particular project because, due to its extent across WC and its status as a major tributary of the Big River, the MFRS has the potential to be considered a major contributor to the Big River's elevated levels of contamination.

1.1.2. Mineral Fork River System Geology. Part of the reason the Old Lead Belt was so productive was due to the relatively easy access the area offered. Figure 1.2 shows the exposed bedrock formations within a particular part of WC. The areas shaded in dark brown represent the Potosi Dolomite, which is the major host rock for barium and lead ores within the WC area (Brown, Jr. & Missouri Department of Natural Resources (DNR), 2001). The Potosi Dolomite is a Cambrian dolomite similar to other Missouri dolomites that have a relatively high solubility, leading to a karstic nature, and due to the higher solubility of the host rock, the ores within became concentrated over time, , filling void and fractures in the bedrock during chemical weathering processes, resulting in large deposits (Mugel et al. 2017) that are at, or near, the surface (Brown, Jr. & Missouri Department of Natural Resources (DNR), 2001).

Soil types within MFRS range slightly. Rueter, Sonsac, Goss, Bender, Lily, Coulstone, and Gravois Serries soils are all present and prevalent within the area, and are considered to be, respectively: very gravelly silt loam; extremely gravelly silt loam; very cobbly silt loam, very gravely sandy loam; fine sandy loam; very gravely fine sandy loam; and silt loam (Hansen et al., 2005) (Natural Resources Conservation Service (NRCS) Missouri & United States Department of Agriculture (USDA), 2005). This indicates that the soils in the MFRS are poorly sorted, and so the small diameter particles in a given sample are likely to be silt or clay as opposed to coarse sand.

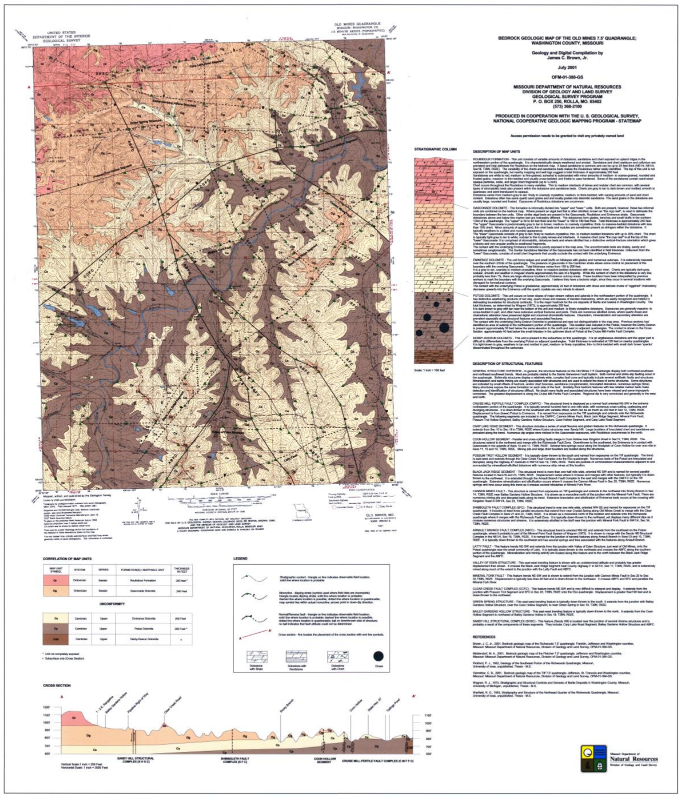


Figure 1.2 Bedrock Geologic Map of the Old Mines 7.5’ Quadrangle, Washington County, Missouri. (Brown, Jr. & Missouri Department of Natural Resources (DNR), 2001).

1.1.3. Mineral Fork River System Hydrogeology. Illustrated in Figure 1.2, along with expanses of exposed bedrock, are prevalent fault lines. From this, and the previously stated background knowledge regarding the karstic nature of Missouri dolomites, it is likely that there are major interactions between surface water and groundwater within the MFRS. Very near WC and the MFRS is an area of ongoing mining, referred to as the Viburnum Trend Subdistrict, a study was conducted regarding the extent of the connection between groundwater and surface water flow, and found that many streams in the area would have groundwater to surface water (gaining) flow or surface water to groundwater (losing) flow strictly dependent on the level of rainfall within a given time frame (Seeger et al., 2009). Due to the highly connected nature of groundwater and surface water this study will not be considering water samples as it would be difficult to relate the results directly to any particular source.

1.2. PREVIOUS WORK IN THIS AREA

Previous work conducted in this area was completed by Miller in 2020. Miller (2020) attempted to find a relationship between the concentration of three particular contaminants of concern (COCs), lead, zinc, and barium, on suspended sediments and the density of mining activity within the watershed area where a sample was collected. Miller (2020) also included water-level data in relation to the COCs concentrations. No relationships between COC concentration, density of mining activity, and/or water-level/flow rate were identified (Miller, 2020). Sample collection, processing, and analysis methods will be discussed in a later section.

Certain types of data from Miller's (2020) study were made available for use in this project, as seen in Table 1.1 and 1.2.

Table 1.1 Upstream Mining Activity, Previous Work.

Sampler Name (Miller, 2020)	Sampler Name (Current Study)	Upstream Mine Activity Occurances (Miller, 2020)	Area [sq. miles] (Miller, 2020)	Density of Mining Activity [Occurances/sq. mile] (Miller, 2020)
A	W2-S0	2	36.5	0.05
B	W5-S1	3	18.4	0.16
C	W2-S1	7	53.4	0.13
D	W4-S1	26	52.8	0.49
E	W6-S1	37	160.6	0.23
F	W3-S1	6	12.5	0.48

Table 1.2 COC Concentrations in Samples, Previous Work.

Sampler of Origin (Miller, 2020)	Sample	Pb Concentration [ppm] (Miller, 2020)	Zn Concentration [ppm] (Miller, 2020)	Ba Concentration [ppm] (Miller, 2020)	Density of Watershed Mining Activity
A	W2-S0-02	345	648	5634	0.70
A	W2-S0-01	291	615	3260	0.70
A	W2-S0-0	354	830	3101	0.70
C	W2-S1-01	148	263	1634	0.81
C	W2-S1-0	184	456	1758	0.81
F	W3-S1-01	408	558	2992	3.05
F	W3-S1-0	549	1125	2692	3.05
D	W4-S1-01	304	856	1759	2.28
D	W4-S1-0	290	894	1646	2.28
E	W6-S1-05	254	514	2252	2.70
E	W6-S1-04	265	462	2433	2.70
E	W6-S1-03	315	857	2265	2.70
E	W6-S1-02	266	613	2281	2.70
E	W6-S1-01	265	743	2164	2.70
E	W6-S1-0	301	717	2025	2.70

While contaminant concentrations, number of mining activity occurrences, density of mining activity in particular watersheds, and area of watersheds were made available, actual locations of the considered occurrences of mining activity were omitted.

1.3. HYPOTHESIS

The objective of this study is to determine if there is a relationship between the number of mining-related activities (occurrence of a strip mine, tailings pond, etc.) within a particular watershed area (i.e., density of mining activity) and the concentrations of three particular contaminants (lead, zinc, and barium) on suspended sediments collected from that watershed. It is expected that using and building upon data from previous work (Miller, 2020) by extending the timeframe of sample collection, following similar methods of sample collection and preparation, improved processing techniques, and a refinement of data used in analysis, a positive correlation between COC concentrations and density of mining activity will be identified.

2. LITERATURE REVIEW

2.1. MINING ACTIVITY IN MISSOURI

Mining activity in Missouri has been going on since the early 1700s, and still occurs today. Strip mines, surface mines, underground mines, tailing ponds, tailing piles, and tailing dams are all common occurrences within Washington County. The ores that were mined historically were lead and barium, however zinc, iron, cadmium, and copper were also common desirable ores.

The near-surface characteristic of the Potosi Dolomite allowed for easy access to many ore types, so many of the historic mining sites were surface mines, as opposed to underground mines. This is a common tactic that is still used in the area today. (Mugel et al., 2017).

2.2. CONTAMINANTS OF CONCERN

In order to expand on previous work, this study has been limited to three major contaminants of concern: lead, zinc, and barium. These are the same COCs that were considered in Miller's (2020) study of the MFRS and limiting the number of COCs ensures that the study will stay focused. These COSs are all commonly found in the Potosi Dolomite (Mugel et al., 2017).

2.2.1. Lead. Lead is a heavy metal that acts as a neurotoxin when it enters the body. It has major effects on neurological and reproductive systems within humans and other animals, and it bioaccumulates overtime. Children exposed to high amounts of lead often have delayed mental acuity and special needs. Adults exposed to lead run the risk of permanent damage to organ systems and hypertensive toxicity of lead (Agency for Toxic Substances and Disease Registry (ATSDR), n.d.-b).

In soils, the Eco- Soil Screening Levels (SSL) for lead range between 11 ppm and 1,700 ppm (Agency for Toxic Substances and Disease Registry (ATSDR), n.d.-b). Based on the contamination levels reported in this study, which will be discussed later, the MFRS has contamination levels of lead on soils within the upper limits and also exceeds those limits.

2.2.2. Zinc. Zinc is a metal that is considered to be a dietary necessity in human beings. Zinc deficiency is associated with skin and growth problems, as well as impaired immune function. (Agency for Toxic Substances and Disease Registry (ATSDR), n.d.-c)

Zinc’s Eco-SSL ranges between 46 ppm and 160 ppm (Agency for Toxic Substances and Disease Registry (ATSDR), n.d.-c). Based on the contamination results from this study, which will be discussed later, the MFRS far exceeds those values.

2.2.3. Barium. Barium is a relatively safe heavy metal due to the fact that it has a very low mobility in a soil context. Barium usually manifests in a sulfate or carbonate form, making it difficult for humans, plants, and animals to have it enter their body (Agency for Toxic Substances and Disease Registry (ATSDR), n.d.-a).

The Eco-SSL for barium is approximately 2000 ppm (Agency for Toxic Substances and Disease Registry (ATSDR), n.d.-a). Based on the results of this study, which will be discussed later, the barium contamination levels are consistently under, but close to, the limit.

2.3. METHODS FOR MEASURING CONTAMINANTS

The previous work conducted in this area by Miller (2020) used a passive time integrated suspended sediment sampler installed at key positions within the MFRS in order to capture sediments coming from suspected areas of point and nonpoint contamination sources. A handheld ED-XRF was used by a lab technician at the USGS to process the samples and get COC concentrations. The samples were sieved before being processed and only the finest particles were measured. The process for this study will closely follow the work done by Miller (2020) in order to continue and refine the findings from that study. Slight changes to Miller's (2020) process and methods were made in order to improve the process and results of the study. More sampling locations were used in order to improve the resolution of the study, and a more accurate processing tool, a benchtop WD-XRF, was used in order to achieve more accurate concentration values.

3. METHODS

3.1. PRELIMINARY WORK

Before suspended sediment samples could be taken and COC concentrations analyzed, quite a bit of preliminary work had to be done to prepare. Sampler locations had to be chosen, maps had to be made, routes had to be planned out, and background data had to be collected.

3.1.1. Mine Data Collection. Finding sources that provided locations of historic mines or mining activities was quite difficult, and the majority sources that supply information on mining activities had very little, if anything, reported in WC, let alone in the MFRS watershed.

3.1.1.1. Sources used. The first source that provided sufficient information on mining activities was the Mineral Resources Data System (MRDS) (Mason & Arndt, 1996-2011). Figure 3.1 below shows the occurrences of mining activity within WC from the MRDS, displayed as a shapefile in QGIS. Sampler locations were based upon this data, as it was found early on in the process of this study.

At the end of the study a second, more inclusive list of mine activity occurrences was discovered. The second list was from the Missouri Mine Inventory (Missouri Department of Natural Resources (DNR), 2021). Included in the Missouri Mine Inventory are four key data sets: the Inventory of Mines, Occurrences and Prospects (IMOP); Abandoned Mine Lands Project; Industrial Mineral Mines; and Metallic Mineral Waste Management Areas. When these four data sets are displayed independently within a GIS system, the only significant contributor to the Missouri Mine Inventory within WC was the IMOP, as the other three data sets had little or no data within WC.

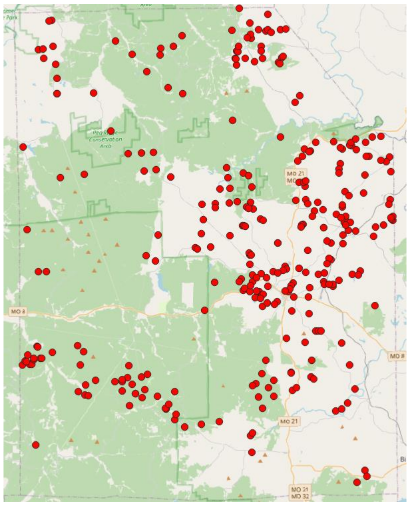


Figure 3.1 Occurrences of Mining Activity in Washington County, MO as Reported by the Mineral Resources Data System. (Mason & Arndt, 1996-2011).

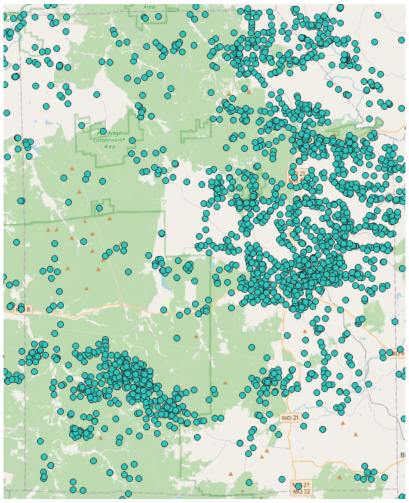


Figure 3.2 Occurrences of Mining Activity in Washington County, MO as Reported by the Missouri Mine Inventory. (Missouri Department of Natural Resources (DNR), 2021).

Figure 3.2 displays the occurrences of mining activity in WC according to the Missouri Mine Inventory. The differences between the two data system are quite significant, with the Missouri Mine Inventory documenting a far greater number of occurrences compared to the MRDS. However, both appear to have similar patterns relating to the areas in which the occurrences are located, with most appearing in the southwest and northeast portions of WC, and both systems served in characterizing the nature of mining activity within WC.

To further characterize the MFRS, and to determine the exact area of interest, elevation data was obtained from the Missouri Spatial Data Information Service (MSDIS), which was compiled by the Center for Applied Research and Environmental Systems (CARES). This data was then stitched together in QGIS for the purpose of this study, and can be seen in Figure 3.3

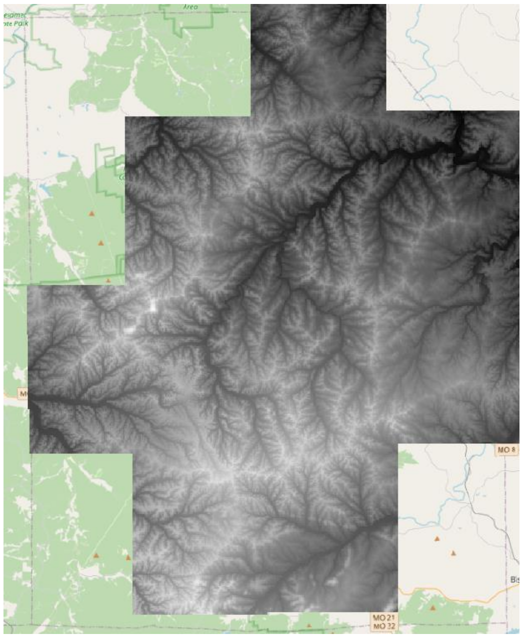


Figure 3.3 Compilation of 10m DEM Elevation Data for the Mineral Fork River System. (Center for Applied Research and Engagement Systems (CARES) & Missouri Spatial Data Information Service (MSDIS), 2005).

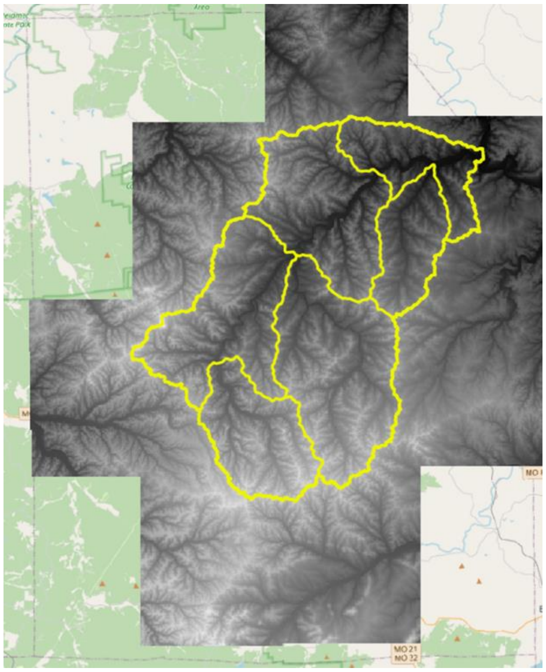


Figure 3.4 Compilation of 10m DEM Elevation Data for the Mineral Fork River System with Sub-watershed Boundaries. (USGS Watershed Boundary Dataset (2013)), (CARES & MSDIS, 2005).

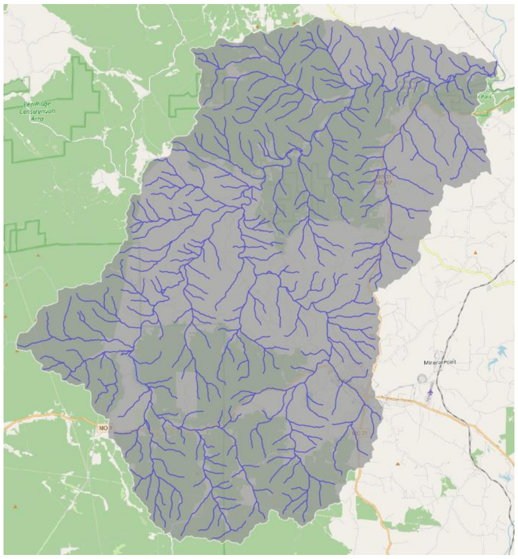


Figure 3.5 Mineral Fork River System Delineated Watershed With Stream Outlines. (Watershed Boundary Dataset from the USGS (2013)).

Watershed data from the USGS Watershed Boundary Dataset (2013) was also utilized during the preliminary work of this study. Figure 3.4 illustrates how officially recognized sub-watersheds of the MFRS were used to characterize a general outline of the whole watershed. These outlines were also useful in checking the delineations of sampler-specific watersheds, as well as developing a naming scheme that was clear and consistent. Figure 3.5 also displays an aspect of the Watershed Boundary Dataset. The blue lines, which are layered over the delineated MFRS watershed, are stream outlines. These outlines helped in choosing locations for samplers and delineating sampler-specific watersheds, as they could be viewed on top of the GIS road map. This allowed for rapid identification of areas that would be likely to have stream access from the road.

3.1.1.2. Related and unrelated mining sites. Using the Missouri Mine Inventory data system, the occurrences of mining activities could be counted and classified by COC involvement. Below are several tables that illustrate how COC information regarding mine activity was used to develop the relationships.

Table 3.1 Upstream Mining Activity, Total.

Sampler Name	Watershed Area [sq. miles]	Total Occurrences of Upstream Mining Activity	Density of Mining Activity [occurrences/sq. mile]
W1-S1	14.4	9	0.63
W2-S0	37.1	26	0.70
W2-S1	53.2	43	0.81
W3-S0	22.2	82	3.69
W3-S1	15.1	46	3.05
W3-S2	7	36	5.14
W4-S1	116	264	2.28
W4-S2	13.1	35	2.67
W5-S1	13.7	73	5.33
W6-S1	160.9	435	2.70

Table 3.2 Upstream Mining Activity, Lead.

Sampler Name	Watershed Area [sq. miles]	Pb Related Occurrences of Upstream Mining Activity	Density of Pb Related Mining Activity [occurrences/sq. mile]	Density of Mining Activity Unrelated to Pb [occurrences/sq. mile]
W1-S1	14.4	4	0.28	0.35
W2-S0	37.1	18	0.49	0.22
W2-S1	53.2	32	0.60	0.21
W3-S0	22.2	35	1.58	2.12
W3-S1	15.1	4	0.26	2.78
W3-S2	7	19	2.71	2.43
W4-S1	116	134	1.16	1.12
W4-S2	13.1	11	0.84	1.83
W5-S1	13.7	29	2.12	3.21
W6-S1	160.9	227	1.41	1.29

Table 3.3 Upstream Mining Activity, Zinc.

Sampler Name	Watershed Area [sq. miles]	Zn Related Occurrences of Upstream Mining Activity	Density of Zn Mining Activity [occurrences/sq. mile]	Density of Mining Activity Unrelated to Zn [occurrences/sq. mile]
W1-S1	14.4	2	0.14	0.49
W2-S0	37.1	3	0.08	0.62
W2-S1	53.2	3	0.06	0.75
W3-S0	22.2	4	0.18	3.51
W3-S1	15.1	0	0.00	3.05
W3-S2	7	4	0.57	4.57
W4-S1	116	30	0.26	2.02
W4-S2	13.1	2	0.15	2.52
W5-S1	13.7	14	1.02	4.31
W6-S1	160.9	41	0.25	2.45

Table 3.4 Upstream Mining Activity, Barium.

Sampler Name	Watershed Area [sq. miles]	Ba Related Occurrences of Upstream Mining Activity	Density of Ba Mining Activity [occurrences/sq. mile]	Density of Mining Activity Unrelated to Ba [occurrences/sq. mile]
W1-S1	14.4	3	0.21	0.42
W2-S0	37.1	7	0.19	0.51
W2-S1	53.2	8	0.15	0.66
W3-S0	22.2	57	2.57	1.13
W3-S1	15.1	36	2.38	0.66
W3-S2	7	20	2.86	2.29
W4-S1	116	162	1.40	0.88
W4-S2	13.1	28	2.14	0.53
W5-S1	13.7	53	3.87	1.46
W6-S1	160.9	258	1.60	1.10

Table 3.5 Upstream Mining Activity, Other.

Sampler Name	Watershed Area [sq. miles]	Non-Pb, Zn, or Ba (Other) Occurrences of Upstream Mining Activity	Density of Other Mining Activity [occurrences/sq. mile]
W1-S1	14.4	4	0.28
W2-S0	37.1	5	0.13
W2-S1	53.2	5	0.09
W3-S0	22.2	3	0.14
W3-S1	15.1	3	0.20
W3-S2	7	0	0.00
W4-S1	116	12	0.10
W4-S2	13.1	4	0.31
W5-S1	13.7	1	0.07
W6-S1	160.9	14	0.09

The Tables 3.1 through 3.5, all of which are above, define particular densities of mining activities for a sampler-specific watershed. Table 3.1 considers all occurrences of mining activity, while Tables 3.2, 3.3, and 3.4 only consider mining activities regarding lead, zinc, and barium, respectively. Table 3.5 considers all other possible ores of interest, which would be out of scope for this study.

3.1.2. Watershed Delineations and Sampler Locations. Using: the DEM elevation data from the Center for Applied Research and Engagement Systems (CARES) & Missouri Spatial Data Information Service (MSDIS), (2005), the stream outlines from the USGS Watershed Boundary Dataset (2013), the USGS MRDS (Mason & Arndt, 1996-2011), and the locations for samplers used in previous work conducted in the area (Miller, 2020), sampler locations were chosen. Sampler locations for this study and from previous work (Miller, 2020) and can be seen in Figure 3.6.

Sampler locations were chosen in a way that would provide varying densities of mining activity for each watershed, as well as proximity to a major road and access to the waterway from the road that avoided any trespassing.

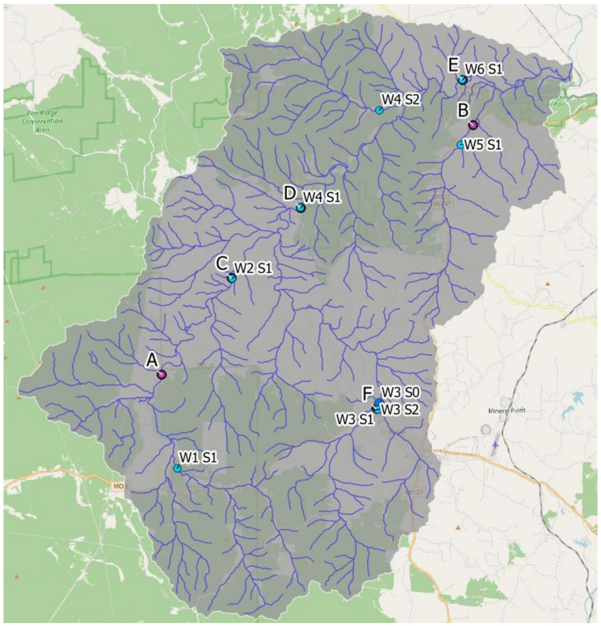


Figure 3.6 Locations of Samplers in the MFRS, Previous and Current Work.

Sampler names were developed based on the official sub-watersheds identified by the USGS Watershed Boundary Dataset (2013) and if the sampler was the first, second, third, etc. sampler to be installed within that watershed. Watersheds are denoted as W1 through W6, and samplers are denoted as S1, S2, etc. These two alphanumerical values are paired together, separated by a hyphen, to create unique sampler names. Samplers within the boundaries of their sub-watersheds can be seen in Figure 3.7.

Once sampler locations were identified and/or chosen, sampler-specific watersheds were delineated. Figure 3.8 shows all sampler-specific watersheds in an overlapping format.

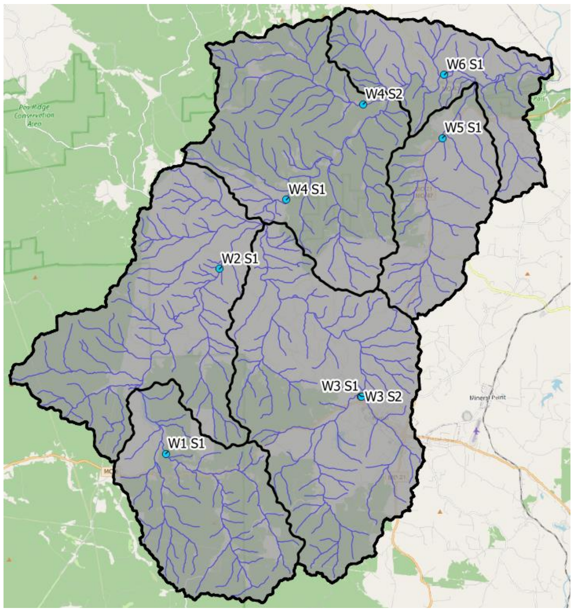


Figure 3.7 Sampler Locations Within the Official Sub-watersheds of the Mineral Fork River System. Data from the USGS Watershed Boundary Dataset (2013).

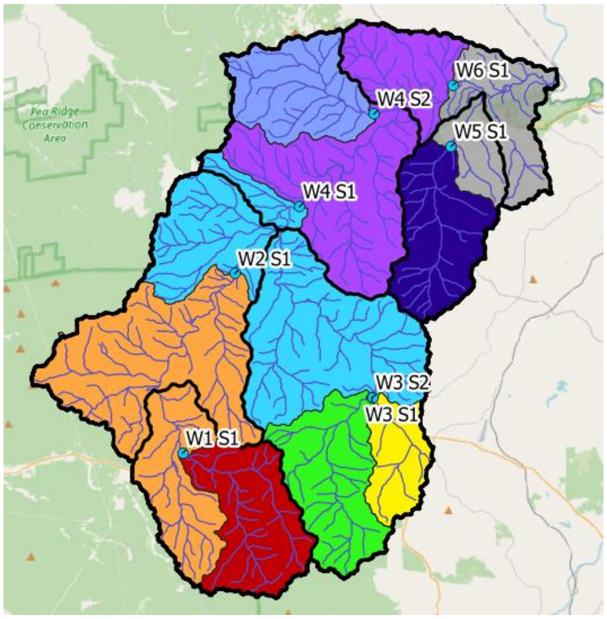


Figure 3.8 Sampler Locations and Sampler Watersheds Within the Mineral Fork River System. Delineated in QGIS and Overlain With Stream Outlines From the USGS Watershed Boundary Dataset (2013).

3.2. FIELD WORK

A significant portion of this project consisted of the field work required to gather samples. Field work often required 12-hour days in extremely remote parts of southeastern Missouri.

3.2.1. Getting to the Sites. Service in the MFRS area is scarce, and essential nonexistent. Desired locations for samplers were identified using QGIS and their corresponding GPS coordinates were obtained. These coordinates were marked in Google Maps, labeled, and then the Offline Google Maps that were extensive enough to navigate between all the sites, as well as to and from the laboratory, were downloaded to ensure safety and efficiency.

3.2.2. Installing Samplers. Sampler stations (referred to as samplers) consisted of: a PVC time integrated passive suspended sediment sampler (sampler) shaped like a diffuser, or a large crayon, with a hole in the pointed end and in the flat end (which would also unscrew using a wrench); two, 5-foot poles (SuperStruts); and two 6-inch duct clamps. To install the samplers, the SuperStrusts were hammered into the streambed using a 4 pound engineering hammer until at least 2 feet of SuperStruts were in the ground, which you can see happening in Figure 3.7.

Once the SuperStruts were hammered into the ground, the sampler was positioned with the pointed end of the sampler facing upstream and was attached to the SuperStruts using the duct clamps. Figures 3.8 and 3.9 shows fully installed passive sediment samplers. Writing on the samplers with Extreme Sharpies was necessary to keep nearby landowners at ease, prevent any tampering, and ensure that there was a contact so that the sampler could be returned in case of a removal by human interaction or natural forces.

Figure 3.9 Installation of SuperStruts Into a Streambed by the Author, T.N. Mortensen.

Figure 3.10 A Fully Installed Sampler.

Figure 3.11 A Fully Installed Sampler With Identifying Information.

3.2.3. Collecting Samples. To collect samples from the sampler, Duct Tape or saran wrap would be used to cover the pointed end of the sampler to prevent sample loss, then the duct clamps would be loosened, and the sampler slid out, ensuring to keep the pointed end downwards or the hole on the flat (back) end of the sampler covered.

The sampler would be shaken, rolled, or tipped end to end over and over again in order to disturb the sample inside of the sampler. This was done in order to ensure the maximum amount of recovery for the sample as possible. One or more large gallon bag would then be prepared with the proper sampler notation as well as the number of times that we went out to the field (EX: if taking a sample from the first sampler installed in watershed #6, and it was the fourth trip out to the field, then the notation would read W6-S1-4). The duct tape or Saran wrap would then be removed from the pointed end of the sampler and the contents of the sampler would be allowed to flow freely into the prepared gallon bag(s) until the bag(s) were, at maximum, 3/4 full. The bags would then be put in an additional gallon bag and stored in a repurposed Kitty litter container for transportation back to the laboratory. once the contents of the sampler were empty, the flat end of the sampler would be unscrewed using a wrench and the inside would be inspected for any residual sample. If residual sample remained, then, keeping the pointed and covered, water would be scooped up into the sampler and splashed around in order to remove the rest of the sample. The water and sample mix would then be put into another gallon bag. If there were multiple gallon bags, they all added up to be one singular sample.

Once the sampler was clean on the inside, and all possible sample was removed, the flat end of the sampler would be replaced, and the sampler would slide back through the duct clamps to be secured again.

3.3. LAB WORK

After bringing the samples back from the field to the laboratory, there was a little bit of prep work that would need to be done in order to prepare the samples to be processed. This included decanting and drawing out the samples to remove as much excess water as possible, preparing them for the XRF processing.

3.3.1. Decanting and Drying Samples. Figure 3.10 illustrates the process used to decant the samples.

First, the additional exterior plastic bag would be removed and the primary plastic bag, full of water and sediment sample, would be positioned in a way such that a corner of the plastic bag would be pointing down to the ground, and all other corners would be gathered up at the top. The sample would then be disturbed to ensure any sample sticking to the sides of the bag would be removed.

Once the sediment had settled out again, and there was a clear definition of sediment and water, a stainless-steel push pin would be used to poke holes in the bag near the top of the water. This would allow the water to flow out of the bag slowly as to not allow much sediment to escape. this would be continued until very little water was left in the bag.

At this point the sample should look like a very thick, muddy mixture. There may be sand, or organic matter, mixed in with the silt and clay. This was to be expected and would be dealt with later.

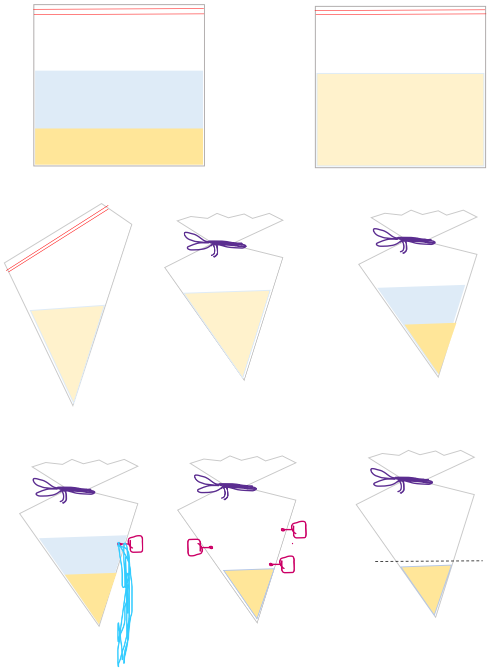


Figure 3.12 Illustration of the Decanting Process.

Using stainless steel scissors, the plastic bag would be cut just above the line of the thick sediment and water mixture, and the resulting mixture would be poured out onto a waterproof plastic plate with edges that would not allow water to flow off the edges.

Distilled water in a clean spray bottle would be used to clean out any residual sample that was clinging to the corner of the bag.

The sample then would be left to air dry. This would take several days. when in a time crunch, and oven was used at a temperature of 150 degrees Celsius to hasten the evaporation of water from the sample.

3.3.2. XRF Sample Preparation. Once the samples were entirely dried out, they were collected from the plastic plates. Depending on the sample, and when it was taken, the sample may be stored in a quart sized plastic bag and then ground up to a fine powder using a mortar and pestle, or it may be ground into a fine powder first, as shown in Figure 3.11, and then stored in a plastic bag. This is done to keep moisture out of the sample and keep the sample ready to be made and to a pellet for XRF processing.

Figure 3.13 Sample After Being Ground Into a Fine Powder.

3.3.3. XRF Pellet Making. To turn the sample into a pellet that can be used in the XRF, the sample would be mixed with a binder. The binder ratio would be chosen based on the amount of sample available. Regardless of the amount of binder used, the results from the XRF would be accurate due to the XRF software accounting for the binder and omitting it from any calculations. The XRF that was used was a Rigaku Supermini200 Benchtop WD-XRF. The pellet making process was based off of the Rigaku Journal Article (Takahashi, 2015).

Once you have a finely ground sample, you add binder into the sample at the desired ratio and grind both the sample and the binder in a mortar and pestle until it is a homogeneous mixture. Then you take a pellet cap and fill it with the mixture of binder and sample. Once you have done this, you can load the cap into a press machine to apply 25 Mpa to the sample. This compacts everything into a very nice pellet. Figure 3.12 illustrates what a full pellet cap should look like.

Figure 3.14 A Filled Pellet Cap Being Loaded Into a Press Machine Chassis.

3.3.3.1. Problem with small sample sizes. Small sample sizes pose a problem to creating a pellet for the XRF. The average sample size, including binder, should be around 6 or 7 grams of sample. When there is not enough sample to reach this limit, more binder must be used or the total size of the sample must be decreased.

3.3.3.2. Test samples. In order to become familiar with how to use the XRF machine, test samples were prepared using bank sediment from one location within the MRFS. These test samples were not intended to be included as values for COC concentrations.

When the test sample results came back, a method for processing the small sample sizes was created. It was decided that as much sample would be used as possible, and the rest of the sample would be made up of a cellulose binder comma the same binder used for the standard pellets. If necessary, alterations would be made to the pellet caps in order to prevent any complications, such as splitting caps or overlapping flaps that altered the results. Figure 3.13 is an example of an altered cap, where the edges were folded over to make the cap shallower.

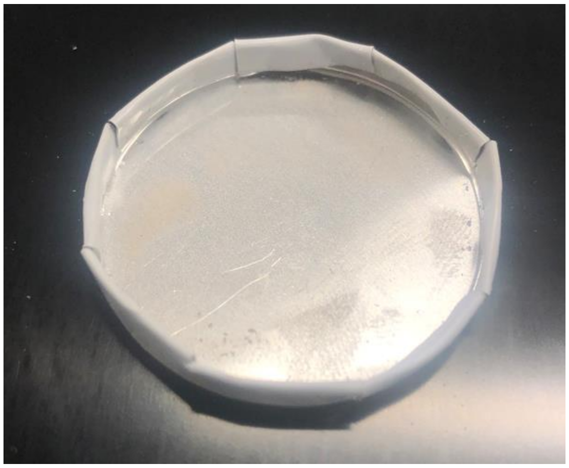


Figure 3.15 An Altered Pellet Cap.

4. DATA AND RESULTS

4.1. TEST SAMPLE RESULTS AND OBSERVATIONS

Test samples were run on one large sample of bank sediment in order to gain familiarity with the XRF system while using a similar material that could be assumed to be homogeneous in composition. Results were not deemed necessary to the objectives of this study, however future studies should consider taking consistent background samples using bank sediments to establish a baseline of what, at that point in time, is expected to be in the area.

4.2. SAMPLE RESULTS AND ANALYSIS

In this study, COC concentrations were determined with a highly accurate benchtop, WD-XRF called the Rigaku Supermini200. Miller’s (2020) study also used XRF processing to determine the COC concentrations, however the XRF used in Miller’s (2020) study was a handheld, ED-XRF, which are considered less accurate overall when compared to a WD-XRF. Because of the differences between the accuracy levels, COC concentration results from this study and Miller’s (2020) study are analyzed independently. However, because the goal of this project is to expand upon the previous work conducted in this area, the combined set of COC concentrations were also evaluated.

4.2.1. Results from this Study. When considering the COC concentrations from samples taken during the duration of this study and the density of total mining activity as calculated in this study, there appears to be a strong ($R^2>0.6$), positive correlation between all three COC concentrations and the density of total mining activity. Figure 4.1 illustrates these relationships between lead, zinc, and barium and the density of mining activity in a sampler-specific watershed within the MFRS.

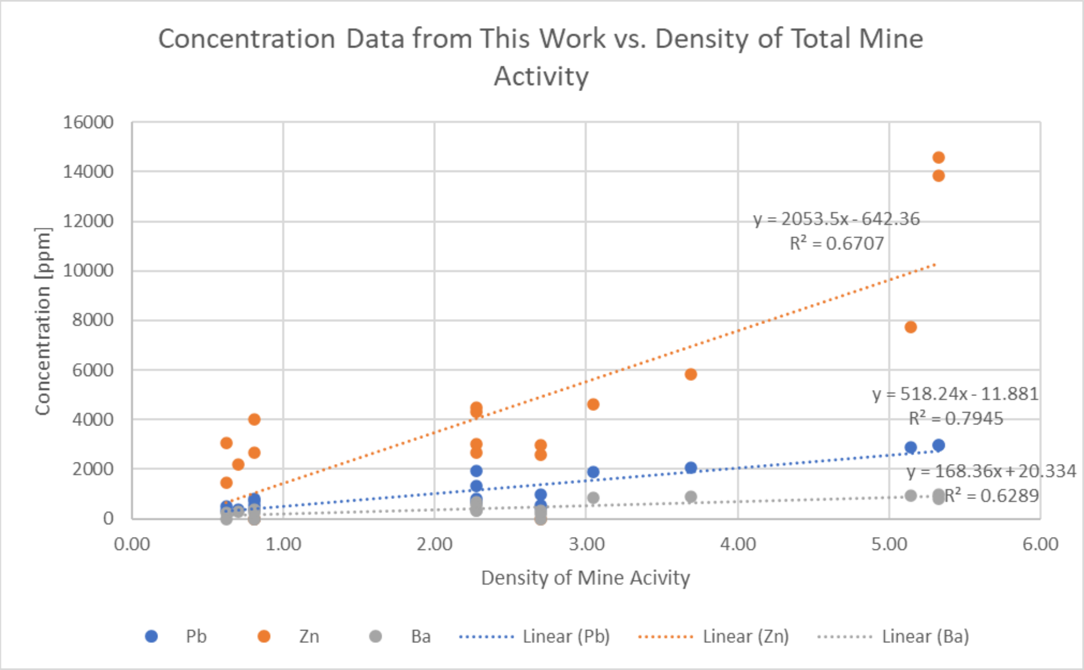


Figure 4.1 Concentration Data from This Work vs. Density of Total Mine Activity.

4.2.2. Results Regarding Data from Previous Study. The results from previous work done in this area (Miller, 2020) were deemed largely inconclusive. When the COC concentrations from Miller's (2020) study were taken and compared to the calculated density of total mining activity from this study, there appears to be a slight positive relationship between lead and zinc concentrations and the density of total mining activity, while there is a slight negative correlation between barium concentrations and the density of total mining activity. However, these relationships are weak ($R^2<0.4$), as illustrated in

Figure 4.2. This presents a stark contrast between the results from this study and Miller's (2020) study, which could be a result of the XRF used to process the samples.

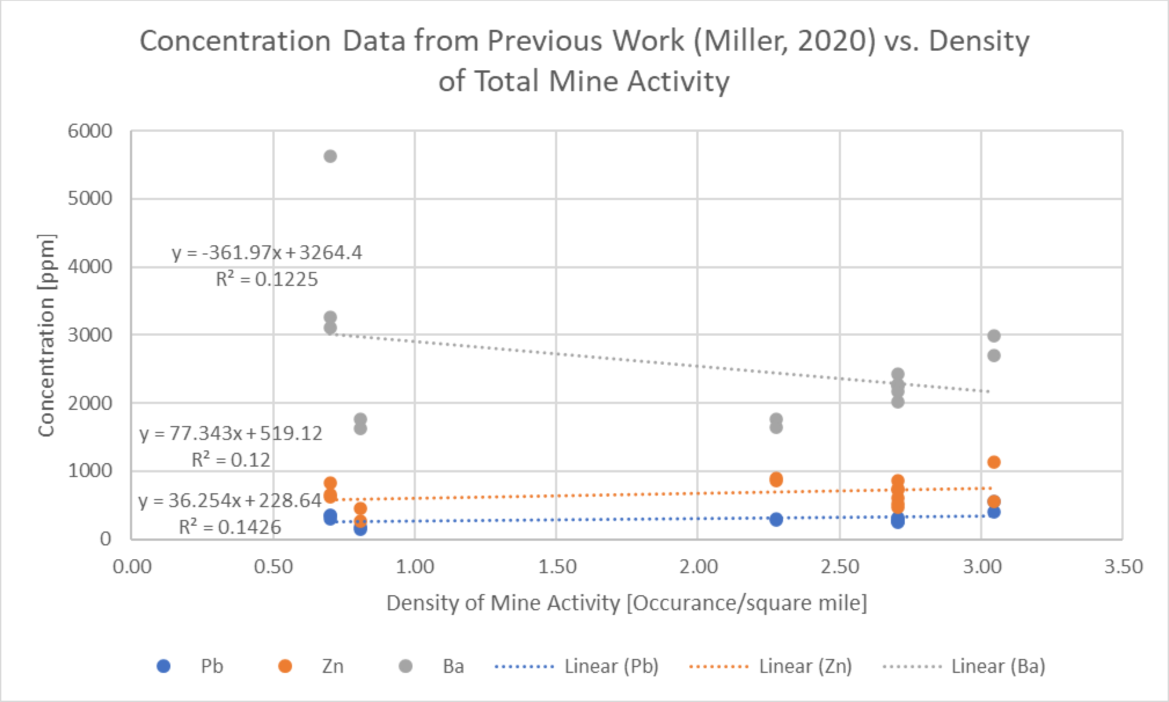


Figure 4.2 Concentration Data from Previous Work (Miller, 2020) vs. Density of Total Mine Activity.

4.2.3. Combined Results. Considering COC concentration data collected from both studies, and the density of mining activity calculated in this study.

4.2.4. COC Concentrations vs. Density of Total Mining Activity. When looking at all concentration data vs. the density of total mining activity in Figure 4.3, there appears to be a moderate correlation ($0.4<R^2<0.6$) between the COC concentrations of lead and zinc and density of total mining activity, similar to what was seen in the results from Figure 4.1. However there appears to be no relationship (R^2=~0) between the two factors when considering barium. This observation aligns more with Miller's (2020) observation, so long as only barium is considered.

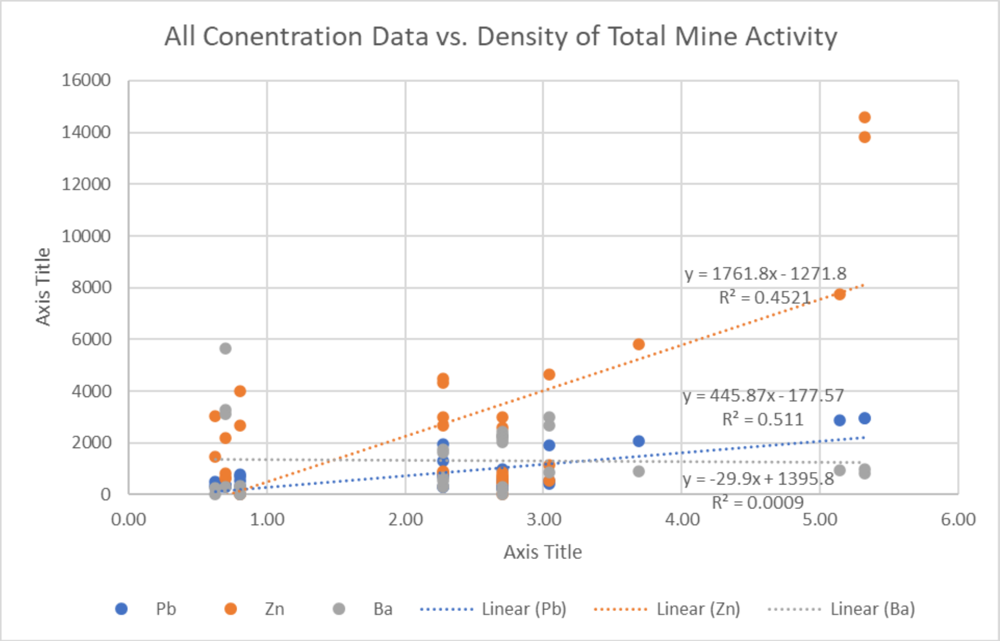


Figure 4.3 All Concentration Data vs. Density of Total Mine Activity, Linear Plot.

The positive correlation regarding lead and zinc, as well as the lack of correlation regarding barium, are further emphasized by Figure 4.4. The visual given by Figure 4.4 for Zinc is especially impactful and very clear. The positive correlation between the density of mining activity and lead is also able to be seen in the box and whisker plot below.

These correlations, or lack thereof, are only for the density of total mining activity, which includes all occurrences of mining activity. Contemplating the relationship between a COC and it's related, and unrelated, mining activities is important, as it will help determine if mining of any sort will increase the concentration of contamination regardless of the COC, or if a particular COC is going to be more concentrated due to a higher density of mining activity occurrences related to that COC.

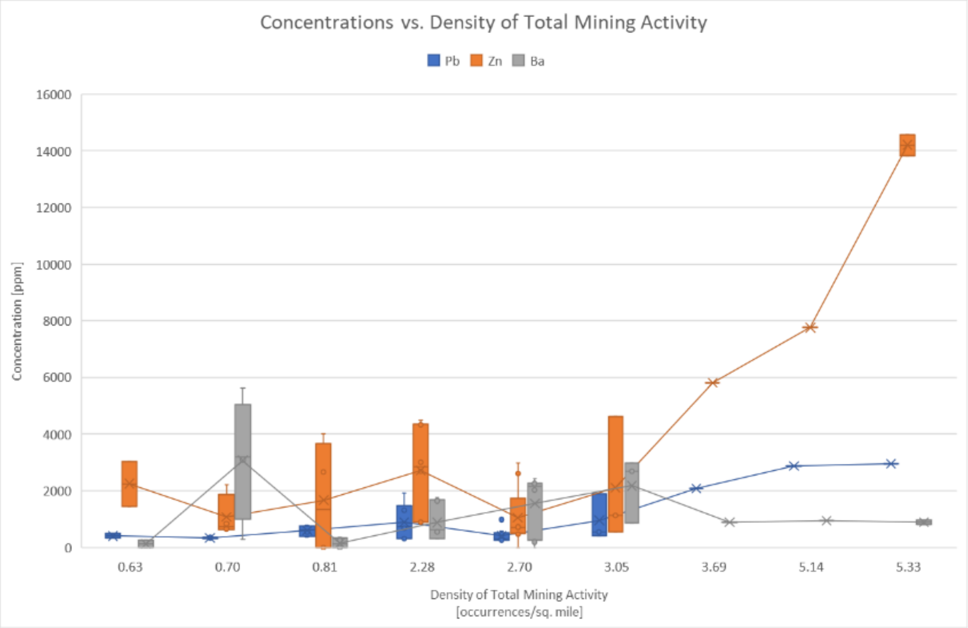


Figure 4.4 All Concentration Data vs. Density of Total Mining Activity, Box and Whisker Plot.

4.2.5. COC Concentrations vs. Density of Related Mining Activity. The relationship between COC concentrations and the density of related mining activity will indicate whether or not the COC has a higher likelihood of occurring in high concentrations in areas where the mining activity is related to that COC.

Below, in Figures 4.5 and 4.6, we can see that lead has a moderate ($0.4<R^2<0.6$) positive correlation regarding concentration and density of related mining activity.

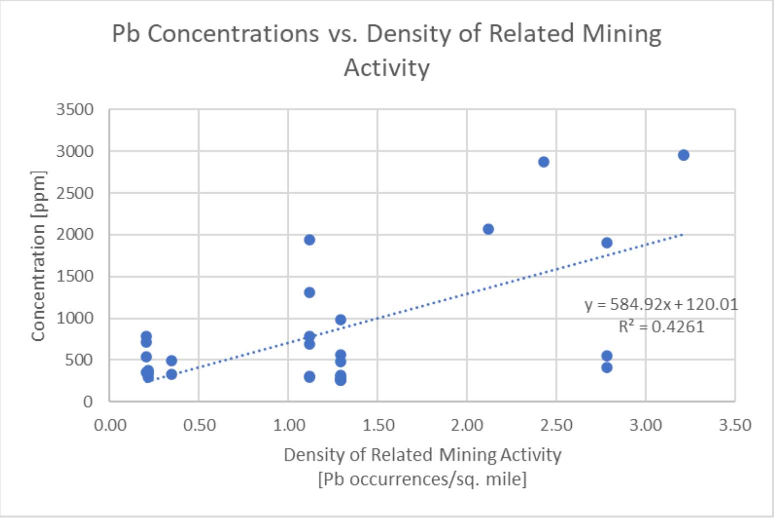


Figure 4.5 Pb Concentration vs. Density of Related Mining Activity, Linear Plot.

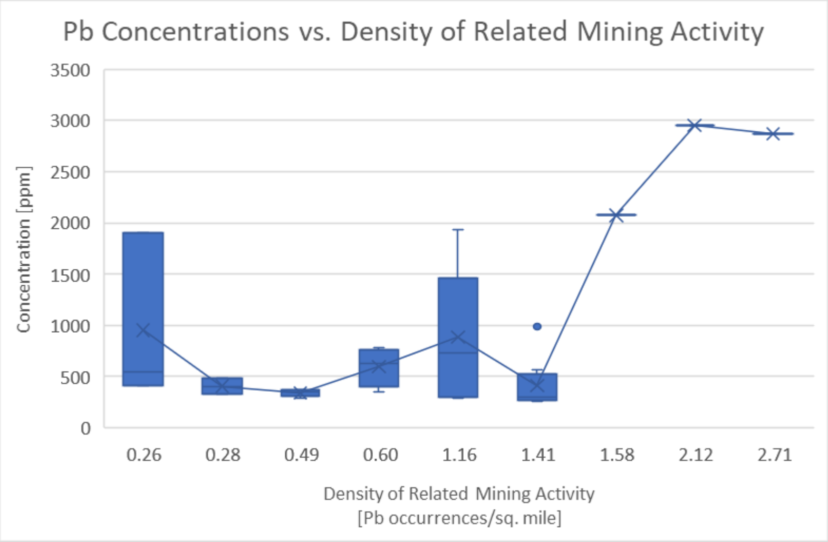


Figure 4.6 Pb Concentrations vs. Density of Related Mining Activity, Box and Whisker Plot.

Figure 4.7 and Figure 4.8 demonstrate a strong (R^2>0.6) positive correlation between the concentration of zinc and the density of related mining activity.

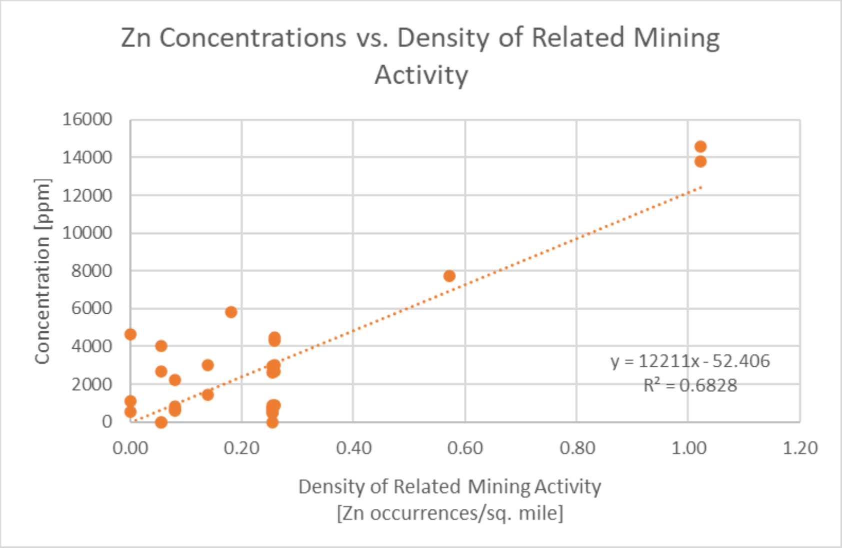


Figure 4.7 Zn Concentrations vs. Density of Related Mining Activity, Linear Plot.

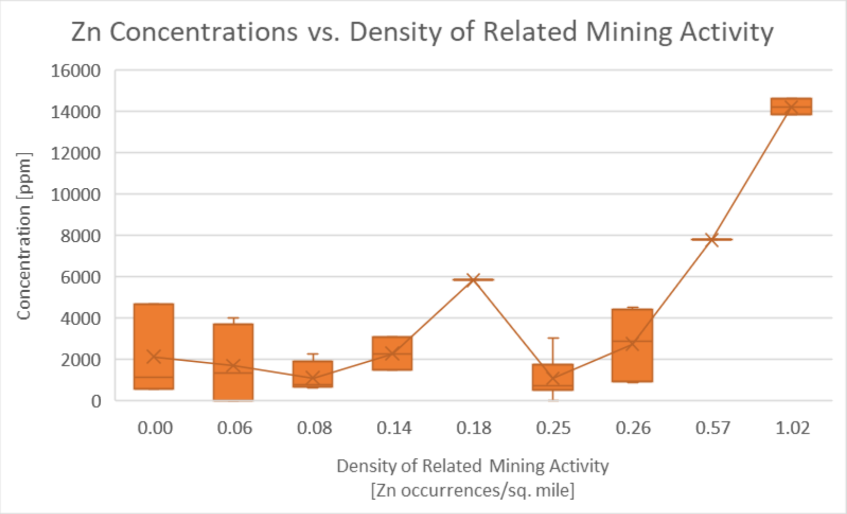


Figure 4.8 Zn Concentrations vs. Density of Related Mining Activity, Box and Whiskers Plot.

Figure 4.9 and Figure 4.10 show no relationship (R^2= ~0) between the concentration of Barium and the density of related mining activity.

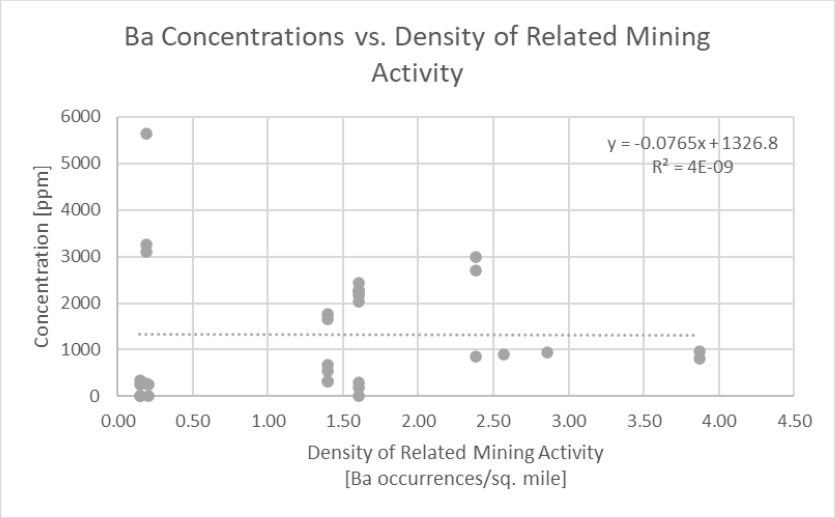


Figure 4.9 Ba Concentrations vs. Density of Related Mining Activity, Linear Plot.

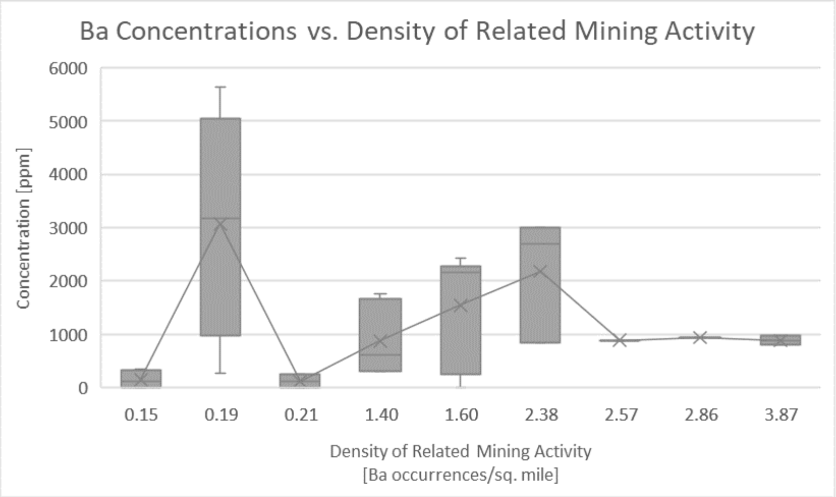


Figure 4.10 Ba Concentrations vs. Density of Related Mining Activity, Box and Whiskers Plot.

4.2.6. COC Concentrations vs. Density of Unrelated Mining Activity. The Relationship between COC concentrations and the density of unrelated mining activity is important as it demonstrates the likelihood of a COC occurring in high concentrations regardless of what ore is being mined. Unrelated mining activity has more serious implications than related mining, as this indicates that there is a chance for a serious contaminant to be released into the environment unknowingly, as the COC would likely be considered a naturally occurring background contaminant. This could also cause significant harm to those who live in environments where contaminants naturally occur.

Lead shows a weak (R^2<0.4) positive correlation between concentration and the density of unrelated mining activity, as shown in Figure 4.11 and Figure 4.12.

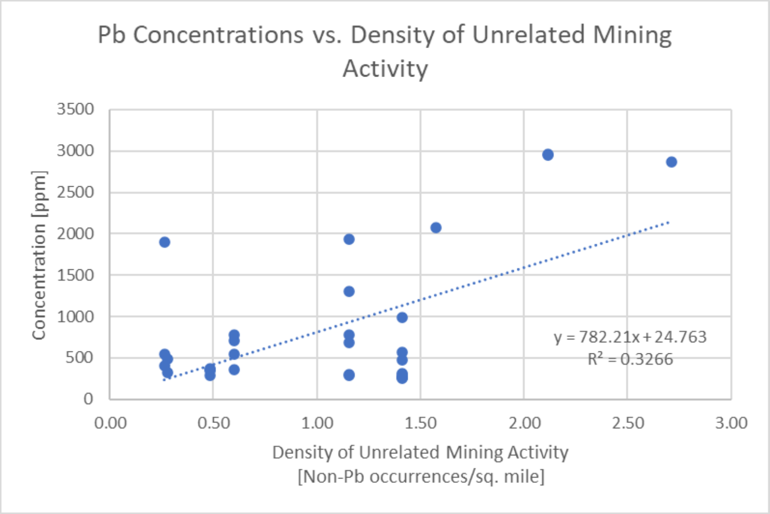


Figure 4.11 Pb Concentrations vs. Density of Unrelated Mining Activity, Linear Plot.

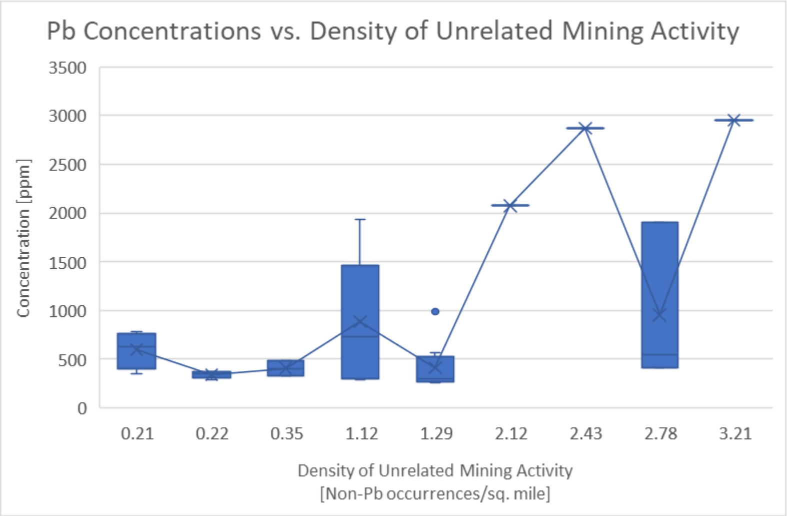


Figure 4.12 Pb Concentrations Vs. Density of Unrelated Mining Activity, Box and Whiskers Plot.

Zinc also shows a weak ($R^2<0.4$) positive correlation between concentration and density to unrelated mining activity, as shown in Figure 4.13 and Figure 4.14.

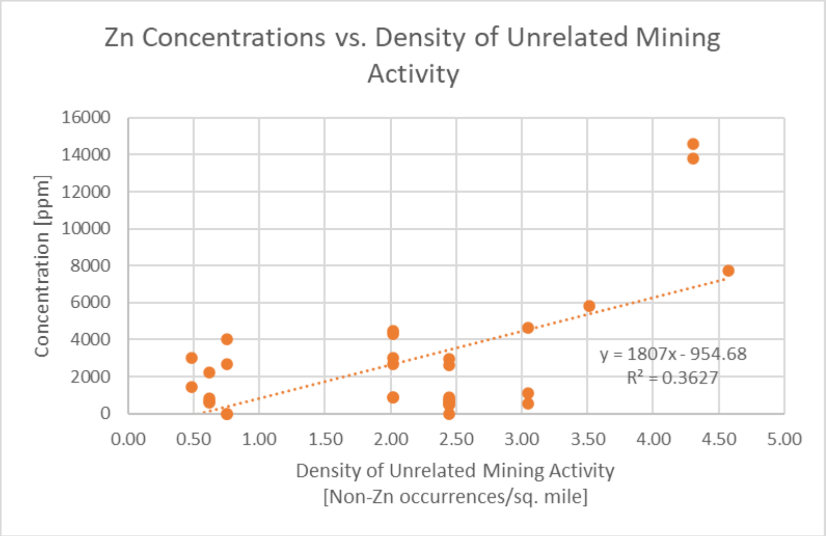


Figure 4.13 Zn Concentrations vs. Density of Unrelated Mining Activity, Linear Plot.

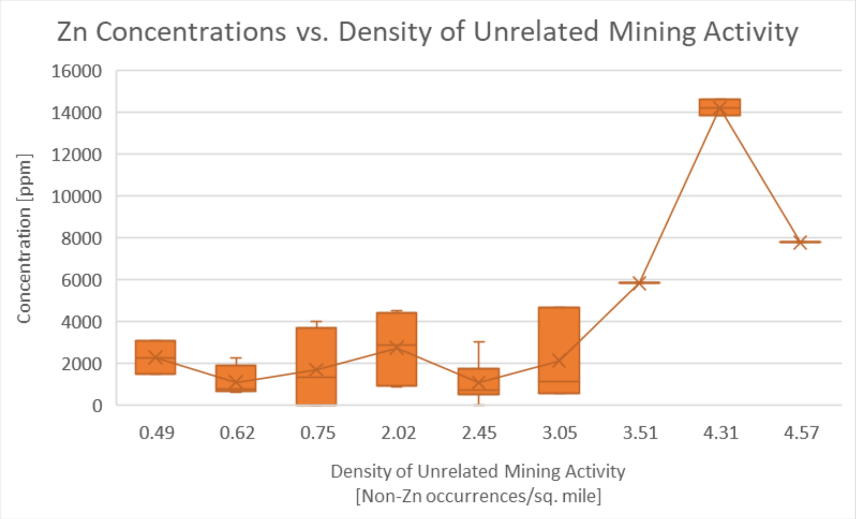


Figure 4.14 Zn Concentrations vs. Density of Unrelated Mining Activity, Box and Whisker Plot.

It appears that there is no relationship between barium concentrations and unrelated mining activity (R^2=~0) according to Figure 4.15 and Figure 4.16.

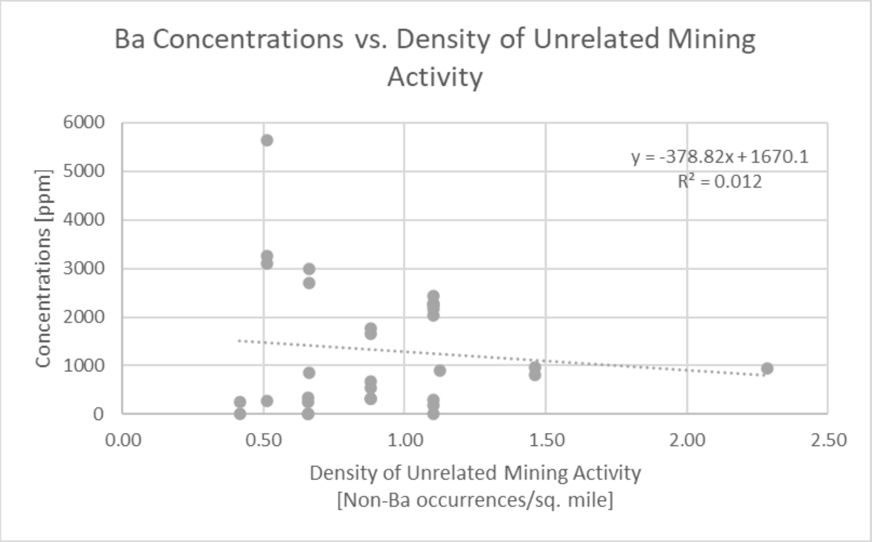


Figure 4.15 Ba Concentrations vs. Density of Unrelated Mining Activity, Linear Plot.

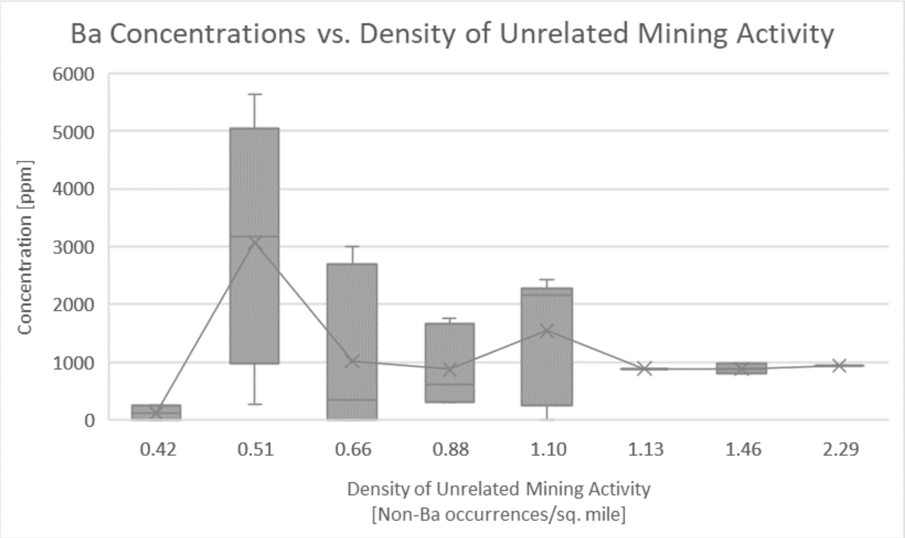


Figure 4.16 Ba Concentrations vs. Density of Unrelated Mining Activity, Box and Whisker Plot.

4.3. COC CONCENTRATIONS VS. WATER FLOW

When considering the same data used in Miller's (2020) study regarding water-level and COC concentrations at a W6-S1, whose watershed encompasses the majority of the other sub-watersheds, we can see a relationship between all three COC's and the water-level.

When water-level decreases, flowrate generally decreases. Figure 4.17 shows that when the flowrate decreases, the barium concentrations decrease (a positive correlation). However, when flow-rate decreases, lead and zinc concentrations increase (two negative correlations). Miller (2020) stated that due to the conflicting positive and negative correlations, there was no relationship. However, it is this authors belief that the behaviors of the contaminants were not considered fully. Due to barium's natural state being a form of barium sulfate, barium would only be likely to occur as a sediment in its sulfate form, not as barium sorbed to another particle, so concentrations would likely be higher at times of faster flow when streams would have the capacity to carry larger particles of barium sulfate downstream.

On the other side, lead and zinc would be more likely to travel sorbed onto the finest particles available (clay sized particles) and are naturally attracted to clay minerals. Because of these behaviors, when flowrates are high larger particles are carried to the sampler where they would settle out and the fine particles have a higher likelihood of bypassing the sampler, should the sampler not diffuse the flow enough, and being carried on downstream. This would result in a diluted sample with diluted levels of lead and zinc since the more contaminated particles bypassed the sampler.

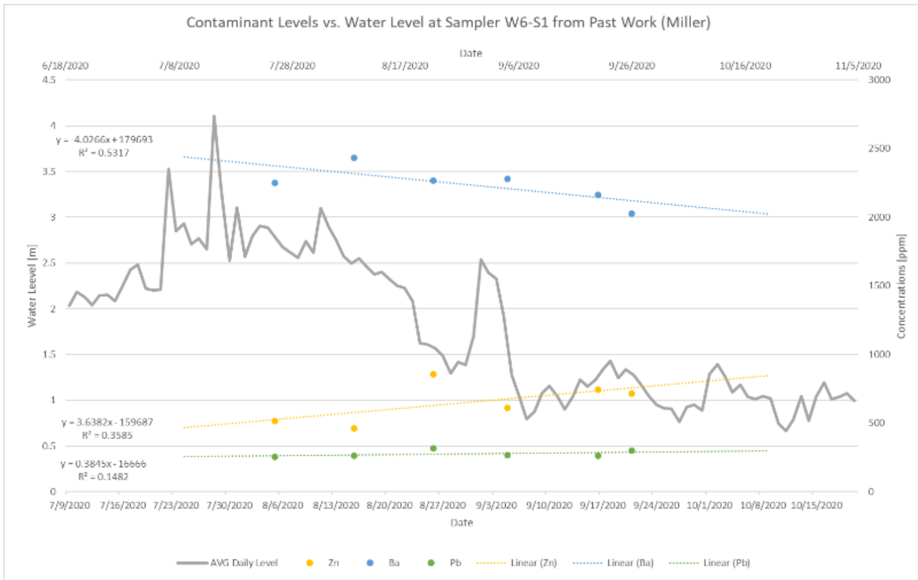


Figure 4.17 Contaminant Levels vs. Water Levels at Sampler W6-S1. (Miller, 2020).

However, at times of low flow fine particles are more likely to settle out in the samplers and larger particles would not be able to be carried to the sampler at all, resulting in a sample that is less diluted from less contaminated larger particles, and therefore would have higher concentrations of lead and zinc. Therefore, it is this authors opinion that there is a relationship between flowrate/water-level and COC contaminations in suspended sediment loads.

5. FINDINGS AND DISCUSSION

5.1. KEY ASSUMPTIONS MADE

In order to make this study as straightforward and the results as clear as possible, several assumptions must be made. Below is a list of several key assumptions that should be made when analyzing the COC concentrations and density of mining activities. This list is not meant to be entirely comprehensive, but to guide the reader towards the mindset used during the analysis of this study.

The first assumption is that there were no instances of sample contamination that would significantly alter the COC concentration results. This means that one should assume that all provisions taken to produce a pure, representative sample were successful.

Another assumption that should be made is that the COC concentrations from this study are more accurate and offer a better representation of COC concentrations in relation to density of mining activity than the COC concentrations reported in Miller's (2020) study, and therefore when considering the two studies separately, the data presented in this study should be considered to have a higher value.

All current mining operations within the watershed are considered to be part of the historic mining activity so long as the sites were in operation before the beginning of this study in 2021.

EPA cleanup actions within the watershed are not considered to contribute to ongoing releases of contamination from historic mining sites, as the EPA will follow strict guidelines to contain the contaminants and prevent further releases.

It should be assumed that all procedures were followed as accurately as possible, and that no deviations were made in the course of this study unless they have been specifically pointed out.

This study acknowledges that there is no such thing as perfect when it comes to procedures, studies, or sampling that requires field work, but assumes that the minute sources of error that occur in the process of such procedures, studies, or samplings can be ignored for the purpose of this study.

5.2. LIKELY SOURCES OF ERROR

Though all possible efforts were taken in this study to prevent gross contamination of the samples, any study that requires fieldwork is bound to have certain sources of error, and this study is no different. Below is a list of the most likely sources of error within this study; it is not meant to be a comprehensive list, however.

One likely source of error that could affect COC concentrations in samples are the samplers themselves. When collecting the samples from the samplers, if the sample is not collected in its entirety, then it is possible that there may be cross contamination between the samples, resulting in overly diluted or saturated COC concentrations between samples depending on what the COC concentrations were and how much of the previous sample was left in the sampler.

Another source of error is a result of inaccurate mining data. Without access to the source material, no verification can be made that occurrences of mining activity were omitted or counted twice in their reporting.

Contaminated laboratory materials are another source of error. Without a sterile environment, cross contamination, either between samples or from outside sources, is a possibility, no matter what precautions are taken.

Samples are double bagged in zip-lock bags when collected and transported from the field to the lab in sealed containers. However, it was not always possible to use the same container for any given station thought the study, and occasionally multiple samples had to be transported in the same container. Though no leaks of the bags were noted, it is still possible that cross contamination happened in these scenarios and could have altered the COC concentration results.

Improper XRF calibration or usage is a possible source of error. The majority of the sample processing using the Rigaku Supermini200 was self-taught, and no sources outside of those already mentioned were available for training or questions. Miller's (2020) study also has possible XRF error sources, as the samples were sent off to a USGS lab for analysis, so Miller could not verify the results firsthand. A less accurate XRF models was also used in Miller's (2020) study.

5.3. OBSERVED OR SPECULATED RELATIONSHIPS

The stark contrast between the concentration values found in this study compared to the concentration values found in Miller's (2020) study are quite drastic. When the values are combined and then compared to various densities of mining activity, the findings are only somewhat consistent, with two of the three COCs following the same patterns and the third not having any relationship to the densities of mining activity. While this study appears to have at least partially accomplished the goal of expanding

Miller’s (2020) previous study and increasing the resolution of the data, there are several things that should be discussed before drawing any conclusions

5.3.1. Between COC Concentrations and Density of Mining Activity. Overall there appears to be a positive correlation with the density of mining activity and the concentrations of lead and zinc. mining activity. Barium concentrations do not appear to have any relationship with the density of mining activity.

Lead and zinc both appear to have stronger correlations with total mining activity and related mining activity densities and concentrations.

5.3.2. Between COC Concentrations and Mine Production. Although it would have been a great qualifier, there was not enough data regarding mind productions in tonnage for this to play a significant role in data analysis within this project.

5.3.3. Between COC Concentrations and Population Density. the area surrounding the MFRS has an incredibly low population density. Figure 5.1 illustrates the land use classifications for the MFRS and a nearby watershed.

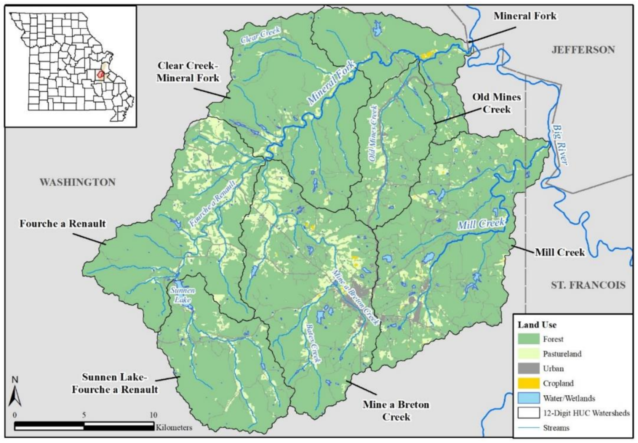


Figure 5.1 USDA-NASS 2017 Land Use Classification for Several Big River Tributaries. (Coonen, 2020).

We can see here that the majority of the area is either forest or farmland, with a very small portion on the fringes of the MFRS being classified as populated. Because of this, population density is not considered to play a large enough factor in contaminant transportation within this study.

5.3.4. Between COC Concentrations and Precipitation. The MFRS is a highly unmonitored portion of land. Despite best efforts, accurate precipitation data was unable to be located. Although, based on the results from the concentrations at sampleR W6-S1, It is hypothesized that precipitation plays a large factor in the transportation of contaminated sediments within the MFRS.

5.3.5. Between COC Concentrations and Time. Due to the different methods used to process the sediment samples, a comparison of the COC concentrations would yield inaccurate results period further study within the same area and using the same methods of processing samples will be needed before COC concentrations can be compared two temporal data.

5.3.6. Between COC Concentrations and Historic Mining Practices. There was not enough existing data to compare COC concentrations and the historic mining practices used within that watershed.

6. CONCLUSIONS

6.1. HYPOTHESIS SUPPORT

Based on the COC concentrations and their relationships with total, related, and unrelated mine activity densities that have been identified, it can be said that there is partial support for the original hypothesis that this study was based upon.

Lead and zinc concentrations both have strong enough positive correlations with all three types of mine activity densities and therefore there is sufficient evidence to claim that there is a relationship between these two factors.

Barium, however, does not appear to have any relationship with mining activity densities.

Continued investigation, sampling, and evaluations of the Mineral Fork River System would be expected to further strengthen the claim that lead and zinc have a relationship with mine activity densities, and may establish a relationship with barium and mining activity densities.

6.2. SUGGESTIONS MOVING FORWARD

Moving forward, any further study within this area should be conducted over uneven longer period of time and should integrate data from all previous works in order to establish a cohesive picture. More investigation into mining practices, mine production, area covered by mining activities, and other such topics would be helpful in establishing further relationships between contaminant concentrations and particular mining practices. The number contaminants of concern should also be expanded to include other heavy metals. This would also aid in developing a better picture of what is going on within the Mineral Fork River System. Examining other watersheds within Washington County, Or other watersheds that contribute to the Big River, would also give an interesting perspective on contaminant transports via suspended sediments. Biological assessments, such as micro invertebrate studies, should also be conducted near sampling sites, As it would give further strength to any claims regarding the effects of contamination within the watershed.

APPENDIX

All images, figures, and supplemental materials will be found within the appendix in order to provide a clear and concise body while still providing relevant information.

1. FIGURES

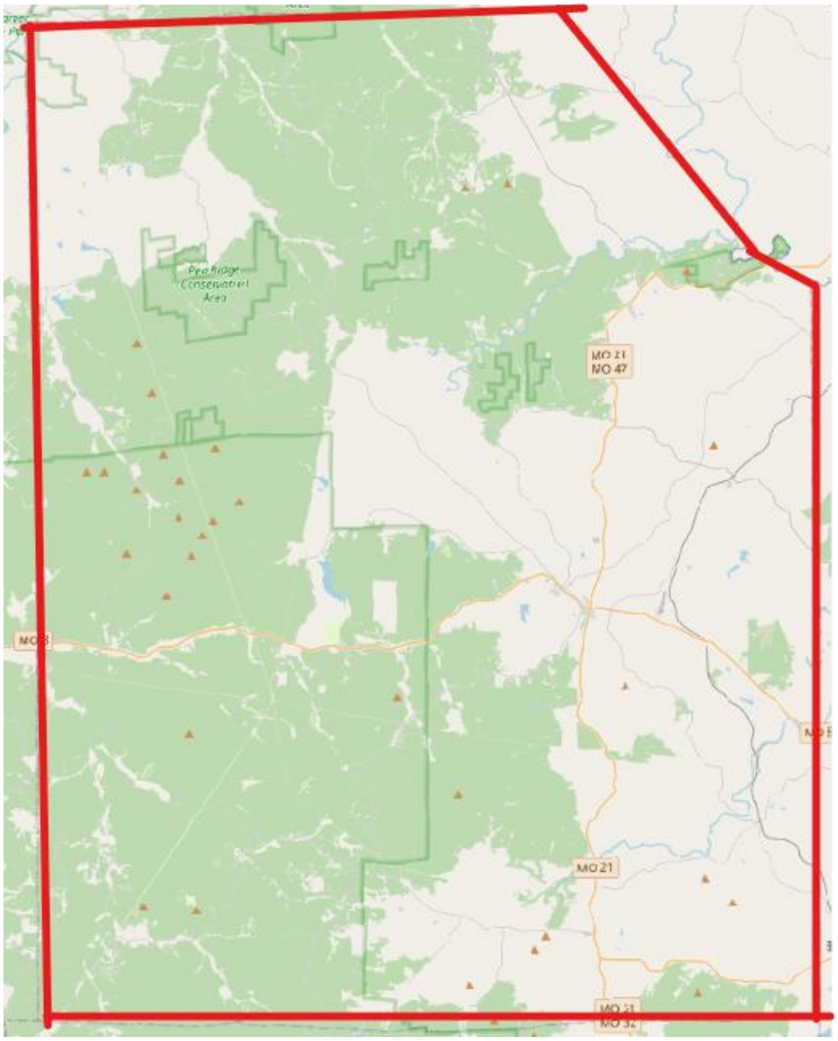


Figure A.1 Border Outline of Washington County, MO

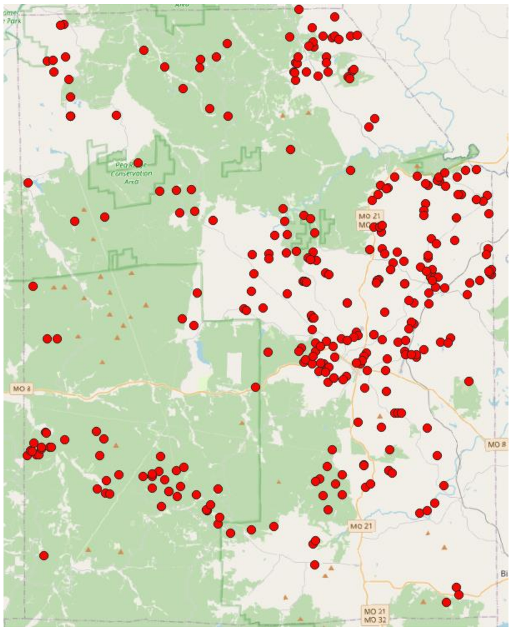


Figure A.2 Occurrences of Mining Activity in Washington County, MO as Reported by the Mineral Resources Data System (Mason & Arndt, 1996-2011).

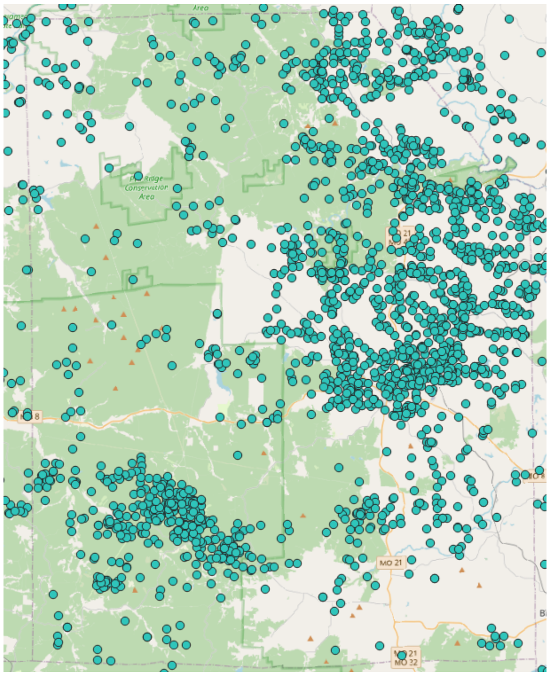


Figure A.3 Occurrences of Mining Activity in Washington County, MO as Reported by the Missouri Mine Inventory (Missouri Department of Natural Resources (DNR), 2021).

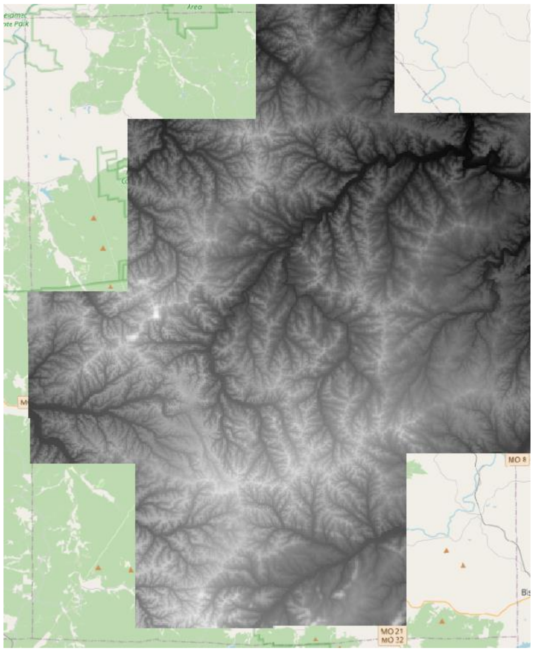


Figure A.4 Compilation of 10m LiDAR DEM Elevation Data for the Mineral Fork River System (Center for Applied Research and Engagement Systems (CARES) & Missouri Spatial Data Information Service (MSDIS), 2005).

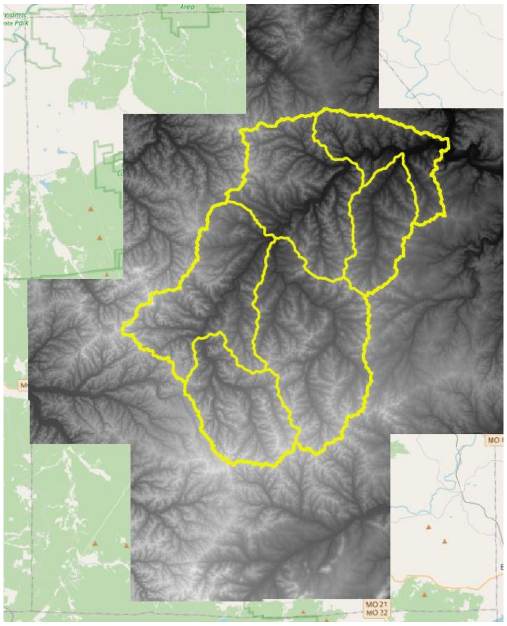


Figure A.5 Compilation of 10m DEM Elevation Data (CARES & MSDIS, 2005) for the Mineral Fork River System with Sub-watershed Boundaries from the USGS Watershed Boundary Dataset (2013).

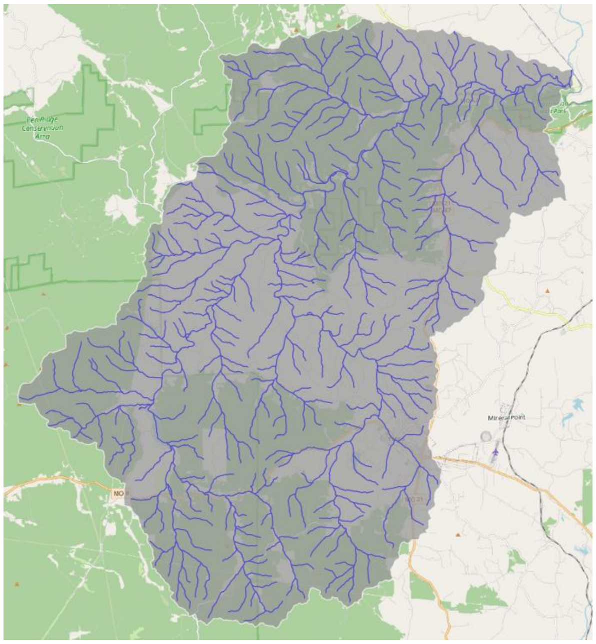


Figure A.6 Mineral Fork River System Delineated Watershed With Stream Outlines from the Watershed Boundary Dataset from the USGS (2013).

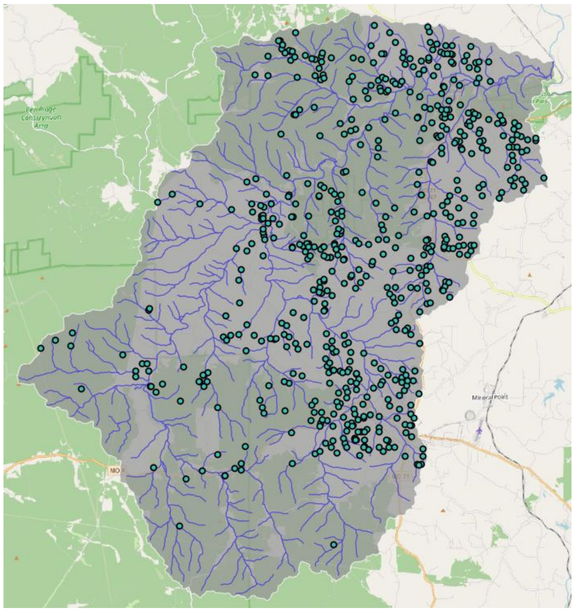


Figure A.7 Mineral Fork River System Delineated Watershed With Stream Outlines from the Watershed Boundary Dataset from the USGS (2013) and Occurrences of Mining Activity as Reported by the Missouri Mine Inventory (Missouri Department of Natural Resources (DNR), 2021).

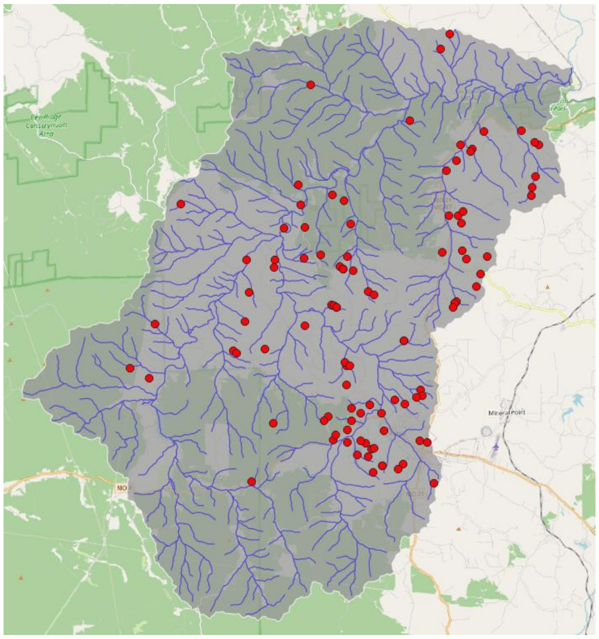


Figure A.8 Mineral Fork River System Delineated Watershed With Stream Outlines from the Watershed Boundary Dataset from the USGS (2013) and Occurrences of Mining Activity as Reported by the Mineral Resources Data System (Mason & Arndt, 1996-2011).

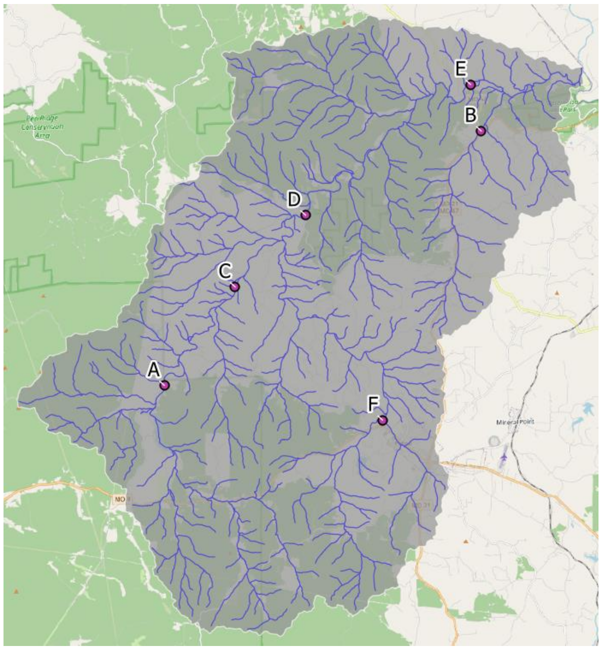


Figure A.9 Sampler Locations in the Mineral Fork River System Watershed from Miller, 2020.

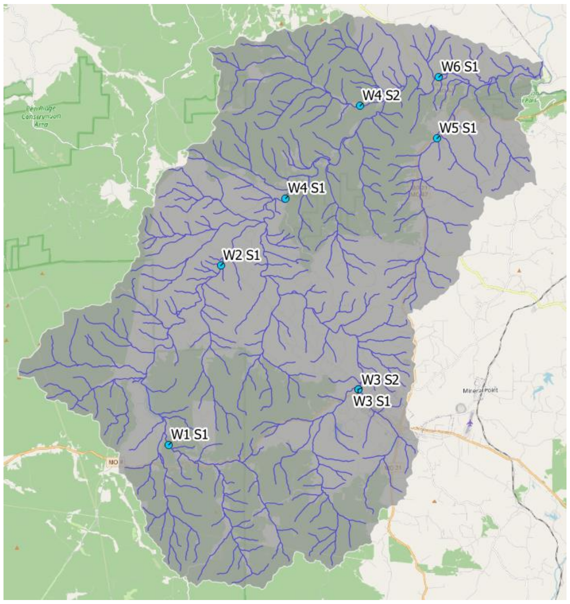


Figure A.10 Sampler Locations in the MFRS Chosen in This Study

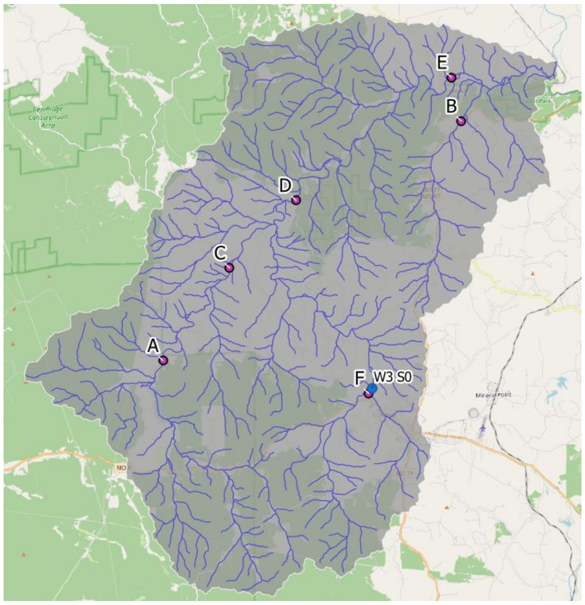


Figure A.11 Sampler Locations in the MFRS, From Miller, 2020, and One Which Was Removed During this Study (W3-S0).

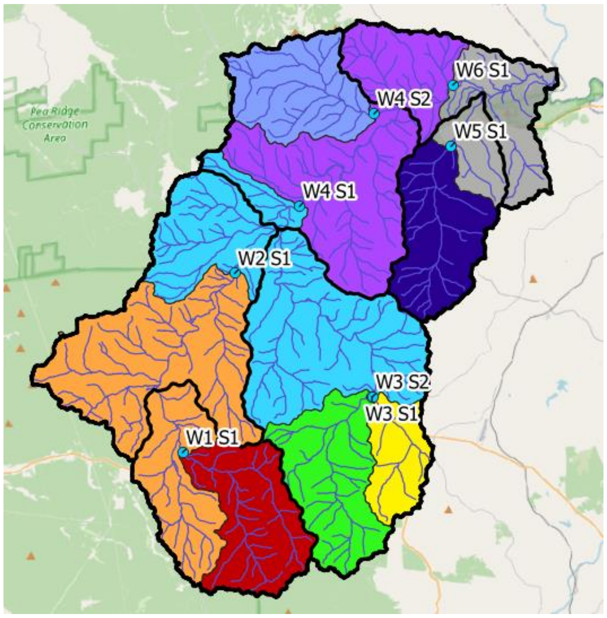


Figure A.12 Sampler Locations and Sampler Watersheds Within the Mineral Fork River System, Delineated in QGIS, Overlain With Stream Outlines From the USGS Watershed Boundary Dataset (2013).

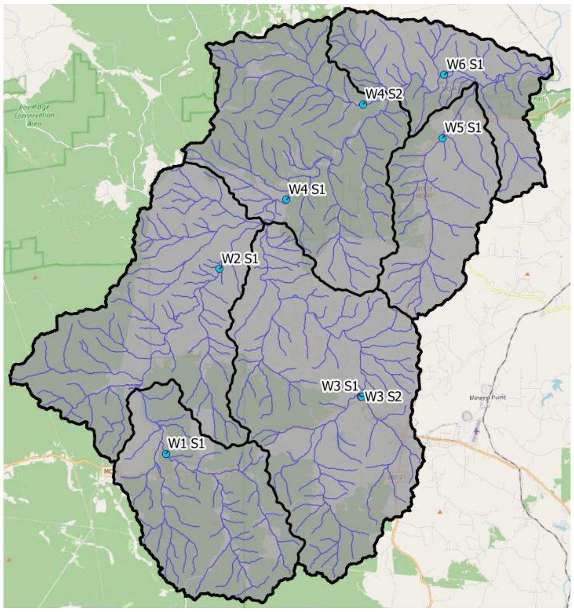


Figure A.13 Smpler Locations Within the Official Sub-watersheds of the Mineral Fork River System from the USGS Watershed Boundary Dataset (2013).

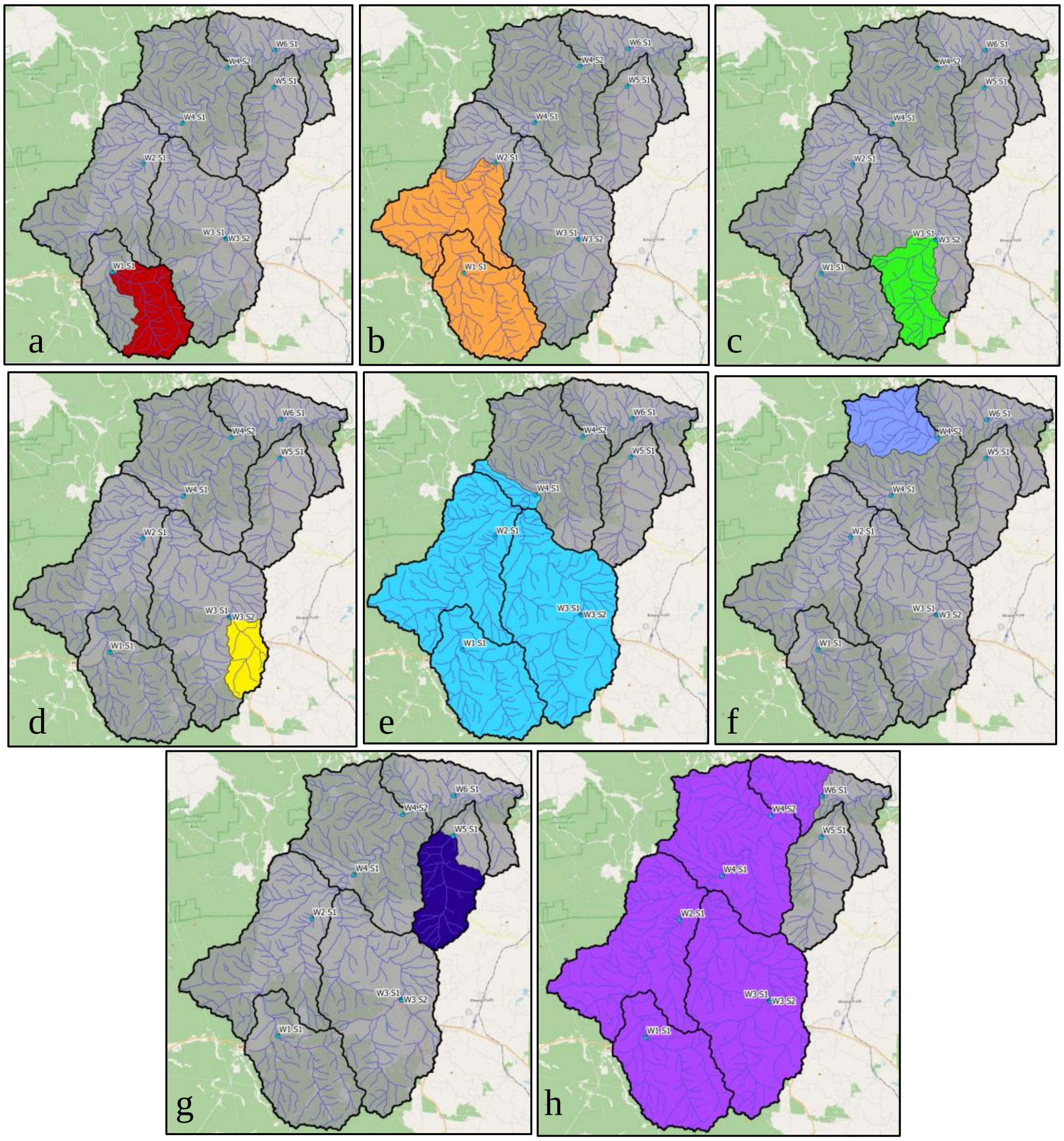


Figure A.14 Watersheds of Samplers. a) W1-S1, b) W2-S1, c) W3-S1, d) W3-S2, c) W4-S1, d) W4-S2, e) W5-S1, and f) W6-S1.

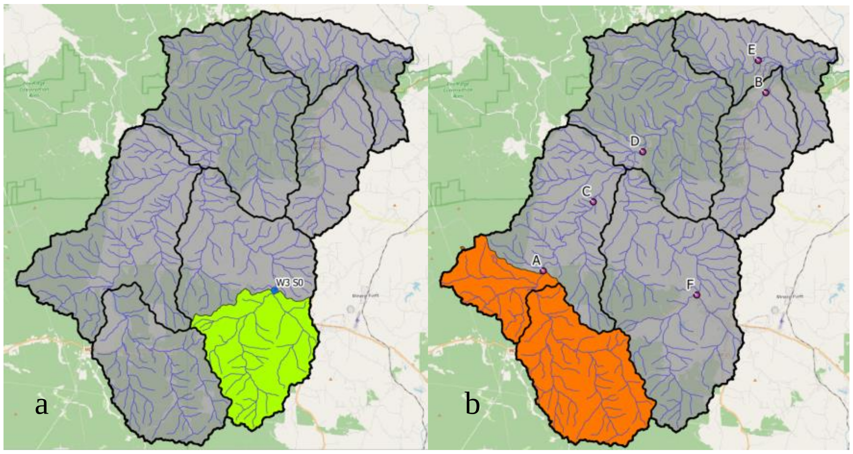
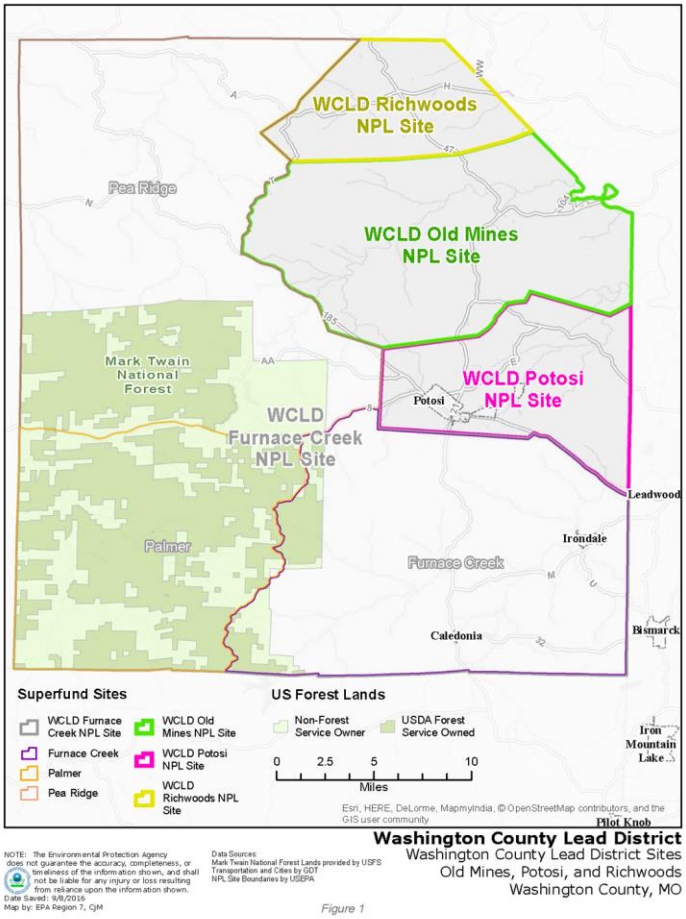


Figure A.15 Watersheds of Removed Samplers. a) W3-S0 and b) Sampler A, aka W2-S0.



Washington County Lead District
Washington County Lead District Sites
Old Mines, Potosi, and Richwoods
Washington County, MO

NOTE: The Environmental Protection Agency does not guarantee the accuracy, completeness, or timeliness of the information shown, and shall not be liable for any injury or loss resulting from reliance upon the information shown.
Date Saved: 9/8/2016
Map by: EPA Region 7, CJM

Data Sources:
Mark Twain National Forest Lands provided by USFS
Transportation and Cities by GDT
NPL Site Boundaries by USEPA

Figure 1

Figure A.16 Map of the Washington County Lead District (Environmental Protection Agency (EPA), 2021).

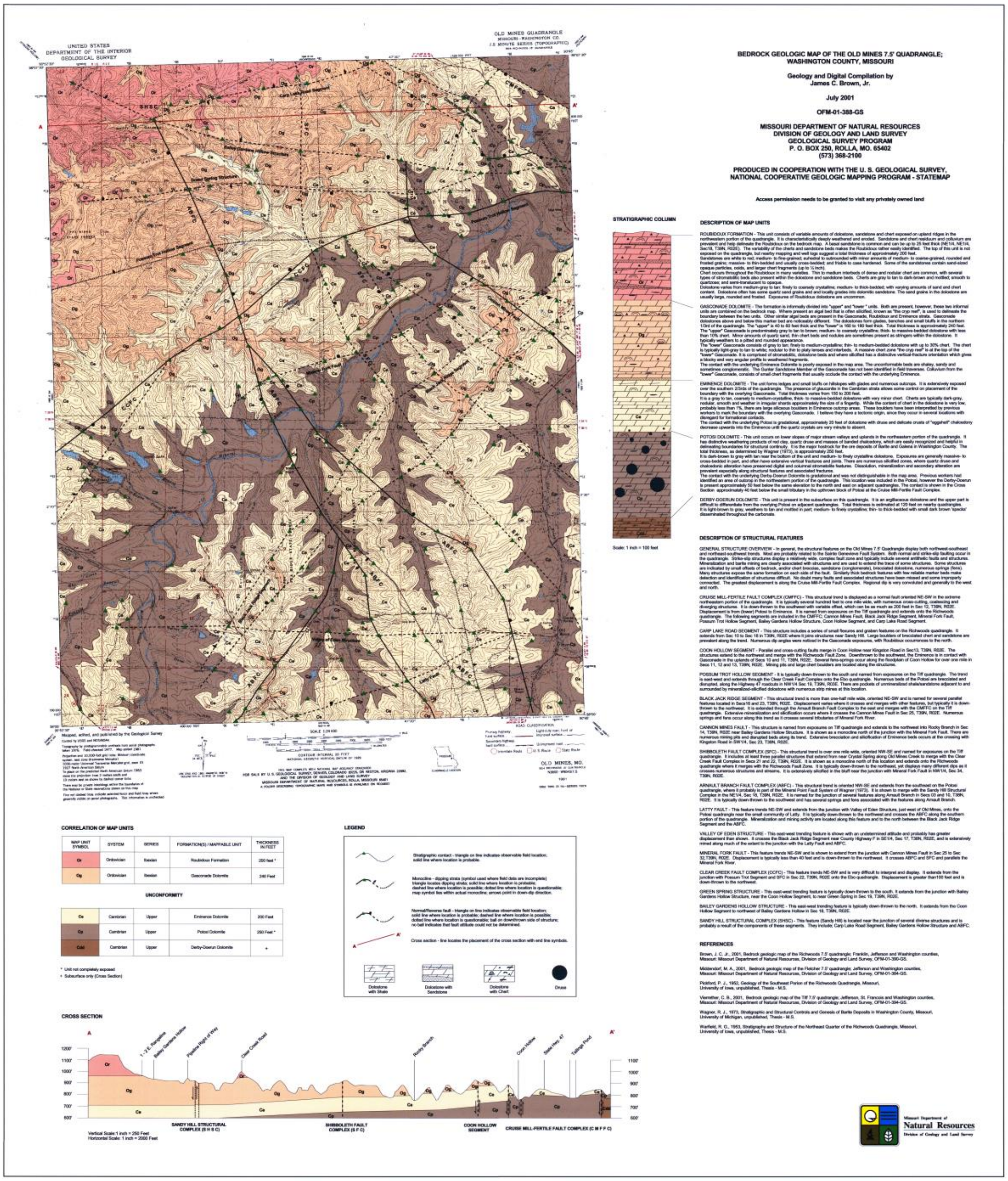


Figure A.17 Bedrock Geologic Map of the Old Mines 7.5’ Quadrangle, Washington County, Missouri (Brown, Jr. & Missouri Department of Natural Resources (DNR), 2001).

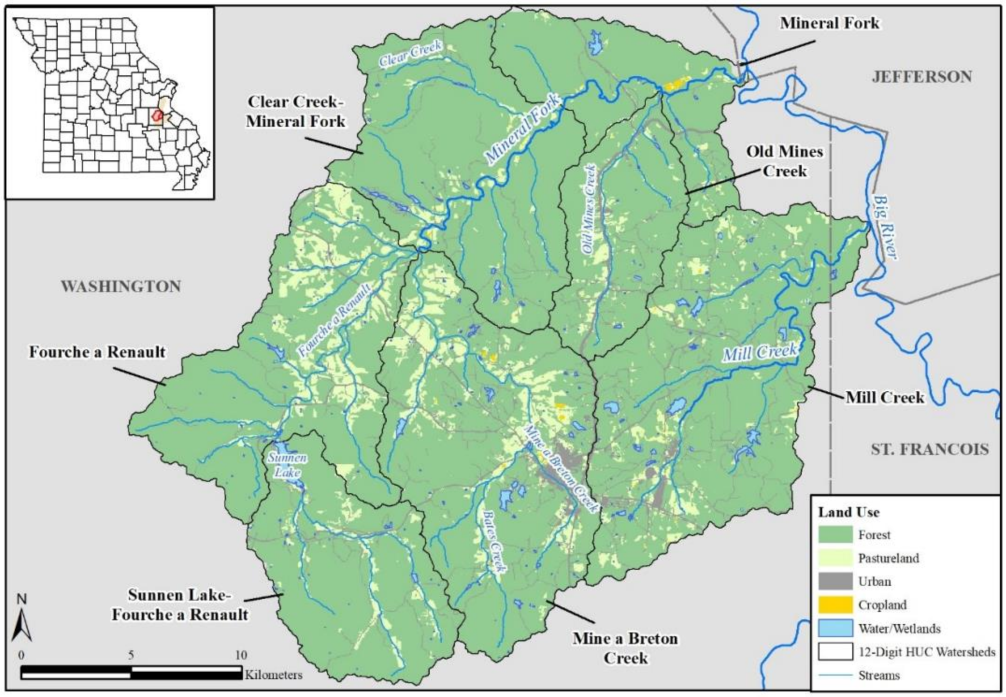


Figure A.18 USDA-NASS 2017 Land Use Classification for Several Big River Tributaries (Coonen, 2020).

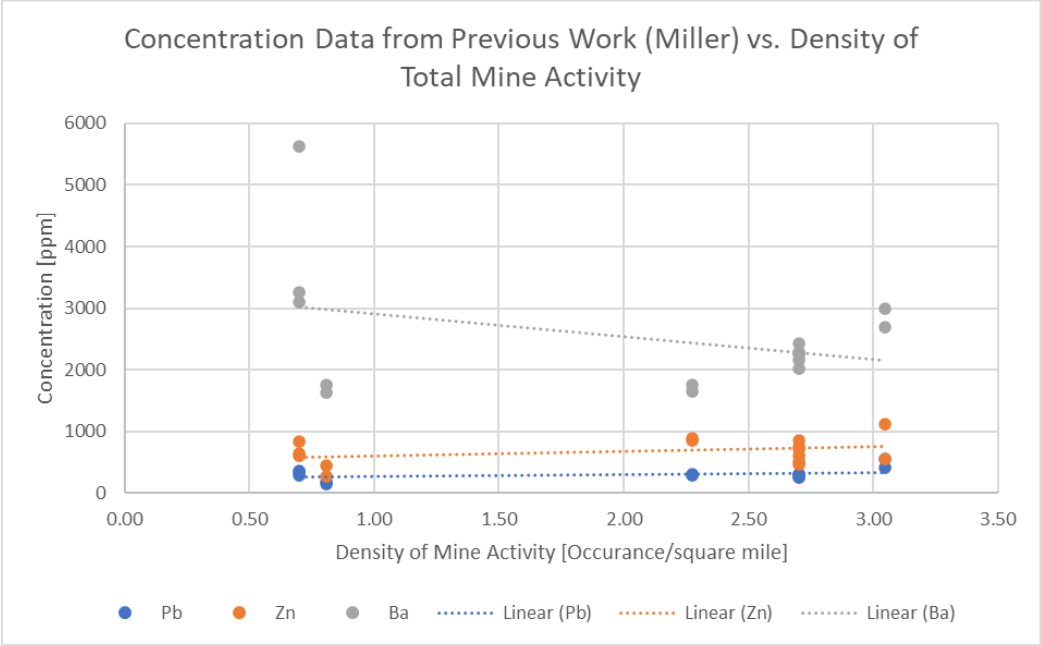


Figure A.19 Concentration Data from Previous Work (Miller, 2020) vs. Density of Total Mine Activity.

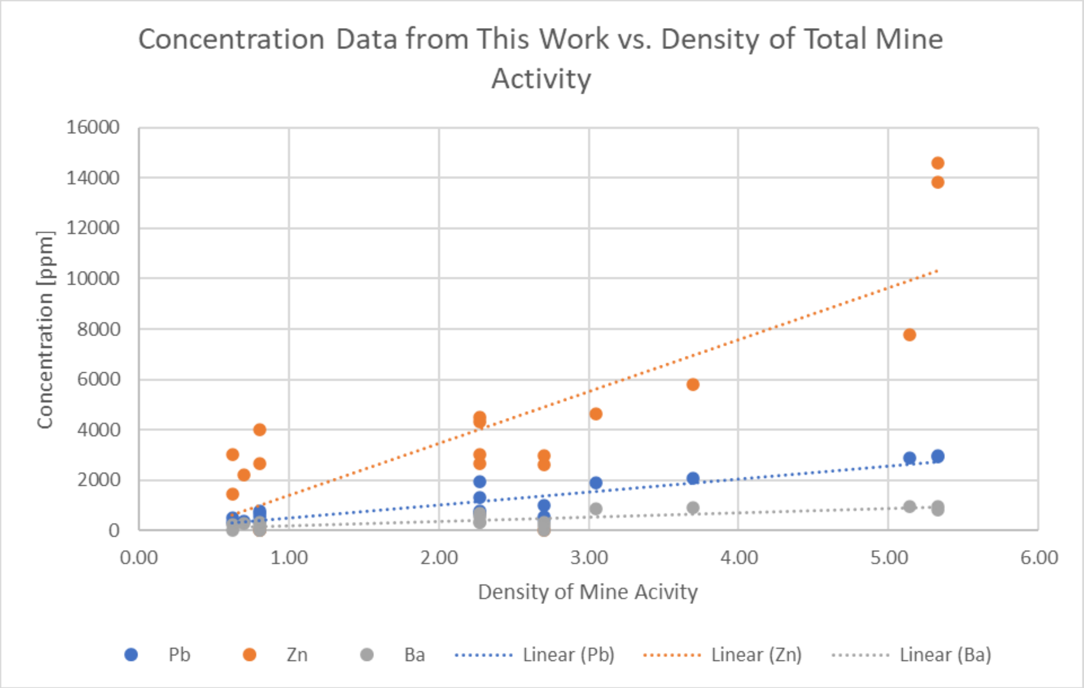


Figure A.20 Concentration Data from This Work vs. Density of Total Mine Activity.

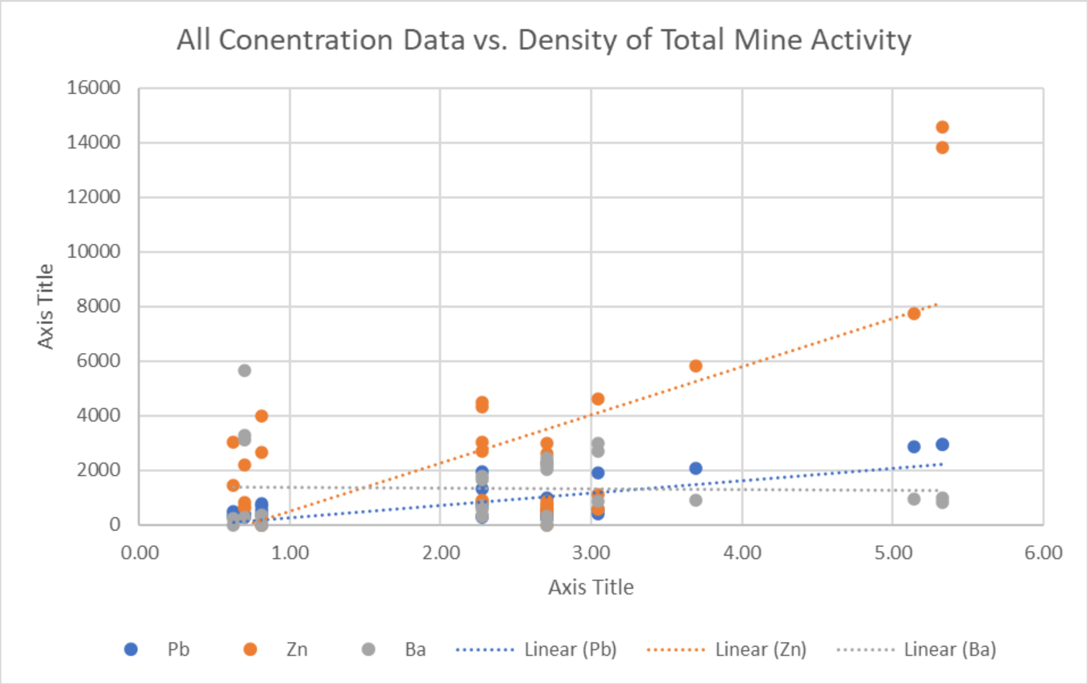


Figure A.21 All Concentration Data vs. Density of Total Mine Activity, Linear Plot.

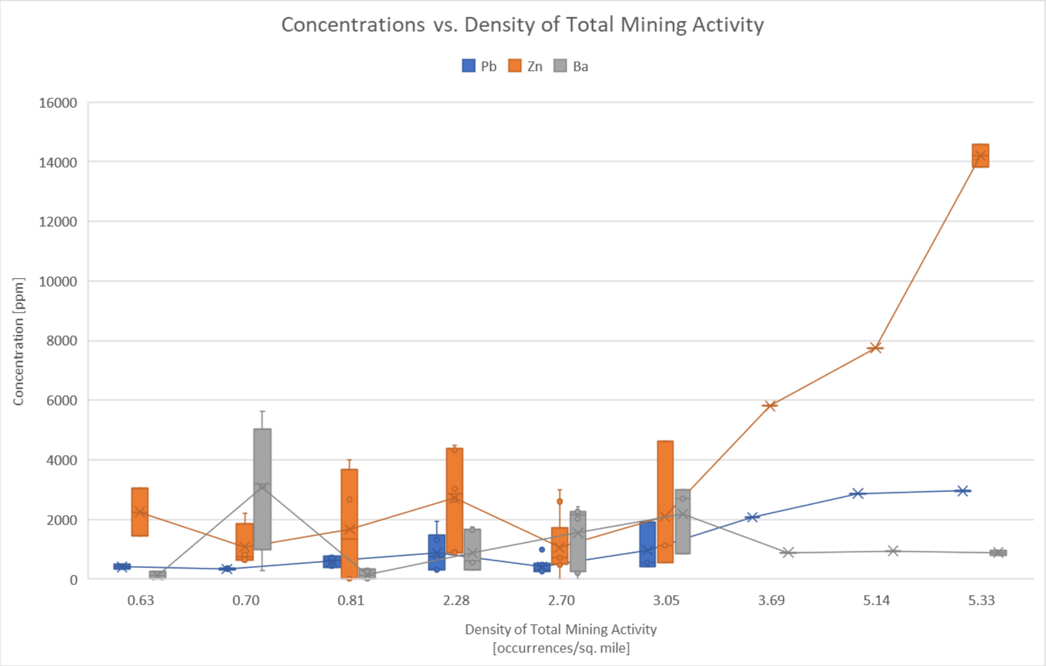


Figure A 22 All Concentration Data vs. Density of Total Mining Activity, Box and Whisker Plot.

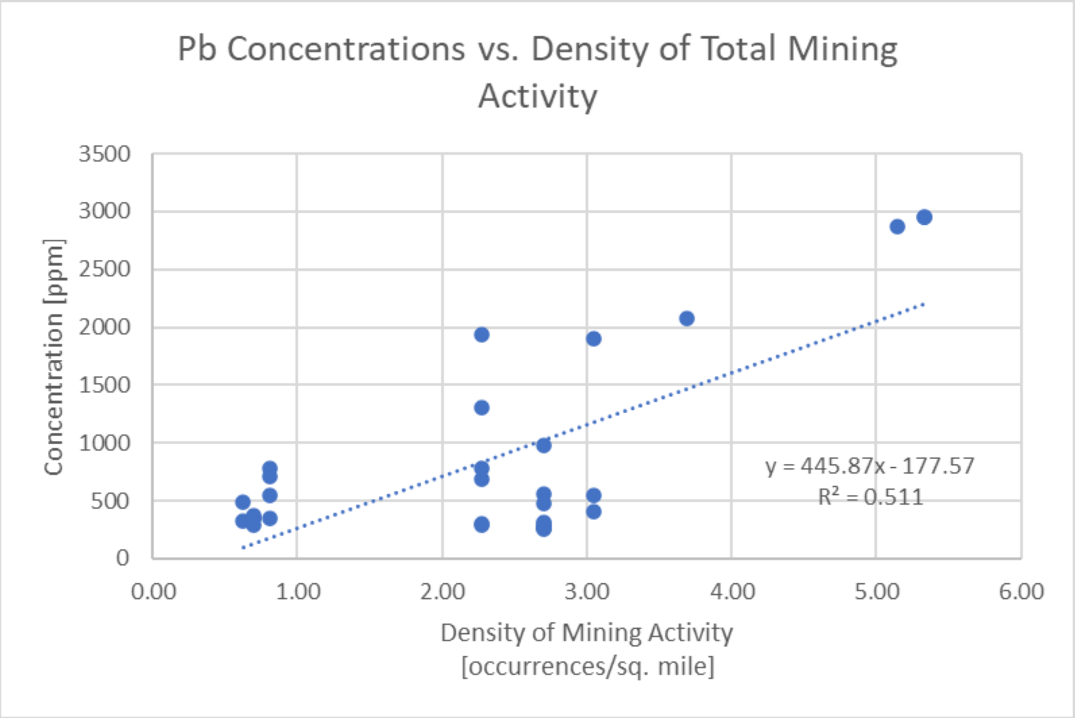


Figure A.23 Pb Concentration vs. Density of Total Mining Activity, Linear Plot.

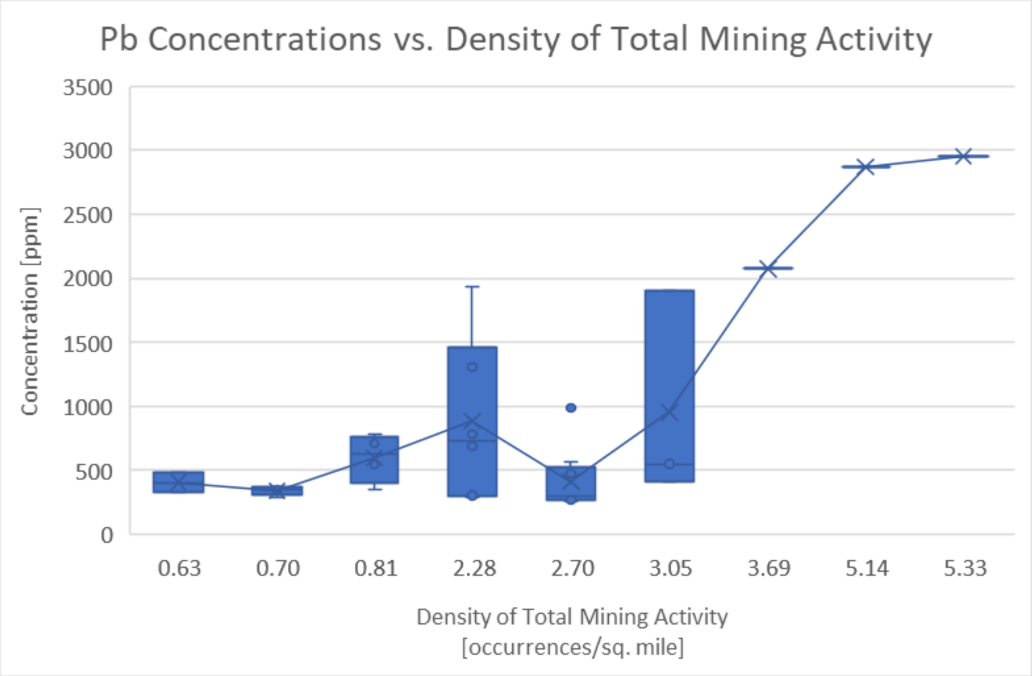


Figure A.24 Pb Concentrations vs. Density of Total Mining Activity, Box and Whisker Plot.

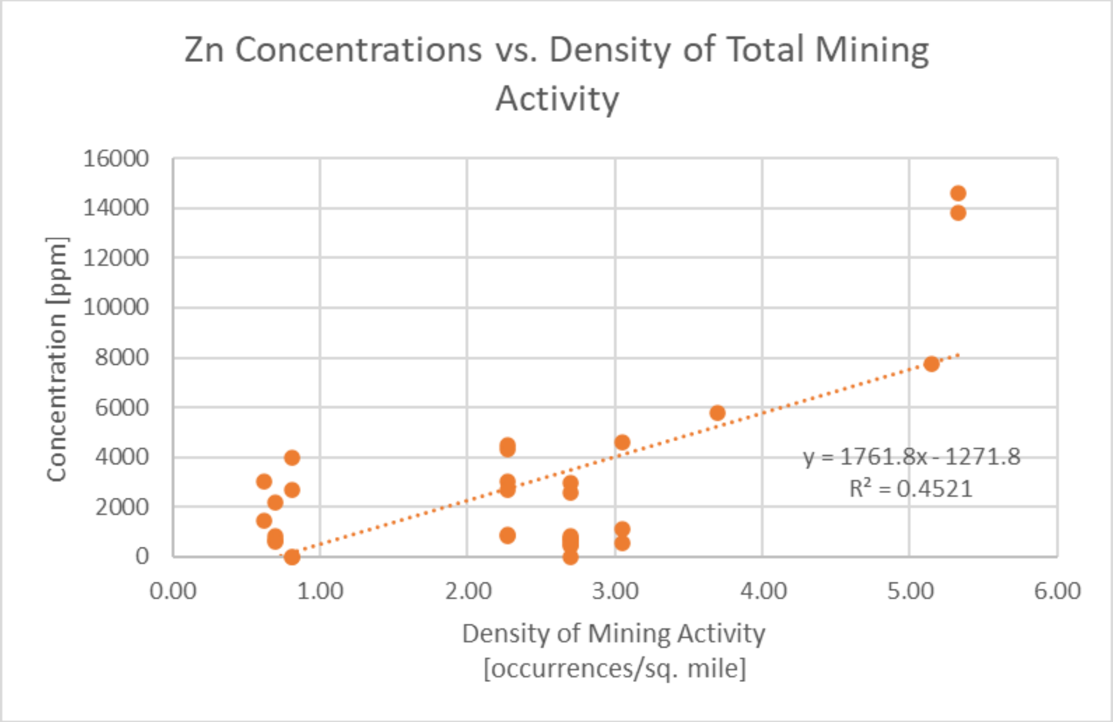


Figure A.25 Zn Concentrations vs. Density of Total Mining Activity, Linear Plot.

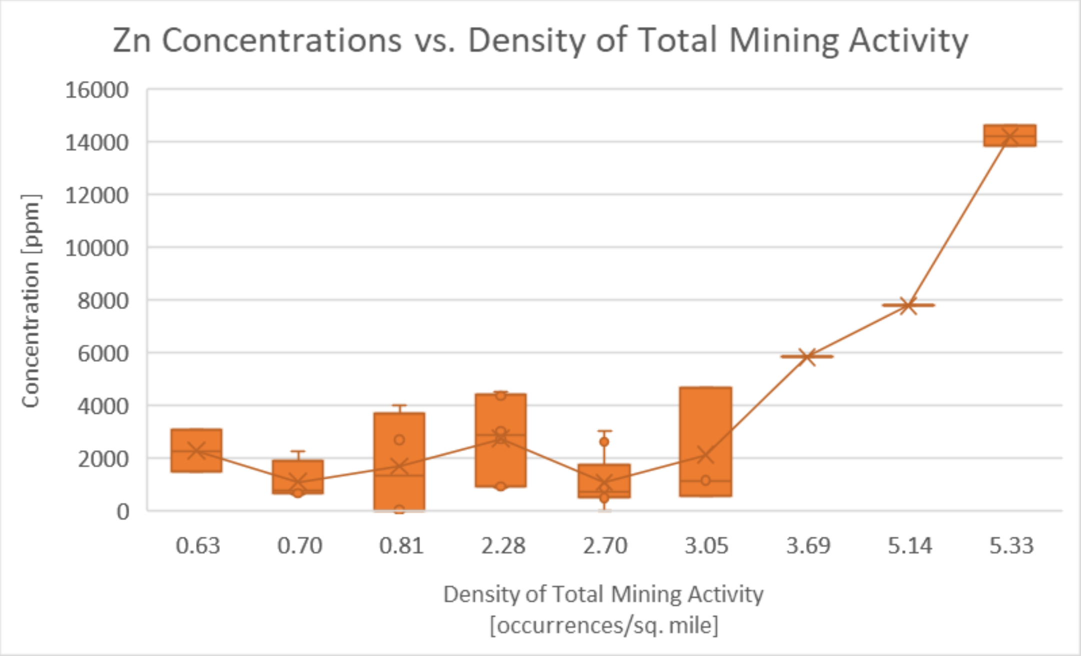


Figure A.26 Zn Concentrations vs. Density of Total Mining Activity, Box and Whiskers Plot.

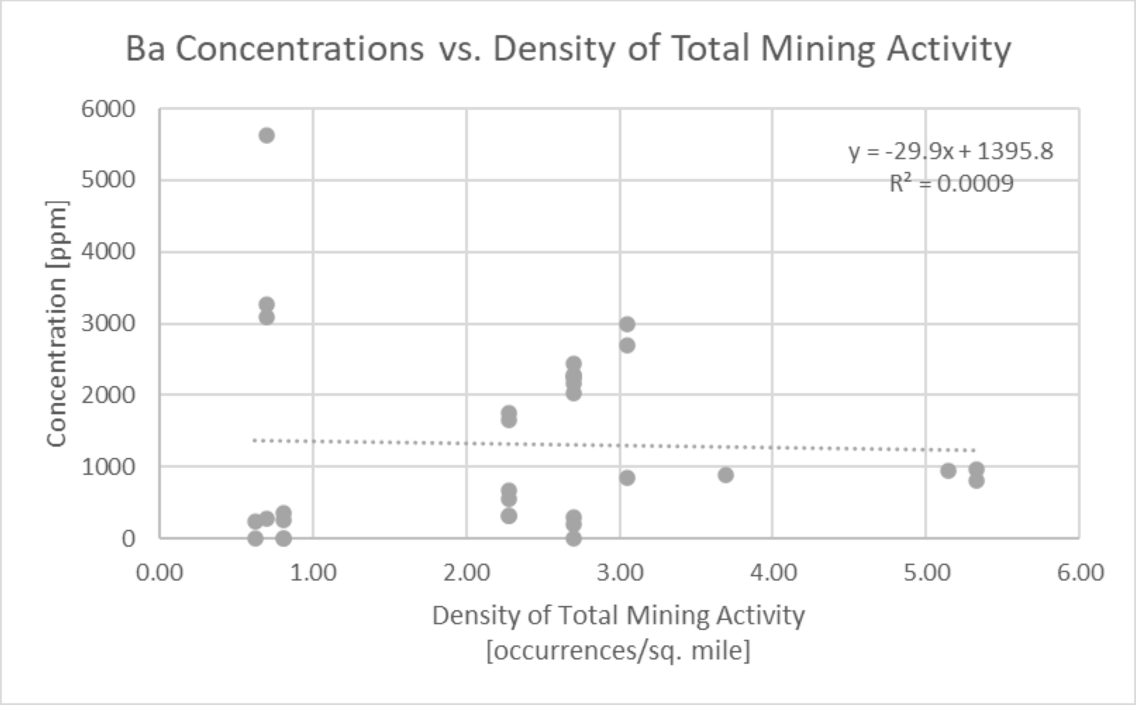


Figure A.27 Ba Concentrations vs. Density of Total Mining Activity, Linear Plot.

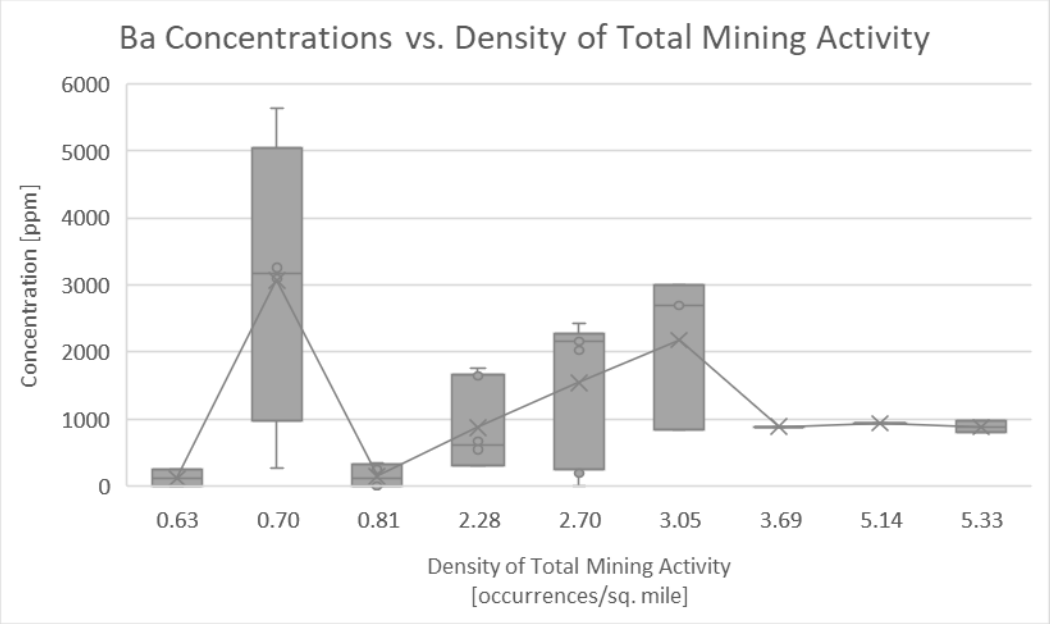


Figure A.28 Ba Concentrations vs. Density of Total Mining Activity, Box and Whiskers Plot.

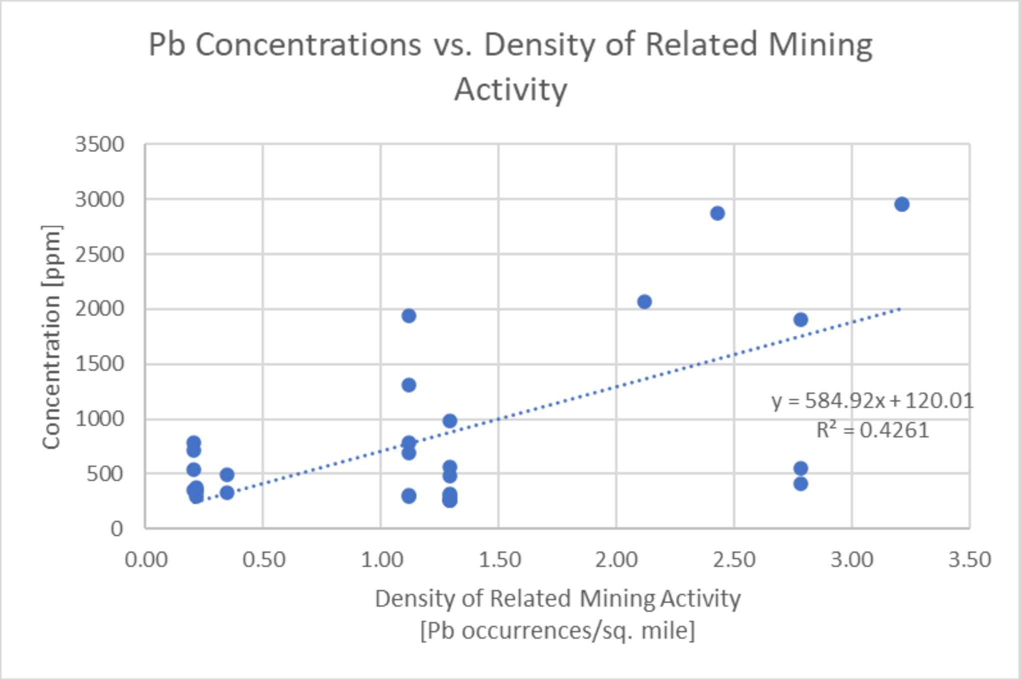


Figure A.29 Pb Concentrations vs. Density of Related Mining Activity, Linear Plot.

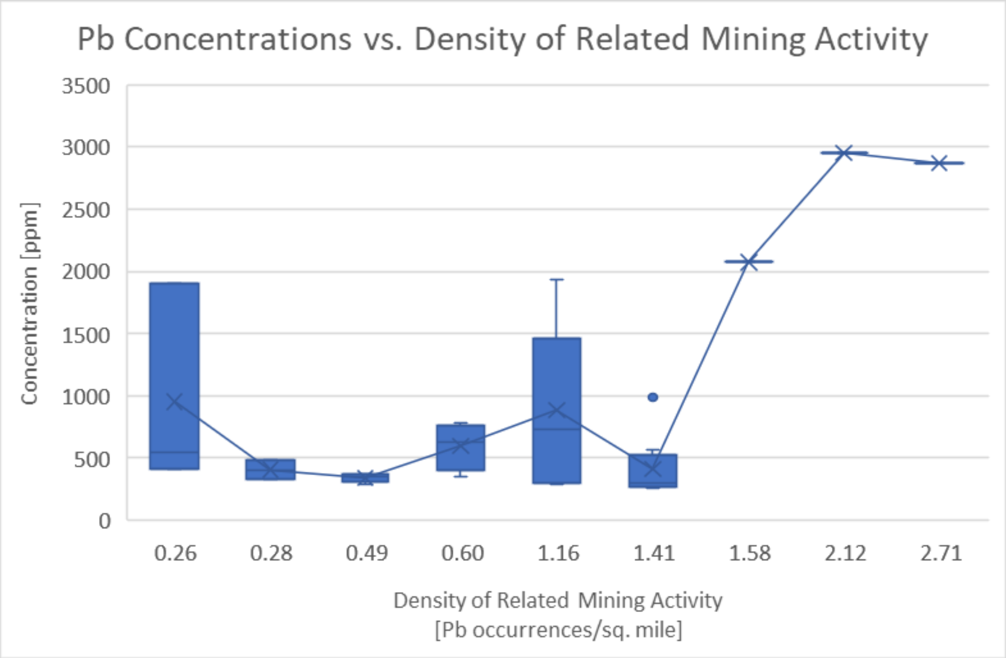


Figure A.30 Pb Concentrations Vs. Density of Related Mining Activity, Box and Whiskers Plot.

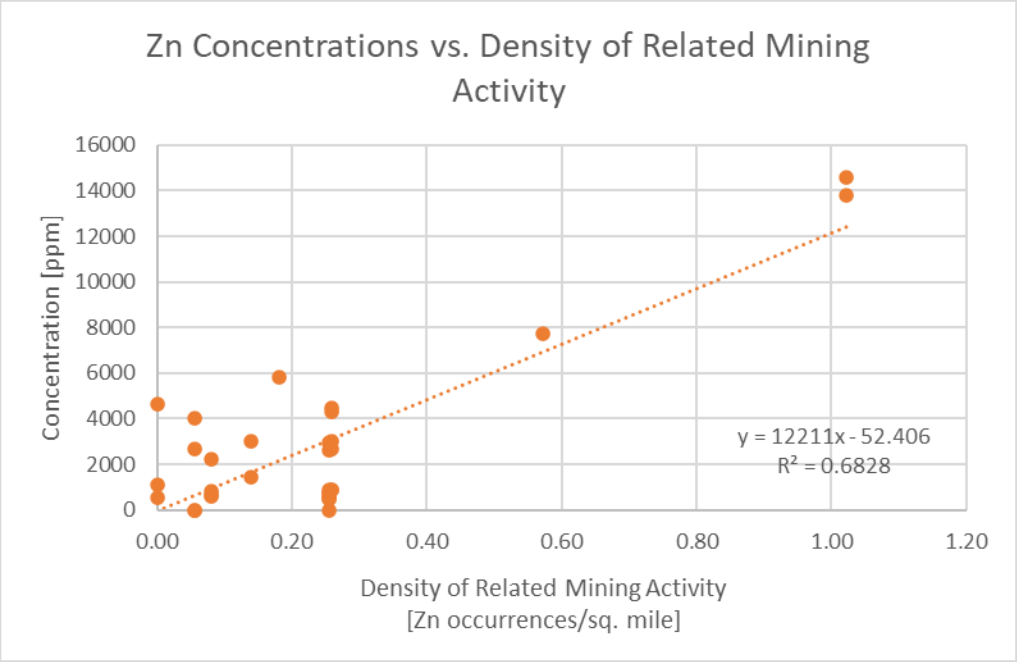


Figure A.31 Zn Concentrations vs. Density of Related Mining Activity, Linear Plot.

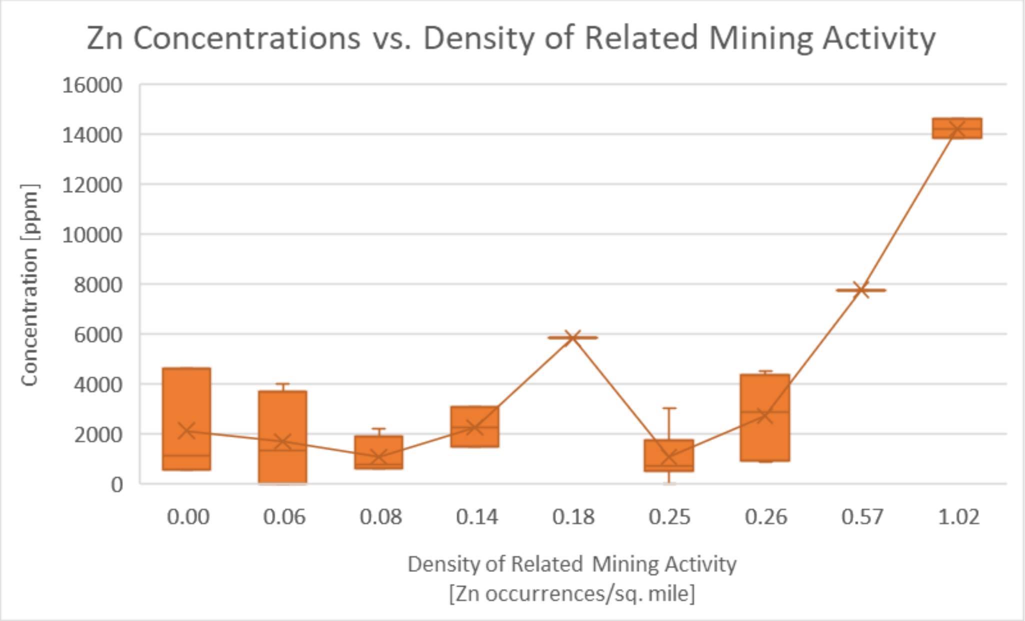


Figure A.32 Zn Concentrations vs. Density of Related Mining Activity, Box and Whisker Plot.

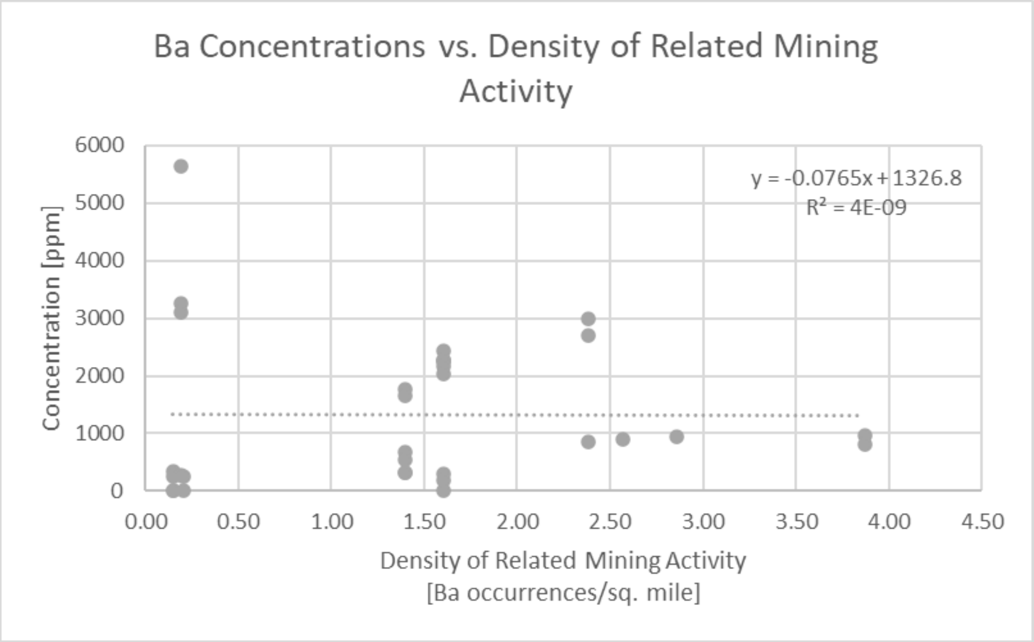


Figure A.33 Ba Concentrations vs. Density of Related Mining Activity, Linear Plot.

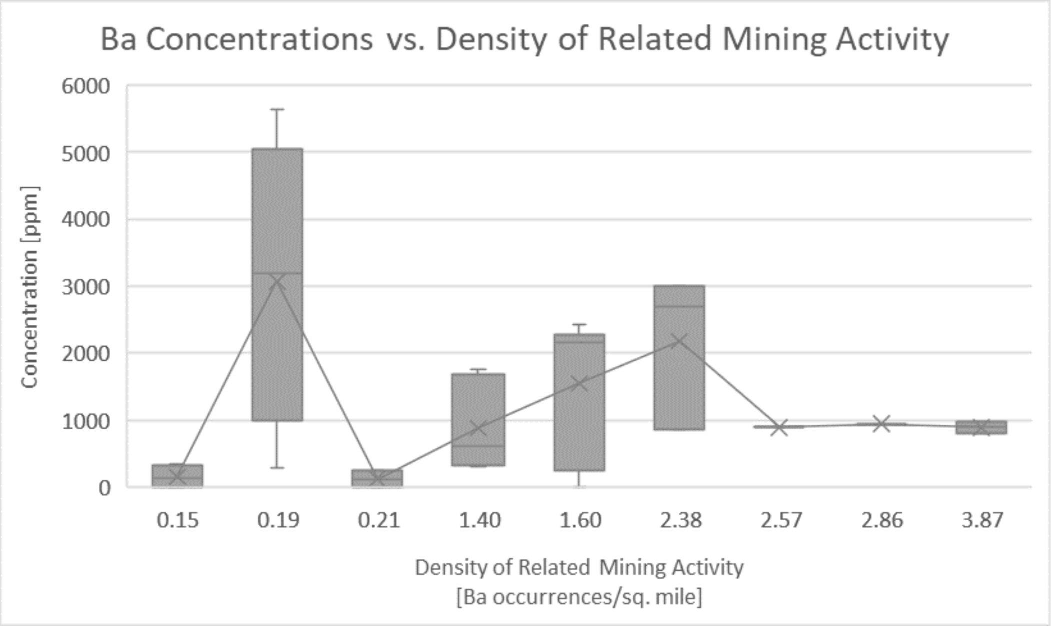


Figure A.34 Ba Concentrations vs. Density of Related Mining Activity, Box and Whisker Plot.

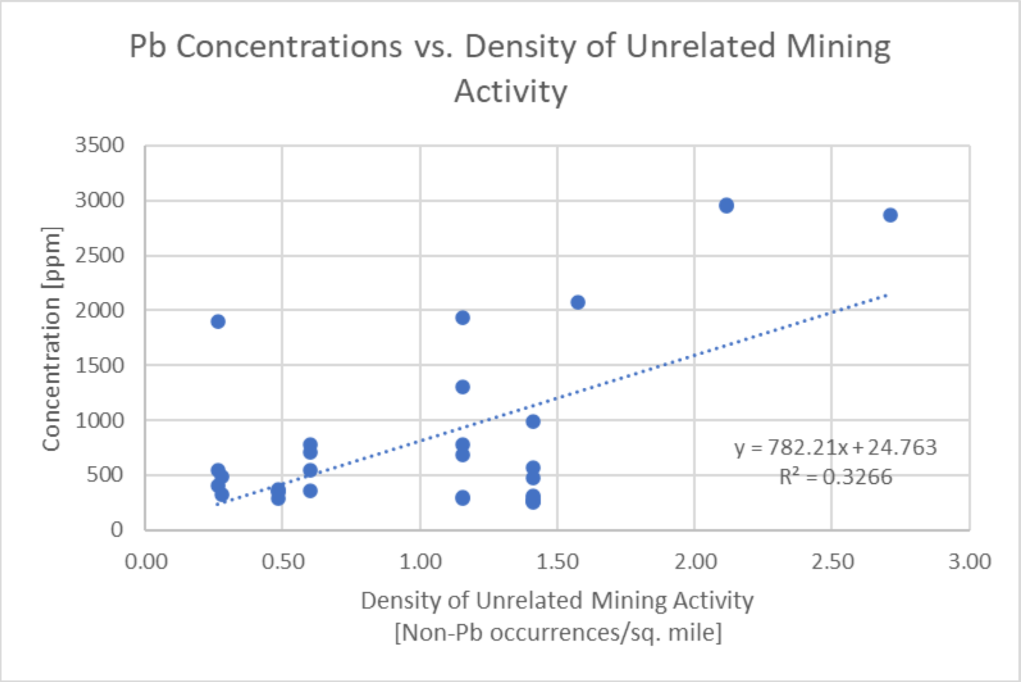


Figure A.35 Pb Concentrations vs. Density of Unrelated Mining Activity, Linear Plot.

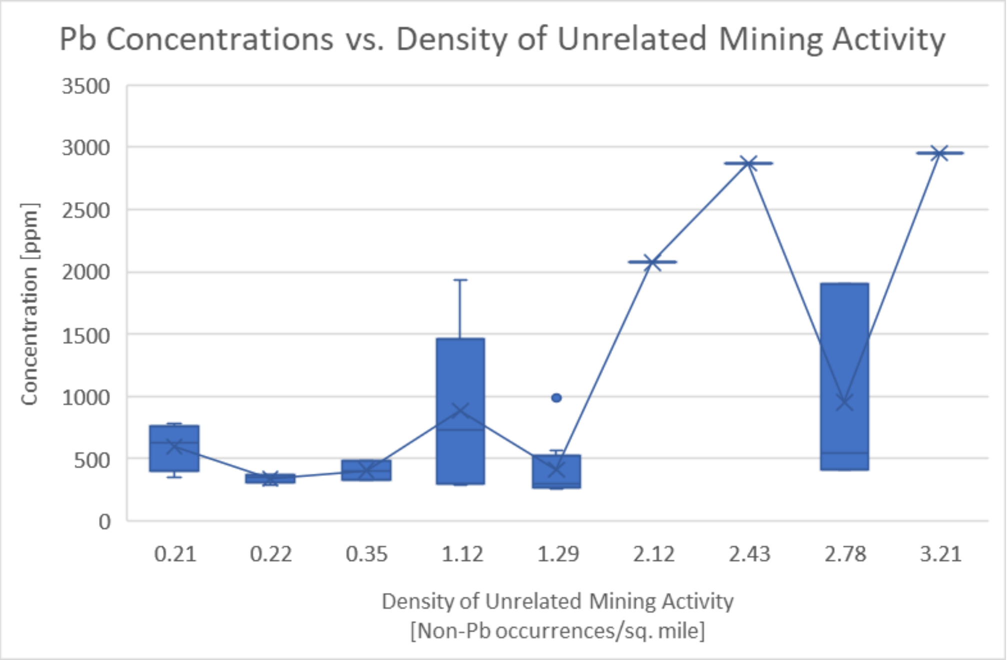


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Figure A.36 Pb Concentrations Vs. Density of Unrelated Mining Activity, Box and Whiskers Plot.

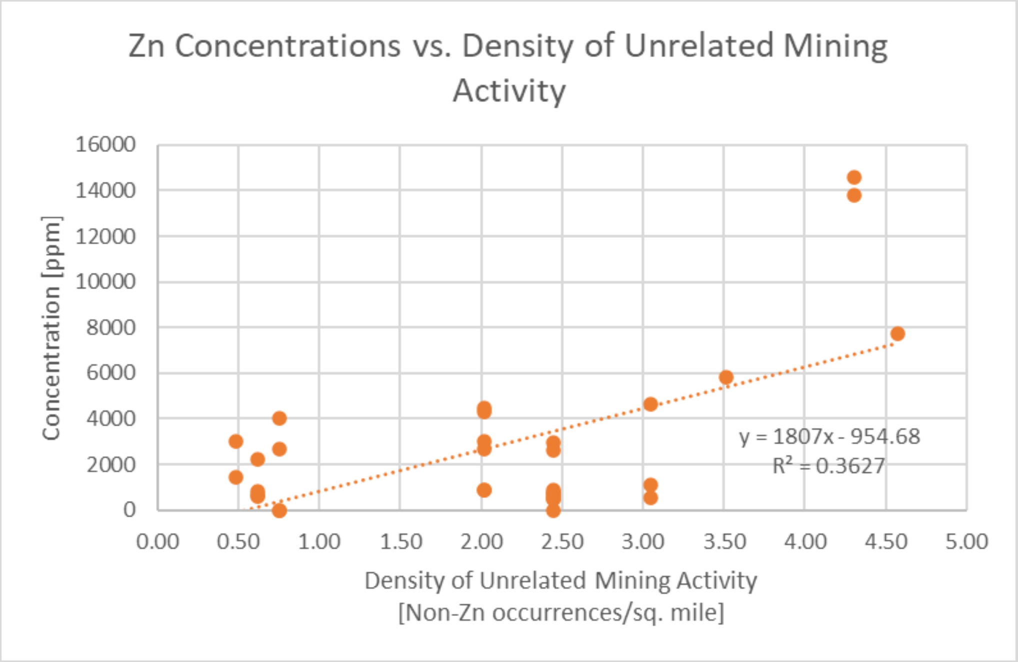


Figure A.37 Zn Concentrations vs. Density of Unrelated Mining Activity, Linear Plot.

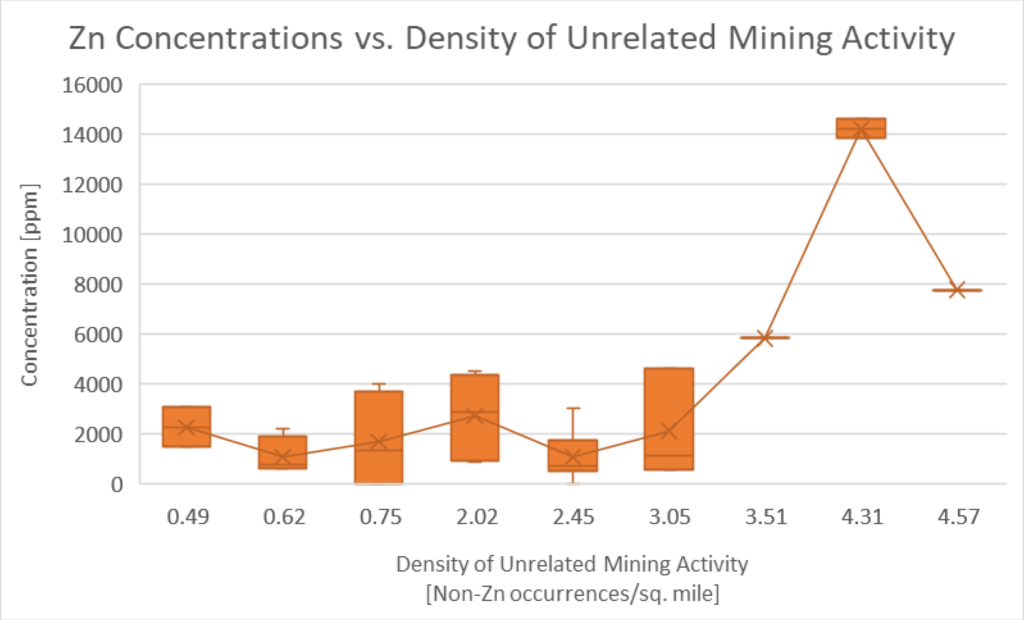


Figure A.38 Zn Concentrations vs. Density of Unrelated Mining Activity, Box and Whisker Plot.

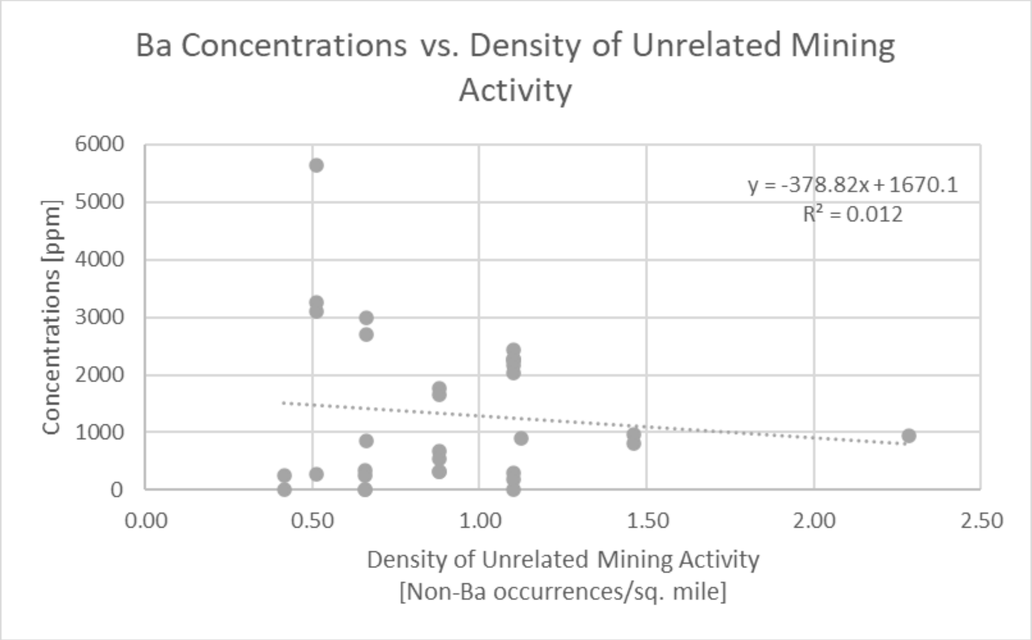


Figure A.39 Ba Concentrations vs. Density of Unrelated Mining Activity, Linear Plot.

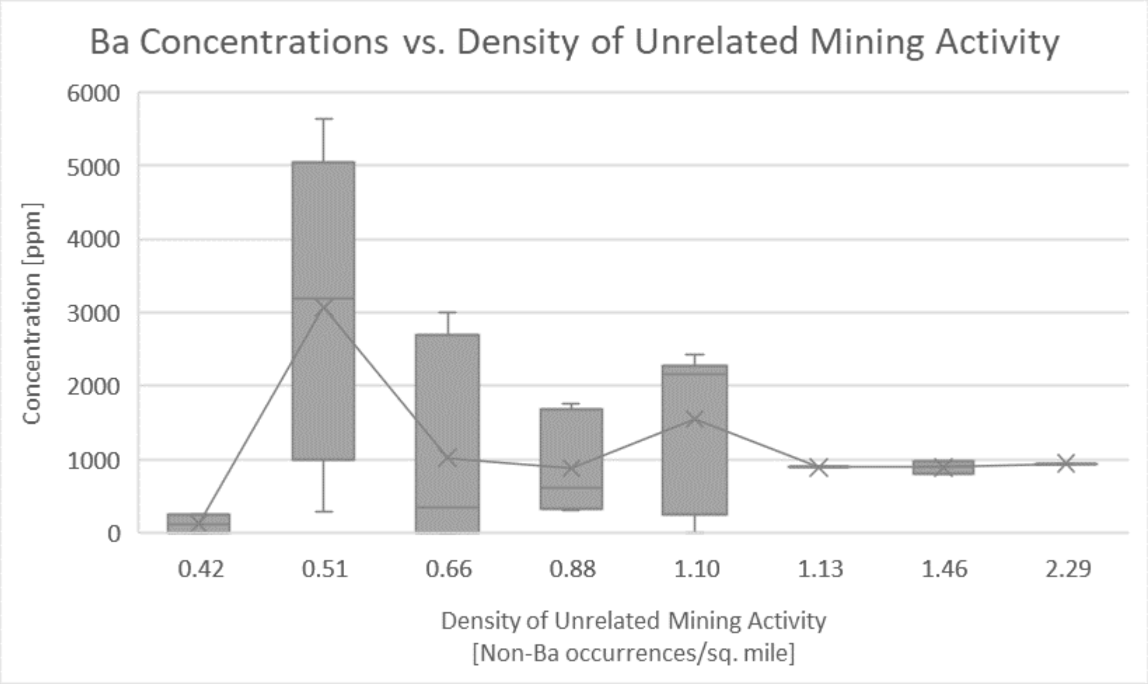


Figure A.40 Ba Concentrations vs. Density of Unrelated Mining Activity, Box and Whisker Plot.

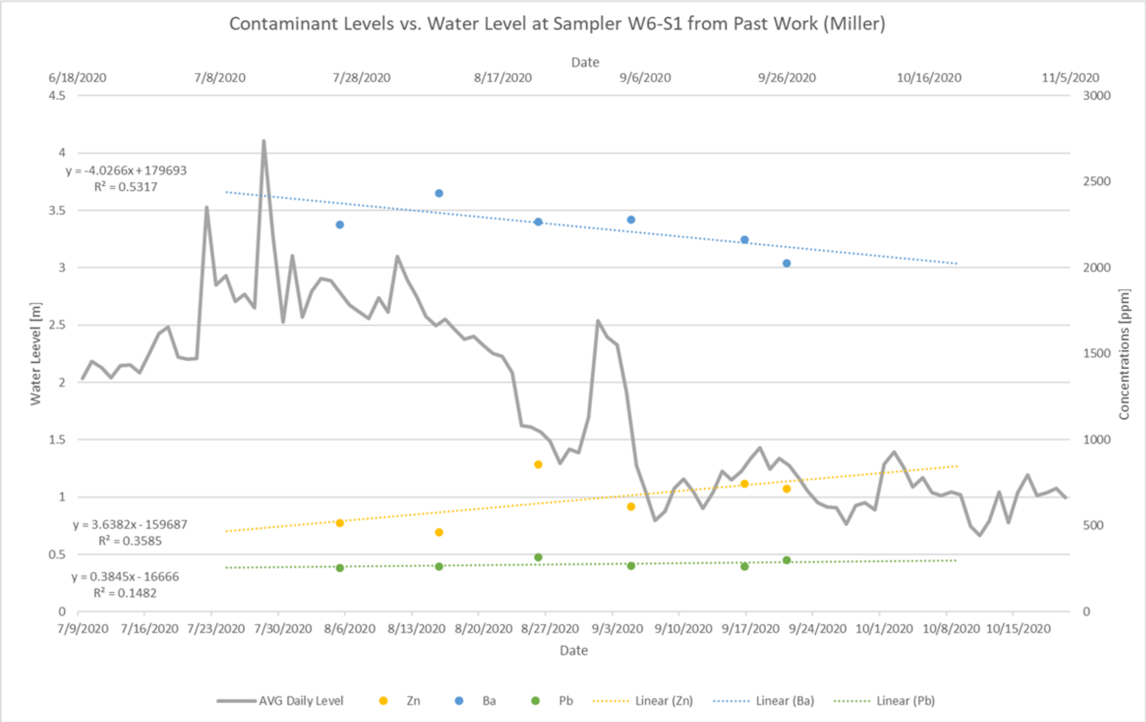


Figure A.41 Contaminant Levels vs. Water Levels at Sampler W6-S1 (Miller, 2020).

Figure A.42 Installation of SuperStruts Into a Streambed by the Author, T.N. Mortensen.

Figure A.43 A Fully Installed Sampler.

Figure A.44 A Fully Installed Sampler With Identifying Information.

Figure A.45 A Sample After It Has Been Ground Into A Fine Powder.

Figure A.46 Steps for Pressing a Sediment Sample Into a Pellet, where a) Mixing of the Sample and Binder, b) Filling of the Pellet Cup, and c) the Loading of the Pellet Cup Into the Press Machine Chassis.

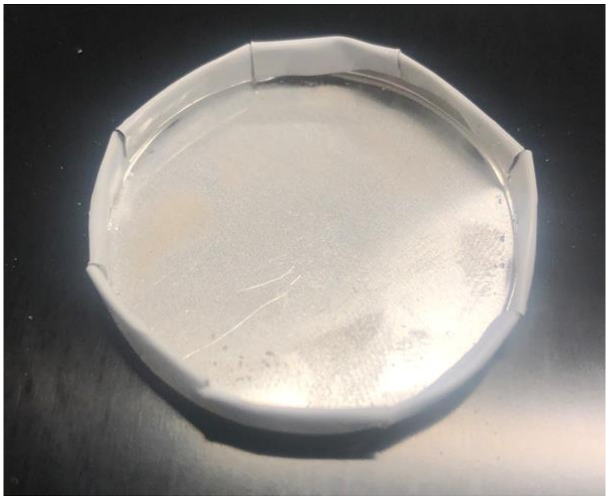


Figure A.47 An Altered Pellet Cup.

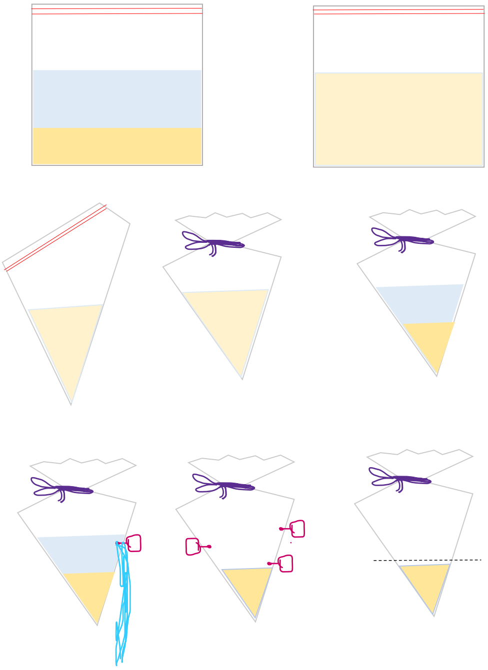


Figure A.48 Illustration of the Decanting Procedure.

2. TABLES

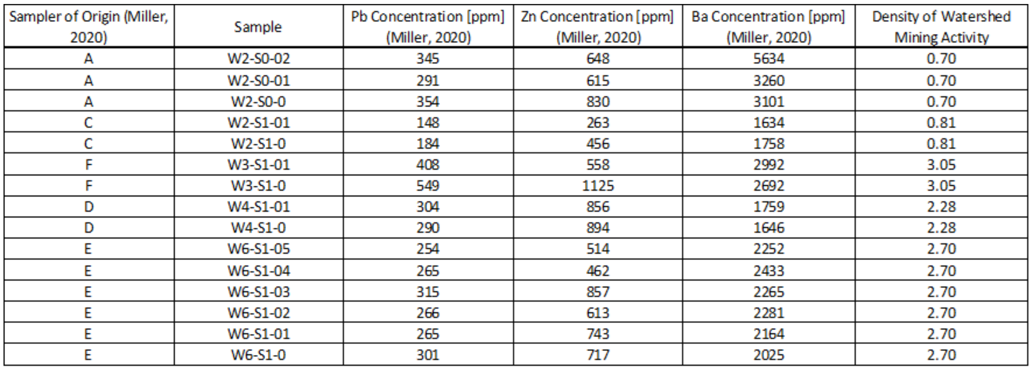
Table A.1 Mine Activity Densities from Past Work (Miller, 2020).

Sampler Name (Miller, 2020)	Sampler Name (Current Study)	Upstream Mine Activity Occurances (Miller, 2020)	Area [sq. miles] (Miller, 2020)	Density of Mining Activity [Occurances/sq. mile] (Miller, 2020)
A	W2-S0	2	36.5	0.05
B	W5-S1	3	18.4	0.16
C	W2-S1	7	53.4	0.13
D	W4-S1	26	52.8	0.49
E	W6-S1	37	160.6	0.23
F	W3-S1	6	12.5	0.48

Table A.2 Mine Activity Occurrences.

Sampler Name From Current Work	Total Occurrences of Upstream Mining Activity	Lead (Pb) Related Occurrences of Upstream Mining Activity	Zinc (Zn) Related Occurrences of Upstream Mining Activity	Barite (Ba) Related Occurrences of Upstream Mining Activity	Non-Pb, Zn, or Ba (Other) Occurrences of Upstream Mining Activity
W1-S1	9	4	2	3	4
W2-S0	26	18	3	7	5
W2-S1	43	32	3	8	5
W3-S0	82	35	4	57	3
W3-S1	46	4	0	36	3
W3-S2	36	19	4	20	0
W4-S1	264	134	30	162	12
W4-S2	35	11	2	28	4
W5-S1	73	29	14	53	1
W6-S1	435	227	41	258	14

Table A.3 Sample Concentrations From Past Work (Miller, 2020).



Sampler of Origin (Miller, 2020)	Sample	Pb Concentration [ppm] (Miller, 2020)	Zn Concentration [ppm] (Miller, 2020)	Ba Concentration [ppm] (Miller, 2020)	Density of Watershed Mining Activity
A	W2-S0-02	345	648	5634	0.70
A	W2-S0-01	291	615	3260	0.70
A	W2-S0-0	354	830	3101	0.70
C	W2-S1-01	148	263	1634	0.81
C	W2-S1-0	184	456	1758	0.81
F	W3-S1-01	408	558	2992	3.05
F	W3-S1-0	549	1125	2692	3.05
D	W4-S1-01	304	856	1759	2.28
D	W4-S1-0	290	894	1646	2.28
E	W6-S1-05	254	514	2252	2.70
E	W6-S1-04	265	462	2433	2.70
E	W6-S1-03	315	857	2265	2.70
E	W6-S1-02	266	613	2281	2.70
E	W6-S1-01	265	743	2164	2.70
E	W6-S1-0	301	717	2025	2.70

Table A.4 Upstream Mining Activity, Total.

Sampler Name from Previous Work (Miller)	Sampler Name From Current Work	Total Occurrences of Upstream Mining Activity	Watershed Area [sq. miles]	Density of Mining Activity [occurrences/sq. mile]
-	W1-S1	9	14.4	0.63
A	W2-S0	26	37.1	0.70
C	W2-S1	43	53.2	0.81
-	W3-S0	82	22.2	3.69
F	W3-S1	46	15.1	3.05
-	W3-S2	36	7	5.14
D	W4-S1	264	116	2.28
-	W4-S2	35	13.1	2.67
B	W5-S1	73	13.7	5.33
E	W6-S1	435	160.9	2.70

Table A.5 Densities of Mining Activity.

Sampler Name From Current Work	Density of Pb Mining Activity [occurrences/sq. mile]	Density of Zn Mining Activity [occurrences/sq. mile]	Density of Ba Mining Activity [occurrences/sq. mile]	Density of Other Mining Activity [occurrences/sq. mile]
W1-S1	0.28	0.14	0.21	0.28
W2-S0	0.49	0.08	0.19	0.13
W2-S1	0.60	0.06	0.15	0.09
W3-S0	1.58	0.18	2.57	0.14
W3-S1	0.26	0.00	2.38	0.20
W3-S2	2.71	0.57	2.86	0.00
W4-S1	1.16	0.26	1.40	0.10
W4-S2	0.84	0.15	2.14	0.31
W5-S1	2.12	1.02	3.87	0.07
W6-S1	1.41	0.25	1.60	0.09

Table A.6 Upstream Mining Activity, Lead.

Sampler Name	Watershed Area [sq. miles]	Pb Related Occurrences of Upstream Mining Activity	Density of Pb Related Mining Activity [occurrences/sq. mile]	Density of Mining Activity Unrelated to Pb [occurrences/sq. mile]
W1-S1	14.4	4	0.28	0.35
W2-S0	37.1	18	0.49	0.22
W2-S1	53.2	32	0.60	0.21
W3-S0	22.2	35	1.58	2.12
W3-S1	15.1	4	0.26	2.78
W3-S2	7	19	2.71	2.43
W4-S1	116	134	1.16	1.12
W4-S2	13.1	11	0.84	1.83
W5-S1	13.7	29	2.12	3.21
W6-S1	160.9	227	1.41	1.29

Table A.7 Upstream Mining Activity, Zinc.

Sampler Name	Watershed Area [sq. miles]	Zn Related Occurrences of Upstream Mining Activity	Density of Zn Mining Activity [occurrences/sq. mile]	Density of Mining Activity Unrelated to Zn [occurrences/sq. mile]
W1-S1	14.4	2	0.14	0.49
W2-S0	37.1	3	0.08	0.62
W2-S1	53.2	3	0.06	0.75
W3-S0	22.2	4	0.18	3.51
W3-S1	15.1	0	0.00	3.05
W3-S2	7	4	0.57	4.57
W4-S1	116	30	0.26	2.02
W4-S2	13.1	2	0.15	2.52
W5-S1	13.7	14	1.02	4.31
W6-S1	160.9	41	0.25	2.45

Table A.8 Upstream Mining Activity, Barium.

Sampler Name	Watershed Area [sq. miles]	Ba Related Occurrences of Upstream Mining Activity	Density of Ba Mining Activity [occurrences/sq. mile]	Density of Mining Activity Unrelated to Ba [occurrences/sq. mile]
W1-S1	14.4	3	0.21	0.42
W2-S0	37.1	7	0.19	0.51
W2-S1	53.2	8	0.15	0.66
W3-S0	22.2	57	2.57	1.13
W3-S1	15.1	36	2.38	0.66
W3-S2	7	20	2.86	2.29
W4-S1	116	162	1.40	0.88
W4-S2	13.1	28	2.14	0.53
W5-S1	13.7	53	3.87	1.46
W6-S1	160.9	258	1.60	1.10

Table A.9 COC Concentrations of Samples.

	Concentrations			Density of Mining Activity [occurrences/sq. mile]				
Sample	Pb [ppm]	Zn [ppm]	Ba [ppm]	Total	Pb	Zn	Ba	Other
W1_S1_5	487	3039	248	0.63	0.28	0.14	0.21	0.28
W1_S1_6	325	1455	0	0.63	0.28	0.14	0.21	0.28
W2-S0-02	345	648	5634	0.70	0.49	0.08	0.19	0.13
W2-S0-01	291	615	3260	0.70	0.49	0.08	0.19	0.13
W2-S0-0	354	830	3101	0.70	0.49	0.08	0.19	0.13
W2_S0_3	372	2210	283	0.70	0.49	0.08	0.19	0.13
W2_S1_1	783	4004	351	0.81	0.60	0.06	0.15	0.09
W2_S1_2	353	2669	0	0.81	0.60	0.06	0.15	0.09
W2_S1_5	709	0	0	0.81	0.60	0.06	0.15	0.09
W2_S1_6	544	0	251	0.81	0.60	0.06	0.15	0.09
W3_S0_4	2074	5810	891	3.69	1.58	0.18	2.57	0.14
W3_S1_5	1902	4626	852	3.05	0.26	0.00	2.38	0.20
W3-S1-01	408	558	2992	3.05	0.26	0.00	2.38	0.20
W3-S1-0	549	1125	2692	3.05	0.26	0.00	2.38	0.20
W3_S2_6	2872	7755	943	5.14	2.71	0.57	2.86	0.00
W4_S1_1	1305	4324	678	2.28	1.16	0.26	1.40	0.10
W4_S1_2	783	3012	311	2.28	1.16	0.26	1.40	0.10
W4_S1_3	687	2681	320	2.28	1.16	0.26	1.40	0.10
W4_S1_6	1935	4495	548	2.28	1.16	0.26	1.40	0.10
W4-S1-01	304	856	1759	2.28	1.16	0.26	1.40	0.10
W4-S1-0	290	894	1646	2.28	1.16	0.26	1.40	0.10
W5_S1_5	2952	13826	970	5.33	2.12	1.02	3.87	0.07
W5_S1_6	2956	14578	807	5.33	2.12	1.02	3.87	0.07
W6-S1-05	254	514	2252	2.70	1.41	0.25	1.60	0.09
W6-S1-04	265	462	2433	2.70	1.41	0.25	1.60	0.09
W6-S1-03	315	857	2265	2.70	1.41	0.25	1.60	0.09
W6-S1-02	266	613	2281	2.70	1.41	0.25	1.60	0.09
W6-S1-01	265	743	2164	2.70	1.41	0.25	1.60	0.09
W6-S1-0	301	717	2025	2.70	1.41	0.25	1.60	0.09
W6_S1_1	984	0	0	2.70	1.41	0.25	1.60	0.09
W6_S1_4	564	2988	308	2.70	1.41	0.25	1.60	0.09
W6_S1_6	476	2601	191	2.70	1.41	0.25	1.60	0.09

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VITA

Tessa Nicole Mortensen began her secondary education at Missouri University of Science and Technology in August of 2015 and received her Bachelor of Science in Petroleum Engineering in December of 2020. She chose to continue her studies at Missouri University of Science and Technology and started her master's program in January of 2021. In May 2022 she received her Master of Science in Geological Engineering. She conducted her research within the Mineral Fork River System from June 2021 to March 2022, and in August 2021 she began her work as a Graduate Research and Teaching Assistant where she continued to work up until her graduation.