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The Distribution of Potentially Toxic Elements (PTEs) in Core Sediments from Industrial Areas Along the James River in Lynchburg, Virginia Using Microwave Plasma-Atomic Emission Spectrometry (MP-AES)

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Abstract:

This research analyzed the origin, distribution, and contamination levels of eight potentially toxic elements (PTEs) in order to identify if industrial sites adjacent to the James River were releasing Zn, Cd, Ni, Cu, Pb, Mn, Co, and/or Cr into the environment. The results indicated that there were significant differences between sites, layers, and elements. A statistical analysis indicated that one of the target locations had significantly higher concentrations in regard to all of the selected metals found in its lower layers, therefore suggesting that it may have been a previous source of metal pollution in the past. An additional study must be conducted with a larger sample size in order to verify the results from this research.

Introduction:

Human activities, such as industrial and agricultural operations, mining, and waste disposal, are contributing to an increase in metal pollution within the natural environment. Metals have low solubility in water, which causes them to adsorb and accumulate in sediments[1]. Adsorption is a surface-based process in which atoms, ions, or molecules from a substance adhere to the surface of the adsorbent. Potentially toxic elements (PTEs) are easily adsorbed on sediments and can just as easily be released back into the environment under certain conditions[2]. This includes factors such as the quantity and type of PTEs present within a system, their concentration levels, and the type of sediment that PTEs are adsorbing to[2]. The ability of PTEs to be able to adsorb to sediments also increases with the presence of organic material and finer mineral grains. A higher adsorption capacity of sediments increases their ability to store and retain the amount of PTEs present [3]. This can be concerning for aquatic habitats with sediments that have high adsorption capacities in relation to an element's mobility rate. Mobility is the rate by which an element is able to migrate from any soil compartment to another. This includes the ability of PTEs to leach into different soil profiles, enter the water column, and be absorbed into plant and animal systems[4].

While it is essential for some elements to exist at certain levels within the natural environment, the ability of PTEs to persist and accumulate over time is a concern due to naturally occurring concentrations combined with human activities. As a result, PTEs can eventually become toxic once they surpass the range at which they naturally occur in the environment[5]. Essential elements within the environment are those that are necessary for biotic organisms to survive. Metals such as iron, zinc, copper, and manganese are examples of elements that are naturally occurring and become toxic at higher concentrations, whereas metals such as lead and cadmium are examples of non-essential elements that are toxic even at low concentrations[1].

The primary concerns of PTE contamination in sediments are the conditions that allow them to have high mobility in soils, biomagnify within the food chain, and to reach high toxicity levels within the surrounding environment. Soil toxicity can impact soil and water quality in addition to plant, animal, and human health. Studies have shown that high mobility rates in soils can result in PTEs leaching and infiltrating groundwater, which can eventually lead to drinking water contamination[6]. Another concern is the bioaccumulation and biomagnification of PTEs within plants and animals[7]. Bioaccumulation is the accumulation of toxic substances within an individual organism, whereas biomagnification is the buildup of toxic substances between increasing trophic levels. As toxins pass between trophic levels, they increase in concentration levels. At lower trophic levels, plants primarily uptake PTEs through their root systems, but are prone to contamination from the surrounding soil, water, and air. This not only impacts the plant's health by altering its characteristics and functions, but it can also expose other organisms at higher trophic levels to potential health risks through exposure and ingestion[8]. The combined effect can be especially problematic for larger organisms with longer lifespans at higher trophic levels. Larger organisms are at risk of bioaccumulating more toxic substances. At a higher trophic level, they will have accumulated more toxins at higher concentrations. A longer lifespan means that these organisms have a longer time to accumulate potentially fatal element concentrations within their systems. It also means that they are more likely to live long enough to suffer the effects of the toxins, potentially impacting their health and fitness within the ecosystem.

Similarly, marine organisms can be exposed due to chemical pollution in the water, leading to bioaccumulation that can eventually pose risks to human health depending on dietary intake of individuals[9]. The types of health effects vary based on the types of PTEs people are exposed to. For instance, those exposed to chromium (Cr) can experience lung inflammation and tumors; copper (Cu) can cause liver and kidney damage; whereas lead (Pb) and manganese (Mn) can affect the central nervous system[7,9]. Other general human health risks include tissue damage, decreased fertility, dysfunction of organs, and cell death[1]. Therefore, it is important to monitor ecosystems in order to reduce the threats of PTE pollution to plant, animal, and human health.

The interaction between industrial activities, PTEs, and their mobility within the environment through different mediums poses a potential risk to the James River, which according to the James River Association, is the largest river in Virginia. With its size of roughly 10,000 square miles, it accounts for approximately 25% of the entire state. The James River watershed is home to various endangered terrestrial and aquatic species in addition to being valued by the community for its recreational capacity and drinking water supply. As a result, industrial areas situated along the James River are more prone to disrupting the health of the natural environment due to the river's ability to transport contaminants. Not only are ecosystems in close proximity to industrial sites prone to being affected, but ecosystems downstream as well. And once PTEs are introduced into the equation, they persist in the environment for a long time among soils, sediments, vegetation, and animals. Therefore, even small outputs of PTE concentrations, combined with the outputs of multiple industrial sites, can impose serious environmental and safety concerns, especially over time.

The main objectives of the study were to: (1) identify PTEs in sediment samples from industrial sites in Lynchburg, Virginia, along the James River. (2) quantify the concentrations of

PTEs within sediment samples. (3) identify potential sources of origin of PTE pollutants by comparing PTE concentrations from above and downstream of industrial sites to target locations. (4) analyze for significant differences in PTE concentrations between upper and lower core sediment samples. (5) provide reference and baseline data for organizations such as the James River Association in order to improve the health of ecosystems along the James River and Chesapeake Bay watershed.

Methods:

Study areas:

Two industrial areas were chosen as target locations for this research. Appalachian Tank Car Services is located in northern Lynchburg (37.44692, -79.17264), and U.S. Pipe is located in northeast Lynchburg (37.41692, -79.13897). Appalachian Tank Car Services is currently involved in the repair and maintenance of freight and tank cars, including cleaning, inspection, and storage. While there is limited information available regarding the history of the Appalachian Tank Car Services property, U.S. Pipe has an extensive history of working with PTEs.

The Virginia Department of Environmental Quality published a statement of basis for Griffin Pipe in 2017, now U.S Pipe. A statement of basis describes the actions that the Environmental Protection Agency has selected in order to contain and clean up a hazardous waste facility. This statement included historical information about the property and its facilities, in addition to facility investigations regarding environmental health and risk assessments. Originally established in 1882 as Lynchburg Foundry and Machine Works, Griffin Pipe Products Foundry took over the company in 1971. Since 1972, Griffin Pipe has manufactured ductile cast iron pipes for both potable water and sewage systems. In 1986, the facility was issued a Hazardous Waste Management Permit for the Storage and Treatment of Hazardous Waste. The waste that was managed under this permit was limited to cupola dust emissions generated in the iron melting process, dust emissions generated during the molten iron desulphurization and magnesium treatment process, and for used air pollution control bags. In 2010, a facility investigation took place that analyzed soil samples, groundwater, surface water and sediment. Soil samples revealed high concentrations of lead and resulted in future soil sampling endeavors in 2013 and 2015. By 2015 the lead concentrations in the soil samples were still high but were deemed to not be of concern by the Adult Lead Methodology (ALM). The ALM is a mathematical equation used by the Environmental Protection Agency to predict the risk of lead in non-residential settings such as human exposure to soils. Groundwater samples revealed elevated levels of arsenic, lead, cobalt, nickel, and vanadium that exceeded screening criteria in at least one location. Additionally, various semi volatile organic compounds (SVOCs) were identified and suspected to be a result of historical petroleum releases. Sediment samples revealed concentrations of arsenic and barium that exceeded screening criteria in at least one location. And in relation to surface water samples, the arsenic and barium exceedances among the sediment samples were detected at similar concentrations in all surface water samples collected. Aside from the facility investigation, the facility has had multiple instances of releases and pollution complaints since 1989. The first being in 1989 with a leak from a steel underground storage tank, which closed in 2002. Another instance occurred in 1991 regarding an underline pipeline. Oil could be seen spreading out along the riverbank. The facility initially responded by installing a product recovery system. However, this system was removed in 2007, and the facility now periodically removes the product manually. Lastly, the facility found free petroleum product during a routine inspection in 2008. The issue was addressed and closed in 2011. Corrective action was taken by the facility and is reported to have met the Environmental Protection Agency's (EPA's) environmental clean-up indicators for human health and groundwater in 2011[8].

Monacan Park was chosen as a control site above stream of both target locations in Madison Heights, Virginia (37.48767, -79.21706). An additional site was chosen downstream of the two target locations in eastern Lynchburg (37.39106, -79.06019). Sites were relatively equidistant from one another, with approximately 5 miles separating adjacent sample sites, as seen in figure 1.

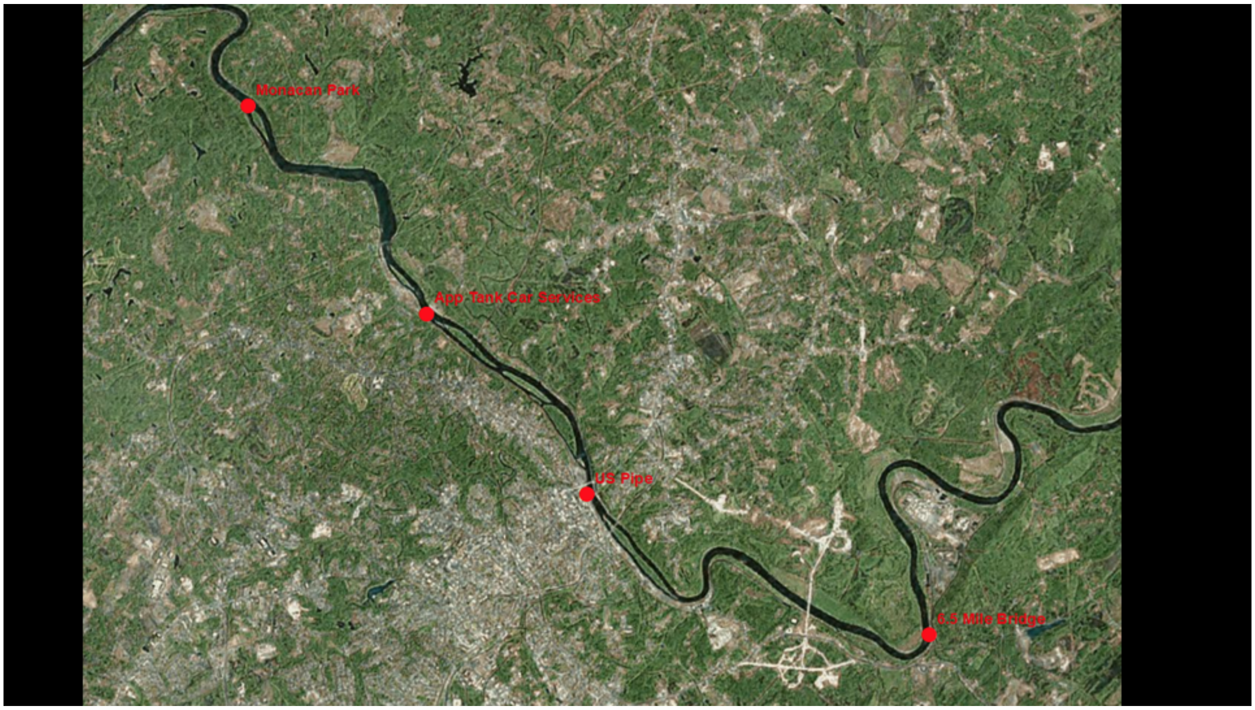


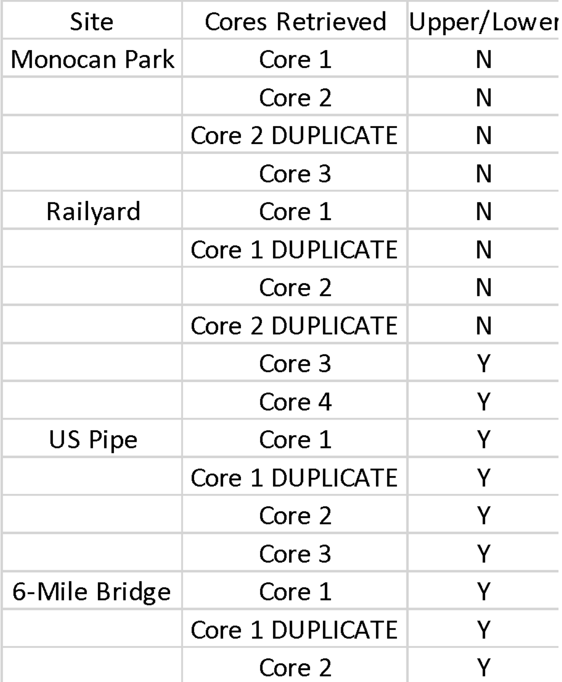
Figure 1: Satellite Image Map of Sampling Site Coordinates and Locations. From top left to bottom right the four sites shown are Monacan Park (upstream of other sites), Appalachian Tank Car Service, and 6-Mile Bridge.

Sampling Methods:

A total of 12 sediment sample cores were collected from site locations over the span of 3.5 weeks through the months of October and November of 2019. A minimum of 3 core samples were extracted from each sampling site, with the actual number of cores that were analyzed in this study shown in table 1 and resulting in a total of 12 cores. All of the cores were extracted from the same site on the same day. Different sites were visited on different days, which resulted in the 3.5-week collection period. A GPS was used to record the exact location of each sampling site. Sediment cores were collected using two different models of hand core sediment samplers. One was constructed in-house and consisted of PVC pipe that allowed for the collection of longer cores. The other sampler was purchased commercially and manufactured by WildCo (Forestry Suppliers, Jackson, MS). Two different models were used initially for core sampling in order to observe if one was more efficient than the other. It was determined that both models were equivalent in their efficiency and were used throughout data collection interchangeably. Samples were retrieved underwater when water levels were low, with a capacity between 1-1.5 feet. In terms of spacing between cores at individual sampling sites, each core was collected at a minimum distance of 2-3 feet from one another, but overall varied based on factors such as water levels and sediment availability. This also impacted some of the sediment samples in that some sediment samples were retrieved underwater, and in others they were exposed and closer to the riverbank. Core sample sizes ranged from 7.5-25 inches, with cores that exceeded 12 inches having been divided into upper and lower layers.

In some cases, duplicates were chosen from sampling sites in order to assess precision. Meaning, that two samples were taken from the same specific core and were exposed to the same analytical methods. Table 1 indicates all of the cores that were retrieved from their respective site locations. At Monacan Park, none of the cores exceeded 12 inches. As a result, none of the samples were divided into upper and lower layers. Of the three cores, one core was chosen to take a duplicate from. Table 1 also indicates that two of the cores retrieved from Appalachian Tank Car Services (Railyard) exceeded 12 inches. As a result, those two samples were divided into upper and lower layers. Of the four cores, two were chosen to take duplicates from. At U.S. Pipe, all three cores exceeded 12 inches. As a result, all three of the samples were divided into upper and lower layers. Of the three cores, one was chosen to take a duplicate from. At 6-Mile Bridge, all three cores exceeded 12 inches. As a result, all three samples were divided into upper and lower layers. Of the three cores, one was chosen to take a duplicate from.

Table 1: Cores Retrieved from Site Locations



Site	Cores Retrieved	Upper/Lower
Monocan Park	Core 1	N
	Core 2	N
	Core 2 DUPLICATE	N
	Core 3	N
Railyard	Core 1	N
	Core 1 DUPLICATE	N
	Core 2	N
	Core 2 DUPLICATE	N
	Core 3	Y
	Core 4	Y
US Pipe	Core 1	Y
	Core 1 DUPLICATE	Y
	Core 2	Y
	Core 3	Y
6-Mile Bridge	Core 1	Y
	Core 1 DUPLICATE	Y
	Core 2	Y

For quality control purposes, a Standard Reference Material (SRM 2586) was analyzed along with all of the sediment samples. Acid-washed beach sand was also analyzed as a negative control. Measured values were compared to certified values for SRM 2586 in an effort to insure the validity of the results.

Sample Processing*:*

The samples were dried for 7 days in an Isotemp Oven Model 630G set at 40°C. The dried sediment samples were sieved with a USGS standard 2.0 mm brass sieve and placed in either glass containers or plastic bags for storage. Each dried sediment sample was subjected to a coning and quartering method to insure homogeneity. Each resulting sample was then weighed out into a 110 mL capacity Teflon digestion vessel. The mass of each sample placed into the digestion vessel was carefully recorded and ranged between 0.50 and 1.0 grams.

Sample Digestion Process:

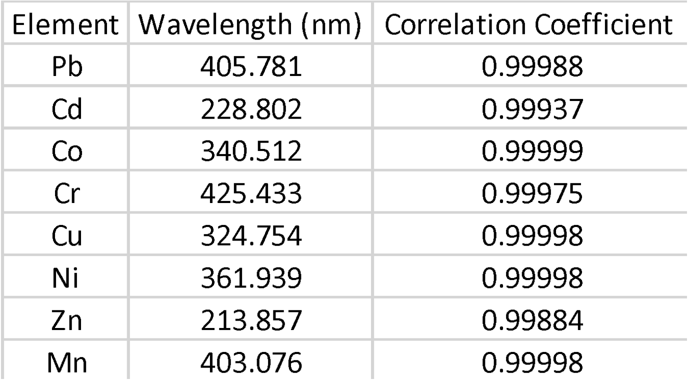
A sample pre-digestion process was conducted on all of the samples in the Teflon digestion vessels over a 24-hour period to prepare for the full digestion process. 10 mL of concentrated nitric acid was pipetted into each vessel and caps were sealed with teflon plugs. Samples were then allowed to pre-digest over a 24-hour period to begin the process of degradation of the organic material present in the sediment samples.

For the full acid digestion process, the samples in the Teflon vessels were placed into a CEM Corporation MARS 5 Microwave Digestion System (Matthews, NC), physically located at Randolph College in Lynchburg, VA. The microwave digestion system was programmed using onboard software (“Soil XPress”) which is equivalent to the U.S. EPA Method 3051A recommended for the digestion of sediments for elemental analysis. Starting at an initial temperature of 37 degrees Celsius, the temperature was raised to a maximum of 180 degrees Celsius where it was held for 10 minutes. This was followed by a 10-minute cool down cycle. Once cool enough, the samples were removed from the microwave and transferred to a fume hood so that they could be safely opened and diluted with DI water. Samples were then transferred from the Teflon digestion vessels into 100 mL volumetric flasks through Whatman 1 filter paper and a gravity filtration funnel. The samples were fully brought up to volume and thoroughly mixed. Samples were then transferred into 100 mL Nalgene bottles for multi-elemental analysis by the MP-AES.

MP-AES Analysis:

An Agilent Technologies MP-4200 MP-AES (Santa Clara, CA) was used to analyze the diluted digests as prepared previously. A multi-elemental calibration stock solution (Inorganic Ventures IV-24, Blacksburg, VA) was used in order to prepare a series of working calibration standards. Seven calibration standards were prepared: 0 mg/L, 0.5 mg/L, 1 mg/L, 2 mg/L, 5 mg/L, 10 mg/L, and 15 mg/L. For each standard, a specific amount of stock solution was pipetted into appropriate volumetric flasks. For standards 0.0, 0.5, 1.0, 2.0, and 3.0, stock solution was added in 50 mL volumetric flasks and diluted with 2 mL of concentrated HNO3. For standards 10.0 and 15.0, stock solution was added in 25 mL volumetric flasks and diluted with 1 mL of concentrated HNO3. All of the standards were brought up to volume using DI water, sealed and mixed with Parafilm, and then transferred into 100 mL bottles. Eight elements were analyzed in this research as seen in table 2: zinc (Zn), cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), manganese (Mn), and chromium (Cr).

Table 2: PTEs with Corresponding Wavelengths and Calibration Curve Correlation Coefficients



Element	Wavelength (nm)	Correlation Coefficient
Pb	405.781	0.99988
Cd	228.802	0.99937
Co	340.512	0.99999
Cr	425.433	0.99975
Cu	324.754	0.99998
Ni	361.939	0.99998
Zn	213.857	0.99884
Mn	403.076	0.99998

The MP-AES was optimized for peak performance at the wavelengths corresponding to the metals of interest prior to analysis. MPExpert (Agilent Technologies) software was used to set up a worksheet indicating the elements to be analyzed and all associated instrumental parameters. Calibration standards were analyzed first, followed by all of the sediment sample digests. Calibration curves reflected high correlation coefficient values, as seen in table 2. Correlation coefficient values closer to 1 indicate a more robust linear relationship between concentration and intensity.

Triplicate measurements per element were recorded by the software. Raw concentrations of each measurement were recorded by the software, and then imported into Excel where dilution factors were accounted for and raw measurements (in mg/L) were converted into mg metal/kg dried sediment sample.

Statistical Analysis:

Statistical methods were applied in order to analyze the data using standard descriptive statistical analyses in relation to its distribution and correlation among the studied parameters. Correlation analyses were used to examine the relationships between soil sampling sites, PTEs, and upper and lower soil layers. Confidence interval testing was used to assess the significance between variables and PTE concentrations. In order to examine the statistical significance of the results, Levene's Test and a Q-Q plot were used to test for variance and normality. A univariate statistical analysis was performed using a three-way ANOVA. IBM SPSS Statistics software was used in order to complete the data analysis.

Results and Discussion:

Distribution of Elements in Core Sediments:

The averaged levels of Zn, Cd, Ni, Cu, Co, Pb, Mn, and Cr at different depths of core sediments from site locations are listed in table 3. It is clear that the concentration levels vary between PTEs and site locations. In some cases, concentration levels were not detectable (ND) by MP-AES, as seen in table 3. This does not equate to an absence of PTEs within the sample, but rather a concentration below the threshold for which the MP-AES instrument could detect. Nickel was one of the PTEs that had no detectable levels among any of the site locations. Another was cobalt, in which there were no detectable levels among any of the site locations aside from one of the lower layer cores retrieved from 6-Mile Bridge with a concentration of 1.05 mg/kg. Since there is only one detectable concentration across all of the sites, and it is at a low level, this result is likely insignificant. More samples would need to be taken and analyzed to be sure.

The PTEs with detectable concentrations followed the order of Mn > Zn > Cr > Pb > Cu based on averages taken from all sites. Due to both target locations being downstream of the upstream control site, PTE concentrations should be lowest at Monacan Park. The target locations should have increased concentrations if they are actively releasing PTEs into the environment. The Railyard was positioned above stream of U.S Pipe, so it would be expected for the U.S Pipe site to have higher concentrations of PTEs due to sediment transport downstream.

The control site downstream of both target locations, 6-Mile Bridge, was investigated to determine whether or not PTEs are being transported downstream, and if so, to what extent based on the concentration values from upstream sites. Based on upper and lower layers, it is expected for lower layers to have higher concentrations due to accumulation overtime. For an upper layer to have a higher concentration, it would indicate that the particular site is actively releasing PTEs into the environment. As a result, sites with higher concentrations found in their upper layers than lower layers are a greater cause for concern.

Table 3: Averaged PTE Concentrations in Sediment (mg/kg)

Site	Cores Retrieved	Zn (mg/kg)	Cd (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Co (mg/kg)	Pb (mg/kg)	Mn (mg/kg)	Cr (mg/kg)
Monacan Park	core 1	99.1	1.80	ND	9.01	ND	18.0	248.7	9.01
	core 2	90.9	1.62	ND	8.12	ND	16.2	251.6	9.74
	core 2 DUPLICATE	91.6	2.65	ND	6.64	ND	14.6	242.9	9.29
	core 3	80.2	3.09	ND	7.72	ND	15.4	189.8	10.8
Railyard	core 1	86.2	ND	ND	11.7	ND	19.0	230.8	16.1
	core 1 DUPLICATE	81.7	ND	ND	10.7	ND	17.4	194.1	16.1
	core 2	78.2	ND	ND	15.6	ND	21.5	320.5	19.5
	core 2 DUPLICATE	94.0	1.77	ND	14.2	ND	23.0	374.1	21.3
	core 3 upper layer	82.0	1.44	ND	11.5	ND	18.7	251.7	12.9
	core 3 lower layer	83.6	1.52	ND	10.6	ND	19.8	284.3	15.2
	core 4 upper layer	78.4	1.22	ND	9.80	ND	15.9	182.5	13.5
	core 4 lower layer	80.7	1.22	ND	23.2	ND	14.7	184.7	13.5
US Pipe	core 1 upper layer	19.7	ND	ND	11.6	ND	12.7	118.1	20.8
	core 1 DUPLICATE upper layer	20.6	ND	ND	7.22	ND	18.6	133.1	20.6
	core 1 lower layer	34.3	ND	ND	11.0	ND	19.6	211.6	29.4
	core 1 DUPLICATE lower layer	22.5	ND	ND	7.16	ND	10.2	166.8	25.6
	core 2 upper layer	26.2	ND	ND	7.71	ND	13.9	178.9	23.1
	core 2 lower layer	57.8	ND	ND	14.8	ND	46.8	331.0	56.6
	core 3 upper layer	38.4	ND	ND	9.60	ND	21.3	268.7	37.3
	core 3 lower layer	188.2	ND	ND	23.3	ND	25.0	483.0	58.3
6-Mile Bridge	core 1 upper layer	49.8	ND	ND	19.6	ND	13.1	292.1	19.6
	core 1 lower layer	48.5	0.0	ND	20.6	ND	11.8	251.5	16.2
	core 2 upper layer	45.1	ND	ND	16.8	1.05	12.6	268.3	18.9
	core 2 DUPLICATE upper layer	38.0	0.0	ND	15.2	ND	10.8	214.8	13.0
	core 2 lower layer	54.7	0.0	ND	22.2	ND	14.8	334.0	20.7
	core 2 DUPLICATE lower layer	50.5	0.0	ND	20.0	ND	11.7	270.0	24.6

As seen in table 3, the highest Zn concentration was detected in one of the lower layers retrieved from U.S Pipe, whereas the lowest Zn concentration was detected in one of the upper layers retrieved from U.S Pipe with a range of 168.5 mg/kg. The sites followed the order of Monacan Park > Rail Yard > U.S Pipe > 6 Mile Bridge based on average Zn concentrations, as seen in figure 2. This indicates that target locations are not actively releasing Zn into the environment. Although it is interesting that Monacan Park, the upstream control site, has the highest average levels of Zn. This is likely due to pollution upstream of the site caused by an industrial area's methods in how they deal with their heavy metals and waste. There is also a trend of decreasing Zn levels further downstream, aside from the spike in Zn in one of the lower layers from U.S Pipe. This would support that target locations are not actively releasing Zn into the environment, but due to high concentration levels in their lower layers, may have in the past.

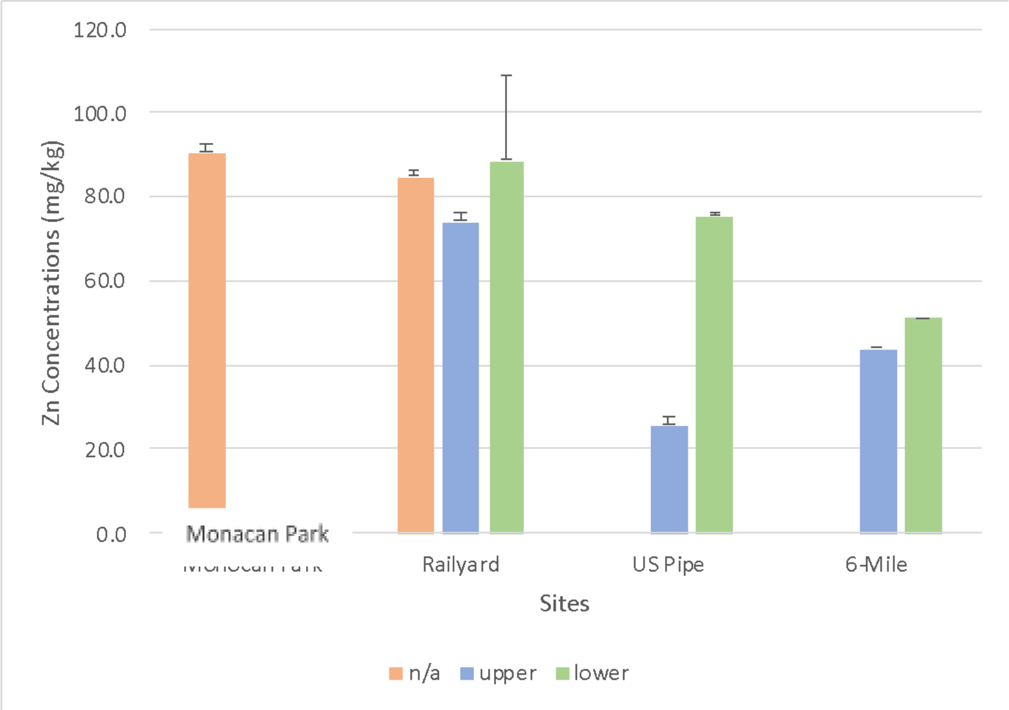


Figure 2: Average Zn Concentrations in Upper and Lower Layers Across All Sites with Standard Error Bars. Cores that were not divided into upper and lower layers are labeled as "n/a". Sites are arranged from upstream to downstream, as shown from left to right.

As seen in table 3, the highest Cd concentration was detected in one of the cores retrieved from Monacan Park, whereas the lowest detectable Cd concentrations were from 6-Mile Bridge with a range of 1.80 mg/kg. As seen in figure 3, there were a lot of non-detectable Cd concentrations across the Railyard, U.S Pipe, and 6-Mile Bridge sites. Monacan Park was the only site to have detectable Cd levels in all of its core samples. Similar to the trend of Zn in the upper sediment layers, it is likely that the Cd concentrations are a result of pollution upstream of Monacan Park. Considering there are no detectable levels in the upper or lower layers downstream of the Railyard, it is likely that the Railyard site was either a source of Cd pollution in the past, or there was a source further upstream that released Cd into the environment. However, additional data would need to be collected in order to determine a trend for the lower layers since there is nothing to compare it to.

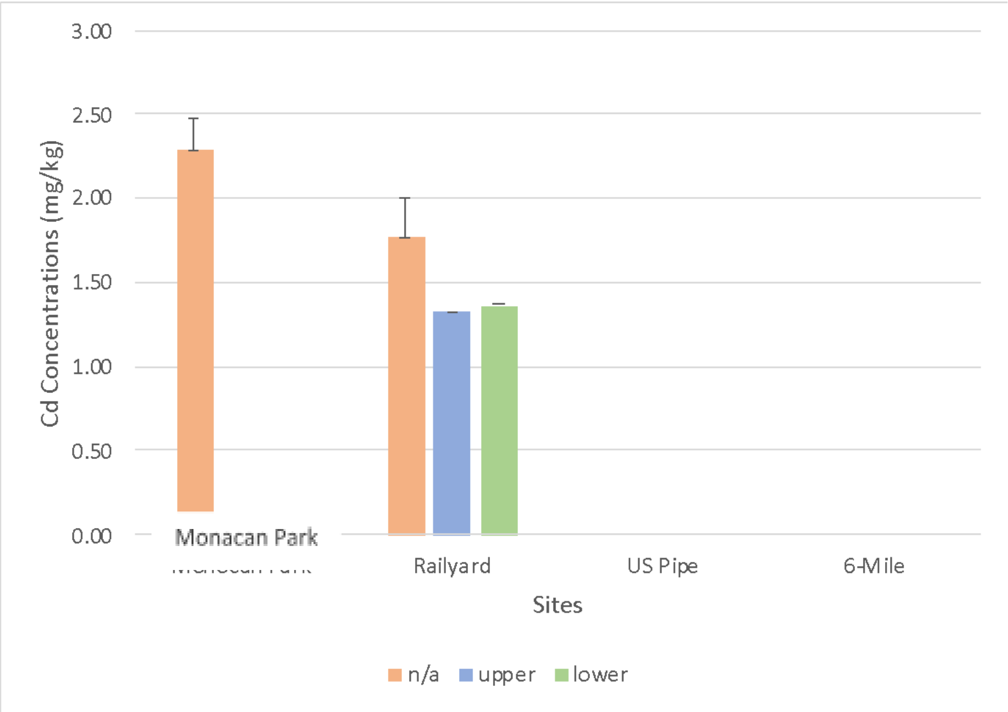


Figure 3: Average Cd Concentrations in Upper and Lower Layers Across All Sites with Standard Error Bars. Cores that were not divided into upper and lower layers are labeled as “n/a”. Sites are arranged from upstream to downstream, as shown from left to right.

As seen in table 3, the highest Cu concentration was detected in one of the lower layers retrieved from U.S Pipe, whereas the lowest detectable Cu concentration was detected in one of the cores from Monacan Park with a range of 16.66 mg/kg. Figure 4 shows that the sites followed the order of 6-Mile Bridge > Rail Yard > U.S Pipe > Monacan Park based on average Cu concentrations. This would indicate that the target locations could potentially be emitting Cu into the environment, since the concentration levels gradually increase downstream. Additional data is needed regarding element mobility in this study in order to determine an exact source that may be releasing Cu into the environment.

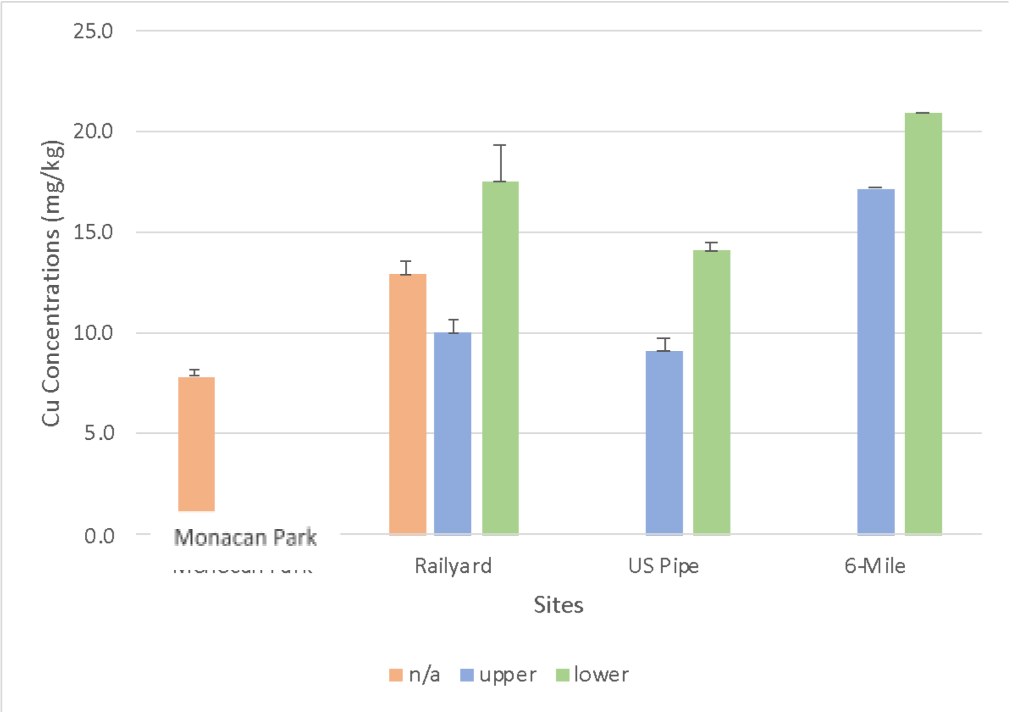


Figure 4: Average Cu Concentrations in Upper and Lower Layers Across All Sites with Standard Error Bars. Cores that were not divided into upper and lower layers are labeled as "n/a". Sites are arranged from upstream to downstream, as shown from left to right.

As seen in table 3, the highest Pb concentration was detected in one of the lower layers retrieved from U.S Pipe, whereas the lowest detectable Pb concentration was detected in one of the lower layers also retrieved from U.S Pipe with a range of 36.6 mg/kg. Figure 5 shows that the sites followed the order of U.S Pipe > Rail Yard > Monacan Park > 6 Mile Bridge based on average Pb concentrations. This would suggest that the two target locations are releasing Pb into the environment, with U.S Pipe more so than the Railyard.

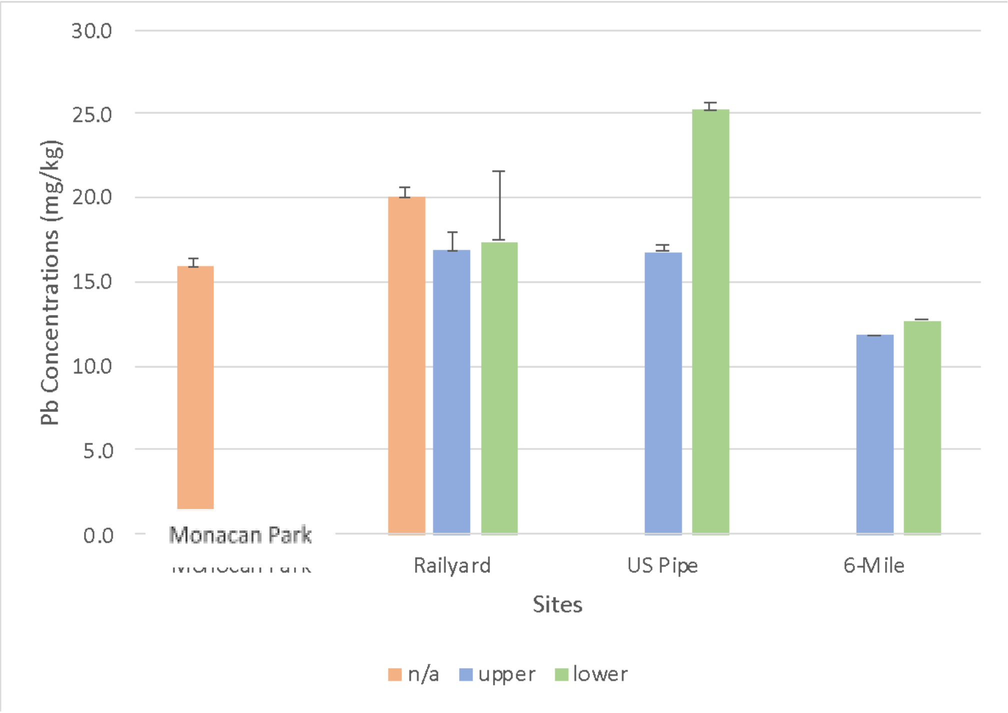


Figure 5: Average Pb Concentrations in Upper and Lower Layers Across All Sites with Standard Error Bars. Cores that were not divided into upper and lower layers are labeled as “n/a”. Sites are arranged from upstream to downstream, as shown from left to right.

Mn concentrations were the highest compared to all of the other observed PTE concentrations, but are likely from natural sources based on the known geological deposits within the area. As seen in table 3, the highest Mn concentration was detected in one of the lower layers retrieved from U.S Pipe, whereas the lowest detectable Mn concentration was detected in one of the upper layers from U.S Pipe with a range of 364.9 mg/kg. As seen in figure 6, the sites followed the order of 6-Mile Bridge > Rail Yard > U.S Pipe > Monacan Park based on average Mn concentrations. This pattern is identical to the trend of Cu concentrations found across all four sites. It is possible that the target locations could be releasing Mn into the environment, as the concentration levels are higher immediately after the upstream control site. However, the levels are still relatively high at Monacan Park, meaning that there is likely an unidentified source further upstream that is contributing to contaminants accumulating in the control site downstream in addition to Mn being released by target locations. It is also likely that this downstream accumulation is from runoff as a result of the geological deposits of Mn in the area.

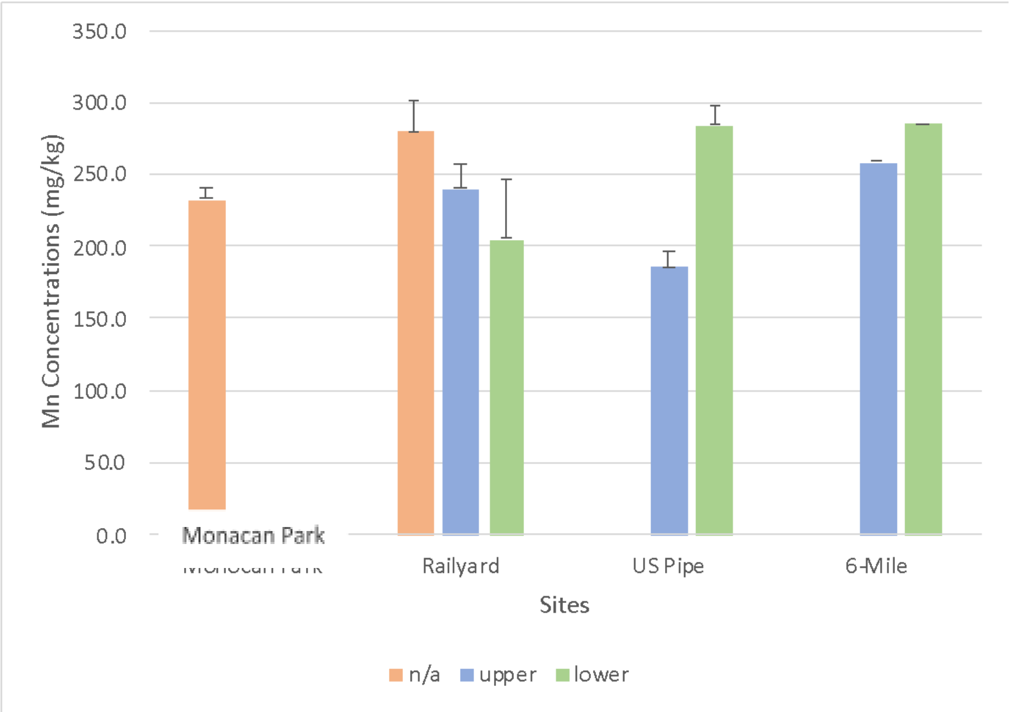


Figure 6: Average Mn Concentrations in Upper and Lower Layers Across All Sites with Standard Error Bars. Cores that were not divided into upper and lower layers are labeled as “n/a”. Sites are arranged from upstream to downstream, as shown from left to right.

Lastly, as seen in table 3, the highest Cr concentration was detected in one of the lower layers retrieved from U.S Pipe, whereas the lowest detectable Cu concentration was detected in one of the cores from Monacan Park with a range of 47.59 mg/kg. As seen in figure 3, the sites followed the order of U.S Pipe > 6-Mile Bridge > Railyard > Monacan Park based on average Cr concentrations. This would indicate that the target locations are releasing Cr into the environment. Since the Railyard has higher concentration levels than the control site upstream, it is likely that Cr is accumulating at the U.S Pipe location. Since the U.S Pipe location has the highest concentration levels, it is likely that they are depositing Cr into the environment, which is supported by the fact that the site with the second highest Cr levels was immediately downstream at 6-Mile Bridge.

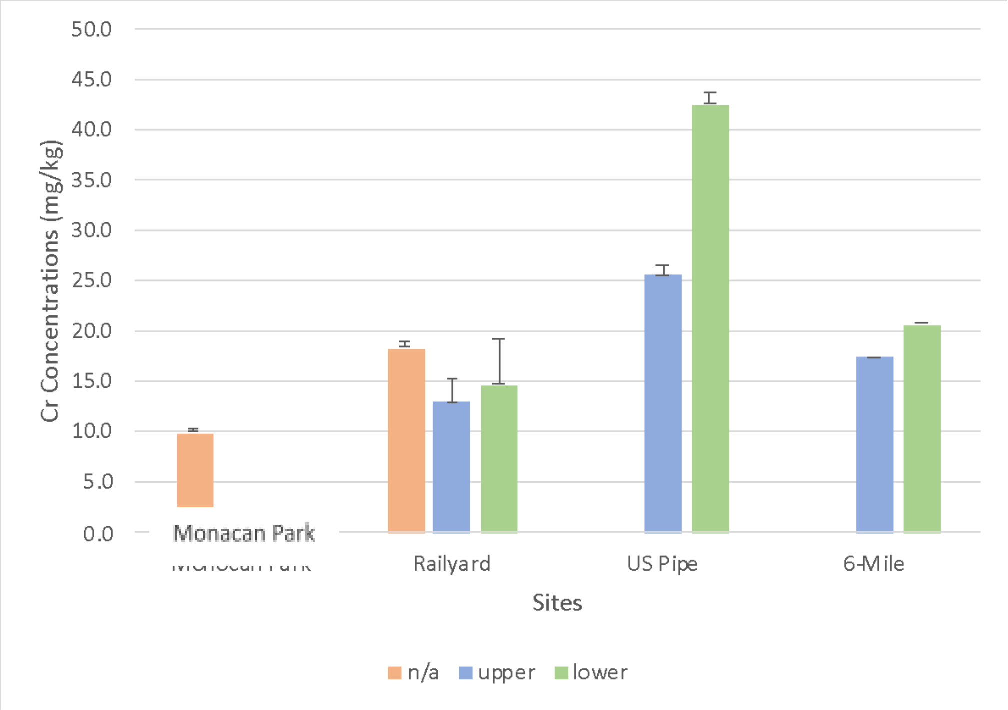


Figure 7: Average Cr Concentrations in Upper and Lower Layers Across All Sites with Standard Error Bars. Cores that were not divided into upper and lower layers are labeled as “n/a”. Sites are arranged from upstream to downstream, as shown from left to right.

The results from table 3 indicate that there is a general trend for higher concentrations to be found in lower layers of sediments. It also reflects that there tends to be higher concentrations of PTEs found in the lower layers of cores retrieved from the U.S Pipe location. This could be a result of U.S Pipe’s extensive history in dealing with PTEs, ultimately leading to an accumulation of certain elements in lower sediment layers over time.

Quality Control Checks:

It is very important to have accurate and precise data in order to effectively be able to interpret the results. To assess accuracy in this study, a NIST SRM 2586 (National Institute of Standards and Technology Standard Reference Material) containing a certified value for Pb was analyzed in the exact same way as the other sediment samples. A Percent recovery for Pb was calculated using Equation 1. Percent recovery calculates the percentage of an original substance that is recovered after a complete analysis process, thus also acting as a measurement of the reaction's efficiency. In analyzing a standard reference material (SRM) containing a known amount of "substance" in a matrix similar to that of the sample being analyzed, it is possible to test for controllable errors in the entire analysis process. Percent recoveries between 75-100% are considered acceptable.

$$Equation\ 1:$$

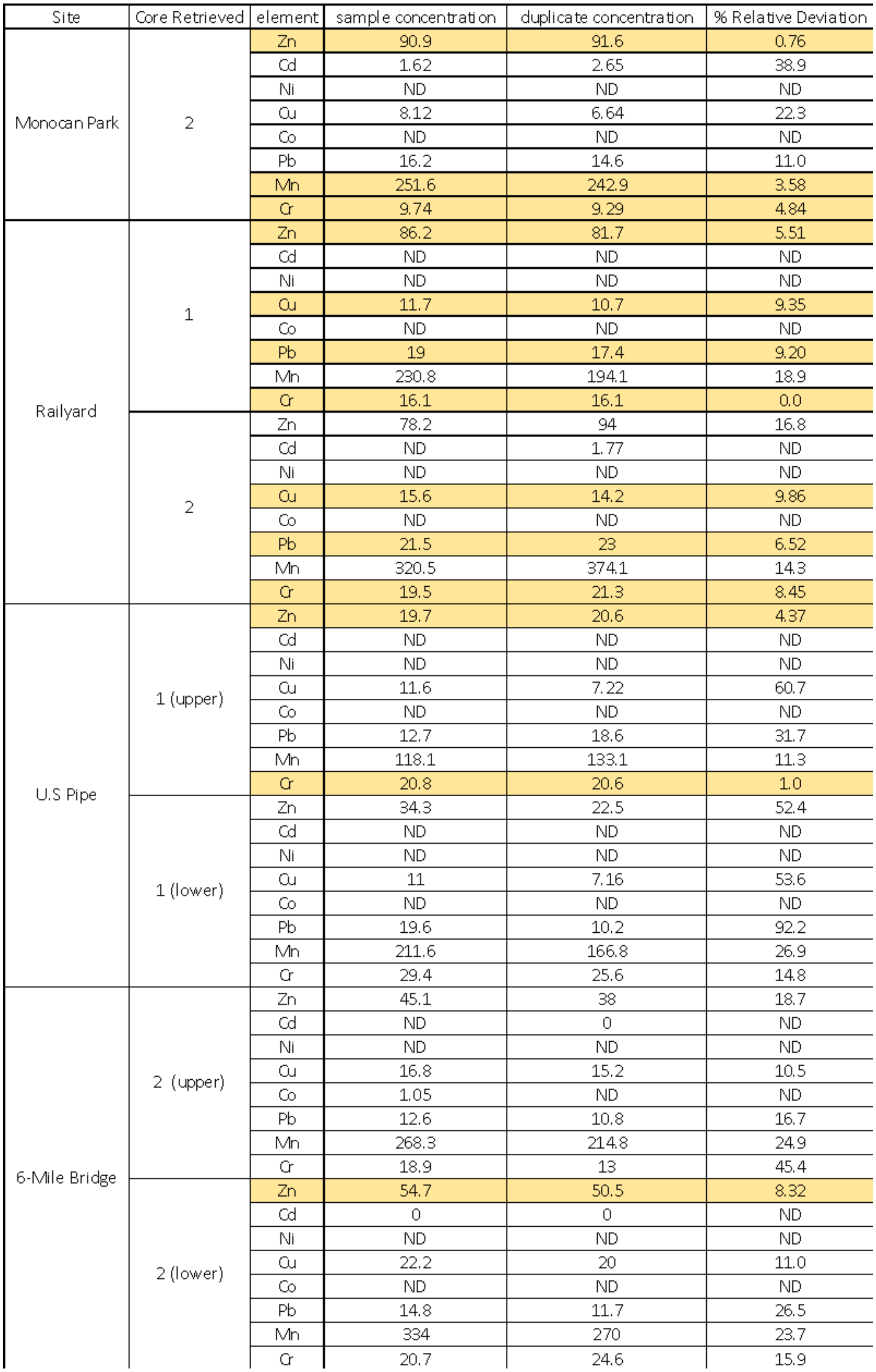
$$\%\ Recovery = \left(\frac{actual\ value}{certified\ value}\right) x\ 100$$

To assess precision, the results of duplicate samples were compared to their original core sample. Table 4 indicates the calculated precision values of duplicate samples using equation 2. In this case, smaller deviation values (<10%) are more desirable.

Equation 2:

$$\% \, Relative \; Deviation = \left(\frac{|sample \; concentration - duplicate \; concentration|}{sample \; concentration}\right) x \; 100$$

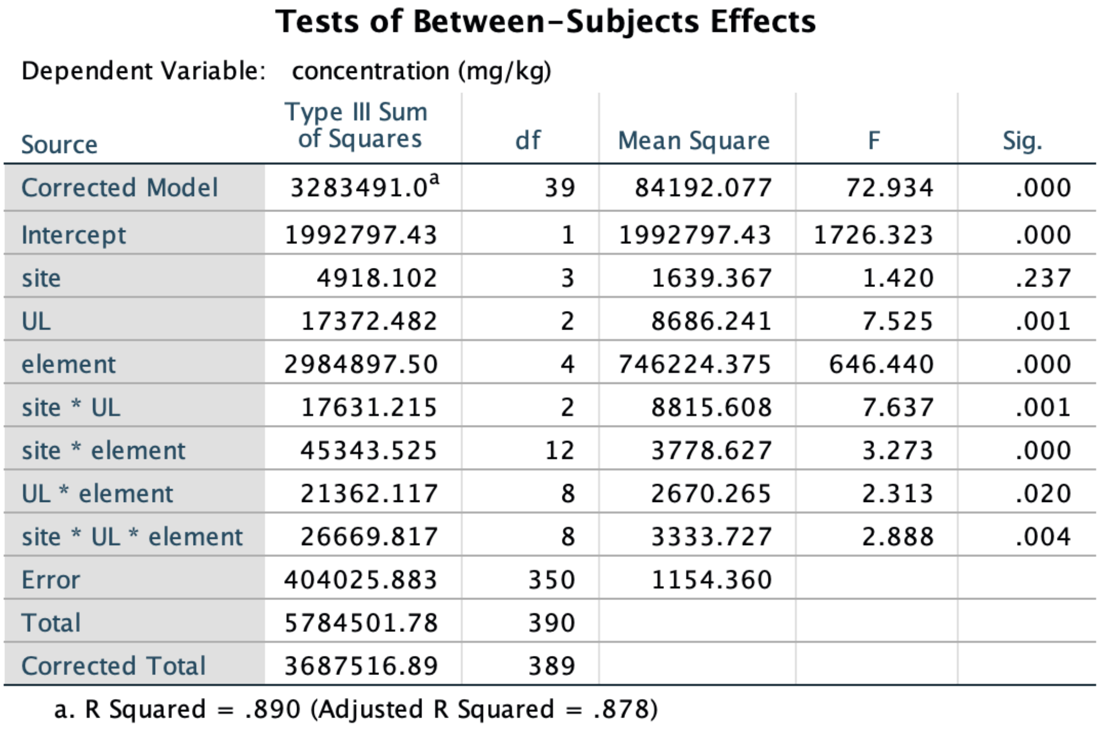
Table 4: Percent Relative Deviation of Duplicate Samples



Site	Core Retrieved	element	sample concentration	duplicate concentration	% Relative Deviation
Monocan Park	2	Zn	90.9	91.6	0.76
		Cd	1.62	2.65	38.9
		Ni	ND	ND	ND
		Cu	8.12	6.64	22.3
		Co	ND	ND	ND
		Pb	16.2	14.6	11.0
		Mn	251.6	242.9	3.58
		Cr	9.74	9.29	4.84
Railyard	1	Zn	86.2	81.7	5.51
		Cd	ND	ND	ND
		Ni	ND	ND	ND
		Cu	11.7	10.7	9.35
		Co	ND	ND	ND
		Pb	19	17.4	9.20
		Mn	230.8	194.1	18.9
		Cr	16.1	16.1	0.0
	2	Zn	78.2	94	16.8
		Cd	ND	1.77	ND
		Ni	ND	ND	ND
		Cu	15.6	14.2	9.86
		Co	ND	ND	ND
		Pb	21.5	23	6.52
		Mn	320.5	374.1	14.3
		Cr	19.5	21.3	8.45
U.S Pipe	1 (upper)	Zn	19.7	20.6	4.37
		Cd	ND	ND	ND
		Ni	ND	ND	ND
		Cu	11.6	7.22	60.7
		Co	ND	ND	ND
		Pb	12.7	18.6	31.7
		Mn	118.1	133.1	11.3
		Cr	20.8	20.6	1.0
	1 (lower)	Zn	34.3	22.5	52.4
		Cd	ND	ND	ND
		Ni	ND	ND	ND
		Cu	11	7.16	53.6
		Co	ND	ND	ND
		Pb	19.6	10.2	92.2
		Mn	211.6	166.8	26.9
		Cr	29.4	25.6	14.8
6-Mile Bridge	2 (upper)	Zn	45.1	38	18.7
		Cd	ND	0	ND
		Ni	ND	ND	ND
		Cu	16.8	15.2	10.5
		Co	1.05	ND	ND
		Pb	12.6	10.8	16.7
		Mn	268.3	214.8	24.9
		Cr	18.9	13	45.4
	2 (lower)	Zn	54.7	50.5	8.32
		Cd	0	0	ND
		Ni	ND	ND	ND
		Cu	22.2	20	11.0
		Co	ND	ND	ND
		Pb	14.8	11.7	26.5
		Mn	334	270	23.7
		Cr	20.7	24.6	15.9

Statistical Analysis of PTEs Metals:

Of the eight PTEs of interest, Cd, Ni, and Co had concentration levels that were not detectable by the instrument, so they were not further considered in the statistical analysis. As a result, only Zn, Cu, Pb, Mn, and Cr were analyzed. In order to ensure the most accurate results, raw data and concentrations were used as opposed to the previous average values as seen in table 3. Equivalent calculations were performed in order to account for dilutions and conversions. The main reasons for incorporating statistical analyses were to answer two questions: (1) Is there a significant difference between upper and lower layers within a single site? (2) Is there a significant difference in a specific element across all four sites?



Tests of Between-Subjects Effects

Dependent Variable: concentration (mg/kg)

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	3283491.0[a]	39	84192.077	72.934	.000
Intercept	1992797.43	1	1992797.43	1726.323	.000
site	4918.102	3	1639.367	1.420	.237
UL	17372.482	2	8686.241	7.525	.001
element	2984897.50	4	746224.375	646.440	.000
site * UL	17631.215	2	8815.608	7.637	.001
site * element	45343.525	12	3778.627	3.273	.000
UL * element	21362.117	8	2670.265	2.313	.020
site * UL * element	26669.817	8	3333.727	2.888	.004
Error	404025.883	350	1154.360		
Total	5784501.78	390			
Corrected Total	3687516.89	389			

a. R Squared = .890 (Adjusted R Squared = .878)

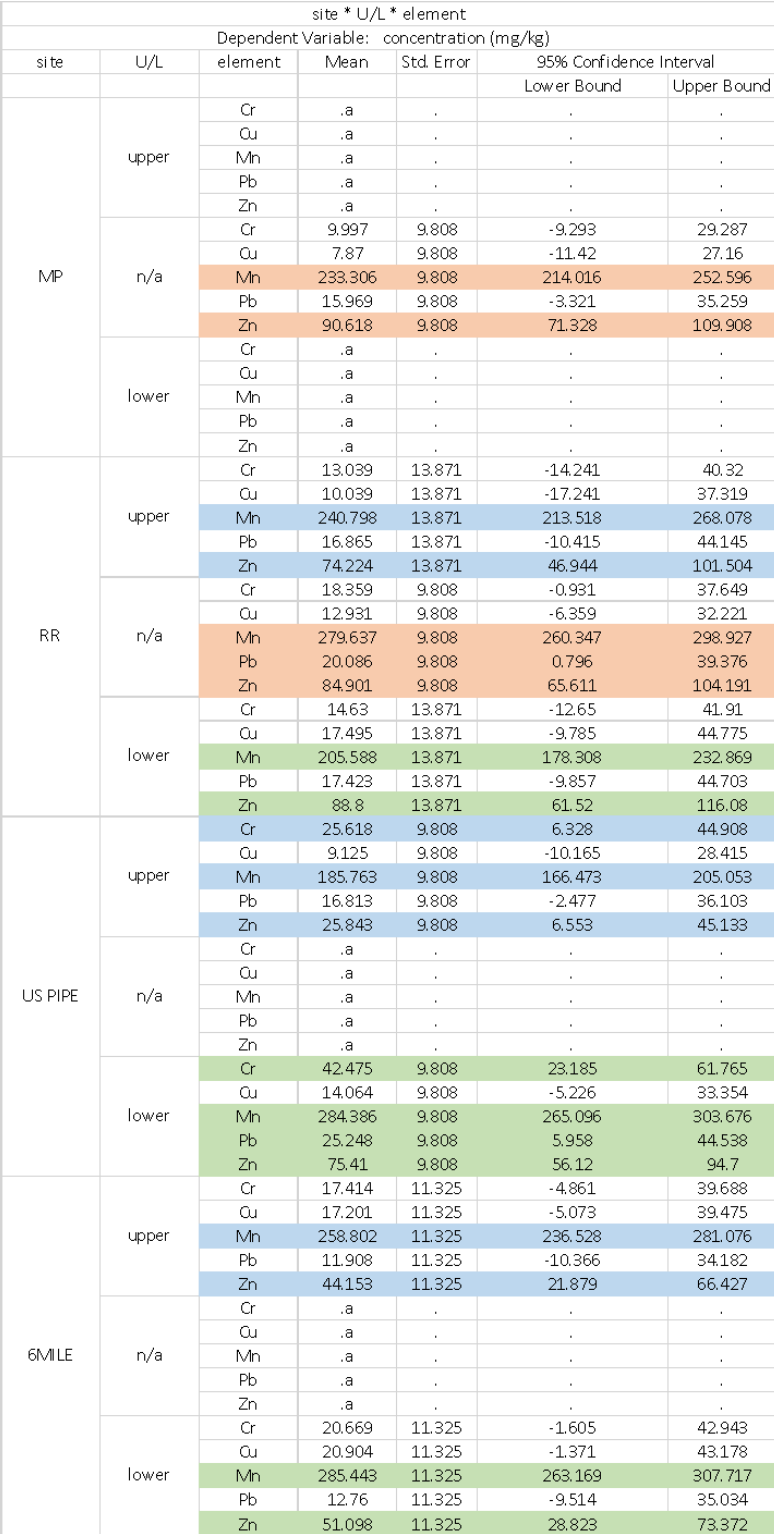
Figure 8: Significance of Measured Variables Using a Three-Way ANOVA

The results from Figure 8 are a reflection of different types and levels of interactions between variables. A significance value less than 0.05 indicates that a variable or interaction among variables is significant. Since the three-way interaction between site location, upper and lower layers, and PTEs is significant, the other variables and their single or two-way interactions are unable to be interpreted, regardless of their significance. This means that all three independent variables interact with one another to influence the outcome of the dependent variable.

Significant Differences Compared to Zero:

Figure 9 reflects the specific interactions between site location, upper and lower layers, and PTE elements. Cores that were not able to be separated into upper and lower layers were labeled as n/a. The confidence intervals as seen in figure 9 indicate whether or not a PTE has a concentration that is significantly higher than 0 mg/kg. Confidence intervals that contain zero are considered insignificant. Figure 9 is able to identify PTEs with concentrations significantly higher than zero among upper and lower layers of different site locations.

U.S Pipe was the only location to have Cr concentrations significantly higher in its upper and lower layers. There were no sites that had Cu concentrations significantly higher than zero. All of the sites had Mn concentrations significantly higher than zero in both upper and lower layers, including the “n/a” sites. U.S pipe was one of two locations to have Pb concentrations significantly higher than zero in its upper and lower layers. Even so, the concentrations are low overall. The Railyard’s “n/a” core also indicated having Pb concentrations significantly higher than zero, although just barely. Considering that there are no significant differences in the upper and lower layers at the Railyard, it is likely not a cause for concern. Lastly, all of the sites followed the same pattern as with Mn. All had Zn concentrations significantly higher than zero, including the “n/a” sites. Based on these results, the most common elements with concentrations significantly higher than zero are those that were common across all sites- Mn and Zn. However, this is understandable as these two elements are more naturally occurring in the environment, and only become toxic at much higher concentrations.



site * U/L * element

Dependent Variable: concentration (mg/kg)

site	U/L	element	Mean	Std. Error	95% Confidence Interval	
					Lower Bound	Upper Bound
MP	upper	Cr	.a	.	.	.
		Cu	.a	.	.	.
		Mn	.a	.	.	.
		Pb	.a	.	.	.
		Zn	.a	.	.	.
	n/a	Cr	9.997	9.808	-9.293	29.287
		Cu	7.87	9.808	-11.42	27.16
		Mn	233.306	9.808	214.016	252.596
		Pb	15.969	9.808	-3.321	35.259
		Zn	90.618	9.808	71.328	109.908
	lower	Cr	.a	.	.	.
		Cu	.a	.	.	.
		Mn	.a	.	.	.
		Pb	.a	.	.	.
		Zn	.a	.	.	.
RR	upper	Cr	13.039	13.871	-14.241	40.32
		Cu	10.039	13.871	-17.241	37.319
		Mn	240.798	13.871	213.518	268.078
		Pb	16.865	13.871	-10.415	44.145
		Zn	74.224	13.871	46.944	101.504
	n/a	Cr	18.359	9.808	-0.931	37.649
		Cu	12.931	9.808	-6.359	32.221
		Mn	279.637	9.808	260.347	298.927
		Pb	20.086	9.808	0.796	39.376
		Zn	84.901	9.808	65.611	104.191
	lower	Cr	14.63	13.871	-12.65	41.91
		Cu	17.495	13.871	-9.785	44.775
		Mn	205.588	13.871	178.308	232.869
		Pb	17.423	13.871	-9.857	44.703
		Zn	88.8	13.871	61.52	116.08
US PIPE	upper	Cr	25.618	9.808	6.328	44.908
		Cu	9.125	9.808	-10.165	28.415
		Mn	185.763	9.808	166.473	205.053
		Pb	16.813	9.808	-2.477	36.103
		Zn	25.843	9.808	6.553	45.133
	n/a	Cr	.a	.	.	.
		Cu	.a	.	.	.
		Mn	.a	.	.	.
		Pb	.a	.	.	.
		Zn	.a	.	.	.
	lower	Cr	42.475	9.808	23.185	61.765
		Cu	14.064	9.808	-5.226	33.354
		Mn	284.386	9.808	265.096	303.676
		Pb	25.248	9.808	5.958	44.538
		Zn	75.41	9.808	56.12	94.7
6MILE	upper	Cr	17.414	11.325	-4.861	39.688
		Cu	17.201	11.325	-5.073	39.475
		Mn	258.802	11.325	236.528	281.076
		Pb	11.908	11.325	-10.366	34.182
		Zn	44.153	11.325	21.879	66.427
	n/a	Cr	.a	.	.	.
		Cu	.a	.	.	.
		Mn	.a	.	.	.
		Pb	.a	.	.	.
		Zn	.a	.	.	.
	lower	Cr	20.669	11.325	-1.605	42.943
		Cu	20.904	11.325	-1.371	43.178
		Mn	285.443	11.325	263.169	307.717
		Pb	12.76	11.325	-9.514	35.034
		Zn	51.098	11.325	28.823	73.372

Figure 9: Three-Way Interactions Between Site Locations, Upper and Lower Layers, and PTEs. Sites are arranged from upstream to downstream, as shown from top to bottom. PTEs with significantly higher concentrations than zero are highlighted based on their core layers: lower=green; upper=blue; n/a=orange.

Significant Differences in Upper and Lower Layers Within a Single Site:

In order to evaluate if there were significant differences between upper and lower layers in a single site, new confidence intervals were developed by using equation 3 and values from figure 9. The t-value was determined using five percent significance and a value of 350 (figure 8) for the degrees of freedom. Mean values were used as x-values for the upper and lower layers, with the lower layer values being used as $\overline{x}_1$.

$$\text{Equation 3:}$$

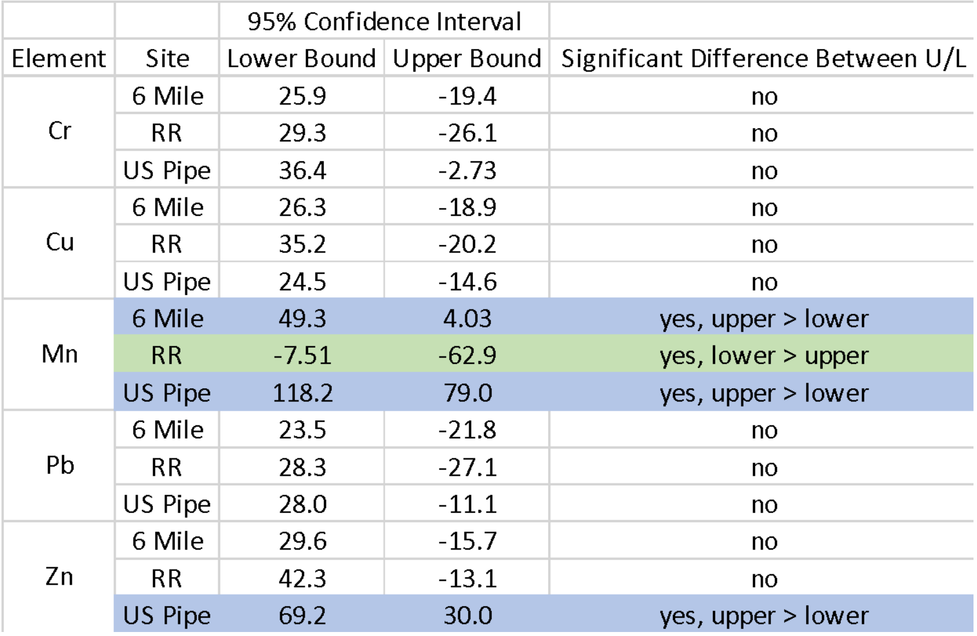
$$confidence\ interval = \overline{x_1} - \overline{x_2} \pm (t - value)(st.error\ value)$$

This equation allows us to determine if there were significant differences between upper and lower layers in a single site based on whether or not zero was included in the confidence intervals or not, as seen in table 5. In order for there to be a significant difference between upper and lower layers, the confidence intervals cannot include zero. Sites that did not have upper and lower layers were not included in this analysis. Confidence intervals with a positive range indicate that the lower layers had significantly higher concentrations than the lower layers. Confidence intervals with a negative range indicate that the upper layers had significantly higher concentrations than the lower layers.

Table 5 indicates that there are significant differences between upper and lower layers in relation to two elements. For Mn, there are significant differences between the upper and lower layers across all three sites. The Railyard was the only site to have significantly higher concentrations of Mn in its upper layers compared to its lower layers. Both U.S Pipe and 6-Mile sites had significantly higher concentrations of Mn in their lower layers compared to their upper layers. Zn was the only other element to show a significant difference between upper and lower layers. In this case, U.S Pipe also had significantly higher concentrations of Zn in its lower layers compared to its upper layers.

Higher concentrations in upper layers not only indicate more recent PTE deposits, but can also be a sign that a greater amount of PTEs are being actively released into the environment than before. Without knowing the specific ages of the core layers, time can be only assessed as relative between upper and lower layers. Upper surface layers are indicators of more recent deposits, whereas lower subsurface layers are indicators of older deposits. Higher concentrations in lower layers likely suggest that sites have changed their practices so that they no longer release as many PTEs into the environment.

Table 5: Significant Differences of PTE Concentrations Between Upper and Lower Layers Within a Single Site



		95% Confidence Interval		
Element	Site	Lower Bound	Upper Bound	Significant Difference Between U/L
Cr	6 Mile	25.9	-19.4	no
	RR	29.3	-26.1	no
	US Pipe	36.4	-2.73	no
Cu	6 Mile	26.3	-18.9	no
	RR	35.2	-20.2	no
	US Pipe	24.5	-14.6	no
Mn	6 Mile	49.3	4.03	yes, upper > lower
	RR	-7.51	-62.9	yes, lower > upper
	US Pipe	118.2	79.0	yes, upper > lower
Pb	6 Mile	23.5	-21.8	no
	RR	28.3	-27.1	no
	US Pipe	28.0	-11.1	no
Zn	6 Mile	29.6	-15.7	no
	RR	42.3	-13.1	no
	US Pipe	69.2	30.0	yes, upper > lower

Significant Differences in PTE Concentrations Across All Sites:

In order to evaluate if there was a significant difference of a single element across all four sites, new confidence intervals were developed using equations 4 and 5 and values from figure 9. After solving for the standard error value in equation 5, new confidence intervals were calculated using equation 3.

Equation 4:

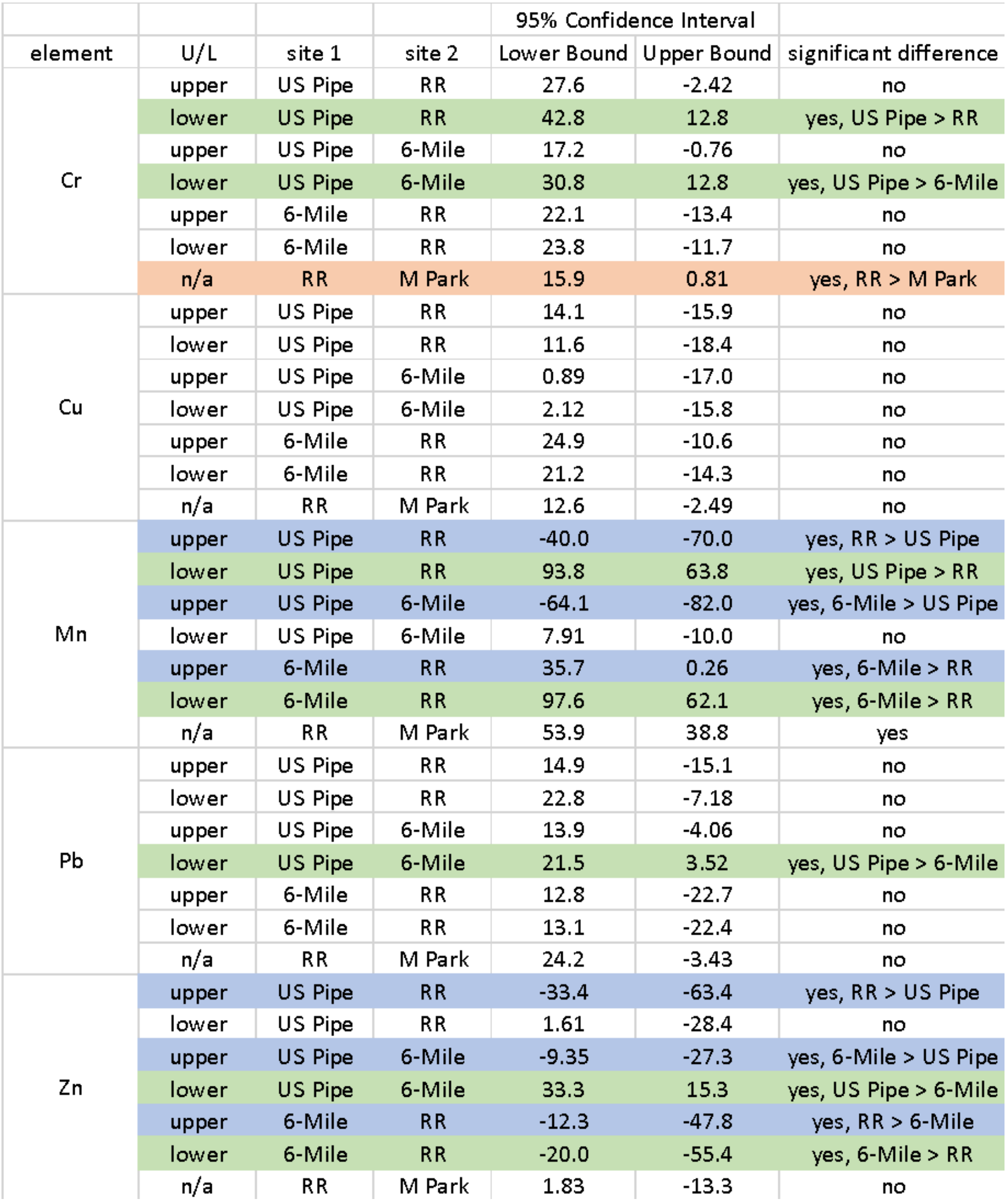
$$s_p = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}$$

$Equation\ 5$:

$$st.error\ value = s_p\sqrt{\frac{1}{n_1}+\frac{1}{n_2}}$$

Table 6 indicates the significant differences between a single element across the upper and lower layers of all sites. As a result, sites with cores that did not include upper and lower layers could only be compared to one another. Therefore, PTE concentrations at target sites could only be compared to the downstream control site. Not being able to observe if there were significant differences between target locations and an upstream control site meant that results were less accurate since sediments are transported downstream. Confidence intervals with a positive range indicate that site 1 had significantly higher concentration levels when compared to site 2. Confidence intervals with a negative range indicate that site 2 had significantly higher concentration levels when compared to site 1.

Table 6: Significant Differences of PTE Concentrations Between Upper and Lower Layers Across All Sites



				95% Confidence Interval		
element	U/L	site 1	site 2	Lower Bound	Upper Bound	significant difference
Cr	upper	US Pipe	RR	27.6	-2.42	no
	lower	US Pipe	RR	42.8	12.8	yes, US Pipe > RR
	upper	US Pipe	6-Mile	17.2	-0.76	no
	lower	US Pipe	6-Mile	30.8	12.8	yes, US Pipe > 6-Mile
	upper	6-Mile	RR	22.1	-13.4	no
	lower	6-Mile	RR	23.8	-11.7	no
	n/a	RR	M Park	15.9	0.81	yes, RR > M Park
Cu	upper	US Pipe	RR	14.1	-15.9	no
	lower	US Pipe	RR	11.6	-18.4	no
	upper	US Pipe	6-Mile	0.89	-17.0	no
	lower	US Pipe	6-Mile	2.12	-15.8	no
	upper	6-Mile	RR	24.9	-10.6	no
	lower	6-Mile	RR	21.2	-14.3	no
	n/a	RR	M Park	12.6	-2.49	no
Mn	upper	US Pipe	RR	-40.0	-70.0	yes, RR > US Pipe
	lower	US Pipe	RR	93.8	63.8	yes, US Pipe > RR
	upper	US Pipe	6-Mile	-64.1	-82.0	yes, 6-Mile > US Pipe
	lower	US Pipe	6-Mile	7.91	-10.0	no
	upper	6-Mile	RR	35.7	0.26	yes, 6-Mile > RR
	lower	6-Mile	RR	97.6	62.1	yes, 6-Mile > RR
	n/a	RR	M Park	53.9	38.8	yes
Pb	upper	US Pipe	RR	14.9	-15.1	no
	lower	US Pipe	RR	22.8	-7.18	no
	upper	US Pipe	6-Mile	13.9	-4.06	no
	lower	US Pipe	6-Mile	21.5	3.52	yes, US Pipe > 6-Mile
	upper	6-Mile	RR	12.8	-22.7	no
	lower	6-Mile	RR	13.1	-22.4	no
	n/a	RR	M Park	24.2	-3.43	no
Zn	upper	US Pipe	RR	-33.4	-63.4	yes, RR > US Pipe
	lower	US Pipe	RR	1.61	-28.4	no
	upper	US Pipe	6-Mile	-9.35	-27.3	yes, 6-Mile > US Pipe
	lower	US Pipe	6-Mile	33.3	15.3	yes, US Pipe > 6-Mile
	upper	6-Mile	RR	-12.3	-47.8	yes, RR > 6-Mile
	lower	6-Mile	RR	-20.0	-55.4	yes, 6-Mile > RR
	n/a	RR	M Park	1.83	-13.3	no

For Cr, there are significant differences in the lower layers across all of the sites. This contradicts the results from table 5, which indicated that none of the sites had significant differences between their upper and lower layers. Perhaps this is an indication of the mobility and transport of Cr within soils and the environment, and it has ended up in upper layers further downstream. U.S Pipe has significantly higher Cr concentrations in its lower layers compared to the lower layers of the Railyard and 6-Mile Bridge sites. This can be an indication that U.S Pipe or the Railyard used to be a source of Cr pollution, since the Railyard is directly upstream of U.S Pipe. In terms of upper layers, there were no significant differences in Cr concentrations across all of the sites. This means that there were similar concentration levels of Cr in all of the upper layers at all of the sites. Table 6 also indicates that the Railyard had significantly higher Cr concentrations than Monacan Park. This would indicate that Cr pollution is occurring around the target locations, since there are higher concentrations present downstream. However, without an upstream control site with upper and lower layers to compare the target location concentrations to, this cause is unclear.

For Cu, there were no significant differences in any of the upper- or lower-layer concentrations at any of the sites. Meaning, that there were similar concentration levels of Cu at all of the sites, including upper and lower layers. This indicates that there is no cause for concern for past or present metal pollution of target locations in regard to Cu levels.

For Mn, there are significant differences in the upper and lower layers across all of the sites. There are significantly higher Mn concentrations in the upper layers of 6-Mile when compared to both of the target locations. This can be an indication of Mn deposition occurring from upstream. So, by looking at the Railyard and U.S Pipe, the Railyard has higher Mn concentrations in its upper layers compared to the upper layers of U.S Pipe. This can indicate that the Railyard is a source of Mn pollution, or it can be a result of a site further upstream. Without an upstream control site, this cause is unclear. It can also indicate, since U.S Pipe is situated between the Railyard and 6-Mile sites, that there is a source between U.S Pipe and the 6-Mile Bridge that is emitting Mn into the environment. Additionally, there are significantly higher concentrations of Mn in the lower layers of both U.S Pipe and 6-Mile compared to the lower layers of the Railyard. When compared to each other, there is no significant difference between the lower layers of U.S Pipe and 6-Mile, meaning that they have similar Mn concentration levels in their lower layers. This indicates that U.S Pipe could have been a source of past Mn pollution, and carried some of it downstream to 6-Mile. It could also indicate that an upstream source, maybe the Railyard, could have been a source of pollution. Ultimately, 6-Mile had significantly higher Mn concentrations in both its upper and lower layers compared to all of the other sites. When comparing these results to table 5, there are significantly higher Mn concentrations in the lower layers of 6-Mile. Meaning, that target locations used to emit higher levels of Mn pollution into the environment compared to recently.

For Pb, there are significant differences in the lower layers of sites. There are significantly higher Pb concentrations in the lower layers of U.S Pipe compared to the lower layers of 6-Mile. Similar to Cr, these results contradict with the results from table 5. Perhaps this is an indication of the mobility and transport of Pb within soils and the environment, and it has ended up in upper layers further downstream. However, since the highest Pb concentrations were in the lower layers of U.S Pipe, it is likely that U.S Pipe used to be a source of Pb pollution. This is supported by U.S Pipe's extensive history in dealing with Pb and other PTEs in the past. Since there are insignificant levels of Pb in the upper levels across all of the sites, this means that there are similar Pb concentrations at each site. Meaning, that target locations are not currently a cause for concern based on current Pb levels.

For Zn, a pattern very similar to Mn in that there are significant differences in the upper and lower layers across all of the sites. However, unlike Mn, the Railyard has significantly higher concentrations than U.S Pipe and 6-Mile. This can be a result of the Railyard being a source of current Zn pollution, or it can be a result of a source further upstream. Without an upstream control site, this cause is unclear. U.S Pipe has significantly higher concentrations of

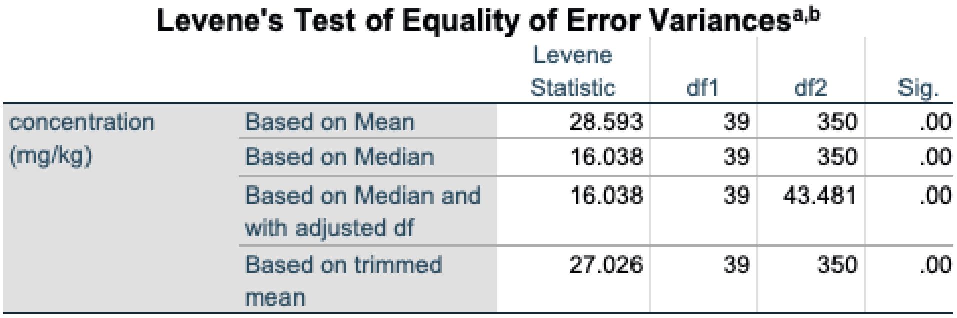
Zn in its lower layers compared to 6-Mile and the Railyard. Due to the fact that 6-Mile had significantly higher concentrations of Zn in its lower layers than the lower layers of the Railyard, it is likely that U.S Pipe used to be a source of Zn pollution.

Ultimately, there was no definitive pattern in regard to the upper layers between sites. Different individual sites had significantly higher concentrations in regard to different elements. Sites with higher concentrations in their upper layers further downstream can be an indicator of pollution occurring upstream, such as with Mn and 6-Mile. However, since there was no upstream control site to compare results to, it is unclear if target locations with higher concentrations are a source of metal pollution, or if there is a source further upstream, or if it can be explained by a combination of the two. There was, however, a general pattern related to U.S Pipe lower layers. For all of the PTEs with significant differences in their lower layers including Cr, Mn, Pb, and Zn, all were found to have the highest concentrations in cores taken from the U.S Pipe site. This indicates that U.S Pipe was likely a source of metal pollution in the past.

Statistical Significance of Results:

Levene’s test was used to assess the equality of variances between the measured variables using SPSS. As seen in Table 7, Levene’s test failed, meaning that there was a difference in variances. However, because there is a general trend of large variance associated with large sample size, we would not falsely reject the null hypothesis. Therefore, the results from this test would be considered valid, and Levene’s test would be considered significant.

Table 7: Levene’s Test Results



Levene's Test of Equality of Error Variances^{a,b}

		Levene Statistic	df1	df2	Sig.
concentration (mg/kg)	Based on Mean	28.593	39	350	.00
	Based on Median	16.038	39	350	.00
	Based on Median and with adjusted df	16.038	39	43.481	.00
	Based on trimmed mean	27.026	39	350	.00

A Q-Q plot was created for the concentration by site location, PTE elements, and upper and lower layers in order to test for normality. As seen in figure 10, the results presented are questionable due to what appears to be a significant departure from normality, as seen by the nonlinear shape. Therefore, the results from this study are rendered statistically unusable. As a result, further studies should be performed with a larger sample size in order to verify the findings identified in this research.

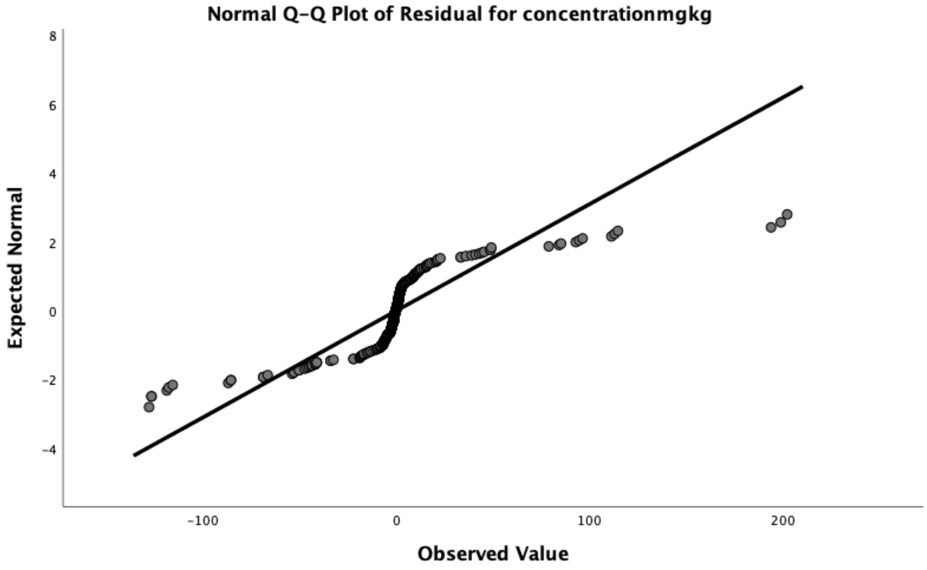


Figure 10: Q-Q Plot Testing for Normality of Results.

Conclusion:

Detectable PTEs followed a general trend of having higher concentrations in lower layers across the sampling sites. U.S Pipe, one of the target locations, was observed to have significantly higher concentrations of Cr, Mn, Pb, and Zn in its lower layers compared to the other sampling sites. This is likely due to the extensive history that U.S Pipe has in dealing with PTEs in the past. A lack of significant PTE concentrations in the upper layers at the sample sites indicates that target locations are not currently releasing toxic levels of PTEs into the environment. PTEs Mn and Zn had significantly higher concentrations in upper layers between different sites but are also naturally occurring and therefore common at higher concentrations within the environment. Overall, another study should be conducted with a larger sample size in order to verify the findings identified in this research due to the data from this study reflecting a significant deviation from normality. In addition to a larger sample size, these results would benefit from having a control site upstream of target locations with upper and lower layers. Since there were no reference values or standards to compare PTE concentrations to, the findings from this study are an approximation of PTE pollution from chosen industrial areas. There were also no measurements of mobility, bioavailability, or chemical speciation of elements. As a result, this study provides a baseline for the current status of contamination of the studied sites based on the elements observed. This information can be used as supplementary material for government and non-profit organizations working to restore and conserve the James River Watershed.

Some ideas for future research would be to include an Environmental Risk Assessment of the sampling sites. This way permissible limits of PTEs in soils can be compared to the concentration levels of PTEs identified from core extractions and would be better able to evaluate the risks that those concentrations may pose to the ecosystem. Another idea would be to look at alternate PTEs. Due to the significance of the three-way interaction from the three-way

ANOVA test, it was not possible to isolate for possible effects of variables, such as sites and/or layers, on individual elements. It might be beneficial for future research to decrease the number of elements of interest, and to analyze essential and non-essential elements separately. This would decrease the range of average concentration levels between PTEs, as seen in the high concentrations of Mn and the low concentrations of Cd in this study. Looking at different PTEs would also allow for an extended evaluation of patterns and relationships among PTEs, similar to the identified correlation between Mn and Zn concentrations in this study. In order to improve the accuracy of data, it would be useful to use alternative methods for layer classifications. For example, instead of dividing cores into upper and lower layers, instead to analyze the cores in increments of soil profiles. This would also likely help in better understanding the mobility of PTEs. Similarly, classifying the soil types at each of the sampling sites would help to better understand the mobility and behavior of PTEs. As mentioned in the introduction, soil type, grain size, and the amount of organic material present can influence the types and quantities of PTEs found in soils as well as their concentration levels. Other variables to evaluate in future research include water quality and soil and water pH levels. Lastly, it would be interesting to conduct a seasonal analysis that would assess changes in water levels as well as whether or not there is a change in PTEs being released into the environment.

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