The Influence of Land Use on Sediment Quality in the Mill Creek Watershed

By

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Abstract

The aquatic ecosystem of Mill Creek Watershed (MCW) is currently susceptible to pollution from nutrients and heavy metals due to the various human activities within the watershed. Sediment quality parameters such as trace metals, organic matter (OM%), pH, total phosphorus (TP) and particle sizes were measured at 13 sampling points along Mill Creek. The overall objective of the research was to determine the immediate land use around each of the 13 sampling sites and how that impacts the sediment quality. Each of these sampling points were used as watershed outlets to delineate 13 distinctive drainage areas, with their individual land uses. The results showed most of the parameters measured were within acceptable values. TP values within the southern watershed were higher than all other sites (MacDonalds et.al, 2005).

These observations were explained by the land use of the delineated drainage areas around each of these sites. Site 9 had about 30% of its drainage area covered by agricultural land row crops, site 10 had 20% and site 8 had 14%. Agricultural runoffs may have played a role in the TP concentration. A more direct impact may be the location of the Boardman Waste Water Treatment Plant at site 8, the semi buffered cattle ranch located by the creek at site 9 and the crop farm located at site 10. Geospatial statistical maps created showed the northern portions especially site 2A and 4 as well as some middle areas of the watershed which include mostly site 8, 9 and 10, to have higher levels of most of the trace metals compared to the sediment reference values. The calculated correlations among percentages of land use, trace metals, TP, pH & OM%, showed Ba to be statistically significant to agricultural land use. TP was also positively correlated with agricultural land use but not statistically significant. pH was significantly correlated residential areas. The other trace metals were not statistically significant with any land use which may be because of the dominant sandy particle sizes and flow dynamics of the river. The predominant residential land use and CSOs locations were perhaps the contributing sources.

Ongoing studies would benefit from analyzing samples in both dry and wet seasons, and after precipitation events. Researchers may have to Incorporate sediment texture properties when sampling. Researchers may also combine Soil and Water Assessment Tools (SWAT) with sediment geochemistry to model trace metals and TP loadings if Mill Creek watershed establishes a gauge station on its main-stem.

These will augment the understanding of the relationship between human activities, sediment and water quality and the importance to ecological health.

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Chapter 1 Introduction

Sediment quality has a crucial impact on the overall condition of aquatic ecosystem. Often, sediments stockpile contaminants that may be moved upright to the water column when a physical disturbance, diffusion, or biological activities occur (Box & Mossa, 1999; Cheung et al, 2003; Dou et al, 2013; Ciparis et al, 2012; Nowrouzi & Pourkhabbaz, 2014). Sediments are a fundamental source of contaminant exposure to organisms that live in sediments as well as those organisms that feed at the bottom of the waterbody, such as crabs and flatfishes (Li et al, 2012). The exposure can result in adverse impacts on the sediment- dwelling organism communities (Tobin et al, 2000) and it can lead to indirect effects on human health and other organisms due to bioaccumulation of contaminants along the food chain (Barnett et. al, 2008).

Anthropogenic activities, including land use changes such as (e.g. housing developments, industries, agricultural produce, waste water treatment plants, impervious surfaces) associated with population growth, influences the physical, chemical and biological conditions of water bodies. Since all freshwater systems, the sea and the atmosphere are interconnected through the hydrologic cycle, it makes it easier for pollutants to be transferred from one medium to the other. A simple diagram below displays pollutant pathways within the aquatic environment (Chapman, 1996; Besten et. al, 2003).

Figure 1.0: Displays pollutant pathways within the aquatic environment (Clifford, 2016)

The contamination of surface water by pollutants such as trace metals and nutrients can be a serious ecological problem. Metals for instance can be toxic even at low concentrations; because they are non-degradable and are capable of bio-accumulating through food chain (Besten et. al, 2003). Sediments act as sinks for the various contaminants of heavy metals and can become a source of pollution within water bodies (Hieu, et al, 2002). Trace metals and nutrients accumulate in the sediments through physical and chemical adsorption mechanisms depending on the characteristics of the sediment particles and that of the pollutant being adsorbed. Many human diseases have been linked to trace metals. Some of which include delayed growth, kidney damage, cancer, and decreased cognitive abilities (Xie et. al, 2014). The extremely toxic trace metals, including Cr, Ni, Pb, Cd and As. Cr (VI), Ni and Cd are known to be carcinogenic; As and Cd are teratogenic and Pb causes neurological impairment and poor function of the central nervous system (Chen et. al, 2007). Nutrients such as phosphorus and nitrogen cause eutrophication because of excessive growth of algae. Nitrogen also causes blue-baby syndrome if it happens to get into the groundwater system and consumed by infants (Hassan et. al, 2015).

The Mill Creek Watershed (MCW) is located in Columbiana and Mahoning Counties, which comprises parts of Youngstown, Canfield, Beaver, Boardman, and Austintown townships, as well as Mill Creek Park and the Canfield Fairgrounds. Water quality concerns, particularly bacteria issues, have been reported regionally, perhaps related to land use and infrastructure (Hanna, 2017). Research by the Ohio Environmental Protection Agency states that due to the considerable water holding capacity of the three dams in MCW the hydrology and water quality of Mill Creek can be affected as the retention of stream water in reservoirs promotes settling solids, including bacteria and particulate forms of nutrients, and allows time for nutrient conversions and bacterial decay (OEPA, 2002). In as much as natural processes contribute to these stated activities, studies have shown that land changes and usage have a strong influence on the intensity of the degradation process (Bing et. al, 2013; Ciparis et al, 2012; Martinez et al, 2012; Ong & Yunus, 2009; Qiongfang et al, 2012). Considering erosion and sediment deposition by natural and man-made sources, the Mill Creek watershed is one area that has been prone to erosion over the years (Poesen & Hooke, 1997).

A previous study resulting in MCW action plan (McCracken, 2007) states that most of the watershed has been impacted through various land uses such as industrial and commercial development, residential development, resource extraction such as timber harvesting and coal mining, building within the floodplain, destruction of wetlands and agricultural practices and mentioning that the watershed has no large sections of land that are exhibiting little to no human impact. However, questions remain about the details on the distribution, magnitude and extent of the impact (McCracken, 2007).

Sediments analyses offer vital information on the impact of close and distant human activities on an ecosystem. The composition of sediment provides the best record of environmental changes. Sediments act as both source and transport of contaminants in an aquatic environment and can serve as a pool that can retain or release contaminants to the water column by various hydrological processes (Barnett et. al, 2008). Therefore, it is important to assess the sediment quality of the Mill Creek watershed. It will help stakeholders to make important decisions that will protect the MCW for posterity.

1.1 Hypothesis

Previous research data collected from the Mill Creek watershed through various agencies like the Ohio Environmental Protection Agency and (Korenic, 1999) shows that the major sources of point source nutrients in the MCW are many, but the largest contributor is the Boardman Waste Water Treatment Plant. Others include Combined Sewer Overflows and fertilizer application from agricultural fields. According to the article, about 55-63% of total phosphorus (TP) originate from point sources whereas 37-45% originates from nonpoint sources (Korenic, 1999). If the later research is relevant, then there should be higher total phosphorus and total metals concentrations in samples collected at these sites in proximity to these point source pollutions compared to the other sites whose pollutants are mostly non-point source.

1.2 Objectives of the study were as follows:

1. Determine the concentrations of total metals and phosphorus in the bottom and upper 7.5cm of core sediments for each sample site in the MCW.
2. Compare the concentrations of total metals and TP in sediments core for each site to other sample sites within the MCW.
3. Evaluate the TP and total metal concentrations to the percentage of land use in the Mill Creek drainage areas.
4. Identify possible land use activities/facilities within the MCW and their impact on the total metal and phosphorus concentrations within the drainage areas.
5. Assess MCW sediment concentrations relative to sediment reference values determined by the Ohio EPA (table 4.0).

Chapter 2 Literature Review

2.0 Sediments in Aquatic Ecosystems

Sediments are referred to as complex mixture of gaseous, dissolved, and particulate compounds, living and/or dead organic material, derived from various sources (native and nonnative), controlled by numerous physical, chemical, and biological processes and factors, which prevail in an environment (Reuther, 2009; Chapman & WHO, 1996). The physical aquatic sediments are divided into three main categories; suspended sediments, bottom sediment, and the pore or interstitial water.

Sediments usually accumulate inorganic and organic constituents that enter a lake or river and adsorb to particulates or dissolve in the porewater. Watershed sediment sources can be put into two main categories based on their origin: uplands and hillslopes, and stream corridors (Gellis, Fitzpatrick & Berigan, 2016). Upland sediment sources most often include soil erosion from various land use and land cover types, such as forest, cropland, pasture, construction sites, and roads (Nelson & Booth, 2002). Stream corridor sources often include streambanks and channel beds. Others include mass wasting where channels intersect valley sides and terrace walls. Floodplains, lakes and alluvial areas are usually sediment sinks, where sediments transported from streams and rivers get deposited (Figure 2.0); which is what makes it a challenge when analyzing stream sediments (Gellis, Fitzpatrick & Berigan, 2016).

Generally, the fate of trace metals and TP are influenced by physical parameters such as pH, particle size, OM%, physical disturbance et cetera. pH normally speeds up the mobilization of trace metals under slightly acid to strongly acidic conditions in sediments. Slightly basic to highly basic conditions results in immobilization of trace metals in sediments in aquatic ecosystems (Yao et al., 2015). Particle size is also another factor that govern heavy metal contamination in sediments within an aquatic ecosystem. Usually, fine particles have a higher affinity for heavy metals due to the larger surface area, and the presence of clay minerals, organic matter, as well as Fe/Mn/Al oxides connected with the formation of fine-sized aggregates (Gambrell et al, 1991). Physical disturbance of waterbody has also been identified as one of the factors that influence the rapid removal of trace metals and TP attached to sediments into the water stream (Atkinson, Jolley & Simpson, 2007).

Human activities have enhanced sedimentation as well as sediment loss. Sedimentation activities can be land-based (i.e., agriculture, forestry, construction, urbanization, recreation) and water-based (i.e., dams, navigation, channelization, wetlands loss). These activities could impact the entire environment by altering the amount of light that gets to a stream, the temperature of the stream in question, the extent of erosion, pollutant transport to stream amongst others (Ryan & Packman, 2006; Engler, 2015).

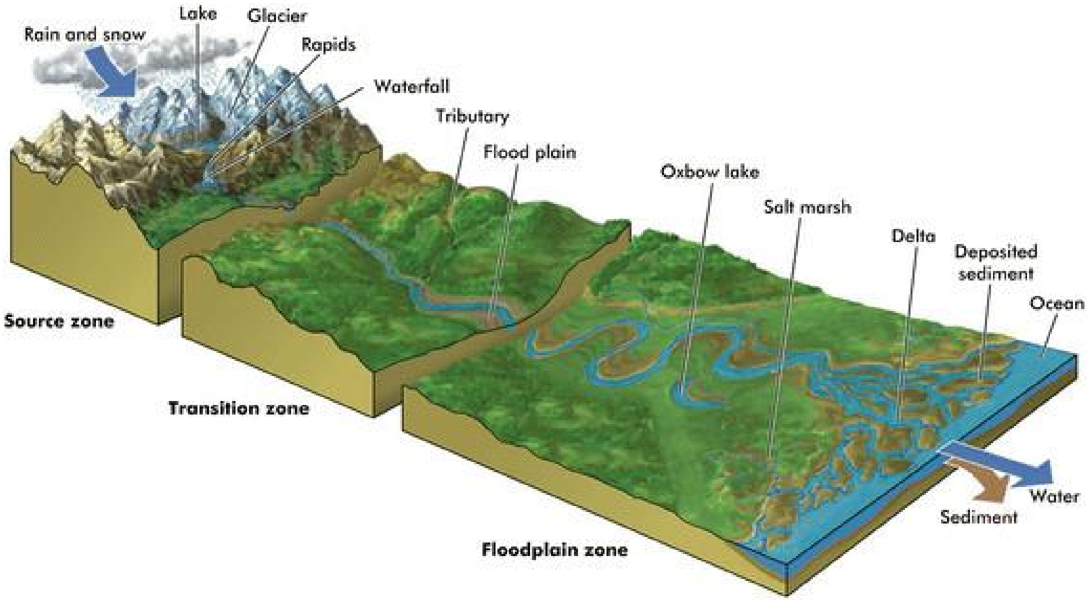


Figure 2.0: Displaying sedimentation process in a river (Isha, 2017).

Agriculture and urban activities are major sources of phosphorus and other nutrients to aquatic ecosystems. These nonpoint inputs of nutrients are difficult to control because they derive from activities dispersed over wide areas of land and change with the effects of weather (Skaggs, Breve & Gillian, 1994). In aquatic ecosystems, these nutrients cause several problems such as algal blooms, hypoxia, fish kills, loss of biodiversity, loss of aquatic plant beds, and other problems. Nutrient enrichment seriously degrades aquatic ecosystems and undermines the use of water for drinking, industry, agriculture, recreation, and other purposes (Carpenter et. al., 1998).

Trace heavy metals are also very crucial environmental pollutants, particularly in areas that are highly populated. Sources of trace metals are normally industrial, but some research have shown that certain metals such as arsenic and others are used in the manufacture of fertilizers which implies that they could also be linked to agricultural fields (Aprile & Bouy, 2008). The presence of trace heavy metals in the atmosphere, soil, and water can cause serious problems to all organisms due to their ability to bioaccumulate in the food chain which can be highly dangerous to human health. Trace metal contaminations affects drinking water quality, ecological environment, and food chain. Moreover, the toxicity in contaminated water, soil, and vegetables poses serious threat to human health (Waseem et al., 2014).

Urbanization is another major land use which strongly impacts water quality (Hall et. al, 1999). Research has shown that imperviousness affects pollutant transportation and concentrations. Differences in TP, Al, Cr, Zn and Pb concentrations have been observed especially between city center catchments with high and intermediate imperviousness and residential catchment having low imperviousness; while total suspended solids, Mn, Co, Ni and Cu concentrations increase with increasing imperviousness (Bing et. al, 2013). Regarding pollutant loads, it has been noted that imperviousness is strongly related to TP, Al, Mn, Zn, Cr, Co, Ni and Cu transportation. The effects of urbanization on runoff quality have also been noted to be season dependent: urbanization increases runoff volumes and pollutant loads, especially during warm seasons (Brabec, Schulte & Richards, 2002). Highest pollutants transport has been observed in catchments during spring. Nevertheless, warm periods produce comparable loads to spring at city center catchments. Pollutant concentrations, especially in city center catchments, sometimes exceed thresholds set for surface waters, indicating a need for runoff treatment in water quality protection (Valtanen et. al., 2014).

Combined Sewer Overflows (CSOs) are also sources of pollution in a watershed. A combined sewer system is defined by EPA as a system that collects rainwater runoff, domestic sewage, and industrial wastewater into one pipe. In an ideal situation, it carries all the wastewater it collects to a sewage treatment plant for treatment before it is discharged into a water body. Sometimes, the quantity of wastewater can exceed the capacity of the combined sewer system especially during storm events and could cause untreated stormwater and wastewater to be discharged directly into water bodies (Even, et. al., 2007). CSOs are a water pollution concern for most areas in U.S. that have Combined Sewer Systems, including Mill Creek watershed. Below is a map for the CSOs in Mill Creek Watershed (USEPA, 2016).

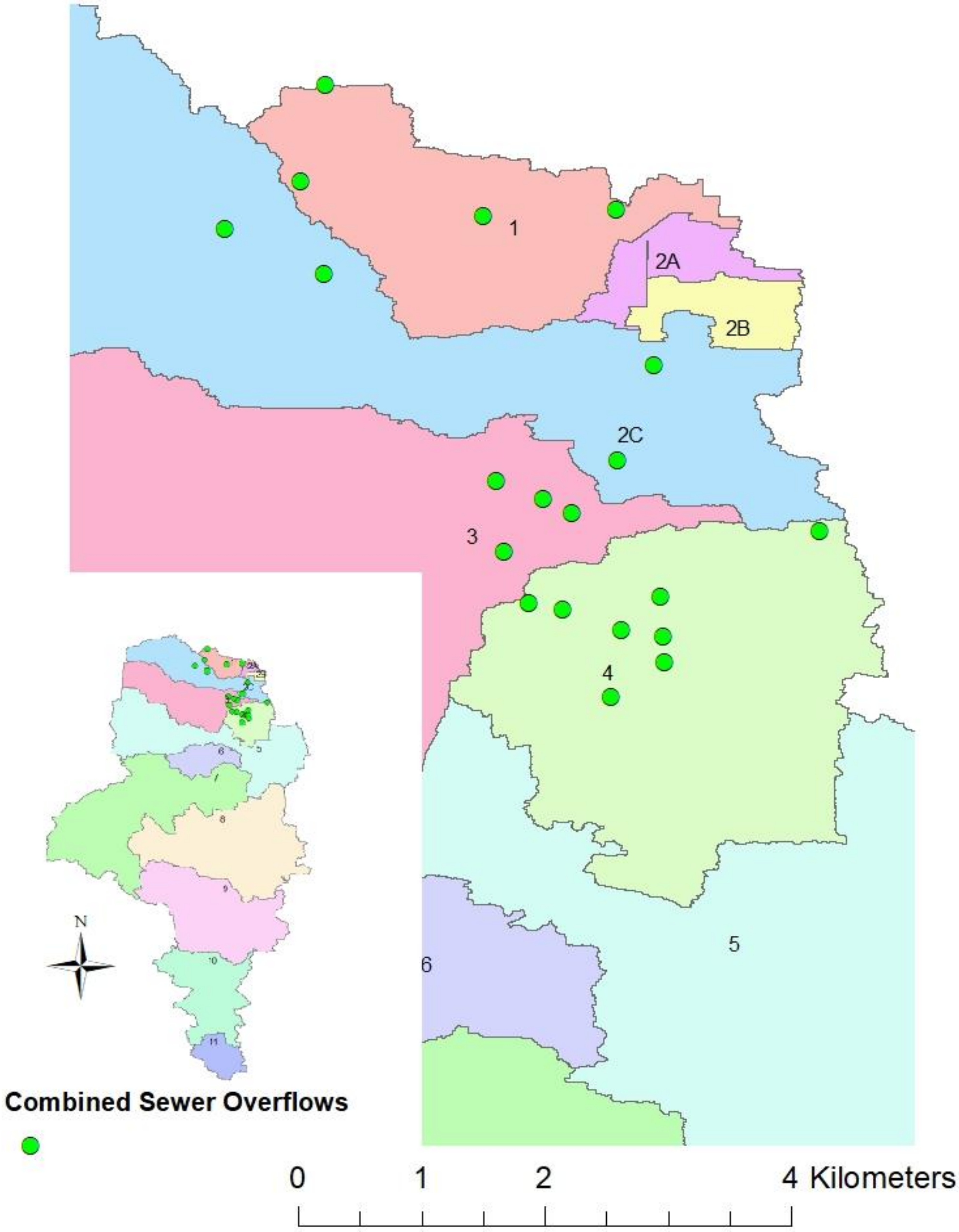


Figure 2.1: Locations of CSOs within Mill Creek Watershed

The pollutants from CSOs could also form complexes with soil and eventually get driven into waterbodies which is one of the reasons why sediments should be analyzed.

Table 2.0: Sources of trace metals and nutrient pollutants (Paul, 2017; Carpenter et. al, 1998; Dore, 2014)

Element	**Sources**
Arsenic (As)	Pesticides, fungicides, metal smelters (Paul, 2017).
Barium (Ba)	Mineral deposits, smelting of copper, disposal of drilling wastes, manufacturing of car parts, groundwater, atmospheric transport (Carpenter et. al, 1998).
Cadmium (Cd)	Welding, electroplating, pesticides, fertilizers, batteries, nuclear fission plants (Dore, 2014).
Chromium (Cr)	Mining, electroplating, tanning industry, textile (Paul, 2017).
Copper (Cu)	Electroplating, pesticides, mining (Carpenter et. al, 1998).
Lead (Pb)	Pesticides, mining, burning of coal, paints, automobile emissions, batteries (Dore, 2014).
Manganese (Mn)	Welding, fuel additions, ferromanganese production (Paul, 2017).
Nickel (Ni)	Electroplating, zinc base casting, battery industries (Carpenter et. al, 1998).
Zinc (Zn)	Refineries, brass manufacturing, metal plating, immersion of painted idols (Dore, 2014).
Vanadium (V)	Combustion of fossil fuels, coal mining, atmospheric deposition (Paul, 2017).
Total P	Fertilizers, agricultural and urban activities, atmospheric deposition, Waste Water Treatment Plants, CSOs (Carpenter et. al, 1998).

There are many reasons why researchers analyze sediments. Some of these reasons include; fine-grained particles and organic matter being natural accumulators of major water constituents in streams and lakes, due to their highly sorptive properties and association with particulate matter in many streams and lakes (Zhang et al., 2009). Chemical constituents such as Cu, Pb, Ni, As, Cd, TP, Cr among others usually associate with the fine-grained sediment fraction, mostly clay and silt particles, and with particulate organic matter. Even though the water may contain only a small portion of these constituents, suspended and bed sediments may contain relatively large concentrations, which makes it easier to detect and to analyze (Tam & Wong, 2000).

Another reason for analyzing sediments is that sources of many waterborne pollutants may be sporadic, or storm related, and as a result, they may not be detectable in single or periodic water samples. On the other end, sediments in depositional aquatic environments allow a time-integrated sampling of waterborne particulate matter. Sediment concentrations provide a useful measure of the bioaccumulation potential of organic contaminants that have less affinity for water at a site when combined with biological tissue analysis (Milenkovic et. al, 2004).

2.1 Mill Creek Watershed Description

The Mill Creek watershed is located in two counties in Ohio, which include Columbiana and Mahoning. According to the USGS watershed delineation, the Mill Creek watershed have been sub-divided into 3 sub watershed areas. But for the purposes of this research, the Mill Creek watershed was divided into 13 drainage basins based on the sampling sites for the research; to do a more detailed comparison of land use to sediment properties.

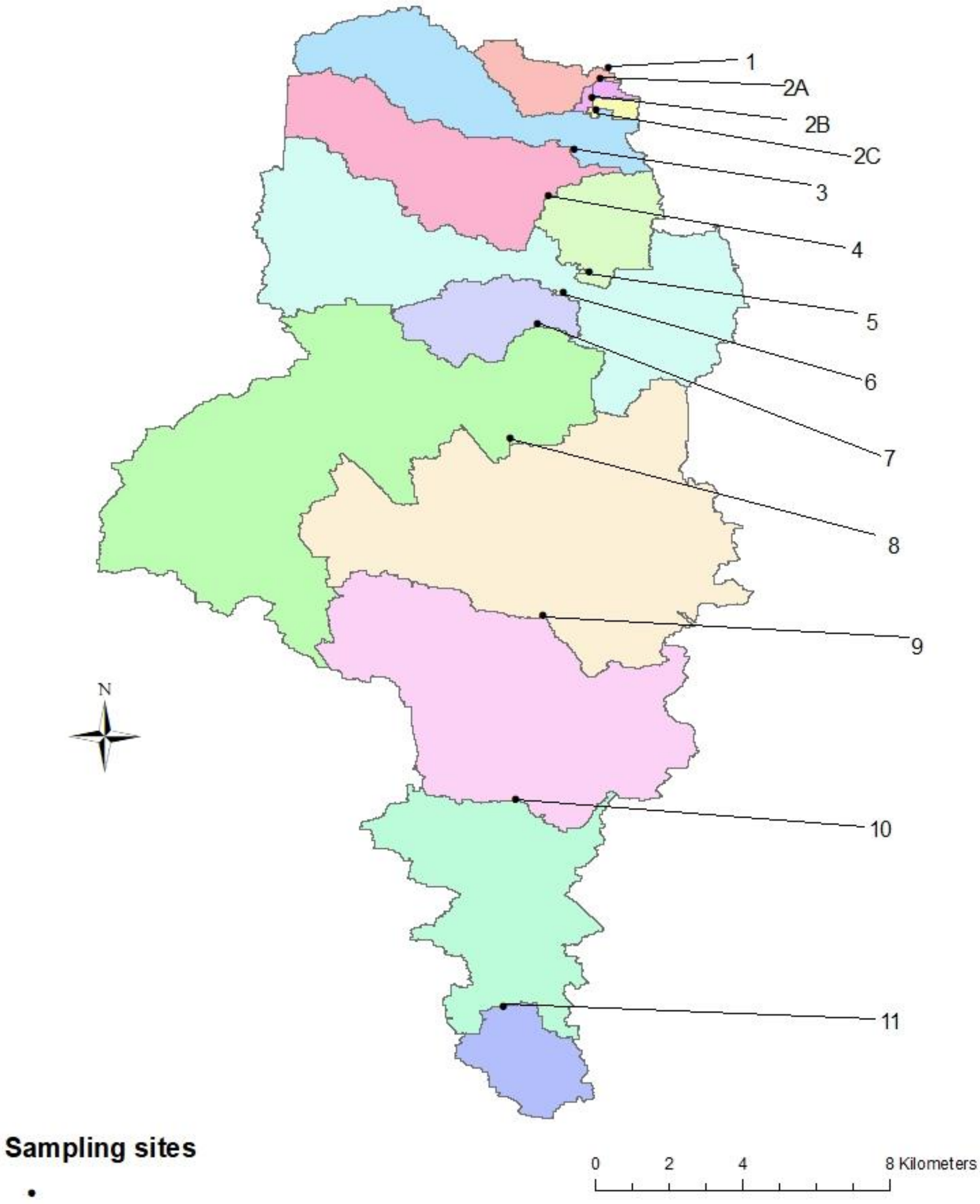


Figure 2.2: Map of drainage areas and sampling sites with drainage areas shown in different shades of colors and samplings sites displayed as dark dots

The Mill Creek Watershed consists of approximately 1,204 acres of ponds and lakes. There are 193.1 acres of lakes within the watershed. The largest lakes in the watershed are the impoundments on the mainstream of Mill Creek. Of these three, Lake Glacier is the farthest north, with its dam located approximately 500 feet from the Mill Creek confluence with the Mahoning River. Lake Glacier covers a surface area of 38.3 acres. Lake Cohasset covers 23.8 acres and is the center lake in the chain with its dam situated near where Old Furnace Road crosses Mill Creek. Lake Newport is the southern most of the Mill Creek impoundments and covers 75.2 acres. The Newport dam is just within the Youngstown city limits, south of the US 62 bridges over Mill Creek. The Mill creek watershed has approximately 303 miles of streams. The mainstem of the Mill Creek is 20.9 miles long, according to the Gazetteer of Ohio Streams, however, according to county GIS the mainstem of Mill Creek is 23.9 miles long. Mill Creek has 7 tributaries which are named by the Gazetteer, but several more which are recognized as being named locally. These include the Bears Den Run, Axe Factory Run, Andersons Run, Cranberry Run, Indian Run, Saw Mill Run, Turkey Run, Calvary Run, Little Indian Run and North Lima Creek (McCracken, 2007).

The majority of soils in the Mill Creek Watershed were formed from glacial deposits from Wisconsin glacier (McCracken, 2007). Soils on the floodplains formed in alluvium deposited more recently. The most common soils on the floodplains along the mainstem of Mill Creek are Wayland and Orrville soils (USDA, 2017) These are nearly level, poorly to somewhat poorly drained soils.

The most common soils on the stream terraces and near uplands for most of the length of the watershed are Bogart, Chili, and Jim town soils. They are sloping to gently sloping, well drained to somewhat poorly drained soils with gravely subsoil.

In the lower watershed, the most common soil types in the riparian and near uplands are Loudonville, Muskingum and DeKalb soils. These soils are mainly deep over sandstone or siltstone figure 2.3 (McCracken, 2007).

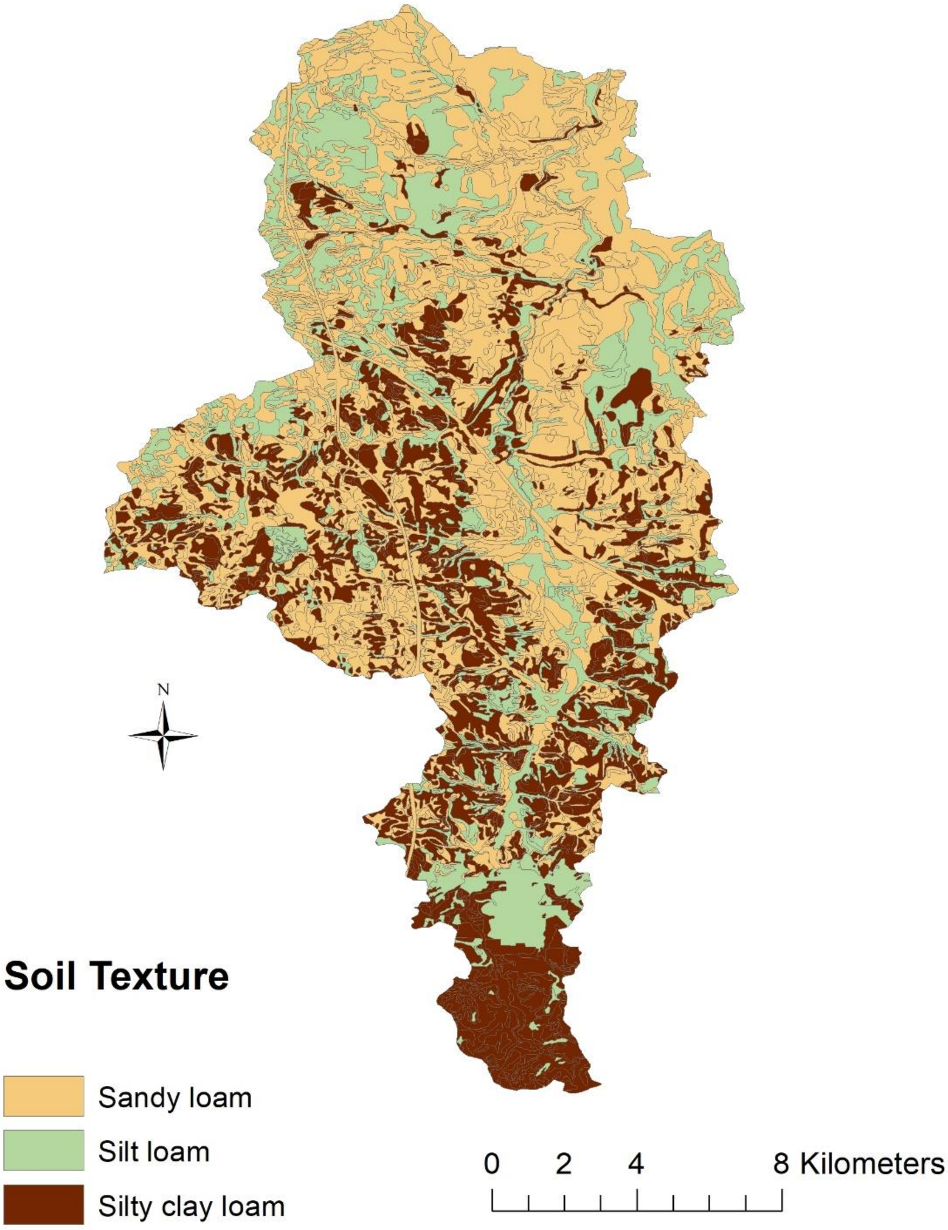


Figure 2.3: Soil texture within Mill Creek watershed

Also, due to the glaciated nature of the Mill Creek watershed, the physiography tends toward rolling plains and rounded hills, gentle slopes and broad valleys. Except for steep gorges adjacent to the northern portion of the Mill Creek Channel and adjacent to Indian Run near Canfield, the topography of the watershed is relatively flat to gently rolling (McCracken, 2007). The upper watershed consists mostly of developed urban and suburban areas whereas the lower watershed consists mostly of agricultural areas as shown in figure 2.4 of the Mill Creek watershed land use map.

Furthermore, special districts within the watershed consist of the Mill Creek MetroParks, which owns the protected lands, Youngstown, Columbiana and Canfield with approximately 96,500 citizens living within the Mill Creek Watershed (McCracken, 2007).

Sections of the Mill Creek Watershed Action Plan reports that YSU Center for Urban and Regional Studies generated maps that depict the erosion potential for bare soils in the watershed; with a gross total of 34,643 acres within the Mill Creek watershed having the potential to be susceptible to erosion. The Mahoning County Board of Commissioners came up with Erosion and Sediment Control Rules in the Spring of 2007 to establish doable and reasonable erosion and sediments control standards to reduce soil erosion and pollution of waterbodies of the State by soil sediment as result of land use but has not really materialized. Hence, it can be assumed that there has been impact of land use on the sediments deposits in the watershed (McCracken, 2007; Mahoning County Board of Commissioners, 2007).

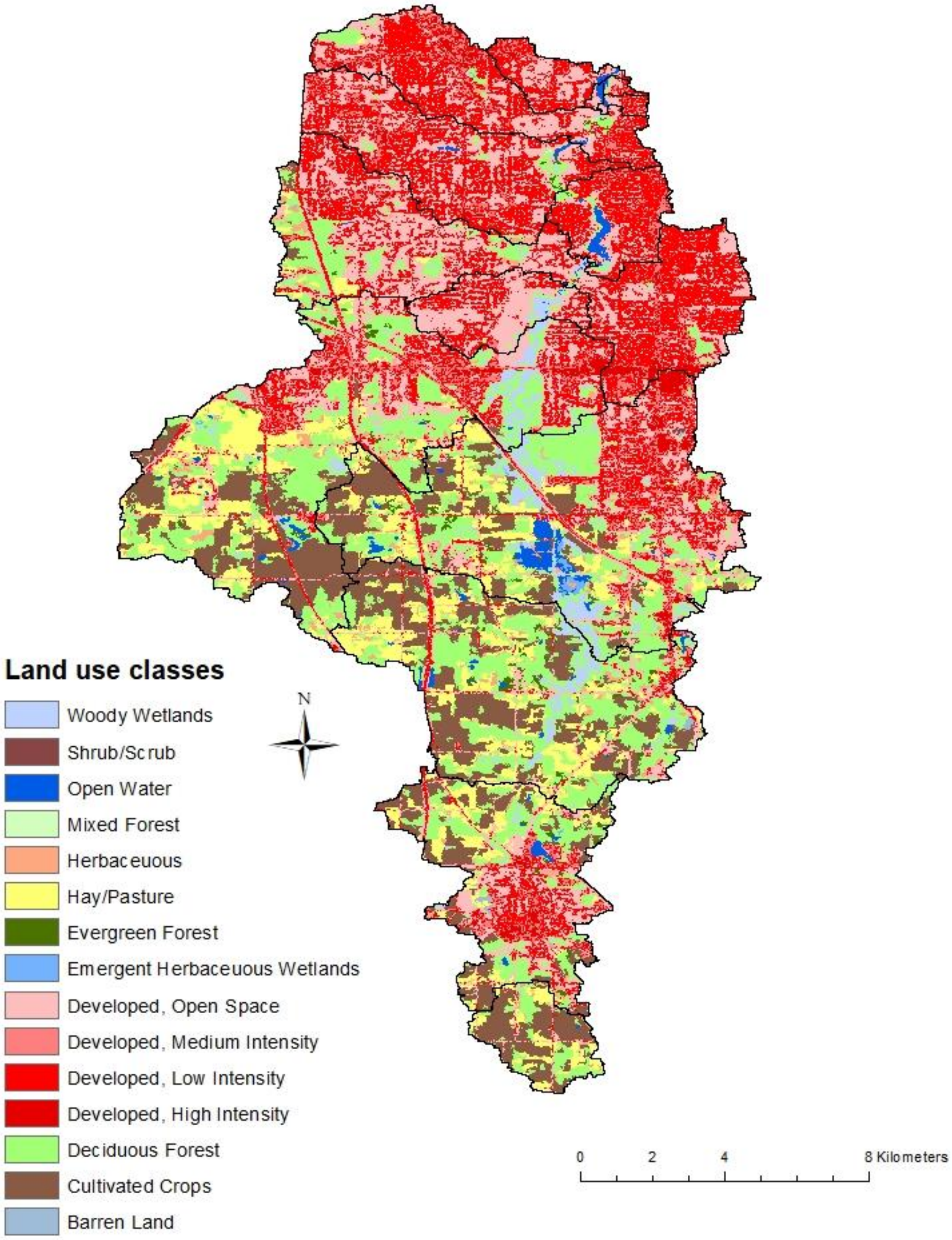


Figure 2.4: Map of land use classes in shades of color according to the National Land Cover Data (NLCD) designation

Table 2.1: Showing entire watershed land use by acreage and percentage

Land Use	Land Area (acres)	Percentage (%)
Water	583	1.15
Residential	24905	49.1
Industrial	1260	2.48
Forest	10096	19.9
Range	976	1.91
Hay	4764	9.36
Agricultural	6875	13.5
Wetlands	1293	2.55

Table 2.2: Drainage area 1 land use by acres and percentage with sample site 1 as outlet

Land Use	Land Area (acres)	% Drainage Area
Water	583	1.6
Residential	24905	67.6
Industrial	1260	3.4
Forest	10096	27.4

Table 2.3: Drainage area 2 land use by acres and percentage with sample site 2A as outlet

Land Use	Land Area (acres)	% Drainage Area
Water	572	1.6
Residential	24196	67.0
Industrial	1243	3.4
Forest	10096	28.0

Table 2.4: Drainage area 3 land use by acres and percentage with sample site 2B as outlet

Land Use	Land Area (acres)	% Drainage Area
Water	550	1.5
Residential	24104	66.9
Forest	10090	28.0
Wetlands	1293	3.6

Table 2.5: Drainage area 4 land use by acres and percentage with sample site 2C as outlet

Land Use	Land Area (acres)	% Drainage Area
Water	545	1.3
Residential	23997	55.9
Industrial	1242	2.9
Forest	10089	23.5
Range	976	2.3
Hay	4764	11.1
Wetlands	1292	3.0

Table 2.6: Drainage area 5 land use by acres and percentage with sample site 3 as outlet

Land Use	Land Area (acres)	% Drainage Area
Water	538	1.5
Residential	21477	60.9
Industrial	1067	3.0
Forest	9946	28.2
Range	965	2.7
Wetlands	1285	3.6

Table 2.7: Drainage area 6 land use by acres and percentage with sample site 4 as outlet

Land Use	Land Area (acres)	% Drainage Area
Water	516	1.7
Residential	18187	59.0
Industrial	996	3.2
Forest	9828	31.9
Wetlands	1280	4.2

Table 2.8: Drainage area 7 land use by acres and percentage with sample site 5 as outlet

Land Use	Land Area (acres)	% Drainage Area
Water	440	1.0
Residential	16967	40.4
Industrial	969	2.3
Forest	9765	23.2
Range	953	2.3
Hay	4758	11.3
Agricultural	6875	16.4
Wetlands	1273	3.0

Table 2.9: Drainage area 8 land use by acres and percentage with sample site 6 as outlet

Land Use	Land Area (acres)	% Drainage Area
Water	432	1.9
Residential	11407	49.8
Industrial	789	3.4
Forest	9050	39.5
Wetlands	1241	5.4

Table 2.10: Drainage area 9 land use by acres and percentage with sample site 7 as outlet

Land Use	Land Area (acres)	% Drainage Area
Water	428	1.3
Residential	10107	29.9
Industrial	788	2.3
Forest	9005	26.6
Range	852	2.5
Hay	4632	13.7
Agricultural	6821	20.2
Wetlands	1181	3.5

Table 2.11: Drainage area 10 land use by acres and percentage with sample site 8 as outlet

Land Use	Land Area (acres)	% Drainage Area
Water	371	1.6
Residential	6237	3.9
Industrial	554	2.4
Forest	6135	26.5
Range	544	2.3
Hay	3272	14.1
Agricultural	5214	22.5
Wetlands	841	3.6

Table 2.12: Drainage area 11 land use by acres and percentage with sample site 9 as outlet

Land Use	Land Area (acres)	% Drainage Area
Water	122	0.9
Residential	2907	21.5
Industrial	162	1.2
Forest	3745	27.7
Range	291	2.1
Hay	2172	16.1
Agricultural	3854	28.5
Wetlands	273	2.0

Table 2.13: Drainage area 12 land use by acres and percentage with sample site 10 as outlet

Land Use	Land Area (acres)	% Drainage Area
Water	47	0.8
Residential	2005	33.8
Industrial	132	2.2
Forest	1205	20.3
Range	89	1.5
Hay	822	13.8
Agricultural	1604	27.0
Wetlands	36	0.6

Table 2.14: Drainage area 13 land use by acres and percentage with sample site 11 as outlet

Land Use	Land Area (acres)	% Drainage Area
Water	1.11	0.09
Residential	105.4	8.06
Forest	252	19.3
Range	20.49	1.57
Hay	261	19.9
Agricultural	666	50.91
Wetlands	2.44	0.19

Chapter 3 Methods

3.0 Sampling, watershed delineation and sample preparations

Short sediments cores (15cm) samples were taken from the shores of Mill Creek main water stem including Lake Newport, Lake Cohasset and parts of Lake Glacier. There were 13 sample sites where samples were taken. Each of these sampling points were then used as an individual watershed outlet to create separate, distinctive drainage area with their unique land use. The watershed was delineated using the Soil and Water Analysis Tool (SWAT) edition 10.4. Digital Elevation Model (DEM), Soil and Land use data (2011) were used in the delineation of the watershed. Hydrologic Response Units (HRUs) were created for MCW and reports exported to excel for further analysis.

Samples were stored in sealed plastic bags in an ice chamber at <4 degrees Celsius. Upon arrival in the lab, each core sediment was divided into two equal parts thus top 7.5cm and lower 7.5cm. The samples were dried in the oven at 105 degrees Celsius for 24 hours. The samples were crushed, sieved at 2mm and stored in plastic bags for analysis.

3.1 Organic Matter Analysis (Loss on Ignition)

All crucibles to be used for the organic matter analysis were washed and heated in furnace at 400 degrees Celsius for 2 hours. Soil samples were sieved to 2mm and approximately 2.5g of each soil sample and replicate were weighed into crucibles and heated in furnace at 400 degrees Celsius for 16 hours. Furnaces were turned off afterwards, samples transferred into a desiccator to cool for about 30 minutes and then weighed. The difference between the weight of the sample at 105 degrees Celsius and the weight at 400 degrees Celsius was the organic matter content. The resulting samples after the organic matter determination were bagged in plastics for particle size analysis (Nelson & Sommers, 1996).

3.2 pH determination

The pH meter was first standardized. Two 10g sample of soil (sieved at 2mm) was weighed in a 50mL centrifuge tube. 10 mL of deionized water was measured into the two soil samples. In cases where soil was very organic, more solution was added to produce a soil suspension. Using a stir rod, all samples were stirred for 1 minute so that soil was equally mixed and allowed to stand for a minimum of 30 minutes. The pH electrode was then lowered into the soil suspension and the pH reading recorded when meter stabilized (SSSA, 1996).

3.3 Sediment texture determination and particle size analysis

Sediments were analyzed using the particle size analyzer since there were not enough of each sample for the application of hydrometer method. Particle sizes measured were clay<2um, silt<50um, very fine sand<100um, fine sand<250um, medium sand<500um, coarse sand<1000um and very coarse sand<2000um. All particles were measured according the Natural Resource Conservation Service (NRCS) soil subdivisions (SSSA, 1996).

3.4 Trace metals and Total Phosphorus Analysis

For trace metals and total phosphorus analysis, 2mm sediment samples were sieved to 0.4191mm. 0.5 ± 0.01 grams of samples and Standard Reference were measured into digestion tubes. The EPA method 3050B was used in the digestion of the samples.

Spikes for two random samples were prepared accordingly. 5ml (1:1) HNO3 + Deionized water were added to each sample and heated to 95 degrees Celsius without boiling. Upon cooling, 2ml of deionized was added to each sample followed by 1ml of hydrogen peroxide (h202). The samples were then allowed to react for about 10 minutes and then heated to 95 degrees Celsius for 2 hours. The samples were left to cool and then 5ml of HCL added to the solution. The samples were again heated at 95 degrees Celsius for 15 minutes and diluted to 35ml mark for analysis (USEPA, 1996).

Inductively Coupled Plasma instrument was then used to analyze the samples for trace metals and TP.

3.5 Quality Assurance and Quality Control

In ensuring quality assurance and quality control of all analytical processes involved in the total metal and TP analysis, the guidelines stated by Environmental Protection Agency in method 3050B were used. Blanks and spikes were prepared whenever any new sample matrix was to be analyzed to avoid errors and bias in all cases (Arsenic et.al, 1996).

3.6 Geostatistical methods and Statistical methods

The geostatistical maps were created with the Inverse Distance Weight (IDW) tool in ArcGIS version 10.41. With help of shapes created from the SWAT watershed delineation, maps were created to depict the distribution of each parameter of interest in the research.

The statistical methods were done using IBM SPSS Statistics 24. Correlation analysis was used in finding the correlation coefficient (Pearson’s R) and significance between different land use percentages within the watershed and the individual parameters (trace metals, TP, pH, and organic matter content (OM%) analyzed within the watershed). Another correlation analysis was done within all parameters to help in source identification of pollutants. All correlations analysis was done at 95% confidence level. Principal Component Analysis (PCA) and Cluster Analysis were also done on the variables, land use with variables, sites and sediment horizons analyzed in the research to reduce variables and find associations within parameters. For cluster analysis, Z-scores were used in standardizing the cases and variables. The cluster method used was between groups linkage. The measure intervals used in the cluster analysis were Pearson correlation and squared Euclidean distance.

Chapter 4 Results and Discussions

4.0 Assessment and Evaluations of Sites Using Sediment Guidelines

Using the Guidance for Conducting Ecological Risk Assessment by Ohio EPA, the various trace metals concentrations for each site was evaluated.

Table 44.0: Displaying freshwater sediment reference values for Erie Ontario lake plains(EOLP) (Ohio EPA, 2008)

Metals	**EOLP mg/kg**
As	25
Ba	190
Cd	0.79
Cr	25
Cu	32
Fe	41000
Pb	(47)
Mg	7100
Mn	1500
Ni	33
V	(40)
Zn	160

Note: Pb and V are statewide sediment reference values

According to table 4.0, none of the sampling sites showed elevated concentrations of As with all values being below the sediment reference values.

Barium was seen to be elevated in sites 8, 10 and 11. Site 11 was slightly above the sediment reference levels with a value of 191 mg/kg. Sites 8 and 10 on the other hand had Ba concentrations highly above the sediment reference which depicts a potential source of contamination. Site 8 has the Boardman Waste Water Treatment plant situated in its area whereas site 10 is located near a cattle farm. These plus other sources like atmospheric deposition and runoff from stormwater could be the reason for the elevated levels of Ba at these sites.

Cadmium elevation was observed in most of the sample sites. The most elevated values were noticed at site 2A, followed by site 5, 2B, 2C, 3, 4, 8, 9, 10 and 11 in descending order. Other specific horizons included site 1 deep lower and site 6 except shallow upper horizon. Site 7 had contamination levels less than 0.79 mg/kg. There were several explanations for the sites that exhibited values greater than the sediment reference values. At site 2A, there existed a drain discharging into the area that may have had pollutants accompanying it into the water body. Most of the Combined Sewer Overflows were also found in the northern part of the watershed where sites 2A, 2B,2C, 3, 4 and site 5 were located. Site 8 has the Boardman Waste Water Treatment Plant and site 9 also has a similar drain as observed at site 2A into the Creek. These may have influenced the Cd levels in the Creek. Other sources could be atmospheric deposition since research has shown that it is one of the main sources of Cd in the environment (Tucker, 2008). We cannot attribute them to the geology of the area since most of the values are way above the 0.79 mg/kg sediment reference value set by Ohio EPA for the Lake Erie Ontario Plains.

Elevated Cr concentrations were also observed at site 2A with 7.4% of organic matter content. The values were above the sediment reference values. The land use data derived from SWAT analysis indicated that approximately 77% of the drainage area within which this sample site is located is made up of residential areas as well as bounded by roads which could have had runoff from it into the site. Site 4 also depicted elevated levels of Cr except site 4 shallow regions. That may also be due to the predominant CSOs within its drainage areas. On the contrary, the sample for 2A had sand particles dominating it with a moderately neutral pH.

Copper elevation was also observed at site 2A and site 4. This may be because of the runoff from residential areas, parking lots, CSOs among other things within the vicinity of Site 2A and Site 4.

Nickel and Pb were also seen to be elevated at site 1 shallow, 4 & 5. The runoff from surrounding areas could have contributed to the concentrations of Ni and Pb. Another possible source could be the CSOs predominant in site 1, 4 and 5. One site that could expose people to Pb was site 1. Unfortunately, people fish within the area sampled and as Pb has been known to be toxic and bioaccumulate in tissues of organisms, there could be some risks to the public who consume fish from this area (Barnett et. al, 2008). However, the scope of this study does not cover the population risk. Further studies will have to be conducted to ascertain the risk levels.

Table 4.1: Displays the average shallow upper and lower Pb, P, Ba, Cd concentrations, % sand, %silt, %clay, pH, and %OM.

	Ba	Cd	P	Pb	pH	OM%	Clay%	Silt%	Sand%
Site 1 Shallow	88.71	0.32	547.3	55.83	6.91	3.69	5.18	64.02	30.80
Site 2A Upper	74.12	3.43	660.7	39.96	6.38	7.42	2.38	30.25	67.37
Site 2B Upper	101.3	1.74	323.0	30.95	6.81	3.07	3.26	58.87	37.88
Site 2C Upper	61.84	0.98	216.6	13.80	5.67	3.68	2.09	29.47	68.45
Site 3 Shallow	35.87	1.04	291	13.50	6.49	3.79	2.11	34.30	63.59
Site 4 Shallow	155	1.74	545.0	37.94	7.28	2.78	3.35	39.16	57.49
Site 5 Shallow	96.20	2.39	801.1	65.47	6.85	3.59	4.40	68.00	27.60
Site 6 Shallow	73.15	1.09	597.5	14.19	5.65	2.52	2.83	41.64	55.53
Site 7 Shallow	30.74	0.50	267.1	5.77	6.67	1.19	1.53	17.15	81.32
Site 8 Shallow	341.9	2.16	902.0	18.63	5.73	6.45	4.95	71.35	23.71
Site 9 Shallow	167.9	2.31	1240	25.63	5.77	6.39	4.50	67.97	27.54
Site 10 Shallow	331.1	1.51	1148	29.71	6.44	6.79	3.30	59.92	36.78
Site 11 Shallow	208.2	1.09	318.2	8.40	5.42	2.07	2.85	34.73	62.43

Shallow site averages were used because they were the values that depicted the best results when used for statistical analysis.

4.1 Description of site 2A, 2B and 2C, their parameters and why they are different

Site 2A, 2B and 2C were different in concentrations and percentages of the measured parameters (Ba, pH, Cd, Pb, OM%, silt%, sand%, clay%). These three sites were close to each other but varied a lot in terms of measured parameters. Site 2A was a depositional area, site 2B had flow occurring at the area and site 2C had materials being transported from the area. These may have been the reason why the parameters in site 2A, 2B and 2C were different from one site to the other even though they were close.

Also, Zn, V and Mn were observed to be elevated in certain areas of the watershed according to table 4.0. These include V in site 2A and 8 deep upper, Zn in site 5 and 9, and then Mn in site 2A and 4. Because these are metals used in alloying, they could have been washed from impervious surfaces around their drainage basins. Vanadium can be toxic in certain compounds. It is used with Cr in steel alloys, both of which were found in high concentrations at Site 2A (Venkataraman & Sudha, 2005). This may also be because both metals originate from a similar source.

pH in the samples analyzed at the sites were relatively neutral. This implies there are probably few activities that is either increasing or decreasing the pH levels within the watershed.

Total phosphorus could not be discussed using table 4.0 guidelines for sediment quality assessment because the Ohio EPA did not include total phosphorus. Using the "Guidelines for the Protection and Management of Sediment in Ontario", TP was evaluated.

Table 4.2: Trace metals and TP levels indicating concentrations that negatively impact sediment dwelling organisms and some sensitive water uses.

Substance	**Lowest Effect Level (mg/kg)**	**Severe Effect Level (mg/kg)**
As	6	33
Cd	0.6	10
Cr	26	110
Co	50	*
Cu	16	110
Fe	2	4
Pb	31	250
Mn	460	1100
Ni	16	75
Zn	120	820
P	600	2000

No Effect Levels and * symbol is "Not Established"

None of the sampling sites displayed concentrations of TP at the Severe Effect Level (table 4.2) but comparing sites to one another, high concentrations of TP was noticed in sites 5 shallow upper, 6 shallow upper, 8, 9 and 10. The high TP concentrations in site 5 shallow upper and 6 shallow upper could have been due to the CSOs located within its drainage areas. The two sample sites also had the same amount of organic matter content and approximately neutral pH. With regards to samples from site 8,9 and 10, it was noted that site 10 had the highest TP, followed by site 9 and then site 8. The explanation to this observation was reflected in the land use of the drainage area within which the sites were located. Site 8 had about 23% of its drainage area covered by agricultural land row crops, site 9 had 29% and site 10 had 27%. Agricultural runoffs could have played a role in the increase in the TP content. A more direct impact may be the location of the Boardman Waste Water Treatment Plant at site 8, the semi buffered cattle ranch located by the creek at site 10 and the crop farm located by site 9.

According to the sediment quality guidelines for metals in freshwater ecosystem that reflect Probable Effect Concentrations (PECs) (i.e. concentrations above which harmful effects are likely to be observed in organisms that live in sediment), none of the samples showed harmful levels of As, Cd, Cr and Cu to sediment dwelling organisms except site 4 deep lower and 5 deep lower for Pb and Ni respectively. Here also, the predominant residential land use and CSOs locations could be the contributing sources of TP.

Table 4.3: Showing sediment quality guidelines for metals in freshwater ecosystem that reflect Probable Effect Concentrations (PECs) (MacDonalds et.al, 2005)

Metals	PEL (mg/kg)	SEL (mg/kg)	TET (mg/kg)	ERM (mg/kg)	Consensus based PEC (mg/kg)
As	17	33	17	85	33
Cd	3.53	10	3	9	4.98
Cr	90	110	100	145	111
Cu	197	110	86	390	149
Pb	91.3	250	170	110	128
Ni	36	75	61	50	48.6
Zn	315	820	540	270	459

TET denotes Toxic Effect Threshold

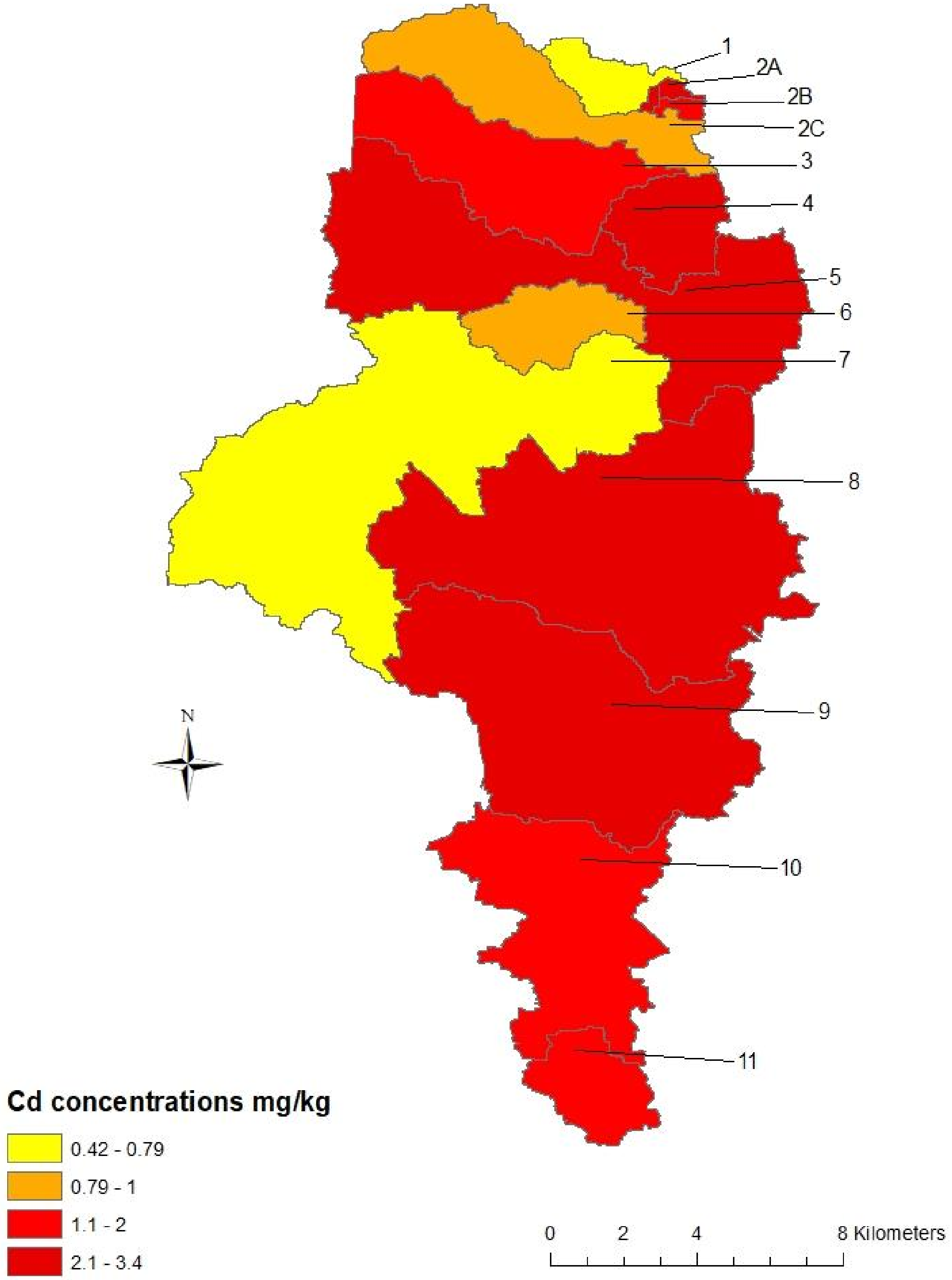
SEL denotes Severe Effect Level

ERM denotes Effect range median

PEL denotes Probable Effect Level

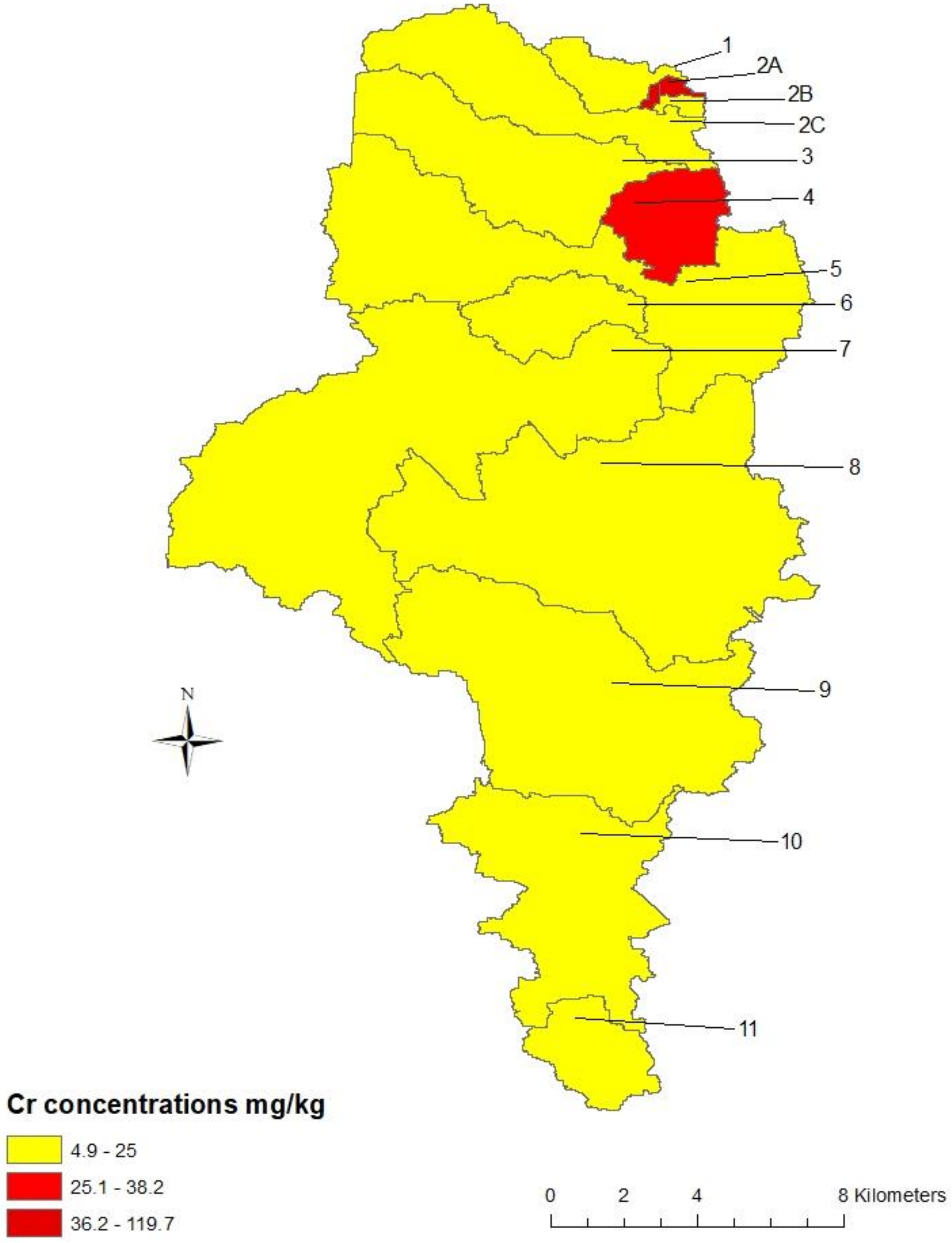
4.2 Geospatial Distributions of Trace Metals

The spatial distribution maps below were designed to give a pictorial view of how the parameters measured through the analysis were distributed geospatially over the MCW sampled areas. The blue and yellow shades depicted areas of concentrations below the sediment reference value, and gold and red areas indicated sample areas with concentrations above the sediment reference values. In general, it can be noted that some of the parameters analyzed had similar distributions across MCW. In the northern areas of MCW there were similar distributions of Pb and Ni, Cr, V, Mn and Cu concentrations. According to research, such similar distributions may have been because of the elements having a similar source (Niu et. al., 2015). Arsenic concentrations were below the sediment reference values. Barium concentrations were elevated in sites 8 ,10 and 11. The elevation of Ba in those sites may be as a result of the fracking activities in proximity to the sites 8, 10 and 11. Cd concentrations were elevated on majority of the sites except site 7 and 1. Site 7 and site 11, in most cases had the lowest values of the trace metals; which may be because of the high sand percentages in the sediment collected for analysis in those areas, since, most metals and nutrients have a high affinity for very small soil fractions like clay and silt (Zhang et. al, 2009).



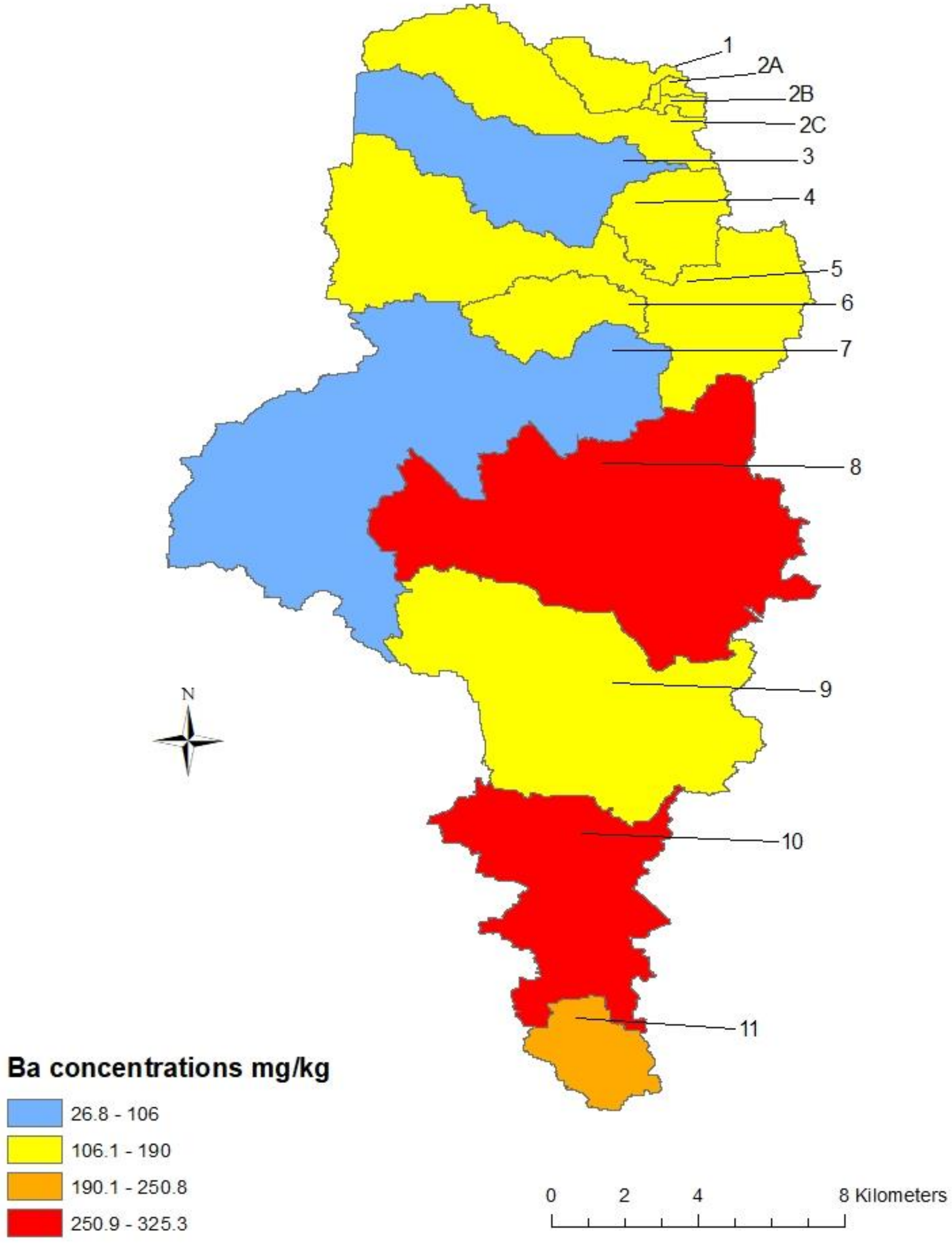
EOLP Cd Sediment Reference Value is 0.79mg/kg

Figure 4.0: Spatial distribution of Cd concentrations across the sampling areas with yellow depicting values below the sediment reference and shades of red depicting concentrations above sediment reference values



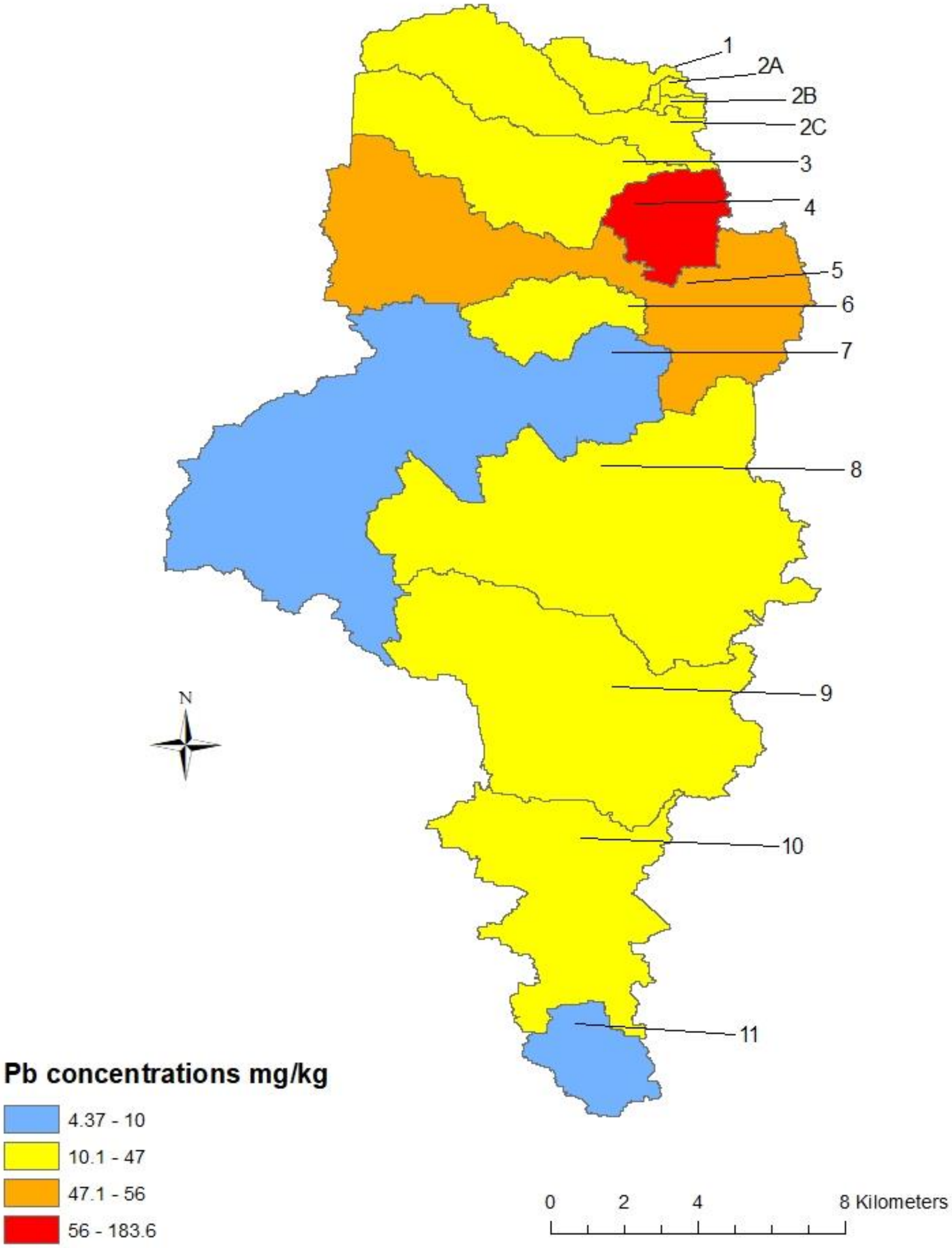
EOLP Cr Sediment Reference Value is 25mg/kg

Figure 4.1: Spatial distribution of Cr concentrations across the sampling areas with yellow depicting values below the sediment reference value (SRV) and shades of red depicting concentrations above SRV



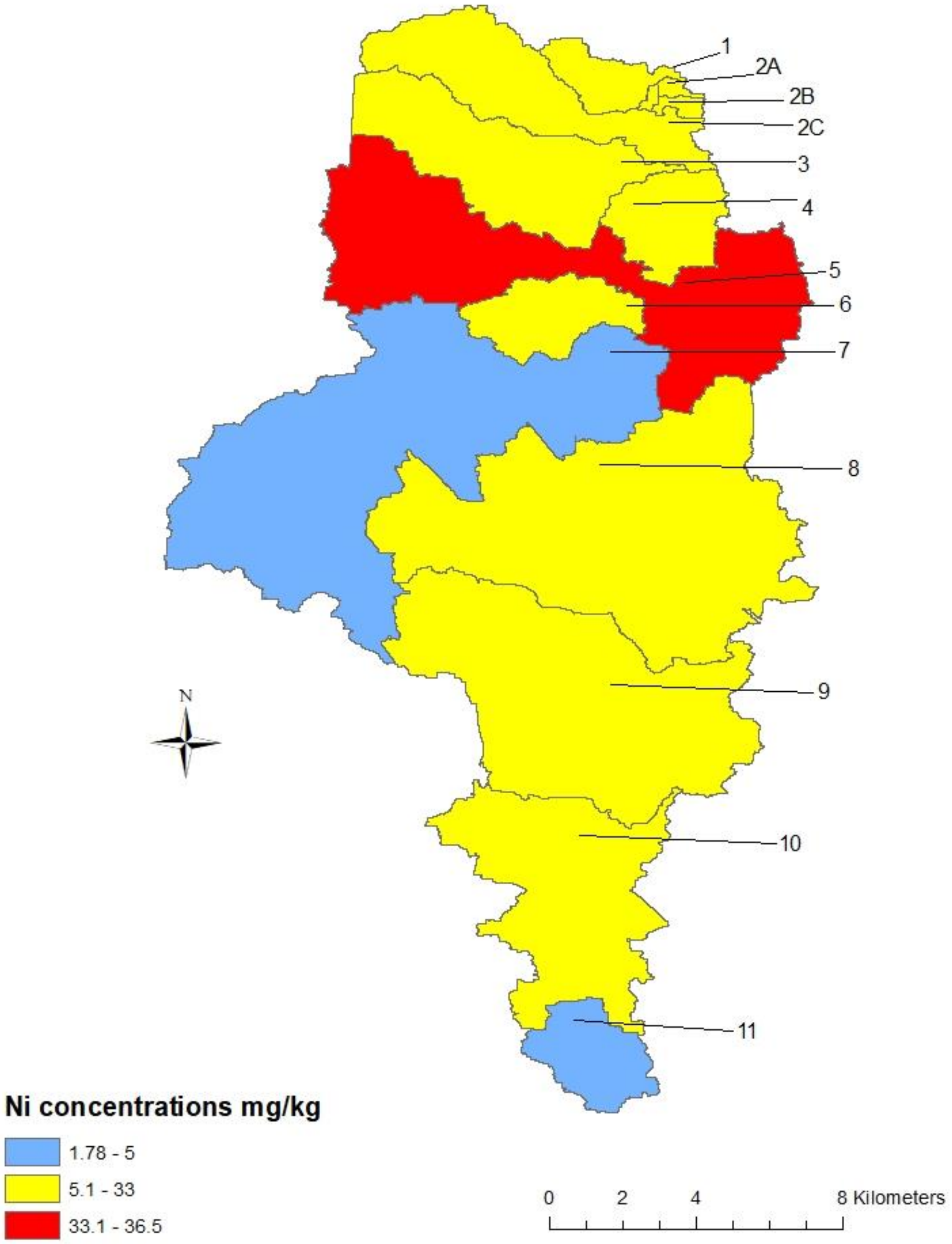
EOLP Ba Sediment Reference Value is 190mg/kg

Figure 4.2: Spatial distribution of Ba concentrations across the sampling areas with blue and yellow depicting values below the sediment reference and gold and red depicting concentrations above SRV



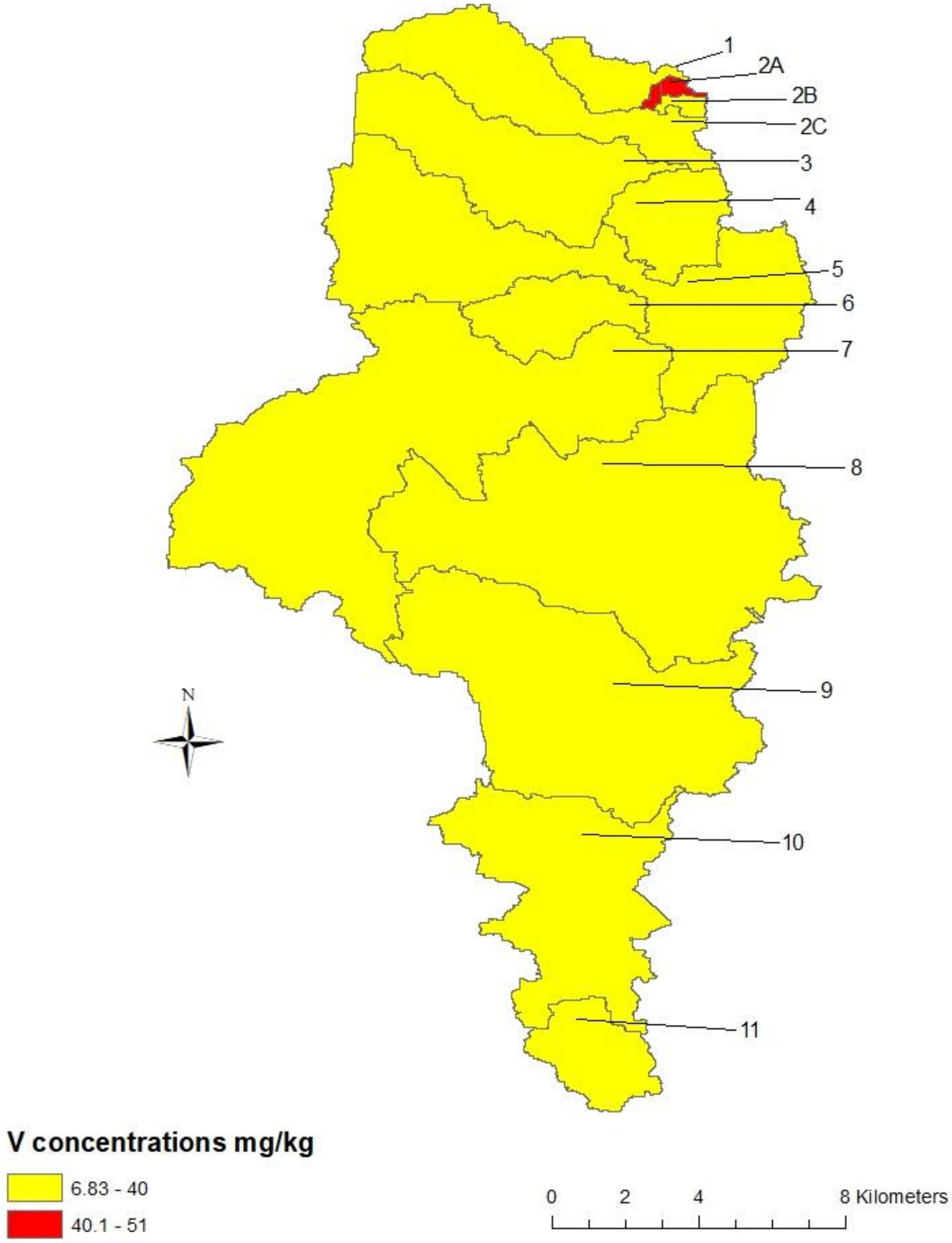
EOLP Pb Sediment Reference Value is 47mg/kg

Figure 4.3: Spatial distribution of Pb concentrations across the sampling areas with blue and yellow depicting values below the sediment reference value (SRV) and gold and red depicting concentrations above SRV



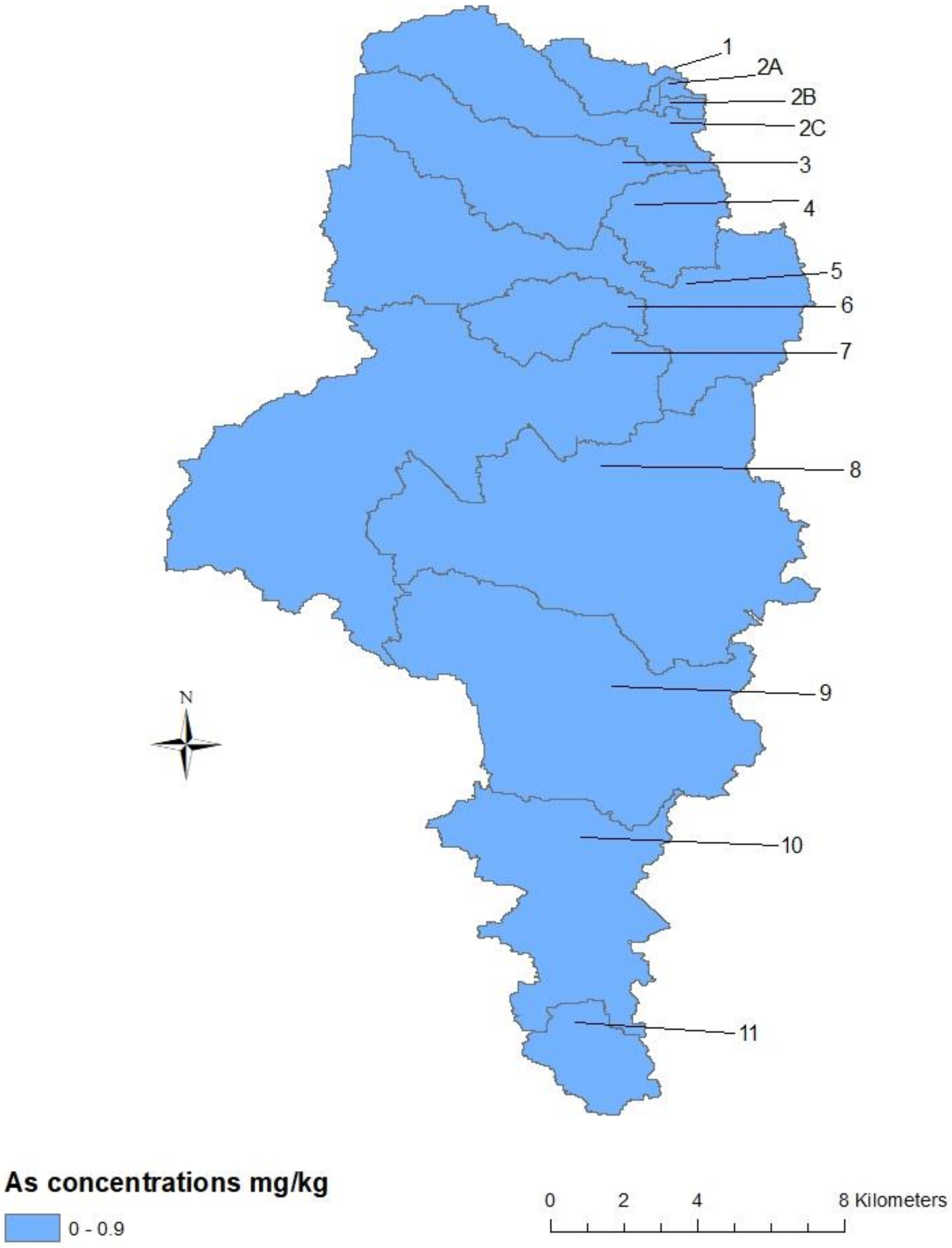
EOLP Ni Sediment Reference Value is 33mg/kg

Figure 4.4: Spatial distribution of Ni concentrations across the sampling areas with blue and yellow depicting values below the sediment reference value (SRV) and red depicting concentrations above SRV



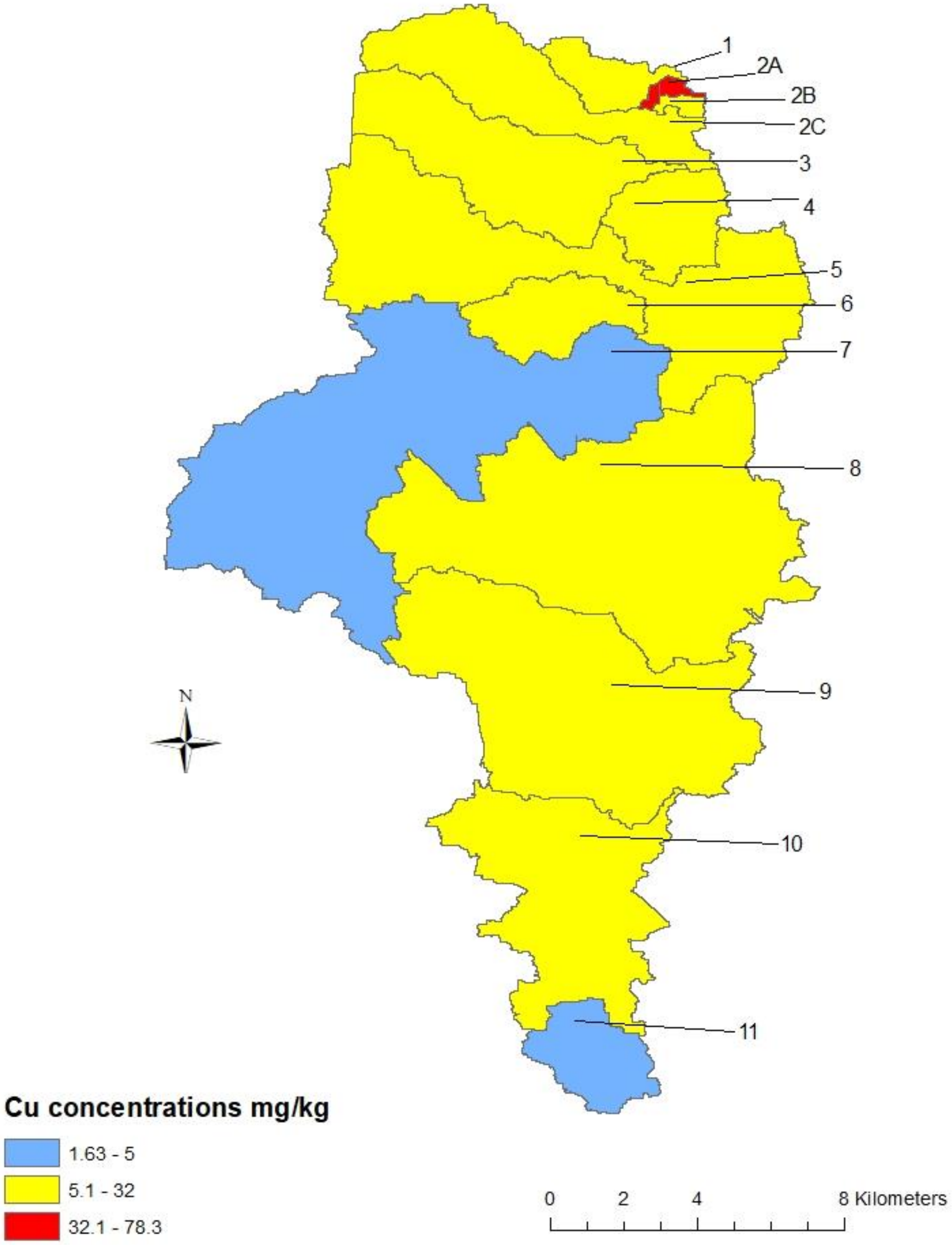
EOLP V Sediment Reference Level is 40mg/kg

Figure 4.5: Spatial distribution of V concentrations across the sampling areas with yellow depicting values below the sediment reference value (SRV) and red depicting concentrations above SRV



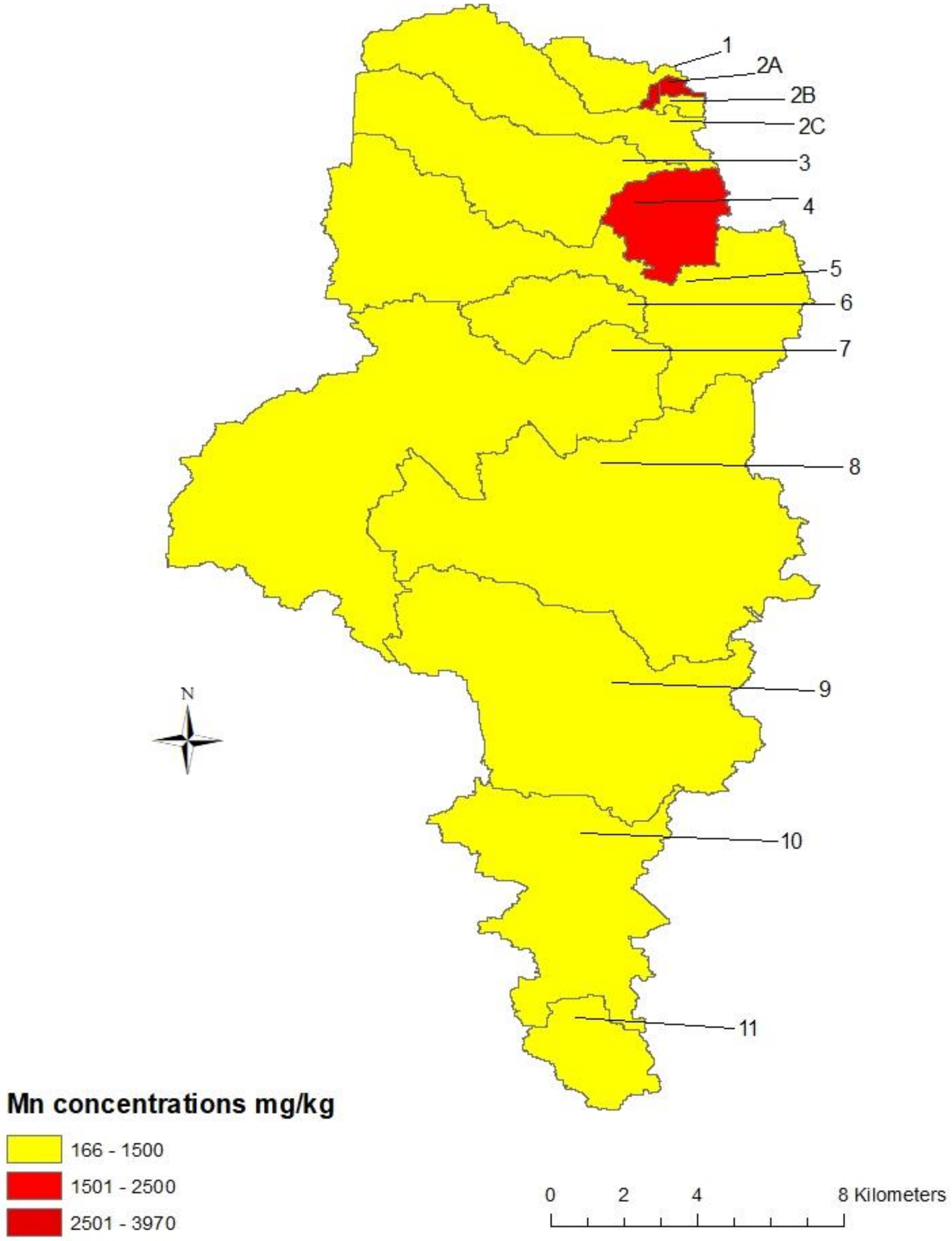
EOLP As Sediment Reference Level is 25mg/kg

Figure 4.6: Spatial distribution of As concentrations across the sampling areas with blue depicting values below the sediment reference value



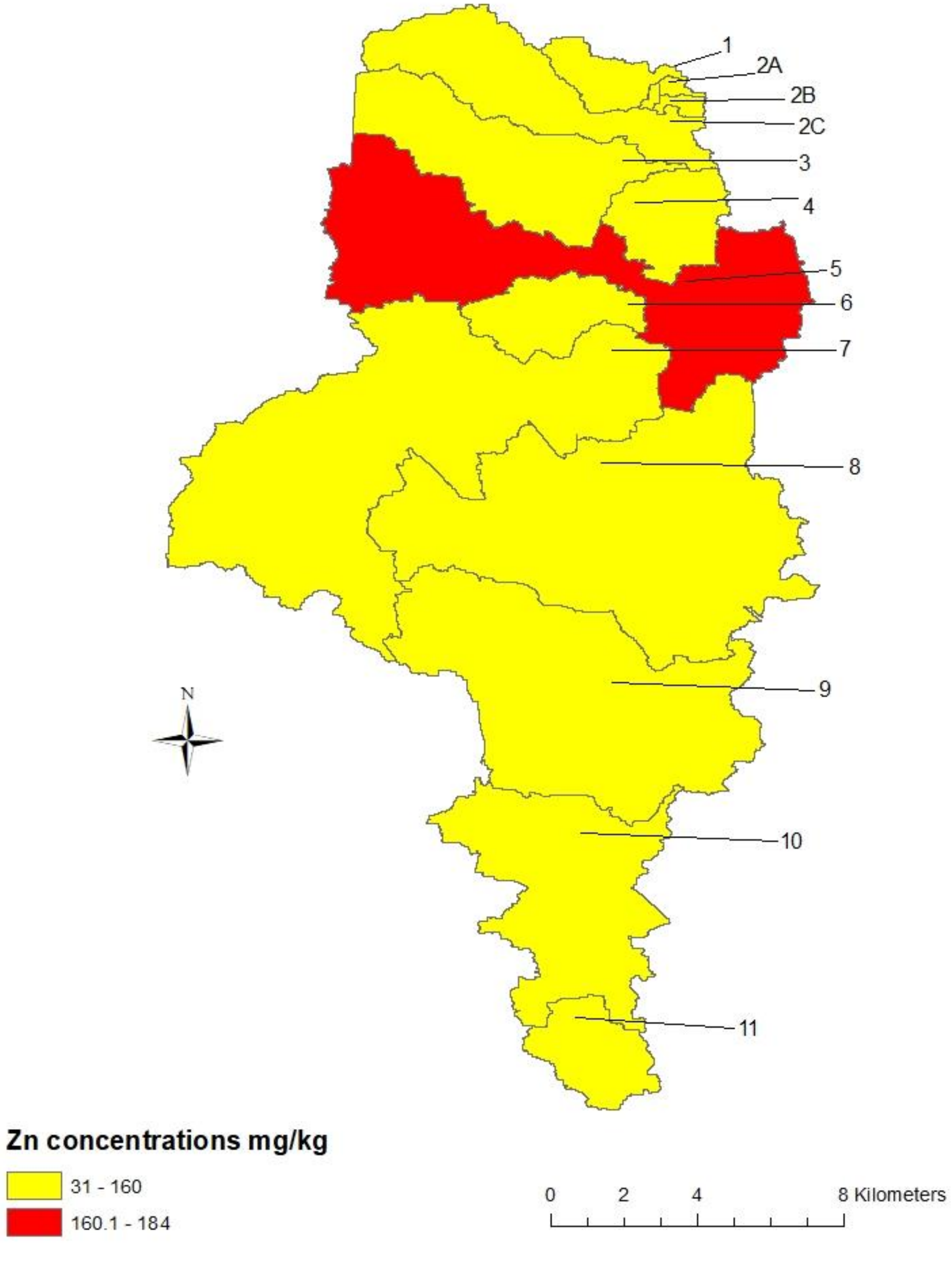
EOLP Cu Sediment Reference Value is 32mg/kg

Figure 4.7: Spatial distribution of Cu concentrations across the sampling areas with blue and yellow colors depicting values below the sediment reference value (SRV) and red depicting concentrations above SRV



EOLP Mn Sediment Reference Value is 1500mg/kg

Figure 4.8: Spatial distribution of Mn concentrations across the sampling areas with yellow colors depicting values below the sediment reference value (SRV) and shades of red depicting concentrations above SRV



EOLP Zn Sediment Reference Value is 160mg/kg

Figure 4.9: Spatial distribution of Zn concentrations across the sampling areas with yellow depicting values below the sediment reference value (SRV) and red depicting concentrations above SRV

4.3 Statistical analysis for further source assessments

A statistical correlation analysis between land use percentages, trace metals, total P, pH and OM% had the correlation coefficients (Pearson's r) between Ba and agricultural areas to be significant, TP and agricultural areas to be positive and the pH and residential areas to be significant. This indicates that increasing agricultural areas impacts the Ba and TP concentrations (Elrashidi et. al, 2007). Also, residential areas influence the pH of the sediments significantly. Some of the other parameters on the hand did not show significant correlations with land use. Sediments samples that were analyzed from the sites were dominated with sand particles which may have accounted for the insignificance of some of the correlations within parameters. The flow dynamics of river systems may also have impacted the lack of significance within some of the correlated parameters.

Table 4.4: Correlation matrix between land use and parameters: * correlation is significant at the 0.05 level (2-tailed), ** correlation is significant at the 0.01 level (2-tailed) as determined by shallow sediment averages.

	As	Ba	Cd	P	Pb	pH	OM %	Clay %	Silt %	Sand %
As	1.00	0.17	0.60*	0.55	0.69**	0.27	0.34	0.49	0.58*	-0.57*
Ba	0.17	1.00	0.23	0.63*	-0.04	-0.26	0.51	0.49	0.55	-0.55
Cd	0.60*	0.23	1.00	0.51	0.37	-0.01	0.68*	0.20	0.28	-0.28
P	0.55	0.63*	0.51	1.00	0.34	-0.10	0.74**	0.62*	0.70**	-0.70**
Pb	0.69**	-0.04	0.37	0.34	1.00	0.62*	0.25	0.61*	0.55	-0.55
pH	0.27	-0.26	-0.01	-0.10	0.62*	1.00	-0.16	0.09	0.06	-0.06
OM%	0.34	0.51	0.68*	0.73**	0.25	-0.16	1.00	0.36	0.45	-0.45
Clay%	0.49	0.49	0.20	0.62*	0.61*	0.09	0.36	1.00	0.92**	-0.93**
Silt%	0.58*	0.55	0.28	0.70**	0.55	0.06	0.45	0.92**	1.00	-1.00**
Sand%	-0.57*	-0.55	-0.28	-0.70**	-0.55	-0.06	-0.45	-0.93**	-1.00**	1.00
Resident	-0.06	-0.65*	-0.04	-0.38	0.40	0.58*	-0.10	-0.22	-0.22	0.22
Industrial	0.14	-0.28	-0.04	0.01	0.22	0.24	0.15	-0.06	-0.21	0.20
Forest	0.00	-0.38	-0.01	-0.07	-0.05	0.10	-0.18	-0.04	-0.10	0.10
Agric	-0.03	.58*	0.01	0.32	-0.28	-0.47	0.05	0.14	0.15	-0.15

Wetlands	0.11	-0.23	-0.13	-0.21	-0.29	0.04	-0.42	-0.18	-0.10	0.10

Table 4.5: Showing statistics for the parameters in table 4.4 (all values are in kg/mg)

	Mean	Std. Dev.	N
As	0.27	0.21	13
Ba	135.9	102.7	13
Cd	1.56	0.86	13
P	604.5	336.8	13
Pb	27.68	18.27	13
Ph	6.31	0.60	13
OM%	4.11	1.99	13
Clay%	3.29	1.16	13
Silt%	47.45	18.14	13
Sand%	49.27	19.21	13
Residential	43.44	22.38	13
Industrial	2.30	1.21	13
Forest	26.93	5.12	13
Agricultural	12.73	16.35	13

Table 4.6: Correlation matrix for trace metals, total P, pH, OM%, clay%, silt% and sand%: ** correlation is significant at the 0.01 level (2-tailed) and * correlation is significant at the 0.05 level (2-tailed)

	As	Ba	Cd	Cr	Cu	Mg	Mn	Ni	P	Pb	V	Zn	pH	OM%	Clay%	Silt%	Sand%
As	1.000	0.115	0.745**	0.274	0.301*	0.545**	0.235	0.748**	0.388**	0.601**	0.534**	0.776**	0.118	0.276	0.419**	0.468**	-0.467**
Ba	0.115	1.000	0.273	-0.050	-0.047	0.227	-0.059	0.167	0.496**	0.021	0.224	0.253	-0.354*	0.212	0.395**	0.398**	-0.399**
Cd	0.745**	0.273	1.000	0.592**	0.535**	0.771**	0.583**	0.727**	0.480**	0.355*	0.788**	0.750**	-0.094	0.547**	0.458**	0.500**	-0.499**
Cr	0.274	-0.050	0.592**	1.000	0.804**	0.703**	0.821**	0.106	0.136	0.259	0.726**	0.185	0.040	0.430**	-0.012	-0.056	0.053
Cu	0.301*	-0.047	0.535**	0.804**	1.000	0.661**	0.713**	0.178	0.109	0.192	0.615**	0.269	0.150	0.485**	0.070	0.062	-0.063
Mg	0.545**	0.227	0.771**	0.703**	0.661**	1.000	0.685**	0.560**	0.392**	0.273	0.877**	0.672**	0.039	0.559**	0.577**	0.570**	-0.572**
Mn	0.235	-0.059	0.583**	0.821**	0.713**	0.685**	1.000	0.239	0.171	0.139	0.570**	0.260	0.311*	0.395**	0.010	-0.049	0.045
Ni	0.748**	0.167	0.727**	0.106	0.178	0.560**	0.239	1.000	0.529**	0.242	0.599**	0.932**	-0.058	0.408**	0.716**	0.723**	-0.725**
P	0.388**	0.496**	0.480**	0.136	0.109	0.392**	0.171	0.529**	1.000	0.011	0.481**	0.638**	-0.136	0.639**	0.460**	0.537**	-0.534**
Pb	0.601**	0.021	0.355*	0.259	0.192	0.273	0.139	0.242	0.011	1.000	0.169	0.294*	0.166	-0.080	0.012	-0.025	0.023
V	0.534**	0.224	0.788**	0.726**	0.615**	0.877**	0.570**	0.599**	0.481**	0.169	1.000	0.662**	-0.233	0.590**	0.567**	0.549**	-0.552**
Zn	0.776**	0.253	0.750**	0.185	0.269	0.672**	0.260	0.932**	0.638**	0.294*	0.662**	1.000	-0.023	0.500**	0.722**	0.776**	-0.775**
pH	0.118	-0.354*	-0.094	0.040	0.150	0.039	0.311*	-0.058	-0.136	0.166	-0.233	-0.023	1.000	-0.188	-0.300*	-0.292*	0.293*
OM%	0.276	0.212	0.547**	0.430**	0.485**	0.559**	0.395**	0.408**	0.639**	-0.080	0.590**	0.500**	-0.188	1.000	0.368*	0.471**	-0.466**
Clay%	0.419**	0.395**	0.458**	-0.012	0.070	0.577**	0.010	0.716**	0.460**	0.012	0.567**	0.722**	-0.300*	0.368*	1.000	0.947**	-0.953**
Silt%	0.468**	0.398**	0.500**	-0.056	0.062	0.570**	-0.049	0.723**	0.537**	-0.025	0.549**	0.776**	-0.292*	0.471**	0.947**	1.000	-1.000**
Sand%	-0.467**	-0.399**	-0.499**	0.053	-0.063	-0.572**	0.045	-0.725**	-0.534**	0.023	-0.552**	-0.775**	0.293*	-0.466**	-0.953**	-1.000**	1.000

Table 4.7: Displaying the descriptive statistics for trace metals in table 4.6 (all values are in kg/mg)

	As	*Ba*	*Cd*	*Cr*	*Cu*	*Mg*	*Mn*	*Ni*
Mean	0.30	137.0	1.56	17.06	14.97	1902.3	780.8	13.99
Standard Deviation	0.26	111.8	0.90	23.41	18.33	945.1	904.9	11.72
Count	46	46	46	46	46	46	46	46

Table 4.8: Displaying the descriptive statistics for trace metals, pH, OM%, clay%, silt% and sand% in table 4.6 (all values are in kg/mg)

	TP	*Pb*	*V*	*Zn*	*pH*	*OM%*	*Clay%*	*Silt%*	*Sand%*
Mean	587.0	37.58	18.78	102.0	6.34	3.51	3.33	47.54	49.13
Standard Deviation	335.7	80.54	11.07	51.01	0.65	2.06	1.59	24.09	25.60
Count	46	46	46	46	46	46	46	46	46

Table 4.6 displayed correlation matrix for trace metals, TP, pH, OM%, clay%, silt% and sand% and their associated significance levels. Among them are significantly correlated parameters like V and Pb, Mg and Mn, OM% and TP, Ni & Zn, clay% and Cd and clay% and Ni. There were significant intercorrelation of the trace metals which suggest the sources of the trace metal pollutants were different. Clay% was also significantly correlated with Ni and Cd which suggest a positive affinity of these metals for fine sediment fractions. Sand had very negative correlations with virtually all parameters analyzed which was obviously because they are of greater particle sizes.

4.4: Cluster analysis

Cluster analysis divides or separates data into groups according to certain properties shared by the individual parameters. Clustering groups according to these shared characteristics helps in data summarization as well as analysis. Using this technique also reveals similarities and dissimilarities between a given set of data to assist the experimenter in making useful deductions on shared characteristics (Tan, Steinbach & Kumar, 2013).

According to figure 4.10, it can be deduced that sites 3, 7,2C, 2B, 7 and 11 were clustered in a similar zone (zone 1), sites 2A, 6, 1, 4 and 5 also in another similar zone (zone 2) and finally sites 9,10 and 8 in the last zone (zone 3). It can be noted that in zone 1 sites 3, 7,2C, 2B, 7 and 11 shared a common characteristic of showing lower concentrations for most of the parameters measured, hence their grouping into a similar cluster. The second cluster displaying sites 2A, 6, 1, 4 and 5 also displayed higher levels for metals and TP in some cases which resulted in being grouped into a similar cluster. Lastly, sites 9, 10 and 8 also showed higher and similar levels of TP and Ba concentrations which may have been the reason why they fell into a similar group.

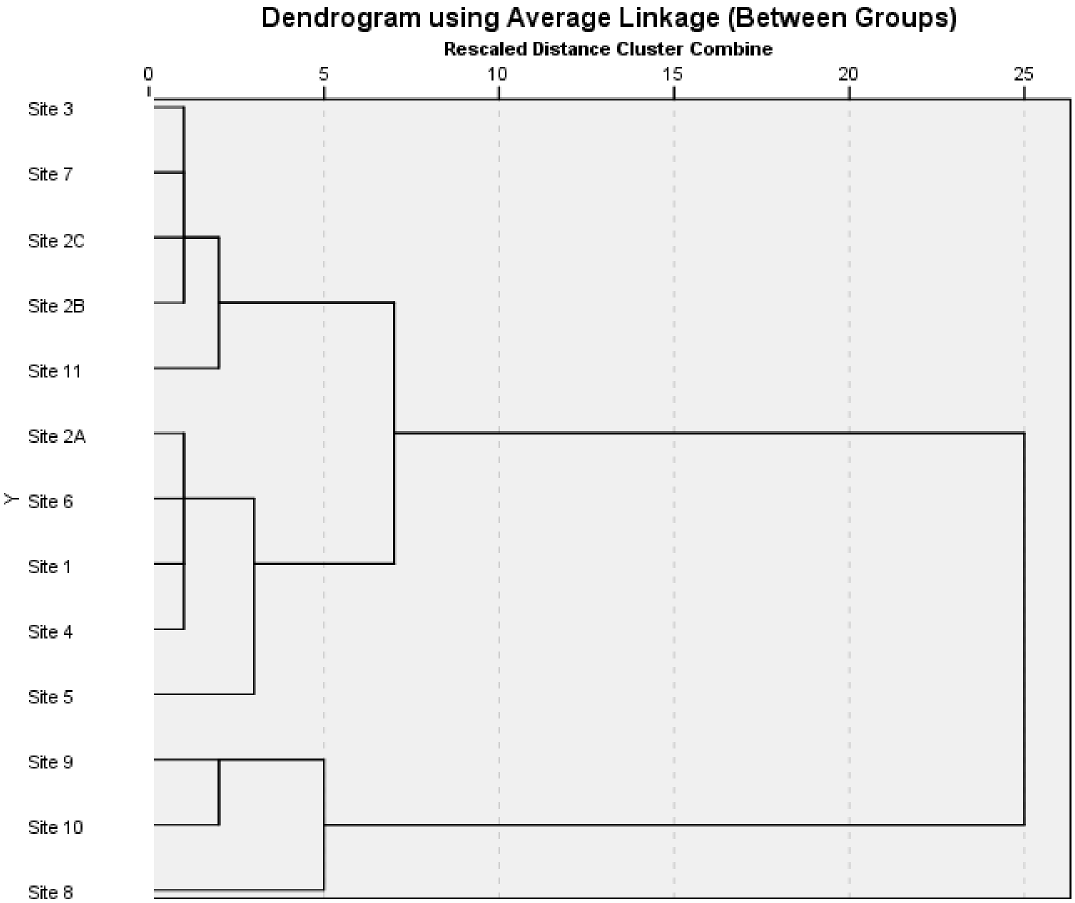


Figure 4.10: Cluster analysis for the sites based on related parameters

4.5: Principal Component Analysis

Principal component analysis (PCA) is a technique used to emphasize variation and discerning patterns in large environmental datasets. That was why it was employed in the study to find strong patterns in the datasets. PCA helps to eliminate dimensions and reduce factors that have less influence on researcher's area of interests. It also brings out very strong patterns and variations within variables (Reid and Spencer, 2009).

Regarding the analysis shown in figures 4.11 and 4.12 and observing TP concentrations, sites 3 and 7 were grouped and characterized by residential, forested and industrial land use within the sections of the watershed. The concentrations of TP in sites 2A, 2C, and 6 were grouped and characterized by pH within those areas of the MCW. Sites 1, 2B, and 4 relationships was characterized by Pb. Sites 5 and 11 relations were characterized by Cd. Sites 8, 9 and 10 relationships were also characterized by the clay%, silt% and Ba concentrations. Component 1 and 2 explained 37 and 28 percent of variances between the variables respectively.

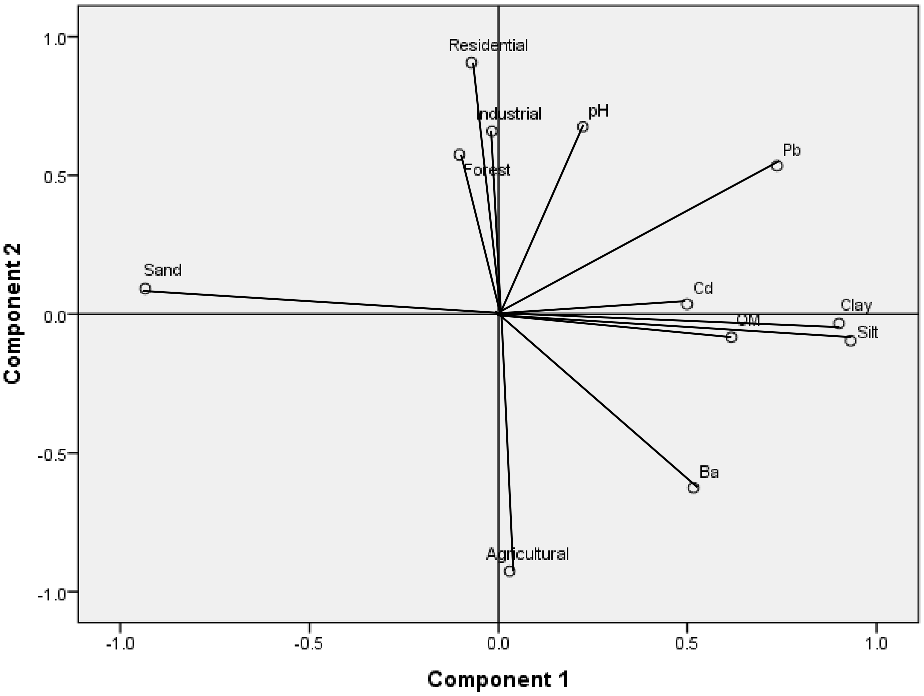


Figure 4.11: Principal Component Analysis for TP and (residential%, industrial%, forest%, agricultural%, pH, Ba, Cd, Pb, OM%, sand%, clay% and silt%).

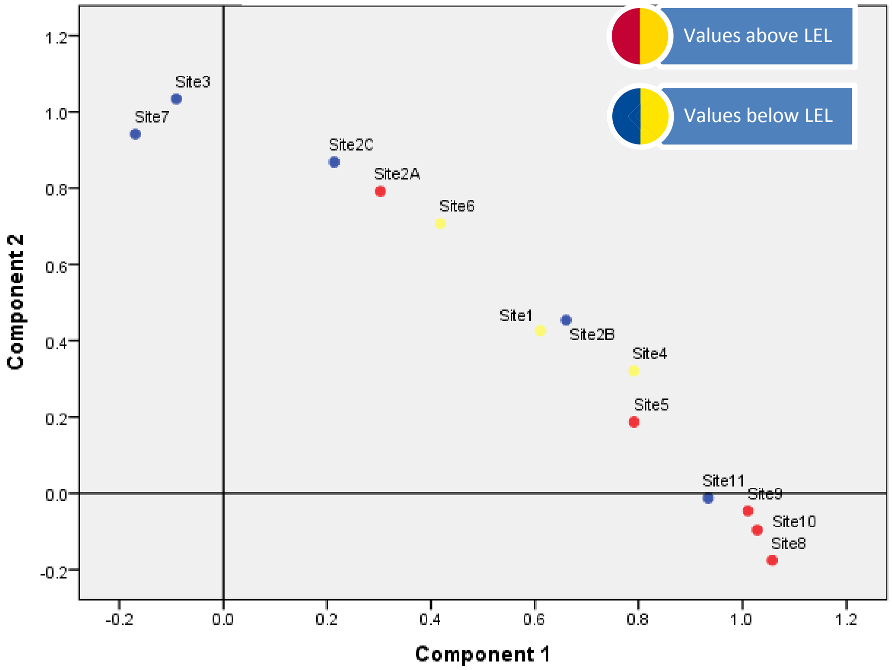


Figure 4.12: PCA for sites based on TP and other applicable parameters thus (residential%, industrial %, forest%, agricultural%, pH, Ba, Cd, Pb, OM%, sand%, clay% and silt%)

According to the PCA analysis shown in figures 4.13 and 4.14 and regarding Ba concentrations in the various sites, it was observed that sites 2C was characterized by pH. Sites 7 and 3 were related and characterized by Pb. Sites 2B and 11 were also related and characterized by Cd. Sites 1 6, and 4 were grouped and characterized by TP, OM%, silt% and clay%. Sites 5, 8, 9 and 10 were also related but were not characterized by any specific parameter of the analysis. Component 1 and 2 explained about 38 and 27 percent of the variance within the variables.

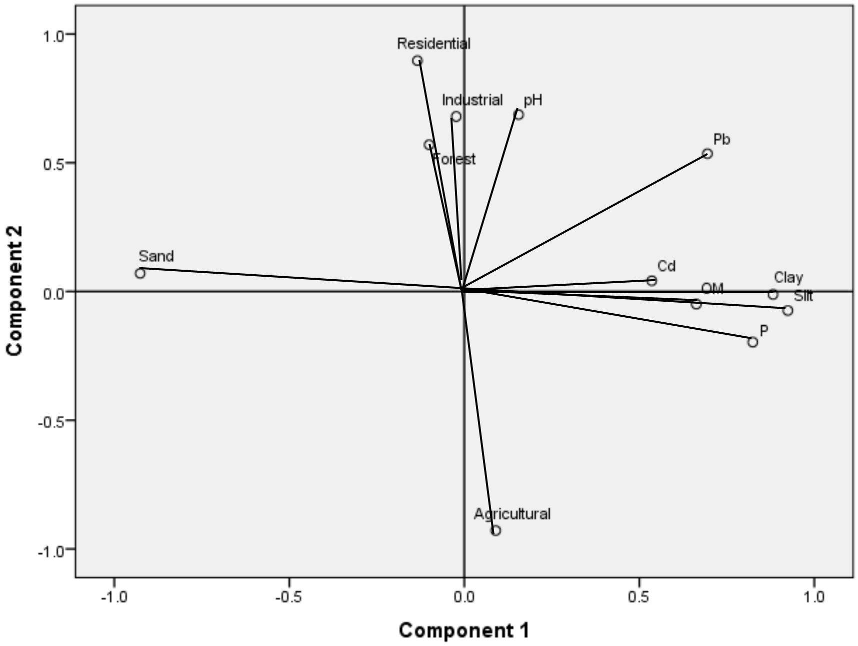


Figure 4.13: PCA for Ba, parameters applicable to it and land use thus (residential%, industrial %, forest%, agricultural%, pH, Cd, TP, Pb, OM%, sand%, clay% and silt%).

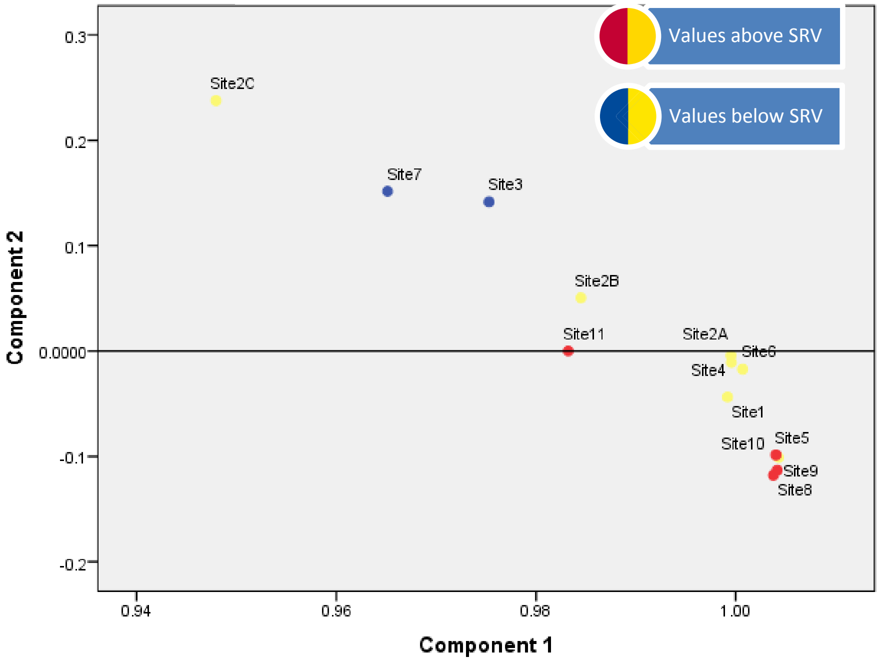


Figure 4.14: PCA of sites based on Ba and applicable parameters thus (residential%, industrial %, forest%, agricultural%, pH, Cd, Pb, TP, OM%, sand%, clay% and silt%)

The PCA analysis shown in figures 4.15 and 4.16 regarding Cd concentrations depicts sites 11 was characterized by pH. Site 8 was characterized by Pb. Sites 2B, 4 and 10 were characterized by clay%. Site 9 was characterized by silt%. Sites 1, 2A, 2C, 5 and 6 were characterized by OM% and TP. Sites 7 and 3 were not characterized by any specific parameter. Component 1 and 2 explained 41 and 27 percent of the variations within the variables respectively.

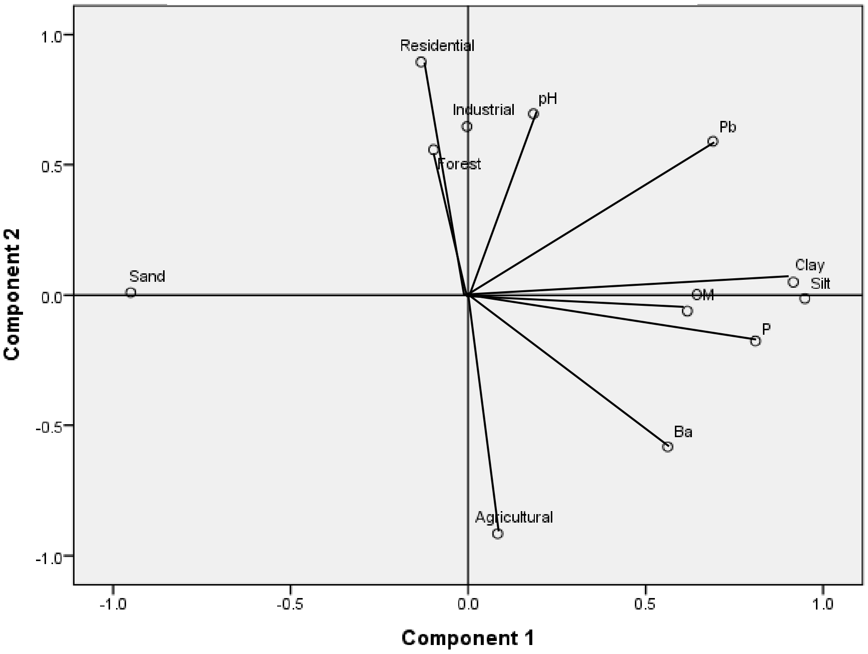


Figure 4.15: PCA for Cd, parameters closely related to it and land use (residential%, industrial %, forest%, agricultural%, pH, Ba, TP, Pb, OM%, sand%, clay% and silt%).

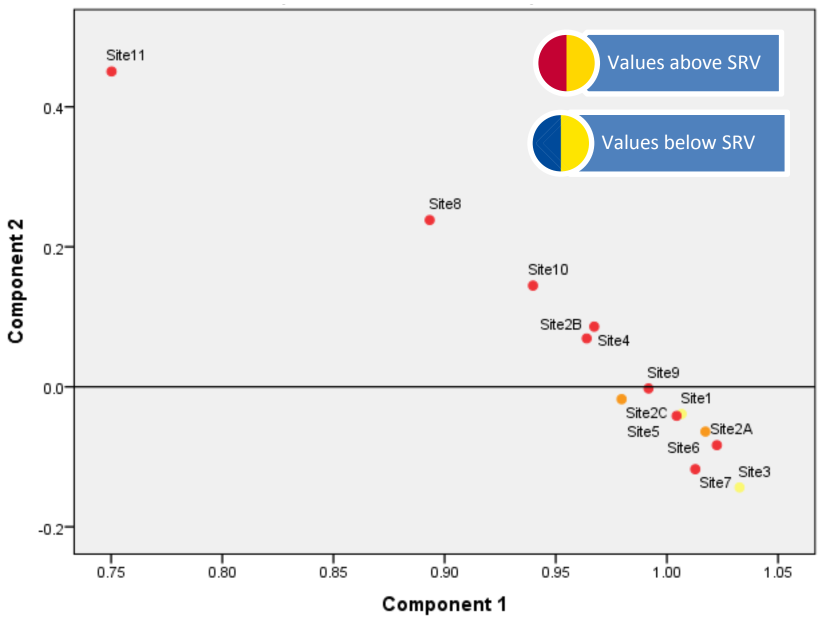


Figure 4.16: PCA of sites based on Cd and parameters applicable to it thus (residential%, industrial %, forest%, agricultural%, pH, Ba, TP, Pb, OM%, sand%, clay% and silt%)

The PCA analysis shown in figures 4.17 and 4.18 regarding Pb concentrations depicts sites 11 was characterized by pH and industrial land use. Sites 8 and 10 were related and characterized by Cd. Sites 2B and 4 were related and characterized by OM%. Site 9 was characterized by clay%. Sites 1, 2C and 5 were related and characterized by TP and silt%. Sites 2A, 3, 6 and 7 were not characterized by any specific parameter in the analysis. Component 1 and 2 explained 41 and 23 percent of the variations within the variables respectively.

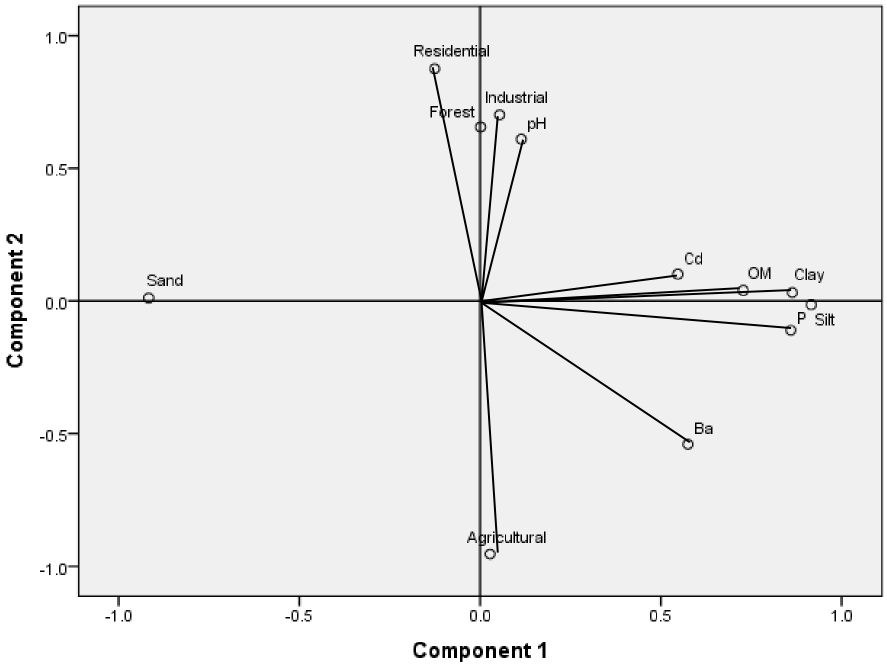


Figure 4.17: PCA for Pb, parameters related to it and land use thus (residential%, industrial %, forest%, agricultural%, pH, Ba, Cd, TP, OM%, sand%, clay% and silt%).

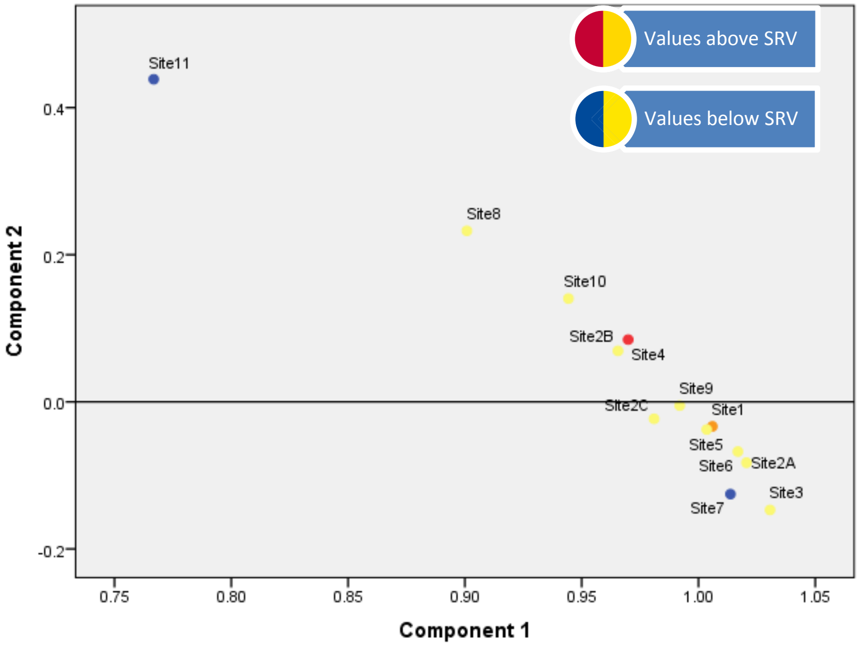


Figure 1.18: PCA for sites based on Pb and parameters applicable to it (residential%, industrial %, forest%, agricultural%, pH, Ba, Cd, TP, OM%, sand%, clay% and silt%)

4.6: Sources of Uncertainties

Low Spike recovery: Not all of the spiked concentration was recovered during the total metals and TP analysis. Only about 60-75% for most of trace metals and TP was recovered. This may have been due to adsorption and desorption of the total metals and TP between the extraction and analysis period.

Chapter 5 Conclusions

The hypothesis for the analysis was partially accepted. The results from the analysis showed that there were some significant relationships between land use, trace metals and TP. Barium significantly correlated with agricultural land use. TP was also positively correlated with agricultural land use but not statistically significant. pH was significantly correlated to residential areas. The other trace metals were not significantly correlated with any land use which may be because of the dominant sandy particle sizes and flow dynamics of the river. The TP concentrations at site 8, 9 and 10 were approximately twice the lowest effect range (Ohio EPA, 2008). Geospatial statistical maps created showed some areas of the lower watershed (especially site 2A, 4 and 5, in predominantly urban areas), had higher concentrations of most of the trace metals compared to the sediment reference values. This suggests a source of pollutants associated with land use from these areas into the creek. The elevated concentration of trace metals above the sediment reference indicate potential impacts of sediment quality by land uses within the watershed. Additionally, residential areas were significantly correlated with pH whereas agricultural and forested areas were positively correlated with TP, though not significant.

Future studies would benefit from analyzing samples in both dry and wet seasons, and after precipitation events. Researchers may have to Incorporate sediment texture properties when sampling. Researchers may also combine Soil and Water Assessment Tools (SWAT) with sediment geochemistry to model trace metals and TP loadings if Mill Creek watershed establishes a gauge station on its main-stem.

With further analysis by other researchers, the knowledge from this work can be used in improving upon buffer strip application along the watershed, fertilizer application management, discharge of treated waste water and where to tackle pollution sources from. These efforts will consequently increase citizen awareness of how their everyday acts impact the health of Mill Creek Watershed.

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Appendix A - General Mill Creek Watershed Information

Water depth for each sample point and the general description of sample areas

Site	Water Depth (m)	General Description
Site 1 Shallow	0.44	Quite rocky, murky water, impervious roads over and by it, lots of housing developments across the streets by it, has five CSOs within its drainage area
Site 1 Deep	1.32	
Site2A	0.88	bounded on both sides by roads, storm draining into lake through pipe, has lots of housing development in area
Site2B	0.61	has a tributary to Mill Creek, bounded on both sides by roads, storm draining into lake, lots of housing development
Site 2C	0.88	bounded on both sides by roads, storm draining into lake, lots of housing development
Site 3 Shallow	0.3	Minimal deposition of sediment in main channel, very rocky area, has trails on both sides, downslope of housing developments
Site 3 Deep	0.4	
Site 4 Shallow	0.4	Mostly rocky, foam and precipitates around area, downslope housing developments, bounded by two roads and one trail, has four CSOs within its drainage area,
Site 4 Deep	0.45	
Site 5 Shallow	0.3	has very fine sediment, upstream of a wetland by Newport Wetland Parking, bounded by roads on both sides, has four CSOs within its drainage area
Site 5 Deep	0.9	
Site 6 Shallow	0.2	after storm drain, east of hike and bike trail, bounded by roads on both sides, lots trees around creek, dead trees, parking lots on the side, has 8 CSOs within its drainage area, housing developments upslope
Site 6 Deep	0.5	
Site 7 Shallow	0.3	Close Mill Creek Golf Course, housing developments upslope, hiking trail by creek, has a road by creek
Site 7 Deep	0.66	
Site 8 Shallow	0.5	Boardman Waste Water Treatment Plant drains into it, lots of forest and trees within vicinity, housing development upslope
Site 8 Deep	0.7	
Site 9 Shallow	0.3	Cattle ranch right around area and partially buffered with strip, bounded on one side by road, minimal housing developments
Site 9 Deep	0.6	
Site 10 Shallow	0.2	crop farm by area, drains into stream, trees in vicinity, road by the side of creek, moderate housing developments
Site 10 Deep	0.7	
Site 11 Shallow	0.29	Very Sandy area, bounded by roads on one side and across it, minimal housing developments, following agricultural fields by creek
Site 11 Deep	0.44	

Appendix B - Soil Types

dominant soil types and map unit names at each sample area (USDA, 2017)

Site	Soil Types & Map Unit Names	Slope (%)
Site 1	Dekalb very stony loam	25 to 50
	Chili-Urban land complex	Undulating
	Londonville-Urban complex	Undulating
Site 2A	Chili gravelly loam	12 to 18
	Dekalb very stony loam	12 to 25
	Londonville-Urban land complex	Undulating
Site 2B	Dekalb very stony loam	25 to 50
	Chili-Urban land complex	Undulating
	Londonville-Urban land complex	Undulating
Site 2C	Rittman-Urban land complex	2 to 6
	Londonville loam	6 to 12
	Dekalb very stony loam	25 to 50
Site 3	Londonville-Urban land complex	Undulating
	Londonville loam	6 to 12
	Bogart loam	2 to 6
Site 4	Londonville loam	12 to 18
	Bogart loam	2 to 6
	Jimtown loam	2 to 6
Site 5	Jimtown- Urban land complex	Undulating
	Chili loam	2 to 6
	Rittman-Urban land complex	2 to 6
Site 6	Wayland silt loam	Undulating
	Lorain silty clay loam	Undulating
	Bogart loam	2 to 6
Site 7	Papakating silt loam	Undulating
	Wooster silt loam	2 to 6
	Damascus loam	Undulating
Site 8	Wayland silt loam	Undulating
	Bennington silt loam	2 to 6
	Canfield silt loam	2 to 6
Site 9	Canfield silt loam	2 to 6
	Bogart loam	2 to 6
	Glenford silt loam	2 to 6
Site 10	Bogart loam	2 to 6
	Canfield silt loam	2 to 6
	Wooster silt loam	2 to 6
Site 11	Ravenna silt loam	2 to 6
	Canfield silt loam	2 to 6
	Bogart silt loam	2 to 6

Appendix C - Sample area elevation, description of main channel and its sides

Site	Elevation(m)		Channel & Side Description
Site 1	Elevation(m)	301.6	Fairly deep main channel with relatively flat sides
	Min (m)	255	
	Max (m)	334	
Site 2A	Elevation(m)	283.4	Deep & wide main channel with very steep sides
	Min (m)	255	
	Max (m)	325	
Site 2B	Elevation(m)	299.5	Fairly deep & wide main channel with moderately steep sides
	Min (m)	259	
	Max (m)	324	
Site 2C	Elevation(m)	317.2	Deep & wide main channel with moderately steep sides
	Min (m)	259	
	Max (m)	352	
Site 3	Elevation(m)	324.9	Shallow & fairly wide main channel with fairly steep sides
	Min (m)	271	
	Max (m)	355	
Site 4	Elevation(m)	315.8	Deep main & wide channel with steep sides
	Min (m)	276	
	Max (m)	338	
Site 5	Elevation(m)	332.6	Fairly deep & moderately wide main channel with steep sides
	Min (m)	298	
	Max (m)	365	
Site 6	Elevation(m)	315.1	Shallow & fairly wide main channel with Steep sides
	Min (m)	299	
	Max (m)	354	
Site 7	Elevation(m)	342.6	Shallow & fairly wide main channel with moderately steep sides
	Min (m)	300	
	Max (m)	386	
Site 8	Elevation(m)	329.3	Fairly deep & narrow main channel with very steep sides
	Min (m)	303	
	Max (m)	390	
Site 9	Elevation(m)	341.5	Fairly deep & narrow channel with steep sides
	Min (m)	306	
	Max (m)	378	
Site 10	Elevation(m)	339.6	Shallow & narrow channel with very steep sides
	Min (m)	313	
	Max (m)	379	
Site 11	Elevation(m)	366	Shallow & narrow main channel with moderately steep sides
	Min (m)	335	
	Max (m)	396	

Appendix D

Daily Weather History & Observations for Youngstown before and during sampling period (Underground weather, 2017)

2017	Temp. (°F)			Humidity (%)			Wind (mph)			Precip. (in)	Events
May	high	avg	Low	High	Avg	Low	High	avg	High	Sum	
1	74	63	52	87	70	52	47	13	67	0.74	Fog , Rain , Thunderstorm
2	53	49	45	80	67	54	37	15	48	0.06	Rain
3	57	50	42	89	61	32	17	7	22	0.1	Rain
4	58	52	45	86	68	50	20	12	28	0.2	Rain
5	55	50	44	96	91	86	21	13	26	0.51	Rain
6	46	44	41	96	89	82	25	14	34	0.23	Rain
7	53	44	35	92	66	39	24	10	33	0.02	Rain
8	54	42	30	92	61	29	21	7	25	0	
9	64	47	29	85	56	26	17	4	19	0	
10	67	55	43	76	50	24	12	5	17	0	
11	64	56	48	86	70	54	14	8	17	0.14	Rain
12	59	53	47	83	73	62	10	6	13	0	
13	68	54	40	100	70	40	15	5	22	0.06	Fog , Rain
14	64	54	43	100	74	47	22	10	27	T	Fog
15	68	53	37	92	63	34	18	7	23	0	Fog

Appendix E – Organic Matter

Average organic matter determined by loss ignition method and an estimate of total organic carbon content for each sample sites

Site	OM%	%TOC
Site 1 Shallow Upper	5.11	2.97
Site 1 Shallow Lower	2.27	1.32
Site 1 Deep Upper	2.6	1.51
Site 1 Deep Lower	4.46	2.59
Site 2A Upper	9.91	5.76
Site 2A Lower	4.93	2.86
Site 2B Upper	2.43	1.42
Site 2B Lower	3.7	2.15
Site 2C Upper	2.58	1.5
Site 2C Lower	4.78	2.78
Site 3 Shallow Upper	2.62	1.52
Site 3 Shallow Lower	4.96	2.88
Site 3 Deep Upper	4.58	2.66
Site 3 Deep Lower	2.22	1.29
Site 4 Shallow Upper	2.12	1.23
Site 4 Shallow Lower	3.45	2.01
Site 4 Deep Upper	1.66	0.96
Site 4 Deep Lower	1.7	0.99
Site 5 Shallow Upper	3.78	2.19
Site 5 Shallow Lower	3.41	1.99
Site 5 Deep Upper	3.96	2.3
Site 5 Deep Lower	4.01	2.33
Site 6 Shallow Upper	3.78	2.2
Site 6 Shallow Lower	1.26	0.74
Site 6 Deep Upper	1.81	1.05
Site 6 Deep Lower	2.21	1.28

Site	OM%	%TOC
Site 7 Shallow Upper	1.77	1.03
Site 7 Shallow Lower	0.6	0.35
Site 7 Deep Upper	0.73	0.43
Site 7 Deep Lower	0.57	0.33
Site 8 Shallow Upper	8.4	4.89
Site 8 Shallow Lower	4.5	2.62
Site 8 Deep Upper	5.82	3.38
Site 8 Deep Lower	3.67	2.13
Site 9 Shallow Upper	6.97	4.05
Site 9 Shallow Lower	5.81	3.38
Site 9 Deep Upper	3.32	1.93
Site 9 Deep Lower	3.54	2.06
Site 10 Shallow Upper	7.96	4.63
Site 10 Shallow Lower	5.61	3.26
Site 10 Deep Upper	2.25	1.31
Site 10 Deep Lower	2.21	1.28
Site 11 Shallow Upper	1.45	0.84
Site 11 Shallow Lower	2.7	1.57
Site 11 Deep Upper	1.5	0.87
Site 11 Deep Lower	1.84	1.07

Minimum Value	0.57	0.33
Maximum Value	9.91	5.76
Mean	3.51	2.04
Standard deviation	2.06	1.2

Appendix F - pH of sediment of sampling site

Site	pH
Site 1 Shallow Upper	6.76
Site 1 Shallow Lower	7.07
Site 1 Deep Upper	5.69
Site 1 Deep Lower	6.1
Site 2A Upper	6.16
Site 2A Lower	6.59
Site 2B Upper	6.39
Site 2B Lower	7.23
Site 2C Upper	5.58
Site 2C Lower	5.76
Site 3 Shallow Upper	6.28
Site 3 Shallow Lower	6.7
Site 3 Deep Upper	6.71
Site 3 Deep Lower	6.82
Site 4 Shallow Upper	7.42
Site 4 Shallow Lower	7.14
Site 4 Deep Upper	7.23
Site 4 Deep Lower	6.64
Site 5 Shallow Upper	6.78
Site 5 Shallow Lower	6.91
Site 5 Deep Upper	6.87
Site 5 Deep Lower	6.89
Site 6 Shallow Upper	6.02
Site 6 Shallow Lower	5.29
Site 6 Deep Upper	6.64
Site 6 Deep Lower	6.26

Site	pH
Site 7 Shallow Upper	6.72
Site 7 Shallow Lower	6.63
Site 7 Deep Upper	6.98
Site 7 Deep Lower	7.22
Site 8 Shallow Upper	6.32
Site 8 Shallow Lower	5.15
Site 8 Deep Upper	5.22
Site 8 Deep Lower	4.78
Site 9 Shallow Upper	6.02
Site 9 Shallow Lower	5.53
Site 9 Deep Upper	6.46
Site 9 Deep Lower	5.85
Site 10 Shallow Upper	6.48
Site 10 Shallow Lower	6.41
Site 10 Deep Upper	6.79
Site 10 Deep Lower	6.62
Site 11 Shallow Upper	5.96
Site 11 Shallow Lower	4.88
Site 11 Deep Upper	6.08
Site 11 Deep Lower	5.85

Minimum	4.78
Maximum	7.42
Count	46

Appendix G – Particle Size

Sediment particle sizes for each site in percentages as well as its textural class (USDA,2017)

Site	Clay%	Silt%	Sand%	Textural Class
Site 1 Shallow Upper	4.66	61.8	33.55	Silt Loam
Site 1 Shallow Lower	5.71	66.24	28.06	Silt Loam
Site 1 Deep Upper	4.2	59.07	36.74	Silt Loam
Site 1 Deep Lower	6.55	84.78	8.68	Silt
Site 2A Upper	2.74	36.69	60.58	Sandy Loam
Site 2A Lower	2.03	23.82	74.16	Loamy Fine Sand
Site 2B Upper	2.16	31.74	66.11	Sandy Loam
Site 2B Lower	4.35	86.01	9.65	Silt
Site 2C Upper	2.98	43.77	53.26	Sandy Loam
Site 2C Lower	1.2	15.18	83.63	Loamy Fine Sand
Site 3 Shallow Upper	1.47	26.29	72.25	Loamy Fine Sand
Site 3 Shallow Lower	2.76	42.3	54.94	Sandy Loam
Site 3 Deep Upper	2.11	44.65	53.25	Sandy Loam
Site 3 Deep Lower	2.08	45.84	52.09	Sandy Loam
Site 4 Shallow Upper	3.84	42.04	54.12	Sandy Loam
Site 4 Shallow Lower	2.87	36.28	60.86	Sandy Loam
Site 4 Deep Upper	1.87	20.66	77.47	Loamy Fine Sand
Site 4 Deep Lower	2.5	29.62	67.89	Sandy Loam
Site 5 Shallow Upper	3.99	63.58	32.44	Silt Loam
Site 5 Shallow Lower	4.82	72.43	22.76	Silt Loam
Site 5 Deep Upper	4.99	72.03	22.99	Silt Loam
Site 5 Deep Lower	5.34	76.46	18.21	Silt Loam
Site 6 Shallow Upper	3.31	47.06	49.64	Sandy Loam
Site 6 Shallow Lower	2.35	36.23	61.43	Sandy Loam
Site 6 Deep Upper	1.49	16.74	81.78	Loamy Fine Sand
Site 6 Deep Lower	1.92	26	72.09	Loamy Fine Sand
Site 7 Shallow Upper	2.01	24.84	73.16	Loamy Fine Sand
Site 7 Shallow Lower	1.05	9.47	89.49	Fine Sand
Site 7 Deep Upper	1.38	12.69	85.94	Fine Sand
Site 7 Deep Lower	0.89	7.95	91.17	Fine Sand
Site 8 Shallow Upper	3.64	57.08	39.29	Silt Loam
Site 8 Shallow Lower	6.27	85.62	8.12	Silt Loam
Site 8 Deep Upper	5.52	89.75	4.73	Silt
Site 8 Deep Lower	6.32	93.3	0.39	Silt
Site 9 Shallow Upper	4.24	65.96	29.81	Silt Loam
Site 9 Shallow Lower	4.76	69.98	25.27	Silt Loam
Site 9 Deep Upper	4.73	64.99	30.28	Silt Loam
Site 9 Deep Lower	6.43	87.83	5.74	Silt
Site 10 Shallow Upper	3.58	64.15	32.28	Silt Loam
Site 10 Shallow Lower	3.02	55.7	41.29	Silt Loam
Site 10 Deep Upper	2.07	31.64	66.29	Sandy Loam
Site 10 Deep Lower	1.92	26.1	71.99	Loamy Fine Sand
Site 11 Shallow Upper	2.47	27.01	70.52	Loamy Fine Sand
Site 11 Shallow Lower	3.22	42.45	54.33	Sandy Loam
Site 11 Deep Upper	2.12	24.83	73.06	Loamy Fine Sand
Site 11 Deep Lower	3.46	38.32	58.23	sandy Loam

Appendix H – Trace Metals

Trace metals As, Ba, Cd, Cr, Cu and Mg concentrations

Site	**As (mg/kg)**	**Ba (mg/kg)**	**Cd (mg/kg)**	**Cr (mg/kg)**	**Cu (mg/kg)**	**Mg (mg/kg)**
Site 1 Shallow Upper	0.22	85.96	0.35	16.69	21.6	2761.46
Site1 Shallow Lower	0.16	91.47	0.3	14.36	27.3	2756.14
Site 1 Deep Upper	0.1	84.09	0.17	10.13	7.47	1681.88
Site 1 Deep Lower	0.22	108.72	*2.03	13.47	17.42	2663.42
Site 2A Upper	0.41	77.12	*3.57	*119.36	112.4	4015.84
Site 2A Lower	0.32	71.12	*3.28	*120.12	*44.2	4680.46
Site 2B Upper	0.17	51.38	*1.41	6.23	10.3	1400.68
Site 2B Lower	0.3	151.24	*2.07	9.94	20.08	3100.8
Site 2C Upper	0.09	79.88	*0.94	6.62	7.86	1179.14
Site 2C Lower	0.06	43.8	*1.02	5.77	5.43	1078.82
Site 3 Shallow Upper	0.15	40.93	*1.14	7.4	11.47	1629.06
Site3 Shallow Lower	0.1	30.81	*0.94	5.36	21.99	1252.1
Site 3 Deep Upper	0.3	50.97	*1.39	11.24	15.38	1749.52
Site 3 Deep Lower	0.29	41.74	*1.44	9.61	17.15	1520.76
Site 4 Shallow Upper	0.28	153.82	*1.82	*26.69	14.57	3017.2
Site 4 Shallow Lower	0.22	156.14	*1.66	13.46	10.88	2208.56
Site 4 Deep Upper	0.34	*221.92	*1.79	*27.63	*58.9	2301.28
Site 4 Deep Lower	1.14	129.92	*3.03	*46.08	21.54	2640.24
Site 5 Shallow Upper	0.9	98.61	*2.23	17.5	26.8	2342.32
Site 5 Shallow Lower	0.82	93.78	*2.55	13.72	16.89	2652.02
Site 5 Deep Upper	0.79	89.41	*2.46	14.5	16.92	2408.82
Site 5 Deep Lower	0.92	110.12	*3.39	13.52	17.16	2511.8
Site 6 Shallow Upper	0.44	96.14	*1.44	21.44	10.11	1416.26
Site 6 Shallow Lower	0.14	50.16	0.75	5.92	4.59	1065.9
Site 6 Deep Upper	0.1	43.79	0.51	4.37	2.46	621.98
Site 6 Deep Lower	0.18	46.03	0.66	7.42	4.47	827.64
Site 7 Shallow Upper	0.14	37.4	0.67	8.47	3.5	835.24
Site 7 Shallow Lower	0.11	24.08	0.33	3.56	1.03	432.36
Site 7 Deep Upper	0.08	20.54	0.21	3.68	1.2	384.33
Site 7 Deep Lower	0.08	25.22	0.48	4.04	0.8	542.3
Site 8 Shallow Upper	0.38	110.54	*1.86	21.6	12.55	2224.14
Site 8 Shallow Lower	0.46	*573.31	*2.47	15.51	13.13	2801.36
Site 8 Deep Upper	0.64	*216.98	*2.93	21.26	19	2916.12
Site 8 Deep Lower	0.51	*277.67	*2.53	15.75	14.65	2976.92
Site 9 Shallow Upper	0.27	164.92	*2.34	9.94	9.36	1977.14
Site 9 Shallow Lower	0.3	170.96	*2.27	10.1	9.14	1987.4
Site 9 Deep Upper	0.26	124.56	*2.06	14.27	10.01	1976
Site 9 Deep Lower	0.3	191.41	*1.79	16.82	6.57	2538.4
Site 10 Shallow Upper	0.37	*330.56	*1.58	10.08	10.28	2027.3
Site 10 Shallow Lower	0.29	*331.66	*1.44	11.26	9.36	1865.8
Site 10 Deep Upper	0.16	*296.97	*1.14	7.82	5.45	1347.48

Site 10 Deep Lower	0.11	*342.04	*1.03	5.86	4.95	1108.08
Site 11 Shallow Upper	0	110.43	*0.92	8.85	2.47	923.78
Site 11 Shallow Lower	0.04	*305.9	*1.25	10.08	4.3	1250.2
Site 11 Deep Upper	0.02	131.94	0.75	8.06	2.23	741.76
Site 11 Deep Lower	0.03	*215.76	*1.23	9.3	3.28	1163.56
Mean	0.3	137	1.56	17.06	14.97	1902.26
Standard Deviation	0.26	111.81	0.9	23.41	18.33	945.06
Reference	2.15	175.56	4.51	126.62	63.66	5912.8

*Means concentration above sediment reference value (table 4.0) or above Lowest effect range (table 4.1)

Trace metals Mn, Ni, P, Pb, V and Zn concentrations

Site	Mn (mg/kg)	Ni (mg/kg)	P (mg/kg)	Pb (mg/kg)	V (mg/kg)	Zn (mg/kg)
Site 1 Shallow Upper	528.09	16.71	553.28	55.02	23.43	133
Site1 Shallow Lower	596.18	16.43	541.31	56.64	26.03	128.59
Site 1 Deep Upper	316.73	10.1	459.04	12.18	17.31	78.07
Site 1 Deep Lower	699.92	18.58	540.13	17.9	23.67	91.05
Site 2A Upper	*3865.74	13.62	*724.62	36.26	*49.2	116.77
Site 2A Lower	*4075.88	10.31	596.87	43.65	*52.86	91.16
Site 2B Upper	436.05	9.26	284.13	24.47	10.88	89.82
Site 2B Lower	745.64	15.9	361.87	37.44	17.83	134.48
Site 2C Upper	165.38	7.16	226.1	18.21	10.08	43.17
Site 2C Lower	340.21	6.25	207.06	9.38	10.63	43.54
Site 3 Shallow Upper	352.07	5.64	324.94	15.63	11.08	65.59
Site3 Shallow Lower	348.19	4.29	256.96	11.38	7.68	57.98
Site 3 Deep Upper	411.31	7.65	451.71	20.63	13.42	82.39
Site 3 Deep Lower	358	8.11	397.06	16.96	13.13	122.93
Site 4 Shallow Upper	*2869.38	15.63	572.96	53.85	17.1	117.53
Site 4 Shallow Lower	*2512.18	12.38	517.03	22.04	12.71	96.98
Site 4 Deep Upper	*2018.94	11.32	354.35	104.88	15.16	90.63
Site 4 Deep Lower	890.72	22.75	447.64	553.74	23.34	152
Site 5 Shallow Upper	690.73	24.1	*1039.68	70.28	22.44	*164.05
Site 5 Shallow Lower	657.7	35	562.59	60.67	22.58	*182.48
Site 5 Deep Upper	916.18	32.72	*693.84	40.56	24.41	*171.34
Site 5 Deep Lower	*1608.92	*54.17	*604.92	51.06	31.67	*218.08
Site 6 Shallow Upper	579.77	12.81	*958.36	20.63	15.23	104.16
Site 6 Shallow Lower	148.12	6.62	236.63	7.76	11.83	61.77
Site 6 Deep Upper	256.65	1.56	268.62	4.31	7.95	31.31
Site 6 Deep Lower	253.38	4.42	282.57	8.3	9.7	55.41
Site 7 Shallow Upper	449.08	4.73	326.42	7.67	9.31	43.65
Site 7 Shallow Lower	241.6	1.16	207.78	3.87	5.68	29.38
Site 7 Deep Upper	290.02	0	171.3	0.73	5.38	17.92
Site 7 Deep Lower	333.22	1.24	244.07	5.19	6.97	35.65

Site 8 Shallow Upper	942.78	17.58	*1097.82	16.2	21.72	141.82
Site 8 Shallow Lower	311.3	23.1	*706.27	21.06	29.13	145.88
Site 8 Deep Upper	368.3	*33.89	*1288.58	28.9	*48.34	*205.16
Site 8 Deep Lower	247.53	22.02	*692.36	24.98	36.53	142.88
Site 9 Shallow Upper	1442.1	*34.73	*1341.02	24.49	20.39	*174.46
Site 9 Shallow Lower	1011.18	*34.26	*1139.62	26.76	25.75	*171.04
Site 9 Deep Upper	725.61	28.1	*983.44	48.99	21.86	*167.77
Site 9 Deep Lower	480.78	15.86	*709.99	18.13	25.87	119.02
Site 10 Shallow Upper	573.8	9.38	*1203.46	26.7	18.84	105.15
Site 10 Shallow Lower	463.22	8.86	*1092.88	32.73	16.3	114.8
Site 10 Deep Upper	335.31	4.68	*947.34	16.48	12.31	62.61
Site 10 Deep Lower	392.92	3.82	*1091.36	17.93	11.08	60.29
Site 11 Shallow Upper	156.29	3.41	295.68	8.13	11.57	57.14
Site 11 Shallow Lower	114	6.28	340.78	8.67	13.75	66.71
Site 11 Deep Upper	119.55	1.66	287.28	6.5	8.08	57.59
Site 11 Deep Lower	276.56	5.28	369.97	10.55	13.52	50.6
Mean	780.81	13.99	586.99	37.58	18.78	102.04
Standard Deviation	904.86	11.72	335.65	80.54	11.07	51.01
Reference	661.81	39.54	774.44	374.68	86.64	303.16

Appendix I - Quality Control and Quality Assurance

QC-1	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn
Avg	4.61	4.612	NA	4.6	4.685	5.965	5.309	5.705	NA	NA	NA
%	92.2	92.24		92	93.7	119.3	106.18	114.1			
QC-1	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn
Avg	4.81	5.146	NA	4.827	4.976	5.449	4.039	5.184	NA	NA	NA
%	96.2	102.92		96.54	99.52	108.98	80.78	103.68			
QC-1	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn
Avg	4.81	5.146	NA	4.827	4.976	5.449	4.039	5.184	NA	NA	NA
%	96.2	102.92		96.54	99.52	108.98	80.78	103.68			
QC-NUT	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn
Avg	NA	NA	9.925	NA	NA	NA	NA	11.12	19.54	12.34	9.229
%			99.25						97.7	82.27	92.29
QC-1	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn
Avg	4.972	5.235	NA	5.049	5.198	5.49	3.796	5.232	NA	NA	NA
%	99.44	104.7		100.98	103.96	109.8	75.92	104.64			
QC-1	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn
Avg	4.974	5.654	NA	5.097	5.226	6.928	3.66	5.215	NA	NA	NA
%	99.48	113.08		101.94	104.52	138.56	73.2	104.3			

QC-1	Mo	Na	Ni	P	Pb	Se	Sn	Ti	V	Zn	Y	Y
Avg	5.452	NA	4.755	NA	5.05	5.028	5.173	5.591	4.9	5.359	5778.2	12476
%	109.04		95.1		101	100.56	103.46	111.82	98	107.18		
QC-1	Mo	Na	Ni	P	Pb	Se	Sn	Ti	V	Zn	Y	Y
Avg	5.405	NA	5.044	NA	5.337	4.957	5.337	5.36	4.885	5.384	4949.2	9981.8
%	108.1		100.88		106.74	99.14	106.74	107.2	97.7	107.68		
QC-1	Mo	Na	Ni	P	Pb	Se	Sn	Ti	V	Zn	Y	Y
Avg	5.405	NA	5.044	NA	5.337	4.957	5.337	5.36	4.885	5.384	4949.2	9981.8
%	108.1		100.88		106.74	99.14	106.74	107.2	97.7	107.68		
QC-NUT	Mo	Na	Ni	P	Pb	Se	Sn	Ti	V	Zn	Y	Y
Avg	NA	10.01	NA	11.9	NA	NA	NA	NA	NA	NA	4900.5	9819.5
%		100.1		119								
QC-1	Mo	Na	Ni	P	Pb	Se	Sn	Ti	V	Zn	Y	Y
Avg	5.838	NA	5.274	NA	5.685	5.231	5.723	5.413	4.745	5.832	4811.1	9610.2
%	116.76				113.7	104.62	114.46	108.26	94.9	116.64		
QC-1	Mo	Na	Ni	P	Pb	Se	Sn	Ti	V	Zn	Y	Y
Avg	6.036	NA	5.304	NA	5.818	5.423	5.902	5.349	5.267	6.053	4765.1	9562.9
%	120.72				116.36	108.46	118.04	106.98	105.34	121.06		

	As ppm	Ba ppm	Ca ppm	Cd ppm	Cr ppm	Cu ppm	Mg ppm
Site 6 Shallow (Unspiked)	0.00	0.96	16.65	0.01	0.17	0.10	16.25
Site 6 Shallow(SPIKE)	2.47	3.49	9.35	2.50	3.10	2.21	14.37
Recovery%	49.40	58.54	43.19	49.78	59.97	43.40	67.64
Site 9 Shallow(Unspiked)	0.00	4.35	75.15	0.02	0.15	0.14	26.72
Site 9 Shallow(SPIKE)	2.95	6.89	54.06	3.01	3.66	2.45	25.22
Recovery%	58.84	73.67	67.45	59.85	70.95	47.75	79.52
	Mn ppm	Ni ppm	P ppm	Pb ppm	V ppm	Zn ppm	*
Site 6 Shallow (Unspiked)	4.62	0.13	7.96	0.17	0.17	1.32	*
Site 6 Shallow(SPIKE)	4.23	2.72	3.02	2.83	0.00	3.54	*
Recovery%	44.00	53.10	23.26	54.70	0.00	55.99	*
Site 9 Shallow(Unspiked)	7.20	0.12	15.84	0.35	0.25	1.38	*
Site 9 Shallow(SPIKE)	8.15	3.29	13.52	3.72	0.05	4.58	*
Recovery%	66.75	64.12	64.89	69.59	0.93	71.81	*
Formula (spiked/(5+Unspiked)*100							

Appendix J – Pearson Correlations

	As	Cr	Cu	Mg	Mn	Ni	V	Zn	pH	OM%	Resdnt%	Indusrl%	Forest%	Rnge%	Hay%	Agric %	Wetland %
As	1.000	0.210	0.294	0.475	0.200	0.678*	0.424	0.737**	0.267	0.336	-0.065	0.144	-0.003	0.049	0.018	-0.031	0.105
Cr	0.210	1.000	0.954**	0.787**	0.855**	0.019	0.894**	0.099	0.071	0.521	0.302	0.334	0.104	-0.405	-0.326	-0.245	-0.405
Cu	0.294	0.954**	1.000	0.859**	0.796**	0.102	0.904**	0.206	0.224	0.532	0.455	0.357	0.076	-0.404	-0.450	-0.369	-0.436
Mg	0.475	0.787**	0.859**	1.000	0.797**	0.412	0.903**	0.574*	0.369	0.634*	0.358	0.275	0.075	-0.504	-0.423	-0.324	-0.388
Mn	0.200	0.855**	0.796**	0.797**	1.000	0.171	0.754**	0.218	0.315	0.445	0.353	0.339	0.234	-0.480	-0.396	-0.312	-0.224
Ni	0.678*	0.019	0.102	0.412	0.171	1.000	0.385	0.934**	0.055	0.429	-0.203	-0.093	0.031	0.068	0.164	0.114	-0.021
V	0.424	0.894**	0.904**	0.903**	0.754**	0.385	1.000	0.485	0.049	0.719**	0.148	0.256	0.011	-0.354	-0.194	-0.124	-0.514
Zn	0.737**	0.099	0.206	0.574*	0.218	0.934**	0.485	1.000	0.185	0.524	-0.140	-0.083	0.003	-0.108	0.045	0.090	-0.130
pH	0.267	0.071	0.224	0.369	0.315	0.055	0.049	0.185	1.000	-0.162	0.575*	0.243	0.096	-0.316	-0.526	-0.465	0.038
OM%	0.336	0.521	0.532	0.634*	0.445	0.429	0.719**	0.524	-0.162	1.000	-0.100	0.148	-0.181	0.030	0.084	0.048	-0.416
Resdnt%	-0.065	0.302	0.455	0.358	0.353	-0.203	0.148	-0.140	0.575*	-0.100	1.000	0.446	0.398	-0.567*	-0.883**	-0.888**	0.058
Indusrl%	0.144	0.334	0.357	0.275	0.339	-0.093	0.256	-0.083	0.243	0.148	0.446	1.000	0.463	-0.148	-0.504	-0.626*	0.154
Forest%	-0.003	0.104	0.076	0.075	0.234	0.031	0.011	0.003	0.096	-0.181	0.398	0.463	1.000	-0.493	-0.678*	-0.620*	0.629*
Rnge%	0.049	-0.405	-0.404	-0.504	-0.480	0.068	-0.354	-0.108	-0.316	0.030	-0.567*	-0.148	-0.493	1.000	0.673*	0.450	0.113
Hay %	0.018	-0.326	-0.450	-0.423	-0.396	0.164	-0.194	0.045	-0.526	0.084	-0.883**	-0.504	-0.678*	0.673*	1.000	0.892**	-0.247
Agric %	-0.031	-0.245	-0.369	-0.324	-0.312	0.114	-0.124	0.090	-0.465	0.048	-0.888**	-0.626*	-0.620*	0.450	0.892**	1.000	-0.377
Wetlnd%	0.105	-0.405	-0.436	-0.388	-0.224	-0.021	-0.514	-0.130	0.038	-0.416	0.058	0.154	0.629*	0.113	-0.247	-0.377	1.000

Appendix K - Smoothed land use data

	Water%	Residential%	Industrial%	Forest%	Range %	Hay%	Agricultural %	Wetlands%
Site 1	1.58	67.60	3.42	27.40	0.00	0.00	0.00	0.00
Site 2A	1.58	67.01	3.44	27.96	0.00	0.00	0.00	0.00
Site 2B	1.53	66.89	0.00	28.00	0.00	0.00	0.00	3.59
Site 2C	1.27	55.93	2.90	23.51	2.27	11.10	0.00	3.01
Site 3	1.53	60.88	3.03	28.19	2.73	0.00	0.00	3.64
Site 4	1.67	59.04	3.23	31.90	0.00	0.00	0.00	4.16
Site 5	1.05	40.40	2.31	23.25	2.27	11.33	16.37	3.03
Site 6	1.89	49.77	3.44	39.49	0.00	0.00	0.00	5.41
Site 7	1.27	29.89	2.33	26.63	2.52	13.70	20.17	3.49
Site 8	1.60	3.94	2.39	26.48	2.35	14.12	22.51	3.63
Site 9	0.90	21.49	1.20	27.69	2.15	16.06	28.49	2.02
Site 10	0.80	33.76	2.22	20.28	1.49	13.84	27.00	0.61
Site 11	0.09	8.06	0.00	19.30	1.57	19.90	50.91	0.19