5-7-2016

Interweaving Geochemical and Geospatial Data to Identify High Concentrations of Metal Contamination from Copper, Lead, and Zinc within Utoy Creek, Atlanta Ga

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INTERWEAVING GEOCHEMICAL AND GEOSPATIAL DATA TO IDENTIFY HIGH CONCENTRATIONS OF METAL CONTAMINATION FROM COPPER, LEAD, AND ZINC WITHIN UTOY CREEK, ATLANTA GA

by

Ryan Walker

Under the Direction of Katie Price PhD

ABSTRACT

Utilizing geochemical and geospatial data to explore the spatial variability of metals within streambed sediment of a local waterway may help to identify anthropogenic input of copper, lead, and zinc in urbanized streams. Utoy Creek is an urbanized stream located just southwest of downtown Atlanta. Baseline trace metal values and a reference site were used to determine if copper, lead, and zinc concentrations were higher or lower than baseline or reference site values. The Atlanta Metro Region had over 2,100 miles of impaired streams listed on the 2008 303(d) list. This type of study can be used as a proxy to help determine how "impaired" local urbanized streams really are and identify areas of interest for future studies. For this study, 42 sites were selected for streambed sediment collection, chemical analysis was preformed, and GIS and statistical analysis were performed. This study shows that several areas in Utoy Creek show elevated metal concentrations of copper, lead, and zinc.

INDEX WORDS: Utoy Creek, Copper, Lead, Zinc, Stream Network, Atlanta

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by

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A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

Masters of Science

in the College of Arts and Sciences

Georgia State University

2016

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December 2016

DEDICATION

First and foremost this is for my mother for always providing an example of a person I should strive to be, for always being there to push me further, and for always being there for me. This is also for Kelsey and the rest of the Brennan family for pushing me forward and believing in me when I had trouble believing in myself.

ACKNOWLEDGEMENTS

I would like to thank Dr. Price, Dr. Deocampo, Dr. Dai, Dr. Horowitz, Dr. Meyer, Kent Elrick, and William Ballow for their time, guidance, help, and wisdom they have provided. I would also like to thank everyone in the Geoscience Department at Georgia State University.

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1 INTRODUCTION

Toxic metals, defined as individual or compound metals that negatively affect human or ecosystem health, are often byproducts produced by numerous industries and are a prime concern in regards to addressing water quality from urban runoff (US EPA, 1983). Urban runoff ranks as the second highest source of surface pollutants entering rivers (Walker et al., 1999). Urban runoff, specifically overland flow, typically contains significant amount of toxic metals (Sansalone, 1999) as well as nutrients, sediments, and other anthropogenic compounds (Jang et al., 2005). Up to 50% of the toxic metal content in urban runoff is in dissolved form (Erickson et al., 2013). In natural waters, these metals have low solubility and generally are removed by sedimentation or sorption (Pitt et al., 1999). However, as the water becomes more acidic, toxic metals readily dissolve into ion form. In this form, toxic metals are generally non-degradable and build up in food chains via bioaccumulation (Chen & Ray, 2001).

Zinc is a particularly troubling toxic metal because it can be detected at frequencies of 90% in urban runoff samples (Rangsivek & Jekel, 2005). It is one of the most prevalent toxic metals along with copper and lead (Rose et al., 2001). This is due to Zinc's diverse anthropogenic usage (Rose et al., 2001). Zinc comes from such sources as the manufacturing of brass and bronze alloys (Sen & Khoo, 2013), runoff from galvanized roofs (Rose et al., 2001), wear from brake pads (Walker et al., 1999), and wear from tire tread (Councell & Duckenfield, 2004). Zinc is essential for humans (US EPA, 2005) as well as for plant development (Rout & Das, 2003) at low to moderate levels where it only has low toxicity. At higher concentrations zinc can be toxic to plants (Rout & Das, 2003) and can decimate aquatic communities (USGS, 1993).

Like zinc, copper has diverse anthropogenic uses. Copper comes from such sources as wear from brake pads (Hulskotte et al., 2006), copper plumbing (Pavissich et al., 2010), treated lumber (Stilwell & Gorny, 1997) and algaecide (Bishop & Rodgers, 2012). Cooper is essential for plants at low concentrations (Yruela, 2005). At high concentrations, both acute and chronic, it may be toxic to biota (USEPA, 1985). Thee toxicity of copper is dependent upon the alkalinity of the water (USGS, 1999) as well as hardness and pH (Santore et al., 2001). The higher the acidity of the water the more toxic copper concentrations become to biota (USGS, 1999).

Lead has been used by humans since antiquity and comes from such sources as plumbing in older housing (Beattie et al., 1972), car batteries (Weijma et al., 2002), lead based paint (Farfel & Chisolm, 1990), and glass making (Hynes & Jonson, 1997). The toxicity of lead to humans has been well documented as it may effect multiple body systems including the brain, liver, and kidneys (WHO, 2016). Lead is a common environmental contaminant and may cause vascular, neurological, and genetic damage to mammals (Patrick, 2006), causes phytotoxicity and inhibits plant seed germination (Pourrut et al., 2011), and effects reproduction of fish (Tulasi et al., 1989).

The urbanization of the Atlanta Metro Region (AMR) has led to increased amounts of copper, lead, and zinc in the local water systems. Since 1970, the population of AMR has risen from about 1.5 million residents to about 4.2 million residents in 2013 (ARC, 2013). Corresponding to the population growth has been the rise in residential, industrial, commercial, and transportation sectors within the AMR. These sectors are projected to continue their rapid growth rate through 2030 (Miller, 2012). The increase in urbanization leads to changes in the AMR land cover. Greater areas of vegetation are covered with impervious surfaces which leads to stormwater being rerouted directly into stream channels as overland flow (Rose & Peters, 2001). This increased amount of urbanization can have a negative effect on the water quality, aquatic habitat, and biotic communities for local waterways in the AMR by changing the physical and chemical characteristics of the waterways (Fitzpatrick et al., 2004).

1.1 Objectives

The overarching objective of this study is to utilize geochemical and geospatial data to explore the spatial variability of metals within streambed sediment from Utoy Creek, a local waterway, which is located in an urbanized setting. The United States Geological Survey (USGS) has a monitoring station at the mouth of Utoy Creek (USGS Station #02336728). One specific objective was to determine whether the metal concentrations are higher or lower than the nationwide "baseline" estimates. An additional objective was to observe values from Utoy Creek to observed values in a nearby, non-urban, non-industrialized watershed.

1.2 Hypothesis

Due to the diverse anthropogenic use of copper, lead, and zinc as well as the high population density and traffic areas surrounding Utoy Creek, the original hypothesis was that copper, lead, and zinc concentrations will not be spatially uniform. Furthermore, metal concentrations should be higher in industrialized areas than non-industrialized areas.

2 Methods

2.1 Study watershed

Utoy Creek is located in the Piedmont region in the state of Georgia in the United States. Utoy Creek is a tributary of the Chattahoochee River, and this confluence is located approx. 3.5 miles southwest of downtown Atlanta. It is a part of the HUC #03130002 Middle Chattahoochee-Lake Harding Watershed (USEPA, 2016). The stream length of Utoy Creek is approximately 35 km. Both the north fork and main stem sections of Utoy Creek flow under Interstate-285 (Figure 1) on the way to the Chattahoochee River. Most of the land cover in the Utoy Creek drainage basin is urban, and the stream flows through both residential and industrial areas. The bedrock geology is primarily porphyritic granite, biotitic gneiss, and mica schist/gneiss/amphibole (Lawton, 1976). There were 42 sample sites chosen and five random duplicate samples were taken for quality control. The primary objective was to identify copper, lead, and zinc concentrations. However, other known metals that are primarily contributed by population density were measured as well.

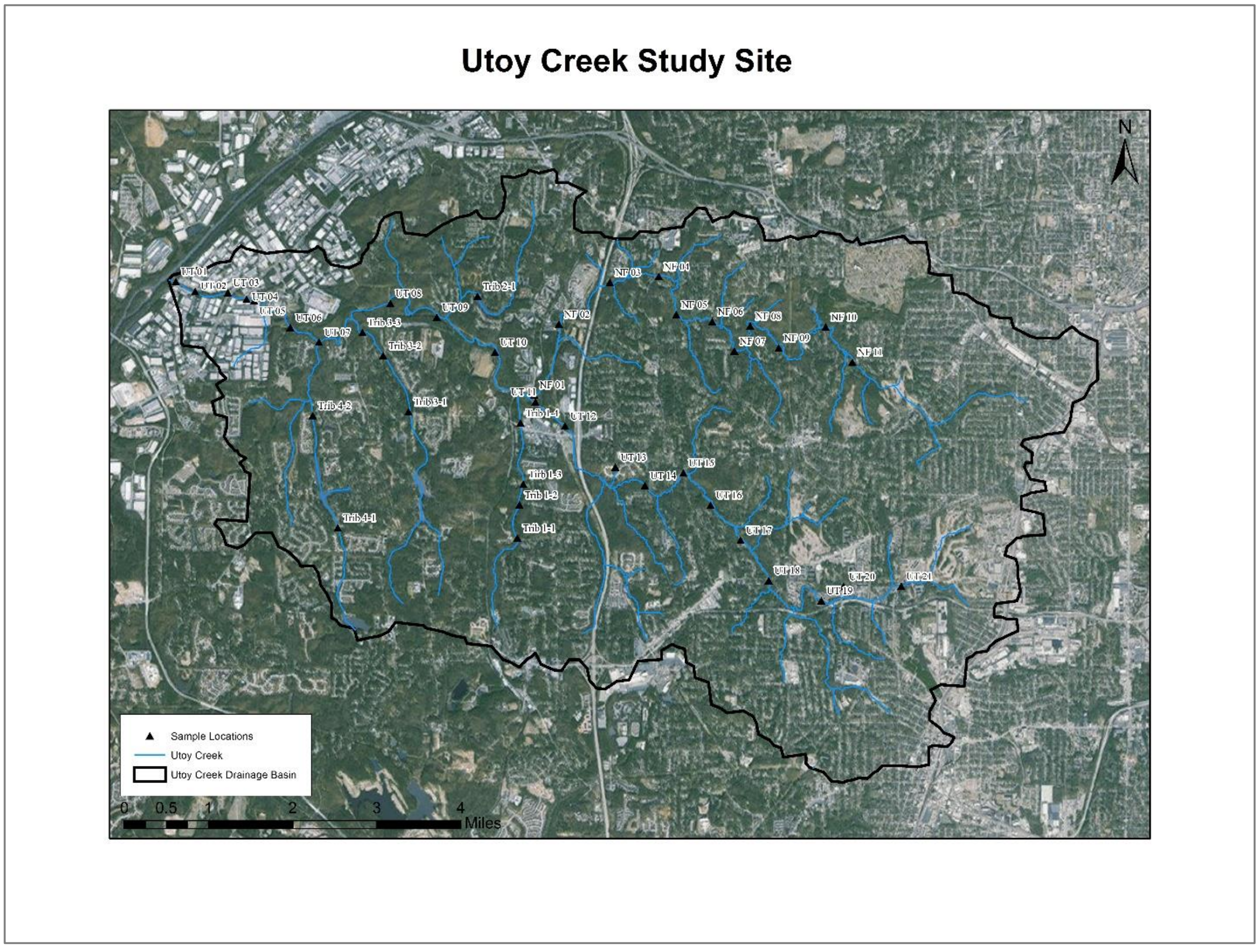

Figure 1. Utoy Creek study site. This map shows the drainage basin for Utoy Creek as well as the sample locations taken for this study. For reference, Interstate-285 can be seen running north-south in the middle of the drainage basin. Interstate-20 is located just north of the drainage basin going from east to west, and the Chattahoochee River can be seen in the northwest portion of this map.

2.2 Sample Collection

Streambed sediment sampling of Utoy Creek occurred from October to December of 2014. Representative composite samples were taken from the left bank, right bank, and any sand bars present at each of the 42 sampling sites. Sediment was collected near the water's edge and only the upper most 0.5 inch of sediment was collected. This type of sample was collected because streambed sediment in these areas have been shown to accumulate trace elements that may not be detectable in a water grab sample (Horowitz, 1985). For every ten sites sampled, a duplicate sample was taken at a random site for quality control. All samples were placed in an iced cooler after being taken and transferred to a lab for chemical analysis. GPS coordinates were collected at each site using a standard handheld Garmin (+/- 3m).

2.3 Chemical Analysis

All samples were mixed thoroughly for homogenization prior to wet sieving. The wet sieving technique was used to retain all grains < 63 µm. The sediment grains in this size fraction was chosen because they have the ability to accumulate trace metals as well as toxins and may reenter the water column as suspended sediment (FL EPD, 2002). The wet sieved sediment was then freeze dried (Horowitz & Elrick, 1987; Horowitz & Elrick 1988). The < 63 µm sediment was then broken down through acid digestion through HNO_3-HF-$HClO_4$. All samples, including replicates, were then run through chemical analysis by use of Atomic Absorption Spectroscopy (AAS) at Georgia State University, Department of Geoscience. Once metal concentrations were determined, the values were then compared to Georgia's Environmental Protection Division's (EPD) freshwater fishing streams water quality standards (GA R&R, 2016).

2.4 Baseline

Baseline values were used for comparison purposes and are intended to represent a "natural" geochemical signature in the absence of human impact. The baseline values were taken from Horowitz (1991) and were estimated using models derived from a combination of multiple regression and principal components analyzed from 61 samples taken from un-impacted watersheds across the United States and calibrated to reflect local geological signatures. The baseline values are estimates from samples all over the United States and will be compared to

Bear Creek which represents a local reference site. Bear Creek metal concentration values represent actual conditions of a mostly forested watershed.

2.5 Reference Site: Bear Creek

A lightly-impacted watershed (Bear Creek) was identified, for comparison of metal concentrations between our primary, urbanized watershed (Utoy Creek). The mouth of Bear Creek is approximately located 30 miles southwest of downtown Atlanta and the stream length is perennial stream length is approximately 15 miles. Like Utoy Creek, Bear Creek is located in the Piedmont physiographic region and is a part of the Middle Chattahoochee-Lake Harding Watershed. The bedrock is mineralogically similar to Utoy Creek and primarily contains porphyritic granite, aluminous schist, biotitic gneiss, and calc-silicate granite gneiss (Lawton, 1976). Five sample site locations were chosen, and one duplicate sample was collected for quality control.

Bear Creek samples were collected in November 2015. Sample collection followed the same protocol as used in Utoy Creek sampling. However, the samples were shipped to ALS Minerals for chemical analysis via ICP-AES. The samples were again wet sieved to retain < 63 µm fraction, and samples were then oven dried. This element of the research design was included to understand stream metals concentrations in a relatively undisturbed stream system (Gregory & Calhoun, 2007), as opposed to a direct, pairwise comparison between Utoy and Bear Creeks.

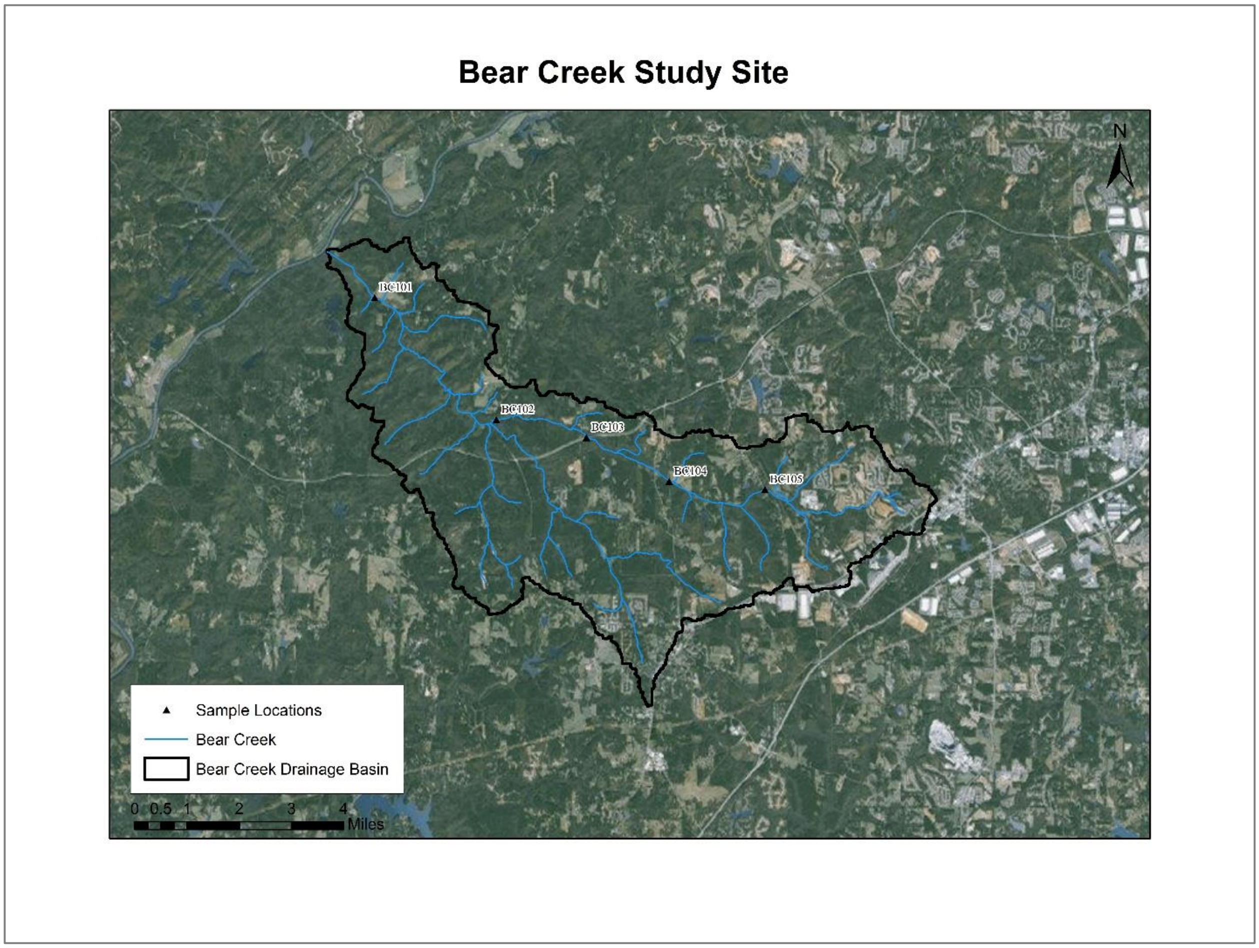

Figure 2. Bear Creek drainage basin with sample locations. Bear Creek is located just west of Fairburn, Georgia. The Chattahoochee River is located in the northwestern portion of the map.

2.6 GIS

The chemical analyses were linked to geospatial coordinates collected during sampling and entered into ArcGIS 10.1. Concentrations were visualized using graduated symbols to easily determine where the highest metal concentrations were located along Utoy Creek. Additionally, concentrations of copper, lead, and zinc were related to downstream distance for visualization of network sources and their downstream propagation (Lecce et al., 2011). Also, 2010 population density data was obtained from the US Census Bureau (US Census, 2010) for visual analysis of metal concentrations and high density areas within the Utoy Creek watershed.

2.7 Statistical Analysis

SPSS Statistics 23 was utilized to analyze the metals concentration data. The chemical analysis data was run through using histograms, scatter plot graphs, Pearson's and Spearman's correlations, and the Mann-Whitney U Test. Histograms were utilized to see the distribution of frequency of metal concentrations. Scatter plot graphs were utilized to determine regression analysis as well as correlations between metal concentrations and ratios between metals and iron and aluminum. Pearson's and Spearman's correlations were utilized to quantify the relationships between metal concentrations for metals that were normally distributed (Pearson's) and metal concentrations that were not normally distributed (Spearman's). The Mann-Whitney U Test was utilized to compare metal concentrations between Utoy Creek and Bear Creek.

3 RESULTS

3.1 Metal Concentrations

Table 1. Lists the results of metal concentration of all 42 sample sites (Figure 1). Cu, Co, Cd, Pb, and Zn are in ppm. Al and Fe are in percent. Easting and Northing refer to UTM NAD 83 Zone 16 N.

Site	Cu	Co	Cd	Pb	Zn	Al %	Fe %	Easting	Northing
NF 01	45	17	0.3	76	180	10.2	4.4	730677.0	3734882.0
NF 02	44	16	0.4	84	170	9.3	4.0	731060.7	3736036.6
NF 03	63	21	0.5	120	320	10.9	5.0	731840.0	3736695.0
NF 04	51	18	0.5	100	220	9.9	4.1	732614.0	3736806.0
NF 05	45	19	0.4	80	160	10.1	3.7	732910.0	3736209.0
NF 06	69	22	0.7	140	310	10.5	5.0	733484.0	3736112.0
NF 07	64	22	0.6	120	290	10.4	4.7	733849.0	3735653.0
NF 08	59	18	0.4	110	220	12.5	5.0	734089.0	3736056.0
NF 09	66	23	0.3	120	200	12.6	5.6	734553.0	3735721.0
NF 10	90	26	0.9	180	370	10.9	6.1	735294.0	3736068.0
NF 11	74	19	0.6	140	255	10.6	5.1	735731.0	3735524.0

Trib 1-1	24	16	0.2	62	160	12.2	5.1	730462.0	3732606.0
Trib 1-2	16	16	0.1	40	100	11.5	2.8	730481.0	3733133.0
Trib 1-3	23	19	0.1	56	150	11.5	4.0	730539.0	3733461.0
Trib 1-4	43	26	0.2	64	200	10.8	5.3	730469.0	3734429.0
Trib 2-1	41	16	0.2	67	210	10.3	5.4	729725.7	3736450.4
Trib 3-1	29	20	0.1	48	120	10.5	3.7	728681.0	3734566.0
Trib 3-2	39	26	0.1	57	160	11.0	4.6	728255.0	3735446.0
Trib 3-3	37	24	0.2	43	140	10.4	4.2	727918.0	3735807.0
Trib 4-1	47	21	0.2	38	120	11.4	5.0	727599.0	3732699.0
Trib 4-2	43	32	0.1	45	150	10.0	6.2	727156.0	3734468.0
UT 01	56	25	0.4	72	860	10.2	4.3	724927.0	3736541.0
UT 02	37	17	0.1	58	330	12.0	3.7	725238.0	3736392.0
UT 03	57	20	0.3	81	560	10.2	4.4	725758.0	3736385.0
UT 04	51	24	0.4	70	550	9.6	4.6	726073.7	3736388.9
UT 05	51	22	0.3	67	460	10.8	4.5	726339.3	3736161.9
UT 06	55	30	0.4	75	910	9.8	4.7	726766.0	3735855.0
UT 07	60	29	0.4	77	590	10.5	4.7	727229.0	3735636.0
UT 08	60	22	0.3	85	220	10.7	4.6	728288.0	3736278.2
UT 09	57	19	0.3	78	190	9.8	4.5	729083.0	3736114.2
UT 10	51	20	0.2	110	160	10.6	4.3	730068.0	3735554.9
UT 11	62	28	0.4	81	220	9.5	5.4	730698.0	3734770.0
UT 12	68	23	0.4	78	210	9.8	4.9	731179.0	3734400.0
UT 13	39	19	0.2	60	130	11.9	5.4	731937.2	3733476.9
UT 14	95	26	0.4	95	250	11.4	5.1	732476.0	3733486.0
UT 15	80	26	0.3	87	220	10.8	5.3	733082.0	3733702.0
UT 16	110	27	0.4	100	280	10.8	5.3	733529.0	3733202.0
UT 17	70	19	0.2	50	160	12.4	3.4	734022.0	3732657.0
UT 18	120	31	0.5	120	360	10.3	5.7	734484.0	3732029.0
UT 19	110	35	0.7	200	350	9.7	6.0	735332.0	3731731.0
UT 20	76	32	0.4	96	290	11.4	6.5	735723.4	3731813.2
UT 21	110	30	0.4	110	280	11.3	6.7	736495.8	3732018.9

Copper was found to be within the range of 16-120 ppm. Site Trib 1-2 was the lowest concentration at 16 ppm and site UT 18 was the highest concentration at 120 ppm. Cobalt was found to be within the rage of 16-35 ppm. Sites Trib 4-1, Trib 1-2, NF 02 and Trib 2-1 were the lowest concentration at 16 ppm and site UT 19 was the highest concentration at 35 ppm. Cadmium concentrations ranged from 0.1 to 0.9 ppm. Six sites, most of which are tributaries for Utoy Creek, were at the lowest concentration at 0.1 ppm and site NF 10 was the highest concentration at 0.9 ppm. Lead was found to be within the rage of 38-200 ppm. Site Trib 4-1 was the lowest concentration at 38 ppm and site UT 19 was the highest concentration at 200 ppm. Zinc was found to be within the range of 100-910 ppm. Site Trib 1-2 was the lowest concentration at 100 ppm and site UT 06 was the highest concentration at 910 ppm. Aluminum was found to be within the rage of 9.3-12.6%. Site NF 02 was the lowest concentration at 9.3% and site NF 09 was the highest concentration at 12.6%. Iron was found to be within the range of 2.8-6.7%. Site Trib 1-2 was the lowest concentration at 2.8% and site UT 21 was the highest concentration at 6.7%.

Table 2. Lists the results of metal concentration of all five sample sites and duplicate sample. Cu, Co, Cd, Pb, and Zn are in ppm. Al and Fe are in percent.

Site	Cu	Co	Cd	Pb	Zn	Al%	Fe%
BC101	8	5	0.5	29	40	5.74	1.77
BC102	9	10	0.5	16	25	3.81	1.73
BC103	10	8	0.5	14	27	3.25	2.06
BC104	9	8	0.5	13	25	3.47	1.87
BC105	7	4	0.5	11	18	2.60	1.56

Copper was found to be within the range of 7-10 ppm. Site BC 105 was the lowest concentration at 7 ppm and site BC 103 was the highest concentration at 10 ppm. Cobalt was found to be within the range of 4-10 ppm. Site BC 105 was the lowest concentration at 4 ppm and site BC 102 was the highest concentration at 10 ppm. Cadmium at every sample site was found to be 0.5 ppm. Lead was found to be within the range of 11-29 ppm. Site BC 105 was the lowest concentration at 11 ppm and site BC 101 was the highest concentration at 29 ppm. Zinc was found to be within the range of 18-40 ppm. Site BC 105 was the lowest concentration at 18 ppm and site BC 101 was the highest concentration at 40 ppm. Aluminum was found to be within the range of 2.60-5.73 percent. Site BC 105 was the lowest concentration at 2.60 percent and site BC 101 was the highest concentration at 5.74 percent. Iron was found to be within the range of 1.56-2.06 percent. Site BC 105 was the lowest concentration at 1.56 and site BC 103 was the highest concentration at 2.06 percent.

Table 3. Lists the minimum and maximum metal concentration values for copper, lead, and zinc for Bear Creek (ppm), Regional Baseline (ppm), Utoy Creek (ppm), Georgia Rules and Regulations (391-3-19) for regulated substances and soil concentrations that trigger notification. Georgia EPD water quality standards for freshwater streams is also shown.

	Cu		Pb		Zn	
	Min	Max	Min	Max	Min	Max
Bear Creek (ppm)	7	10	11	29	18	40
Regional Baseline(ppm)	14	26	14	26	71	110
Utoy Creek (ppm)	16	120	38	200	100	910
GA R&R Soil Limits (ppm)		1500		400		2800
GA EPD Water Quality Limits (ppm)	0.005	0.007	0.0012	0.03	0.065	0.065

Table 4. Lists the error estimations for metal concentrations of the sample sites where duplicate samples were taken as well as the differences between the two samples. Also lists the ICP-AA and ICP-AES analytical errors.

		Cu	Co	Cd	Pb	Zn	Al	Fe
UT 06	Sample 1	55	30	0.4	75	910	9.8	4.7
	Sample 2	55	28	0.4	74	830	10.0	4.5
	Difference	0	2	0	1	80	0.2	0.2
UT 15	Sample 1	80	26	0.3	87	220	10.8	5.3
	Sample 2	74	22	0.3	80	210	9.8	4.6
	Difference	6	4	0.0	7	10	1.0	0.7
UT 12	Sample 1	68	23	0.4	78	210	9.8	4.9
	Sample 2	75	27	0.4	83	240	10.0	5.3

	Difference	7	4	0.0	5	30	0.2	0.4
NF 04	Sample 1	51	18	0.5	100	220	9.9	4.1
	Sample 2	57	19	0.5	110	240	10.1	4.3
	Difference	6	1	0.0	10	20	0.2	0.2
UT 09	Sample 1	57	19	0.3	78	190	9.8	4.5
	Sample 2	48	18	0.2	73	170	9.4	4.2
	Difference	9	1	0.1	5	20	0.4	0.3
ICP-AA (NIST 2709a)	Reference	34±1	13±1	0.4	17±1	103±4	7.4±0.2	3.4±0.1
	Sample 1	33	14	0.4	17	100	7.3	3.3
	Sample 2	34	12	0.4	17	110	7.4	3.4
ICP-AES*		<10%	<10%	<10%	<10%	<10%	<10%	<10%

*Errors reported for ALS minerals in Pavlowsky et al. 2010

3.2 Statistics

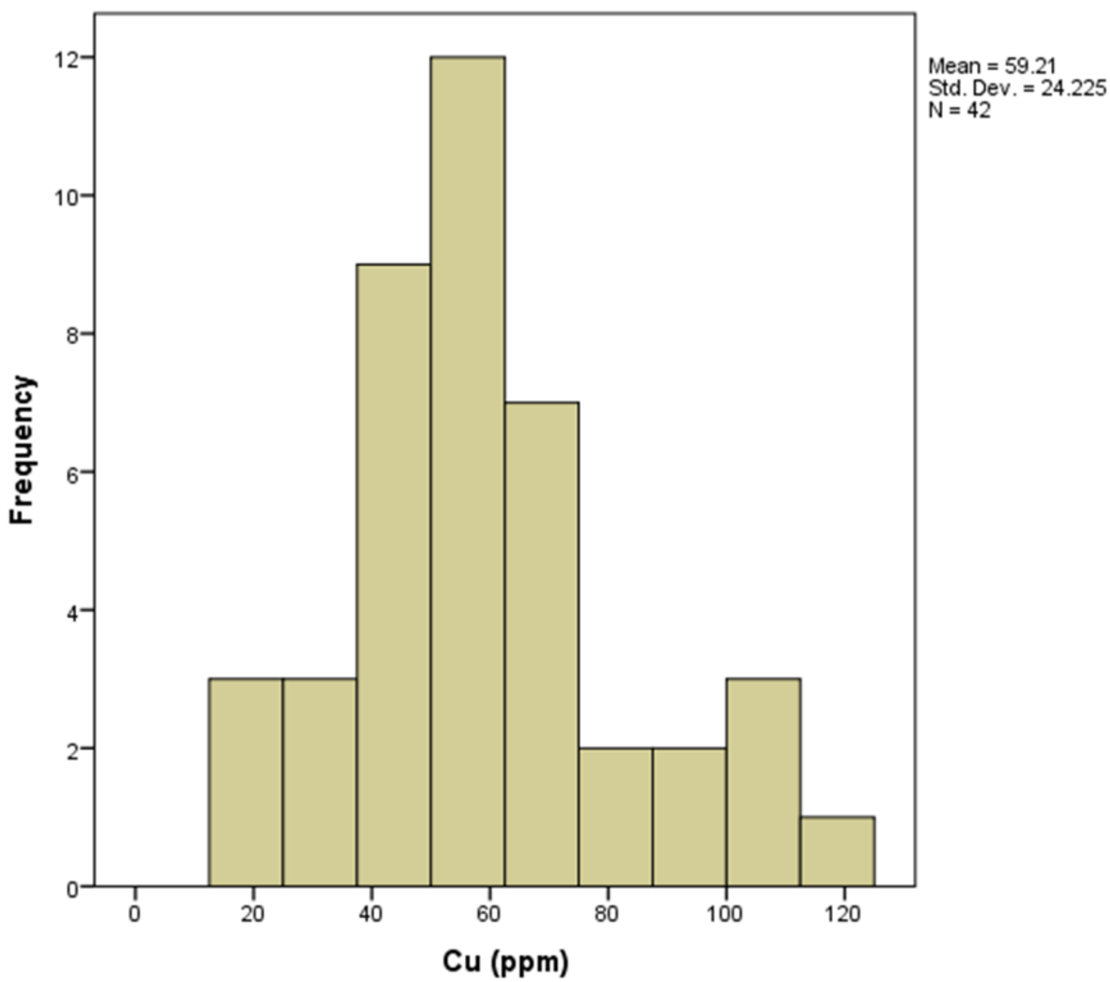

Figure 3. Histogram of copper. The y-axis is the number of occurrences (Frequency) and the x-axis is the concentration level (ppm) of copper.

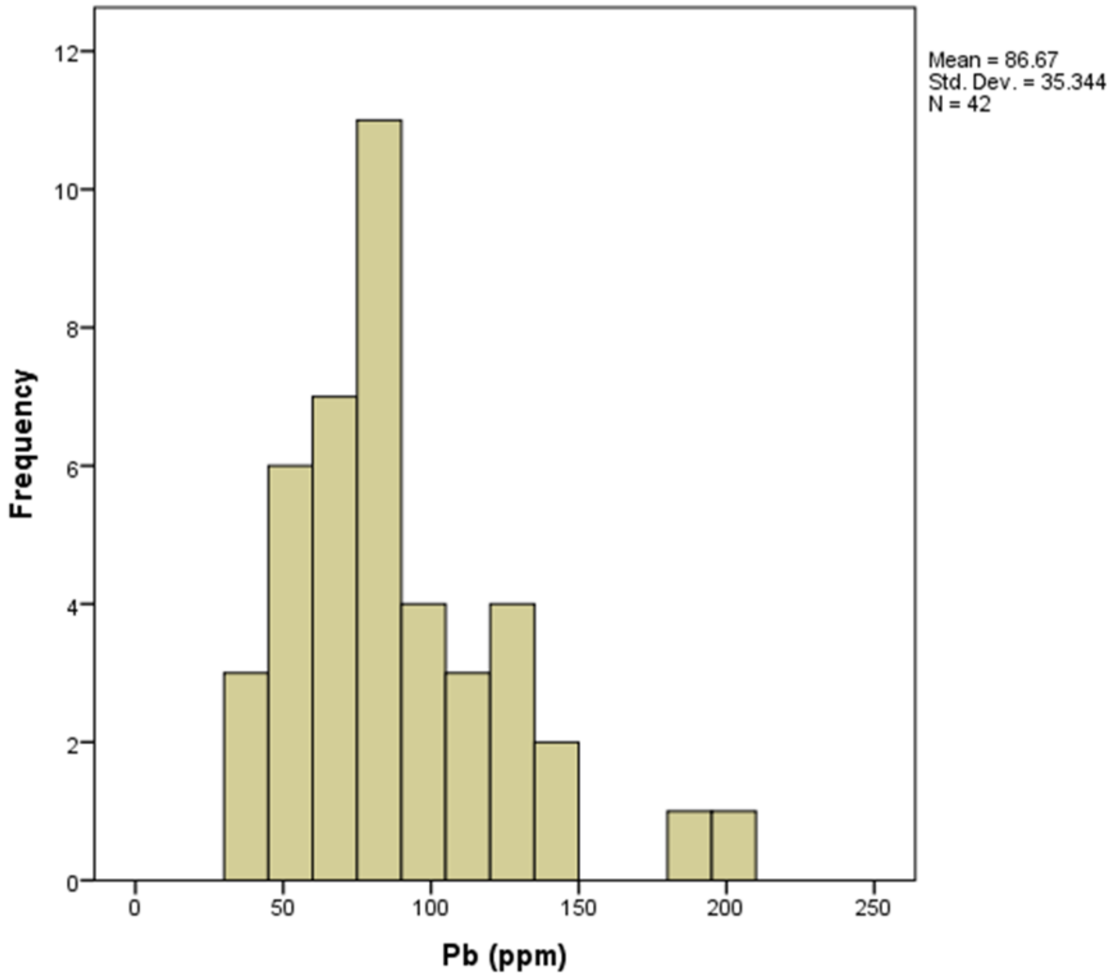

Figure 4. Histogram of Lead. The y-axis is the number of occurrences (Frequency). The x-axis is the concentration level (ppm) of lead.

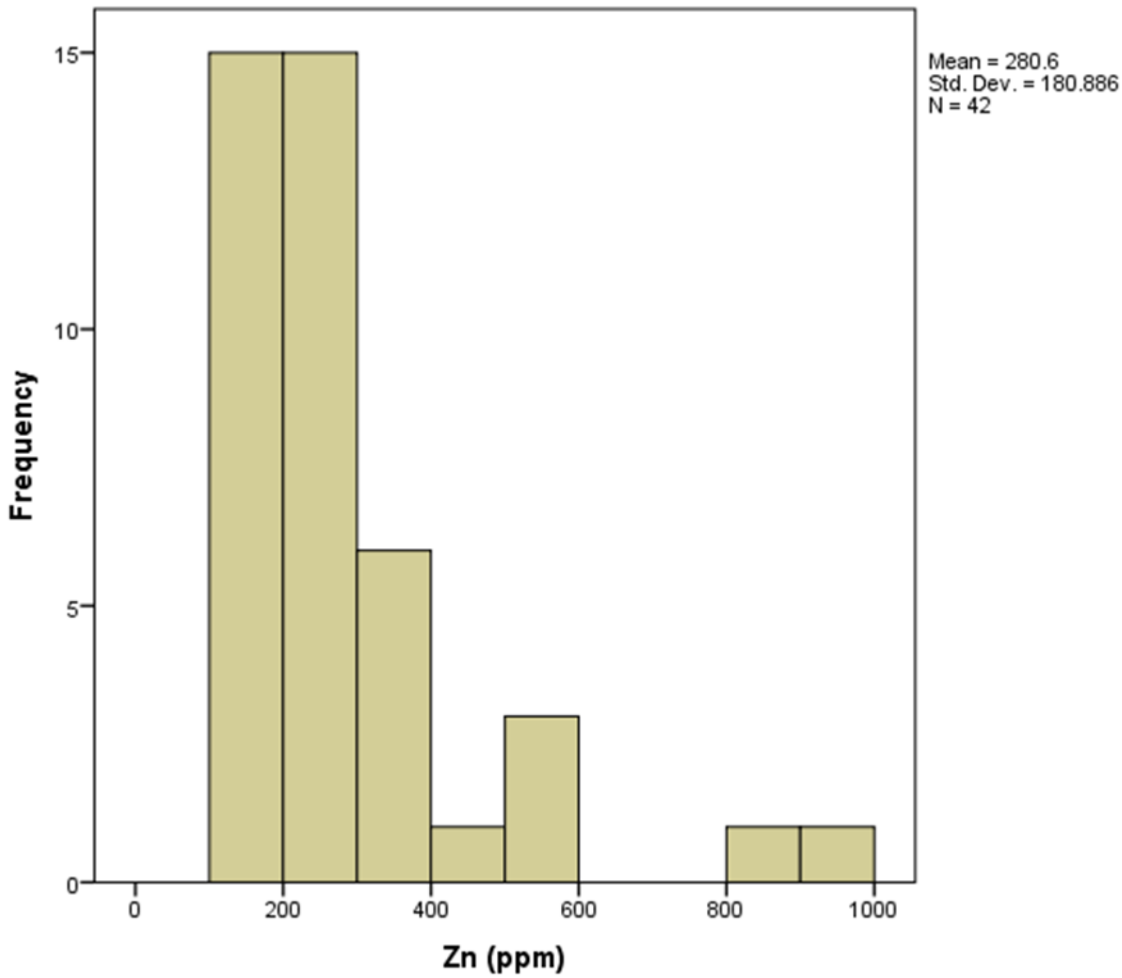

Figure 5. Histogram of Zinc. The y-axis is the number of occurrence (Frequency). The x-axis is the concentration (ppm) of zinc.

This histogram of copper (Figure 3) shows a mean concentration of 59 ppm and a standard deviation of 24. The histogram of lead (Figure 4) shows a mean concentration of 86 ppm and a standard deviation of 35. The histogram of zinc (Figure 5) shows a mean concentration of 280 ppm and a standard deviation of 180. The three histograms used 42 samples. All mean averages are above the baseline levels.

Table 5. Pearson's Correlation between Cu, Co, Cd, Pb, Zn, Al, and Fe for Utoy Creek.

Correlations

		Cu	Co	Cd	Pb	Zn	Al	Fe
Cu	Pearson Correlation	1	.623**	.655**	.701**	.223	-.086	.609**
	Sig. (1-tailed)		.000	.000	.000	.078	.293	.000
	N	42	42	42	42	42	42	42
Co	Pearson Correlation	.623**	1	.315*	.328*	.372**	-.244	.660**
	Sig. (1-tailed)	.000		.021	.017	.008	.060	.000
	N	42	42	42	42	42	42	42
Cd	Pearson Correlation	.655**	.315*	1	.869**	.347*	-.310*	.400**
	Sig. (1-tailed)	.000	.021		.000	.012	.023	.004
	N	42	42	42	42	42	42	42
Pb	Pearson Correlation	.701**	.328*	.869**	1	.165	-.123	.493**
	Sig. (1-tailed)	.000	.017	.000		.149	.219	.000
	N	42	42	42	42	42	42	42
Zn	Pearson Correlation	.223	.372**	.347*	.165	1	-.297*	.061
	Sig. (1-tailed)	.078	.008	.012	.149		.028	.351
	N	42	42	42	42	42	42	42
Al	Pearson Correlation	-.086	-.244	-.310*	-.123	-.297*	1	.014
	Sig. (1-tailed)	.293	.060	.023	.219	.028		.465
	N	42	42	42	42	42	42	42
Fe	Pearson Correlation	.609**	.660**	.400**	.493**	.061	.014	1
	Sig. (1-tailed)	.000	.000	.004	.000	.351	.465	
	N	42	42	42	42	42	42	42

**. Correlation is significant at the 0.01 level (1-tailed).

*. Correlation is significant at the 0.05 level (1-tailed).

A significant correlation at the 0.01 level for a 1-tailed test was found between Cu and Co, Cu and Cd, Cu and Pb, Cu and Fe, Co and Zn, Co and Fe, Cd and Pb, Cd and Fe, and Pb and

Fe. A significant correlation at the 0.05 level for a 1-tailed test was found between Co and Cd, Co and Pb, Cd and Zn, Cd and Al, and Zn and Al.

Table 6. Spearman's rho correlations of Easting and Northing for Utoy Creek.

Spearman's rho Correlations

		Cu	Co	Cd	Pb	Zn	Al	Fe	Easting	Northing
Cu	Correlation Coefficient	1.000	.556**	.740**	.777**	.574**	-.052	.537**	.638**	-.202
	Sig. (1-tailed)		.000	.000	.000	.000	.371	.000	.000	.100
	N	42	42	42	42	42	42	42	42	42
Co	Correlation Coefficient	.556**	1.000	.321*	.255	.436**	-.187	.591**	.125	-.321*
	Sig. (1-tailed)	.000		.019	.051	.002	.118	.000	.216	.019
	N	42	42	42	42	42	42	42	42	42
Cd	Correlation Coefficient	.740**	.321*	1.000	.832**	.669**	-.359**	.344*	.538**	.160
	Sig. (1-tailed)	.000	.019		.000	.000	.010	.013	.000	.156
	N	42	42	42	42	42	42	42	42	42
Pb	Correlation Coefficient	.777**	.255	.832**	1.000	.539**	-.124	.442**	.679**	.098
	Sig. (1-tailed)	.000	.051	.000		.000	.217	.002	.000	.269
	N	42	42	42	42	42	42	42	42	42
Zn	Correlation Coefficient	.574**	.436**	.669**	.539**	1.000	-.247	.250	.010	.338*
	Sig. (1-tailed)	.000	.002	.000	.000		.057	.055	.475	.014
	N	42	42	42	42	42	42	42	42	42
Al	Correlation Coefficient	-.052	-.187	-.359**	-.124	-.247	1.000	.090	.233	-.317*
	Sig. (1-tailed)	.371	.118	.010	.217	.057		.286	.069	.020
	N	42	42	42	42	42	42	42	42	42
Fe	Correlation Coefficient	.537**	.591**	.344*	.442**	.250	.090	1.000	.469**	-.376**
	Sig. (1-tailed)	.000	.000	.013	.002	.055	.286		.001	.007
	N	42	42	42	42	42	42	42	42	42
Easting	Correlation Coefficient	.638**	.125	.538**	.679**	.010	.233	.469**	1.000	-.422**
	Sig. (1-tailed)	.000	.216	.000	.000	.475	.069	.001		.003
	N	42	42	42	42	42	42	42	42	42

Northing	Correlation Coefficient	-.202	-.321*	.160	.098	.338*	-.317*	-.376**	-.422**	1.000
	Sig. (1-tailed)	.100	.019	.156	.269	.014	.020	.007	.003	
	N	42	42	42	42	42	42	42	42	42

**. Correlation is significant at the 0.01 level (1-tailed).

*. Correlation is significant at the 0.05 level (1-tailed).

Spearman's rho correlations were used primarily for easting and northing as these two parameters are not normally distributed. A significant correlation at the 0.01 level for a 1-tailed test was found between Easting and Cu, Easting and Cd, Easting and Pb, and Easting and Fe. Northing and Fe were also significantly correlated at the 0.01 level. A significant correlation at the 0.05 level for a 1-tailed test was found between Northing and Co, Northing and Zn, and Northing and Al.

Table 7. Pearson's Correlation between Cu, Co, Cd, Pb, Zn, Al, and Fe for Bear Creek.

Correlations

		BCZn	BCPb	BCFe	BCCu	BCCo	BCAl
BCZn	Pearson Correlation	1	.956**	.299	.137	-.089	.963**
	Sig. (1-tailed)		.005	.313	.413	.443	.004
	N	5	5	5	5	5	5
BCPb	Pearson Correlation	.956**	1	.016	-.116	-.228	.984**
	Sig. (1-tailed)	.005		.490	.426	.356	.001
	N	5	5	5	5	5	5
BCFe	Pearson Correlation	.299	.016	1	.911*	.498	.072
	Sig. (1-tailed)	.313	.490		.016	.196	.454
	N	5	5	5	5	5	5
BCCu	Pearson Correlation	.137	-.116	.911*	1	.806*	-.026
	Sig. (1-tailed)	.413	.426	.016		.050	.483
	N	5	5	5	5	5	5

BCCo	Pearson Correlation	-.089	-.228	.498	.806*	1	-.097
	Sig. (1-tailed)	.443	.356	.196	.050		.438
	N	5	5	5	5	5	5
BCAl	Pearson Correlation	.963**	.984**	.072	-.026	-.097	1
	Sig. (1-tailed)	.004	.001	.454	.483	.438	
	N	5	5	5	5	5	5

**. Correlation is significant at the 0.01 level (1-tailed).

*. Correlation is significant at the 0.05 level (1-tailed).

A significant correlation at the 0.01 level for a 1-tailed test was found between Zn and Pb, Zn and Al, and Pb and Al. A significant correlation at the 0.05 level for a 1-tailed test was found between Fe and Cu, and Cu and Co. Both Utoy Creek and Bear Creek had significant correlations between Zn and Al as well as Cu and Co.

Table 8. Spearman's rho Correlations of Easting and Northing for Bear Creek.

Spearnman's rho Correlations

		BCZn	BCPb	BCFe	BCCu	BCCo	BCAl	Easting	Northing
BCZn	Correlation Coefficient	1.000	.821*	.616	.368	.132	.667	-.821*	.821*
	Sig. (1-tailed)		.044	.134	.271	.416	.109	.044	.044
	N	5	5	5	5	5	5	5	5
BCPb	Correlation Coefficient	.821*	1.000	.200	.205	.359	.900*	-1.000**	1.000**
	Sig. (1-tailed)	.044		.374	.370	.276	.019		
	N	5	5	5	5	5	5	5	5
BCFe	Correlation Coefficient	.616	.200	1.000	.821*	.359	.100	-.200	.200
	Sig. (1-tailed)	.134	.374		.044	.276	.436	.374	.374
	N	5	5	5	5	5	5	5	5
BCCu	Correlation Coefficient	.368	.205	.821*	1.000	.763	.051	-.205	.205
	Sig. (1-tailed)	.271	.370	.044		.067	.467	.370	.370
	N	5	5	5	5	5	5	5	5

BCCo	Correlation Coefficient	.132	.359	.359	.763	1.000	.359	-.359	.359
	Sig. (1-tailed)	.416	.276	.276	.067		.276	.276	.276
	N	5	5	5	5	5	5	5	5
BCAl	Correlation Coefficient	.667	.900*	.100	.051	.359	1.000	-.900*	.900*
	Sig. (1-tailed)	.109	.019	.436	.467	.276		.019	.019
	N	5	5	5	5	5	5	5	5
Easting	Correlation Coefficient	-.821*	-1.000**	-.200	-.205	-.359	-.900*	1.000	-1.000**
	Sig. (1-tailed)	.044		.374	.370	.276	.019		
	N	5	5	5	5	5	5	5	5
Northing	Correlation Coefficient	.821*	1.000**	.200	.205	.359	.900*	-1.000**	1.000
	Sig. (1-tailed)	.044		.374	.370	.276	.019		
	N	5	5	5	5	5	5	5	5

*. Correlation is significant at the 0.05 level (1-tailed).

**. Correlation is significant at the 0.01 level (1-tailed).

Spearman’s rho correlations were used primarily for easting and northing as these two parameters are not normally distributed. A significant correlation at the 0.01 level for a 1-tailed test was found between Easting and Pb, and Easting and Al. A significant correlation at the 0.01 level was also found between Northing and Pb, and Northing and Easting. A significant correlation at the 0.05 level for a 1-tailed test was found between Easting and Zn, and Easting and Al. A significant correlation at the 0.05 level was also found between Northing and Zn, and Northing and Al.

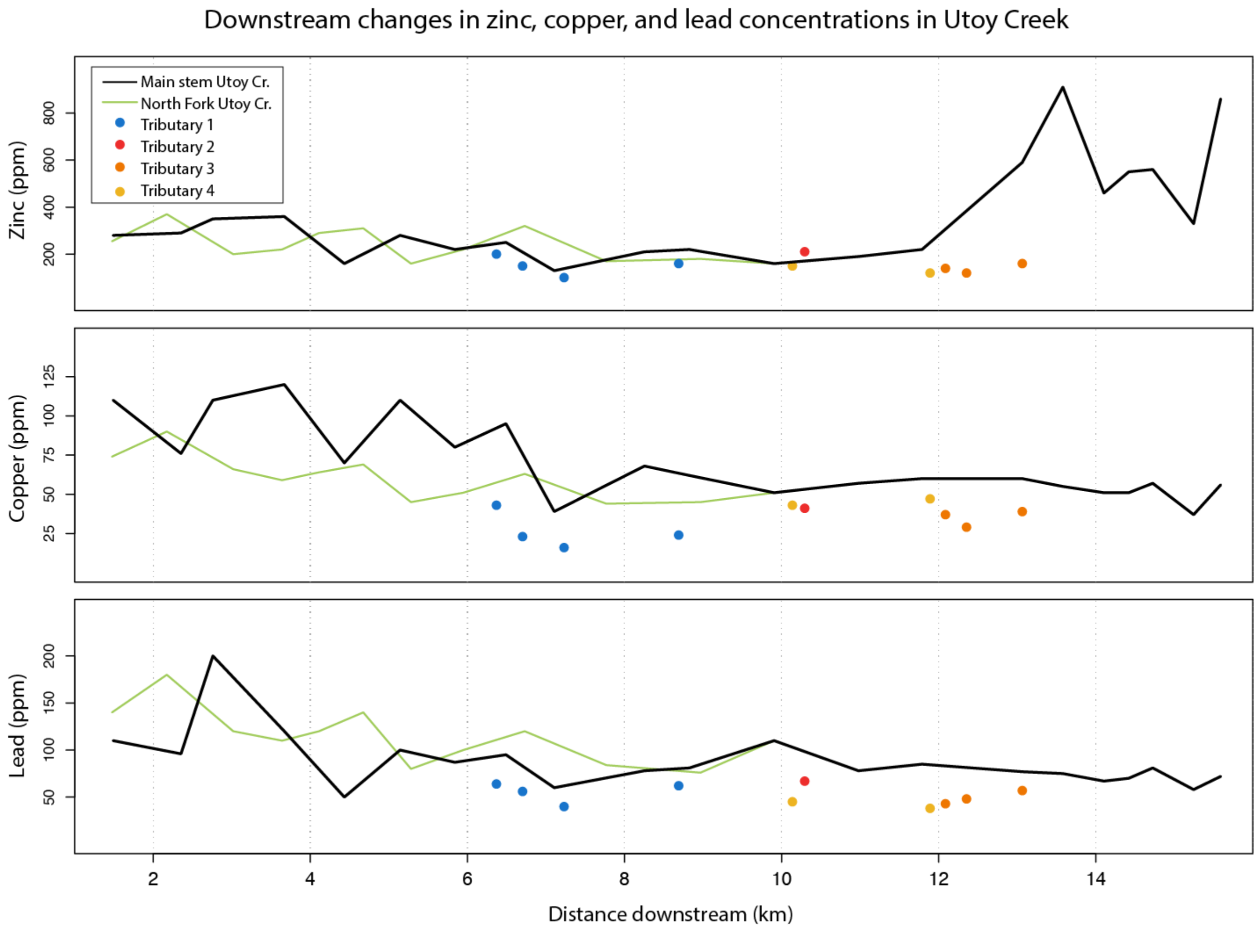

Figure 6. Shows zinc, copper, and lead concentrations as a function of downstream distance in the Utoy Creek system. The two main branches of Utoy Creek, the mainstem and North Fork, are shown as solid lines. Tributaries (corresponding to Figure 1) are shown as point values in the relative positions to the downstream distance where they enter Utoy Creek.

Figure 6 shows clear downstream trends of increasing zinc but decreasing copper and lead. It is evident from the figure that key point sources of these metals are located on the main branches, as concentrations are consistently lower in the smaller tributaries. While levels of copper and lead decline with distance from apparent sources in the upper portions of the watershed, zinc levels near the mouth of Utoy Creek are higher than all tributary levels, baseline values, and reference site (Bear Creek) values.

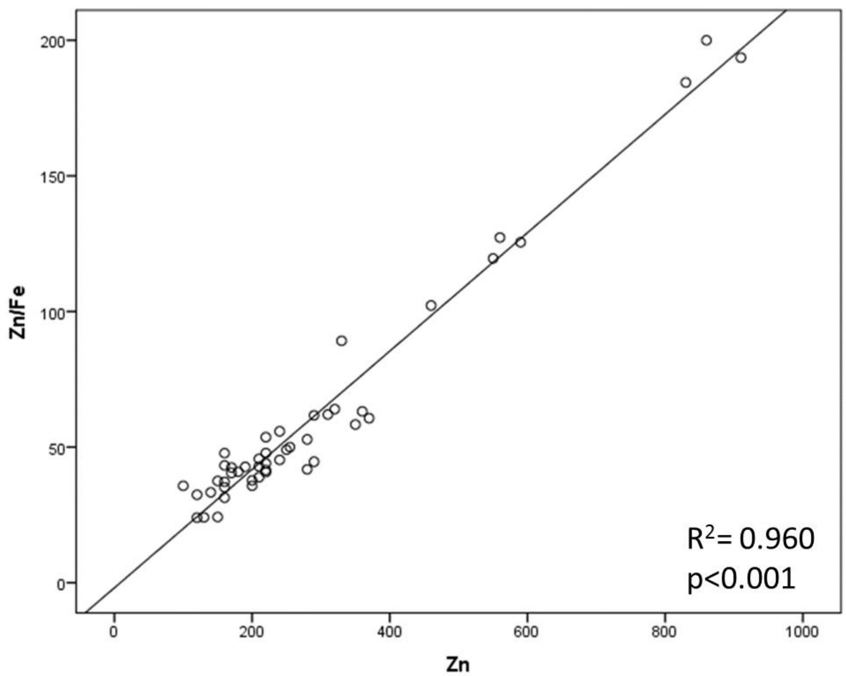

Figure 7. Graph showing the ratio of zinc to iron on the y-axis and zinc concentration (ppm) on the x-axis. This indicates that zinc is significantly correlated to the ratio of zinc to iron.

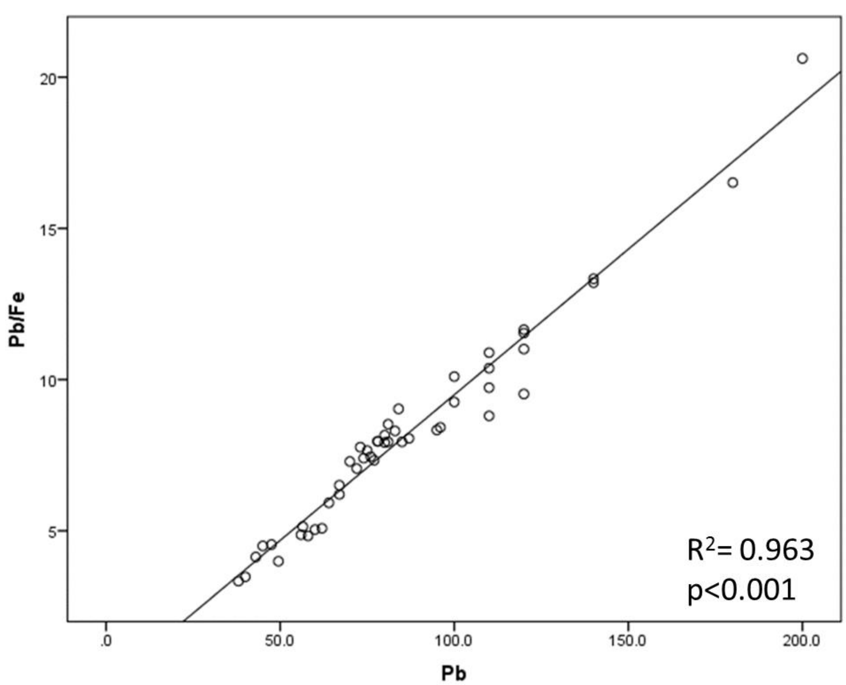

Figure 8. Graph showing the ratio of lead to iron on the y-axis and lead concentration (ppm) on the x-axis. This indicates that lead is significantly correlated to the ratio of lead to iron.

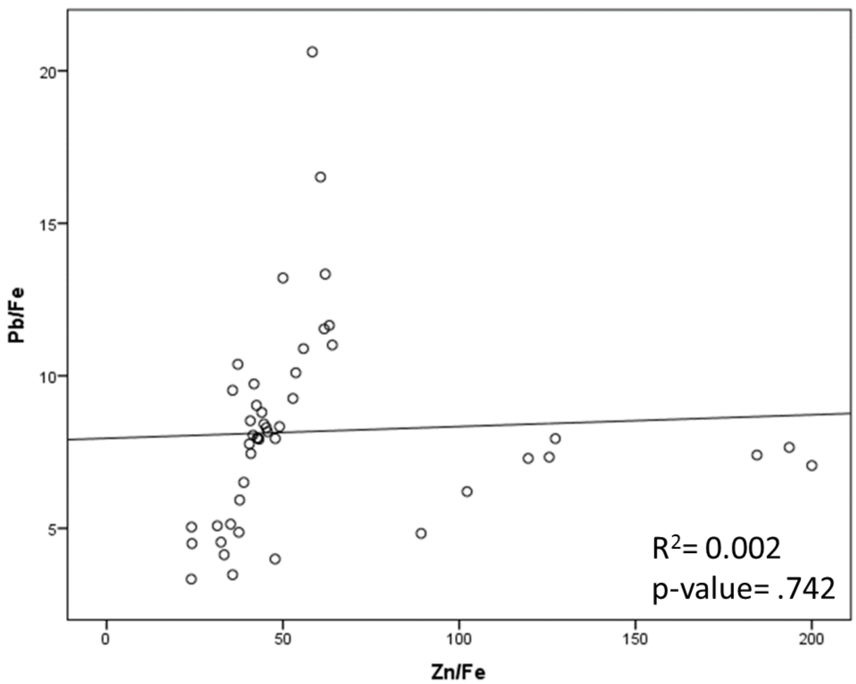

Figure 9. Graph showing the ratio of lead to iron on the y-axis and the ration of zinc to iron on the x-axis. This indicates that there is a correlation of the ratio of lead to iron and the ratio of zinc to iron when the ratio of zinc to iron is around 30-50.

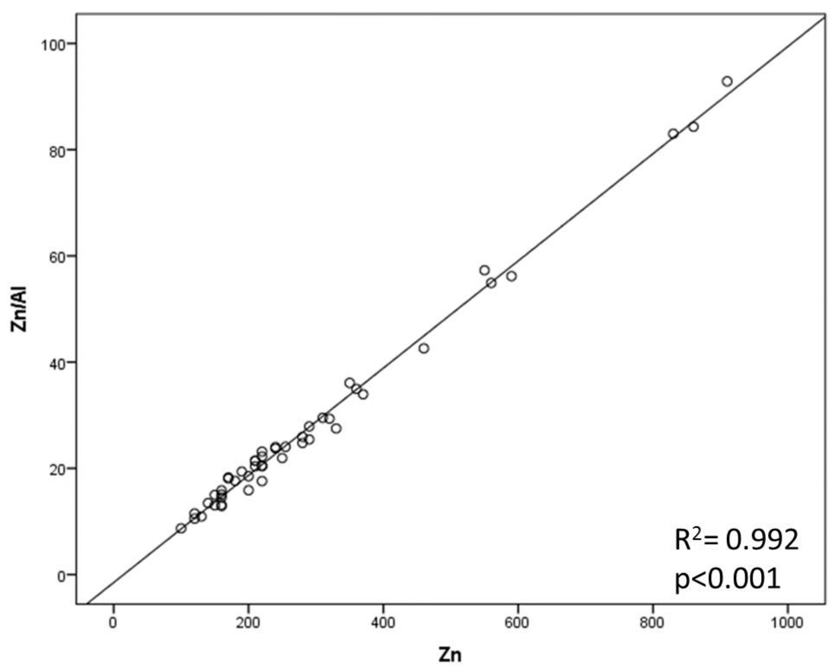

Figure 10. Graph showing the ratio of zinc to aluminum on the y-axis and the concentration of zinc (ppm) on the x-axis. This indicates that the concentration of zinc is significantly correlated to the ratio of zinc to aluminum.

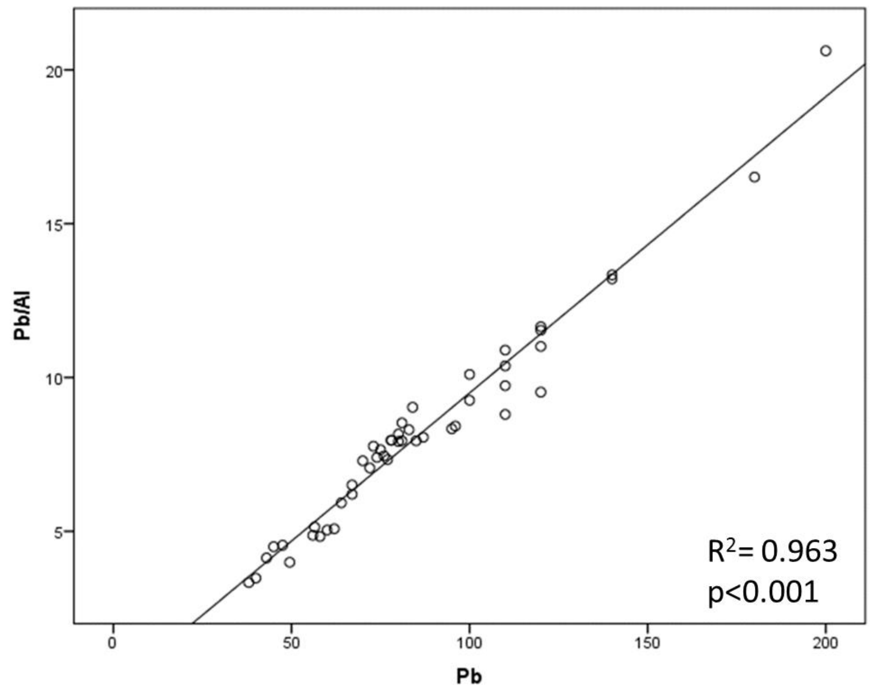

Figure 11. Graph showing the ratio of lead to aluminum on the y-axis and the concentration of lead (ppm) on the x-axis. This indicates that the concentration of lead is significantly correlated to the ratio of lead to iron.

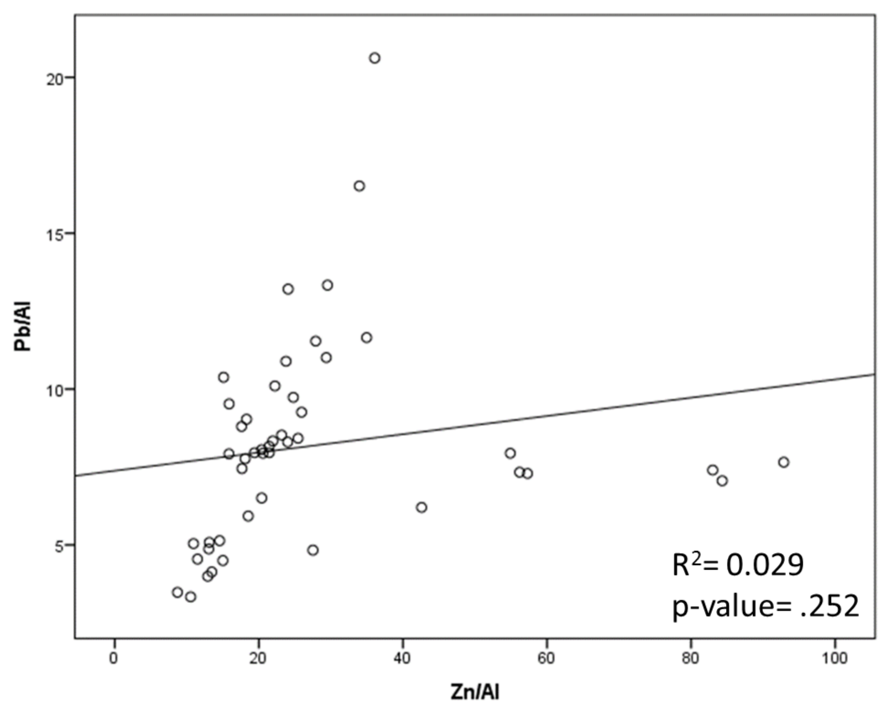

Figure 12. Graph showing the ratio of lead to aluminum on the y-axis and the ratio of zinc to aluminum on the x-axis. This indicates that there is correlation between the ratio of iron to aluminum and zinc to aluminum when the ratio of zinc to aluminum is between 10-40.

Figures 7 – 12 show the correlation between zinc and lead concentrations and the ratios of those metals with iron or aluminum. Figures 9 and 10 show that zinc and lead concentrations are significantly correlated to the ratio of zinc or lead to iron. Figure 11 indicates that there is a correlation of the ratio of lead to iron and the ratio of zinc to iron when the ratio of zinc to iron is around 30-50.

Figures 12 and 13 show that zinc and lead concentrations are significantly correlated to the ratio of zinc or lead to aluminum. Figure 14 indicates that there is correlation between the ratio of iron to aluminum and zinc to aluminum when the ratio of zinc to aluminum is around 10 - 40.

Table 9. Mann-Whitney U Test between Utoy and Bear Creek samples for Cu, Pb, and Zn. The "0" under the stream column represents Utoy Creek. The "1" under the stream column represents Bear Creek.

Ranks

Stream		N	Mean Rank	Sum of Ranks
Cu	0	42	26.50	1113.00
	1	5	3.00	15.00
	Total	47		
Pb	0	42	26.50	1113.00
	1	5	3.00	15.00
	Total	47		
Zn	0	42	26.50	1113.00
	1	5	3.00	15.00
	Total	47		

Test Statistics[a]

	Cu	Pb	Zn
Mann-Whitney U	0.000	0.000	0.000
Wilcoxon W	15.000	15.000	15.000
Z	-3.625	-3.625	-3.628
Asymp. Sig. (2-tailed)	.000	.000	.000
Exact Sig. [2*(1-tailed Sig.)]	.000[b]	.000[b]	.000[b]

a. Grouping Variable: Stream

b. Not corrected for ties.

The Mann-Whitney U Test results showed a significant difference in metal concentrations between Utoy Creek and Bear creek for copper, lead, and for zinc (Table 9). The 42 sample sites for Utoy Creek and the five sites for Bear Creek for the Mann-Whitney U Test.

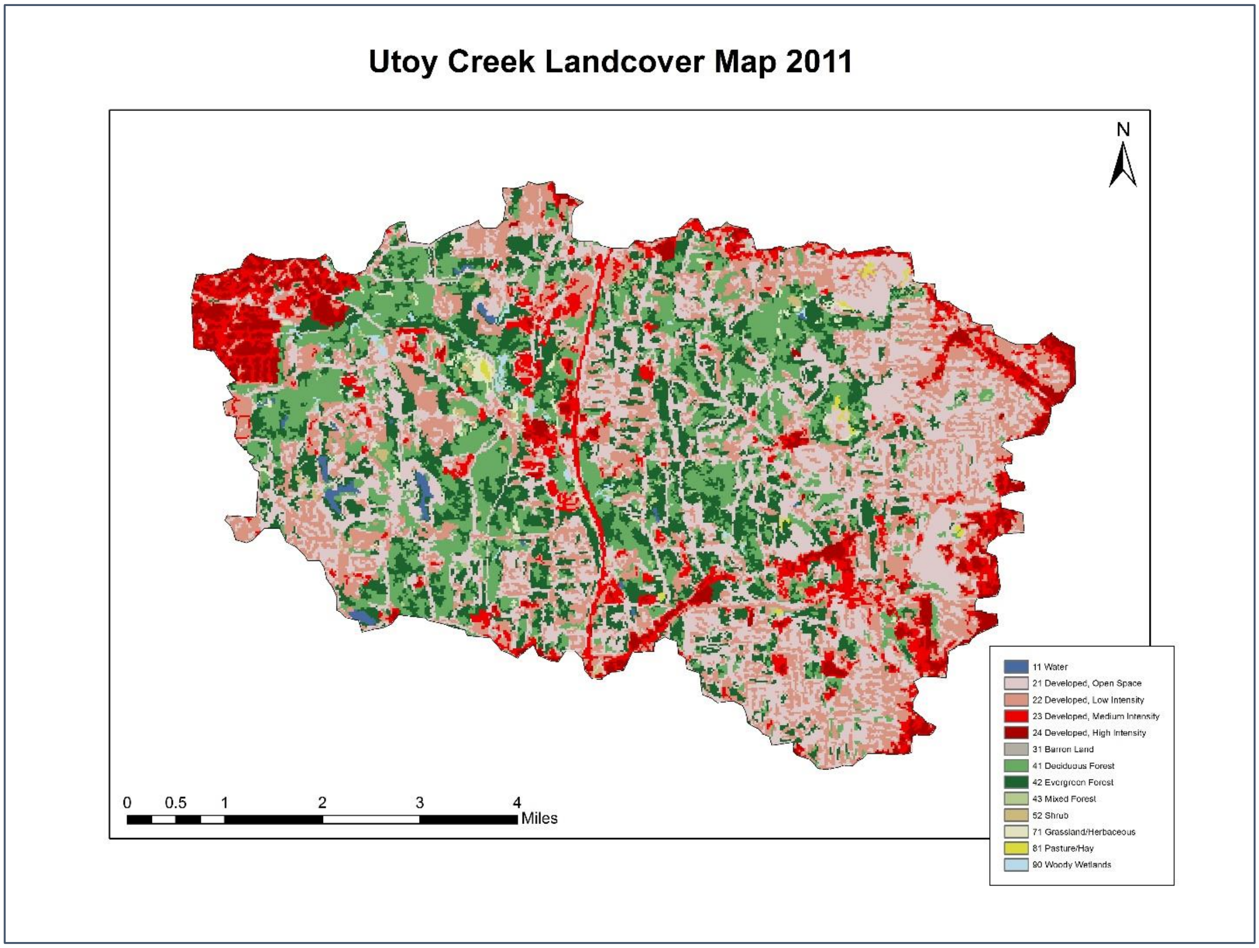

Figure 13. Land cover map of Utoy Creek drainage basin (Homer et al., 2015).

The highest percentage of landcover for Utoy Creek was the Developed, Open Space at 29% followed by Developed, Low Intensity at 22%. The next highest percentage of landcover was for Deciduous Forest at 16% and Evergreen Forest at 17%.

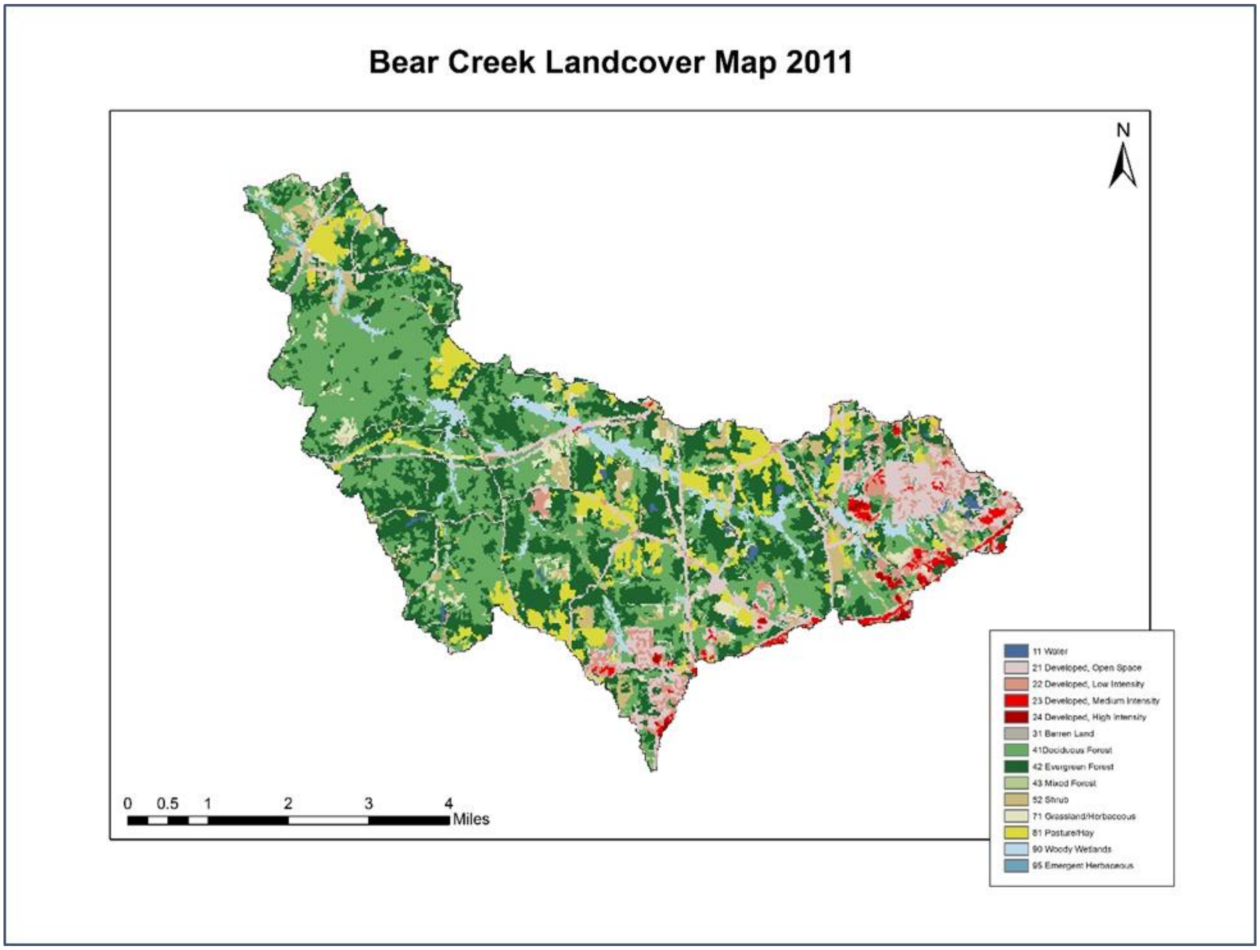

Figure 14. Land cover map of Bear Creek drainage basin. (Homer et al., 2015)

Table 10. Landcover classification breakdown for Bear Creek.

Landcover Classification	**Bear Creek** Percent	**Utoy Creek** Percent
11 - Water	0.62	0.50
21 - Developed, Open Space	10.68	28.93

22 - Developed, Low Intensity	3.82	22.45
23 - Developed, Medium Intensity	1.27	8.41
24 - Developed, High Intensity	0.32	4.59
31 - Barren Land	0.15	0.02
41 - Deciduous Forest	33.67	15.98
42 - Evergreen Forest	28.54	16.66
43 - Mixed Forest	0.47	0.73
52 - Shrub	4.44	0.36
71 - Grassland/Herbaceous	3.93	0.73
81 - Pasture/Hay	8.22	0.22
90 - Woody Wetlands	3.77	0.40
95 - Emergent Herbaceous	0.11	0.00

The highest percentage of landcover for Utoy Creek was for Developed, Open Space at 29% and Developed, Low Intensity at 22%. The highest percentage of landcover for Bear Creek was the Deciduous Forest at 34% followed by Evergreen Forest at 29%. The developed landcover classifications were lower than Utoy Creek with the highest percentage being for Developed, Open Space at 11%

4 Discussion

Baselines were created to help evaluate stream quality (Horowitz et al., 1991). The chemical analysis results show that most copper, lead, and zinc concentration levels were found to contain amounts higher than the max baseline (Table 1 & 2). Copper, lead and zinc are common in urban runoff and the increase in Atlanta's population could be the reason behind the high levels of zinc concentration found around Utoy Creek. Atlanta area's population has increased 125% from 1970 to 2000 (ARC, 2009) and is predicted to nearly double again by 2040 (ARC, 2009).

The metal concentration values determined for copper, lead, and zinc for both Utoy Creek and Bear Creek exceeded GA EPD water quality standards (Table 3) for freshwater streams. This study helps show how important streambed sediment sampling can be. Trace metals sorb to the < 63 µm sediment. This size of sediment can be deposited along the stream banks and stream beds and may also reenter the water column if stream discharge increases. Streambed sediment analysis is more likely to show what types of trace metals are in the stream as opposed to water grab samples (Horowitz, 1991).

All cooper concentration levels were found to be below the Georgia Rules and Regulations Soil Contamination levels (Table 3). The mean of the copper concentrations was found to be 59 ppm (Figure 3) and only three sample sites fell within the established baseline levels. The highest concentrations of copper were found near the mouth of Utoy Creek. Sites UT 14, UT 18, UT 19, UT 16, and UT 21 are all located near the headwaters of Utoy Creek (Figure 1, Figure 15) and had copper concentrations ranging between 95-120 ppm (Table 1). Sections of the headwaters of Utoy Creek run adjacent to Arthur B. Langford Jr. Parkway which is a limited access freeway. Wear from brake pads is one of the leading sources of copper for urban contaminant (Horowitz, 2009). The cause for the high copper levels in this area are most likely caused by high traffic volume.

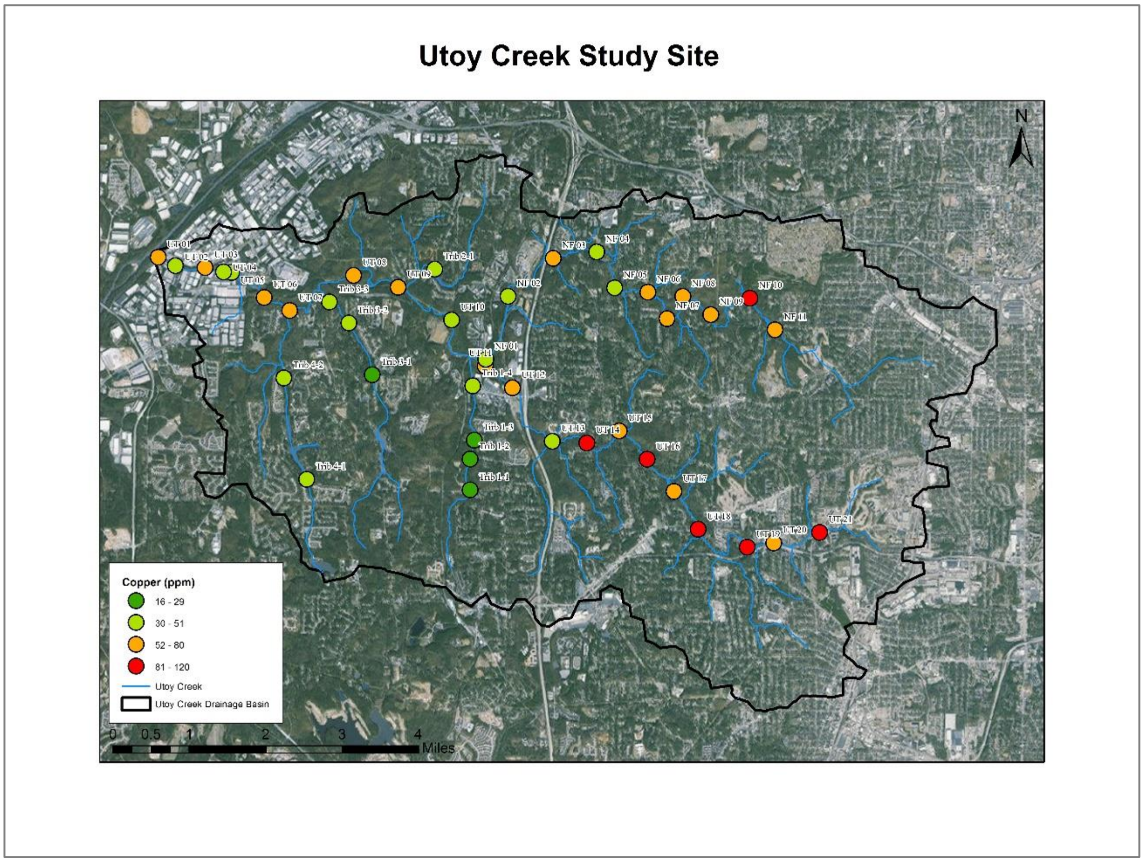

Figure 15. Graduated color map of copper concentration in Utoy Creek.

All lead concentration levels were found to be below the Georgia Rules and Regulations Soil Contamination levels (Table 3). The mean of the lead concentrations was found to be 86 ppm (Figure 4) and no sample sites fell within the established baseline levels. The highest concentrations of lead were found near the mouth of both North Utoy Creek and on the main stem of Utoy Creek. Site UT 19 is located near the headwaters of Utoy Creek (Figure 16) and had a lead concentration of 200 ppm. Site NF 10 is located in North Utoy Creek and had a lead concentration of 180 ppm. Site UT 19 is located in a densely populated area (Figure 18). Plumbing, car batteries, and paint are all the leading sources of lead contaminates and could be the causes of high lead levels. Site NF 10 is not located in a densely populated area. There could possibly be a few different sources at this location. This site is located near Westview Cemetery which is one of the oldest cemeteries in Atlanta. Lead has been used to line coffins and could be leaching into Utoy Creek (Jonker and Oliver, 2012). Also, there could be illegal dumping in the area. Further research is needed to determine the sources of these high lead levels.

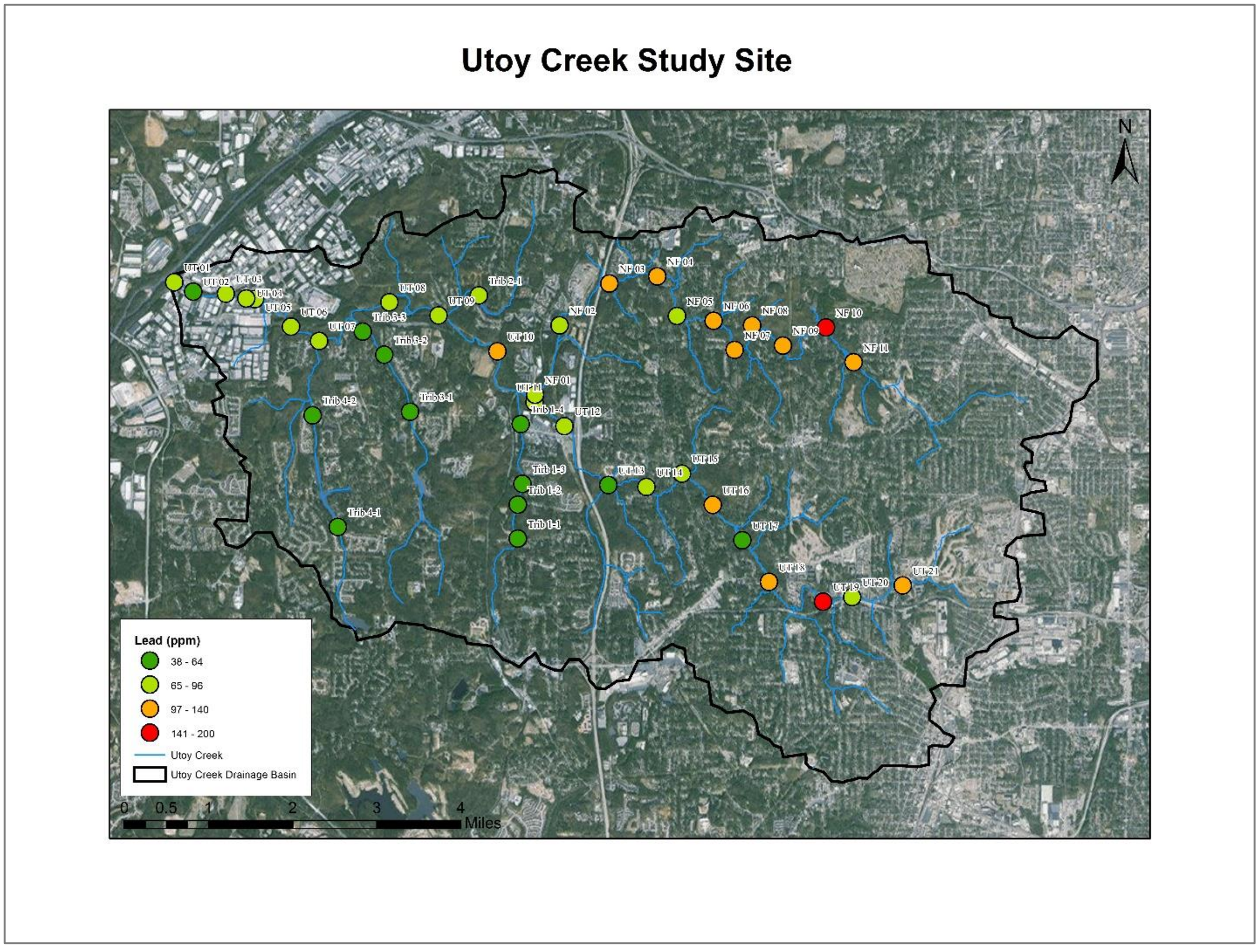

Figure 16. Graduated color map of lead concentration in Utoy Creek.

In comparison to Bear Creek, Utoy Creek has a much higher lead concentration. Bear Creek lead levels were between 11-29 ppm (Table 3) and Utoy Creek lead levels were between 38-200 ppm (Table 3). The primary anthropogenic sources of lead contamination are car batteries, plumming from old housing, and paint (Horowitz, 2009). As shown in the landcover tables, Utoy creek has a higher percentage of developed areas (Table 9, Table 10). The increased amount of developed areas is the most likely cause of the higher elevated lead concentrations in Utoy Creek as opposed to Bear Creek.

For this study all zinc concentration levels were found to be below the Georgia Rules and Regulations Soil Contamination levels (Table 3). However, USGS has recorded zinc concentration levels that exceed the Georgia Rules and Regulations Soil Contamination levels in the past which has caused the State of Georgia to implement a TMDL for Utoy Creek. There are specifically four areas in Utoy Creek where zinc concentration were especially high; UT 18 located near the headwaters of Utoy Creek (Figure 1, Figure 17) has a zinc concentration of 360 ppm, NF 10 located in the north fork of Utoy Creek (Figure 1) has a zinc concentration of 370 ppm, UT 01 located near the mouth of Utoy Creek (Figure 1) has a zinc concentration of 860 ppm, and UT 06 located near the Metaplating Galvanizing plant (Figure 19) has a zinc concentration of 910 ppm.

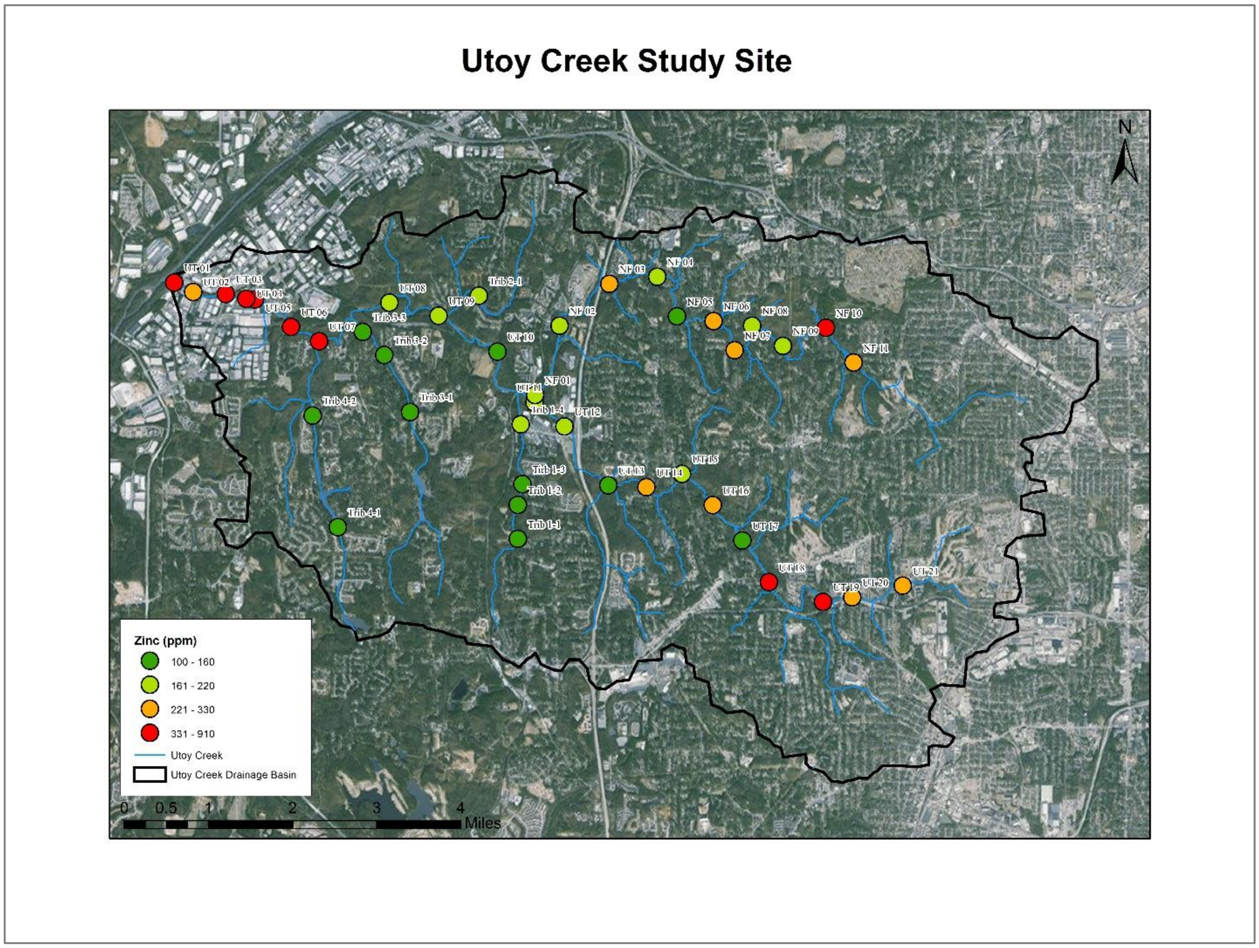

Figure 17. Graduated color map of Zinc concentration in Utoy Creek

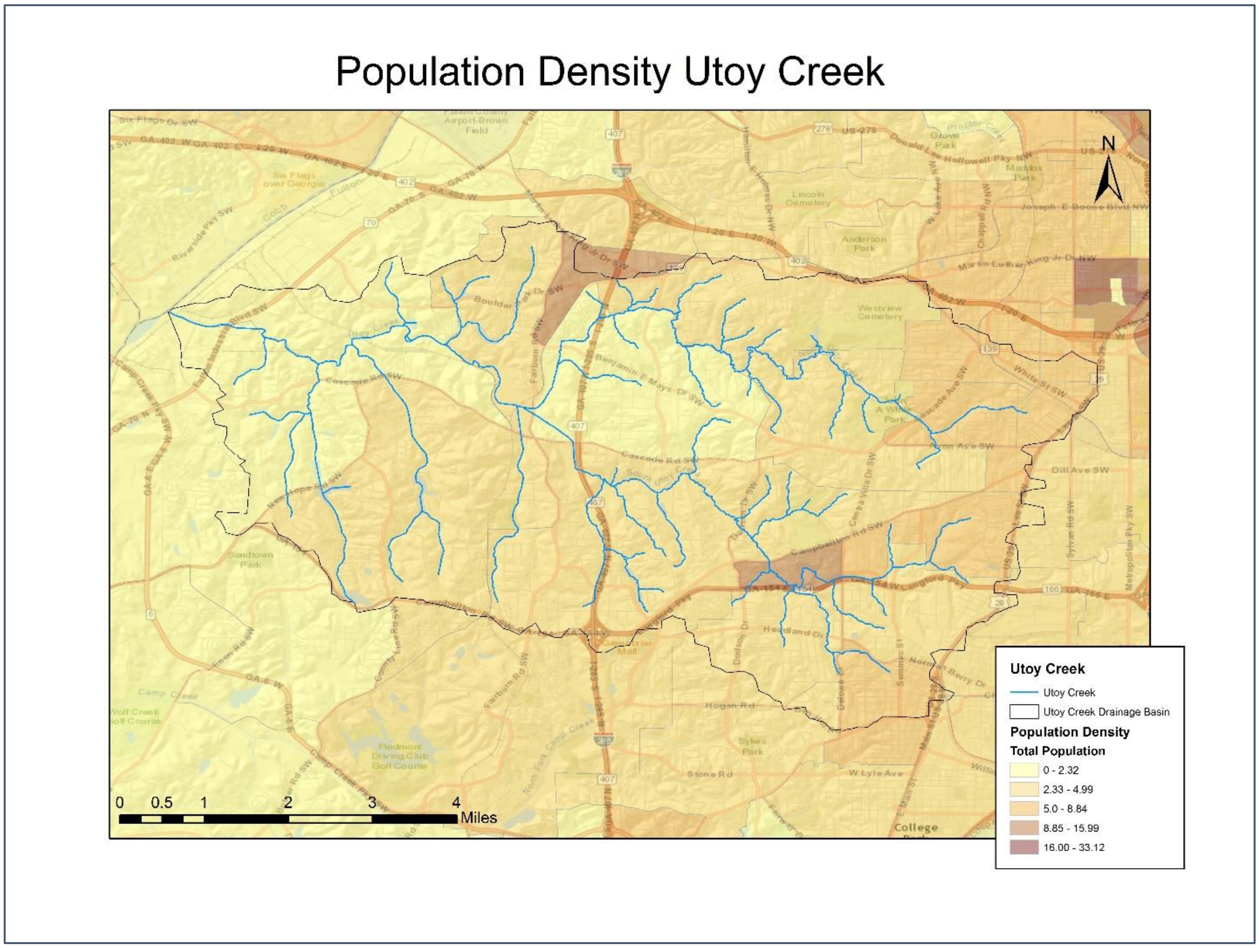

Figure 18. Population density map from US Census data 2010 (US Census, 2010). Map shows Utoy Creek drainage basin and corresponding population density near Utoy Creek.

Sites UT 18 and NF 10 are both located in residential areas, while sites UT 01 and UT 06 are located in industrialized areas. Zinc concentrations were visually compared to population density values in Utoy Creek (Figure 18). Site UT 18, located in near the headwaters of Utoy Creek (Figure 1), is inside a high population density area which is most likely the reason for high zinc levels due to heavy traffic, roofing, and galvanized piping. However, site NF 10, located in the north fork of Utoy Creek, does not correspond to high density and is not located near a major road. NF 10 is located near the Westview Cemetery which opened in October of 1884. Further investigations are needed to pinpoint the source of the zinc in this area.

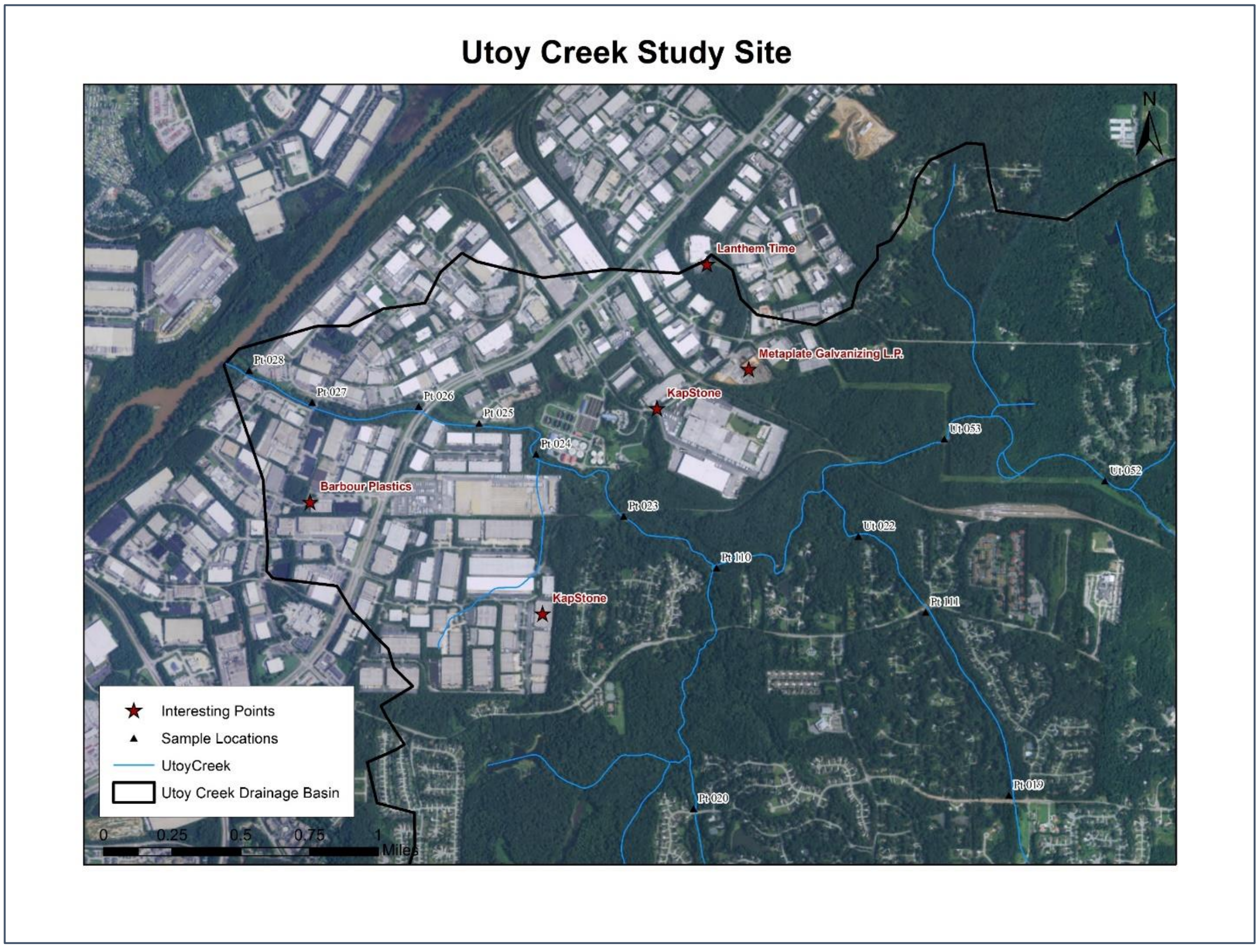

Figure 19. A close up view near the mouth of Utoy Creek. This map shows the locations of some the sample site locations as well as points of interest. For reference purposes, the mouth of Utoy Creek is at the northwest quadrant of the map. From north to south the interesting points are Lanthem Time, Metaplate Galvanizing L.P., KapStone, Barbour Plastics, and anther KapStone location.

Site UT 06 is located near the Metaplating Galvanization plant as well as a KapStone faclility (Figure 19) and shows the highest levels of zinc concentration recorded at 910 ppm (Table 1). Site UT 01 is located near Barbour Plastics facility (Figure 19) and shows the second highest levels of zinc concentration recorded at 860 ppm (Table 1). Both locations are located in a heavily industrialized area. The zinc concentrations are well above the max baseline level (Table 3) as well as the mean zinc concentration (Figure 5). Galvanizing is one of the leading sources of zinc contamination. At least one if not all of these facilities are contributing to high zinc concentrations in Utoy Creek.

Copper, lead, and zinc concentrations were normalized by comparing those values to a reference metal, i.e. iron and aluminum (Figures 7-12). The reference metals must originate from non-anthropogenic sources and help create a baseline to determine anthropogenic input from trace metals (FL EPD, 2002). All metals show a positive relationship with the reference metals. The zinc to iron graph (Figure 7) and zinc to aluminum graph (Figure 10) shows that most of the sites are clustered at lower concentrations of zinc with a few sites that are not grouped together at high zinc concentrations. The high cluster of points at the lower zinc concentration show a type of “baseline” and the higher zinc concentration points show human input of zinc. The same can be said for the lead to iron graph (Figure 8) and the lead to aluminum graph (Figure 11). The high cluster of points in the lower lead concentration show a type of “baseline” and the higher metal concentration sites show anthropogenic inputs.

Overall, Utoy Creek metal concentration values for copper, lead, and zinc were found to mostly be higher than the regional baseline values. However, Bear Creek metal concentration values for copper, lead, and zinc were found to be lower than the regional baseline values. This could indicated that the models used to create the baseline values might be over-predicting copper, lead, and zinc under natural conditions for the region.

4.1 Implications for Metro Atlanta

Utoy Creek and Bear Creek are just two tributaries of the Chattahoochee River. The differences between the metal concentrations in an urbanized, industrial watershed (Utoy Creek) to a less-developed stream (Bear Creek) are significant. AMR's impact on local waterways can be seen in the 2008 303(d) list that showed over 2,100 miles of stream in the AMR are classified as impaired (ARC, 2011). As such, Utoy Creek may be seen as a proxy relative to other highly urbanized streams in the AMR.

Something else to take note of is that the larger copper and lead metal concentration values were higher at the head of Utoy Creek than at the mouth of the stream. This is important to note because the USGS monitoring station for Utoy Creek is located on Great Southwest Parkway SW and is approximately 365 meters upstream from the mouth of Utoy Creek. The copper metal concentration values reach 120 ppm at UT 18 (Table 1) and are 56 ppm near the mouth of stream at UT 01 (Table 1). Lead metal concentration values reach 200 ppm at UT 19 (Table 1) and are at 72 ppm near the mouth of the stream at UT 01 (Table 1). This shows that the metal concentration values are being diluted by the time they reach the USGS monitoring station. This indicates that monitoring just the mouth of the stream is not capturing what is truly happening further upstream in the rest of the drainage basin. USGS may need to reexamine their sampling methodology to capture what is occurring in the entire drainage basin. High zinc concentrations have been recorded at the USGS station but zinc metal concentration values are highest near the mouth of the stream at 910 ppm at UT 06 and 860 ppm (Table 1) at UT 01.

4.2 Future Research Questions

We were able to satisfy our objects by determining that metal concentrations of copper, lead, and zinc are spatially variable within Utoy Creek. We were also able to determine that the metal concentration levels were found to be above the baseline value which shows anthropogenic effected areas. Also, we were able to determine that metal concentrations were higher in the industrialized watershed as opposed to the non-industrialized watershed.

However, the results also indicate that several key areas of further research are needed. Further research includes to locate the non-point source lead plume located in the north fork section of Utoy Creek and identify the source, locate the non-point source zinc plume located near the mouth of Utoy Creek, to quantify the relationships between population density and metals concentrations, to obtain traffic density information around Utoy Creek, and to look into new stream water quality policies and stream sampling methodology to more accurately reflect what is occurring in the entire stream drainage basin.

5 CONCLUSIONS

By combining geochemical data with geospatial methods we were able to determine the spatial distribution of copper, lead, and zinc concentrations along Utoy Creek. This study could be a good proxy for similar streams in the AMR, since most regional watersheds have been similarly affected by AMR’s increase in population. Numerous streams in the AMR are currently listed on the 303d list, including Utoy Creek (GA EPD, 2012). By repeating this process in other watersheds, we may be able to identify streams where it would take minimal effort to turn the impaired stream into a supporting stream (i.e. remove it from the EPA 303(d) list) and which streams would need more attention. This would then lead to better water quality in the region.

While lead and copper concentrations are located in residential areas, the highest zinc concentrations were found in the industrialized section of Utoy Creek. Zinc is a known toxin of certain fish and benthic macroinvertebretes (Besser and Leib, 1999). Since the industrialized section of Utoy Creek is near the mouth of the stream there is no chance for the concentration to dilute before it enters the Chattahoochee River. As stated previously, Utoy Creek can be used as a proxy stream for AMR streams. If high concentrations of metals such as zinc enter the Chattahoochee River, the biota of the stream may be greatly affected.

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APPENDICES

Appendix A

Appendix A.1

Appendix A.2

Appendix B

Appendix C