

Spatial Distribution of Lead, Zinc, Cadmium, and Nickel in the South Creek
Watershed, SW Missouri

Battlefield
Mall

Jimmy Trimble
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ABSTRACT

Many non-point source contaminants in fluvial systems originate in urban landscapes.

Metals are an important component of urban run off and are attributed to water quality degradation. Detention ponds can act as environmental buffers and impede the downstream transport of these contaminants. The current study examines metal contaminants in the South Creek Watershed which drains the urban area Springfield, Missouri. South Creek is heavily affected by urban landuse, however, an in stream detention pond exists on the creek and may serve to trap sediment bound metals. To test the effectiveness of the detention pond, sediment samples were collected from seven sites upstream of the pond and seven sites downstream. The $<0.63\ \mu\text{m}$ size fraction of each sample was analyzed for lead, zinc, cadmium, and nickel using an Inductively Coupled Plasma (ICP) spectrometer. Metal concentrations for lead, zinc, and cadmium generally decrease downstream. Nickel concentrations are more variable throughout the watershed. A T-test indicates that concentrations of zinc and cadmium are significantly different upstream and downstream of the pond at the 90% confidence level. Lead and nickel concentrations are not significantly different upstream and downstream of the pond at the 90% confidence level. The detention pond in the South Creek Watershed is not a significant trap for sediment bound metals originating in Springfield, MO.

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INTRODUCTION

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Recent water quality degradation in streams has been partly attributed to the affects of urbanizing areas. Degradation has been linked both to elevated nutrient input and metal input. Both point and non-point sources are to blame for water quality degradation. Much focus has been placed on regulating point sources such as

industrial discharge and wastewater treatment plants. More and more research is focusing on the affects of urban non-point sources such as parking lots, lawn care, construction sites, and roads.

A related body of research has developed that focuses on the usefulness of detention ponds and constructed wetlands as environmental buffers against these non-point source contaminants. These areas serve to trap sediment and the associated pollutants including metals and nutrients. Researchers have investigated the usefulness of wetlands and detention ponds to attenuate the impact of urbanizing areas and contaminant introduction in general. Studies have also examined phytoremediation in constructed wetlands as opposed to terrestrial phytoremediation. When compared to terrestrial phytoremediation, the anoxic soils in wetland areas immobilize pollutants and metals are held in nontoxic forms (Horne, 2000).

Watersheds that drain the urbanizing area of Springfield, Missouri suffer from degraded water quality due to non-point source introduction of metals and nutrients. The current study is focused primarily on four metal contaminants. The metals examined in this study are lead (Pb), zinc (Zn), Cadmium (Cd), and Nickel (Ni). The streams that drain this area empty into table rock lake, a very tourist dependent area. Degraded water quality has a detrimental affect on this tourism.

There is a lack of research concerning urban area influence on metal contaminants in Ozark streams. Much research has been conducted on the affects landfills have on sediment bound metal concentrations in Ozark streams (Mantei and Coonrod, 1989; Mantei and Sappington, 1994). Another study has evaluated the phases of metal contamination from several sources, including a relatively densely populated area of Springfield, MO. (Mantei and Foster, 1991). However, this study did not evaluate metals solely originating in the urban area from non-point sources.

Another study has examined the importance of various urban functions as sources of metals (Xanthopolous and Hahn, 1993). Xanthopolous and Hahn (1993)

concluded that urban streets are an important non-point source of metals. A study by the U.S. Environmental Protection Agency (EPA) (1990) identified sources of lead and zinc in an urban setting. According to this study, sources of lead include: gasoline; batteries; paint; and lead pipe. Sources of zinc include: metal corrosion; tires; road salt; wood preservatives; and paint. Bannerman (1991) related increases in zinc and lead concentrations to increases in traffic densities. Marsalek (1986) studied urban runoff in both water column samples and sediment samples and concluded that the most prominent toxic contaminants in urban runoff are trace metals. The most frequently encountered metals were zinc (98% of samples), nickel (87% of samples), and lead (78% of samples). Another study by Pitt and Baron (1989) studied important sources of dissolved metals in the urban system. Table 1 illustrates their findings for lead, zinc, cadmium, and nickel. The authors found that roof runoff has the highest input of dissolved zinc. According to the authors parking areas are important sources of dissolved nickel and lead. Streets and vehicle service areas are important sources of cadmium.

Table 1 Dissolved Metal Concentrations from Urban Runoff (adapted from Pitt and Baron, 1991)

Constituent μg/l	Urban Sources					
	roofs	parking	storage	streets	vehicle service	landscapes areas
Cadmium	0.8-30	0.7-70	2.4-10	0.7-220	8-30	0.04-1
Lead	13-170	30-130	30-330	30-150	75-110	9.4-70
Nickel	5-70	40-130	30-90	3-70	35-70	30-130
Zinc	100-1580	30-150	66-290	58-130	67-130	32-1160

Specifically, this study is focused on sediment bound metal contamination in South Creek, a tributary of Wilson Creek and ultimately the James River. South Creek is strictly an urban stream and suffers from the associated land uses. South Creek heads near the Battlefield Mall and essentially runs due west to its confluence with Wilson's Creek (Figure 1). A large portion of South Creek is channelized and is

confined to a concrete channel. South Creek receives many small tributaries that run through various subdivisions and other urban landscapes. A detention pond exists in the course of South Creek upstream of its confluence with Wilson's Creek. This study is focused on assessing sediment bound metal levels upstream and downstream of this detention pond. The research hypothesis is that this pond will attenuate the downstream affects of urbanization. Metal concentrations in stream sediments should be much lower than concentrations above the pond and concentrations of metals in the pond sediment should be the most elevated.

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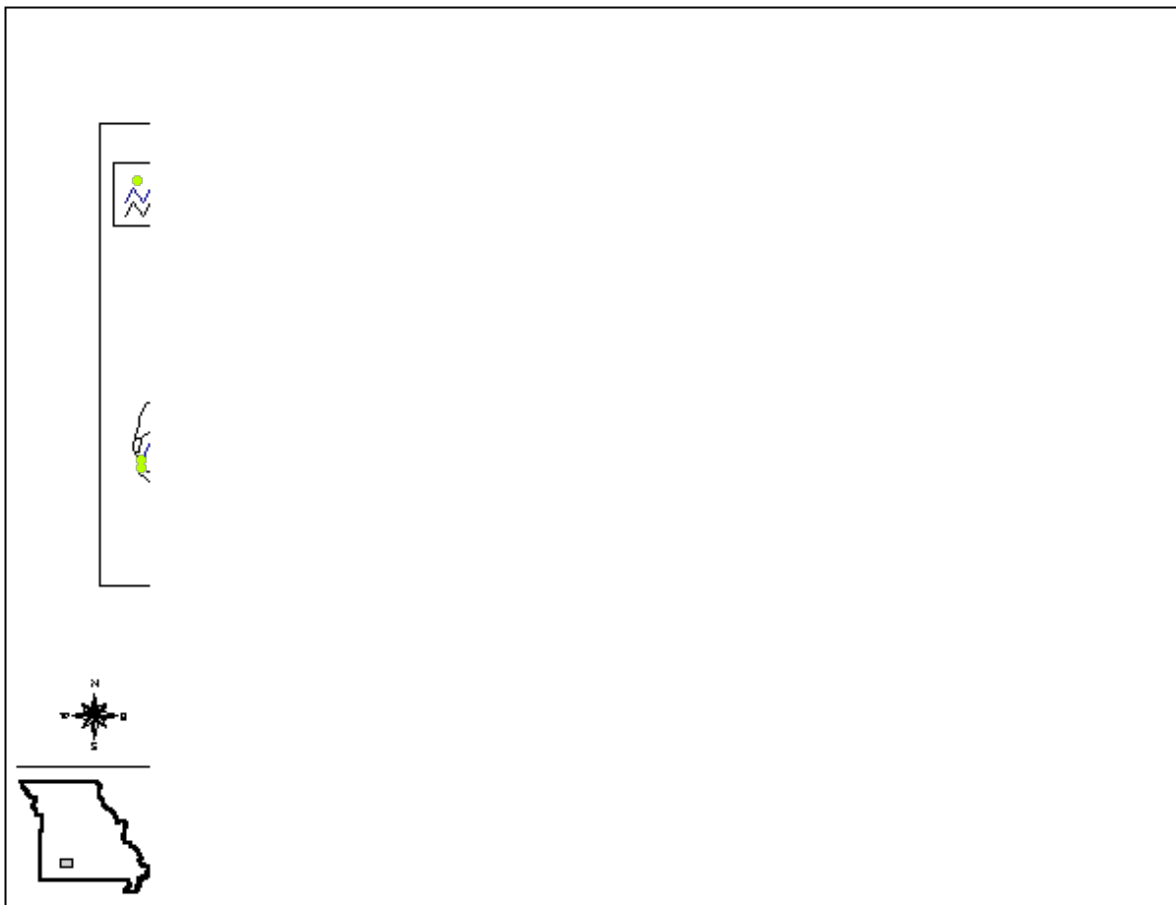


Figure 1 Regional Setting and Sample Site Locations

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METHODS

Methodology for the current study consisted of field work, sample preparation and analysis, data analysis, and gis analysis.

Field Methods Field methods consisted largely of collecting sediment samples from both in-channel and pond sites. Sediment samples were collected from fourteen in-channel sites (Figure 1). Fine grained sediment was collected from seven sites upstream of the pond and seven sites were sampled downstream of the pond. The samples were collected at an approximately equal interval both downstream and upstream of lake. Seven samples were also taken from a pit dug into the pond sediment. The pit was dug to a sufficient depth to represent the sediment in the pond. The geochemical results of these seven samples were averaged to represent the level of contamination in the lake sediment.

Each sample site was recorded with a handheld GPS unit for entry into a GIS. After sample collection, each was immediately bagged, sealed, and labeled for transport back to the lab.

Sample Preparation and Analysis Upon delivery back to the geomorphology lab at Missouri State University, each sample was wet sieved to pass through a 0.63 μm mesh sieve. The $<0.63 \mu\text{m}$ fraction of the samples were retained for geochemical analysis. When necessary, samples were disaggregated with a mortar and pestle to pass through the brass sieve. The sieved sediment was poured into a 250 ml beaker. Two grams of the sample were weighed and retained in a sample vile for analysis. An acid solution was created to dissolve samples and suspend the metals. Dionized water was used to dilute nitric acid (HNO_3) to a 500 ml, 2N solution. The 2g portion of each sample was treated with a single wash of the 2N HNO_3 solution and placed in a shaker

bath at 80°C for 24 hours. Once the samples were thoroughly dissolved they were centrifuged in order to further separate the dissolved sample from any particulate matter that remained. The dissolved sample solution for each sample was decanted into a vile for geochemical analysis. An Inductively Coupled Plasma (ICP) spectrometer was used to analyze the metal concentrations in each sample.

Prior to geochemical analysis, two standards and one blank were created in order to correctly calibrate the ICP for analysis of Pb, Zn, Cd, and Ni. A two point standard method was used. Standards were mixed using metal stock solution, nitric acid, and diionized water. One standard was created at the estimated low concentration of the samples which was estimated to be 20 ppm. The standard was diluted by a factor of ten, so the actual concentration evaluated by the ICP was 2 ppm. Another standard was created at 100 ppm and was likewise diluted by a factor of 10 to 10 ppm. A “blank” was also created to be analyzed by the ICP. The blank consisted of only diionized water and nitric acid. The blank was analyzed by the ICP in order to calibrate the instrument for any metals that may be present in these substances.

The ICP instrument was programmed to analyze the wavelength emitted from the four metals under investigation. Initially the two standards and the blank were analyzed in order to properly calibrate the machine. Each sample was subsequently analyzed and a printout of the results was produced. After analysis the samples were discarded and the lab equipment cleaned.

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Data Analysis The geochemical results were recorded in a spreadsheet program for analysis and display. Microsoft Excel was used to produce trend charts of the spatial distribution of the four metals under examination. The geochemical results were transferred to another software package and a student *t*-test was conducted in order to compare the mean of the samples upstream of the pond with the mean of the samples collected downstream of the pond.

GIS Methodolgy A GIS was used to organized and display spatial data. Relevant spatial data layers were downloaded from ESRI Inc. (www.esri.com) and stored in the GIS. Urban areas, street files, and stream files were downloaded and visually displayed. Sample site locations were downloaded from the GPS unit to a PC and combined with the other data layers. The sample site theme was joined with the spreadsheet of the sample analysis in order to qualitatively assess and display downstream spatial distribution of zinc, lead, cadmium, and nickel within South Creek.

Results

The original research hypothesis is that the control sample sites (upstream of pond) should have higher concentrations than sample sites downstream of the pond. The concentrations of Pb, Zn, Ni, and Ca at the all sample sites are shown in Table 2. The mean concentrations for the four metals at both upstream and downstream sites are given in Table 3. Average metal concentrations in the pond (site 8) are not abnormally high and do not suggest that the pond is a major sink for metals.

site	lead	zinc	cadmium	nickel	ds_dist(km)	X-coord	Y-coord
1	293.70	436.36	5.37	12.00	0	476248.81	4113128.49
2	196.40	441.32	5.74	10.58	0.35	475897.87	4113156.87
3	45.33	125.07	0.77	5.88	0.85	475559.79	4113511.34
4	114.00	213.04	2.61	11.67	1.29	475128.81	4113522.12
5	25.46	209.32	2.09	3.39	1.82	474581.19	4113551.13
6	66.48	214.15	2.52	5.40	3.22	473215.64	4113361.96
7	40.96	98.37	0.90	8.03	3.99	472448.34	4113355.50
8	40.40	99.74	1.41	8.68	4.61	471874.00	4113509.16
9	102.70	176.36	2.45	13.51	6.26	467142.22	4111658.22
10	40.81	101.26	1.16	10.69	7.26	467143.06	4111749.26
11	21.05	174.09	0.53	6.32	8.53	467358.50	4112026.34
12	32.63	91.16	0.88	9.87	9.32	468072.86	4112361.05
13	49.95	111.95	1.54	10.59	10.53	468431.65	4113029.80
14	42.75	129.04	1.30	7.88	10.9	469531.72	4113507.79
15	45.54	93.61	1.29	10.84	10.99	470382.21	4113746.38

Table 2. Metal Concentrations, upstream of pond (1-7), in pond (8) and downstream of pond

(9-15).

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Table 3. Mean Metal Concentrations Upstream and Downstream of Pond

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<u>Metal</u>	<u>Upstream Mean (ppm)</u>	<u>Downstream Mean (ppm)</u>
<u>Lead</u>	<u>111.76</u>	<u>47.92</u>
<u>Zinc</u>	<u>248.23</u>	<u>125.35</u>
<u>Cadmium</u>	<u>2.856</u>	<u>1.308</u>
<u>Nickel</u>	<u>8.135</u>	<u>8.409</u>

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Concentrations for all of the metals except Ni generally decrease longitudinally downstream (Figures 2-5). All metals have a second major spike in concentrations downstream of the pond and then generally decrease longitudinally. Nickel has a rather sporadic downstream trend, but also spikes downstream of the pond (Figure 5). Nickel is a component in some fertilizers and its trend could be influenced by the non-point sources of fertilizer throughout the stream. At the location where Ni spikes downstream of the pond is a golfcourse that could be contributing to the high Ni concentrations due to fertilizing of grass. Cadmium, zinc, and lead have similar downstream trends reflecting the similarity in sources of these metals (Figures 2,3,4).

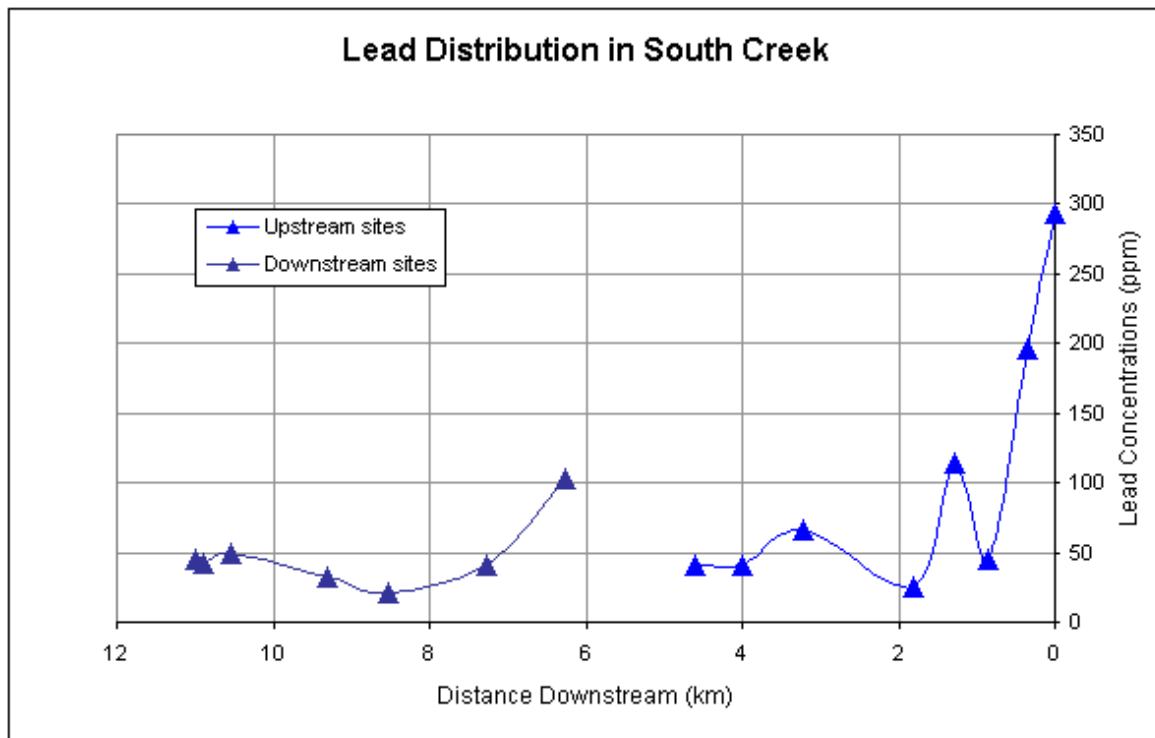


Figure 2. Downstream distribution of lead sampled at sites upstream and downstream of pond.

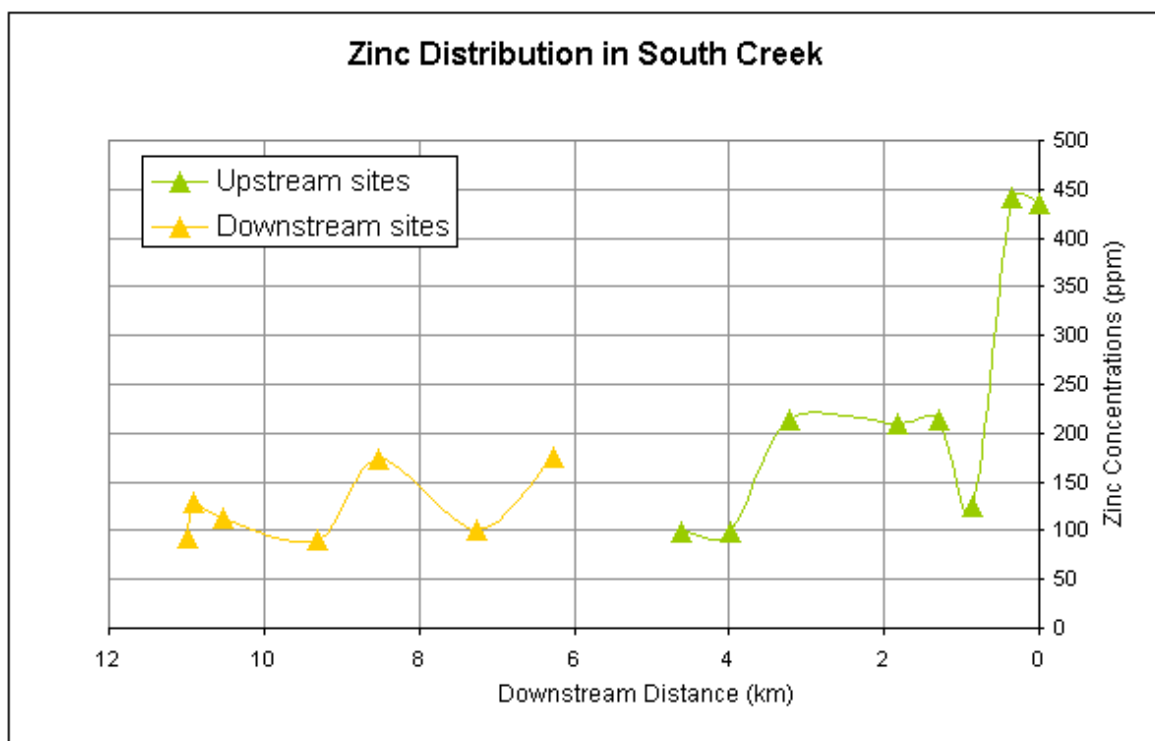


Figure 3. Downstream distribution of zinc sampled at sites upstream and downstream of pond.

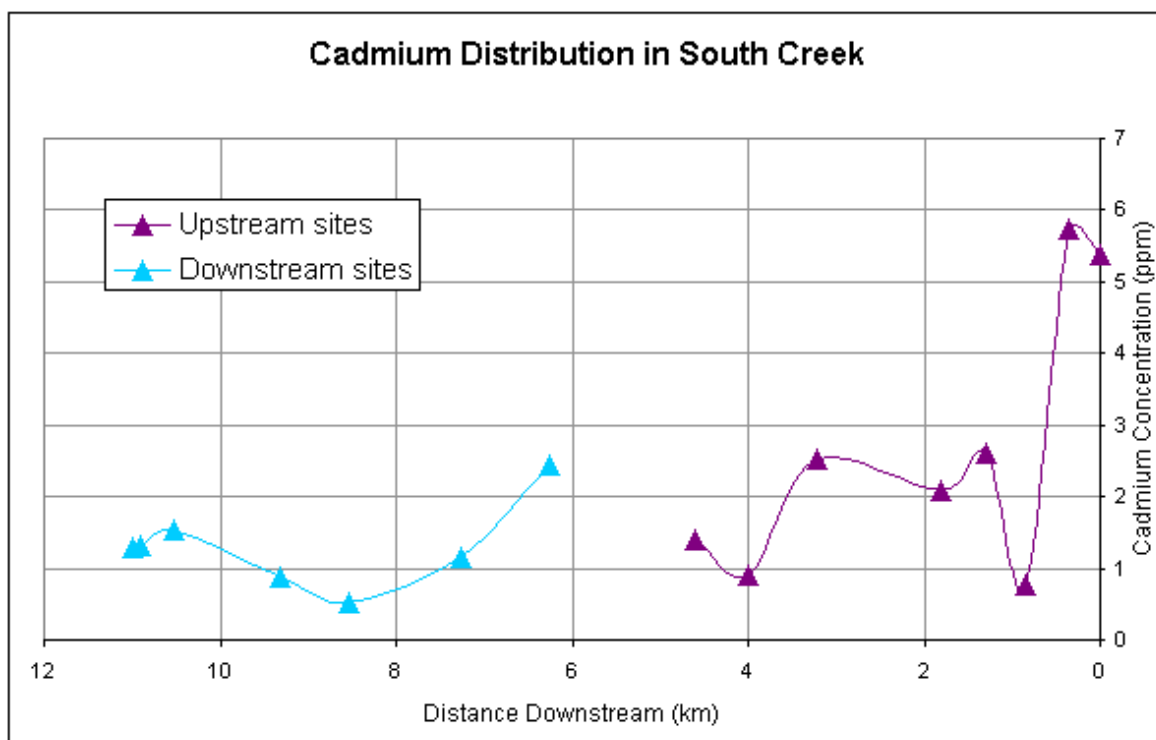


Figure 4. Downstream distribution of cadmium sampled at sites upstream and downstream of pond.

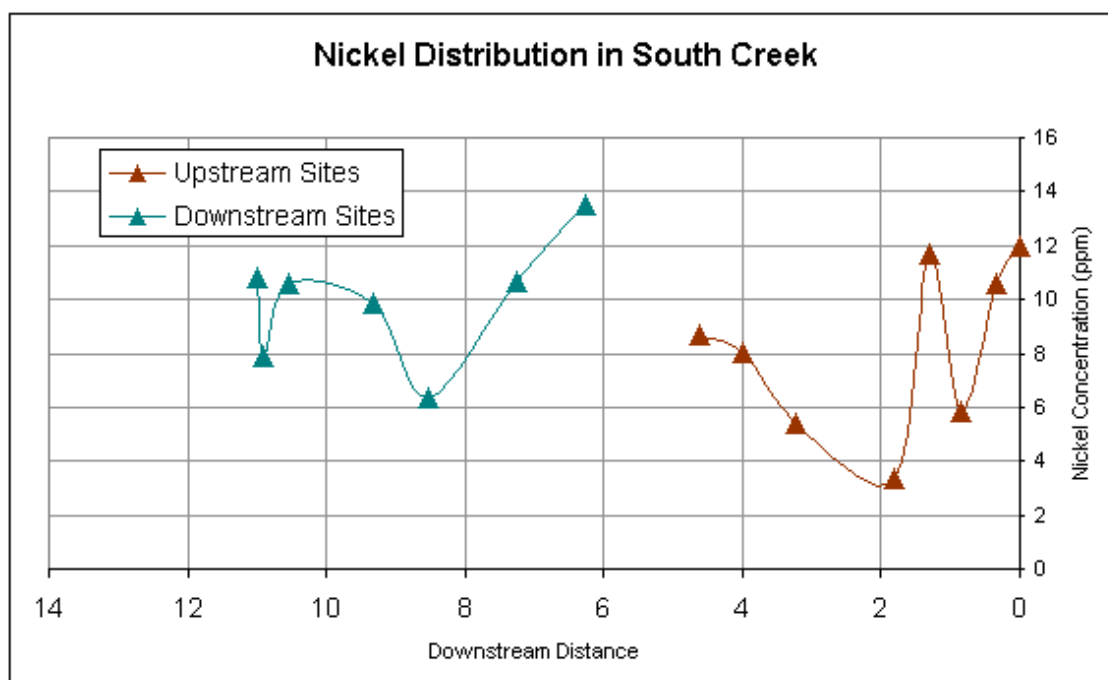


Figure 5. Downstream distribution of Nickel sampled at sites upstream and downstream of pond.

To test the research hypothesis a two sample *t*-test was conducted to evaluate the differences in the mean concentrations of the metals upstream and downstream of the pond. Table 4 displays the *t*-values and two tailed critical values for each metal. Supporting the research hypothesis would require the samples downstream to be significantly lower than samples upstream of the pond. Lead concentrations were not significantly different upstream and downstream of the pond at the 0.1 alpha (90%) confidence level. Zinc concentrations are significantly different upstream and downstream at the 0.1 alpha (90%) level. Cadmium concentrations were also significantly different at the 0.1 alpha (90%) confidence level in the upstream sites vs. the downstream sites. Mean nickel concentrations were not significantly different at the 0.1 alpha level (90%). The results for zinc and cadmium support the research hypothesis while the results for lead and nickel reject the hypothesis.

Table 4. *t*-test results for upstream and downstream samples

Metal	Upstream Mean	Downstream Mean	0.1 Alpha	
			<i>t</i> -value	critical value
-	-	-	-	-
Zinc	248.23	125.35	2.2786	1.8945
Lead	111.76	47.92	1.645	1.895
Cadmium	2.856	1.308	1.976	1.895
Nickel	8.135	8.409	0.131	1.796

CONCLUSION

Two of the metals, Zn and Cd, examined in the study are slightly affected by the

pond. Two of the metals, Pb and Ni, are not affected by the pond. The most likely reason why the pond does not greatly reduce downstream metal concentrations is the fact that many non-point sources of metals exist downstream of the pond. Any attenuation of metal concentrations by the pond is negated by sources downstream. In fact, the sediment contained in the pond does not have an abnormally high metal content.

Another complication with sediment bound metal transport in South Creek is sediment residence times. Most sediment does not reside in the channel for long periods of time, thus reducing the absorption time of metals by the sediment. South Creek is very flashy in nature and much of the channel is concrete. This scenario creates an efficient conduit for material carried by the stream. Any sediment deposited in the channel is most likely completely washed from the system during the next flow event. It could be suggested, by looking at the trend charts, that metal enrichment in South Creek is nearly syngenetic in nature. The metals get deposited with the sediment and are washed out of system during the next event. The sediment does not remain in the channel where it has a chance to absorb metals from subsequent flow events.

Future recommendations would be to sample more extensively and to sample Wilson's Creek. Samples taken in Wilson's Creek upstream and downstream of the confluence with South Creek would reveal metal inputs from South Creek. This type of sampling scheme would provide more evidence for amounts of metals that may be originating from the urban landscape.

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