An Analytical Study of Heavy Metal Concentrations In Soils at Pierce Cedar Creek Institute

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Introduction:

Lead, copper, and zinc metals occur naturally in the earth's soil at low to moderate levels, but sometimes these elements can be found in higher concentrations that can be toxic to organisms, according to the United States Department of Agriculture. Zereini, et al. (2005) analyzed concentration and distribution of heavy metals in urban particulate matter (PM) and found higher levels of lead, copper, and zinc PM in air collected near roadways than in other urban environments[1]. These metals are considered to be "road-specific" because they are mainly derived from combustion residues, fuels (gasoline and diesel), engine/transmission oil, abrasion from tires, and brake linings[1]. These vehicle components provide the majority of copper and zinc emission[2]. Since the phase out of leaded gasoline in the 1970's the main source of lead in roadside soils has been attributed to the pulverization of lead wheel weights that fall off vehicles[3].

Studies done by Battelle Memorial Institute suggest that the concentration of lead increases with traffic volume. Leaded gasoline emissions as the source of lead-soil contamination has been assessed in four ways: distance from the roadways, association with ambient air-lead levels, association with traffic volume, and community area pattern [4]. Our study will examine two of these effects, distance from the roadway and traffic volume for three metals: lead, copper, and zinc.

Lead is considered dangerous to the human body, especially to children, even at low levels according to the EPA. Lead accumulates in the blood, bones, muscles, and fat; this can lead to damaged kidneys, liver, and can also affect the brain and nerves, leading to seizures, mental retardation, mood changes, and memory problems. High levels of lead in the blood can increase the risk of heart disease as it raises blood pressure[5]. Lead also reduces iron utilization resulting in anemia, the shortage of red blood cells[6].

Zinc is present in some enzymes of the human body making it one of the most important metals biologically. Carboxypeptidase A and carbonic anhydrase are the most recognized enzymes containing zinc. Carboxypeptidase A plays a part in digestion, catalyzing the hydrolysis of proteins during digestion; carbonic anhydrase catalyzes the equilibrium reaction of hydration and dehydration in red blood cells of mammals. Another important function of zinc is its ability to recognize base sequences in DNA, consequently regulating the transfer of genetic information during replication[7]. Clinical manifestations of excessive levels of zinc in the body include acute, life-threatening gastrointestinal and pulmonary effects, which are generally treated with oxygen therapy or bronchodilators. Chelation therapy is suggested for excessive amounts of zinc in the blood[8].

Copper also helps to sustain life as its redox chemistry has a role in the oxidation processes of iron, erythro- and leukopoiesis, bone mineralization, elastin and collagen cross-linking, oxidative phosphorylation, catecholamine metabolism, melanin formation, myelin formation, glucose homeostasis, and antioxidant protection of the cell. Excessive amounts of copper result in upset stomach, kidney damage, and the inability to excrete the metal from the liver (Wilson's disease)[9].

A study by Martinez & Motto (2000) suggests that pH affects the solubility of metals in soil. They concluded that the solubility of Pb, Zn, and Cu "increased with a decrease in [soil] pH." The favorable pH levels for each metal are slightly acidic, lead is most soluble in soil with a pH of 5.2; a soil pH of 5.5 gives copper the greatest solubility; and zinc is most soluble in soil with a pH of 6.2[10].

The Pierce Cedar Creek Institute (PCCI) is a 661 acre ecological preserve in Southwest Michigan (in Barry County, nine miles south of Hastings) that provides visitors and scientists with a diverse selection of habitats to explore. PCCI contains wetlands, forests, marshes, streams, lakes, and prairies[11]. Of the 661 acres of land, approximately 70 acres was farmed in the past 60+ years. Cloverdale Road (a dirt road that has been in existence for at least 100 years) transects the property inputting nearly the only vehicle traffic[12].

The purpose of this study is to elucidate what role (if any) that vehicle traffic has on lead, copper, and zinc levels in soils. PCCI was selected for this research because it offers acres of pristine land that have been minimally impacted by the urbanization of rural communities. The samples collected within the preserve will serve as controls for measuring the background concentrations of these heavy metals in each soil type. East Beltline and Fulton Street are paved urban moderately trafficked (>1000 vehicles per day) roads located in Grand Rapids, MI. The samples collected along Cloverdale Road, Fulton Street, and East Beltline will serve as the vehicle traffic affected soils. Cloverdale Road receives significantly less traffic than the two urban roads (as observed at sampling times). It was hypothesized that increased lead, copper, and zinc concentrations in soil would be correlated with increased traffic volumes of the roads sampled. The pH of each soil sample collected was also analyzed to determine whether there was a correlation between soil pH and the amount of heavy metals in the soil. It was hypothesized that soils with lower pH would contain higher concentrations of lead, copper, and zinc due to the conclusions of previous case studies[10].

The six questions that to be investigated in this project were:

(1) Are the lead concentrations of soils near and away from Cloverdale Road the same?
(2) Are the copper concentrations of soils near and away from Cloverdale Road the same?
(3) Are the zinc concentrations of soils near and away from Cloverdale Road the same?
(4) Do soils with lower pH possess higher concentrations of lead, copper, and zinc than soils with higher pH?
(5) Among the soil samples collected near the road, does the concentration of any or all metals decrease with increasing distance from the road?
(6) Do the concentrations of lead, copper, and zinc in roadside soils increase with increased traffic volumes?

Experimental Section:

Sampling. Nine sets of soil samples were taken during a seven week period from 21 May 2006 to 4 July 2006. Seven sets were collected on Pierce Cedar Creek Institute (PCCI) property and two sets were collected beside major roads in Grand Rapids. Three different soil types (Marlette, Perrinton, Thetford) were represented in the PCCI sets. Perrinton soil type was represented in the Fulton St. and East Beltline sets from Grand Rapids. Two different sampling sites (one beside Cloverdale Road and one located in PCCI's interior) were utilized for each of the Perrinton and Thetford soils. Three different sampling sites (one near Cloverdale Road and two located in PCCI's interior) were used for the Marlette soil. Sampling sites on the PCCI property were selected using a GIS soil type/texture projection map that PCCI provided. During each sampling, a Thales Navigation MobileMapper handheld GPS unit was employed to mark the sampling coordinate position (the GPS coordinates were not utilized in the GIS projection map. See the GIS map at the conclusion of this report).

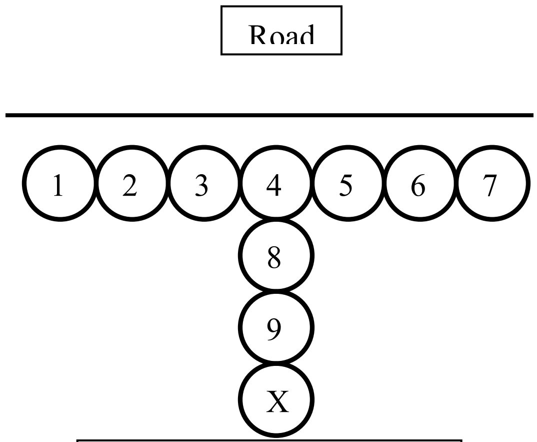

Figure 1: Roadside Sampling Grid

For the five sample sets collected near a road a sampling grid (see figure 1) composed of ten sampling points (marked with 71-cm stakes with red biodegradable tape wrapped around the crown) spaced one meter apart was constructed. An eighteen inch Oakfield Apparatus Company stainless steel soil corer was implemented to collect the top six inches of soil at each sampling point in the grid. Prior to sampling each point ground cover was removed to minimize sampling irregularities. The top six inches of soil was removed and placed into a labeled Fisher Scientific 3-inch x 7-inch Twirl Em' bag. The bag was then tightly sealed for transportation and storage. At each sample site a compass was used to record the bearing to which the sampling grid was constructed.

The four sample sets collected in the interior of PCCI were collected following the same protocol outlined for the roadside sample sites except that a different sampling grid (see figure 2) was utilized.

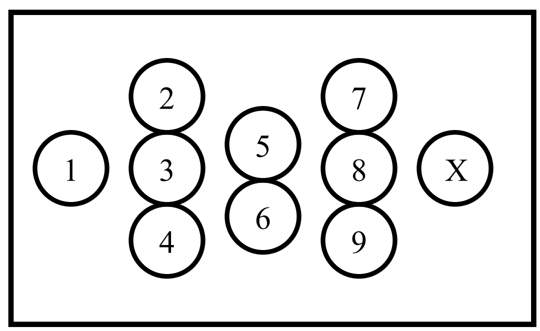

Figure 2: Interior Sampling Grid

The protocol utilized for pH analysis and heavy metal analysis was adapted from the Recommended Chemical Soil Test Procedures for the North Central Region[9] published by Missouri Agricultural Station.

Before laboratory analysis, each Twirl Em' bag was emptied into two Solo 3-oz plastic or Meijer-brand paper cups. Each of the two cups contained approximately the same amount of soil. The cups were then dried in an American Sterilizer Company drying oven for approximately 24-hours at 40 °C. After drying, the soil was crushed to a floury consistency using a mortar and pestle. Large pebbles, grass, and other organic material were manually removed.

pH Analysis. Using a 4.93-mL Fisher Scientific sterile plastic spoon approximately 5.00-mL of each dry/crushed soil sample was placed into an empty 3-oz cup, previously used for drying the same soil sample. Following this, 5-mL of reverse osmosis (RO) water was pipetted into each of the ten plastic cups and the mixture was stirred for approximately five seconds. The samples were allowed to stand for ten minutes before pH measurement.

An Accumet AP62 portable laboratory pH meter was utilized in measuring soil pH. The pH meter was standardized using Fisher Scientific 4.00-pH, 7.00-pH, and 10.00-pH buffer solutions before each use. The pH electrode was placed into the soil slurry and used to homogenize the slurry during the pH reading. Immediately after the initial pH was recorded, a drop of 0.0124 M aqueous $CaCl_2$ (prepared from Aldrich Chemicals, technical grade solid) was added to each soil sample to "mask the effects [that] differential soluble salt concentrations"[13] would have on pH. The samples were stirred for approximately ten seconds before a second pH measurement was recorded .

Diethylenetriaminepentaacetic acid (DTPA) Extraction. Using a 4.93-mL Fisher Scientific sterile spoon twice approximately 10.0-mL of each dry/crushed soil sample was placed into a clean 50-mL Erlenmeyer flask. Immediately following, 20.0-mL of an extracting solution composed of approximately 0.005 M DTPA (GFS Chemicals, 98.0 %), 0.01 M $CaCl_2$ (Aldrich Chemicals, technical grade), and 0.1 M triethanolamine (TEA) (unknown source) in RO water was pipetted to each flask. An additional 20.0-mL of extracting solution was added to an eleventh 50-mL Erlenmeyer flask to serve as a blank. The mouths of the Erlenmeyer flasks were then wrapped tightly in Parafilm. The flasks were clamped to a Burrell Wrist-Action Shaker and shaken for approximately 2 hours.

Following shaking, the contents of each flask was filtered by gravity through Whatman #42 filter paper into eleven clean and dry 50-mL Erlenmeyer flasks. If the filtrate remained cloudy after the first filtration it was re-filtered through Whatman #42 filter paper until completely clear (in all tests the filtrate possessed a yellow color of varying intensity).

Atomic Absorption (AA) Spectroscopy Analysis. A Buck Scientific AA Spectrometer Model 210VGP was used to analyze the filtrate for lead (Pb, λ = 274.6 nm), copper (Cu, λ = 324.7 nm), and zinc (Zn, λ = 213.9nm). A lean flame composed of an acetylene/air mix was used throughout analysis. The slit width of the instrument was set at 0.7-nm. Lead (100ppm – 0.1ppm), copper (10ppm – 0.1ppm), and zinc (10ppm – 0.1ppm) standards were prepared from 1000ppm GFS Chemicals standard solutions using extracting solution as the dilutant. A calibration curve was prepared from the standard solution's absorption values and the concentration (ppm) of Pb, Cu, and Zn in the soil samples were elucidated using least-squares analysis.

Results and Discussion:

A large portion of this study has concentrated on the levels of lead, copper and zinc in soils on Cloverdale Road compared to those in soils of the PCCI interior. To compare each interior location to the corresponding road location for each soil type, the Wilcoxon Rank Sum Test at the 95 % confidence level was used.

The first question in our study addressed the difference in lead levels of matching soil types found at different locations, the road vs. the interior. Road locations were expected to show greater levels of lead than interior locations of the same soil type because roadside soils have been subjected to vehicle emissions and greater traffic than the interior locations, increasing the possibility of lead pollution.

Of the four matching soil types, only the Perrinton Road samples were significantly higher with respect to lead concentration than the corresponding Interior samples. However, our hypothesis stating the road samples would have a greater concentration for lead than the Interior samples was true for Thetford and Marlette I soil samples. The exception in this case was the Marlette Interior II location; the average lead concentration (3.692 ± 0.033 ppm) was significantly greater than the average lead concentration of Marlette Road. Figure 3 graphically compares the concentration of lead found in the soil samples of the road vs. the interior.

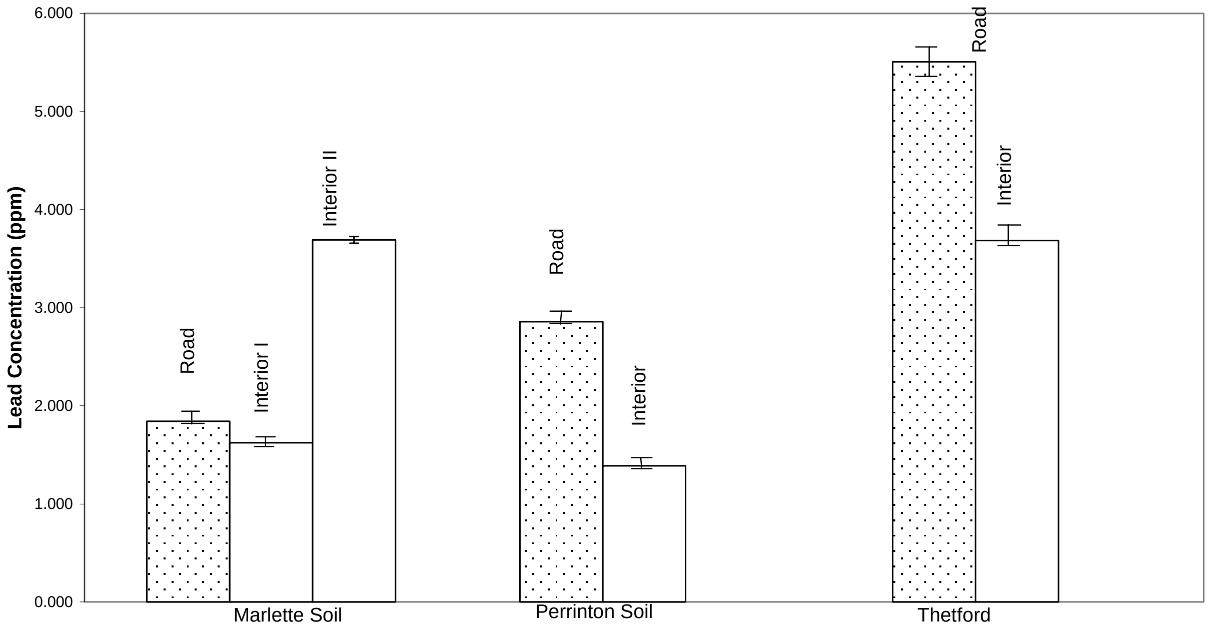

Figure 3: Concentration of lead in soil on road locations vs. interior locations

Analyzing the first set of matching soil samples in Figure 3, the Marlette Interior I soil samples had a mean of 1.623 ± 0.027 ppm lead. With the mean lead concentration being only 9% higher, the difference between the Marlette Road samples and Interior I is not significant (at 95 % confidence). The second set of matching soil type illustrated is Perrinton. The mean levels of lead found in the road samples were found to be significantly higher than the corresponding Interior samples, 2.8576 ± 0.033 vs 1.360± 0.028 ppm, respectively. This result is assumed to be due to increased human traffic and vehicle emissions on Cloverdale Road. The last set of data bars represent Thetford soil. Both of these locations contained higher concentrations of lead than all other PCCI locations. As we hypothesized, the Thetford Road sample mean (5.51 ± 0.0737 ppm) is greater than the corresponding Interior sample mean (3.685 ± 0.074 ppm), however they are not significantly different.

The second question in our study addressed the difference in copper levels of matching soil types found at different locations. Again we hypothesized that the road would have the greater level of metal due to the increased volume of vehicle and human disturbances. This result was found true in each of the matching soil locations, the copper concentrations being significantly different for both Marlette and Thetford soils. These results comparing the levels of copper in the road locations vs. the interior locations are illustrated graphically in Figure 4.

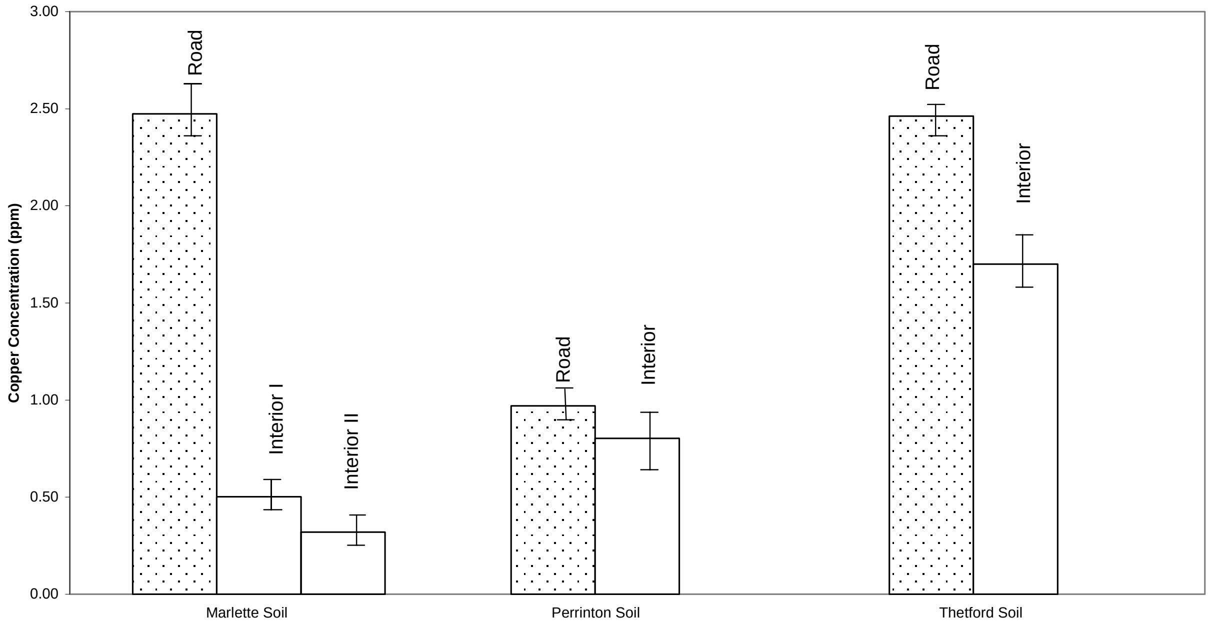

Figure 4: Concentration of copper in soil on road locations vs. interior locations

The Marlette Road samples had a mean of 2.47 ± 0.134 ppm Cu, significantly higher than both Marlette Interior I and Marlette Interior II samples (0.502 ± 0.049 ppm and 0.320 ± 0.054 ppm Cu, respectively). The Thetford Road sample mean (2.463 ± 0.082 ppm Cu) was also significantly higher than the Thetford Interior sample mean (1.70 ± 0.145 ppm). The Thetford Interior soil samples contain the greatest mean concentration of copper among the interior locations. The soil samples with the least amount of copper in general are of Perrinton type, however the same trend of greater copper on the road was found here. The Perrinton soil samples collected on the roadside had a mean of 0.9696 ± 0.0509 ppm Cu compared to the Perrinton Interior samples which had an average of 0.803 ± 0.083 ppm Cu.

The third question in our study follows the first two and compares the differences in zinc levels between matching soil types found at different locations of Cloverdale Road and the PCCI interior. Unlike copper, zinc was more abundant in the Interior soil samples than in Road samples. This is contrary to our hypothesis. Similar to the copper analysis, significant differences were found for each matching soil type, with the exception of Perrinton. Refer to Figure 5 for a comparison of the levels of zinc.

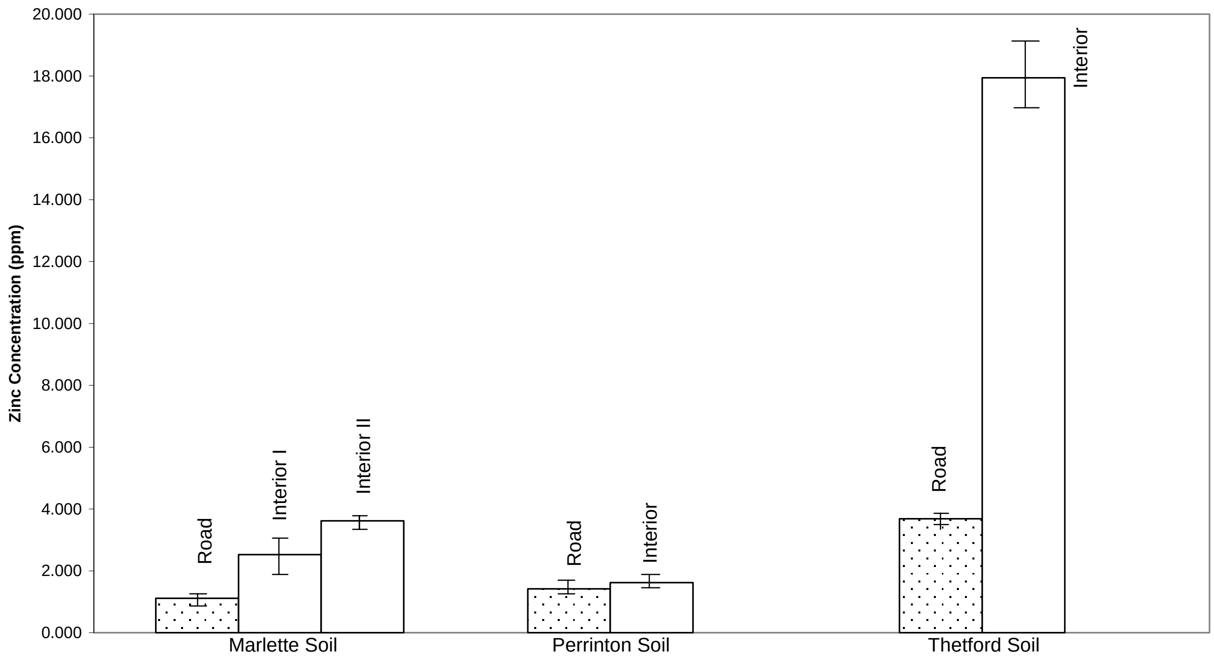

Figure 5: Concentration of zinc in soil on road locations vs. interior

The greatest difference in zinc levels between matching soil types was found in the Thetford locations. The interior location had an average of 17.94 ± 1.625 ppm, the greatest level of zinc found in any of the soil samples by over 400%. Thetford Road had a mean concentration of 3.685 ± 0.074 ppm of zinc, the greatest of all zinc concentrations among road samples.

Marlette Interior I and II were both found to be significantly higher in zinc than the corresponding road location (3.617 ± 0.181 ppm and 2.52 ± 0.55 ppm Zn, respectively).). The road location had less zinc than any other samples collected in this study (1.108 ± 0.066 ppm Zn).

Even though the zinc concentrations of the matching Perrinton locations are not significantly different, Perrinton followed the same trend as the other matching soil samples, having a higher concentration of zinc in interior soil than in road soil. The mean value for the interior (1.622 ± 0.17 ppm) is about 10% greater than the road mean of 1.420 ± 0.18 ppm.

The low concentrations of zinc found on the roadside when compared to the matching interior location has led us to believe that zinc is not easily admitted into the soil through vehicle and human traffic. Perhaps the soil that was more settled was higher in zinc because of its natural occurrence and the lack of disturbance of the soil. The roadside has more opportunity for the nutrients in the ground to be distributed and interrupted. Zinc may be more likely to exist in locations with less movement.

The fourth question our study addressed was the relationship between the acidity of the soil samples and the corresponding heavy metal concentration. The samples were found to be moderately acidic to basic, with values ranging from pH 4.01 to pH 8.34. Interestingly, all of the basic soils (pH>7) were found at the five road sites, while all of the interior sites were acidic. The most basic soil was taken from Fulton Street with an average pH of 8.17; the most acidic soil was found at Marlette Interior II with an average pH of 4.56. The mean pH of all soil samples was 6.54, slightly acidic.

We had predicted more acidic soils would have greater levels of lead, copper, and zinc than basic soils. A study by Martinez & Motto suggest that heavy metals are increasingly soluble in acidic soils[10]. The actual results found in this present study indicate no relationship at all for lead and zinc. For copper, more basic soils were found to have greater concentrations of the metal. This relationship, however, is minute with a correlation constant of only 0.298. This is predominantly due to the Fulton Street soil samples, which had the second-greatest average concentration of copper (7.67 ± 0.36 ppm), and the most basic soil with an average pH of 8.17. The East Beltline soil samples also contribute to the positive correlation, with the greatest average concentration of copper (8.40 ± 0.19ppm) and an average pH of 7.62. In addition, the most acidic soil found at Marlette Interior II (average pH of 4.56) had the smallest average concentration of copper of all nine sites (0.320 ± 0.54 ppm). Figure 6 demonstrates this relationship.

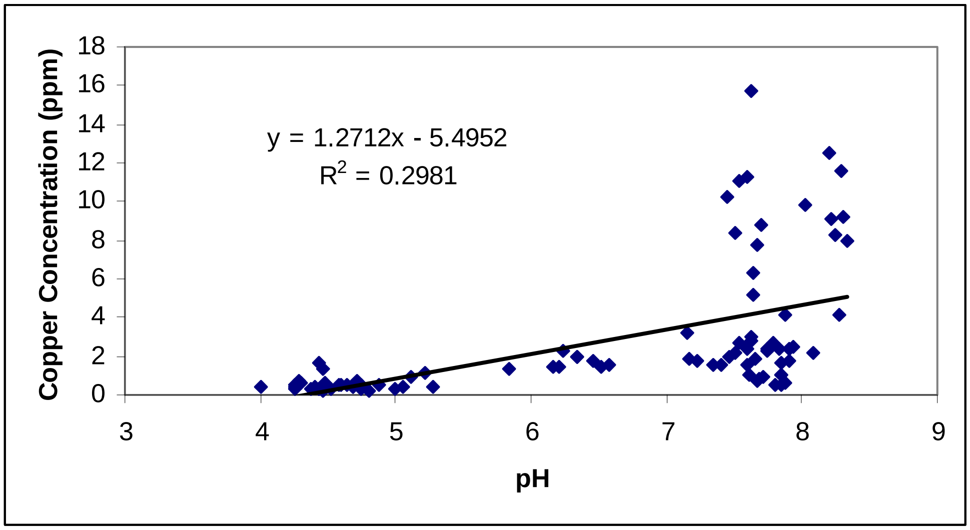

Figure 6: Copper concentration in all soils vs. pH

The Fulton Street and East Beltline soil sites are subjected to more traffic and vehicle emissions than the PCCI sites, and as a result contain a greater than average level of heavy metals. Omitting these sites and looking at only the PCCI territory results, a greater positive correlation exists between the average copper concentrations in the soil samples vs. the pH, 0.386. Figure 7 demonstrates this relationship.

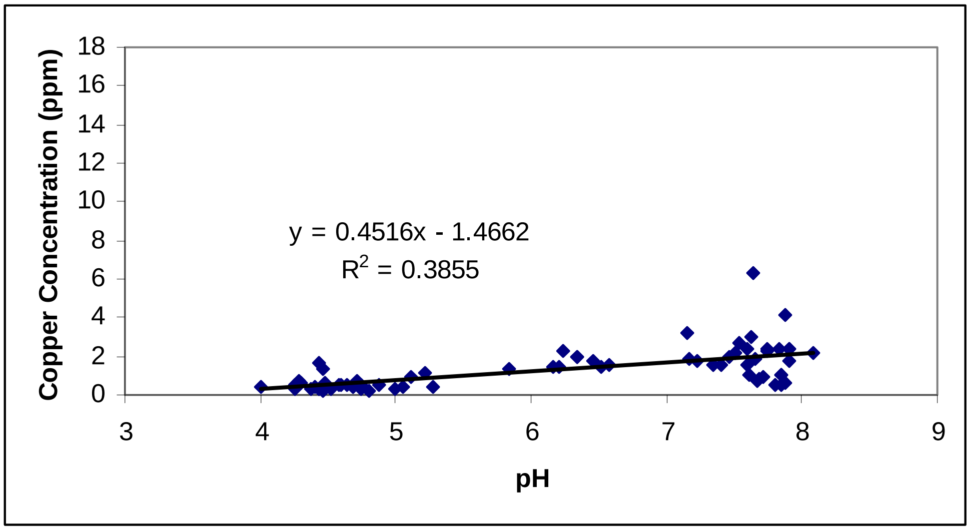

Figure 7: Copper concentration in PCCI soils only vs. pH

The next greatest positive correlation for pH and heavy metal concentration exists in lead (0.147), however this relationship is small enough to be considered dismissable. The data is generally scattered, but the more heavily trafficked roads slightly skew the results. The soil at Fulton Street contains the greatest amount of lead (average 100.0 ± 10.19 ppm), and also the most basic of all the samples, as pointed out before. Refer to Figure 8.

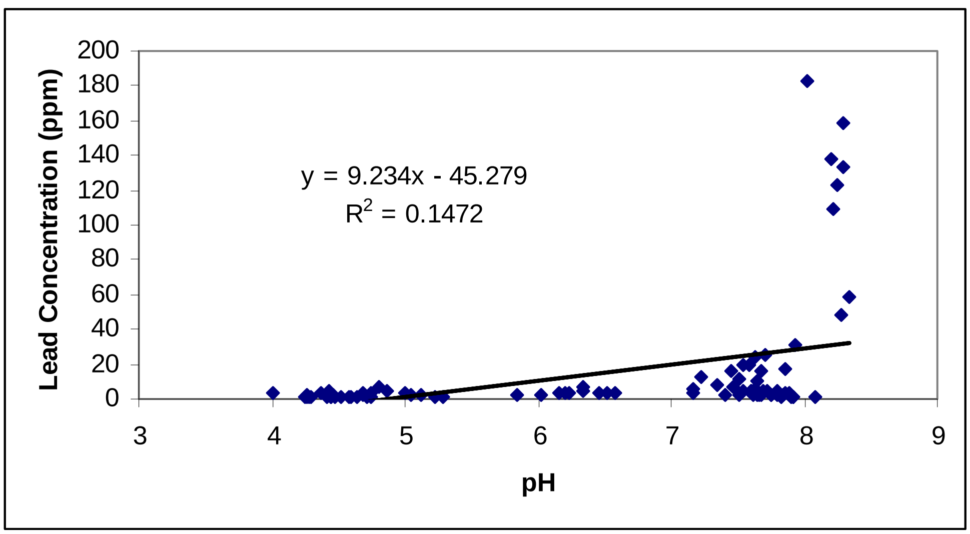

Figure 8: Lead concentration in all soils vs. pH

Omitting the heavy trafficked road sites, the correlation between the lead concentration of the soil samples and pH level is nonexistent, having a correlation constant of less than 0.1 (actual value 0.0616). These results are greatly scattered, refer to figure 9.

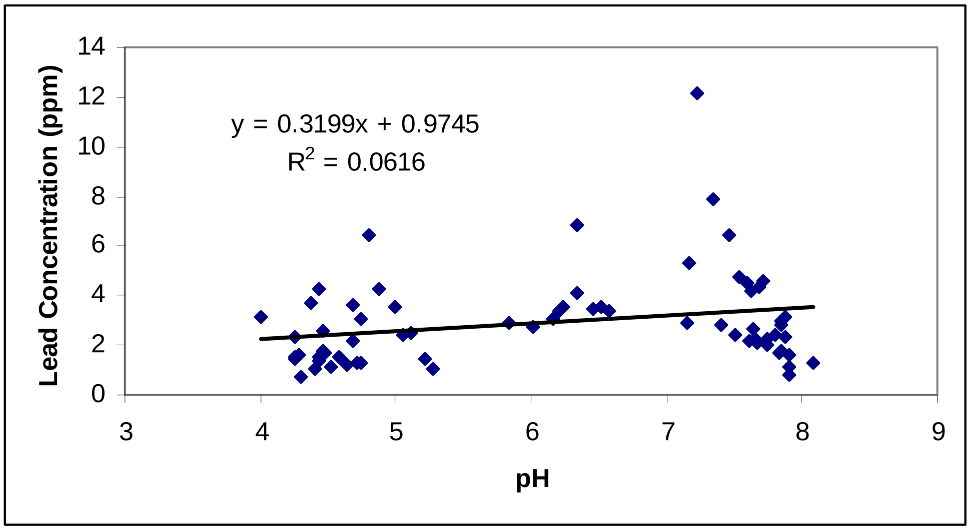

Figure 9: Lead concentration in PCCI soils only vs. pH

The least positive correlation in the relationship between pH and heavy metal concentration was found in zinc, with a correlation constant of 0.0632, again dismissible. The slight positive correlation in this relationship is, again, due to the Fulton Road site which had the second greatest average level of zinc (16.76 ± 2.33 ppm) and also the most basic soil. The soil with the greatest levels of zinc have been found at the Thetford Interior site (17.94 ± 1.7 ppm) which has an average pH of 6.27. See figure 10 below.

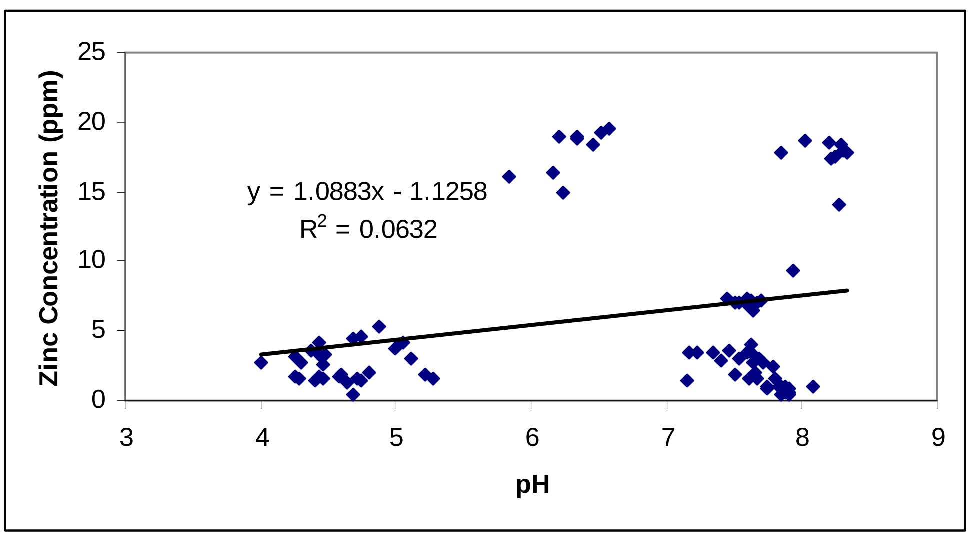

Figure 10 : Zinc concentration in all soils vs. pH

When the Fulton Street and East Beltline soil sites are omitted, the relationship between zinc concentration of the soil and pH level is nonexistent, with a correlation constant of 0.0006. See figure 11.

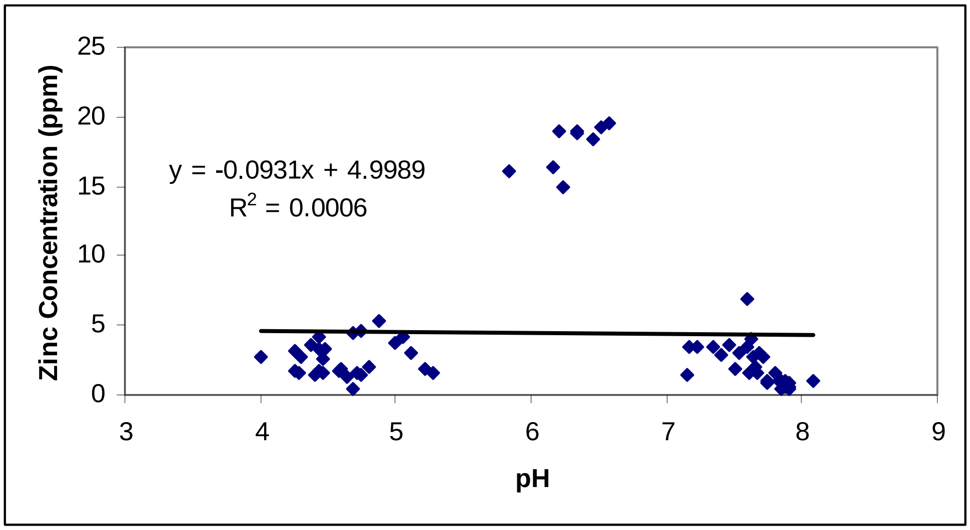

Figure11 : Zinc concentration in PCCI soils only vs. pH

Overall, data suggests that soils with lower pH levels do not possess higher concentrations of heavy metals than soils with higher pH levels. Copper had the greatest relationship, showing a slight tendency for more basic soils to have greater levels of copper.

Soil at nine different locations was sampled during this project. For each of the samples, the lead, copper, and zinc content were determined. The average metal concentrations (sites 1-10 for interior locations, sites 1-7 for road locations) are presented in Table 1.

Sample Location	Pb (ppm)	uncertainty (ppm)	Sample Location	Cu (ppm)	uncertainty (ppm)	Sample Location	Zn (ppm)	uncertainty (ppm)
Fulton Street	129.1	8.5	East Beltline	10.48	0.19	Fulton Street	18.05	2.4
East Beltline	18.79	0.52	Fulton Street	9.78	0.35	Thetford Interior*	17.94	1.6
Thetford Road	4.25	0.14	Thetford Road	2.793	0.082	East Beltline	7.17	0.53
Marlette Interior II	3.692	0.033	Marlette Road	2.47	0.14	Thetford Road	3.787	0.077
Thetford Interior*	3.685	0.074	Thetford Interior*	1.70	0.15	Marlette Interior II	3.617	0.18
Perrinton Road	2.46	0.034	Perrinton Road	1.048	0.051	Marlette Interior I**	2.52	0.54
Marlette Road	1.779	0.028	Perrinton Interior	0.803	0.083	Perrinton Interior	1.622	0.17
Marlette Interior I	1.623	0.027	Marlette Interior I	0.502	0.05	Perrinton Road	0.9886	0.18
Perrinton Interior	1.390	0.028	Marlette Interior II	0.320	0.054	Marlette Road	0.966	0.066

Table 1: Mean Pb, Cu, and Zn concentrations
*indicates only nine samples analyzed due to insufficient sample quantity
**indicates only eight samples analyzed due to insufficient sample quantity

The analysis of lead showed that the two urban roadside locations (Fulton Street and East Beltline) had significantly greater concentrations of lead (Wilcoxon Rank Sum Test $\alpha = 0.05$) than the most concentrated site on PCCI property (Thetford Road).

Copper concentrations demonstrated a similar relationship. Again, the two urban roadside locations had significantly greater concentrations of copper (Wilcoxon Rank Sum Test $\alpha = 0.05$) than the most concentrated site on PCCI property (Thetford Road).

The zinc analysis (excluding Thetford Interior) showed the same type of relationship that both the copper and lead analyses had. The two urban roadside sites had significantly greater concentrations of zinc (Wilcoxon Rank Sum Test $\alpha = 0.05$) than the Thetford Road site, which had the highest concentration of zinc among all PCCI sites except the anomalous Thetford Interior site.

Therefore, the urban roadside (with only one exception) had significantly greater concentrations of lead, copper, and zinc than any of the PCCI sites. Since East Beltline and Fulton Street exist in an urban environment where heavier traffic volumes are common it was hypothesized that the roadside soils along these two roads would contain significantly greater concentrations of lead, copper, and zinc. The data supports that increased traffic volumes play a role in heavy metal concentrations in roadside soils.

Why do the Thetford Interior samples have zinc levels analogous to Fulton Street? The sampling location was located approximately thirty meters south of the wetlab building (see Figure 18, point 4) where a slight downward slope away from the structure toward the wetland area was observed. It is hypothesized that during the wetlab's construction (August 2000) additional zinc was introduced into the soil by construction vehicles and gas powered equipment which would account for the increased level detected.

When only roadside samples are compared against each other the East Beltline and Fulton Street sample locations (sample sites 1-7) are significantly different (Wilcoxon Rank Sum Test $\alpha = 0.05$) from the three PCCI roadside soil locations (sample sites 1-7). This is a key observation in this study because it provides evidence in support of vehicle traffic as a source of roadside soil pollution.

The fifth question that this project aims to answer is: Among the soil samples collected near the road, does the concentration of any or all metals decrease with increasing distance from the road?

This is one of the most important questions to be answered in this project. Since the EPA used this type of analysis to link lead to vehicle emissions[4], the results of lead, copper, and zinc analyses are very important in determining if these metals are linked to vehicle traffic.

Figure 12 graphically illustrates how lead levels decrease as distance from the road increases.

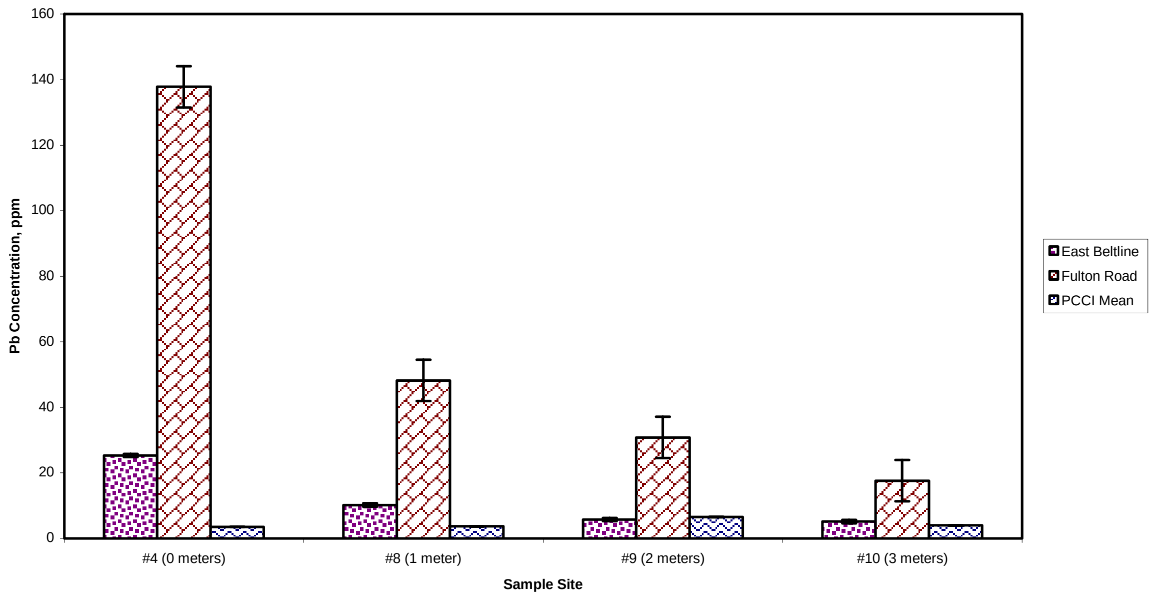

Figure 12: Roadside lead concentrations

The two leftmost bars in each group represent East Beltline and Fulton Street soils (both are Perrinton type). The rightmost bar in each group belongs to the mean of the PCCI roadside soils. It was observed during sampling that East Beltline and Fulton Street experience vehicle volumes far greater than Cloverdale Road. During each sampling at Cloverdale Road locations, fewer than five cars were observed during the hour long process. Conversely, there was constant vehicle traffic at the East Beltline and Fulton Street locations. All roadside samples were collected on weekdays at around 1900 hours. Therefore, all comparisons made in this study should be free of systematic error that could result from sampling each location at different times in the day where traffic volumes may not be comparable. This figure illustrates that the two more heavily trafficked roads show a decrease in lead levels in soil as distance from vehicle traffic increases. The East Beltline location drops a little more than 80 % from 25.27±0.53 ppm Pb (at the edge of the road surface) to 5.13±0.55 ppm Pb (three meters from the edge). The Fulton Street location drops slightly more than 87 % from 137.8±8.3 ppm Pb (at the road surface) to 17.6±1.23 ppm Pb (three meters from the edge). The closest sample to the road was taken within six inches of the road for the Fulton Street sample, whereas the analogous East Beltline sample was displaced approximately two meters from the main road surface by a concrete shoulder. It is hypothesized that that the two meter shoulder attenuates the location's heavy metal concentrations because sampling does not occur less than a meter from the vehicle traffic. The heavy metal particles that accumulate within the barrier's boundaries have a high potential to migrate with rainwater towards a sewer, and not soil.

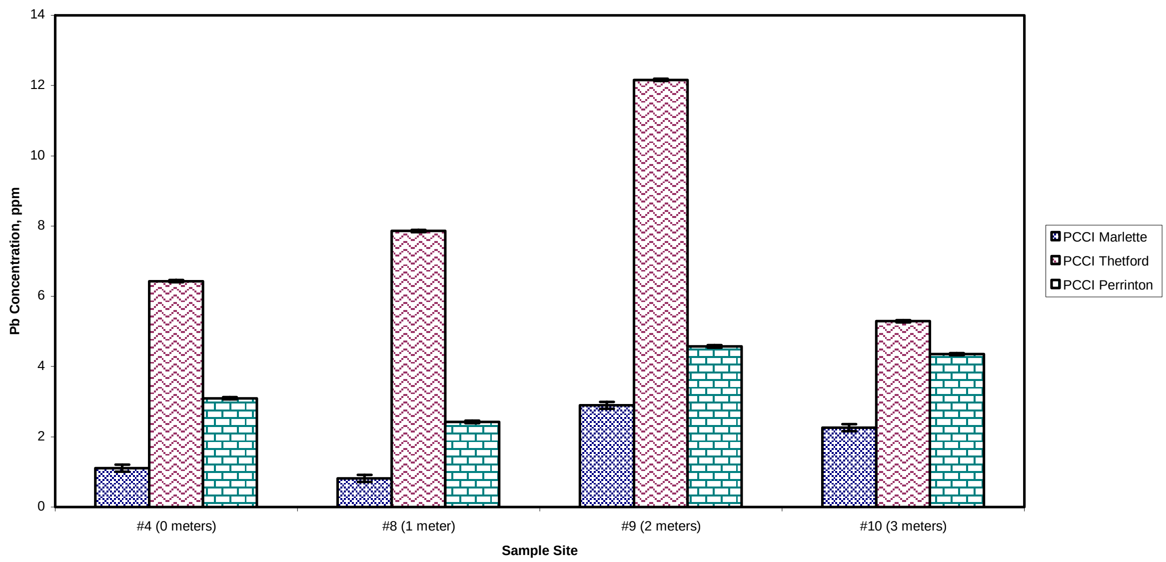

Figure 13: Roadside lead concentrations; PCCI sites only

Figure 13 displays the lead levels in soil as a function of distance from the road of PCCI Marlette, Thetford, and Perrinton roadside locations. This figure does not show the same relationship between distance from the road and soil lead levels as is observed in the East Beltline and Fulton Street samples. The highest lead levels at these locations occur two meters away from the edge of the road (site #9) for each. Among samples taken at this site, Thetford soil had the highest lead concentration of 12.16±0.15 ppm, Perrinton soil had a lead concentration of 4.578±0.033 ppm, and the Marlette soil had the lowest lead concentration at 2.895 ±0.028 ppm.

It was predicted that if vehicle emissions were the primary source of lead in roadside soils then as distance from the road increased the concentration of lead in the soil would decrease. This predicted trend was observed at the East Beltline and Fulton Street locations, but not at the PCCI locations. Why didn't the PCCI locations follow this trend? Robert Root (2000) states that lead wheel weights (the main source of vehicle emitted lead today) usually fall off of vehicles when there is a sudden change in momentum (i.e. braking in traffic and turning onto another road or into a business)[3]. Cloverdale Road does not experience high traffic volume or offer many momentum-changing opportunities so the probability of lead wheel weights falling off on this road is not as high as on East Beltline or Fulton Street. The research collected at PCCI also shows that roadside locations do not have significantly greater concentrations of lead than interior locations do. Thus there may not be enough lead input from vehicle emissions to drastically change the levels of lead in PCCI roadside locations.

Figure 14 graphically illustrates how copper levels are affected as sample distance from the road increases.

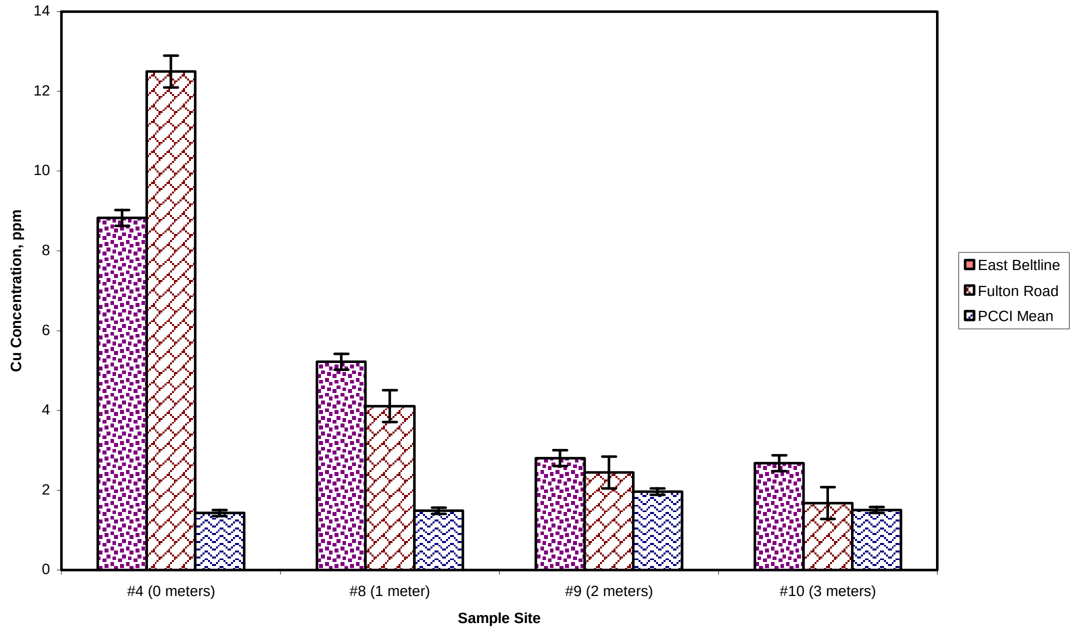

Figure 14: Roadside copper concentrations

The two leftmost bars in each group represent East Beltline and Fulton Street soils. The rightmost bar in each group belongs to the mean of the PCCI roadside soils. This figure illustrates that the two more heavily trafficked roads show a 30-40 % decrease in copper levels in soil as distance from vehicle traffic increases from zero to 3 meters (sample site four: East Beltline = 8.83±0.19 ppm Cu, Fulton Street = 12.5±0.35 ppm Cu; sample site ten: East Beltline = 2.68±0.19 ppm Cu, Fulton Street = 1.68±0.36 ppm Cu). Figure 14 also shows that the copper levels in samples taken from the edge of the road (#4) and one meter away from the road (#8) are much greater than for analogous samples of the PCCI roadside soils. The East Beltline and Fulton Street sample locations (sample sites 1-7) are significantly different (Wilcoxon Rank Sum Test $\alpha = 0.05$) from the three PCCI roadside soil locations (sample sites 1-7). East Beltline's sites two (2.81±0.19 ppm Cu) and three (2.68±0.19 ppm Cu) meters from the road are within experimental error of each other.

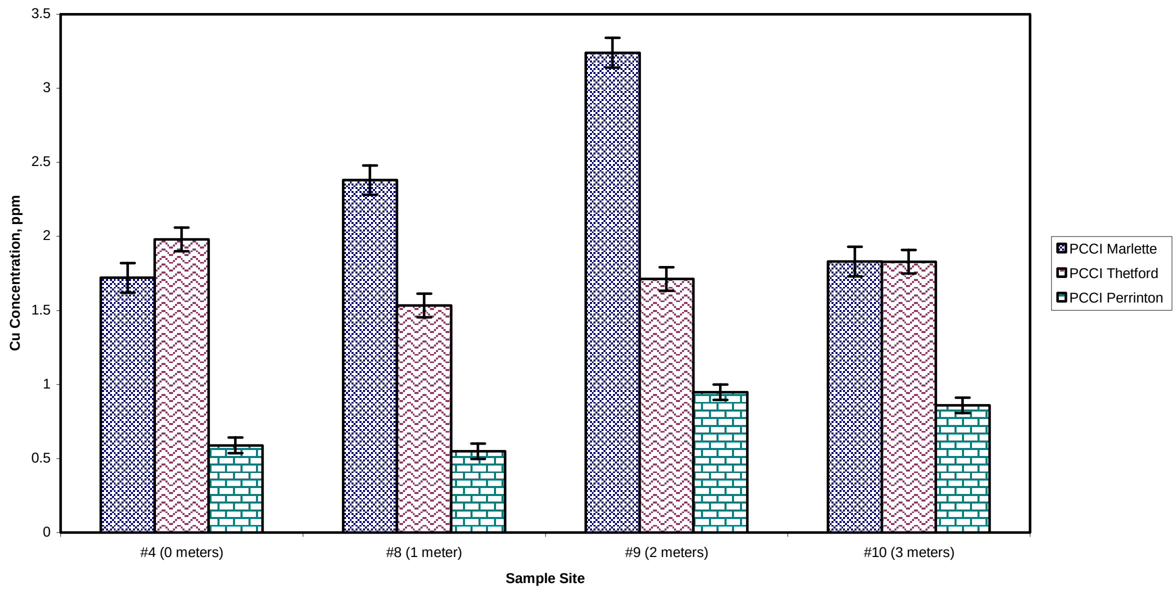

Figure 15: Roadside copper concentrations; PCCI sites only

Figure 15 displays the copper levels in soil as a function of distance from the road of PCCI Marlette, Thetford, and Perrinton roadside locations. This figure does not show the same relationship between distance from the road and soil copper levels that is observed in the East Beltline and Fulton Street samples. The highest copper levels occur at the edge of the road surface for the Thetford Road location (1.980±0.082 ppm Cu) but two meters away from the road edge for the Marlette Road and Perrinton Road locations (3.24±0.14 and 0.948±0.050 ppm Cu, respectively). The trend here is difficult to ascertain. At Marlette sites, copper levels increase for the first two meters and then drop at the third meter. At Thetford and Perrinton locations there is a minor decline from the site on the road shoulder to the site one meter away. At a distance of two meters both concentrations increase and then remain unchanged at three meters from the road.

It was predicted that if vehicle emissions were a source of copper in roadside soils then as distance from the road increased the concentration of copper in the soil would decrease. The East Beltline and Fulton Street samples upheld this prediction. The PCCI locations did not; however, significantly greater concentrations of copper at roadside locations versus interior locations were quantified in two PCCI soil types (Marlette and Thetford). This evidence supports the hypothesis that vehicle emissions do affect roadside soil heavy metal concentrations.

Figure 16 graphically illustrates how zinc levels are affected as sample distance from the road increases.

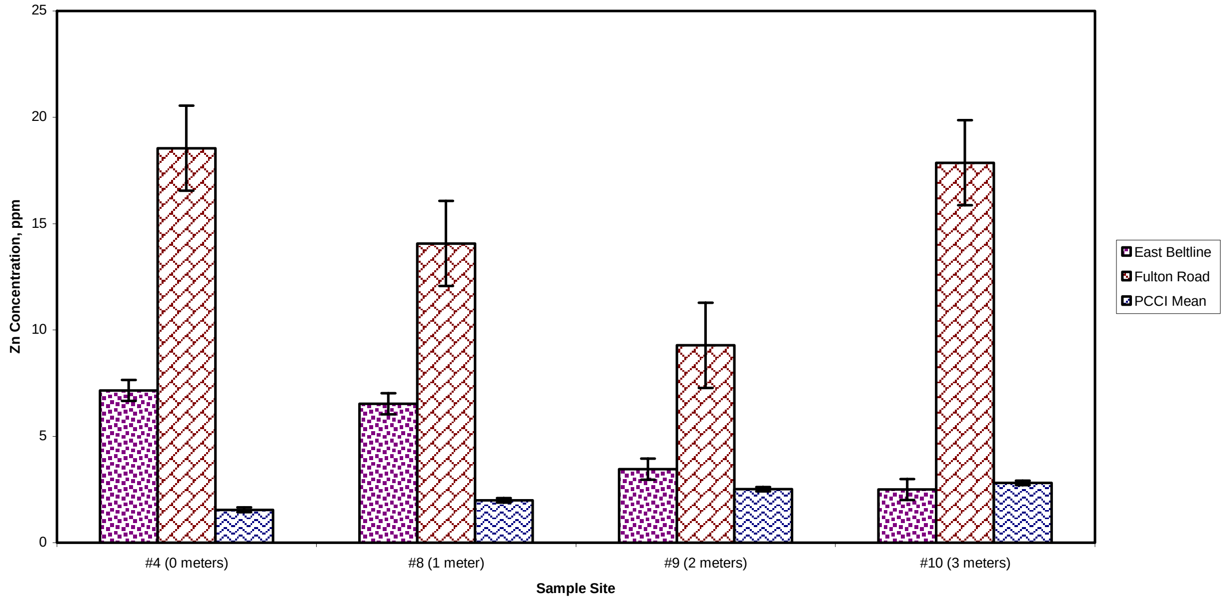

Figure 16: Roadside zinc

The two leftmost bars in each group represent East Beltline and Fulton Street soils. The rightmost bar in each group belongs to the mean of the PCCI roadside soils. Figure 16 shows that Fulton Street has higher zinc levels than all the other roadside locations at every sample distance. The East Beltline and Fulton Street locations (means, sites 1-7) contain significantly (Wilcoxon Rank Sum Test $\alpha = 0.05$) higher concentrations of zinc than the PCCI roadside locations (means, sites 1-7). This figure illustrates that the two *more heavily* trafficked roads have significantly greater concentrations of zinc at the edge of the road surface and one meter from the edge than the PCCI soils (at the edge: East Beltline = 7.16±0.53 ppm Zn, Fulton Street = 18.55±2.4 ppm Zn; one meter: East Beltline = 6.53±0.53 ppm Zn, Fulton Street = 14.07±2.2 ppm Zn).

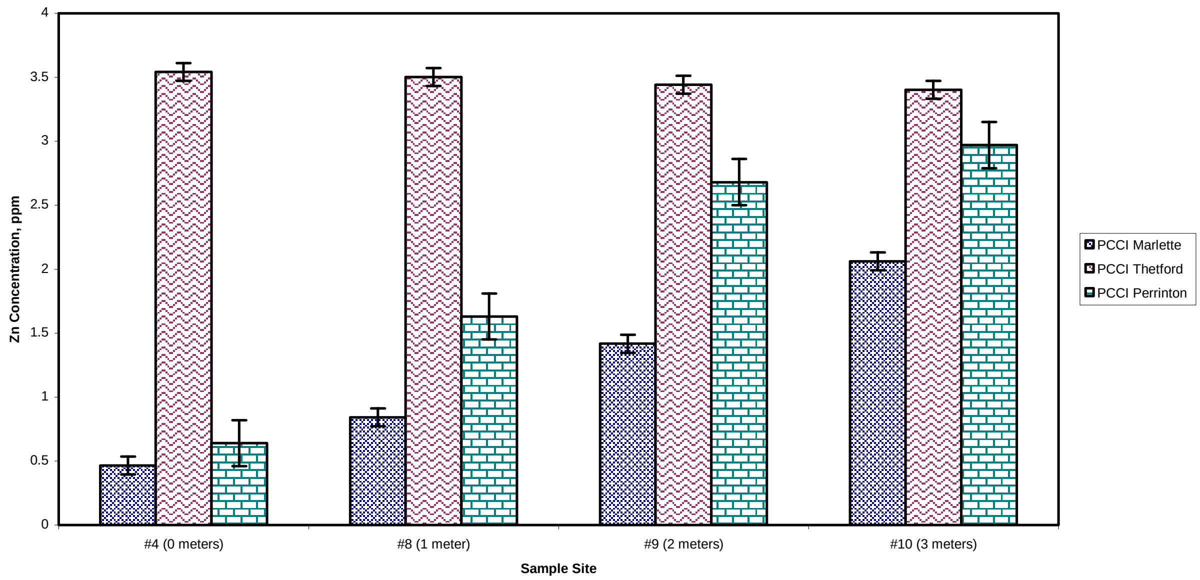

Figure 17: Roadside zinc concentrations; PCCI sites only

Figure 17 displays the zinc levels in soil as a function of distance from the road of PCCI Marlette, Thetford, and Perrinton roadside locations. The zinc levels of Marlette and Perrinton samples steadily increase from 0.466±0.068 ppm to 2.062±0.064 ppm and 0.64±0.18 ppm to 2.97±0.18 ppm, respectively, as distance from the road increases. The zinc levels of the Thetford samples remain constant within experimental error (lowest 3.401 ± 0.070 ppm at three meters from road, highest 3.542±0.071 ppm at the edge of the road surface).

It was predicted that if vehicle emissions were a source of zinc in roadside soils then as distance from the road increased the concentration of zinc in the soil would decrease. The predicted trend was observed at the East Beltline and Fulton locations, although the Fulton Street location showed a substantial increase in zinc concentration between two and three meters from the edge of the road (site #10). However, the Marlette and Perrinton locations at PCCI were observed to follow the reverse trend: as distance from the road increased, soil zinc concentration increased. Since among PCCI locations roadside soils were found not to contain greater concentrations of zinc than interior soils, deposition from vehicle emissions seems an inadequate explanation for the presence of zinc in PCCI soils.

The predicted trend for roadside soils was that heavy metal concentrations would decrease as distance from the road increased. The PCCI roadside soils do not follow the predicted trend for any of the heavy metals analyzed. How can this be explained? At each roadside PCCI location it was observed that as distance from the road increased lead, copper, and zinc (except Thetford) concentrations increased at least once. The slight downward slope of the ground away from the road at all three PCCI locations may be responsible for this divergence. Soluble lead, copper, and zinc (even particulate matter) would drain (or roll) farther from the road because of the slope. If the total amount of lead, copper, and zinc introduced to the environment via vehicle traffic is not great, its gravitational migration may be enough to obscure correlations with distance. The roadside samples (1-7) did contain significantly higher (Wilcoxon Rank Sum Test, $\alpha = 0.05$) levels of copper when compared to corresponding interior locations. Because of this, a soil location that is not heavily polluted by vehicle emissions may not follow the predicted trend, but by comparing roadside locations to interior locations a possible correlation between vehicle traffic and heavy metal deposition can be elucidated. This may be the reason that roadside samples did not contain significantly higher amounts of lead or zinc. Not enough data was collected in this study for a statistical analysis.

Conclusion:

The first three questions of this study addressed concentrations of lead, copper, and zinc in soils near and away from Cloverdale Road. For each of these three metals, it was hypothesized that the road locations would contain the greater concentration of heavy metal. Lead and copper levels near the road were experimentally determined to be greater than the locations away from the road. This observation provides evidence that vehicle traffic may have an affect on lead and copper levels near Cloverdale Road. Zinc did not have the relationship that was hypothesized. Rather than higher concentrations near Cloverdale Road, the locations away from the road were found to contain greater levels of zinc. This suggests vehicle traffic has no positive affect on zinc levels in soils near Cloverdale Road. The fourth question in this study sought to determine if more acidic soils contained greater levels of lead, copper, and zinc. Experimental evidence suggests that the heavy metal concentration in soil is independent of soil pH. The analyzed data revealed no significant relationship between the two variables. The fifth question aimed to qualify if lead, copper, and zinc levels were depleted as distance from the road increased. It has been determined that the urban locations (Fulton Street and East Beltline) follow the hypothesized trend, indicating that vehicle traffic is the main source of increased levels of lead, copper, and zinc. The PCCI locations did not follow the hypothesized relationship, thus the impact of vehicle traffic on locations along Cloverdale Road is inconclusive. The final question pertained to the severity of vehicle traffic and its relationship to lead, copper, and zinc levels at corresponding locations. The greater trafficked urban locations were found to have significantly greater concentrations of these metals than soil locations along the less trafficked soils of Cloverdale Road. This indicates that the levels of heavy metals in soils near road locations increase with vehicle traffic. In order to verify the sixth question's conclusion further studies should be conducted analyzing the particulate matter in the air surrounding varying trafficked roads and particulate matter in isolated areas.

GIS MAP:

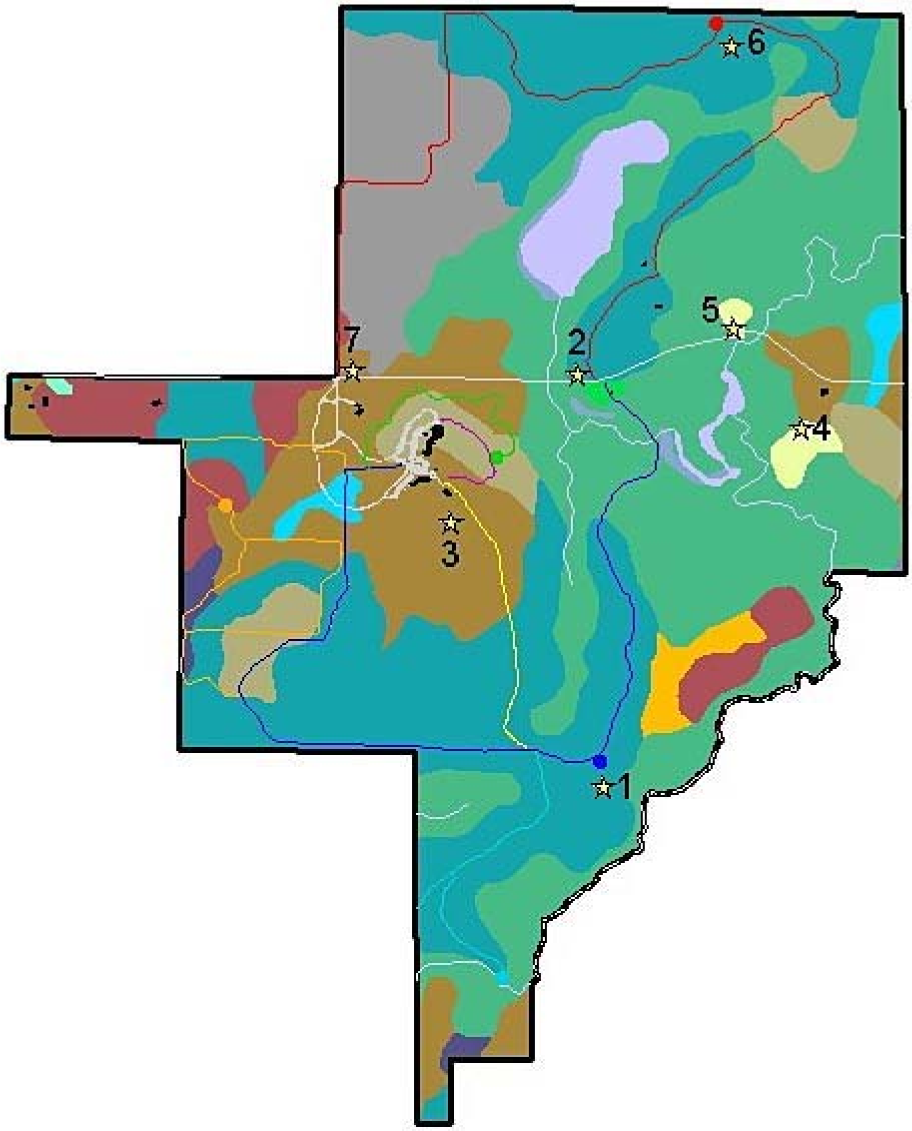

Figure 18: Map of Pierce Cedar Creek Institute property. Stars indicate sampling locations. 1, Marlette Interior I; 2, Marlette Road; 3, Perrinton Interior; 4, Thetford Interior; 5, Thetford Road; 6, Marlette Interior II; 7, Perrinton Road. Collected GPS coordinates were not used to mark the sampling locations due to map projection mismatch, a problem we were unable to solve before the end of the project.

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