

A Legacy of Metal Contamination in Hoosic River Floodplain Soils

Independent Project for ENVI 102: Professors Art, Stoll, and Bingemann

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Good: very systematic organization
graphs tell the story nicely

Possible improvements: inclusion of EPA remediation (for example: zinc is
a nutrient)
- have in-depth discussion of dips
in Protection Area site/disturbances
Experiment performed: March-May 2007

Report submitted: 17-May-2007

Abstract

We tested soil samples taken at five sites in the Hoosic River floodplain between North Adams and Williamstown for various metals—lead, copper, cadmium, zinc, chromium, and nickel—in attempts to determine whether we could trace a legacy of metals left in the soil by industries operating along the river in the past hundred years. We found that the Notch site, closest downstream of the industrial center of North Adams, contained the most metal contamination. In addition, metal contamination at the Airport and Cole sites could have originated at the Aluminum Plant and Williamstown Manufacturing Company, respectively.

Introduction

Toxic metal legacy in soils has become an increasing environmental concern as new scientific research linking toxic concentrations of metals to adverse health risks and problems has emerged. For example, the Agency For Toxic Substances and Disease Registry reports that exposure to high levels of lead can “affect almost every organ and system in your body,” including the central nervous system (DHHS, 1999). While the effects of chromium, cadmium, zinc, copper, and nickel are less familiar, they also impose significant health risks when ingested or inhaled in high quantities, including lung cancer, kidney disease, anemia, and liver damage (DHHS, 2007) and (Gulley, 2007).

Unlike organic substances, metals are non-degradable and have a tendency to bind tightly to soil particles, so they accumulate in soils over time, becoming more toxic at higher concentrations (ENVI 102 PPT, 2007). When humans come into contact with soils, they may inhale or ingest them directly. In addition, humans may ingest metals indirectly by eating plants that have grown in metal-laden soils (DHHS, 1999). Therefore, we wished to postulate whether the concentrations of metals found in our soil samples were high enough to pose health risks by comparing them to concentrations from Hopkins Forest soils not affected by industrial discharge.

We also attempted to trace a legacy of these metals from their point-sources at industries located in North Adams and further along the Hoosic to the sites where they were deposited along the river. Throughout the 20th century, industries and businesses have operated along the Hoosic River, concentrated the most densely in the industrial center of North Adams, from tanneries and iron works to textile dyers and a producer of electrical parts. Many of these manufacturers emitted cocktails of toxic substances into

the river, including the metals we tested for. However, we determined that it was nearly impossible to match specific industries to the metals we found in our samples due to many factors, including the large number of industries present from 1911 to the present, the lack of information about which industries discharged which metals, and the difficulty of correlating the soil depth to the year the metals were deposited. Nonetheless, we were able to make generalizations using our data; the most noticeable trend in our data was that the Notch site situated the closest to North Adams contained greater metal concentrations than the other sites further downstream.

Methods

We dug soil samples at five different locations along the Hoosic River, between Williamstown and North Adams (Appendix 1). The samples from the Notch site were obtained February 21, 2007 by the ENVI 102 class, and included samples from three holes spread out throughout the site. We gathered samples from four other sites in April 2007 by digging one hole at each site. After digging the pits, we used a meter stick to collect soil samples at various depths using a metal core five cm in diameter, defining the depth as the center of the core.

In the lab, after storing the samples in plastic zip-top bags, we followed procedures summarized in the ENVI 102 Laboratory Manual. We placed a five-to-ten gram portion of each sample in a crucible and evaporated the wet soil samples in a 100 degree C oven to determine moisture content. The dry soil was then placed in a 600 degree C oven, burning off any organic matter, to calculate organic content (Loss On Ignition method). To obtain the concentrations of metals in the soil samples, we used

nitric acid digestion followed by filtration, dilution to create a 100mL solution, and analysis in the atomic absorption spectrophotometer, using unique lamps and standards for each metal tested. We filtered half of the samples a few hours after their digestion in 5-10% nitric acid when the acid had not evaporated much. However, the other half was filtered over 24 hours after digestion when the nitric acid had evaporated, so 5% more had to be added and the samples re-boiled. Therefore, the nitric acid added to our samples ranged from 5-15%. We used only 10% nitric acid standards for the AAS, which may not accurately represent the percent nitric acid in the samples, especially the second half filtered. Nonetheless, we expect that this alteration had little effect on the final metal concentration values due to the excellent correlation between organic content, which was not affected by the nitric acid process, and metal concentration (Appendix 12).

Other uncertainties in measurements include core depths, moisture/organic content calculations, and AAS readings. We estimate that core sample depths were accurate to within 10% (for example, 5 cm of a 50 cm depth). The organic content and moisture content measurements are probably accurate to within 10% based on replicate samples of Hopkins Forest soil samples from a previous lab (Gulley, 2007). However, these uncertainty levels do not impact our ability to effectively analyze the data, as we are searching for overall trends in moisture and organic content rather than specific values. According to the lab instructor, the atomic absorption spectrophotometer may have an uncertainty range of $\pm 10\%$. Taking duplicate readings of the 2 ppm and 5 ppm standards in the middle of multiple sample runs confirmed the AAS's uncertainty range of $\pm 10\%$.

We also encountered two minor problems that led us to remove a few of the data points from the graphs. First, while removing the samples from the furnace, samples W4 and D1 were spilled, mixing together. Second, samples W4 and D4 sat adjacently on a hot plate while the nitric acid boiled, and the acid from one spurted into the other. We also omitted sample W13 due to its high inconsistency with neighboring data points (Underlined in Appendix 13). Finally, the main anomaly in the data was due to a large block of black, plastic-like material found at the Airport site, which melted to the sides of the crucible after evaporating the moisture, and left black pieces intact after burning off the organic matter. When we tested these samples, we discovered it was composed of about 10% zinc and also included concentrations of cadmium and nickel much higher than any other sample. Therefore, zinc, cadmium, and nickel were graphed twice, once accounting for the block o' zinc, and once excluding this data.

Results and Discussion

Site Descriptions

Due to the disparity of site locations we chose, it is useful to give brief descriptions of the characteristics and conditions of each site. Differences such as sampling distance from the river, sampling height above the river, and current river conditions demonstrate the difficulty in making spatial and temporal comparisons across sites. Unlike tree rings, in which each year yields a new ring, differences in annual stream flow, flooding patterns, and major flooding events make it difficult to find a direct correlation between date the soil was deposited and soil depth. The disparity between our sites makes this correlation even more unlikely; we cannot assume that samples obtained

from two different sites at 40 cm both contained soil deposited in the same year or even years. The following are brief descriptions of our five sites:

Notch: Sampled 2/21/07 by the ENVI 102 class. We dug three sampling pits, one on a flat, open area close to the river, one in the same area but further from the river, and one further upstream at the base of a small hill surrounded by trees and vegetation (Gulley, 2007). This site is located the closest downstream from the large concentration of industries in North Adams, so metals found at this site are likely to have originated in North Adams.

Protection Avenue: Sampled 4/9/07. Samples were taken about three feet above the water level, and about fifty feet from the water's edge, on a large floodplain. This site is Boulders found 50 cm below the soil surface due to the surrounding flood control structure built about 50 years ago. Therefore, the soil at this site has accumulated for only 50 years and we cannot assume that any metals present originated in industries older than 50 years. The river this day was most likely lower than on our other sampling day, 4/18/07, after it had rained for multiple days.

Cole Avenue: Sampled 4/9/07. Our hole was dug ten feet above the water level and fifteen feet from the water's edge—it appears that this site does not get flooded as often as the others. Lots of large trees and vegetation covered the area. The ground was frozen and leaves covered the top layer of soil.

Ashton: Sampled 4/18/07, 2:00 pm. The site had been recently flooded, perhaps in the last two days. Our sampling hole is located four feet above the water level and about the same distance from the water's edge. Streamflow data from the USGS reports a gage height of 7.11 feet and a stream flow of 1290 cubic feet/second, reflecting a high water

level that followed a large amount of rain a couple of days before (USGS, 2007). The top layer of soil is a mixture of sand and dirt, and the sampling hole is situated between the river and a large berm. Since the river turns relatively sharply near the site, we suspect that the river deposits here frequently. This site is located directly across the river from the Spruces mobile home park, so we are especially concerned about the toxicity levels of the soil here.

Airport: Sampled 4/18/07, 2:45 pm. This site has also been recently deposited with sand that covers the top layer of soil. We dug our hole six feet above the water level and about forty feet from the water. The USGS streamflow and gage height are the same as those for the Ashton site (USGS, 2007). We walked down a large hill to get to the site, so toxic levels of metals here may not represent levels in the soil where development has taken place and people are more likely to be affected, on the top of the hill.

Industries

We gathered a large amount of historical data, including Teresa's research at the North Adams Historical Society. We compiled extensive lists of industries operating in the Williamstown-North Adams region throughout the 20th century in hopes of discovering where some of the metal contamination originated (see Appendix 1 for locations of industries and sites).

In Williamstown, the Williamstown Manufacturing Company, a textile mill that operated from 1865-1988 and is located directly across from the Cole Avenue site is most notable.¹ According to a Williams College report: "Started in 1865, the construction of

¹ Town of Williamstown, Massachusetts, "House of Local History," http://www.williamstown.net/house_of_local_history.htm (accessed 14-May-2007.)

the mill along the Hoosic River at Cole Avenue marked the beginning of the Industrial era in Williamstown.” The report details that until 1910, the mill was used to manufacture products from raw cotton, but was then sold to the Greylock Mills Company and converted into a textile mill. In 1939, it was sold again and used to manufacture photographic paper until it stopped production in 1988 (Endres, 2003).

Moving towards North Adams, we find the R.J. Widen tannery located just upstream of the Ashton Avenue site, in operation until 1976 according to the ENVI 102 project assignment details. Next, we encounter the aluminum plant, established in 1981, between the Airport and Protection Ave sites (North Adams City Directory, 1983). Finally, we move to the industrial center of North Adams, noticing that where Mass MoCA now resides, as the Hoosic River leaves North Adams, Arnold Print works operated from 1876-1942 and was then sold to Sprague Electric (North Adams Historical Society museum). We also gathered data from many other manufacturers and industries open from 1911 through 1983, including dyers, leather goods manufacturers, steel, iron, and aluminum works, a boiler maker, shoemaker, and paper box company. Many of these industries most likely released some combination of metals into the Hoosic, but due to the lack of information available, we cannot be certain. Nonetheless, information included below from ASTDR can help us make good predictions about the sources of metal contamination found in our samples.

Metals

The metals we tested for all occur naturally, and most are abundant and present in the earth's crust and soil. In addition, small amounts of copper and zinc are "essential for maintaining good health" (ASTDR, 2005). However, in large amounts, these metals are all toxic and can cause a variety of adverse health affects (ATSDR). In attempts to establish a baseline of naturally-occurring metal concentrations in soil, we compared our data with that taken from soil samples from Hopkins Forest, which we assumed to not contain metals discharged from industries but may include metals carried through the air from power plants or other operations (Appendix 13).

Lead

The discovery of lead in soil is most often linked to flaking lead paint from nearby buildings or houses. However, the lead in our soil more likely originated from industries that discharged it into the river, because the sites were mostly isolated from buildings. Products yielding lead from industries that also operated in North Adams include metal products, paints, and gasoline (ATSDR, 2005). The Aluminum Plant between the Protection and Airport sites could have also emitted lead.

Looking at our results, we find that at all sites, the lead concentrations lie above those in Hopkins Forest soils (Appendix 2). The Notch site contains the highest lead concentrations by far, followed by the Airport site. These sites are located downstream of North Adams and the Aluminum Plant, respectively, providing good evidence for the lead emissions of these two point sources. The Cole site shows an increased lead concentration compared to the upstream Ashton site. Therefore, we may postulate that the

Williamstown Manufacturing Company located between the two sites discharged lead into the river as well.

Copper

Copper is used in a wide variety of industrial processes, including the production of wire, pipes, and sheet metal, and as preservatives for wood, leather, and fabrics (ATSDR, 2004). In North Adams, copper could have been discharged from the aluminum tubing plant, the various metal works, and tanneries. Again, the Aluminum Plant could have also contributed to the contamination in our soil samples. The R.J. Wilden tannery and Williamstown Manufacturing Company, when it was a textile mill, could also have emitted copper. However, copper is also “commonly in agriculture to treat plant diseases like mildew,” and for water treatment, so these sources are also possibilities (ATSDR, 2004).

Viewing our data, we found an extremely close correlation between the lead levels and copper levels (Appendix 3). Each observation made for lead also applies to copper, including the highest concentrations seen at the Notch and Airport sites. The tight relationship between these two metal concentrations could reveal that the same industries discharged the metals. Again, all sites contained at least one sample that fell above the Hopkins Forest soil levels, although Protection Ave and Ashton Ave seem relatively clean of copper contamination. Therefore, it seems that either the tannery upstream of the Ashton site did not emit copper, the levels were held low, or the metals were not deposited at our site.

Cadmium

Used in battery manufacturing, metal soldering or welding, and pigments, the cadmium in our soils could be traced to such industries as metal works, Sprague Electric which produced capacitors and other electrical components, the Aluminum Plant, or perhaps dyers using pigments.

We found 0 ppm of cadmium in all Hopkins Forest soil (Appendix 13). Therefore, any cadmium detected at our sites probably originated from industries discharging it into the river or emitting it into the air and it settling nearby. Extremely high concentrations of cadmium were found within the "block o' zinc" and nearby soil at the Airport site (Appendix 4). Disregarding these concentrations, all sites had cadmium present, but the concentration never exceeded 3.5 ppm (Appendix 11). Again, the trend holds that the Protection and Ashton sites are relatively uncontaminated compared to the other three sites. Notch samples contain the greatest concentrations, most likely reflecting greater concentrations settling on the site from North Adams. However, no cadmium was detected in the middle layers of the soil, perhaps reflecting a time period where no cadmium was emitted. If this were true, one industry would probably be responsible for the total cadmium at the Notch site, since it would be unlikely for multiple industries to stop discharging cadmium at the same time. The steady amount of cadmium contamination at the Airport site may point to continuous emissions from the Aluminum Plant. One sample at the Cole site has a sharp peak in cadmium, and it is unclear what caused this peak. Overall, it appears that Cole is more contaminated than the Ashton site, which may be due to the presence of the Williamstown Manufacturing Plant.

Zinc

Zinc is found in industries producing batteries, metal alloys, anti-rust coatings, paint, rubber, dyes, and wood preservatives, and is also found in pennies (ATSDR, 2005). We could expect some of the industries in North Adams to be utilizing zinc, such as the metals works and dyers, and perhaps the Aluminum Plant and Williamstown Manufacturing Company.

At the Airport site, the large chunk of black solid was found to contain around 100,000 ppm of zinc, making up around 10% of the material (Appendix 13). The soil directly above the solid still contained pieces of it and carried 66,000 ppm zinc at a depth of 65 cm and 510 ppm zinc at a depth of 55 cm (Appendix 5). All of the other samples taken contained around 500 ppm or less zinc. We predict that this block of material, containing not only zinc but also high amounts of cadmium and nickel, was part of a spill from an industry long ago, since it was located 65 cm below the soil surface. We cannot tell what year it could have been deposited there, but we might be able to postulate that it originated at the Aluminum Plant. If we were to do further studies, we would want to sample closer to the aluminum plant and other areas upstream and downstream to look for more of this black solid.

Viewing the zinc data without accounting for the block, we find that again, all of the sites contained at least one sample with zinc concentrations above those in the Hopkins Forest soil. Our pattern seen with the other metals still holds for zinc: Notch had the highest concentrations, followed by Airport; Cole showed a bit higher concentrations

than Ashton; Protection and Ashton appear the least contaminated. The industries mentioned above may have contributed to the metal deposited.

Chromium

According to ATSDR, "Chromium(III) occurs naturally in the environment and is an essential nutrient. Chromium(VI) and chromium(0) are generally produced by industrial processes. The metal chromium, which is the chromium(0) form, is used for making steel. Chromium(VI) and chromium(III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving" (ATSDR, 2001). Therefore, one future direction for a project could be to try to differentiate between the different types of chromium present in the soil. If we found the chromium(0) form, we could be relatively confident that it originated at the steel plant. Finding chromium (VI) would point to other types of industries such as the dyers, tannery, or textile mill.

Nonetheless, we can assume that our samples contained at least some chromium(0) and/or chromium(IV) because the concentrations at Notch, Airport, and Cole are higher than those found in the Hopkins Forest soils, which most likely contains mostly chromium(III) (Appendix 6). These concentrations could have originated from the industries in North Adams, the Aluminum Plant, and the Williamstown Manufacturing Company, respectively, as we have hypothesized for the other metals. We knew that R.J. Widen tannery, upstream of the Ahston site, was using chromates until 1976. However, we detected chromium concentrations at Ashton that were below those found in Hopkins Forest. Due to the low concentrations of other metals at the Ashton site as well, it is possible that the river used to flow in a different direction and did not deposit at the site until recently. The sharp bend in the river around the Ahston site may testify to this

inside/outside bank
in turn.

hypothesis. Another possibility is that the metals were deposited previous to 1976 and have now washed away. We think this possibility is less likely, since metals bind tightly to soil particles and were found in high concentrations at other sites. Another hypothesis is that the tannery could have not been using much metal, or disposed of the metals elsewhere, although the custom of the time was to wash industrial wastes down the river.

Nickel

Nickel is most commonly used to make stainless steel, and can be used to make various metal alloys which can be crafted into metal products such as jewelry, coins, and pipes. Nickel is also emitted into the air by coal- or oil-burning power plants and trash incinerators (ATSDR, 2005). We could therefore expect to find nickel at the metal works in North Adams and perhaps the Aluminum Plant. Additional sources of nickel could be from the coal-fire power plant in North Adams.

We tested for nickel at only four sites. Again, the block o' zinc was found to contribute a high concentration of nickel not present at the other sites (Appendix 7). Since we did not test the Hopkins Forest soil for nickel, we have no baseline from which to examine possible industrial contamination. Nonetheless, it appears that nickel follows the same general trends as the other metals, in that higher concentrations were found at the Airport and Cole sites (Appendix 10). We suspect the industries were more to blame than the coal-fire power plant for the nickel concentrations, because they followed trends seen in the other metals which could not have originated from the power plant.

Other Trends

We found that in most cases, the depth in the soil does not parallel the metal concentrations (Appendix 14 provides representative examples). We expect that in these cases, the depth of soil closely correlates to the time the soil was deposited, perhaps with older industries depositing more metals in general, due to observed increases in metal concentrations at lower depths in all metals, especially at the Airport and Cole sites. Due to industries opening and closing over time, metals ^{discharged} emitted would be deposited irregularly throughout the soil.

Finally, we found that at the Protection site, the percent organic matter inversely correlates with metal concentration (Appendix 12). This trend makes sense considering that higher concentrations of metals will be found on inorganic particles that have more surface area to bind to than organic matter. We can use this chart as evidence of minimal general errors in our data.

Conclusions

We conclude that we cannot establish a timeline of metal emissions into the Hoosic River using only the data we collected, due to lack of information on specific industries including when they operated and what metals they discharged. However, we can remark on general spatial trends in the data.

First, there were generally higher concentrations of metals at the Notch site than the others, most likely due to its location closely downstream of the North Adams industrial center (Appendix 8). The Airport site was generally the next most contaminated, which could be explained by the Aluminum Plant upstream of the site.

This hypothesis is supported by the lower concentrations of metals found at the Protection site just upstream of the Aluminum Plant. However, we would need more details on the metals used at the plant to make a better prediction. Cole Avenue was also relatively contaminated, even though the sampling site was located ten feet above the water level and appeared to be flooded less often than the other sites. Since the Ashton site upstream of Cole was less contaminated, the Williamstown Manufacturing Company could have been highly polluting. Again, we would need more information to be more confident in our results.

Each metal concentration corresponded to the other metal concentrations extremely well, as the parallel fluctuations in Appendix 8 shows, leading to the suggestion that one metal could be used as an indicator the presence of other metals in the soil.

Except for chromium, all the sites had at least one sample with higher metal concentrations than the Hopkins Forest soil. We can conclude that industries did leave a metal legacy in Hoosic floodplain soils, and in some cases left concentrations that warrant further testing to ensure the health of the public.

Acknowledgements

I would like to acknowledge the ENVI 102 class for the collection and analysis of soil samples from the Notch site, Jay Racela for help collecting data from the AAS, and of course my lab partner Teresa. I obtained Appendix 12 from Teresa.

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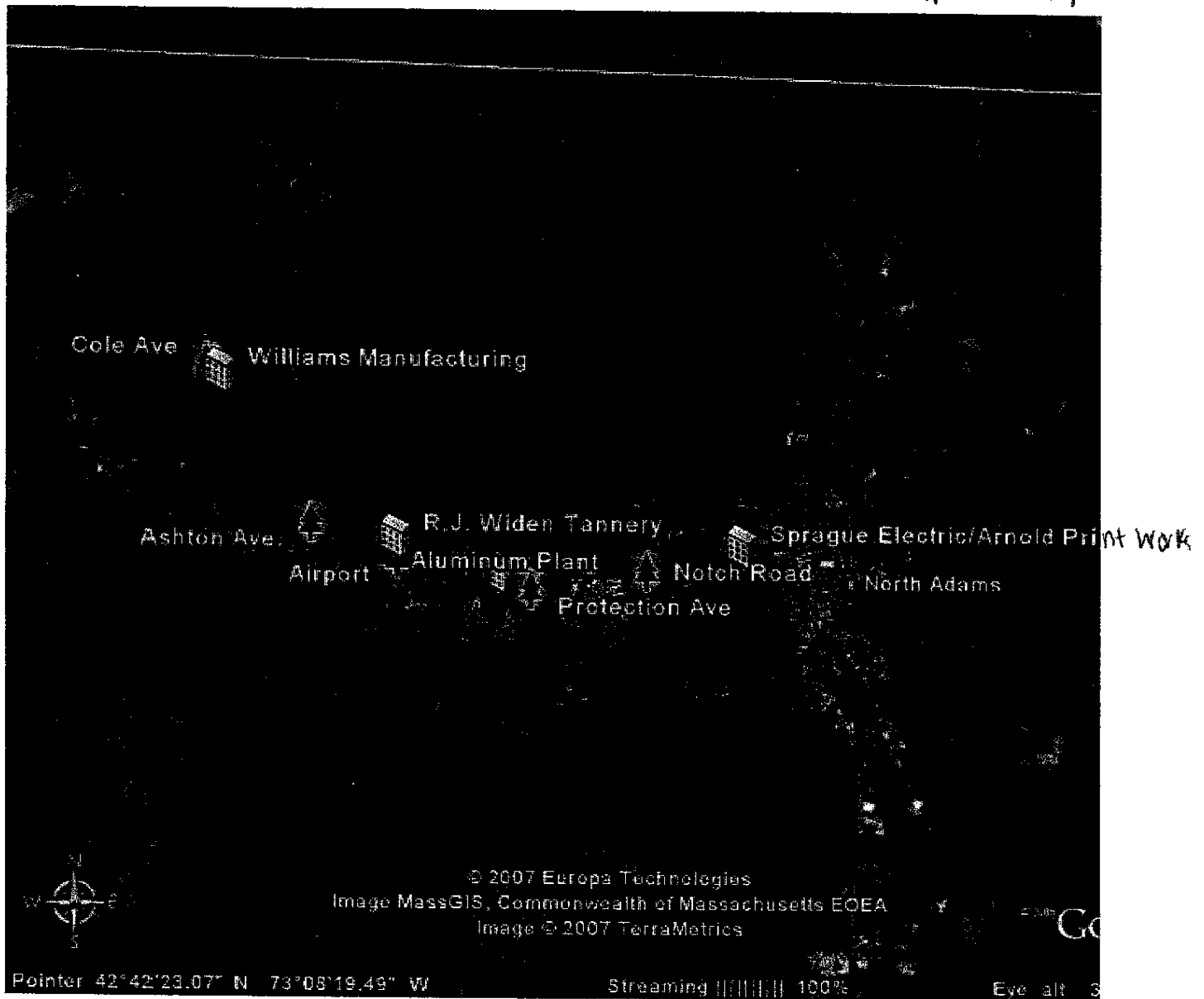
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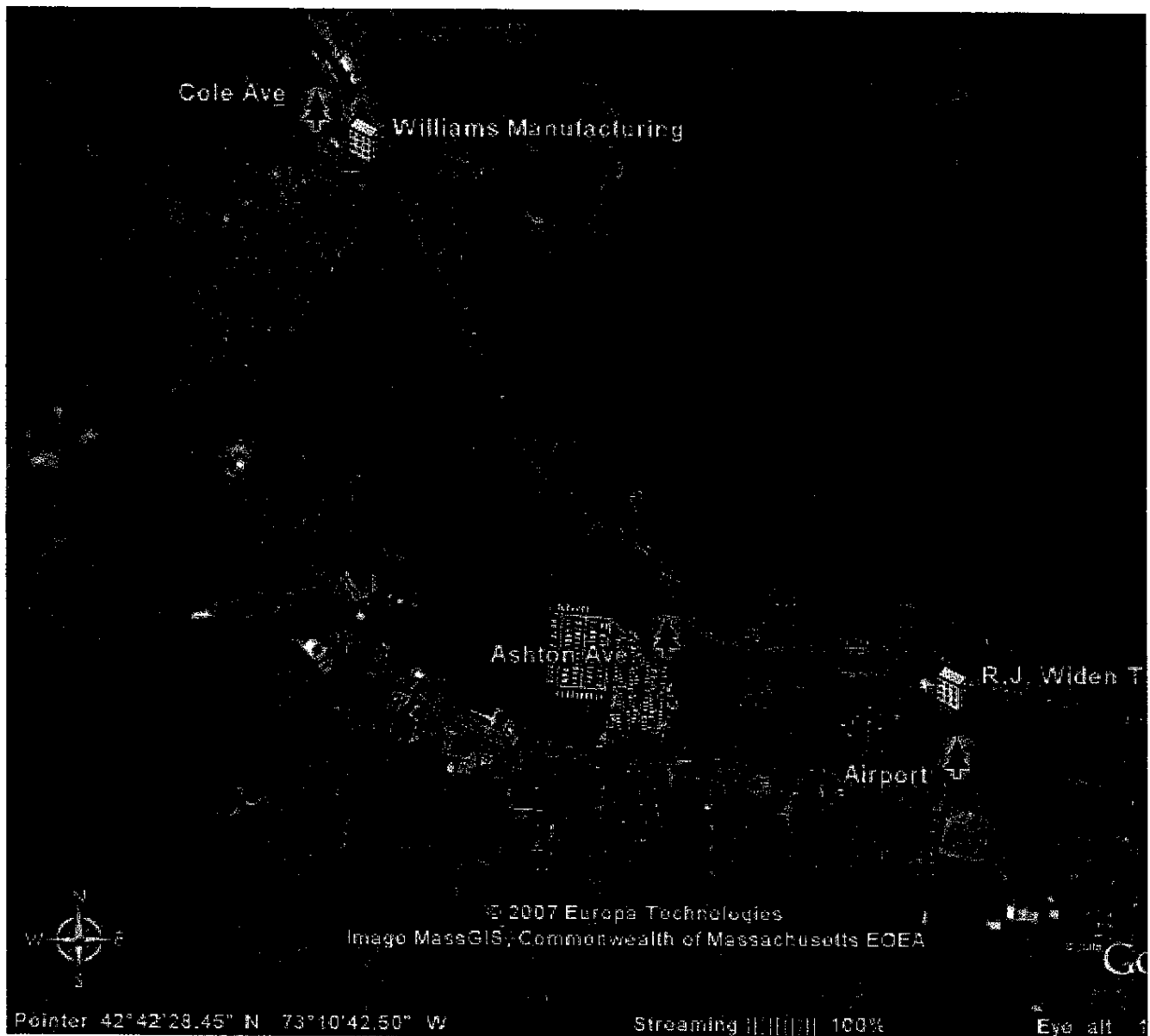
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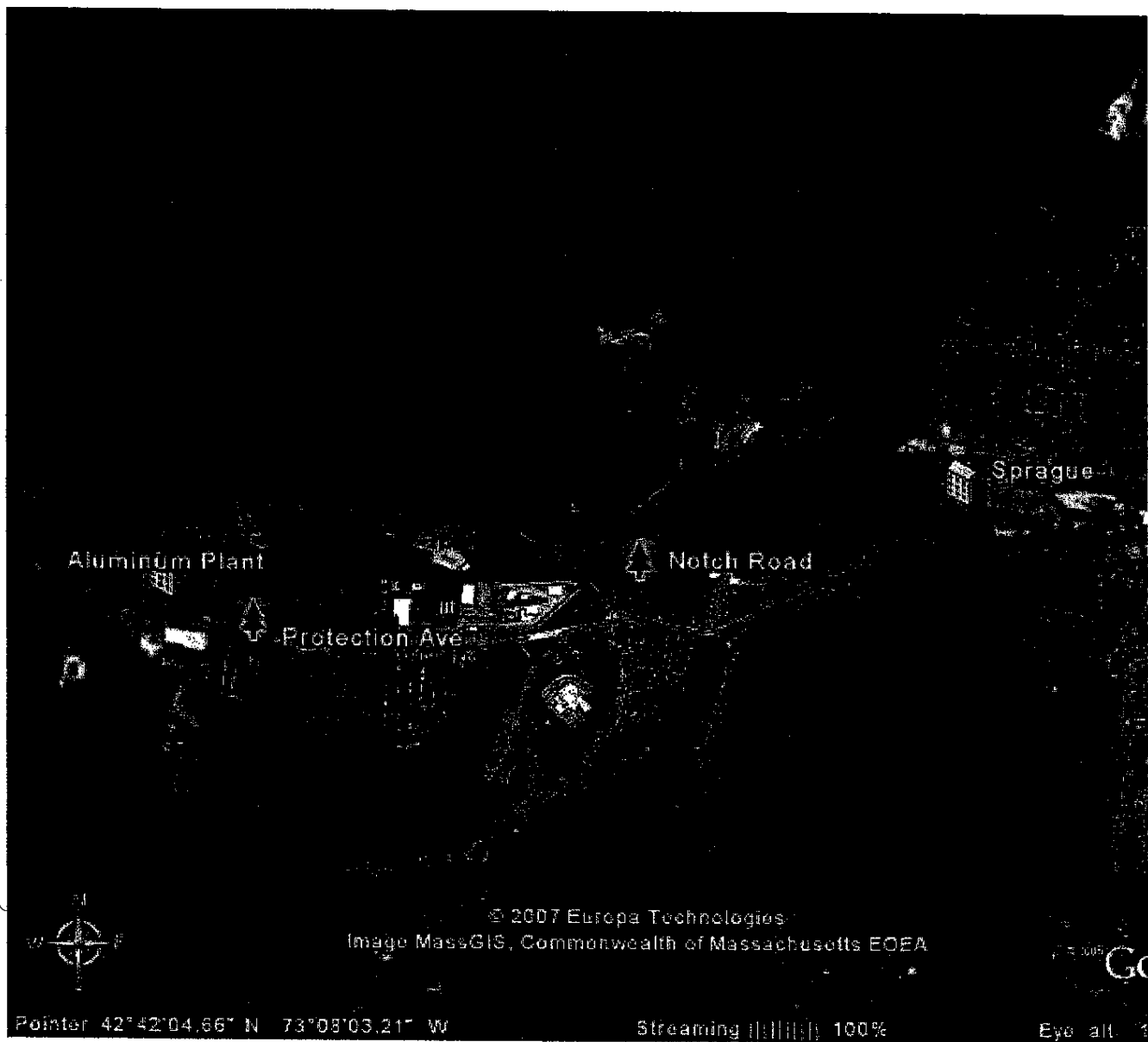
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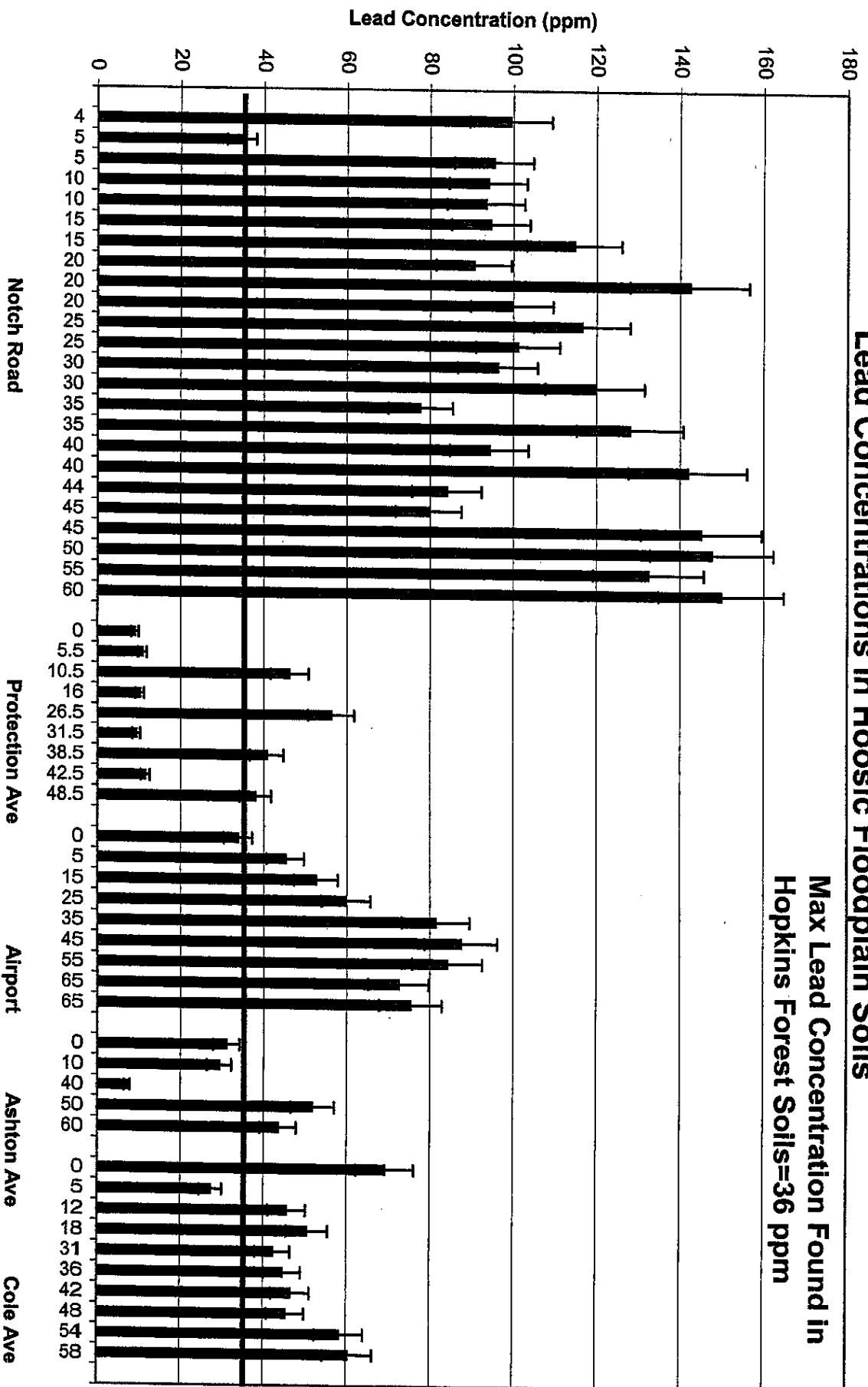






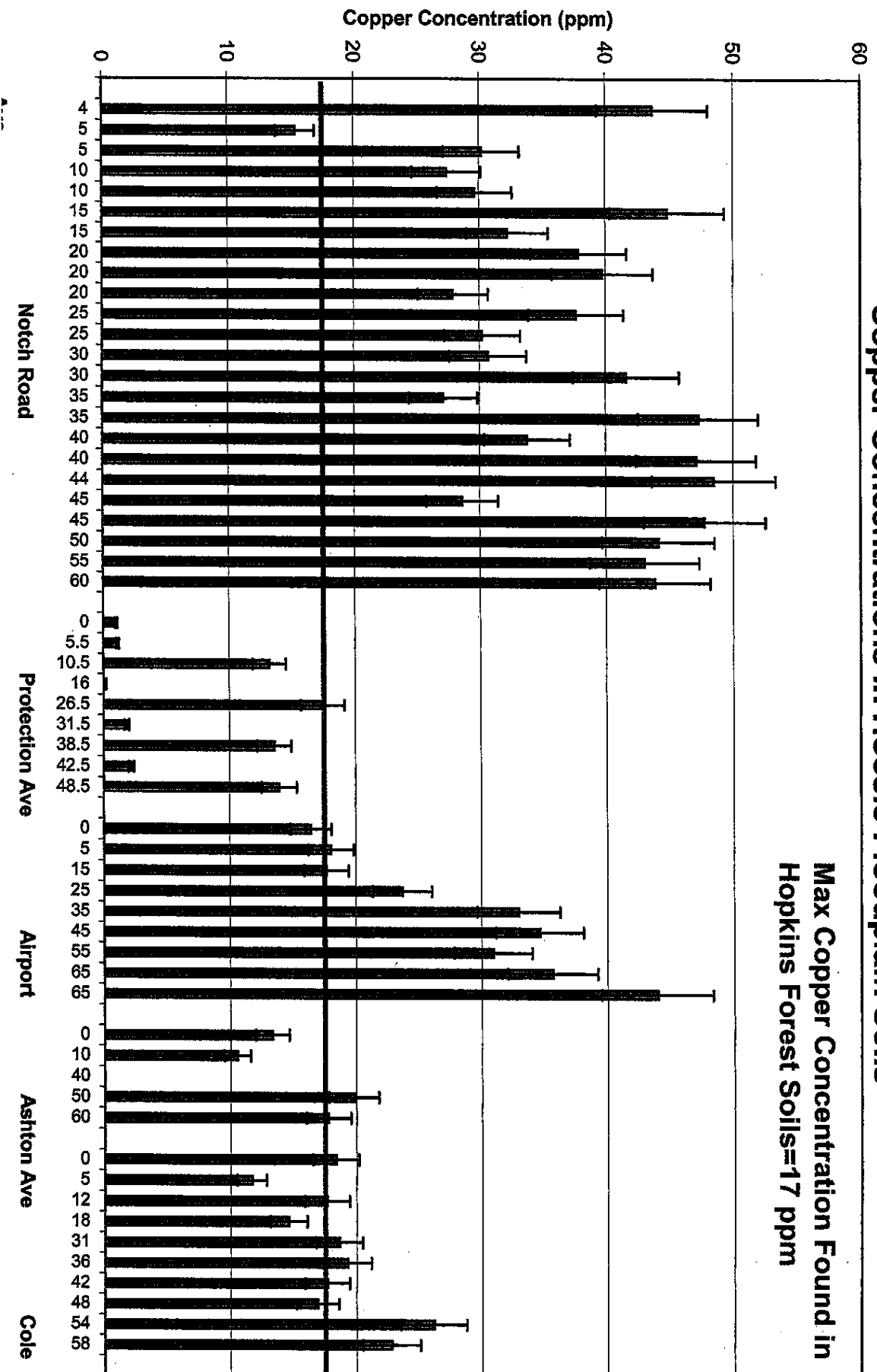
Lead Concentrations in Hoosic Floodplain Soils

Max Lead Concentration Found in
Hopkins Forest Soils=36 ppm

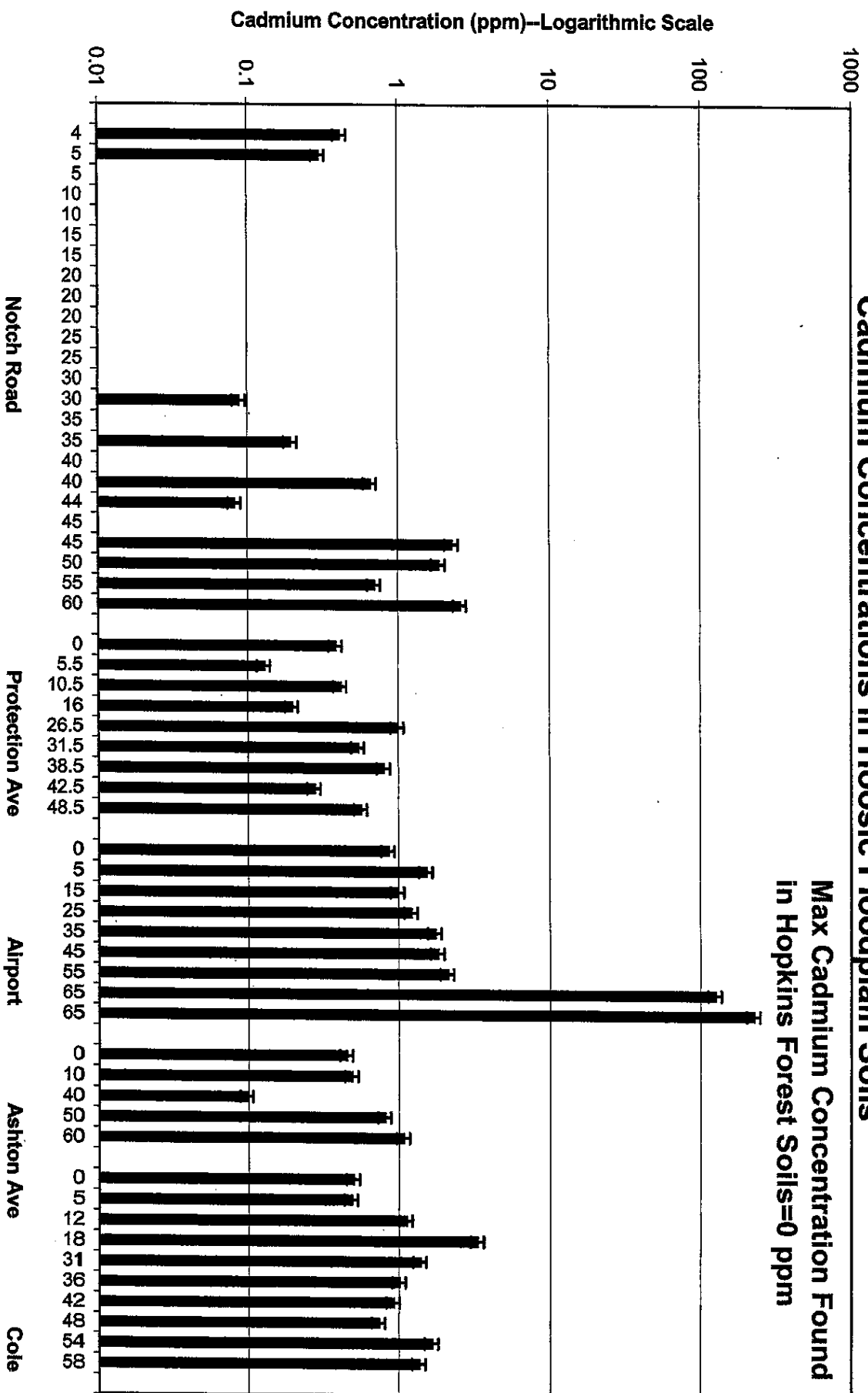


Copper Concentrations in Hoosic Floodplain Soils

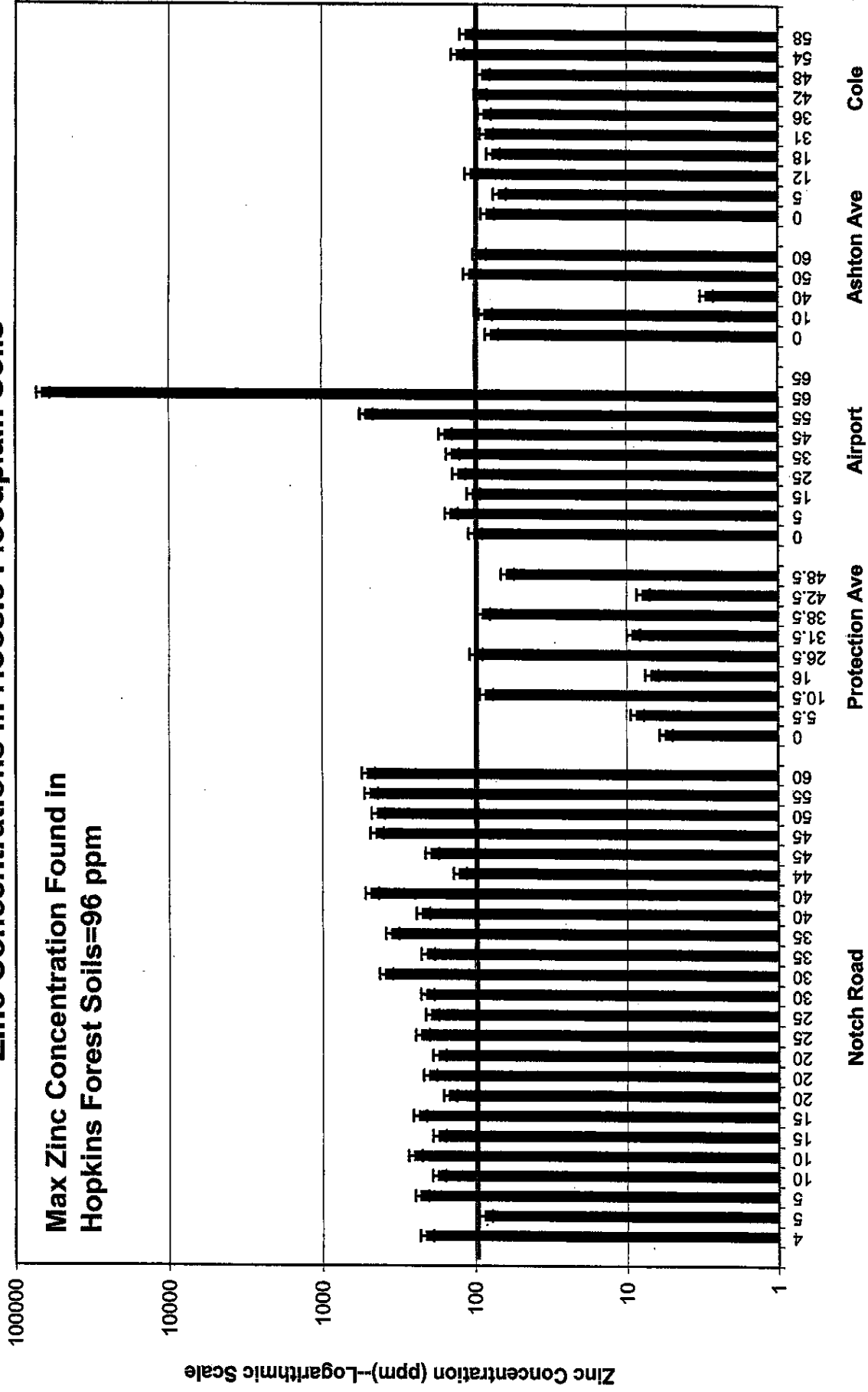
Appendix 3



Cadmium Concentrations in Hoosic Floodplain Soils

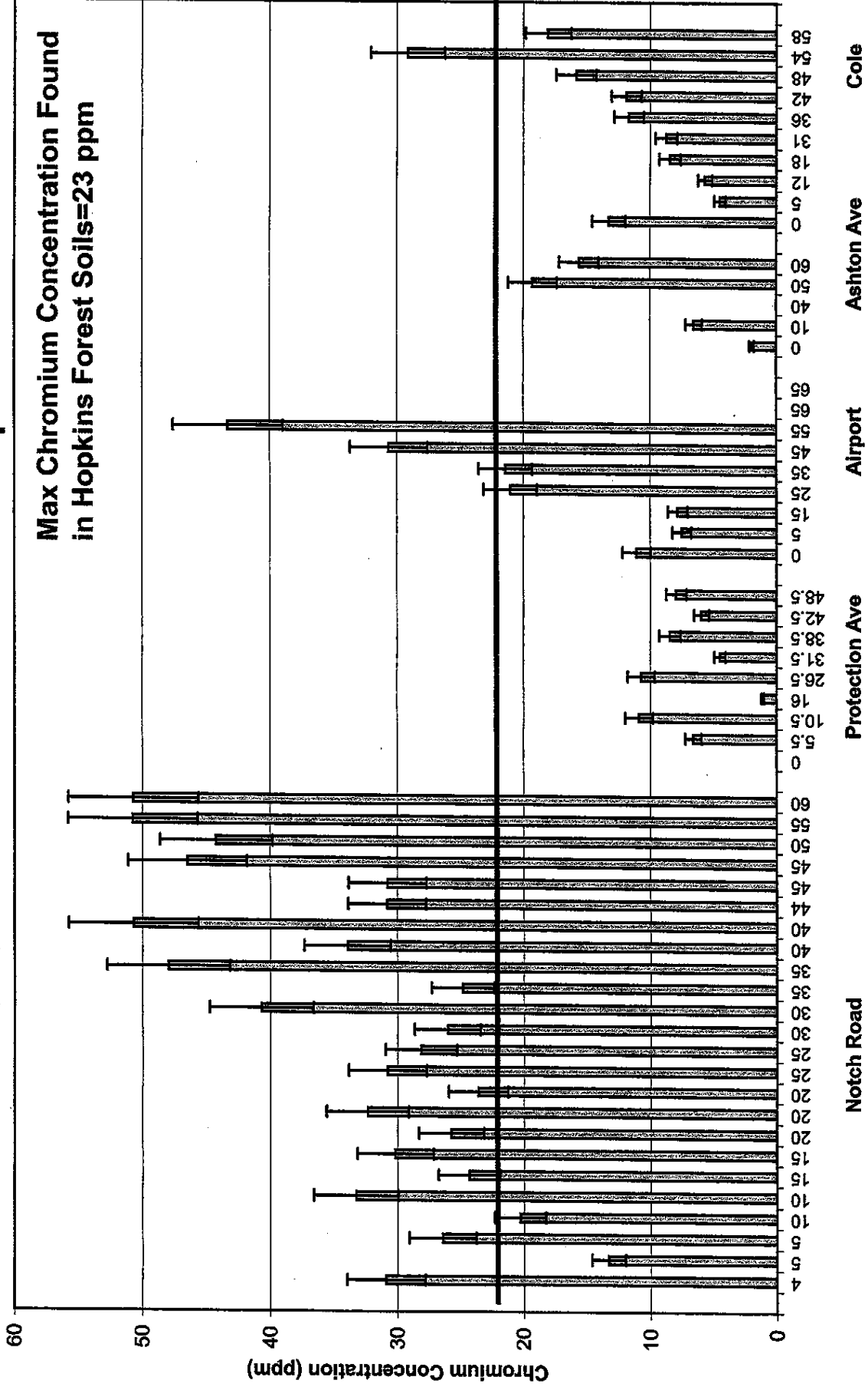


Zinc Concentrations in Hoosic Floodplain Soils

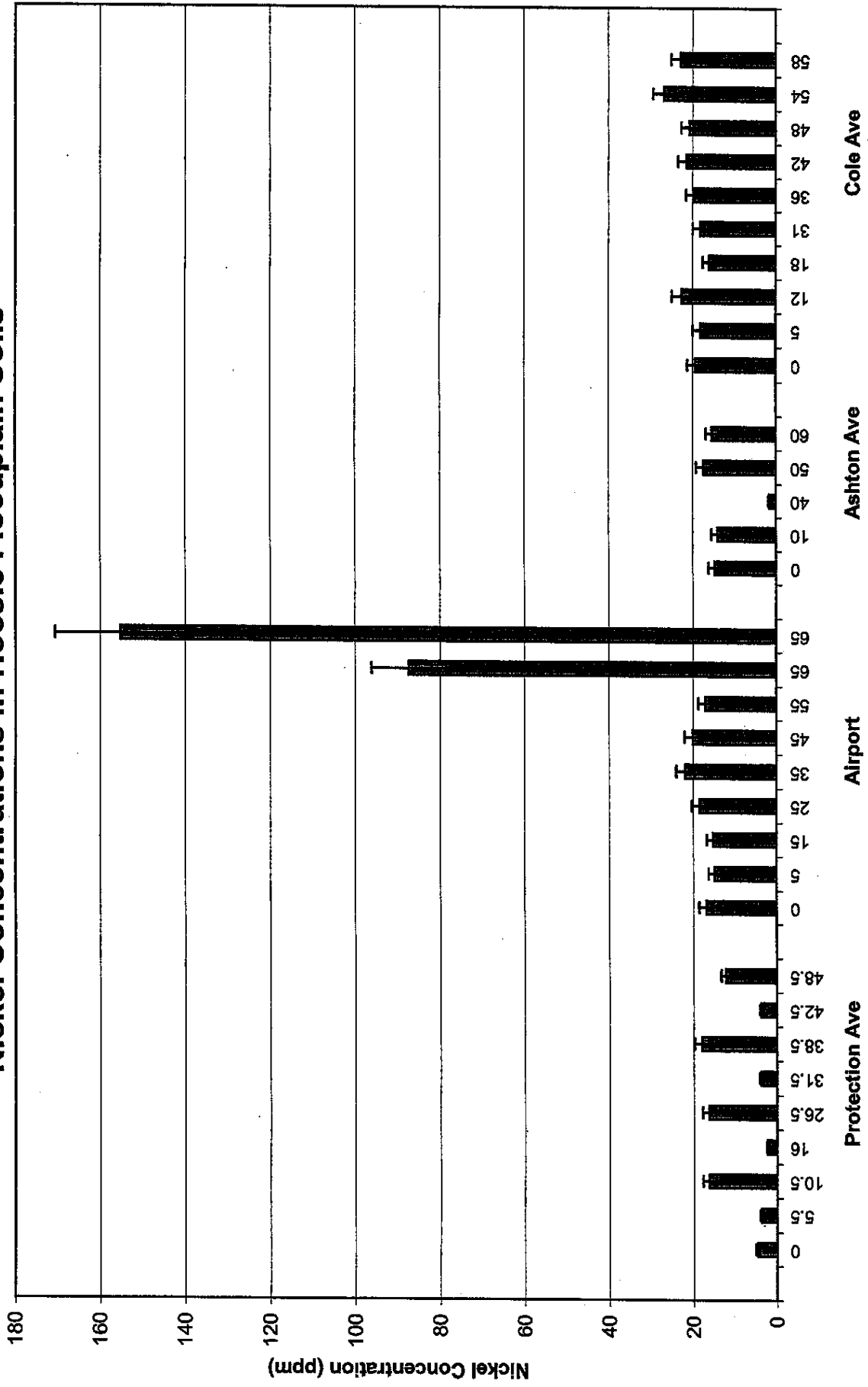


Chromium Concentrations in Hoosic Floodplain Soils

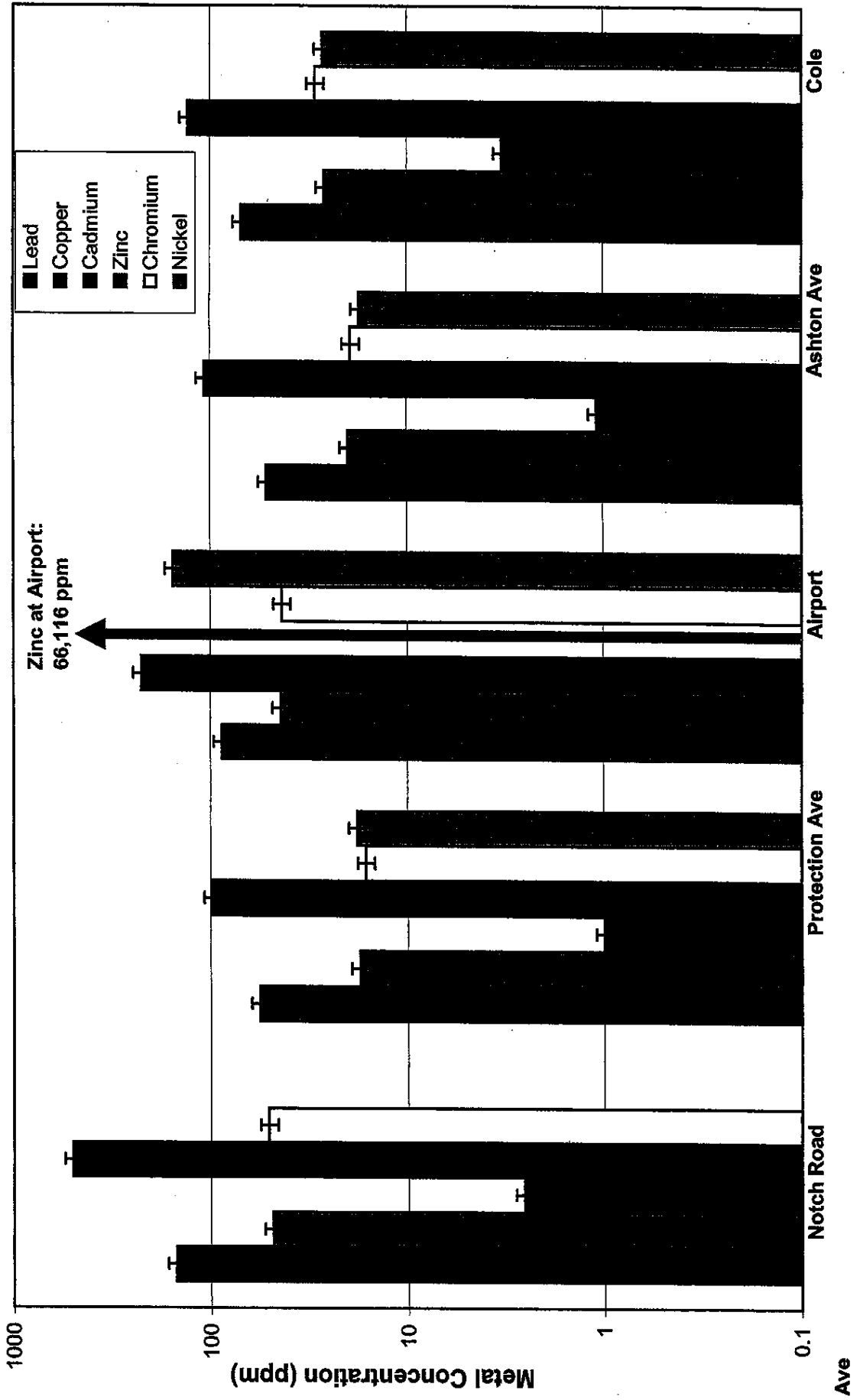
Max Chromium Concentration Found
in Hopkins Forest Soils=23 ppm



Nickel Concentrations in Hoosic Floodplain Soils

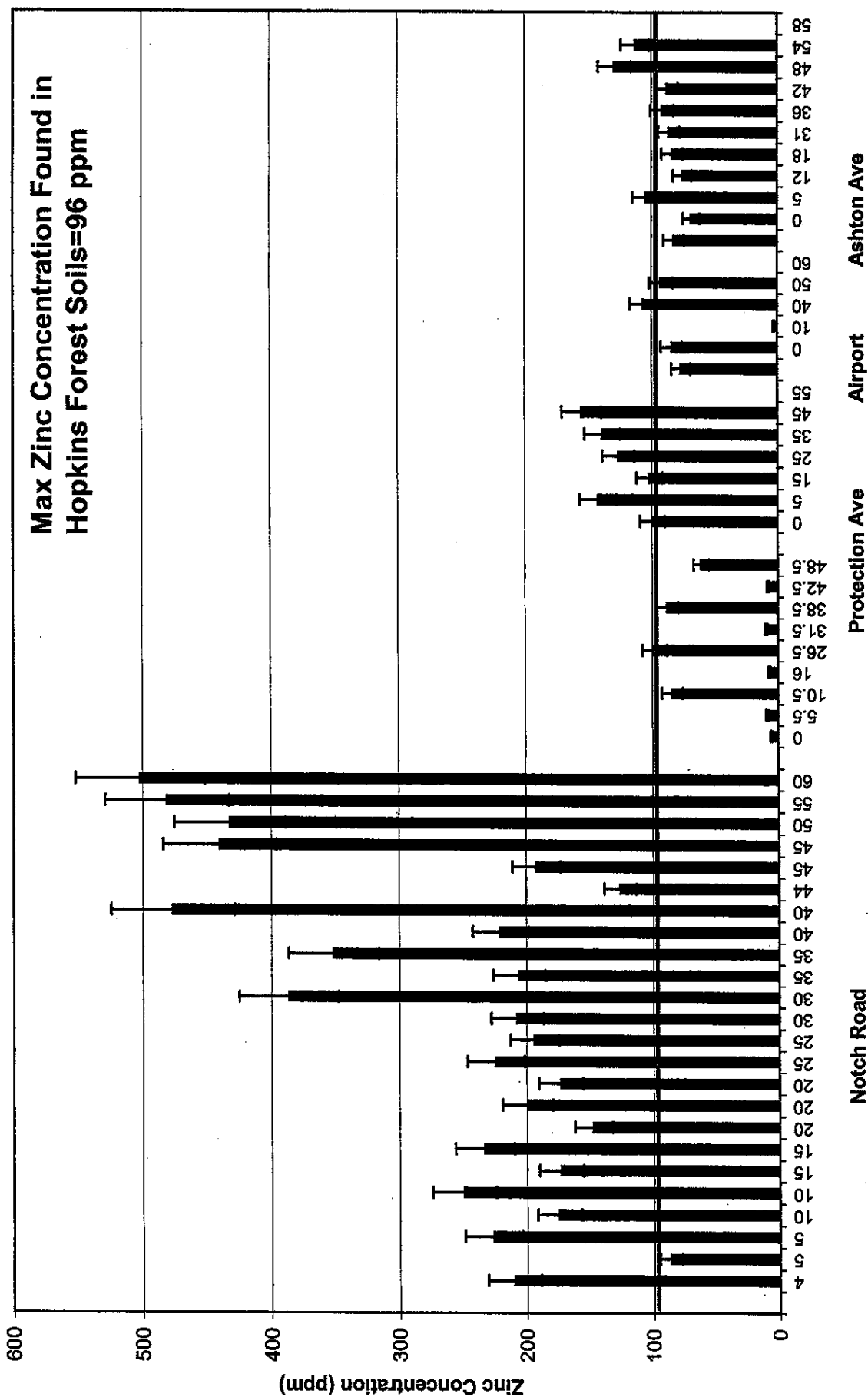


Maximum Concentrations of Metals Found in Hoosic Floodplain Soils

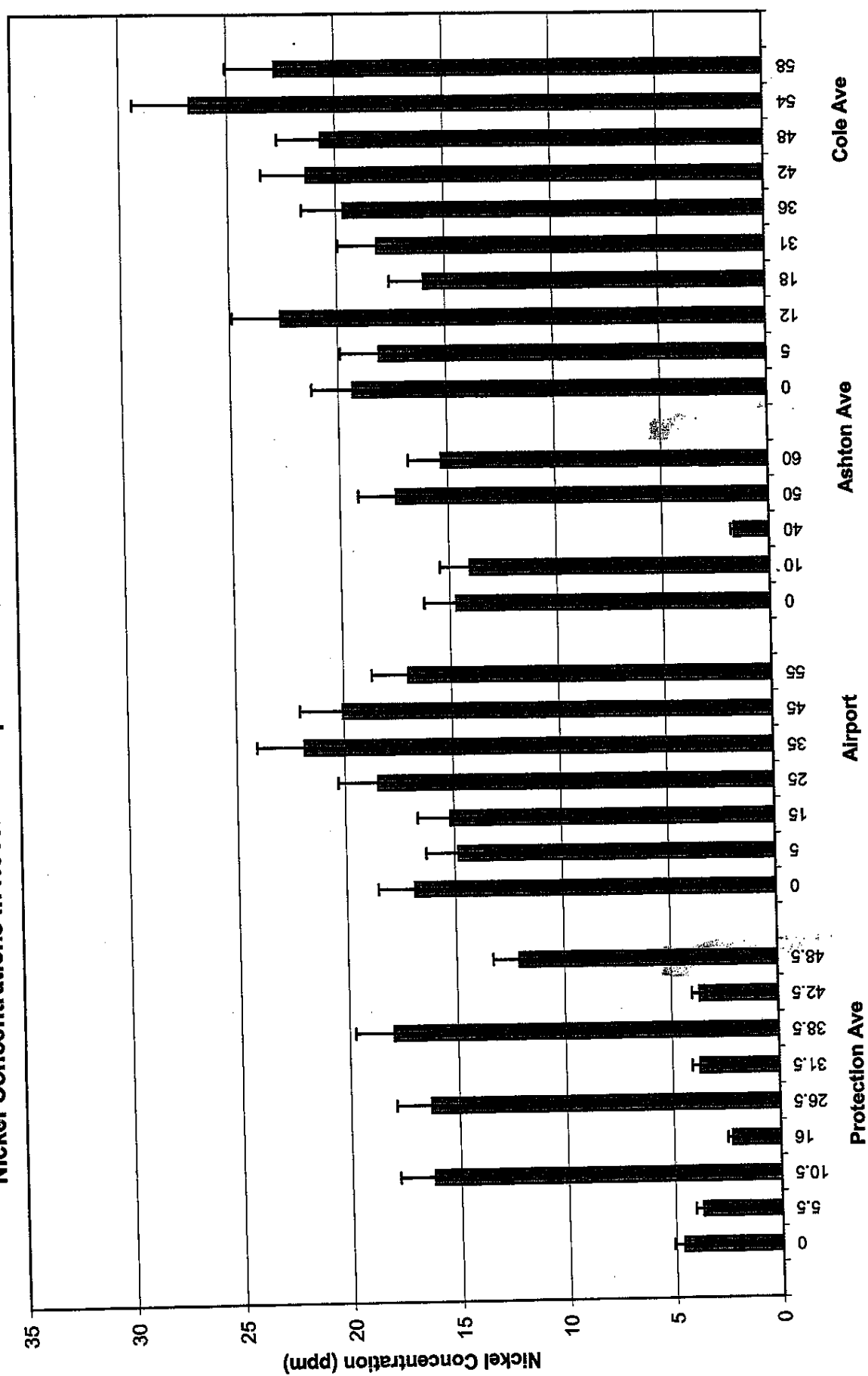


Zinc Concentrations in Hoosic Floodplain Soils, Excluding Outliers (Block of Zinc)

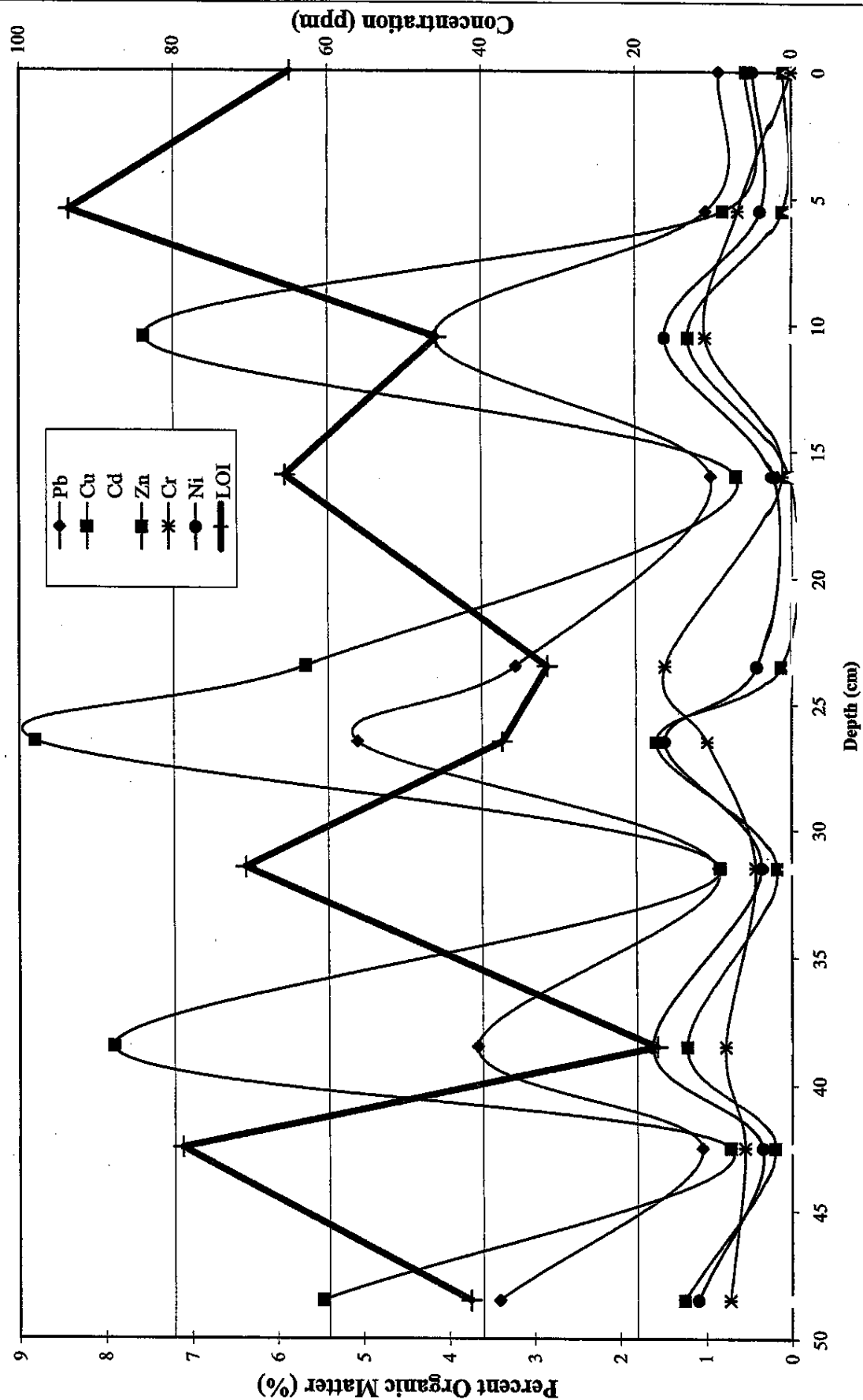
Appendix 9



Nickel Concentrations in Hoosic Floodplain Soils, Excluding Outliers (Block of Zinc)



Correlation Between Metal Concentration and Percent Organic Matter
Protection Ave.



Zinc and Lead Concentrations According to Depth in Soil

