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Study of the Levels of Insoluble Mercury in the Soil of the Lake Calumet and South Chicago Area

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ABSTRACT

Over 100 randomly distributed soil samples were gathered in the Lake Calumet region on the south side of Chicago. The samples were gathered from the top few centimeters of soil. Locations were determined by GPS portable receivers and each site was described. The average mercury content in the samples was 122 parts per billion (ppb) with a large standard deviation of 180 ppb indicating at least a bimodal distribution of values. No significant evidence indicates appreciable deposition of this insoluble mercury pollution can be attributed to a nearby coal-fired power plant. The sites with large concentrations appear to be associated with past or continued use of mercury pesticides, industrial spills, or transportation related emissions.

INTRODUCTION

For over the last decade since the Clean Air Act of 1990 (USEPA, 1990) there has been active research and policy formulation to reduce the emission of mercury from coal fired power plants (USEPA, 1997). In March 2005 a final rule on a mercury emissions cap and trade system (CAMR, 2005) was published. This rule sets nationwide caps for mercury emissions which will slowly decrease over the next 20 years and should allow power plants to trade emission credits as a mechanism for facilitating the process of emission reduction. In preparation for this final rule the United States Environmental Protection Agency has conducted and sponsored analyses and discussions (Sullivan, 2006) about issues pertaining to mercury emissions from coal fired power plants. One of the unresolved issues is whether there are "hot spots" of excess mercury deposition around the plants that would not be ameliorated under the new national standards and caps.

Most predictions of mercury deposition have been based on mathematical dispersion models based on emissions and simple models of deposition (Sullivan, 2006). These models have included atmospheric chemistry processes that affect the partitioning of Hg emissions into elemental (Hg^0) and reactive forms (Hg^{2+} : soluble or insoluble) that may be deposited near sources (Sullivan, 2006). The possible depositions may be in the soil, the plant matter, and in water or aquatic animals. Recent evidence (Edgerton, 2004; Laudel, 2004) has suggested that reactive gaseous mercury in plumes emanating from coal fired power plants quickly reduces to elemental mercury. This effect would greatly

reduce the deposition near coal fired power plants and bring into question whether there are significant “hot spots” near such plants.

A major study of localized mercury deposition by Brookhaven National Laboratory (Sullivan, 2004) surveyed all of the previous literature and conducted a follow up study of two rural power plants. One of these was the Kincaid power plant which is in a rural area just east of Springfield, Illinois and was being studied for a second time. The other studied plant was only identified as Plant A. Including the second Kincaid study there have been five studies of the Hg content of surficial soil samples around coal fired power plants. (Klein, 1973; Anderson, 1977; Crockett, 1979; Sullivan, 2006). The Klein study was conducted near Campbell, MI, around a 650 MW coal fired plant with a 122 m stack. There were 90 samples with a mean concentration of 10.2 ppb (parts per billion by weight, or, equivalently, micrograms of Hg per kilogram of soil) compared to an estimated background of 7.9 ppb. Anderson studied the Kincaid plant near Springfield in 1977. In this study there were 90 soil samples with a mean concentration of 22 ppb over an estimated background of 15.4 ppb. The Crockett study was conducted in the Four Corners area of the southwestern United States and measured 70 samples surrounding the 2150 MW Four Corners power plant. There was no measurement of the background concentration but they found an average concentration of 14.5 ppb in the area. A re-analysis of their concentrations as a function of the distance carried out by Sullivan found a logarithmic derivative of -0.11, though the standard deviations at each distance were up to two thirds of the average values at each distance and this estimate is not significant statistically.

Around Plant A (Sullivan, 2006), which burns locally mined lignite, soil and vegetation samples were collected at 54 selected sites in a region predicted by mathematical precipitation models. The average soil background for Plant A was 28.2 ppb. The soil Hg concentrations for this plant did not show any significant trend with distance and were not distributed as predicted by the deposition model.

The Kincaid plant (Sullivan, 2006) was sampled at 122 sites evenly spaced on a one mile square grid around the plant for radial distance of about 5 miles. The average soil concentration of Hg was found to be 32.4 ppb, with a standard deviation of 17.7 ppb. The range of values was 16.9 to 155.6 ppb. Eight additional sites were chosen along roads far from the plant to serve as background. It is interesting to note that these 8 samples from roadside sites 11 to 23 miles away were higher than sites nearer the plant, with an average value of 41.0 ppb. These samples were taken within 20 feet of the edge of the road in the right-of-way. The 2004 study of Kincaid (Sullivan, 2006) showed roughly the same range of soil samples as the 1977 study, with a number of higher values. Not all of the 1977 data was available so it was not possible to calculate whether the difference between the average values is significant.

All of these power plant site studies have been in rural areas. It is well known that in urban areas there will be a higher level of Hg concentration (Landis, 2002). This study of Hg in soil samples in an urban area was carried out to provide a contrast to the rural sites and to examine the question of “hot spots” in a heavily populated area.

MATERIALS AND METHODS

The process of sampling began by generating 200 random sites within the Lake Calumet quadrangle map of the USGS, covering from (41º37'30''; 87º37'30'') in the lower left hand corner to (41º45'; 87º30') in the upper right hand corner. These 200 random sites were then divided into five groups and each of our researchers culled sites with inaccessible or dangerous locations in the midst of highways, lakes, industrial sites, or rail yards. Sites that were close to each other were merged and the final 100 sites were designated. Each of the five researcher groups were driven to the sites, determined the exact location using a GPS device, wrote a brief description of the site for further correlation, and collected a surface soil sample (1 to 5 cm in depth) (Sullivan, 2006). The soil samples were dredged from the shallow surface soil at each site and collected into a 50 ml centrifuge tube that was labeled by sample number. From each sample were weighed out two replicates of soil that had been separated from any organic material. The samples were then analyzed for mercury according to the protocols outlined as EPA Method 7473 (USEPA, 2000) using a Direct Mercury Analyzer (DMA-80, Milestone, Inc). Of all the 100 pairs of samples which were run for this study, only ten pairs were surprisingly disparate, and these samples were run a second time. Later in the fall one of us (J.F.) collected an additional 20 samples on the west side of the Calumet quadrangle.

SAMPLE SITE GEOGRAPHY AND HISTORY

The Lake Calumet area in Illinois is the area including the southeast section of Chicago bounded on the east by the State of Indiana boundary and on the south by the suburbs of Dolton, Thornton and Calumet City. The area has quite a variety of ecosystems, ranging from densely populated single family residential areas, some multiple family housing, industrial sites (both active and inactive), navigable and re-constructed rivers, canals and basins and natural lakeside, grassland and forest. The soil region is mostly Wisconsian Outwash (NCRS, 2007). The Little Calumet River and the lakes connecting to the southern shore of Lake Michigan made this region a water transportation hub and industrial site almost from the earliest settlements in the region. The area has been an industrial and transportation center of the nation for almost 200 years. In particular, coke plants and steel plants have been very abundant in the northeast part of this area. In the Northeast corner of quadrant is the State Line coal-fired electricity generating plant (525 MW). Near the center of the region is an inactive coke plant that was used for many years to generate coke for use in nearby steel mills. Through the center of the region and across the northern third are two major highways: Interstate 90/94 and the Skyway I-90, connecting to the Indiana Tollway in the northeast. Interstate 57 begins near the center and proceeds to the southwest. Many railroads pass through this region with numerous sidings to active and inactive industrial sites. There are also several large high voltage lines that traverse the region. Two institutions of higher learning are in the area: Chicago State University and Olive Harvey College, one of the City Colleges of Chicago. A number of elementary schools and high schools are also in the area. The area also has a number of landfills and a number of chemical and chemical waste companies.

RESULTS AND DISCUSSION

The average Hg concentrations for this study and the previously discussed studies are reported in Table 1. The average of this study was 122 ppb and the range of samples was 5.9 ppb to 1579.1 ppb.

Previous studies of mercury concentrations in soils by Sullivan (Sullivan, 2006) and Tack (Tack, 2005) have found that the distribution of concentration values follows a lognormal distribution. In order to compare our samples with these previous studies the cumulative distribution of mercury concentrations relative to the average of the distribution was plotted with a lognormal cumulative distribution with a geometric standard deviation of 0.4 and is shown in Figure 1. A cumulative distribution plots the log of the Hg concentration divided by the average concentration against the fraction of the observations with values below that concentration. Thus the value at the highest concentration is one and at the lowest concentration is zero and at the average concentration the value is 0.5.

A slight break in the distribution of concentrations in our sample is apparent in Figure 1 just above the 0.4 value of the sample fraction and just to the left of the zero value for the log of the concentration ratio. It can be seen that the actual distribution is above the lognormal distribution near 0.4 and slightly below at about 0.45, with only a few points in between. This represents a slight break in the distribution near 100 ppb and suggests that there might be a bimodal distribution with two different high and low averages. These Hg soil samples were also examined by a normal Q-Q probability plot of the logarithms of these values. This plot showed the same lognormal behavior as noted for Figure 1. The distribution is very close to lognormal except at the lowest four samples and the highest 25 samples.

To characterize the geographical distribution the Lake Calumet Quadrant was split into six regions, each containing approximately the same number of points. First, the region was split into eastern and western halves. Each of these two halves was then broken into a northern third, the central third and the southern third. Lake Calumet itself occupied most of the middle of the central regions. The concentration averages and their standard deviations by region are tabulated in Table 2.

The average of all six regions is 122 ppb with a standard deviation of 180 ppb. Many of the standard deviations are dominated by a few larger values. Having a large standard deviation suggests that there is at least a bimodal distribution. Indeed, the distribution seems to have many points of smaller concentrations and a collection of much higher concentration sites. The average of the lower 68 values is 49 ± 26 ppb and the average of the 40 values above 100 is: 219 ± 146 ppb.

The East Central Indiana border, which has the smallest average concentration, is the least populated region with the most open water: Eggers Woods Forest Preserve and the Wm. W. Powers Conservation Area of Wolf Lake. At the same time, this area is closest to and just southwest of the State Line coal burning power plant.

The southeast bottom grouping included several industrial sites on the east side of Lake Calumet as well as residential sites in the Hegwich neighborhood of Chicago and the northern neighborhoods of Dolton, Thornton, and Calumet City. In this grouping we have both the highest concentration site as well as some of the lowest concentration sites in residential areas.

The two northern regions of the survey included predominantly urban residential sites from the Dan Ryan expressway east toward Lake Michigan. In this region were found the remaining highest isolated residential sites. These high concentration sites had very neat monoculture yards of grass and highly manicured plants. Because of this observation it was suspected that previously or currently used fungicides or herbicides might be a very important contributor to these isolated high values. Mercury is currently now allowed in herbicides and if this is the source it must reflect use in the past. The Merck Index (Budovari, 1996) lists at least one mercury based herbicide, phenylmercuric acetate, which once was legal.

The distribution of concentrations around the region can further be studied in a number of ways. A GIS plot of the distribution of the mercury concentration throughout the region is shown in Figure 2. As can be seen in Figure 2, the spatial distribution is a mix of large and small quantities in close proximity. The average concentrations for varying intervals are represented by filled circles of increasing radius in the following order: (10, 25, 50, 75, 100, 250 ,500, 750, 1000) ppb. The coal fired power plant is located in the upper right hand corner of the figure on the small rectangular land mass that juts out into Lake Michigan at the Illinois and Indiana border. The power plant's location is indicated by a capital "X".

It is difficult to discern a pattern in the distribution of concentrations from Figure 2. There is a hint of a band of larger values in a semi-circle around the power plant with a radius of about 4 kilometers, but interspersed among these larger values are several smaller values. It is also worth noting that many of the large concentration values were near to roads through industrial areas along the eastern shore of Lake Calumet. There is no clear trend of mercury concentrations decreasing with distance from the power plant for distances less than approximately 6 Km.

The two largest concentrations were in mixed residential areas. The largest sample was from an unimproved lot used to sell used cars and could be the result of dumping. The second largest sample was in a northern section, a residential area with exceptionally well manicured lawns. It would appear that the most likely cause of many of the large mercury values could be residual pesticides, herbicides, or fungicides whose use was banned 15 years ago (ATSDR, 1999). The very largest concentration of the summer was found in a rose bed that had been under cultivation for several decades. This rose bed was not in the Calumet quadrant.

The mercury concentrations were plotted versus the radial distance from the power plant in Figure 3. In this plot, the fact that sites quite near each other in distance from the plant can have significantly different values is manifest in the mix of high and low values at close to the same distance from the power plant.

Several analyses were conducted using Log-Log plots to estimate the exponent of a functional form for the concentration $C(r) = Ar^{\beta}$ where r is the distance from the power plant, A is a constant, and β is the exponent of the distribution. Presumably, if the power plant were the major source of Mercury in the region, this functional form should fit the data with a negative exponent at large distances from the plant. All fits using this form had very small correlation coefficients, primarily because of the intermingling of high and low concentrations as functions of the distance r. If we include all of the points, the best fit value of the exponent is positive. If we consider only points with concentrations below 100 ppb, the exponent was slightly negative (-0.03). However, the Correlation coefficients R^2 for all of the fits that were tried were very low (R^2<0.1) and none of the fits would be considered statistically significant. None of these analyses supports the assumption that the power plant is a significant source of the insoluble mercury concentrations that we measured.

The soil concentrations found in this urban/industrial area were much higher than those found by Sullivan et al. (2006) around two different rural power plants. Their average concentrations were around 30 ppb, while our overall average was four times larger. It must be concluded that the area we studied is significantly more polluted relative to mercury concentrations than rural areas. The EPA website (www.epa.gov) suggests that urban sites which have been occupied for many years would have average concentrations of about 100 ppb. The same website indicates that our levels are significantly below the superfund criterion of 20,000 ppb.

Another possible Hg source is suggested by the geographical distribution of this study as well as by the study of the Kincaid power plant near Springfield, IL, (Sullivan, 2006), in which samples taken within 10-20 feet of the edge of roads had higher mercury concentrations than sites close to the power plant and far from the road right-of-way. Similarly, a number of the larger concentrations in this study, but not all, were taken close to high density roads. It is possible that higher mercury concentrations on road right-of-ways reflect past use of mercury based herbicides to control visibility by suppressing growth of large plants. On the other hand, some evidence (Hoyer, 2002), suggests that some mercury pollution may be associated automobile traffic.

SUMMARY

One hundred surface soil samples were collected in the Lake Calumet area. One has to conclude that in an urban area such as this, any “hot spots” associated with the power plant as measured by the insoluble Hg soil concentration are difficult to find. Soluble compounds would have been washed away by rains and elemental Hg is expected to be widely dispersed so these soil samples may observe only the smallest effects. There is little evidence in the Hg soil distribution that the power plant can be regarded as a major source of that distribution. Other accumulations over history would appear to be much more important. It would be interesting to determine the role of mercury fungicides, and possibly herbicides, used previously in both urban and rural areas. It would also be interesting to pursue the possibility of road traffic as a source of Hg near to roadways.

ACKNOWLEDGMENTS

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REFERENCES

Anderson (1977). Anderson, W.L., Smith, K.E., "Dynamics of Mercury at Coal-Fired Power Plant and Adjacent Cooling Lake," Environ Sci Tech 11, 75-80 (1977).

ATSDR (1999). Agency for Toxic Substances and Disease Registry (ATSDR), Inorganic Mercury, Public Health Service. U.S. Department of Health and Welfare, Atlanta, GA., 1999.

Budavari (1996). Budavari, S., Ed., The Merck Index, 12th Edition, Merck & Co., Inc. , Whitehouse Station, NJ, p. 1257.

CAMR (2005). March 15, 2005. Final Rule of the Clean Air Mercury Rule, www.epa.gov/air/mercuryrule/rule.htm#Oct05a.

Crockett (1979). Crockett, A., Kinnison, R.U., "Mercury Residues in Soil around a Large Coal-Fired Power Plant," Environ Sci Tech 13, 712-5(1979).

Edgerton (2004). Edgerton, E. , Hartsell, B. , Jansen, J. , "Hg Speciation in Coal-fired Power Plant Plumes: Evidence for Reduction of RGM to HG(0)," Seventh Annual Conference on Mercury as a Global Pollutant, Ljubljana, Slovenia, July 3, 2004.

EPRI (2000). An Assessment of Mercury Emissions from U.S. Coal-Fired Power Plants; EPRI Report TR-1000608; EPRI: Palo Alto, CA, 2000.

Hoyer (2002). Hoyer, M., Baklauf, R. W., Scarbro, C., Barres, J., Keeler, G. J., "Mercury Emissions from Motor Vehicles,", Preprint, (*hgtech.com/MTS pdf/Hoyer Vehicle Hg Emissions.pdf), (2002)*.

Klein (1973). Klein, D.H., Russel, P. "Heavy Metals: Fallout around a Power Plant," Eviron Sci Tech 7, 357-8 (1973).

Landis (2003). Landis, M.S., Vette, A.F., Keeler, G.J., "Atmospheric Mercury in the Lake Michigan Basin: Influence of the Chicago/Gary Urban Area," Environ Sci Tech, 36, 4508-17 (2003).

Laudel (2004). Laudel, D., Dunham, G., Levin, L., Mercury Control Technology R&D Review, Pittsburgh, PA, July 14-15, 2004, http://www.netl.doe.gov/publications/proceedings/04/HgReview.

NCRS (2007). Natural Resources Conservation Service, United States Department of Agriculture website for Illinois. http://www.il.nrcs.usda.gov/technical/soils/soil-regions/.

Sullivan (2006). Sullivan, T., Bowerman, B. , Adams, J. , et.al. :Mercury Emissions from Coal Fired Power Plants: Local Impacts on Human Health Risk, Brookhaven National Laboratory, December, 2005, BNL-75594-2006.

Tack (2005). Tack, F.M.G., Vanhaeseebroeck, T., Verloo, M.G., Van Rompaeg, K., Van Ranst, E., "Mercury baseline levels in Flemish soils (Belgium)," Environmental Pollution 34:173-179 (2005).

USEPA (1990). U.S. Environmental Protection Agency. The Clean Air Act Amendments of 1990, Section 114; Government Printing Office, Washington, DC.

USEPA (1997). Mercury Study Report to Congress. Health Effects of Mercury and Mercury Compounds (Vol. V). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Office of Research and Development.

USEPA (2000). U.S. Environmental Protection Agency. Method 7473, Mercury in solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrometry. In Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-486, Update IVA; U.S. Government Printing Office, Washington DC.

Figure 1. The cumulative distribution of the mercury soil samples plotted relative to the average and compared to a lognormal distribution with a geometric standard deviation of 0.4. The closeness of the lognormal distribution of the actual data is consistent with other measurements of similar Hg concentrations.

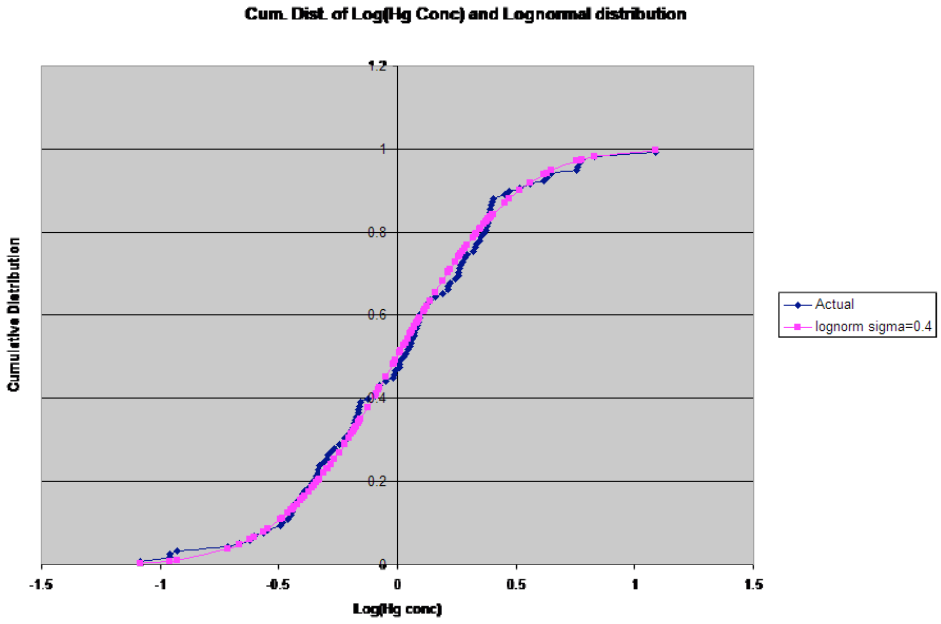


Figure 2. The concentration of mercury in the soil from this study is plotted as an overlay to a map of the Lake Calumet Region showing the incorporation limits, the waterways, and the major Interstate Highways. The average concentrations for varying intervals are represented by filled circles of increasing radius in the following order: (10, 25, 50, 75, 100, 250, 500, 750, 1000) ppb. The power plant, which could have been the source of this distribution is on a rectangular piece of land at the Lake Michigan shore where the Illinois and Indiana boundary intersects the lake. The power plant's location is indicated by a capital "X".

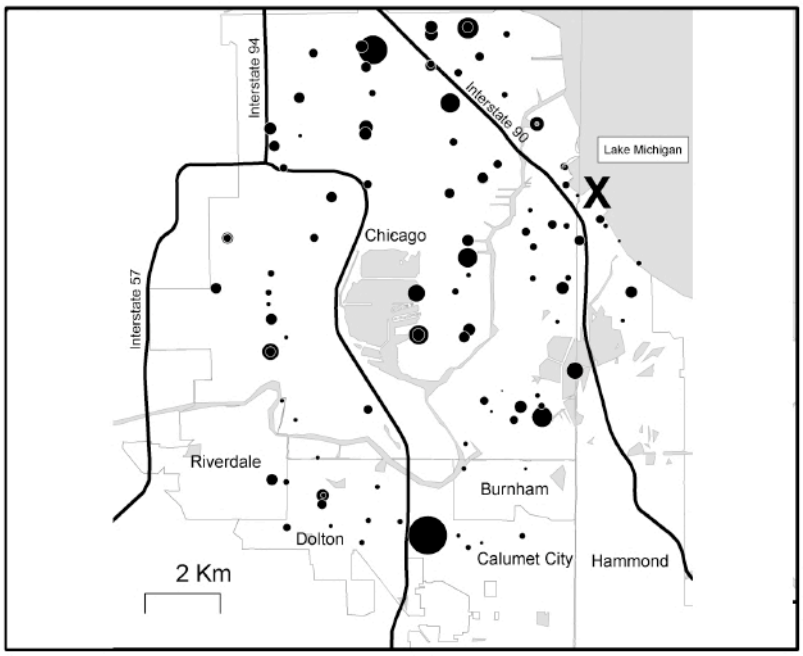
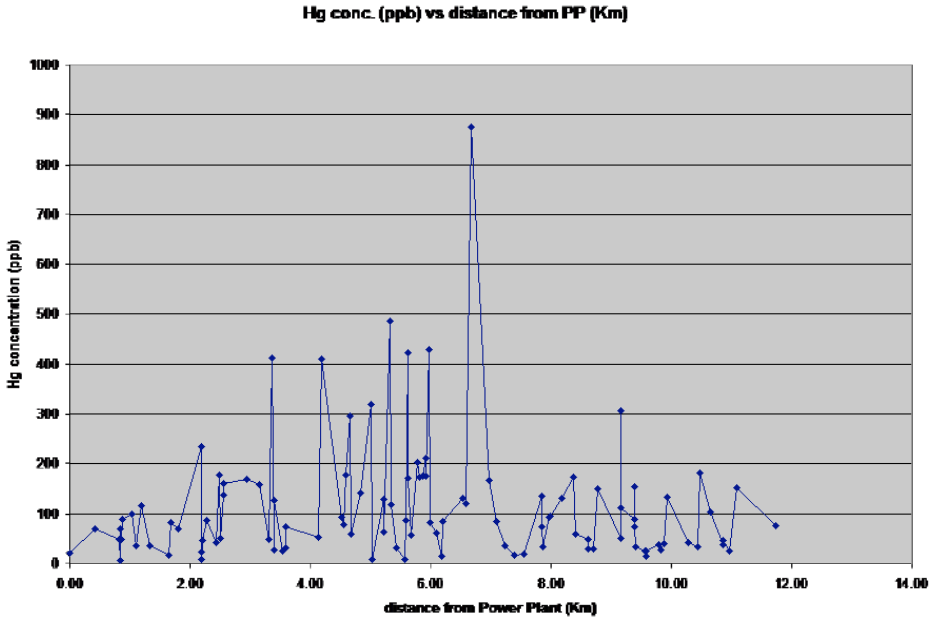


Figure 3. The mercury concentration values are plotted versus the distance from the power plant in kilometers. Note the mix of sites at similar distances with highly different concentration values.



You need a Table 1 description, similar to what you have for the Figures. Perhaps:

Table 1. Average Hg concentrations for this study and other discussed studies.

Study	Average Hg Concentration (ppb)
Klein & Russel (1973)	10.3
Anderson & Smith (1977)	22
Crockett & Kinneson (1979)	14.5
Sullivan et al. (2006), Plant A	28
Sullivan et al. (2006), Kincaid	32.4
Lake Calumet (this study), (2007)	122

You need a Table 2 description, similar to what you have for the Figures. Perhaps:

Table 2. Average Hg concentrations of the six regions of the Lake Calumet Quadrant.

Region, No. of samples ( )	Average Mercury Content (ppb) ± S.D. of samples in region
Northwest top - CSU (14)	160 ± 170
Northeast top - near Lake Michigan (25)	130 ± 120
West Central (13)	100 ± 90
East Central Indiana border (23)	73 ± 47
Southwest bottom (12)	130 ± 330
Southeast bottom (12)	140 ± 140