BNL-74696-2005-CP

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Mercury Associated with Coal-Fired Power Plants***

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*Presented at the ACS Symposium on Mercury Measurement,
Transformations, Control and Related Issues in Power Systems
Anaheim, CA
March 28-April 1, 2004*

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Managed by
Brookhaven Science Associates, LLC
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Contract No. DE-AC02-98CH10886

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ASSESSING THE IMPACTS OF LOCAL DEPOSITION OF MERCURY ASSOCIATED WITH COAL-FIRED POWER PLANTS

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Introduction

Mercury emissions from coal fired plants will be limited by regulations enforced by the Environmental Protection Agency. However, there is still debate over whether the limits should be on a plant specific basis or a nationwide basis. The nationwide basis allows a Cap and Trade program similar to that for other air pollutants. Therefore, a major issue is the magnitude and extent of local deposition.

Computer modeling suggests that increased local deposition will occur on a local (2 to 10 Km) to regional scale (20 to 50 Km) with the increase being a small percentage of background deposition on the regional scale.^{1,2} The amount of deposition depends upon many factors including emission rate, chemical form of mercury emitted (with reactive gaseous mercury depositing more readily than elemental mercury), other emission characteristics (stack height, exhaust temperature, etc), and meteorological conditions. Modeling suggests that wet deposition will lead to the highest deposition rates and that these will occur locally. Dry deposition is also predicted to deposit approximately the same amount of mass as wet deposition, but over a much greater area.² Therefore, dry deposition rates will contribute a fraction of total deposition on the regional scale.

The models have a number of assumptions pertaining to deposition parameters and there is uncertainty in the predicted deposition rates. A key assumption in the models is that the mixture of reactive gaseous mercury (RGM) to elemental mercury Hg(0) is constant in the exhaust plume. Recent work suggests that RGM converts to Hg(0) quickly. Deposition measurements around coal-fired power plants would help reduce the uncertainties in the models.

A few studies have been performed to examine the deposition of mercury around point sources. Measurement of soil mercury downwind from chlor-alkali plants has shown increased deposition within a few Km.³ Studies of soils, sediments, and wet deposition around coal plants typically find some evidence of enhanced deposition; however, the statistical significance of the results is generally weak. A review of these studies is found in Lipfert.⁴

This study combines modeling of mercury deposition patterns with soil mercury measurements. The model used emissions data, meteorological conditions, and plant data to define sample locations likely to exhibit deposition in excess of background, that can be attributed to the power plant. Data were collected at the specified locations in November, 2003.

Deposition Modeling

In this attempt to validate the modeled enhanced deposition of Hg around coal-fired power plants, a field study was conducted around a large coal-fired power plant in the Midwest. The plant typically emits several hundred pounds of mercury per year. Meteorological data for a five year period were reviewed to

determine wind patterns under dry and wet conditions. Under dry conditions, the prevailing winds ran along an axis from the northwest towards the southeast. Winds occurred regularly in each direction along the axis. Under wet conditions, winds were generally from the north and east. This leads to predictions of wet deposition near the plant and to the southwest. Deposition modeling based on the meteorological data predicted highest deposition rates within 10 Km of the plant in a southwesterly direction, Figure 1. Dry deposition rates were lower than wet deposition rates and were not predicted to be a major contributor to deposition in the region. This analysis was used to select appropriate sample locations in the vicinity of the plant.

Experimental

Soil Samples. Soil samples were collected at 54 selected sites around the coal-fired power station as shown in Figure 1. At each site, five samples were collected. Three surface samples from the top five centimeters of soil separated by approximately 3 m, one deep sample at a depth of 5 – 10 cm, and one sample of the vegetation. The general layout of sample locations suggested by the modeling was modified to account for site-specific conditions (e.g., inaccessibility of sample locations, site activities, and changes in soil type which would alter background levels of mercury). The sampling area south and west of the plant covered an approximately square region of 64 km². The land surrounding the power plant was either part of an active strip mine or agricultural. Although many sampling sites were within the strip mine permit area, most of the land had been reclaimed. Strip mine personnel identified sites that had been fully reclaimed, or were at least known not to have been disturbed for at least a year. Agricultural area sampling sites were chosen because they appeared undisturbed for at least one year (i.e. had not been plowed). Many of the agricultural sites were at the crest of roadside ditches, adjacent to a plowed or mowed area.

Figure 1: Soil Sample locations around the power plant.

Samples of approximate 100 grams weight were collected in water-tight wide-mouth 250 mL plastic screw-top cups. Samples were collected using stainless steel trowels, which were rinsed with tap water and wiped dry between each use. Blind field duplicates were collected every 10th sample. Latitude and longitude for each sample location were identified using a GPS locator system (Garmin Etrex) with a resolution of 6 meters.

Mercury Analysis Methods. The soil samples were shipped back to Brookhaven National Laboratory for analysis using a Direct Mercury Analyzer (DMA-80, Milestone, Inc, Monroe, CT). In the DMA-80, controlled heating in an oxygenated decomposition furnace liberates mercury from the solid samples. Flowing oxygen to the catalytic section of the furnace carries the decomposition products, where oxidation is completed and halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are then carried to a gold amalgamator that selectively traps mercury. After the system is flushed, the amalgamator is rapidly heated, releasing mercury vapor, which is then carried through absorbance cells positioned in the light path of a single wavelength (253.7 nm) atomic absorption spectrophotometer. The typical working range for this method is 0.05-600 ng of mercury. Since soil samples are at most about 0.5 grams, the DMA-80 easily measures levels below 1 ppb (ng/g).

DMA-80 analyses were conducted on soil samples as is. Moisture content was determined separately for all samples, and mercury concentrations were adjusted to a dry weight basis.

Quality assurance was evaluated through taking blind duplicates of 10% of the samples, measurement of empty sample boats in the DMA-80, and use of two NIST mercury soil standards (SRM 2709 and SRM 2710) at every 10th measurement. Soil samples will be counted in triplicate to examine for heterogeneity of the samples.

Results and Discussion

Sample analysis is underway and all of the soil locations have been analyzed for mercury, on as received (wet) basis at least once. At each sample location, the three surface soil samples were averaged to give a composite. Typically, the three adjacent surface samples from any site had agreement in the mercury levels to within 10%. At the fifty-four locations the average value was 21.5 ng/g (wet weight basis), with a standard deviation of 5.7. The minimum value was 8.9 ng/g and the maximum value was 43 ng/g.

Comparison between the predicted deposition versus measured mercury concentrations in the soil was accomplished by placing the deposition map over the sampling map coded to measured concentration. Areas of increased deposition are anticipated to have increased soil mercury concentrations. Figure 2 is the graphical representation of the analysis. Predicted regions of enhanced deposition are covered by the dark filled contour. Sample locations with symbols representing measured mercury levels represent the measured data.

Examining Figure 2 shows that the modeled and measured data match reasonably well. The overall shape of the region of excess deposition matches, however, the measured data suggest that the main finger of the plume is slightly south of the area predicted by modeling. There is scatter in the data, as expected with an environmental data set. Statistical analyses will be performed to determine the degree of confidence in these results. The results presented are preliminary and will be refined after completion of the analysis of all soil and vegetative samples.

Although there is evidence of excess deposition near the plant, mass balance calculations comparing emissions with increased soil levels of mercury indicate that less than 5% of emissions are deposited over the sampling domain.

Figure 2 Comparison of modeled deposition pattern (solid contour) with measured data.

Acknowledgment

The National Energy Technology Laboratory, Office of Fossil Energy, U.S. Department of Energy supported this work.

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