DIRECT MEASUREMENT OF MERCURY REACTIONS IN COAL POWER PLANT PLUMES

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ABSTRACT

This project was awarded under U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) Program Solicitation DE-PS26-02NT41422 and specifically addresses Program Area of Interest: #5 – Environmental and Water Resources. The project team includes the Electric Power Research Institute (EPRI) as the contractor and the University of North Dakota Energy & Environmental Research Center (EERC) and Frontier Geosciences as subcontractors. Wisconsin Energies and its Pleasant Prairie Power Plant acted as host for the field-testing portion of the research.

The project is aimed at clarifying the role, rates, and end results of chemical transformations that may occur to mercury that has been emitted from elevated stacks of coal-fired electric power plants. Mercury emitted from power plants emerges in either its elemental, divalent, or particulate-bound form. Deposition of the divalent form is more likely to occur closer to the source than that of the other two forms, due to its solubility in water. Thus, if chemical transformations occur in the stack emissions plume, measurements in the stack may mischaracterize the fate of the material. Initial field and pilot plant measurements have shown significant and rapid chemical reduction of divalent to elemental mercury may occur in these plumes.

Mercury models currently assume that the chemical form of mercury occurring in stacks is the same as that which enters the free atmosphere, with no alteration occurring in the emissions plume. Recent data indicate otherwise, but need to be evaluated at full operating scale under field conditions.

Prestbo and others have demonstrated the likelihood of significant mercury chemical reactions occurring in power plant plumes (Prestbo et al., 1999; MDNR-PPRP, 2000; EERC, 2001). This experiment will thus increase our understanding of mercury atmospheric chemistry, allowing informed decisions regarding source attribution.

The experiment was carried out during the period August 22-September 5, 2003. The experimental site was the Pleasant Prairie Power Plant in Pleasant Prairie, Wisconsin, just west of Kenosha. The experiment involved using an aircraft to capture emissions and document chemistry changes in the plume. While using the airplane for sampling, supplemental fast-response sensors for NOx, connected to data loggers, were used to gauge entry and exit times and transect intervals through plume emissions material. The Frontier Geosciences Static Plume Dilution Chamber (SPDC) was employed simultaneously adjacent to the stack to correlate its findings with the aircraft sampling, as well as providing evaluation of the SPDC as a rapid, less costly sampler for mercury chemistry. A complementary stack plume method, the Dynamic Plume Dilution (DPD) was used in the latter portion of the experiment to measure mercury speciation to observe any mercury reduction reaction with respect to both the reaction time (5 to 30 seconds) and dilution ratio. In addition, stack sampling using the

"Ontario Hydro" wet chemistry method and continuous mercury monitors (CMM) were used to establish the baseline chemistry in the stack. Comparisons among stack, SPDC, DPD and aircraft measurements following data analysis will allow establishment of whether significant chemical changes to mercury occur in the plume, and of the verisimilitude of the SPDC and DPD methods.

This progress report presents the operations and measurements during aircraft flights to measure mercury species within the Pleasant Prairie plume during the experimental period. Simultaneous measurements were being carried out of flue gas composition within the stack, upstream speciation prior to the stack, and mercury speciation during operation of static and dynamic plume dilution simulators at the stack. Results of these measurements and overall project results will be discussed in a future progress report.

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EXECUTIVE SUMMARY

Measurements of stack and stack plume mercury concentrations, by species, were carried out at the We Energies Pleasant Prairie Power Plant (P4) in the period August 22 to September 5, 2003. P4 is a 1210 MW subbituminous coal-fired plant with two boiler units exiting from a single 450-foot exhaust stack. Predictions from the EPA ICR coal, mercury, and chlorine database indicated that both units were expected to emit about 85% elemental mercury, 14% oxidized, and less than 2% particulate-phase.

Flights to measure the mercury in the plume were conducted on August 27, 30, and 31 and September 2 and 4, 2003. Two flights were completed on August 30, including one sounding flight, for a total of six flights. The flights on 8/27, 8/30 (first flight of the day), 8/31, and 9/2 consisted of four sampling points:

1) Upwind of the plant, to characterize baseline mercury concentrations
2) Near the stack
3) 5 miles downwind of the stack
4) 10 miles downwind of the stack

Because weather conditions were marginal on 11/4, sampling was not completed at the 10-mile sample point.

Vertical profiling was conducted on the second flight on 8/30. This consisted of a sample point 10 miles downwind of the plant at four elevations:

1) 500 ft
2) 2500 ft
3) 8500 ft
4) 16,500 ft

PRELIMINARY REPORT ON AIRCRAFT MEASUREMENTS OF MERCURY SPECIES IN THE PLUME OF THE PLEASANT PRAIRIE (WISCONSIN) POWER PLANT, AUGUST-SEPTEMBER 2003

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1. SUMMARY

The work at the Pleasant Prairie Power Plant was completed in early September 2003. Flights to measure the mercury in the plume from the plant were flown August 27, 30, and 31 and September 2 and 4. Two flights were completed on August 30 for a total of six flights. The flights on August 27, 30 (first flight), and 31 and September 2 consisted of sampling points upwind of the plant, near the stack("0 mile sampling point"[1]), 5 miles and 10 miles downwind of the stack. The second flight on August 30 consisted of sample points 10 miles downwind of the plant at elevations of 500, 2500, 8500, and 16,500 ft. The weather conditions were marginal on September 4, and sampling was not completed at the 10-mile sample point. Data reduction is not complete; the following discussion is based on preliminary results. Mercury speciation results indicate a reduction in the reactive gaseous mercury (RGM) right out of the stack and some additional reduction as it moves downstream from the plant. For most of the samples, the mass balance was high, showing more mercury in the plume than was measured in the stack. Some of the plume values are skewed by high dilution rates, which result in high mercury concentrations.

2. METHODS AND MATERIALS

The objective of this program was to measure the elemental, RGM, and particulate-bound mercury concentrations in a plume from a coal-fired utility boiler as the plume moved downwind from the stack. To accomplish this task, instrumentation was installed in a DeHavilland Twin Otter DHC-6 aircraft and flown through a plume at locations near the stack, 5 miles and 10 miles downwind from the stack. An ambient NO_x analyzer, which was modified to reduce response time, was used to verify the presence of the plume trigger mercury sampling and provide data for calculating dilution ratios. At the closest sampling point, ambient air was sampled continuously because the elemental mercury and the RGM concentrations would be much greater than the ambient concentrations. At the 5- and 10-mile locations, zero air was supplied to the mercury system until the NO_x concentration was above a preselected trigger point. The mercury system would then sample from the plume until the NO_x concentration again dropped below the trigger point. A Tekran ambient mercury-monitoring system was used for mercury measurements (see Figure 1). The Tekran system includes modules for collecting particulate-bound mercury (Model 1135) and RGM (Model 1130) which, when coupled with the Model 2537A, provide measurements of elemental, RGM, and particulate-bound mercury. The sample gas enters the bottom of the unit where an impactor removes particulate matter greater than 2. µm in diameter from the sample gas. The gas then flows through an annular denuder, which captures the RGM. The particulate-bound

[1] Aircraft sampling at the point closest to the stack was positioned at the effective stack height (height of plume centerline neutral buoyancy) and at a radial distance accommodating the tilt of plume rise due to wind conditions.

mercury is removed by a quartz fiber filter. At this point, only elemental mercury is left in the sample gas. The system was set up to collect RGM and particulate-bound mercury for 25 minutes, with a 35-minute analysis cycle. During the collection period, the elemental mercury in the sample gas stream is measured. After the collection period, excess zero gas is supplied to the inlet of the impactor. First, the particulate filter is heated to desorb the particulate-bound mercury. The zero gas carries this mercury to the instrument for measurement. Next, the annular denuder is heated to desorb the RGM with the zero gas, carrying the sample to the 2537A for analysis. After cooling, the cycle begins again. The flight sampling procedure was to sample the ambient mercury concentrations upwind of the plant first. While the system was analyzing the particulate and RGM samples, the plume was found near the plant and a flight pattern was set for sampling at this distance. This procedure was also followed for the 5- and 10-mile sampling locations. After completing the collection period at 10 miles, the airplane was landed and the final analysis was completed on the ground. A global positioning system (GPS) unit was used to track the flight path for each sampling flight, and all data were logged to a computer with a data acquisition system.

The NO_x analyzer was calibrated each day using a tank of calibration gas and a tank of zero gas. A dilution system was used to achieve the desired concentrations for calibration. The Tekran instrument was calibrated with primary injections of elemental mercury vapor and zeroed on dry filtered air that was passed through a carbon trap.

3. RESULTS AND DISCUSSION

The plume and stack NO_x concentration data were used to determine the time in the plume and the dilution ratios to apply to the plume mercury data. There were several data points that were removed because of low NO_x concentrations, which caused very high dilution ratios. The low NO_x concentrations were caused by the trigger point being set too low. This resulted in sampling ambient air for a short period of time. After correcting for sample duration and plume concentration, the mercury data were converted to an equivalent stack concentration for each sampling location for each flight. The results are presented in Tables 1–3 along with the corresponding stack concentrations measured with the Ontario Hydro method. The data show that from the stack to the first sampling point, there was a significant increase in the elemental mercury concentration and a corresponding decrease in the RGM concentration. The elemental mercury concentration again increased from the close sample point to the 5-mile sample point, but there was no further change from 5 miles to 10 miles.

Table 1. 0-Mile Sample Point

	Hg Concentration					
Date:	**8/27**	**8/30**	**8/31**	**9/2**	**9/4**	**Average**
Plume						
Hg^0, µg/Nm^3	11.1	9.2	7.7	6.2	9.2	8.7
RGM, µg/Nm^3	1.86	2.44	2.55	1.3	1.96	2.0
Total Hg, µg/Nm^3	13.0	11.7	10.3	7.5	11.2	10.8
% Hg^0	85	79	75	82	82	81
% RGM	14	21	25	17	17	19
Stack						
Hg^0, µg/Nm^3	6.2	4.8	5.3	6.4	6.4	5.8
RGM, µg/Nm^3	3.1	3.7	2.3	2.9	2.9	3.0
Total Hg, µg/Nm^3	9.3	8.5	7.6	9.2	9.2	8.8
% Hg^0	67	56	69	69	69	66
% RGM	33	44	31	31	31	34

Table 2. 5-Mile Sample Point

	Hg Concentration				
Date:	**8/27**	**8/30**	**8/31**	**9/2**	**Average**
Plume					
Hg^0, µg/Nm^3	13.2	11.5	26.3	8.3	14.8
RGM, µg/Nm^3	1.36	2.3	1.95	0.92	1.6
Total Hg, µg/Nm^3	14.6	13.9	28.4	9.2	16.5
% Hg^0	90	83	93	89	89
% RGM	9	17	7	10	11
Stack					
Hg^0, µg/Nm^3	6.2	4.8	5.3	6.4	5.7
RGM, µg/Nm^3	3.1	3.7	2.3	2.9	3.0
Total Hg, µg/Nm^3	9.3	8.5	7.6	9.2	8.7
% Hg^0	67	56	69	69	69
% RGM	33	44	31	31	35

Table 3. 10-Mile Sample Point

	Hg Concentration				
Date:	**8/27**	**8/30**	**8/31**	**9/2**	**Average**
Plume					
Hg^0, µg/Nm^3	14.3	14.7		6.7	11.9
RGM, µg/Nm^3	1.36	2.44		0.96	1.6
Total Hg, µg/Nm^3	15.7	17.3		7.6	13.6
% Hg^0	91	85		87	88
% RGM	9	14		13	12
Stack					
Hg^0, µg/Nm^3	6.2	4.8	5.3	6.4	5.7
RGM, µg/Nm^3	3.1	3.7	2.3	2.9	3.0
Total Hg, µg/Nm^3	9.3	8.5	7.6	9.2	8.7
% Hg^0	67	56	69	69	65
% RGM	33	44	31	31	35

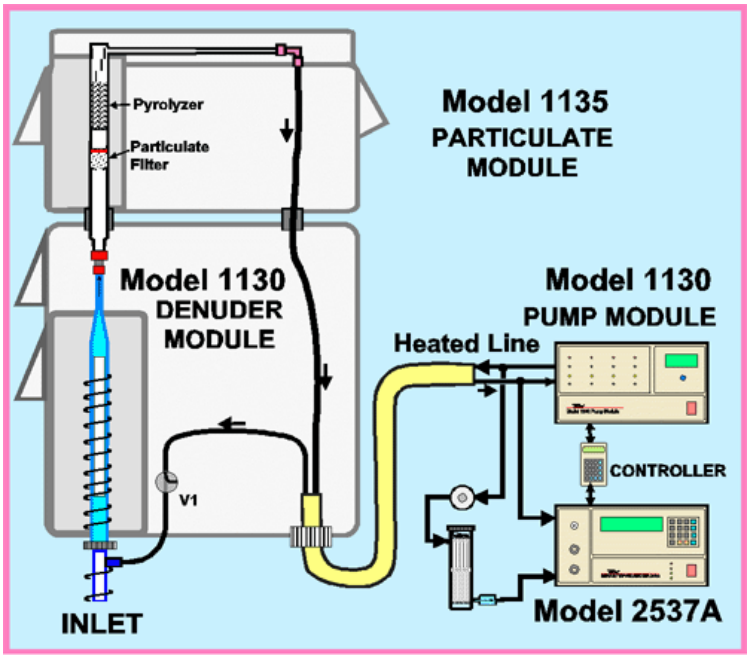

Figure 1. Schematic of the Tekran ambient air mercury speciation unit.

Summary Mercury Measurements at Stack Oxygen, 0°C, and 1 atm (µg/Nm^3)

		Hg_p	Hg^{2+}	Hg^0	Hg_T	Moisture
27-Aug-03	1:20 PM	0.000	3.07	6.25	9.32	12.0
29-Aug-03	2:25 PM	0.000	3.19	5.65	8.84	12.5
30-Aug-03	11:30 AM	0.000	2.81	6.18	8.99	12.1
31-Aug-03	1:30 PM	0.000	3.74	4.76	8.49	12.0
02-Sep-03	11:00 AM	0.000	2.34	5.28	7.62	12.7
04-Sep-03	11:00 AM	0.000	2.86	6.37	9.22	12.2