DIRECT MEASUREMENT OF MERCURY REACTIONS IN COAL POWER PLANT PLUMES

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DISCLAIMER

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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.

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EXECUTIVE SUMMARY

Emissions of mercury from elevated combustion stacks may occur in one or more of three chemical forms, or “species”: elemental mercury [Hg(0)], the uncombined chemical element that, in bulk, is the familiar silvery liquid; divalent mercury [Hg(II)], which is chemically reactive and generally found (at room temperature) combined with other substances into mercury salts; particulate-phase mercury [Hg(p)], which chemically is mostly Hg(II) but barely reactive due to combination with solid-phase material in the atmosphere. Typically no more than 2-5% of coal-fired utility emissions are Hg(p), so the primary forms of interest are Hg(0) and Hg(II).

Since Hg(II) is readily soluble in water and aqueous media (some six orders of magnitude more soluble than is Hg(0)), near-source deposition via solution into precipitation can dominate for sources emitting mostly the divalent form. Hg(0) typically is deposited over much wider areas, at lower concentrations than deposition closer to the sources. Its atmospheric lifetime is about 1 year, until oxidation and deposition occur.

Recent research findings have indicated that the standard method for characterizing the mix of mercury species in emissions may misrepresent the forms dispersing into the atmosphere from the emission plumes. Typically, stack measurements using discrete or “continuous” (short sampling interval) samplers are used in the stack of the facility involved, either at the base or elevated in the structure, to measure total and speciated mercury. These measurements, in turn, are assumed by the atmospheric models to be maintained in the environment, both in the plume and after full dispersion in the atmosphere.

Measurements have been carried out using plume dilution chambers at pilot and full-scale facilities of both power plants and waste combustors, mixing in-stack flue gas with ambient air to simulate dispersion in the atmosphere. The chamber studies found that, at coal-fired power plants, there was evidence of a very rapid reduction of the Hg(II) to Hg(0), of the order of a 30 to 50% conversion within a few minutes of mixing in the chamber. Similarly, measurements at an ambient mercury sampling site in Georgia, south of a major coal-fired power plant, found a six-fold increase in the fraction of elemental mercury, and consequent decrease in divalent mercury, during traverse of the plant plume over the 25 km plant-to-sampler distance. These findings provide important new information on the true speciation of mercury from power plant stacks.

These preliminary results needed to be verified and extended by direct measurement of precursors, products, and rates during the actual reactions that may occur in a plume. To rectify this issue, and provide direct quantitative evidence of whether, how fast, and to what extent, and under what conditions and constraints these reactions might occur, EPRI undertook a field measurement program at a single power plant. This program was an integrated ground, aircraft, and plume chamber study. The aircraft measured mercury species both close to and at a moderate distance from the stack exit in repeated circuits of the plume. Ground measurements of stack mercury speciation and coal feed to the plant boilers were occurring

simultaneously, to allow measurements to establish in-plant speciation for comparison. Both static and dynamic plume chambers were used simultaneously with aircraft and other ground measurements to provide a test of method for a relatively inexpensive sampling and simulation method which, if proven viable, could be used for extensive similar studies at much lower cost.

The site chosen was the We Energies Pleasant Prairie Power Plant (P4). 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.

Field research at the Pleasant Prairie Power Plant was carried out between August 22 and September 5, 2003. 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 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
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

In addition to the airborne tests, stack sampling was conducted using the Ontario Hydro mercury speciation method (ASTM Method D6784-02) and a mercury semicontinuous emission monitor. This sampling was completed September 5, 2003.

Data reduction and analysis for this project are ongoing.

DIRECT MEASUREMENT OF MERCURY REACTIONS IN COAL POWER PLANT PLUMES

1.0 INTRODUCTION

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 U.S. Department of Energy, under “Environmental and Water Resources,” has specified that work to “evaluate the emission, transport, and deposition of mercury” is of interest to the Department. The proposed work is specifically 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. The proposed experiment is designed to authoritatively quantify whether those or other reactions occur; at what rate they occur; and whether efficient, low-cost measurement methods might be used to quantify those reactions at other sites. This project is designed to significantly expand upon, but is separate from, measurements planned for at least one other power plant, in the southeast U.S., since the measurements described in this proposal will be done at a plant with alternative control configurations, at a different location.

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. This experiment is designed to authoritatively quantify whether those or other reactions occur; at what rate they occur; and whether efficient, low-cost measurement methods might be used to quantify those reactions at other sites.

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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.

Currently, environmental assessment of mercury impacts relies on computer models of mercury chemistry and transport in the atmosphere. Although our current understanding of mercury chemistry is incorporated into these models, it is assumed 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. This experiment will accomplish that.

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). These reactions appear to play a significant role in the likely deposition of mercury into nearby waterways, where it may accumulate in food fish to levels considered to pose health risks for humans. If plume reactions alter the amount of mercury from a given power plant that is likely to reach fish, significant public health and environmental management consequences may ensue.

2.0 EXPERIMENTAL

The experiment involved using an aircraft to capture emissions and document chemistry changes in the plume. When using the airplane for sampling, a fast-response sensor for NOx was used to gauge entry points into plume material. Since the initial findings of the fast plume chemistry were in pilot-plant studies using the Frontier Geosciences Static Plume Dilution Chamber (SPDC), that device was used simultaneously on a catwalk attached to the stack to allow its findings to be correlated with the aircraft sampling, and provide 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 the Hg(0) 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 semicontinuous emission monitor (SEM) was carried out to establish the baseline chemistry in the stack. The SEM was placed adjacent to the OH stream at the same stack port, and remained there during the entire project. Comparisons among stack, SPDC, DPD and aircraft measurements will allow establishment of chemical changes that occur in the plume, and of the veracity of the SPDC and DPD simulation methods.

Aircraft sampling – Aircraft sampling flights were carried out in the period August 22 and September 5, 2003, on August 27, 30, and 31 and September 2 and 4, 2003. Two flights were completed on August 30 for a total of six flights. Repeated passes through the plume under relatively steady wind conditions were carried out to allow time-of-flight equivalency for determining reaction rates for any redox reactions noted. Figure-eight or racetrack patterns were used in these passes.

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
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

Sampling of speciated mercury in the utility plume was carried out using the method of Landis et al. 2002. The sample train consisted of an impactor to remove particles larger than 2.5 μm, KCl annular denuder to adsorb gaseous Hg(II), 47-mm quartz fiber filter for particulate mercury collection, followed by a Tekran® 2573A CVAFS continuous mercury monitor to measure the remaining Hg(0) in the sample stream. The sampling train consisted of:

- A heated inlet probe mounted on the forward starboard side of the aircraft, fixed in an otherwise sealed window space.
- A heated manifold with several KCl annular denuders and filters trains upstream of the Tekran® 2537A to allow several samples to be collected during a single flight.
- A valving system to switch flow from denuder to denuder during airplane sampling.
- A mass flowmeter coupled with a variable-speed pump to pull a constant volume through each KCl denuder during airplane sampling. The Tekran® 2537A collects a low flow split stream behind each denuder sample.

Once the samples were collected during airplane operations, the KCl denuders were analyzed on the ground with another, dedicated Tekran® 2537A. Prior to each flight, intercomparisons among the three Tekran® devices were carried out using standard gases to ensure intercomparison among the SPDC/DPD device, the aircraft instrument, and the ground analyzer for the denuders.

Time in plume was assessed by inspection of the NOx analyzer datalogger records; in-plume periods were adjudged to begin when NOx levels began their rise above background, based on upwind measurements made at the onset of each sampling flight. Similarly, in-plume periods ceased when NOx levels returned to background levels following plume segment penetration. Since the plume itself is not evident in the visible light spectrum, test passes were used at the start of each over-stack or downwind segment to correlate aircraft position with GPS coordinates in three dimensions for later data collection.

Plume dilution chamber sampling – Both static (SPDC) and dynamic (DPD) samplers were used during the experiment. The DPD was employed once, during the final aircraft flight on September 4, while the SPDC was used during prior flights. The SPDC method uses a sampling chamber 0.5 m^3 in volume and entirely Teflon® coated. A total of 10 ports with Teflon® fittings allow for plume input and sampling. An insulated heating blanket controls the SPDC temperature. Measurements were made on the device to determine total mercury, particulate-phase mercury, gas-phase mercury (i.e. Hg(0) and Hg(II)) and dry deposition of particulate and Hg(II) via rainwater input.

A known amount of flue gas is introduced into the trace metal-cleaned SPDC using a heated isokinetic sampling probe. The flue gas is quickly diluted with filtered ambient air and allowed to mix and react for a known amount of time, typically 2 to 4 minutes, before sampling begins. The air pressure is maintained near ambient (1 atm) in the SPDC. After the initial mixing Hg speciation measurements are started by pulling a known volume of the plume air through a KCl annular denuder to capture the gaseous Hg(II), followed by a quartz filter to capture the particulate Hg and finally into a Tekran® 2537A continuous mercury monitor to quantify the remaining Hg species, Hg(0). This method has been shown in lab and field tests to be precise, accurate and free of artifacts (Landis et al., 2002). By collecting a number of annular denuder Hg(II) and filter particulate Hg samples in series over the course of 30 minutes, the changes in these species can also be observed with respect to time. Simultaneous to plume introduction into the SPDC, speciation of the injected fluegas will be determined using the Ontario-Hydro and SEM.

A real-time rainwater washout simulation was also done using the SPDC Method. In this part of the experiment, while flue gas plume was introduced into the SPDC, simulated rainwater (10-9 molar H2SO4 and 10-9 M HCl) was continuously sprayed, falling through the plume. The rainwater which collected at the bottom of the SPDC was filtered through 0.2 μm cellulose nitrate filters to separate dissolved verses particulate Hg in the rainwater sample. The plume air remaining in the SPDC was then sampled to determine Hg(0), Hg(II), particulate Hg and Hg wall loss. For non-rainwater experiments, particulate Hg and Hg(II) dry deposition to the walls is determined by spray washing first with a pH 4.5 solution of 10-9 M H_2SO_4 and 10-9 M KCl in double deionized water (simulated rainwater). The wall wash was filtered in real time through a 0.2 μm cellulose nitrate filter. The first wash is followed by a pH 2.0 solution of 0.1% HCl to recover any remaining Hg adsorbed to the SPDC walls for an accurate mass balance.

The Dynamic Plume Dilution (DPD) method is a complementary method to the SPDC and is required to capture the mercury speciation in the 5 to 30 second reaction time frame. It has been observed that the potential conversion of gaseous Hg(II) to Hg(0) is faster than the SPDC can observe (<3-4 minutes). The DPD, unlike the SPDC, has the capability to easily change the flue gas dilution ratio and reaction time during the course of a sample run while observations of Hg(0) are being made.

The DPD has 4 essential parts: 1) Isokinetic inlet, 2) multiple-orifice dispersion plate, 3) Teflon coated reaction cell and 4) sampling manifold. The heated isokinetic inlet is inserted into the flue gas stream to pull a know amount of a representative flue gas sample into the DPD. The flue gas remains at stack temperature until it is quickly diluted with a custom designed, multiple orifice dispersion plate that ensures complete mixing. Ambient air will be used for dilution after passing through a cyclone separator to remove particles larger than 2.5 μm. The diluted plume mixture then travels through the highly cross-linked Teflon reaction cell. The use of the cross-linked Teflon is also important, as it has been shown to be less adsorptive to gaseous Hg(II) than typical Teflon FEP, or PFA. At the end of the DPD is the sampling manifold. Here a set of three KCl-denuders and quartz fiber filter trains will be used to collect 10-minute samples in series, while the Tekran® 2537A is analyzing Hg(0) continuously on a 2.5 minute cycle time. The set of 3 KCl-denuders will have a valve behind them to switch sample trains at 10 minute intervals.

It will also be used to perform periodic in flight calibration tests through the sampling inlet. Detailed documentation of all checklists and precision/accuracy tests will be maintained and kept current to facilitate the QC program.

<u>Plume dilution chamber sample analysis</u> –The KCl denuder and particulate Hg filter media were heated to 40°C during sampling. For the Dynamic Plume Dilution (DPD) chamber, the pump was set to maintain 10 lpm to ensure an impactor aerodynamic aerosol cut point of 2.5μm. In this configuration fine fraction (<2.5 μm) particulate-phase mercury [Hg(P)] is collected downstream of the denuder onto a quartz fiber filter. Field blanks consist of assembling the denuder and filter sampling trains and collecting a sample with only filtered ambient air present in the SPDC or DPD, disassembling the sampling train, and transporting the denuders for analysis.

The manual denuders and filters are analyzed by thermal desorption using a clamshell tube furnace to convert both Hg(II) and Hg(P) into Hg(0) so that it can be quantified using a Tekran® model 2537A vapor phase mercury analyzer (Landis et al., 2002). A separate Tekran® 2537A will be used for the Hg(II) and Hg(P) analysis.

During sampling with both the SPDC and DPD, a dedicated Tekran® 2537A was used to measure Hg(0) continuously in the plume gas, on a 2.5 minute cycle, after the removal of the Hg(II) and Hg(P) by the denuder and filter, respectively. Again, to protect the analyzer from acid gases during sampling, a soda-lime trap was placed behind the denuder and particulate filter at the inlet to the Tekran®.

To ensure that there is no loss of mercury, the water and water filter samples were preserved with a 5% solution of 0.2 N BrCl within 30 minutes after sample collection (FGS

SOP-012.1). A variety of field blanks was employed, consisting of: 1) blank water, 2) blank simulated rain water through the delivery system, 3) blank simulated rainwater through the SPDC, 4) blank pH 2 rinse water through the delivery system, 5) blank pH 2 rinse water through the SPDC, 6) blank filters, and 7) blank filters with blank rainwater through the SPDC.

3.0 ANALYSIS OF RESULTS

As of December 15, 2003, analysis of samples and data is continuing. It is expected that numerical results will be available at the time of the subsequent semiannual report.

FIGURES

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Fig. 1 Ontario Hydro analyzer mounted adjacent to stack port at Pleasant Prairie Power Plant experimental site.

Fig. 2 Semicontinuous Emissions Monitor on-site.

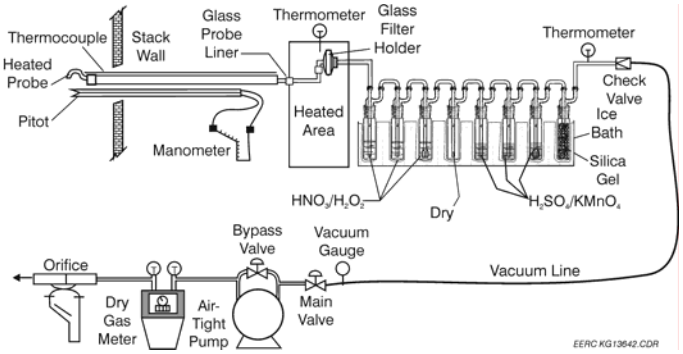

Fig. 3 Ontario Hydro Sampling Train diagram

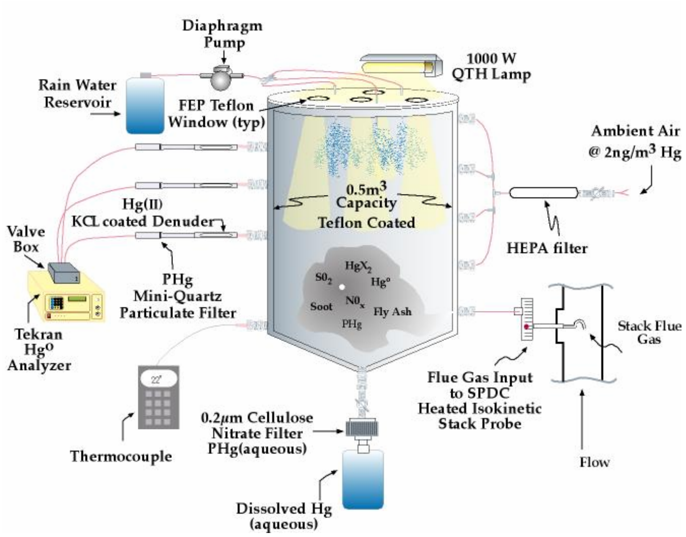

Fig. 4 Static Plume Dilution Chamber schematic