

Statement of Work

Direct Measurement of Mercury Reactions in Coal Power Plant Plumes

A. OBJECTIVES:

The overall objective of the project is to clarify the role, rates and end result of chemical transformations that may occur to mercury that has been emitted from elevated stacks of coal-fired electric power plants. This information is critical in determining the role of coal-fired plants in mercury deposition and in developing cost-effective, environmentally sound policies and strategies for reducing the adverse environmental effects of mercury. In this project, the concentration and speciation of mercury will be measured in the plume of a coal-fired power plant via near-real-time monitors mounted on an aircraft that will fly into the plume. The in-plume data will be compared to similar measurements made within the power plant stack, and in two types of dilution sampling devices that attempt to simulate the mercury transformations occurring within the plume.

B. SCOPE OF WORK:

EPRI, in collaboration with Frontier Geosciences and the University of North Dakota Energy and Environmental Research Center (EERC), will perform precise in-stack and in-plume sampling of mercury emitted from the stack of a coal-fired power plant. The selected plant will ideally have a single boiler feeding a single stack exhaust, have a high proportion of oxidized mercury in its stack emissions, and be located in relatively simple terrain. The purpose of these measurements will be to establish whether significant reduction or oxidation of the mercury occurs near the emission point but within the plume before full dispersion into the atmosphere.

To accomplish the in-plume sampling, aircraft and/or balloon-borne instruments will be carried through the plume to at least two points downwind along the plume centerline, one close to the stack exit and the second some distance downwind. The aircraft sampling approach will be to use valved inlets to the instruments, which will be triggered by fast-response sensors of plume-specific chemical constituents, such as sulfur dioxide. This will allow sampling of isolated plume material. Repeated passes through the plume under relatively steady wind conditions should allow time-of-flight equivalency for determining reaction rates for any redox reactions noted. Measurements of mercury speciation in the stack gases prior to emission will be made simultaneously with the in-plume measurements, and results will be compared to determine the extent of mercury speciation changes.

To complement the in-stack and in-plume sampling, the diluted stack exhaust will be sampled via plume dilution chambers that are designed to simulate the mercury transformation processes that occur as the plume becomes diluted with ambient air. These results will then be compared to the full-scale measurements by aircraft to establish proof-of-method for the dilution chambers. If successful, these chambers can then be

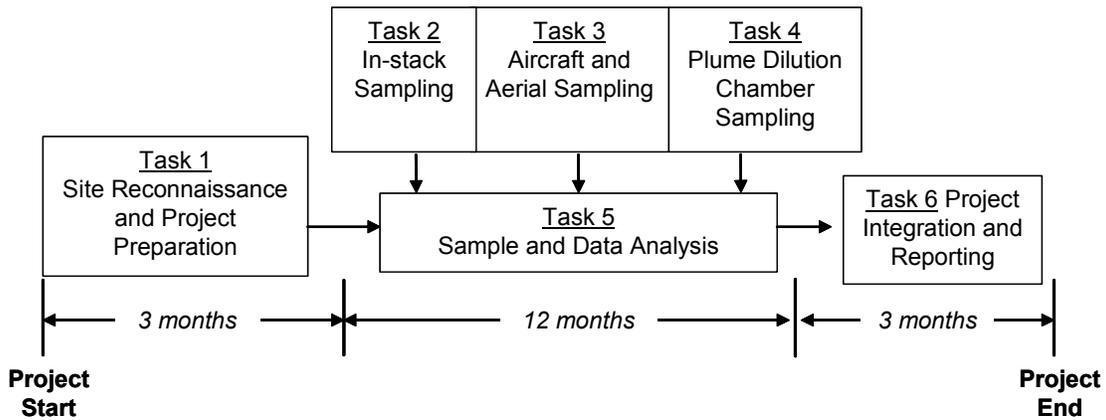
used at a greater number of power plants for inexpensive, rapid simulation of plume chemistry.

Data from all mercury measurements will be assembled, interpreted and integrated by EPRI into a comprehensive final report. A key product of the project will be the best-estimate rate of reduction or oxidation of mercury in the plume as measured during the experiments. This will be expressed as a lower bound value, depending on the distances and equivalent plume transit times sampled.

A technical advisory committee of experts will be selected to provide project guidance and oversight to the project, including review of experimental protocol and assistance with site selection. Specialists in mercury atmospheric chemistry, combustion chemistry, and plume dynamics, as well as participants from the U.S. EPA and U.S. DOE will be sought for this panel.

C. TASKS TO BE PERFORMED:

This section provides a brief summary of the planned approach for this project, which will be broken into six separate tasks to be completed over an 18-month performance period as shown below:



Task 1 consists of selecting the appropriate test plant, establishing agreements with the power plant operating company, establishing physical locations for installation of equipment, developing logistical guidelines for inclusion in the experimental protocol, and selecting a Technical Advisory Committee for the project.

Task 2 consists of measuring the concentrations and chemical speciation of mercury in the power plant stack, using the Ontario Hydro (OH) mercury speciation sampling method and fast-response mercury monitoring devices. The University of North Dakota EERC will have primary responsibility for performing the in-stack measurements.

Task 3 involves the near-real-time measurement of the concentrations and speciation of mercury in the power plant plume at distances of approximately 500 feet to 5 miles downwind of the stack. State-of-the-art instrumentation and procedures will be used to adapt existing mercury measurement equipment to obtain in-plume speciated mercury samples via repeated passes of an airplane through the plume.

Task 4 involves the use of two types of plume dilution devices – one static and one dynamic – to simulate the cooling and dilution processes experienced by the actual plume. Mercury concentrations and speciation of the contents of the plume dilution chambers will be made using the Ontario Hydro (OH) mercury speciation sampling method and fast-response mercury monitoring devices. Frontier Geosciences will have primary responsibility for performing the plume dilution chamber experiments.

Task 5 consists of completing the laboratory analysis of all samples collected under tasks 2, 3, and 4, performing QA/QC checks on the data, and assembling the data to facilitate subsequent interpretation.

Task 6 consists of data integration, interpretation, and reporting functions.

Detailed Task Descriptions

Task 1 - Site Reconnaissance and Project Preparation

Site Selection and Reconnaissance. The selection of a test site will occur upon completion of the award process. Ideal characteristics for the power plant to be measured include:

- Relatively high proportion of divalent mercury in stack emissions.
- Simple terrain surrounding the site for approximately 15 km in all directions
- Dominant wind direction likely for the period of measurement
- Single stack fed by single flue gas duct
- No other nearby significant known sources of mercury atmospheric emissions

Once site selection is complete, in cooperation with the power plant operating company, a site reconnaissance by the experimental team will be carried out; this will take place in Spring 2003. The purpose of the reconnaissance is to establish physical locations for installation of equipment and develop logistical guidelines for inclusion in the experimental protocol.

Selection of Technical Advisory Committee. A critical element is selection of a technical advisory committee of experts to provide project guidance and oversight. Specialists in mercury atmospheric chemistry, combustion chemistry, and plume dynamics, as well as participants from the US EPA and US DOE will be sought for this panel. Its first action will be to review and advise on site selection and the experimental protocol. It is expected

that the panel will generally meet via conference call, although one physical meeting is likely in the later stages of the project. The team assembled in 2002 for the first stack gas measurement at Plant Bowen in Georgia is likely to be continued for this second measurement.

Task 2 - In-Stack Measurements

Mercury sampling at the stack will be completed at the facility over a 5 to 8-day period coinciding with flight operations, using the Ontario Hydro (OH) mercury speciation sampling method and fast-response mercury monitoring devices. Prior to the start of testing, a CMM will be placed at the stack outlet and remain there during the entire project. In addition, three OH samples will be taken to both verify the CMM results and provide additional data. The mercury concentrations in the stack will be differentiated into particulate-bound mercury, Hg^0 , and Hg^{2+} by utilizing the two mercury-sampling methods.

Other flue gas measurements include total and submicron particle concentrations using a condensation particle counter, SO_3 , and chloride concentrations. The sampling methods for these flue gas constituents are well established. It is also expected that the power plant will provide continuous emission monitors (CEM) measurements for SO_2 , NO_x , O_2 , and CO_2 .

During the sampling period, it is expected that the units will be operating at or near normal conditions and that plant operating conditions (i.e., load, O_2 , NO_x , etc.) will be logged by plant personnel and will be available to project management in a suitable format.

Task 3 - Aircraft and Aerial Sampling

Aircraft sampling flights will be conducted in daylight under atmospheric conditions that permit adequate mercury sampling of the stack plume. These include wind speeds of approximately 5 to 10 knots, visibility of at least 5 miles, cloud ceiling of at least 3000 feet, and the absence of precipitation. The optimal wind direction will preclude or minimize sampling of multiple emission sources. A preliminary decision to fly will be made the evening before operations, with the final go/no-go decision made after sunrise on the proposed flight day.

Speciated mercury in the utility plume will be measured using the most sensitive and well-tested method of Landis et al. (2002). The sample train consists of an impactor to remove particles larger than $2.5 \mu\text{m}$, KCl annular denuder to adsorb gaseous $\text{Hg}(\text{II})$, 47-mm quartz fiber filter for particulate mercury collection, followed by a Tekran[®] 2573A CVAFS continuous mercury monitor to measure the remaining $\text{Hg}(0)$ in the sample stream. This equipment will be placed aboard the plane to fly through the plume at various distances downwind. The sampling equipment will consist of:

- A heated specially designed inlet probe mounted to the front or side of the aircraft.
- A heated manifold with several KCl annular denuders and filters trains in front of the Tekran[®] 2537A so that several samples can 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 have been collected during airplane operations, the KCl denuders will be analyzed on the ground with another, dedicated Tekran[®] 2537A.

It will be necessary to control the pumps for the sample traps such that the mercury will only be sampled during the time the aircraft is in the plume. It is proposed that a high-speed correlation spectrometer (COSPEC) calibrated for SO₂ be used. Also, the exact location of the plume will be determined using an SO₂ monitor and a condensation particle counter. Also an infrared thermography camera may be used. The detection of the plume SO₂ gradient along with a GPS system can then be used to determine the location of the plume and control the sample pumps.

The mission flight profiles for the airplane will consist of a series of straight and level segments flown along the axis of the plume from a distance of approximately 500 feet to 5 miles downwind of the stack. These will be followed by short level segments flown transverse to the plume axis at several distances between 500 feet and 5 miles downwind of the stack. Flight altitude and direction will be based on visual identification of the plume and will be verified by real-time measurements of SO₂ concentrations.

For airplane sampling, the Twin Otter aircraft instrumentation will also permit in situ measurements of state parameters (temperature, pressure, water vapor), three-dimensional winds and turbulence, aircraft navigation, and total particle number concentration.

Task 4 - Plume Dilution Chamber Sampling

The Static Plume Dilution Chamber (SPDC) method is described in detail in Prestbo et al. (1999). Briefly, the SPDC is 0.5 m³ 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 are made on the device to determine total mercury, particulate-phase mercury, gas-phase mercury (i.e. Hg⁰) and Hg²⁺) and dry deposition of particulate and Hg²⁺ 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, Hg⁰. 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 Hg²⁺ 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 flue gas will be determined using the Ontario-Hydro and continuous mercury monitoring instrumentation similar to that used in the stack sampling

A real time rainwater washout simulation will also be done using the SPDC Method. In this part of the experiment, while flue gas plume is introduced into the SPDC, simulated rainwater (10⁻⁹ molar H₂SO₄ and 10⁻⁹ M HCl) is continuously sprayed, falling through the plume. The rainwater which has collected at the bottom of the SPDC is immediately filtered through 0.2 μm cellulose nitrate filters to separate dissolved versus particulate Hg in the rainwater sample. The plume air remaining in the SPDC is then sampled to determine Hg⁰, Hg²⁺, particulate Hg and Hg wall loss. For non-rainwater experiments, particulate Hg and Hg²⁺ dry deposition to the walls is recovered by spray washing first with a pH 4.5 solution of 10⁻⁹ M H₂SO₄ and 10⁻⁹ M KCl in double deionized water (simulated rainwater). The wall wash is 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 Hg²⁺ to Hg⁰ 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 Hg⁰ 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 known 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 Hg²⁺ 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 Hg⁰ 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.

Task 5 - Sample and Data Analysis

Stack Sampling. Mercury sampling at the stack will be accomplished using the Ontario Hydro mercury speciation method along with semi-continuous mercury monitors. The Ontario Hydro method is the standard chemistry method for determining mercury speciation in the flue gas generated from coal-fired boilers. A description of the method is presented at <http://www.epa.gov/ttn/emc/prelim.html>. For quality control purposes the liquid samples from this method are analyzed on-site using cold vapor atomic adsorption techniques. In this way if problems occur they can be corrected. A detailed quality control/quality assurance program, in place at the University of North Dakota Energy and Environmental Research Center for ensuring good data when doing this type of sampling, will be adopted for the stack experiment proposed here.

In addition to the Ontario Hydro method the speciated mercury concentrations at the stack will be measured using either a Tekran[®] or a PS Analytical atomic fluorescence fast mercury analyzer. These analyzers have been used successfully in a number of field tests by the EERC. The analyzer will be operated around the clock and the values checked daily using the Ontario Hydro method.

Also, other flue gas constituents such as SO₃, chlorides, and particulate matter will be collected at the stack using standard EPA techniques. SO₃ and chlorides are measured using ion chromatography. Particulate matter is measured using gravimetric techniques. These flue components are important in determining the oxidation level of the mercury being emitted.

Plume Sampling. Details of the plume sampling were described previously in Task 3. Mercury will be collected on gold traps and then desorbed into a Tekran[®] mercury monitor. The aircraft used to do the plume sampling will have the sample probes located near the front of the plane and sampling will take place as the plane flies through the plume. In either case, the exact location of the plume will be determined using an SO₂ monitor and a condensation particle counter. Also an infrared thermography camera may be used.

Because the study involves measuring low levels of various components (mercury, SO₂, etc.) the concentrations in the ambient air are significant. Therefore, the background concentrations for each component will be measured and documented. The planned approach to QC will also include an integrated, automated calibration system that can rapidly provide feedback on the operational readiness of the instrument package before and after every flight. 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. As part of the quality control blank gold traps will be periodically analyzed. Also, steps will be taken to prevent contamination of instruments and sample probes. The EERC has

extensive experience in assessing and developing solutions to ensure good quality control when measuring low levels of mercury.

Plume Dilution Chamber Sample Analysis. The KCl denuder and particulate Hg filter media will be heated to 40°C during sampling. For the Dynamic Plume Dilution chamber (DPD) the pump is set to maintain 10 lpm to ensure an impactor aerodynamic aerosol cut point of 2.5 µm. 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 will be analyzed by thermal desorption using a clamshell tube furnace to convert both Hg²⁺ and Hg_p into Hg⁰ 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 Hg²⁺ and Hg_p analysis.

During sampling with both the SPDC and DPD, a dedicated Tekran[®] 2537A will be measuring Hg⁰ continuously in the plume gas, on a 2.5 minute cycle, after the removal of the Hg²⁺ and Hg_p by the denuder and filter, respectively. Again, to protect the analyzer from acid gases during sampling, a soda-lime trap will be placed behind the denuder and particulate filter at the inlet to the Tekran[®]. The expected plume Hg⁰ concentration should be more than 15 times the detection limit.

To ensure that there is no loss of mercury, the water and water filter samples will be preserved with a 5% solution of 0.2 N BrCl within 30 minutes after sample collection (FGS SOP-012.1). Field blanks will consist 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.

A separate Tekran[®] 2537A will be used for the Hg²⁺ and Hg_p analysis. This instrument will be housed away from the potentially contaminating environment of the flue gas stack area. The manual denuder analysis procedure consists of three steps over 20 minutes: sampling of zero air; heated sampling over 3 cycles to purge any residual mercury; two sample cycles of ambient air. A similar process is used in the analysis of the particulate filters.

Task 6 - Project Integration and Reporting

Following completion of the field measurements, project staff will hold a post-experiment review meeting on-site prior to returning to their respective institutions. The EPRI project manager will then contact the advisory committee to schedule a follow-up meeting in person at a central location about two months following the field experiment, for an initial look by the external reviewers at the data and findings. It is expected that data analysis and task reporting will take 6 to 9 months, typical for analysis of extensive

field samples and quality assurance blanks. The EPRI project manager, working with the other investigators and the advisors, will use task reports as the basis for preparation of an integrated project report. This integrated project report will include the detailed task reports as appendices. A key product of the project will be the best-estimate rate of reduction or oxidation of mercury in the plume as measured during the experiment. This will be expressed as a lower bound value, depending on the distances and equivalent plume transit times sampled.

D. DELIVERABLES

The periodic, topical, and final reports shall be submitted in accordance with the “Federal Assistance Reporting Checklist” and the instructions accompanying the checklist. It is expected that semi-annual reporting of technical progress will be performed. For an 18-month performance period, this translates to two semi-annual reports (one covering the first 6 months and one covering the first 12 months of technical progress), along with a comprehensive final report at the conclusion of the project.

It is anticipated that the preliminary results of the project will be presented at a conference or workshop sponsored by DOE, EPRI, or other organizations. Copies of any manuscripts, presentations, etc. developed in support of such conferences/workshops shall be submitted to DOE for inclusion in the project record.

The following is a schedule of key deliverables/milestones associated with the project, based on a nominal start date of March 18, 2002:

Milestone Schedule	2003										2004							
	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A
Months after project start	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Description																		
Project Kickoff Meeting	▲																	
Select power plant location and project advisory committee members		▲																
Initiate field sampling of power plant plume						▲												
Meeting of project advisory committee to discuss preliminary results								▲										
Complete laboratory analysis and data QA/QC																		▲
Semi-annual Technical Progress Reports								▲						▲				
Final Report																		▲

E. BRIEFINGS/TECHNICAL PRESENTATIONS :

A project kickoff meeting will be held within 60 days after project award. It is anticipated that the project kickoff meeting will be held via teleconference because of the diverse geographic locations of the project participants and the travel costs associated with a face-to-face kickoff meeting. EPRI will prepare a presentation summarizing the objectives and work to be performed during the project, and distribute this presentation to all project participants to facilitate discussion during the kickoff meeting.

After the plant site has been selected and before plume sampling begins, a pre-sampling meeting/briefing will be held at the host plant site. The purpose of this meeting will be to finalize sampling protocols, clear up any remaining issues regarding plant site support, and answer any questions of the project technical advisory committee. This pre-sampling meeting will also be held via teleconference to allow participation by all project technical advisory committee members.

A face-to-face meeting of the project technical advisory committee will be held at a central location about three months following the field experiment, for an initial look by the external reviewers at the data and findings.

It is anticipated that the preliminary results of the project will be presented at a conference or workshop sponsored by DOE, EPRI, or other organizations.