DIRECT MEASUREMENT OF MERCURY REACTIONS IN COAL POWER PLANT PLUMES

Technical Progress Report

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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 NO_x, 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 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 summarizes activities during a period of report revisions and corrections on the draft report from the stack/aircraft subcontractor, further attempts to elicit a data report from the plume dilution chamber subcontractor, and preparation and presentation of emerging results at technical and oversight meetings.

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1) ACTIVITIES DURING THE REPORTING PERIOD

Papers and Presentations

Principal Investigator Leonard Levin presented summary results and interpretation of results for source-receptor relationships to conferences, including:

- Clean Coal Technology Conference, Denver, CO September 2005
- Air Quality V Conference, Arlington, VA, September 2005
- EPRI Environment Division Advisory Council, St. Louis, MO, September 2005
- State of Pennsylvania Mercury Workgroup, Invited Speaker, Harrisburg, PA, October 2005
- International Conference on Heavy Metals in the Environment, Rio de Janeiro, Brazil, June 2005
- Annual meeting, National Atmospheric Deposition Program, Jackson, WY, October 2005
- Petroleum Environmental Research Foundation, Palo Alto, CA, July 2005
- State of Virginia Department of Environmental Quality Mercury Hearing, Richmond, VA, May 2005

Subcontractor Reporting

Subcontractor Frontier Geosciences presented results of the static plume dilution chamber work at Pleasant Prairie during the UNDEERC/U.S. DOE/U.S. EPA/EPRI cosponsored Air Quality V conference in Arlington, VA, in September 2005. The slide presentation is attached as Appendix A.

2) APPENDIX A

PROJECT PRESENTATION AT AIR QUALITY V CONFERENCE

Summary SPDC Mass Balance for P4

MEASUREMENT	Run ID	0828-S1	0829-S2	0830-S3	0831-S4
	Units	Blank			
Expected input to SPDC (CEM results x	ng	-	16.6	19.6	48.8
SPDC Background**	ng	1.52	1.99	1.03	1.11
Expected Total Hg in SPDC	ng	-	18.5	20.6	49.9
Measured SPDC Gas Phase	ng	1.74	10.6	15.1	23.1
Measured SPDC Rinse	ng	-	9.89	4.12	9.68
Measured Total Hg in SPDC	ng	-	20.4	19.2	32.8
Mass Balance - Measured/Expected %		-	110%	93%	66%
Average Mass Balance			90 ± 22%		
Dilution Ratio			260:1	212:1	95:1

- The overall SPDC Hg mass balance was acceptable and the range was similar to other SPDC studies
- Is there a dilution trend (n=3)

Eric Presbo Ph.D. (ericp@frontiergeo.com)

Summary of Hg⁰ Observations for the P4 SPDC Experiments

MEASUREMENT	Run ID	0829-S2	0830-S3	0831-S4
	Units			
Background Hg ⁰	ng/m3	3.46	1.79	1.93
Expected Minimum Hg ⁰	ng/m3	20.6	25.5	44.1
Observed Hg ⁰	ng/m3	20.9	28.3	44.9
Observed %Hg ⁰	%	101%	111%	102%
Dilution Ratio		260:1	212:1	95:1

- Observed plume [Hg⁰] only slightly greater than expected [Hg⁰]
- Hg⁰ is the most accurate and reliable measurement for the SPDC technique!
- No dilution trend for Hg⁰ results

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Was there any interconversion of Hg(II) to Hg⁰ in the SPDC Plume at P4?

MEASUREMENT	Run ID	0829-S2	0830-S3	0831-S4
	Units			
Hg ⁰ Expected	ng/m ³	20.63	25.47	44.14
Hg ⁰ Measured	ng/m ³	20.9	28.3	44.9
Hg ⁰ Net	ng/m ³	0.30	2.8	0.75
	ng	0.15	1.4	0.37
Hg(II) input	ng	8.0	7.7	27.7
Hg(II) to Hg ⁰ conversion		2%	18%	1%

- Average conversion of $7.2 \pm 9.7\%$ of Hg(II) converted to Hg⁰
- Airplane P4 plume results do not compare well with SPDC P4 plume results

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Comparison of SPDC and Airplane Plume Hg Species Interconversion at Bowen and P4

Power Plant	Method	Hg(II) to Hg ⁰ conversion as a percent of total mercury	Mass Balance	n
Bowen, GA	2002	9.4% $\pm$ 2.9%	109% $\pm$ 6.6%	6
"	Aircraft	13%		4
Pleasant Prairie, WI	SPDC	3.1% $\pm$ 3.7%	90% $\pm$ 22%	3
"	Aircraft - 0km	15% $\pm$ 6.5%	123% $\pm$ 24%	5
"	Aircraft - 8km	23% $\pm$ 2.6%	198% $\pm$ 120%	4
"	Aircraft - 16km	24% $\pm$ 5.3%	152% $\pm$ 62%	3

- Note: Airplane results were as of July, 2004

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SPDC – Hg Species Interconversion Results for all Study Sites 1995–2003

Power Plant	Year	Coal	PCD	Hg(II) to Hg ⁰ conversion as a percent of total mercury	Mass Balance	n
Presque Ilse, MI*	1995	W-SB	ESP	33% $\pm$ 6.8%	96% $\pm$ 14%	10
Dickerson, MD*	1998	E-SB	1 Unit Scrubber	41% $\pm$ 7.9%	128% $\pm$ 22%	8
Dickerson, MD	1998	MW	2 Units ESP Scrubber and Carbon Inj.	-23% $\pm$ 12%	84% $\pm$ 15%	7
EERC Pilot Plant	2000	E-B	ESP	23% $\pm$ 6.0%	86% $\pm$ 19%	8
EERC Pilot Plant	2000	E-B	Baghouse	11% $\pm$ 8.0%	75% $\pm$ 9.2%	6
Bowen, GA	2002	E-B	ESP	9.4% $\pm$ 2.9%	109% $\pm$ 6.6%	6
Pleasant Prairie, WI	2003	PRB	ESP/SCR	3.2% $\pm$ 3.7%	90% $\pm$ 22%	3

*value may be biased high due to bias in fluegas speciation measurements

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