JV TASK 10 – CHARACTERIZATION AND MODELING OF THE FORMS OF MERCURY FROM COAL-FIRED POWER PLANTS

Final Report
(for the period August 17, 1998, to September 30, 2000)

Prepared for:

AAD Document Control
U.S. Department of Energy
National Energy Technology Laboratory
PO Box 10940, MS 921-143
Pittsburgh, PA 15236-0940

DOE Cooperative Agreement No. DE-FC26-98FT40321; UND Fund 4770
Performance Monitor: Dr. Richard Read

Prepared by:

Dennis L. Laudal

Energy & Environmental Research Center
University of North Dakota
PO Box 9018
Grand Forks, ND 58202-9018

01-EERC-08-01

August 2001

DOE DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

ACKNOWLEDGMENT

This report was prepared with the support of the U.S. Department of Energy (DOE) National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-98FT40321. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors(s) and do not necessarily reflect the views of DOE.

EERC DISCLAIMER

LEGAL NOTICE This research report was prepared by the Energy & Environmental Research Center (EERC), an agency of the University of North Dakota, as an account of work sponsored by DOE and Minnesota Power, Inc. Because of the research nature of the work performed, neither the EERC nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement or recommendation by the EERC.

TABLE OF CONTENTS

Continued . . .

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF TABLES

CHARACTERIZATION AND MODELING OF THE FORMS OF MERCURY FROM COAL-FIRED POWER PLANTS

EXECUTIVE SUMMARY

The 1990 Clean Air Act Amendments (CAAAs) required the U.S. Environmental Protection Agency (EPA) to determine whether the presence of mercury in the stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk. EPA's conclusions and recommendations were presented in the *Mercury Study Report to Congress* (1) and the *Utility Air Toxics Report to Congress* (1). Given the current state of the art, these reports did not state that mercury controls on coal-fired electric power stations would be required. However, they did indicate that EPA views mercury as a potential threat to human health. In fact, in December 2000, EPA issued an intent to regulate for mercury from coal-fired boilers. However, it is clear that additional research needs to be done in order to develop economical and effective mercury control strategies. The markedly different chemical and physical properties of the different mercury forms generated during coal combustion, appear to impact the effectiveness of various mercury control strategies.

The original "Characterization and Modeling of the Forms of Mercury from Coal-Fired Power Plants" project had two tasks. The first was to collect enough data such that the mercury speciation could be predicted based on relatively simple inputs such a coal analyses and plant configuration. The second was to field validate the Ontario Hydro mercury speciation method (at the time, it had only been validated at the pilot-scale level). However, after sampling at two power plants (at one of which the Ontario Hydro method was validated), EPA issued an information collection request (ICR). The ICR required all coal-fired utilities to submit the mercury concentrations in their coal quarterly for one year, and 80 coal-fired power plants were selected to do mercury flue gas analysis. It was decided by EPRI and the U.S. Department of Energy (DOE) that this project would be suspended until the results of the ICR were known.

This report presents the results that were obtained at the two power plants referred to as Sites 111 and E-29. The EERC teamed with Radian International (now URS Corp.) to do the sampling and analysis at these two power plants.

There were three primary objectives for the project as follows:

- To provide information on the form of mercury present in the gas streams at the two sites tested.
- To more formally validate the Ontario Hydro mercury speciation method in the field using a modified EPA Method 301 procedure.
- To collect data at the power plant for use with mercury speciation-modeling activities being undertaken by EPRI and DOE. However, the modeling was suspended until the results of the ICR became known.

Sites Tested

Two units were tested at Site 111. Each were similar in size (~265 MW). Both Units 1 and 2 fire bituminous and subbituminous western coals and are equipped with low-NO_x burners. At Unit 1, the particulate emissions were controlled with a 10-compartment reverse-gas baghouse. At Unit 2, a lime spray dryer/fabric filter system is used to control both particulate and SO_2 emissions.

Site E-29 was chosen to do the full-scale validation of the Ontario Hydro mercury speciation method. This site was chosen because the high sulfur and chloride content of the coal would provide a challenge to the method. In addition, pilot-scale tests done with the coal burned at this plant indicated that concentrations of Hg^0 and Hg^{2+} were well above the comfort level of detection for the method (>0.5 $\mu g/Nm^3$). This plant has a total capacity of 1426 megawatts. The plant has two electrostatic precipitators (ESPs) to control particulate matter and a limestone wet flue gas desulfurization (FGD) system to control SO_2 emissions. The coal burned at the plant is an eastern bituminous coal.

At both sites, extensive sampling using the Ontario Hydro mercury speciation method was completed for mercury around each of the air pollution control devices. In addition, fly ash and coal samples were taken and the mercury measured. At Site E-29, a Semtech mercury monitor was also used at the stack.

Results

Site 111

At Site 111, the absolute level of mercury measured at the outlet was low (because of adsorption by the fly ash). The results are shown in Table ES-1. This complicates the data interpretation. Since the mercury is highly oxidized and the ash exhibits a strong adsorptive capacity, low levels of mercury (relative to the amount contained in the fuel) are present in the stack gas. Low levels are 1) closer to the analytical detection level and 2) more likely to be caught in the initial stages of the sampling train (and, hence, considered to be oxidized). Current understanding of mercury chemistry in combustion is that it exists in the elemental state at furnace temperatures and then can be oxidized as the gas cools. Once oxidized, it is not expected to be reduced to the elemental state in the flue gas. Therefore, sampling trains, which collect oxidized fractions first, could have a bias if they also promote oxidation (e.g., the presence of fly ash on a filter could promote the oxidation reaction).

Measurements at the Unit 2 inlet show high mercury levels in the particulate phase, which is consistent with low stack emissions (i.e., removal/adsorption across the fabric filters). It is not possible to determine if the mercury is adsorbed once the ash is caught by the filters (and the gas passes through the filter cake) or if adsorption occurs during gas cooling.

Site E-29

The more formal validation of the Ontario Hydro mercury speciation method used a modification of EPA Method 301. Only five sets of quadtrains rather than six were used for the validation test. Analyte spiking was used in two impinger sets of each quadtrain (one-half of the total samples). The statistical results are shown in Tables ES-2 and ES-3.

Table ES-1. Mercury Speciation Results at Site E-111

			Percent Found in Each Fraction		
Location	**Run**	**Total $\mu g/Nm^3$**	**Particulate-Bound Hg**	**Oxidized Hg**	**Elemental Hg**
Unit 1 Outlet	1	0.60	2	88	10
	2	1.3	–	95	5
	3	0.90	1	93	7
	4	1.3	–	96	4
Unit 2 Outlet	1	0.064	–	100	–
	2	0.17	4	48	48
	3	0.071	–	100	–
	4	0.036	11		89
Unit 2 Inlet	1	5.5	100	–	–
	2	6.4	95	5	–
	3	5.7	96	4	–
	4	8.8	84	15	2

Table ES-2. Statistical Results for Precision for the Quadtrain Data from the Ontario Hydro Method

	With Analyte Spiking (spike subtracted)			Without Analyte Spiking		
	Hg^{2+}, $\mu g/Nm^3$	**Hg^0, $\mu g/Nm^3$**	**Total Hg, $\mu g/Nm^3$**	**Hg^{2+}, $\mu g/Nm^3$**	**Hg^0, $\mu g/Nm^3$**	**Total Hg, $\mu g/Nm^3$**
Std. Dev.	0.81	0.82	0.19	0.61	0.62	1.21
% RSD	8.83	21.81	1.49	7.40	19.77	10.55
Mean	9.15	3.78	12.93	8.29	3.13	11.42

Table ES-3. Statistical Results for Bias for the Quadtrain Data from the Ontario Hydro Method

	Hg^{2+}, µg/Nm^3	**Hg^0, µg/Nm^3**	**Total Hg, µg/Nm^3**
Bias	0.86	0.65	1.51
Pooled Std. Dev.	1.01	1.03	1.22
t-value	0.850	0.635	1.237
t-statistic	2.571	2.571	2.571

The statistical results show that the Ontario Hydro method passes the criteria established in EPA Method 301. The relative standard deviation (RSD) is clearly less than 50% in all cases. Also the calculations show that there is no statistical bias (the pooled standard deviation is less than the t-statistic). Based on the mercury speciation results, the mercury generated by this coal was approximately 70% Hg^{2+} and 30% Hg^0. This ratio tended to remain constant regardless of the day-to-day variability in the data.

The Ontario Hydro mercury speciation results at the inlet and the outlet of the FGD are in Figure ES-1. It shows that the FGD system removed about 88% the Hg^{2+}, but little if any Hg^0. This is in agreement with all the mercury data that have been collected in the last several years across wet FGD systems.

The Semtech continuous emission monitor (CEM) was used at the inlet of the FGD system. Although the instrument was developed to only measure Hg^0, by including a conversion system designed at the Energy & Environmental Research Center (EERC), the instrument was able to measure total mercury. An example of the comparison between the Semtech CEM data and the Ontario Hydro method data is shown in Figure ES-2. As can be seen, the CEM results for both total Hg and Hg^0 compare quite well with the results obtained using the Ontario Hydro method.

Conclusions

On the basis of the results from the testing at the two plants, the following conclusions can be drawn:

Site 111

- The fly ash was highly reactive and absorbed mercury. It appeared that inlet Ontario Hydro results may be biased because of the nature of the ash.

- There appeared to be good agreement between the Ontario Hydro and EPA Method 29 for total mercury.

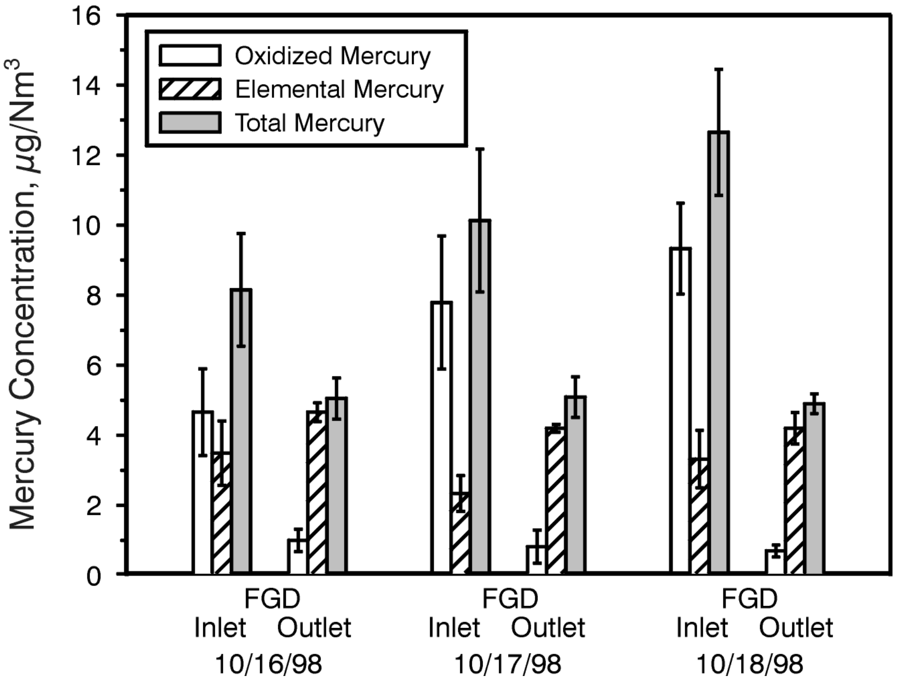


Figure ES-1. The change in vapor-phase speciated mercury across the FGD system.

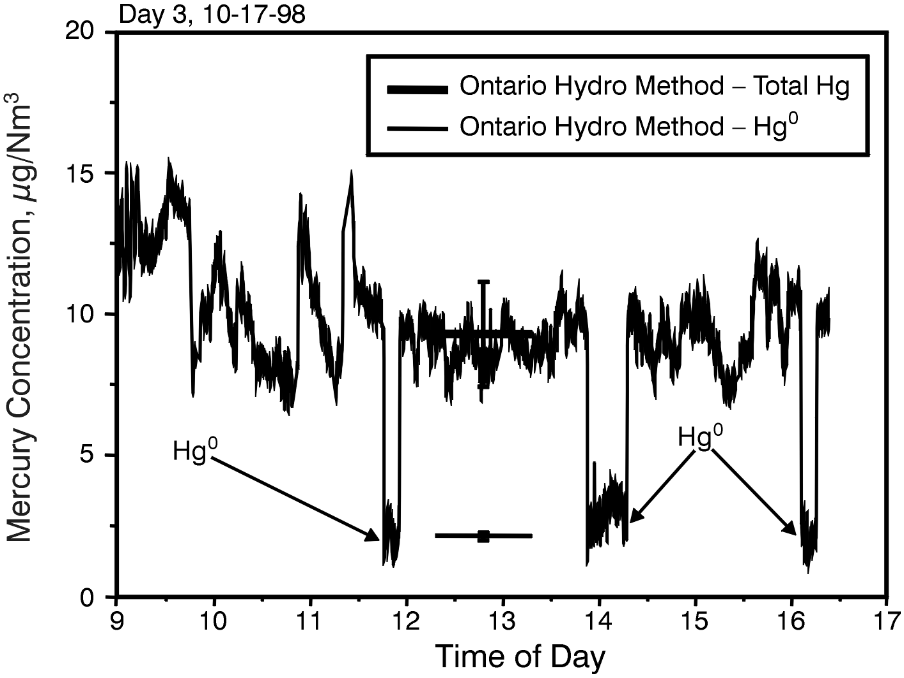


Figure ES-2. Direct comparison between Semtech mercury CEM and Ontario Hydro method for Day 3.

Site E-29

- The Ontario Hydro method results were well within the statistical criteria established by EPA Method 301. The method is valid for measuring mercury speciation in the field.

- The mercury emitted at the stack was about 10% Hg^{2+} and 90% Hg^0.

- No mercury was captured on the filters of the sampling train at either the FGD inlet or the stack.

- The FGD system removed about 88% of the Hg^{2+}. The overall mercury removal of the FGD system was 51%.

- The Semtech Hg 2000 gave total mercury results comparable to those obtained using the Ontario Hydro mercury speciation sampling method for both total Hg and Hg^0.

CHARACTERIZATION AND MODELING OF THE FORMS OF MERCURY FROM COAL-FIRED POWER PLANTS

1.0 INTRODUCTION AND BACKGROUND

The 1990 Clean Air Act Amendments (CAAAs) required the U.S. Environmental Protection Agency (EPA) to determine whether the presence of mercury in the stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk. EPA's conclusions and recommendations were presented in the *Mercury Study Report to Congress* (1) and the *Utility Air Toxics Report to Congress* (1). The first report addressed both the human health and environmental effects of anthropogenic mercury emissions, while the second addressed the risk to public health posed by the emission of mercury and other hazardous air pollutants from steam–electric generating units. Given the current state of the art, these reports did not state that mercury controls on coal-fired electric power stations would be required. However, they did indicate that EPA views mercury as a potential threat to human health. In fact, in December 2000, the EPA issued an intent to regulate for mercury from coal-fired boilers. However, it is clear that additional research needs to be done in order to develop economical and effective mercury control strategies. To accomplish this objective, it is necessary to understand mercury behavior in coal-fired power plants. The markedly different chemical and physical properties of the different mercury forms generated during coal combustion appear to impact the effectiveness of various mercury control strategies.

The original Characterization and Modeling of the Forms of Mercury from Coal-Fired Power Plants project had two tasks. The first was to collect enough data such that mercury speciation could be predicted based on relatively simple inputs such as coal analyses and plant configuration. The second was to field-validate the Ontario Hydro mercury speciation method (at the time, it had only been validated at the pilot-scale level). However, after sampling at two power plants (the Ontario Hydro method was validated at one of them), the EPA issued an information collection request (ICR). The ICR required all coal-fired utilities to submit the mercury concentrations in their coal for one year quarterly, and 80 coal-fired power plants were selected to do mercury flue gas analysis. It was decided by EPRI and the U.S. Department of Energy (DOE) that this project would be suspended until the results of the ICR were known.

This report presents the results that were obtained at the two power plants referred to as Sites 111 and E-29. The EERC teamed with Radian International (now URS Corp.) to do the sampling and analysis at these two power plants.

2.0 PROJECT OBJECTIVES

The three primary objectives for the project are as follows:

- To provide information on the form of mercury present in the gas streams at the two sites tested.

- To more formally validate the Ontario Hydro mercury speciation method in the field using a modified EPA Method 301 procedure.

- To collect data at the power plant for use with mercury speciation-modeling activities being undertaken by EPRI and DOE. However, the modeling was suspended until the results of the ICR became known.

3.0 DESCRIPTION OF THE POWER PLANTS

3.1 Description of Site 111

Two units were tested as Site 111. Each was similar in size (~265 MW). Unit 1 is a coal-fired turbine generator with a net generating capacity of 253.9 MW. The boiler is a balanced-draft, drum type rated at 1.93 million lb of main steam at 2600 psig and 1005°F. The unit burns bituminous and subbituminous western coals and is equipped with low-NO_x burners. The unit was operated at >95% load during all testing periods.

For Unit 1, particulate matter was removed by a 10-compartment reverse-gas baghouse using Teflon-coated fiberglass bags (32' × 11.5" diameter). The baghouse was designed to reduce particulate emissions to a maximum of 14 mg/Nm^3. The designed air/cloth ratio was 1.7 at 1,130,000 Nm^3/hr gas flow and a 300°F inlet temperature.

Unit 2 is also coal-fired turbine generator with a net generating capacity of 267 MW. The boiler is a balanced-draft, drum type rated at 2 million lb of main steam at 2600 psig and 1006°F. The unit burns bituminous and subbituminous western coals and is equipped with low-NO_x burners. The unit was operated at >95% load during all testing periods. Table 1 provides additional information about both units at the facility.

For Unit 2, particulate matter and sulfur dioxide emissions were controlled by a lime spray dryer/fabric filter system. Three parallel spray dryers were used to contact reagent slurry (lime and recycled solids) with the flue gas. The spray dryer was designed for 70% to 76% SO_2 removal depending on the coal source at an inlet gas temperature of 270°F and a 57°F approach temperature. The reagent ratio was 1.25, and the recycle rate was 6 lb recycled spray dryer solids to 1 lb fresh lime. Flue gas bypassing the spray dryer was used to reheat the gas stream before the baghouse. Particulate matter is removed by a 10-compartment reverse-gas baghouse using Teflon-coated fiberglass bags (32' × 11.5" diameter). The baghouse was designed to reduce particulate emissions to a maximum of 14 mg/Nm^3. Design air/cloth ratio is 1.7 at 1,130,000 Nm^3/hr gas flow and a 160°F inlet temperature.

Table 1. Plant Summary for Site 111

Site 111	Unit 1	Unit 2
Maximum Gross Electrical Output, MW	275	290
Particulate Emission Limits, lb/10^6 Btu	0.03	0.03
SO_2 Emission Limits, lb/10^6 Btu	<0.6	<0.6
NO_x Emission Limits,lb/10^6 Btu	0.5	0.5
Air Pollution Controls	Fabric filter	Lime spray dryer/fabric filter
Design SO_2 Removal	NA	70.76[a]
Design Ca:S Ratio, mole basis	NA	1.25
Design Air-to-Cloth Ratio, acf/ft^2	1.7	1.7
Design Maximum Particulate Emission	14 mg/Nm^3	14 mg/Nm^3 (0.005gr/scf)
NO_x Control	Low-NO_x burners	Low-NO_x burners
Design Fuel Rate, tons/hr dry	120	120
Fuel Type	Western bituminous	Western bituminous
Fuel Sulfur Content, % wet	0.38[b]	0.86[b]
Fuel Ash Content, % wet	8.8[b]	17[b]
Fuel Heating Value, Btu/lb wet	12,090[b]	11,430[b]

[a] Design removal varies depending on coal sulfur content.

[b] Mean values measured during sampling.

3.2 Site E-29 Description

Site E-29 was chosen to do the full-scale validation of the Ontario Hydro mercury speciation method. This site was chosen because the high-sulfur and chloride content of the coal would provide a challenge to the method. In addition, pilot-scale tests done with the coal burned at this plant indicated that concentration of Hg^0 and Hg^{2+} was well above the comfort level of detection for the method (>0.5 µg/Nm^3). This plant is located in the Midwest and has a total capacity of 1426 megawatts (MW). Site E-29 was designed to burn up to 3.7 million tons of coal per year. The plant has two electrostatic precipitators (ESPs) to control particulate matter and a limestone wet flue gas desulfurization system (FGD) to control SO_2 emissions. The coal burned at the plant is a bituminous coal that is brought to the plant by rail where it is stockpiled prior to crushing and pulverization. The pulverized coal is fed to the boilers pneumatically and injected into the furnace through the low-NO_x-type burners. A summary for Site E29 is shown in Table 2.

Table 2. Plant Summary for Site E-29

Site E-29	
Maximum Gross Electrical Output, MW	1426
Air Pollution Controls	ESP and limestone wet FGD
NO_x Control	Low-NO_x burners
Fuel Type	Ohio bituminous coal
Fuel Sulfur Content, % wet	4.11*
Fuel Ash Content, % wet	10.51*
Fuel Heating Value, Btu/lb wet	12,305*

* Mean values measured during sampling.

4.0 SAMPLING TEST PLANS

4.1 Site 111

Ash, coal, and spray dryer stream samples were collected by compositing "grab" aliquots over the gas-sampling period. Most gas samples were collected by traversing the stack or duct with probes. The type of sampling done at each location is shown in Table 3. Descriptions of the sampling locations are as follows:

- Stack gas samples were collected from four ports spaced equally around the stack. Three equal area points between the center of the stack and each port were sampled, for a total of 12 sample points per run.

- Spray dryer inlet gas samples were collected at the spray dryer inlet duct feeding the three modules. The duct was traversed using two ports, at two positions. Measurement of vapor-phase species was the objective at this location; therefore, a full traverse was not warranted.

- Coal was sampled from several pulverizers feeding each boiler.

- Fly ash and spray dryer solids were sampled from the hopper transport system as waste solids exited the baghouses.

4.2 Site E-29

Sampling at Site E-29 was completed at two sample points. The first was the inlet sampling to the FGD which was also the sampling location for the ESP outlet. Because the unit has two ESPs, the flue gas was split into two streams, but after passing through the ESPs, the flue gas then is recombined into a single duct. The sample port for the ESP outlet/FGD inlet was located after the flue gas streams had recombined but prior to the FGD modules. At this location, the modified EPA

Table 3. Gas Sampling and Analysis Matrix

Analytes	**Unit 1**		**Unit 2**			
			Full Load		**Reduced Load**	
	Inlet	**Outlet**	**Inlet**	**Outlet**	**Inlet**	**Outlet**
Trace Metals		X		X		
Mercury Speciation		X	X	X	X	X
Mercury Monitor		X		X		X
HCl, Cl_2, HF, F_2, HBr, Br_2		X	X	X	X	
SO_3, H_2SO_4		X	X	X	X	

Method 301 validation procedure was completed for the Ontario Hydro mercury speciation method. However, because of the nature of quadtrains, traversing was not possible, and these samples were taken at a single point. The sampling test plan for Site E-29 is shown in Tables 4 and 5.

Table 4. Test Program Matrix at Site E-29

	Target Species[1]				
Process Stream	**Hg^0**	**Hg^{2+}**	**Total Hg**	**Chlorides (Cl^-)**	**SO_3**
Flue Gas Sample Streams					
ESP Outlet/FGD Inlet	X	X	X	X	X
Stack	X	X	X		
Solid Samples					
Coal Feeders (composite of the feeders)			X	X	X[2]
ESP Hoppers			X		X
Lime			X		

[1] For the flue gas streams, mercury measurements (speciated and total) were made using the Ontario Hydro method; the chlorine (fluoride and bromide) in the flue gas was measured using EPA Method 26 (Cl^- as both HCl and Cl_2), and the SO_3 concentration was measured using the selective condensation method.

[2] For coal, the SO_3 is measured as total sulfur content.

At the FGD inlet, a modified EPA Method 301 test was completed to validate the Ontario Hydro mercury speciation method. The analyte-spiking protocol procedure detailed in EPA Method 301 was used. For this procedure, it is required that six quadtrain replicates be done, with half of the impinger trains being spiked with mercury prior to sampling (two sets of impinger trains in each quadtrain). In this way, the precision and bias of the sampling method being tested can be determined. However, because of time and monetary constraints, it was decided that only five replicate quadtrains, along with all the pilot-scale work that had been done in the past, would provide enough statistical evidence to determine whether the method was valid. This testing resulted in a total of 20 samples being collected at the FGD inlet.

Table 5. Mercury Samples Taken Each Day Using the Ontario Hydro Method

ESP Outlet/FGD Inlet[1,2]	Stack
Ontario Hydro Method	Ontario Hydro Method
1 quadtrain	
1 quadtrain	1duplicate
1 quadtrain	2 duplicates
2 quadtrains	

[1] Three EPA Method 26A samples were also completed for chlorides and selective condensation samples for SO_3.

[2] The Semtech Hg 2000 CEM was to be used to measure total mercury and Hg^0 at the FGD inlet.

At the stack, four sets of duplicated Ontario Hydro method samples were taken. EPA Method 26A (chlorides) and SO_3 (controlled condensation method) samples were taken when the quadtrain samples were being done. These samples were analyzed by Radian. Also, at the stack, a Semtech continuous mercury monitor (CMM) was used to measure total and speciated mercury.

5.0 MERCURY FLUE GAS SAMPLING AND ANALYTICAL METHODS

This section describes the Ontario Hydro mercury speciation method, the Semtech Hg 2000 mercury on-line analyzer, and analytical procedures that were used for this test program to determine the mercury speciation. In addition to mercury for one of the sites (Site 111), a number of flue gas trace elements were determined using EPA Method 29. It should be noted that EPA Method 29 is similar to the Ontario Hydro method described below, with the KCl solutions being replaced with nitric acid–H_2O_2 solution. A detailed description of EPA Method 29 and all other EPA methods can be found at http://www.epa.gov/ttn/emc.

5.1 Ontario Hydro Mercury Speciation Method

The Ontario Hydro method was developed by Keith Curtis and other researchers at Ontario Hydro Technologies in late 1994. Since testing with EPA Method 29 appeared to show that some of the Hg^0 was captured in the nitric acid–hydrogen peroxide (HNO_3–H_2O_2) impingers, an attempt was made to more selectively capture the Hg^{2+} by substituting three aqueous 1 N KCl impinger solutions for one of the HNO_3–H_2O_2 solutions (2). A schematic of the impinger train is shown in Figure 1. The Ontario Hydro method has been extensively tested at the EERC and has been shown to provide accurate mercury speciation data for coal-fired boilers (2, 3). The method is currently being evaluated by American Society for Testing and Materials (ASTM) Subcommittee D22.03.01. A complete description of the Ontario Hydro method in the ASTM format is available at http://www.epa.gov/ttn/emc under preliminary methods

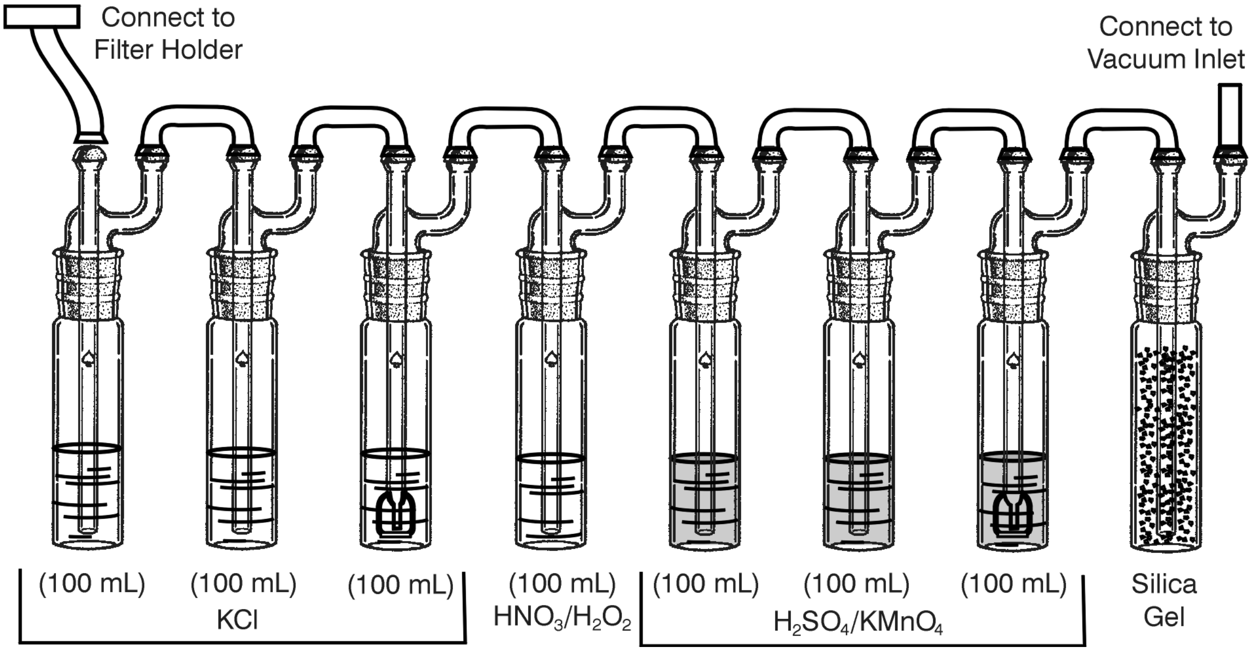
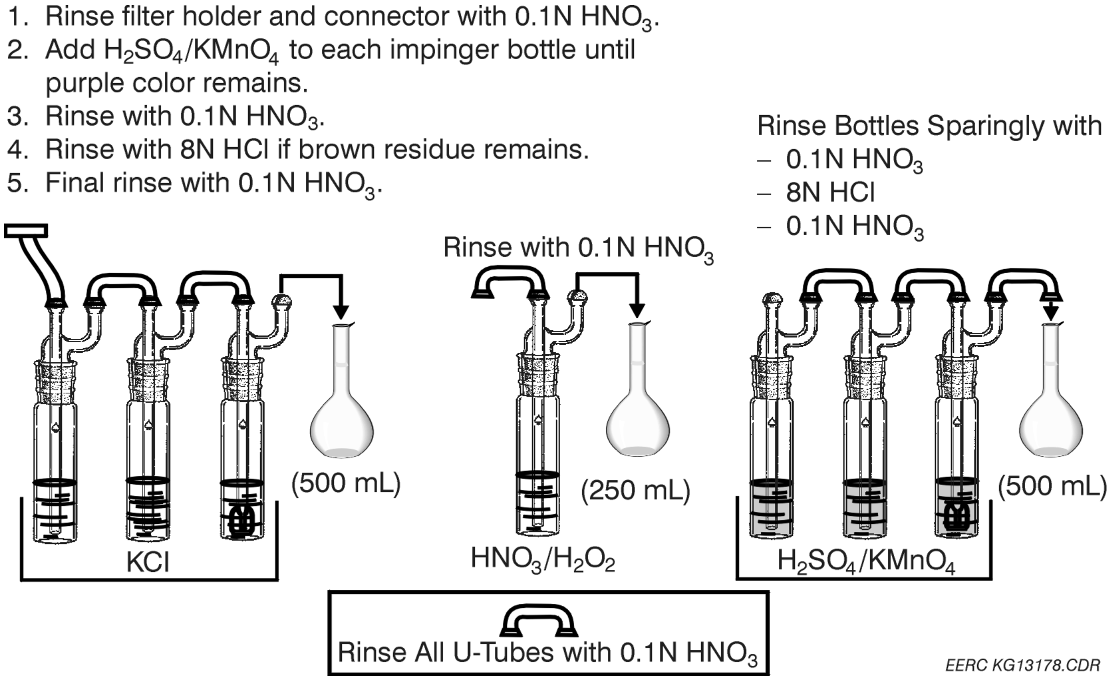


Figure 1. Schematic of the Ontario Hydro mercury speciation method sampling train.

All glassware for the sample trains was precleaned using a 4-hr soak in a 10% HNO_3 solution. No impinger glassware was used more than once in the field test. Samples collected using the Ontario Hydro method were recovered into the following fractions:

- Probe ash and particulate filter and ash – Container No. 1
- Probe rinse with 0.1 N HNO_3 solution – Container No. 2A
- Back half of the filter holder and connecting U-tubes 0.1 N HNO_3 rinses plus the three KCl impinger solutions and their 0.1 N HNO_3 rinses – Container No. 2B
- The HNO_3–H_2O_2 solution and its 0.1 N HNO_3 rinse and the rinse of the U-tube between the last KCl impinger and H_2O_2 – Container No. 3
- H_2SO_4–$KMnO_4$ impinger and rinses (0.1 N HNO_3 rinses and 8 N HCl rinses) and the rinse of the U-tube rinses – Container No. 4

The solutions were analyzed on-site using a Leeman CVAA (cold-vapor atomic absorption) instrument. The particulate fraction, which was taken back to the EERC, was analyzed first using an HCl–HF microwave digestion procedure followed by CVAA analysis for mercury. A schematic of the teardown of the sample train and the different fractions is shown in Figure 2.



1. Rinse filter holder and connector with 0.1N HNO_3.
2. Add H_2SO_4/$KMnO_4$ to each impinger bottle until purple color remains.
3. Rinse with 0.1N HNO_3.
4. Rinse with 8N HCl if brown residue remains.
5. Final rinse with 0.1N HNO_3.

Rinse with 0.1N HNO_3

Rinse Bottles Sparingly with
- 0.1N HNO_3
- 8N HCl
- 0.1N HNO_3

Rinse All U-Tubes with 0.1N HNO_3

EERC KG13178.CDR

Figure 2. Teardown schematic of the Ontario Hydro mercury speciation method sampling train.

For each of the three liquid solutions of the Ontario Hydro method, prior to analyses, a different preparation procedure must be used. The preparation steps for each solution are described below.

KCl Solution. The KCl sample fractions are immediately preserved with acidified $KMnO_4$ after sampling. This solution is then digested using a potassium persulfate digest procedure.

HNO_3–H_2O_2 Solution. The solution is first preserved with 10% $^{v}/_{v}$ HCl, then combined with H_2SO_4–$KMnO_4$ solution until a purple color persists. At this point, hydroxylamine sulfate is added until the solution becomes clear.

H_2SO_4–$KMnO_4$ Solution. Hydroxylamine sulfate is added to the H_2SO_4–$KMnO_4$ sample until the solution turns clear.

For the Ontario Hydro method, the KCl fraction results are reported as Hg^{2+}, and the sum of the mercury measured in the HNO_3–H_2O_2 solution and H_2SO_4–$KMnO_4$ solution is reported as Hg^0. The mercury measured on the filter ash is defined as particulate-bound mercury. The exact form of the mercury on the particulate matter is still unknown.

The procedures are essentially the same for EPA Method 29, except instead of three KCl impingers followed by an impinger HNO_3–H_2O_2 prior to the H_2SO_4–$KMnO_4$, there are only two H_2HO_2–NO_3 and a dry impinger. Standard atomic adsorption techniques were used to measure all the trace elements with the exception of mercury.

5.2 Semtech Hg 2000 Analyzer

A Semtech Hg 2000 mercury CMM manufactured by Semtech Metallurgy AB, Lund, Sweden, was used at the stack location at Site E-29. The instrument measures Hg^0 on a real-time basis using a Zeeman-shifted ultraviolet sensor. The Zeeman shift detection technology eliminates interference from SO_2 absorption. Because the instrument is designed to measure only Hg^0, to get total mercury, the other forms of mercury (Hg^{2+}) must be converted to Hg^0. This is done by passing the flue gas first through a carbonate trap to remove the SO_2 and then a stannous chloride solution. The SO_2 must be removed because it interferes with the ability of stannous chloride to convert Hg^{2+} to Hg^0. The operating range of the instrument is 0.3 $\mu g/Nm^3$ to 20 mg/Nm^3. The Semtech Hg 2000 has been certified by TUEV Rheinland for determining compliance with the German legal limit of 50 $\mu g/Nm^3$ for total mercury from waste incinerators.

5.3 Oxygen Concentration, Flue Gas Velocity, and Moisture

To measure the mercury concentration in the flue gas, it was also necessary that the O_2 levels at each sample location be determined. For these tests, an Orsat procedure was used. Flue gas velocity, moisture, and flow rate determinations were performed according to EPA Methods 2 and 4 in conjunction with the Ontario Hydro method.

6.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

To ascertain data quality obtained during the sampling program, the following procedures were used:

- Process operating data were examined to ensure that sampling took place during steady, representative plant operation.

- Sampling and analytical analysis protocols were reviewed to ascertain how the data compared with other data generated using standard protocols.

- The type and quantity of QA samples were reviewed to qualitatively determine the confidence that can be placed in the results.

- The QA/QC data results were compared with data quality indicators to qualitatively determine the validity of the data in terms of variability and accuracy.

These procedures are part of an overall QA/QC program, in place at the EERC and Radian, that is designed to maintain overall data integrity.

6.1 Process Data Evaluation

Plant operating data were examined to ensure that process operation was stable and representative during the sampling periods. Excessive scatter or significant trends in relevant process variables can indicate periods of nonrepresentative unit operation. Data scatter is useful for identifying periods of operational difficulty; data trends indicate periods when steady-state operation has not been achieved.

6.2 Stack Sampling Quality Control Evaluation

Sampling precision can be estimated by comparing the results for various parameters of the replicate samples, notably velocity, moisture content, and gas composition in the stack. Sampling accuracy is usually inferred from the calibration and proper operation of the equipment and from historical validation of the methods. Field blanks are used to determine any biases that may be caused by contamination or operator errors. Blanks were included for all tests. Sample representativeness also depends on the characteristics of the sampling locations. The sampling location on the stacks were ideal in terms of undisturbed flow distances upstream and downstream of the ports so that the minimum required number of traverse points (12 points) could be used. The FGD inlet sampling locations were not as ideal at either location; however, the purpose of measurements was focused on vapor-phase species, which are not typically stratified.

Sampling comparability depends on the representativeness of the samples and on the use of standard methods consistently applied. The Ontario Hydro mercury speciation method was the newest procedure used and has been extensively studied by the EERC for EPRI. The EPA multimetals procedure (Method 29) is a standard method. EPA Method 26 for chlorine/chloride, although somewhat more recent than others, has been used extensively and is also published as Method 0050 in the EPA Methods Manual for Boilers and Industrial Furnaces. Sampling completeness is mainly a function of providing the requisite number of samples to the analytical laboratories. In most cases, these were triplicate samples.

The isokinetic sampling rate is a measure of the operational performance of sampling for particulate matter and can be used as an indicator of precision, with consequences for representativeness. All of the applicable sampling runs met the acceptance criteria for isokinetic variation, 10%.

6.3 Evaluation of Measurement Data Quality

An evaluation of the measurement's data quality is based on QC data obtained during sampling and analysis. Generally, the type of QC information obtained pertains to measurement precision, accuracy, and blank effects, determined by collecting various types of replicate, spiked, and blank samples. The specific characteristics evaluated depend on the type of QC checks performed. For example, blanks may be prepared at different stages in the sampling and analysis process to isolate the source of a blank effect. Similarly, replicate samples may be generated at different stages to isolate and measure the sources of variability. Table 6 summarizes the QA/QC measures commonly used and the characteristic information obtained. The absence of any of these types of QC checks in this testing does not necessarily reflect poorly on the quality of the data but does limit the ability to identify various sources of measurement error.

Table 6. Elements of the QA/QC Plan

QC Activity	Characteristic Measured
Precision	
Replicate Samples Collected over Time under the Same Conditions	Total variability, including process or temporal, sampling, and analytical but not bias.
Duplicate Field Samples Collected Simultaneously	Sampling plus analytical variability at the actual sample concentrations.
Duplicate Analyses of a Single Sample	Analytical variability at the actual sample concentrations.
Matrix- or Media-Spiked Duplicates	Sampling plus analytical variability at an established concentration.
Laboratory Control Sample Duplicates	Analytical variability in the absence of sample matrix effects.
Surrogate-Spiked Sample Sets	Analytical variability in the sample matrix but at an established concentration.
Accuracy (including precision and bias)	
Matrix-Spiked Samples	Analyte recovery in the sample matrix, indicating possible matrix interferences and other effects. In a single sample, includes both random error (imprecision) and systematic error (bias).
Media-Spiked Samples	Same as matrix-spiked samples. Used where a matrix-spiked sample is not feasible, such as certain stack sampling methods.
Surrogate-Spiked Samples	Analyte recovery in the sample matrix, to the extent that the surrogate compounds are chemically similar to the compounds of interest. Primarily used as indicator of analytical efficacy.
Laboratory Control Samples (LCS)	Analyte recovery in the absence of actual sample matrix effects. Used as an indicator of analytical control.
Blank Effects	
Field Blank	Total sampling plus analytical blank effect, including sampling equipment and reagents, sample transport and storage, and analytical reagents and equipment.
Trip Blank	Blank effects arising from sample transport and storage. Typically used only for volatile organic compound analyses.
Method Blank	Blank effects inherent in analytical method, including reagents and equipment.
Reagent Blank	Blank effects from reagents used.

As shown in Table 6, different QC checks provide different types of information, particularly pertaining to the sources of inaccuracy, imprecision, and blank effects. In general measurement precision and accuracy are typically estimated from QC indicators that cover as much of the total sampling and analytical process as feasible. Precision and accuracy estimates are based primarily on the actual sample matrix.

Data quality objectives (DQOs) are used by the laboratory, not as validation criteria but as empirical estimates of the precision and accuracy that would be expected from existing reference measurement methods and that would be considered acceptable. In some cases, precision and accuracy estimates are not necessarily derived from analyses of the same types of samples being investigated. Although analytical precision and accuracy are relatively easy to control and quantify, sampling precision and accuracy are unique to each site and each sample matrix. Data that do not meet these objectives are by no means necessarily unacceptable. Rather, the intent is to document the precision and accuracy actually obtained, and the objectives serve as benchmarks for comparison. The effects of not meeting the objectives should be considered in light of the intended use of the data.

Specific QC procedures used to measure mercury in the flue gas are described below.

6.3.1 Instrument Setup and Calibration

The instrument used in the field for mercury determination was a Leeman Labs PS200 CVAA. To measure mercury, the instrument was set up for absorption at 253.7 nm with a carrier gas of nitrogen and 10% $^{w}/_{v}$ stannous chloride in 10% $^{v}/_{v}$ HCl as the reductant. Each day, the drying tube and acetate trap were replaced and the tubing checked. The rinse container was cleaned and filled with fresh solution of 10% $^{v}/_{v}$ HCl. After the pump and lamp were turned on and warmed up for 45 minutes, the aperture was set to manufacturer specifications. A four-point calibration curve was then completed using matrix-matched standards. The detector response for a given standard was logged and compared to specifications to ensure the instrument had been properly set up. A QC standard of a known analyte concentration was analyzed immediately after the instrument was standardized in order to verify the calibration. This QC standard was prepared from a different stock than the calibration standards. It was required that the values obtained read within 5% of the true value before the instrument was used. After the initial QC standardizations were completed, standards were run every five samples to check the slope of the calibration curve. All samples were run in duplicate, and one in every ten samples was spiked to verify analyte recovery. A QC chart is maintained at the EERC to monitor the long-term precision of the instrument.

6.3.2 Presampling Preparation

All data sheets, volumetric flasks, and petri dishes used for sample recovery were marked with preprinted labels. The liquid samples were recovered into premarked volumetric flasks and logged, then analyzed on-site. The filter samples were placed in premarked petri dishes and taken back to the EERC, where they were analyzed using mixed-acid digestion techniques. The labels contained identifying data, including date, time, run number, sample port location, and the name of the sampler.

6.3.3 Glassware and Plasticware Cleaning and Storage

All glass volumetric flasks and transfer pipets used in the preparation of analytical reagents and calibration standards were designated Class A to meet federal specifications. Prior to being used for the sampling, all glassware was washed with hot, soapy water, then rinsed with deionized water three times, soaked in 10% $^{V}/_{V}$ nitric acid for a minimum of 4 hours, rinsed an additional three times with deionized water, and dried. The glassware was then stored in closed containers until it was used at the plant.

6.3.4 Analytical Reagents

All acids that were used for the analysis of mercury and other trace elements were trace metal-grade. Other chemicals that were used in the preparation of analytical reagents were analytical reagent-grade. The calibration standards used for instrument calibration and the QC standards used for calibration verification were purchased commercially and certified to be accurate within ±0.5% and were traceable to NIST standard reference materials.

6.3.5 Blanks

As part of the QA/QC procedures, field blanks were completed. A field blank is defined as a complete impinger train including all glassware and solutions that is taken out to the field during sampling and exposed to ambient conditions. These sample trains are then taken apart and the solutions recovered and analyzed in the same manner as those sample trains used for sampling activities. If the field blank shows contamination above instrument background, steps must be taken to eliminate or reduce the contamination to below background levels.

All acids, chemical reagents, and deionized water used for mercury determination were analyzed for background levels of mercury. Each time a new batch of reagents was prepared, an aliquot was immediately taken and analyzed for mercury. Again, no mercury contamination was found.

6.3.6 Spiked Samples

In order to ensure that adequate levels of accuracy were maintained, spiked samples were also submitted for analysis. These samples were made up independently of the chemist doing the analyses. The spikes were required to be within 15% of the true value. If the value is not within the specified limits, then the instrument is recalibrated and the samples reanalyzed. The spiking solutions were from a stock separate from the calibration standard stock.

7.0 RESULTS FROM SITE 111

To evaluate data scatter, the mean and standard deviation was calculated for the following variables: unit load, gas O_2, NO_x and SO_2 contents, and gas temperatures. Table 7 shows the results. Over the test periods, all of these parameters were very steady. Both units were operated at >95%

Table 7. Operating Parameters During Test Periods (mean and standard deviation)

Parameter	Unit 1	Unit 2
Load, MW	268 ± 3	282 ± 4
Excess O_2, %	3.8 ± 0.2	3.3 ± 0.2
Air Preheater Temp, °F	269 ±6	321 ± 2
NO_x, lb/million Btu	0.43 ± 0.02	0.46 ± 0.02
SO_2 to Spray Dryer, lb/million Btu	NA	1.49 ± 0.04
SO_2, lb/million Btu	0.61 ± 0.05	0.28 ± 0.02

of design load during testing periods. These parameters indicate that during the test periods, both units were operating in a steady fashion.

Table 8 presents a summary of the different sampling events, which have been grouped by time period into "runs." The run numbers in Table 8 correspond to those presented later in this section. Coal and ash samples were taken that correspond with these sampling events.

Table 8. Sampling Schedule

Location	Date	Time	Run	Measurements
Unit 1 Stack	Nov 11	AM		OH, M29, M26, M8
		PM	2	OH, M29, M26, M8
	Nov 12	AM	3	OH, M29, M26, M8
		PM		OH, M29
Unit 2 Stack	Nov 13	AM	1	OH, M29, M26, M8
		PM	2	OH, M29, M26, M8
	Nov 14	AM	3	OH, M29, M26, M8
		PM	4	OH, M29, M26, M8
Unit 2 Spray Dryer Inlet	Nov 13	AM	1	OH, M26, M8
		PM	2	OH, M26, M8
	Nov 14	AM	3	OH, M26, M8
		PM	4	OH
	Nov 15*	AM	5, 6	OH

*Reduced load test.

7.1 Coal Results

Table 9 presents coal sample analysis results for both Units 1 and 2. The mean concentration and 95% confidence interval are reported for each analyte. The 95% confidence interval is the range about the sample mean that has a 95% probability of containing the true mean. Only one sample was obtained from Unit 2 during the reduced load test.

Table 9. Coal Analysis

	Unit 1		Unit 2		Reduced Load
As-Received, wt%	**Mean**	**95% CI**	**Mean**	**95% CI**	
Ultimate/Proximate					
Moisture	4.7	0.17	2.7	0.10	2.7
Ash	8.8	0.76	17	1.8	16
Volatile Matter	3.8	0.28	38	0.46	387
Fixed Carbon	48	0.51	42	1.4	43
Heating Value, Btu/lb	12,092	96	11,429	408	11,434
Sulfur	0.38	0.036	0.86	0.031	0.89
Carbon	69	0.64	65	2.0	64.5
Hydrogen	4.6	0.067	4.4	0.082	4.41
Nitrogen	1.2	0.007	1.3	0.044	1.31
Oxygen	11	0.53	8.8	0.75	9.78
Coal Ash Analysis, wt%					
Silica, SiO_2	59	1.5	58	1.2	58.74
Alumina, Al_2O_3	12	1.1	19	0.99	18.46
Titania, TiO_2	0.88	0.12	0.73	0.044	0.77
Ferric Oxide, Fe_2O_3	4.7	0.070	4.6	0.29	4.67
Lime, CaO	12	1.2	6.9	1.1	6.47
Magnesia, MgO	1.4	0.066	2.4	0.31	2.13
Potassium Oxide, K_2O	0.28	0.57	2.1	0.13	1.9
Sodium Oxide, Na_2O	4.1	0.30	1.3	0.23	1.33
Sulfur Trioxide, SO_3	4.7	1.5	3.5	0.58	3.46
Phosphorous Pentoxide, P_2O_5	0.22	0.046	0.17	0.013	0.15
Strontium Oxide, SrO	0.11	0.052	0.20	0.024	0.19
Barium Oxide, BaO	0.065	0.10	0.30	0.033	0.19
Manganese Oxide, Mn_3O_4	0	0	0.008	0.021	0
Undetermined	0.95	0.16	0.34	0.50	1.54
Elemental Coal Ash Analysis, mg/kg					
Aluminum	5,348	246	16,800	1,612	13,700
Antimony	<0.29	---	0.28	0.31	0.09
Arsenic	0.31	0.11	1.1	0.22	0.906
Barium	66	7.7	369	32	300
Beryllium	0.13	0.018	0.45	0.0097	0.43
Cadmium	0.22	0.47	0.49	0.049	0.52
Calcium	7,323	378	8,113	1,017	7,080
Chloride	71	16	356	54	NA
Chromium	5.7	0.54	22	3.4	22.2
Cobalt	0.82	0.11	1.9	0.23	1.89
Copper	4.4	0.30	8.9	0.76	8.8
Fluoride	27	2.3	127	11	NA
Iron	2,880	128	5,073	208	5,060
Lead	2.6	0.41	4.7	0.80	5.04
Magnesium	864	38	2,685	201	2,270
Manganese	14	0.98	20	1.9	17.6
Mercury	0.046	0.003	0.055	0.0093	0.053

Continued . . .

Table 9. Coal Analysis (continued)

	Unit 1		Unit 2		Reduced
As-Received, wt%	**Mean**	**95% CI**	**Mean**	**95% CI**	**Load**
Molybdenum	0.64	0.084	1.2	0.14	1.4
Nickel	2.4	0.24	6.8	0.65	6.7
Potassium	167	12	3,440	533	3,250
Selenium	1.1	0.20	1.4	0.29	1.21
Silver	0.028	0.024	0.015	0.0096	0.0087
Sodium	3,375	376	3,218	1,305	2,080
Strontium	98	6.6	245	30	168
Thallium	0.49	0.10	0.76	0.69	0.83
Tin	0.97	0.15	1.8	0.62	1.8
Titanium	492	16	791	107	800
Vanadium	7.1	0.66	23	3.8	23.9
Zinc	2.3	0.35	14	3.9	14.2

The Unit 1 coal has 0.4% sulfur and 9% ash. Unit 2 fuel has 0.9% sulfur and 17% ash. Unit 1 coal has higher calcium and sodium levels, while Unit 2 aluminum and magnesium levels are higher. Mercury levels in both coals are similar at 0.05 mg/kg.

7.2 Fly Ash Results

Table 10 presents the analyses of the collected fly ash from both units. Note that for Unit 2, this stream includes both coal ash and spray dryer sulfur compounds. This is evident by the higher calcium, sulfate, and chloride levels seen in Unit 2 ash material. Both sets of solids have relatively high mercury levels, indicative of high adsorptive capacity and, therefore, presumably high oxidation conversion efficiency. Gas-phase measurements confirm this observation.

7.3 Gas-Phase Streams

Gas sampling was conducted at three locations: the Unit 1 stack, the Unit 2 spray dryer inlet, and the Unit 2 stack. Sampling of a particular analyte group was conducted concurrently at each location. Table 11 summarizes the analyte concentration means and 95% confidence intervals in the gas entering at the three locations sampled. Also shown in Table 9 is a nominal concentration level for the Method 29 field blanks. Although high-purity filters are used, some trace level of contaminants is seen. Field blank quantities were divided by the average sample gas volume to develop this number for comparison. For many of the elements, the field blank is of the same order of magnitude. For this reason, the sample results should be considered conservative emission estimates. Actual values are probably lower. The actual level of emissions from both units is very low, relative to most other power plants.

Table 10. Ash Analyses

	Unit 1		Unit 2		Reduced
Ash Analyses	**Mean**	**95% CI**	**Mean**	**95% CI**	**Load**
Elemental Analysis, mg/kg					
Aluminum	55,650	5,554	43,725	1,871	52,600
Antimony	4.6	2.1	6.9	1.5	6.53
Arsenic	8.4	1.4	19	2.9	18.9
Barium	1,163	167	2,108	264	2,120
Beryllium	3.0	0.48	3.3	0.307	3.34
Cadmium	0.49	1.2	1.4	0.175	2.19
Calcium	72,450	5,338	166,500	12,316	152,000
Chloride	110	36	4,743	932	3,990
Chromium	76	10	102	11	117
Cobalt	8.5	1.0	8.3	1.1	8.94
Copper	76	64	54	5.8	57.2
Fluoride	107	23	451	104	551
Iron	32,200	4,737	21,575	346	24,100
Lead	23	3.8	32	5.5	35.7
Magnesium	8,930	793	9,878	848	10,100
Manganese	141	32	120	6.9	122
Mercury	0.44	0.20	1.1	0.246	0.901
Molybdenum	7.1	1.5	16	2.5	14.5
Nickel	31	3.2	37	3.7	40.8
Potassium	3,878	748	7,855	523	9,480
Selenium	17	5.5	25	5.5	20.9
Silver	1.5	0.56	1.2	0.43	1.44
Sodium	24,250	6,789	22,275	2,996	19,300
Strontium	1,065	141	1,170	130	1,170
Sulfate	3,755	1,256	15,325	2,647	10,200
Thallium	3.5	1.2	4.0	2.2	4.09
Tin	5.1	1.1	5.9	1.1	5.46
Titanium	4,915	767	2,655	83	2,970
Vanadium	87	16	121	11	138
Zinc	32	3.8	97	8.9	120
Mineral Analysis					
Silica, SiO_2	64	5.5	35	4.9	40
Alumina, Al_2O_3	12	1.6	12	0.5	14
Titania, TiO_2	0.84	0.20	0.61	0.054	0.63
Ferric Oxide, Fe_2O_3	4.6	0.60	4.3	0.044	4.6
Lime, CaO	11	2.0	31	2.3	28
Magnesia, MgO	1.6	0.24	2.3	0.172	2.3
Potassium Oxide, K_2O	0.46	0.082	1.0	0.038	1.05
Sodium Oxide, Na2O	3.2	1.0	3.3	0.6	2.9
Sulfur Trioxide, SO_3	1.3	0.46	6.9	1.9	3.8
Phosphorous Pentoxide, P_2O_5	0.32	0.034	0.36	0.058	0.34
Strontium Oxide, SrO	0.14	0.041	0.19	0.021	0.19
Barium Oxide, BaO	0.11	0.18	0.29	0.138	0.35
Manganese Oxide, MnO	0.025	0.052	0.005	0.014	-

Table 11. Gas Stream Analyses

	Unit 1 Outlet		Unit 2 Outlet		Unit 2 Inlet		Field
	Mean	**95% CI**	**Mean**	**95% CI**	**Mean**	**95% CI**	**Blank**
Gas Flow Rate, dscfm	710,113	10,396	717,398	15,726			
Elemental Concentration, µg/Nm^3							
Aluminum	203	14	147	17			106
Antimony	1.4	1.2	2.5	1.5			1.4
Arsenic	0.59	0.7	0.58	0.85			<1.5
Barium	5.7	0.6	4.9	0.76			3.1
Beryllium	0.08	0.12	0.02	0.008			0.06
Bromine	<78		<95		<353		<100
Cadmium	1.0	0.13	3.4	2.4			4.0
Calcium	446	24	275	62			154
Chlorine	17	16	5.4	7.2	180	207	<18
Chromium	4.4	11	1.1	0.30			0.7
Cobalt	0.74	0.32	0.91	0.41			0.6
Copper	2.3	3.0	1.7	1.5			1.4
Hydrogen Bromide	<104		<146		<540		<100
Hydrogen Chloride	2,879	993	108	39	36,673	4,351	87
Hydrogen Fluoride	995	391	122	37	10,995	1,958	116
Iron	109	62	65	14			34
Lead	1.1	1	1.5	1.3			1.0
Magnesium	46	5.8	31	8.8			20
Manganese	3.2	1.7	4.3	6.2			2.4
Mercury (M29)	0.92	0.49	<0.14				0.0
Mercury (OH)	1.0	0.54	0.09	0.09	5.9	0.8	0.0
Molybdenum	6.4	0.12	6.8	0.34			6.8
Nickel	3.8	10	2.8	3.1			0.7
Potassium	10	13	104	1,160			0.1
Selenium	2.1	1.3	1.6	0.83			0.9
Silver	0.15	0.24	0.68	1.5			<1.3
Sodium	403	152	398	167			281
Strontium	5.3	0.4	2.4	0.61			1.2
Thallium	<3		<3				<2.9
Tin	2.1	1.2	1.4	0.65			0.3
Titanium	12	2.2	5.7	1.6			3.1
Vanadium	0.35	0.34	0.24	0.06			0.1
Zinc	19	14	17	12			10
Particulate, mg/Nm^3	2.7	1.3	1.8	1.4	7,400	1,000	
SO_3, mg/Nm^3	0.50	0.25	0.38	0.08	100	161	
SO_2, mg/Nm^3	645	47	419	25	1,755	184	

Table 12 presents the speciation results for the mercury measurements. Both the Ontario Hydro and Method 29 data are presented for each individual run. Again, there is good agreement between both methods. The absolute level of mercury measured is relatively low (due to adsorption by the fly ash). This complicates the data interpretation. Since the mercury is highly oxidized and the ash exhibits a strong adsorptive capacity, low levels of mercury (relative to the amount contained in the fuel) are present in the stack gas. Low levels are 1) closer to the analytical detection level and 2) more likely to be caught in the initial stages of the sampling train (and hence considered to be oxidized). Current understanding of mercury chemistry in combustion is that it exists in the elemental state at furnace temperatures and then can be oxidized as the gas cools. Once oxidized, it is not expected to be reduced to the elemental state in the flue gas. Therefore, sampling trains, which collect oxidized fractions first, could have a bias if they also promote oxidation (e.g., the presence of fly ash on a filter could promote the oxidation reaction).

Measurements at the Unit 2 inlet show high mercury levels in the particulate phase, which is consistent with low stack emissions (i.e., removal/adsorption across the fabric filters). It is not possible to determine if the mercury is adsorbed once the ash is caught by the filters (and the gas passes through the filter cake) or if adsorption occurs during gas cooling.

Table 12. Mercury Speciation Results

		Ontario Hydro Results				**Method 29 Results**		
			Percent Found in Each Fraction*				**Percent Found in Each Fraction***	
Location	**Run**	**Total $\mu g/Nm^3$**	**Filter**	**KCl**	**$KMnO_4$**	**Total $\mu g/Nm^3$**	**HNO_3–H_2O_2**	**$KMnO_4$**
Unit 1 Outlet	1	0.60	2%	88%	10%	0.5	98%	2%
	2	1.3	–	95%	5%	0.9	98%	2%
	3	0.90	1%	93%	7%	1.2	100%	–
	4	1.3	–	96%	4%	1.1	100%	–
Unit 2 Outlet	1	0.064	–	100%	–	<0.14		
	2	0.17	4%	48%	48%	<0.13		
	3	0.071	–	100%	–	<0.12		
	4	0.036	11%		89%	<0.13		
Unit 2 Inlet	1	5.5	100%	–	–			
	2	6.4	95%	5%	–			
	3	5.7	96%	4%	–			
	4	8.8	84%	15%	2%			
	5**	1.2	lost	19%	81%			
	6**	3.9	76%	14%	10%			

* For the Ontario Hydro method, the mercury in the KCl is considered oxidized mercury and the $KMnO_4$, elemental mercury. For EPA Method 29, the HNO_3–H_2O_2 impingers were thought to remove the oxidized mercury and the $KMnO_4$, elemental mercury.

** Reduced load. On Run 5, the filter fractions was lost; therefore, the fractions reported for the KCl and $KMnO_4$ are biased high. On Run 6, the probe nozzle was turned 180 degrees from the gas flow to collect less ash, in an attempt to determine if mercury was adsorbing on the filter during sampling.

7.4 Quality Control Results

The quality control data evaluated for metal and anion measurements show that most of the results met project objectives. Accuracy data were measured for the coal and ash samples using a Standard Analytical Reference Material (SARM). In addition, a sample was analyzed in duplicate for precision.

7.4.1 Method 29 Results

EPA Method 29 was used to determine the concentration of most elements in the stack gas of Units 1 and 2. Method 29 generates a number of samples per train that are analyzed. These include the filter, which is combined with the probe and nozzle rinse; the nitric acid–peroxide impingers; the potassium permanganate impingers; and an HCl rinse of the permanganate impingers.

All of these fractions were analyzed for mercury, and all of the QC indicators met or exceeded the data quality objective (DQOs). Techniques used included matrix spikes and duplicates (MS/MSD), laboratory control samples and duplicates (LCS/LCSD), and analytical spikes (AS). For the other elements, AS were used. Recoveries were slightly above the DQO for Al, Fe, Ca, Mg, Na, and K. This is most likely due to a matrix effect, since the target elements are present at much lower levels. A lower dilution would probably bring these values into the desired DQO range.

7.4.2 Acid Gases

For these samples, MS/MSD and LCS/LCSD results met DQO targets. A number of the actual samples were analyzed in duplicate. Most of the samples with low concentrations did not meet the precision DQO. This is because of variability seen in results as the detection limit is approached. Samples with higher concentrations meet the precision DQO (±20%).

7.4.3 Ontario Hydro Mercury Results Blanks

The on-site analysis of the OH train components included blank and spike results. No blank contamination was seen. Spike recovery averaged 96% with a range of 73% to 111%.

7.4.4 Coal Analyses

All coal QA/QC data met DQO except as follows. The MS/MSD recovery was slightly high for aluminum and strontium and slightly low for titanium. The analytical spike also had high Al and Sr recovery. MS/MSD levels for chloride showed varied recovery, 65% and 128%, indicating some uncertainty in these values. The Unit 1 coal chloride results were low, under 100 mg/kg. Analysis of a reference coal showed good agreement with certified values, except for a high sodium value.

7.4.5 Ash Analyses

QA samples of ash from both units showed higher variability than seen for the coal. This is typically because digestion of the ash is more difficult. MS/MSD recoveries for aluminum, magnesium, and calcium were slightly below the DQO. Other parameters met DQO levels.

7.4.6 Summary

The data obtained during the sampling events were obtained from two units operating under normal conditions. The samples are representative of the process streams, and the analytical data is believed valid, based on the QA/QC results for all parameters. The actual emission levels for some substances are near the levels seen in the field blanks, primarily as trace contaminants of the particulate sampling filter. The actual magnitude of emissions for these substances may be lower than reported.

8.0 RESULTS FROM SITE E-29

Table 13 summarizes the average load and gas emissions during the mercury speciation test program. The FGD system for this plant was very efficient, as can be seen it was >90%. Although the load data are consistent from day to day there is variability in the inlet SO_2 data. This becomes more apparent when the hourly SO_2 data are plotted as a function of time, as shown in Figure 3. This indicates there was variability in the coal being fired in the boiler. The average moisture and oxygen content at each sample point is shown in Table 13 and 14. The samples taken each day are listed in Table 15.

Table 13. Flue Gas Data

Date	Gross Load, MW	NO_x, ppm (v)	CO_2, %	SO_2 at the FGD Inlet, ppm (v)	SO_2 at the FGD Outlet, ppm (v)	SO_2 removal across FGD, %
10-15-98	1324	211	11.8	2145	133	93.8
10-16-98	1313	207	11.9	2736	184	93.3
10-17-98	1313	195	11.9	2831	161	94.3
10-18-98	1298	198	11.8	2653	142	94.6

Table 14. Average Excess Oxygen and Moisture Content at Sampling Points

Sample Location	Excess O_2 (on a dry basis), %	Moisture Content, %
ESP Outlet/FGD Inlet	7.8	8.6
Stack	9.6	14.4

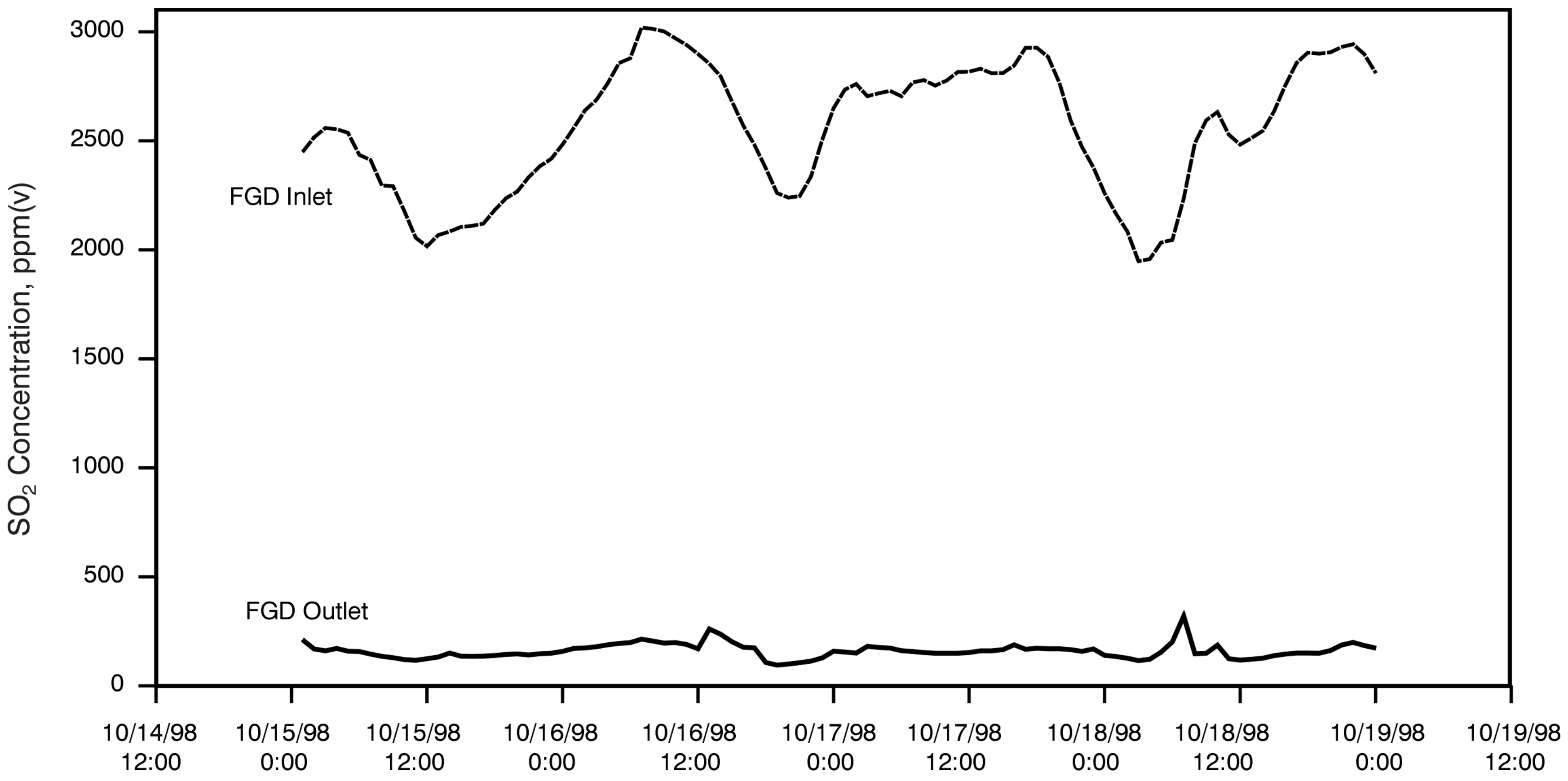


Figure 3. SO_2 concentration at the inlet and outlet of the FGD system.

8.1 Coal Results

Analysis of the coal fired at Site E-29 is shown in Table 15. As can be seen from Table 15, this is a high-sulfur, medium-chloride coal averaging 4.1% and 358 ppm, respectively. The mercury concentration, shown in Table 15, averaged 0.14 ppm.

Table 15. Coal Analysis

Coal Data	1	2	3	4	Avg.
Chloride, mg/kg	203	459	443	327	358
Mercury, mg/kg (dry basis)	0.17	0.12	0.15	0.14	0.14
Moisture, %	6.58	2.54	2.62	4.07	3.95
Heating Value, Btu/lb (as received)	11,524	12,681	12,780	12,235	12,305
Sulfur, % (as received)	3.36	4.48	4.51	4.08	4.11
Ash, % (as received)	10.77	10.46	10.12	10.7	10.51

8.2 Fly Ash and FGD Mercury Results

The concentrations of mercury in the fly ash and the FGD are shown in Table 16.

Although a complete mercury balance was not completed as part of this project, it is clear from Table 16 that little mercury was captured by the ESP. As will be discussed latter in this report the overall mercury removal at Site E-29 was about 56%. This mercury was removed by the FGD system. As had previously been observed (4), the mercury appears to be associated with the FGD solid and not the liquid.

Table 16. Mercury in Fly Ash and FGD

Sampling Location	1	2	3	4	Avg.
ESP Hopper	0.0042	0.0048	0.0018	0.0026	0.0028
FGD Liquids	0.0006	<0.0011	<0.0011	<0.0011	<0.0011
FGD Solids	0.42	0.41	0.37	0.40	0.40

8.3 Flue Gas Mercury Speciation Results

This section presents the flue gas mercury speciation results for the more formal validation tests and the mercury removal across the FGD system. All data are based on 20°C and dry conditions.

8.4 Ontario Hydro Mercury Speciation Validation Results

The more formal validation of the Ontario Hydro mercury speciation method used a modification of EPA Method 301. As described earlier in Section 3.0, only five sets of quadtrains rather than six were used for the validation test. Analyte spiking was used in two impinger sets of each quadtrain (one-half of the total samples). The entire data set is shown in Table 17, and the statistical results are shown in Tables 18 and 19.

Leaks developing across the quadtrain probe, filter, or impinger train can be a major problem in doing quadtrain sampling. This proved to be a problem in the testing at Site E-29. As shown in Table 17, several of the sample trains did not pass the leak check at the end of the sampling period. The leaks resulted in the mercury concentration being less than would be expected. These samples were not used to determine the relative standard deviation and bias results as shown in Tables 18 and 19. Originally, only four quadtrains were planned, but a fifth was done to compensate for the lost sample trains due to leaks in the system.

Table 17. Mercury Speciation Quadtrain Sampling Results Using the Ontario Hydro Method[1]

		Without Analyte Spiking					With Analyte Spiking (spike subtracted)				
Date	Quad-train	Leak Check	Hg on Filter, µg/Nm^3	Hg^{2+}, µg/Nm^3	Hg^0, µg/Nm^3	Total Hg, µg/Nm^3	Leak Check	Hg on Filter, µg/Nm^3	Hg^{2+}, µg/Nm^3	Hg^0, µg/Nm^3	Total Hg, µg/Nm^3
10-15-98	1	Yes	0.01	10.34	4.77	15.12	Yes	0.01	8.94	5.26	14.20
10-15-98	1	No	0.01	5.32	4.88	10.22	Yes	0.01	9.35	4.60	13.96
10-16-98	2	Yes	0.01	4.59	2.43	7.03	No	0.01	2.01	3.96	5.98
10-16-98	2	Yes	0.01	5.93	4.06	10.00	Yes	0.01	3.46	3.97	7.43
10-17-98	3	Yes	0.01	9.27	2.51	11.79	No	0.01	1.42	3.76	5.18
10-17-98	3	Yes	0.01	8.44	2.31	10.76	Yes	0.01	5.65	2.20	7.85
10-18-98	4	Yes	0.01	8.52	2.92	11.45	Yes	0.01	8.38	3.40	11.78
10-18-98	4	Yes	0.00	7.81	2.32	10.13	Yes	0.00	8.48	2.90	11.38
10-18-98	5	Yes	0.01	10.93	4.20	15.14	Yes	0.01	10.84	2.34	13.18
10-18-98	5	Yes	0.00	10.81	4.26	15.07	Yes	0.00	8.90	4.18	13.09

[1] Results are presented on a dry basis and normal conditions (20°C, and 1 atmosphere of pressure).

Table 18. Statistical Results for Precision for the Quadtrain Data from the Ontario Hydro Method

	With Analyte Spiking (spike subtracted)			Without Analyte Spiking		
	Hg^{2+}, µg/Nm^3	Hg^0, µg/Nm^3	Total Hg, µg/Nm^3	Hg^{2+}, µg/Nm^3	Hg^0, µg/Nm^3	Total Hg, µg/Nm^3
Std. Dev.	0.81	0.82	0.19	0.61	0.62	1.21
% RSD	8.83	21.81	1.49	7.40	19.77	10.55
Mean	9.15	3.78	12.93	8.29	3.13	11.42

Table 19. Statistical Results for Bias for the Quadtrain Data from the Ontario Hydro Method

	Hg^{2+}, µg/Nm^3	Hg^0, µg/Nm^3	Total Hg, µg/Nm^3
Bias	0.86	0.65	1.51
Pooled Std. Dev.	1.01	1.03	1.22
t-value	0.850	0.635	1.237
t-statistic	2.571	2.571	2.571

Also based on the speciation results, there does appear to be some variability from day to day. As was shown earlier in Figure 3, there is variability in sulfur content of the coal. It is not unreasonable to assume there could be variability in the mercury content as well. However, the statistical results show that the Ontario Hydro method passes the criteria established in EPA Method 301. The relative standard deviation (RSD) is clearly less than 50% in all cases. Also the calculations show that there is no statistical bias (the pooled standard deviation is less than the t-statistic). Based on the mercury speciation results, the mercury generated by this coal was approximately 70% Hg^{2+} and 30% Hg^0. This ratio tended to remain constant regardless of the day-to-day variability in the data.

One issue that has been extensively discussed with respect to mercury speciation methods is the temperature at which the particulate filter should be maintained. For these tests, the filters were out of stack (EPA Method 5), but the filters and probes were maintained at the temperature of the flue gas (~320°F). As shown in Table 17, the amount of mercury measured on the filter was insignificant. However, because the samples were taken at the outlet of the ESPs, the dust loading was also low.

8.5 Statistical Error/Variability Associated with the Ontario Hydro Method

Data variability results from two sources. The first is actual variability in the compound or element being measured, and the second is error associated with the measurement. The use of paired or quadtrains is designed to help eliminate process variability and determine sample error. Based on very extensive pilot-scale testing using the Ontario Hydro method, the error that can be expected is approximately 10% of the measured value if the measured value is >1.0 µg/Nm^3. These pilot-scale tests were essentially conducted under ideal conditions. It is expected that sampling in the field will result in increased error. People are more cramped, sampling ports are often not ideal, samples must be sent off-site, more chance for contamination error etc. From the field data collected to date using the Ontario Hydro method, the error associated with paired trains (eliminating process variability) has been between 10% and 20%. For example, in two field tests done by the EERC at plants firing North Dakota lignites, the maximum variability for six measurements at the FGD outlet was 12% and 11%.

It has been found that the greatest source of error in the Ontario Hydro procedure is not in the sampling but in the preparation of the impinger solutions following sampling. The preparation steps include 1) tearing down the impinger train, 2) transferring the solutions to flasks or bottles, and 3) digestion of the solutions so that they can be analyzed using CVAA. In the field tests completed in North Dakota, the sample preparation and analysis were done in the field. Assuming qualified people are doing the work, this is expected to reduce overall measurement error, since the sample preparation is done immediately, and samples are not shipped off-site.

In the tests completed at Site E-29. The quadtrain sampling resulted in a maximum variability (%RSD) of 22%. Although the sample preparation and analyses were done on-site, this is on the high end of the expected variability. However, the process variability was also high as shown by the SO_2 data in Figure 3 and the mercury CEM data discussed later in this report (Section 7). The use of bundled quadtrains also can create the potential for data variability because they are clumsy to use and prone to leaks. Indeed, several of the tests did not pass the leak check that must be completed prior to sampling and after sampling is completed. Nevertheless, as stated earlier, the Ontario Hydro method clearly passed the statistical criteria established in EPA Method 301.

8.6 Mercury Removal Across the FGD System

The Ontario Hydro mercury speciation results at the inlet and the outlet of the FGD are shown in Table 20 and, graphically, in Figure 4. It shows in Table 20 that the FGD system removed about 88% of the Hg^{2+}, but little if any Hg^0. This is in agreement with all the mercury data that have been collected in the last several years across wet FGD systems. The overall mercury removal across the FGD system was about 51%. Although it appears that there was an increase in Hg^0 across the FGD, this may not be the case for several reasons. First, all the data are presented on an as-measured O_2 basis. There were not enough O_2 measurements taken at either the stack or the FGD inlet sample point to ensure an accurate O_2 concentration; therefore, O_2 was not taken into account. Secondly, the inlet to the FGD and stack samples were not taken simultaneously, and there was variability in the data. This is shown in Figure 4 by the relatively large error bars on the FGD inlet data. It is also possible that the measured inlet Hg^0 concentration was low. This can occur if there is oxidation of Hg^0 across the sample filter. Although the particulate loading on the sample filter was low, it was not zero. Previous research has shown that particulate matter can convert Hg^0 to Hg^{2+} (2, 5).

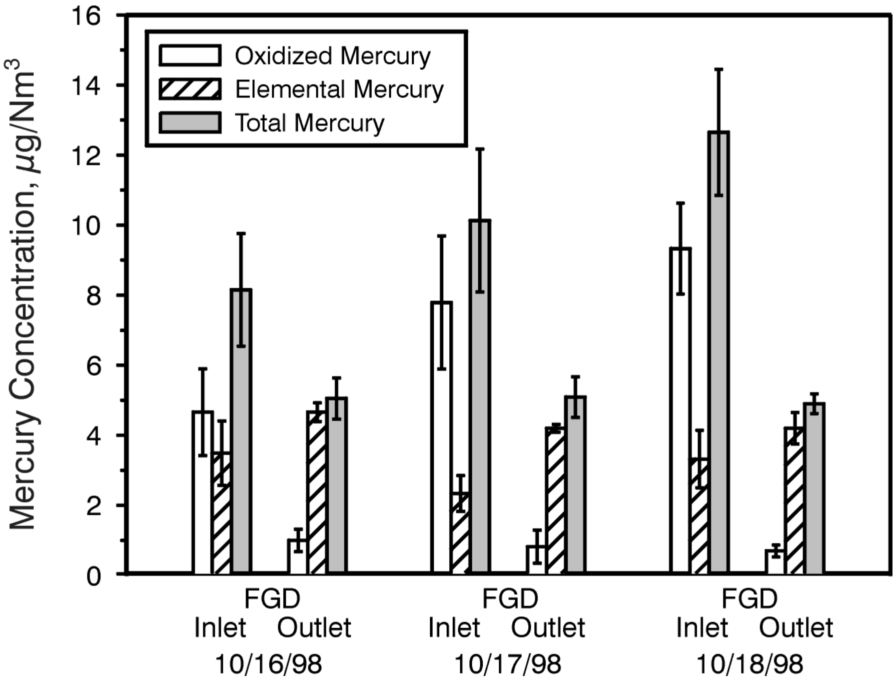


Figure 4. The change in vapor-phase speciated mercury across the FGD system.

Table 20. Mercury Speciation Results Across the FGD System

	Outlet of FGD			**Inlet of FGD**				
Date	**Hg^{2+}, µg/Nm^3**	**Hg^0, µg/Nm^3**	**Total Hg, µg/Nm^3**	**Hg^{2+}, µg/Nm^3**	**Hg^0, µg/Nm^3**	**Total Hg, µg/Nm^3**	**Hg^{2+} Removed, %**	**Total Hg Removed, %**
10-16-98	1.23	4.25	5.47					
10-16-98	0.77	3.86	4.63					
Avg.	1.00	4.05	5.05	4.66	3.49	8.15	78.5	38.0
Stds.	0.32	0.27	0.59	1.24	0.92	1.61		
10-17-98	1.15	4.35	5.50					
10-17-98	0.49	4.19	4.67					
Avg.	0.82	4.27	5.09	7.79	2.34	10.13	89.5	49.7
Stds.	0.47	0.11	0.58	1.90	0.15	2.04		
10-17-98	0.82	3.88	4.70					
10-17-98	0.57	4.52	5.09					
Avg.	0.70	4.20	4.90	9.33	3.32	12.65	92.5	61.3
Stds.	0.17	0.45	0.28	1.30	0.82	1.80		

8.7 Semtech Hg 2000 CEM Results

The Semtech CEM was used at the inlet of the FGD system. Although the instrument was developed to only measure Hg^0, by including a conversion system designed at the EERC, the instrument was able to measure total mercury. To provide mercury speciation data, the conversion system was periodically bypassed to measure Hg^0, and by difference, the concentration of Hg^{2+} in the flue gas could be determined. A comparison between the Semtech CEM data and the Ontario Hydro method data is shown graphically in Figures 5 through 8. As can be seen from the four graphs, the CEM results for both total Hg and Hg^0 compares quite well with the results obtained using the Ontario Hydro method. On Day 4, the carbonate trap of the conversion system was intentionally bypassed to determine the effect it would have on the conversion of Hg^{2+} to Hg^0. As had been speculated, the resulting high levels of SO_2 in the sample gas stream interfered with the ability of the stannous chloride solution to convert Hg^{2+} to Hg^0. As can be seen in Figure 5, eventually no conversion occurred, and the measured total Hg was the same as the measured concentration of the Hg^0. It should be noted that the Semtech and Ontario Hydro method results are presented on the same basis (dry but not corrected for O_2).

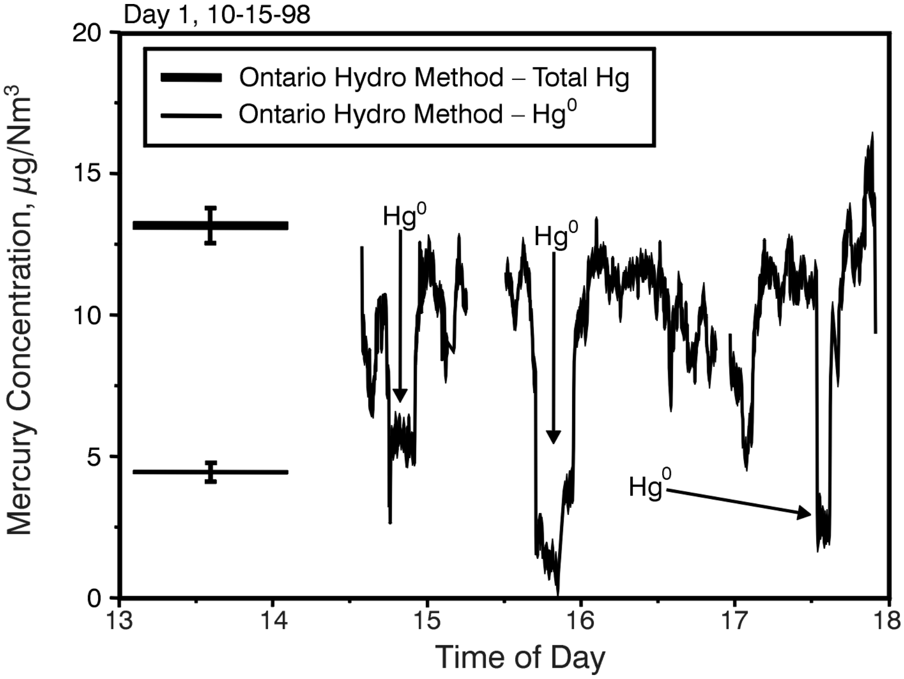


Figure 5. Direct comparison between Semtech mercury CEM and Ontario Hydro method for Day 1.

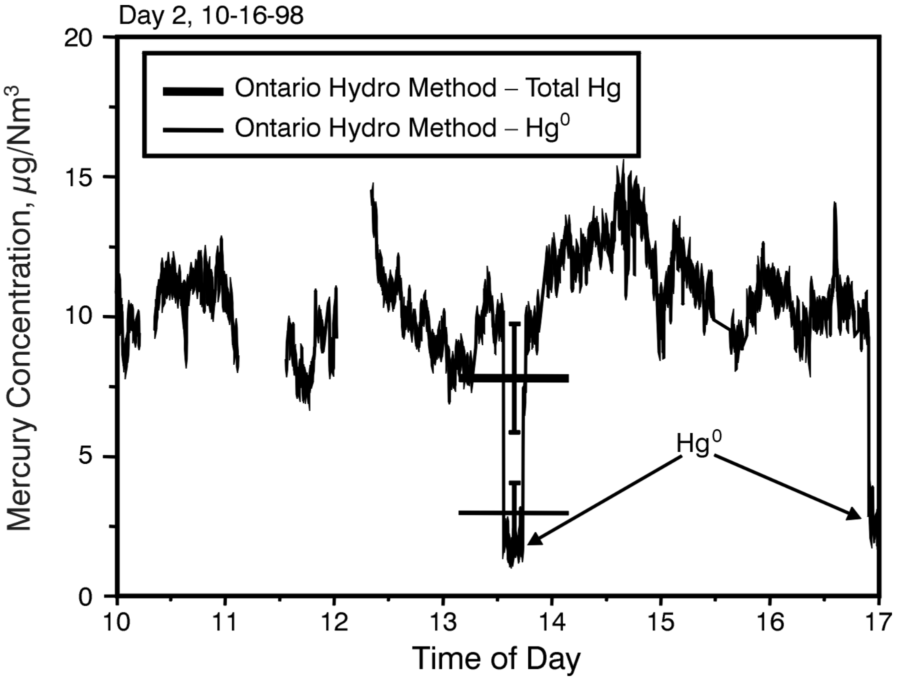


Figure 6. Direct comparison between Semtech mercury CEM and Ontario Hydro method for Day 2.

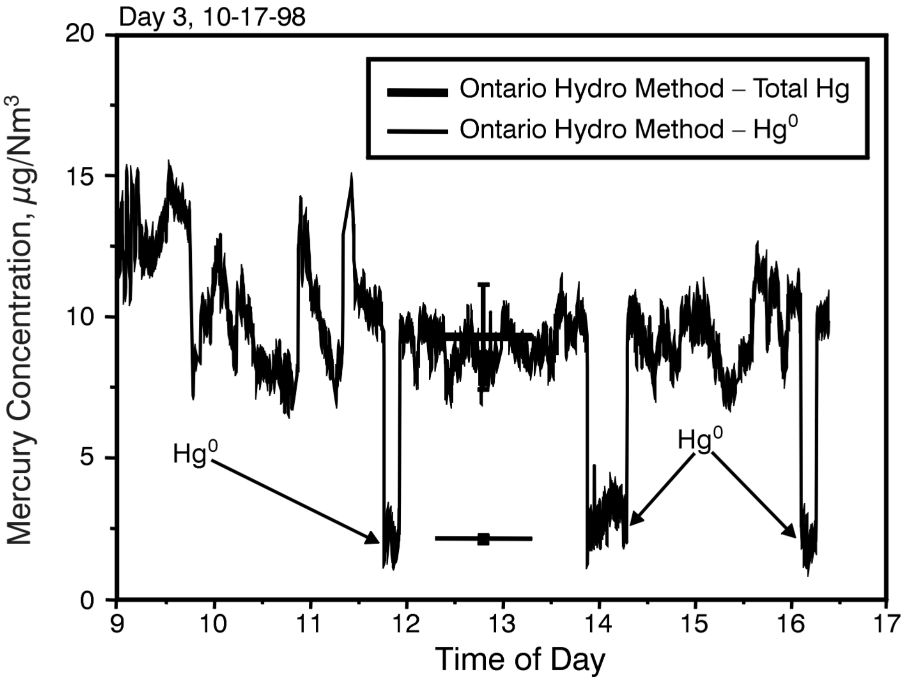


Figure 7. Direct comparison between Semtech mercury CEM and Ontario Hydro method for Day 3.

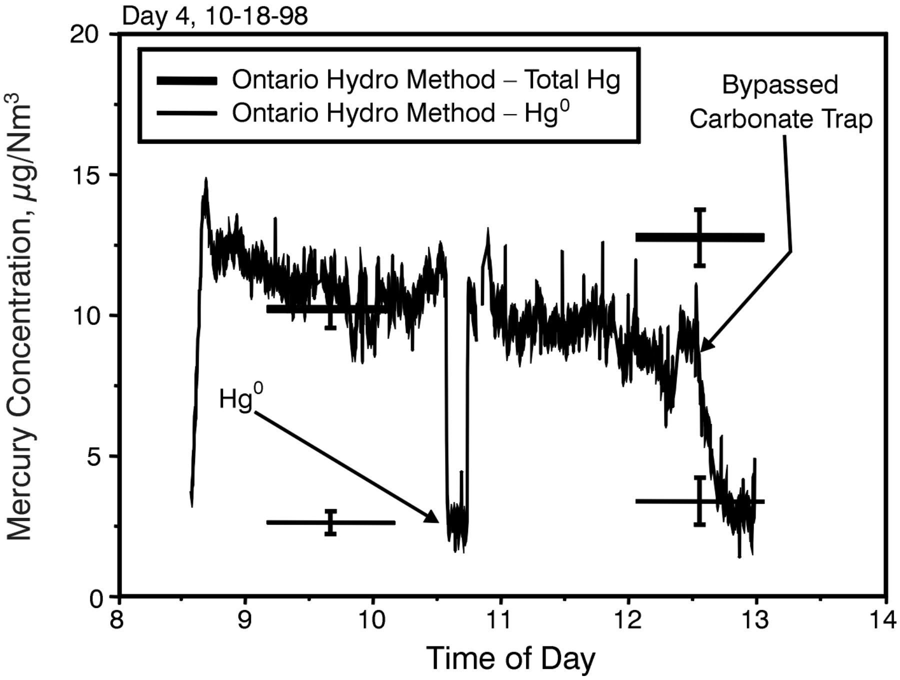


Figure 8. Direct comparison between Semtech mercury CEM and Ontario Hydro method for Day 4.

8.8 Conclusions from the Mercury Speciation Validation Tests

On the basis of the results from the Ontario Hydro mercury speciation validation project completed at Site E-29, the following conclusions can be drawn:

- The Ontario Hydro method results were well within the statistical criteria established by EPA Method 301. The method is valid for measuring mercury speciation in the field.
- The mercury emitted at the stack was about 10% Hg^{2+} and 90% Hg^0.
- No mercury was captured on the filters of the sampling train at either the FGD inlet or the stack.
- The FGD system removed about 88% of the Hg^{2+}. The overall mercury removal of the FGD system was 51%.
- The Semtech Hg 2000 gave total mercury results comparable to those obtained using the Ontario Hydro mercury speciation sampling method for both total Hg and Hg^0.

8.9 QA/QC Results

8.9.1 Blanks

As part of the QA/QC procedures, four field blanks were completed. A field blank is defined as a complete impinger train including all glassware and solutions that is taken out to the field during sampling and exposed to ambient conditions. These sample trains are then taken apart and the solutions recovered and analyzed in the same manner as those sample trains used for sampling activities. If the field blank shows contamination above instrument background, steps must be taken to eliminate or reduce the contamination to below background levels. However, in all cases, the field blanks taken during the sampling activities at Site E-29 were shown to be insignificant, as shown in Table 21.

Table 21. Results of Mercury Speciation Field Blanks

Day	KCl Solution, µg/L	H_2O_2 Solution, µg/L	$KMnO_4$ Solution, µg/L
1	<0.03	<0.03	<0.03
2	<0.03	<0.03	<0.03
3	<0.03	<0.03	<0.03
4	<0.03	<0.03	<0.03

All acids, chemical reagents, and deionized water used for mercury determination were analyzed for background levels of mercury. Each time a new batch of reagents was prepared, an aliquot was immediately taken and analyzed for mercury. Again, no mercury contamination was found.

8.9.2 Spiked Samples

In order to ensure that adequate levels of accuracy were maintained, spiked samples were also submitted for analysis. These samples were made up independently of the chemist doing the analyses. The spikes were required to be within 15% of the true value. If the value is not within the specified limits, then the instrument is recalibrated and the samples reanalyzed. The spiking solutions were from a stock separate from the calibration standard stock. The analytical results for the spiked samples are shown in Table 22. As can be seen, with only a few exceptions, the analyses of these spikes are easily within the tolerance specified.

Table 22. Results of Mercury Speciation Field Spikes

	KCl Solution			H_2O_2 Solution			$KMnO_4$ Solution		
Date	**Measured Value, ppb**	**Spike, ppb**	**Spike Recovery, %**	**Measured Value, ppb**	**Spike, ppb**	**Spike Recovery, %**	**Measured Value, ppb**	**Spike, ppb**	**Spike Recovery, %**
10-15-98	14.70	15	98.0	3.595	4	89.9	4.51	5	90.2
10-15-98	9.94	10	99.4				4.86	5	97.2
10-15-98	10.03	10	100.3	3.87	4	90.8	5.32	5	106.4
10-16-98	15.12	15	100.8	3.60	4	90.0	4.40	5	88.0
10-16-98	10.22	10	102.2	3.72	4	93.0	4.71	5	94.2
10-16-98	10.51	10	105.1	3.78	4	94.5	5.13	5	102.6
10-17-98	13.85	15	92.3	3.94	4	98.5	4.03	5	80.6
10-17-98	9.79	10	97.9	4.38	5	87.6	4.65	5	93.0
10-17-98	9.77	10	97.7	3.64	4	91.0	4.94	5	96.8
10-17-98	10.15	10	101.5	5.75	5	115.0			
10-18-98	13.35	15	89.0	4.48	5	86.2	4.38	5	87.6
10-18-98	9.53	10	95.3	5.12	5	102.4	4.84	5	96.8
10-18-98	9.57	10	95.7	5.30	5	106.0	4.35	5	87.0
10-18-98				5.86	5	117.2			
	Average		98.1	Average		97.5	Average		93.5
	Std. Dev.		4.3	Std. Dev.		10.0	Std. Dev.		7.3

9.0 REFERENCES

1. U.S. Environmental Protection Agency. Airlink Web Site at: http://www.epa.gov/airlinks/.

2. Laudal, D.L.; Galbreath, K.C.; Heidt M.K. *A State-of-the-Art Review of Flue Gas Mercury Speciation Methods*; EPRI Report No. TR-107080 3471; Nov 1996.

3. Laudal, D.L.; Heidt, M.K. *Evaluation of Flue Gas Mercury Speciation Methods*; EPRI Report No. TR-108988; Dec 1997.

4. Laudal, D.L; Kurz, M.D.; Sorensen, J.A.; Bolles, B.A.; Gunderson, L.L. *Mercury Formation and Fate*; Final Report for EPRI Purchase Order No. WO9002-23, Cooperative Power Association Purchase Order No. PO2002350-000, Minnkota Power Cooperative Purchase Order No. PO 97-4630, U.S. Department of Energy Contract No. DE-FC21-93MC30098, and Industrial Commission of North Dakota Purchase Order No. FY98-XXVIII-79; EERC Publication 99-EERC-01-02; Energy & Environmental Research Center: Grand Forks, ND, Jan 1999.

5. Carey, T.R.; Hargrove, O.W., Jr.; Richardson, C.F.; Chang, R.; Meserole, F.B. Factors Affecting Mercury Control in Utility Flue Gas Using Sorbent Injection. Presented at the Air & Waste Management Association 90th Annual Meeting & Exhibition, June 1997, Toronto, ON, Canada; Paper No. 97-WA72A.05.