



Energy &
Environmental
Research
Center

MERCURY SPECIATION SAMPLING AT GREAT RIVER ENERGY'S STANTON STATION

EERC Proposal No. 99-0096

Submitted to:

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Amount Requested: \$44,000

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MERCURY SPECIATION SAMPLING AT GREAT RIVER ENERGY'S STANTON STATION

ABSTRACT

The proposed project is for a 1-year duration, from July 1, 1999, through June 30, 2000 by researchers Dennis L. Laudal and Richard L. Schulz of the Energy & Environmental Research Center (EERC). The total cost of the project is \$135,998, with \$44,000 as the NDIC share.

The project has a twofold purpose. The first, and most important, is to determine the potential impact of mercury emissions from North Dakota lignite-fired power plants on the ecosystem. In doing so, we will also increase our understanding of mercury chemistry. In this way, cost-effective strategies for mercury control can be found in the event mercury controls are required for coal-fired power plants. The second purpose of the project is to provide data to Great River Energy's Stanton Station so that it will be able to meet the requirements mandated by the U.S. Environmental Protection Agency (EPA) Information Collection Request (ICR).

The specific objectives of this work to be conducted by the EERC are to determine the abundance and forms of mercury emitted from the Stanton Station. This is important because the chemical form of mercury affects its transport through air, land, and water, as well as its biological behavior. Knowing the forms of mercury emitted allows determination of deposition rates.

A second important objective is to determine the mercury mass balance across the power plant and, in particular, the air pollution control systems. The Stanton Station has a spray dryer for SO₂ control followed by a baghouse. Very little information exists as to the effectiveness of spray dryers on mercury removal.

A third objective is to meet the requirements of the ICR. As part of the proposed research, the required mercury sampling will be done, and presented in a manner acceptable to EPA.

A second important objective is to determine the mercury mass balance across the power plant and, in particular, the air pollution control systems. This will be done using both the Ontario Hydro (OH) mercury speciation method and two mercury continuous emission monitors (CEMs). The Stanton Station has a spray dryer for SO₂ control followed by a baghouse. It is known that wet SO₂ scrubbers remove a high percentage of the oxidized mercury, but little if any elemental mercury. However, very little information exists as to the mercury collection efficiency of spray dryers or their effect on mercury speciation.

A third objective is to meet the requirements of the ICR. As part of the proposed research, the required mercury sampling will be done, and it will be presented in a manner which is acceptable by EPA.

2.0 PROJECT DESCRIPTION

The 1990 Clean Air Act Amendments (CAAAAs) required 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. Two mercury reports to Congress were issued (2). Given the current state of the art, these reports did not state that mercury controls on coal-fired electric power stations should be required. However, they did indicate that EPA views mercury as a potential threat to human health and additional research and information were necessary. Based on this conclusion, the U.S. EPA issued an ICR. This ICR required a selected group of coal-fired utilities to do mercury speciation sampling at both the inlet of the last air pollution control device and the stack. Two units at Great River Energy's Stanton Station were selected. This provides a unique research opportunity for furthering our understanding of mercury chemistry. For example, the Stanton Station has a dry scrubber, and little if any data are available as to the impact of these devices on mercury speciation.

any flue gas desulfurization (FGD) system. The second unit has a combination of a dry scrubber followed by a reverse-gas fabric filter. Both of these units were selected to be sampled for mercury as part of the ICR.

2.3 Approach

Once the contract is in place, the first activity will be to write a test plan and QA/QC plan for each of the two units to be sampled. This test plan must be provided to EPA by June 1, 1999. It is expected that the test plans developed for EPRI by Fossil Energy Research Corporation will be used as the model. However, the specific details of the test plan will be added during and following a site visit to the plant. The following proposal, which is based on conversations with personnel from Great River Energy, is only tentative. Detailed test plans will be completed once the project is under way.

It is proposed that the sampling done at Unit 1 will be the minimum necessary to meet the requirements of the ICR. This will include doing three consecutive simultaneous OH mercury speciation samples at the inlet to the cold-side ESP and at the stack. In addition, at Unit 1, three coal samples will be collected during the time period that flue gas mercury speciation samples are being done and analyzed for mercury, sulfur, heating value, moisture, and ash.

At Unit 10, a more extensive sampling project is proposed. It is proposed that sampling be done at three locations. The first location will be at the dry scrubber inlet, the second, prior to the baghouse, and the third, at the stack. Table 1 details the proposed sampling test matrix for both Units 1 and 10. Additional coal samples will be collected at Unit 10 to provide a good statistical basis for calculating the mercury mass balance. Also, as part of determining the mass balance, ash samples will be collected from the dry FGD system and the baghouse hoppers. It is expected that OH mercury speciation sampling along with collection of the coal and ash samples will occur over a

at the inlet to the dry FGD system will be done simultaneously with the mercury speciation sampling done at the outlet of the FGD system and at the stack.

2.3.2 Inlet to the Baghouse/Outlet of the Dry FGD

Mercury speciation sampling will be done at this location as part of the mass balance calculations. Sampling at this location is necessary in order to calculate the mercury collection efficiency of the dry FGD system. There is little if any data as to the effect of a spray dryer FGD system on mercury. It is known, for example, that a wet scrubber removes a high percentage of the oxidized mercury but little elemental mercury. The question then is whether or not this is also true for a spray dryer. To answer this question, three consecutive OH mercury speciation samples will be taken at this location, again using a dual-train configuration resulting in a total of six OH trains. However, instead of a multicyclone being used as part of the dual train as was the case at the inlet to the FGD system, a single cyclone with a 1- μm cut point will be used. The purpose of this is to help determine whether the intimate solid-gas interaction that occurs across a standard filter affects mercury speciation as measured by the OH mercury speciation method. A cyclone has much less gas-solid contact and, therefore, is much more similar to the gas-solid contact that is occurring in the duct. As stated earlier, these samples will be taken simultaneously with those at the FGD inlet and at the stack. All OH sampling at this location will be completed with as much traversing as possible.

2.3.3 Stack

This is the second sampling point required by the ICR. The temperature at this location is expected to be $<250^{\circ}\text{F}$; therefore, an EPA Method 5 filtering configuration will be used for the OH mercury speciation sampling train. The dual train to be used at this location will be the OH mercury speciation sampling train coupled with an EPA Method 26A sampling train. EPA Method 26A is

successfully as a research tool to determine mercury speciation at the stack of a power plant. It is expected that a minimum of 10 hr of sampling time at each location can be completed.

2.4 Sampling Procedures

2.4.1 Ontario Hydro Mercury Speciation Method

The OH mercury speciation method, which has been selected by EPA for the ICR for measuring speciated mercury, 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 oxidized mercury (Hg^{2+}) by substituting three aqueous 1 N potassium chloride (KCl) impinger solutions for one of the $HNO_3-H_2O_2$ solutions. After the solutions have been properly prepared, they are analyzed using CVAAS (cold-vapor atomic absorption spectroscopy) techniques. A schematic of the impinger train is shown in Figure 1. The analyses of

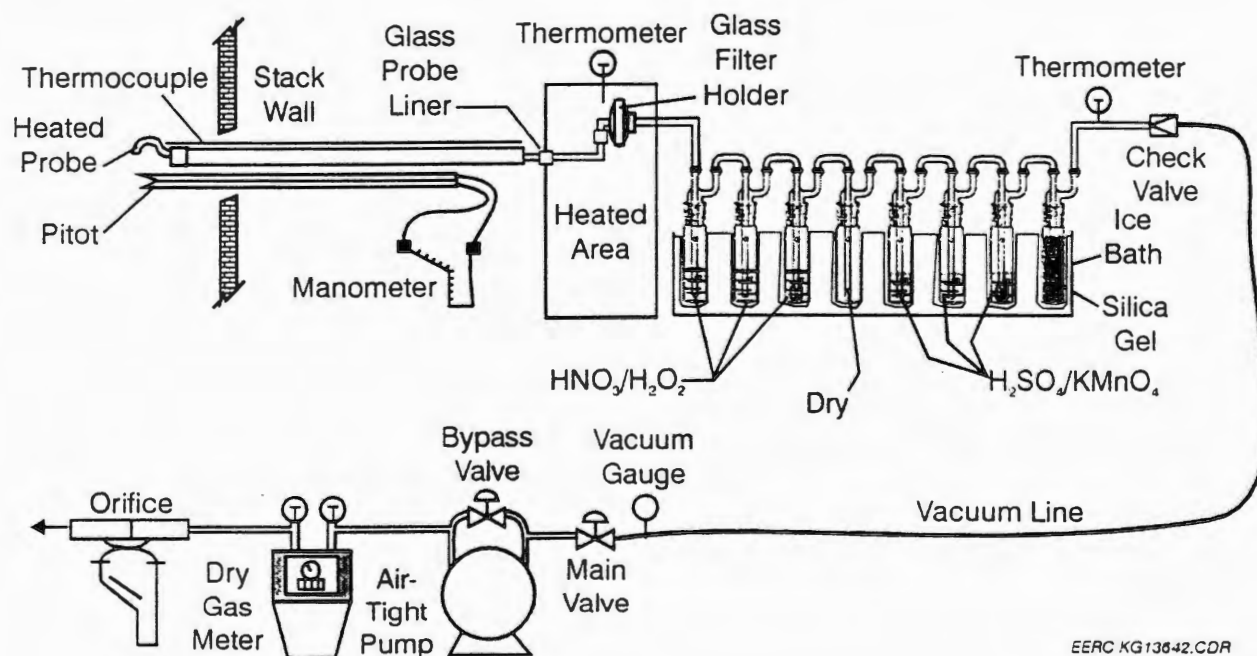


Figure 1. Schematic of the OH speciation impinger train.

HCl/HF and Cl₂ concentrations in the flue gas. During the sampling, the separation of the halides (HCl) from the halogens (Cl₂) is accomplished physically within the impinger matrices. Cl₂ exhibits a low solubility in acid solutions (0.1 N H₂SO₄), but is collected effectively in basic solutions (0.1 N NaOH). The HCl, on the other hand, is captured effectively by the 0.1 N H₂SO₄ solution. The impinger train is operated similarly to other sampling procedures such as EPA Method 5 or EPA Method 29. Once the chlorides/fluorides are collected in the solutions, they are analyzed using ion chromatography techniques.

2.4.3 Coal and Fly Ash Analyses

The EERC has an automated direct mercury analyzer (DMA-80, Milestone, Inc.) that was recently validated as U.S. EPA Method 7473 entitled “Mercury in Solids and Solutions by Thermal Decomposition Amalgamation and Atomic Absorption Spectrophotometry.” Method 7473 integrates thermal decomposition sample preparation, amalgamation preconcentration, and atomic absorption detection, thus reducing the total analysis time of most samples to <5 min in the field setting. The analyzer has an automated sample system that allows multiple samples to be analyzed consecutively. Again, by doing the coal and ash samples on-site, a lot of flexibility can be brought to the test program.

In addition to the automated analysis system, the coal and filter ash samples collected that are a direct part of the ICR requirements will also be analyzed using the more traditional procedures, (microwave digestion for coal and mixed-acid digestion for ash followed by CVAA). For the coal samples collected as part of the ICR, percent sulfur, heating value, percent ash, and chlorine content will be done using EPA-approved methods.

2.4.5 Flue Gas Constituent Concentrations, Particulate Matter, Moisture, and Flue Gas Velocity

To determine the O₂ levels at each sample location, a Teledyne portable O₂ analyzer using a paramagnetic cell will be used. This portable O₂ analyzer's linearity is verified prior to use using EPA Protocol 1 certified gas standards. Flue gas velocity, moisture, and flow rate determinations will be performed according to EPA Methods 2 and 4 in conjunction with the OH method. The particulate matter at each location will be measured in either an EPA Method 17 or EPA Method 5 configuration as part of the OH train. Other flue gas constituents such as CO₂, NO_x, SO₂, and CO will be obtained either using the same portable analyzer which we use to measure O₂ and/or from the plant CEMs.

3.0 STANDARDS OF SUCCESS – QUALITY CONTROL/QUALITY ASSURANCE

The EERC is committed to delivering consistent and high-quality research that meets our clients' needs and expectations. In order to ensure that the goals of this project are realized, an organization-wide quality management system (QMS), authorized and supported by EERC managers, is in effect and governs all programs within the organization. The EERC established and formalized a QMS and QC procedures in August 1988. A *Quality Manual* defines the requirements and the organizational responsibilities for each major element of the QMS and references the supporting documents needed to provide a comprehensive program. Compliance with this manual and its supporting documents assures that the EERC adequately fulfills governmental and private clients' requirements relating to quality and compliance with applicable regulations, codes, and protocols. This project is required to follow the *Quality Manual*, project-specific QA procedures, and all revisions. The EERC QA manager implements and oversees all aspects of QA/QC for all

every five samples to check the slope of the calibration curve. All samples are run in duplicate, and one in every ten samples is spiked to verify analyte recovery. A QC chart is maintained at the EERC to monitor the long-term precision of the instrument.

Prior to testing, all gas-sampling equipment is calibrated according to the *Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III. Stationary Source Specific Methods*. The uncertainty of the individual measurements is determined using the performance test codes in ANSI/ASME PTC 19.1-1985, Part 1, Measurement Uncertainty, as a guideline.

3.2 Presampling Preparation

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

3.3 Glassware and Plasticware Cleaning and Storage

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

15% of the true value. The spiking solutions are made from a stock separate from the calibration standard stock.

4.0 BACKGROUND

The 1990 CAAA required EPA to determine whether the presence of mercury and 188 other trace substances, referred to as air toxics or hazardous air pollutants (HAPs), in the stack emissions from fossil fuel-fired electric utility power plants pose an unacceptable public health risk (5). EPA's conclusions and recommendations as stated earlier were presented in two reports (2): "Utility Air Toxics Report to Congress" and "Mercury Study Report to Congress. Given the current state of the art, these reports did not state that mercury controls on coal-fired electric power stations should be required. However, because it is a mobile and persistent pollutant that becomes more concentrated as it proceeds through the food chain, these reports stated that EPA views mercury as a potential threat to human health. Therefore, one of the conclusions in these reports was that additional research and information were necessary. Based on this conclusion, the EPA issued an ICR.

Mercury is emitted by both natural and human processes and cycles through atmospheric, aquatic, and terrestrial environments. Forms of mercury that appear most important in these environments are elemental mercury, inorganic, oxidized mercury, and monomethylmercury. The chemical form of mercury affects its transport through air, land, and water as well as its chemical and biological behavior. Elemental mercury is known to circulate in the atmosphere for about 1 to 2 years before it deposits (1). Oxidized mercury in the atmosphere can deposit directly onto water bodies or enter them indirectly after depositing on land or surface water through runoff. There appears to be little if any evidence that monomethylmercury is generated from coal combustion. However, there has been substantial speculation as to quantity and ultimate deposition of mercury

measured in combustion and gasification flue gases. Significant improvements and developments in modeling, sampling, analytical, and experimental methods have enabled the elucidation of mercury speciation. In contrast to most trace metals in coal, mercury is highly volatile (boiling point of 357°C) and, therefore, exists almost exclusively in the vapor phase of combustion and gasification flue gases. Thermodynamic calculations and fundamental chemistry reveal that mercury can be volatilized from coals at temperatures as low as 150°C. The very low concentrations of mercury in the bottom ash and slag deposits of boilers and gasifiers also attest to the volatility of mercury. As flue gases cool, it is possible for a significant fraction of the vaporized mercury to condense, especially in the presence of residual carbon particles or other particles with a large surface area-to-volume ratio. Consequently, the speciation of mercury in flue gas involves both gaseous and solid particulate phases. The three oxidation states of mercury, elemental, mercurous, and mercuric, must also be considered in determining speciation. The properties and reactivity of mercury depend strongly on its oxidation state. Measurements indicate that the proportions of the different mercury forms in flue gases vary widely. The variability may be attributable to a number of factors, including the concentration of mercury and its mode of occurrence in the feed coal, flue gas temperature and composition, concentration and physical characteristics of the entrained ash, and the length of time that mercury and its compounds are entrained in the flue gas.

The current understanding of mercury speciation in flue gas is based in part on thermodynamic modeling predictions and experimental investigations of mercury reactions in simulated flue gases and to a limited extent on the interpretation of field test data. Fundamental bench-scale studies have shown that mercury chemistry in combustion systems is extremely complex and is greatly influenced by not only the fly ash, but also Cl_2 , NO_x , SO_2 , and HF components of combustion flue gas. In

technologies, advanced power systems, process development, gasification/combined cycle systems research, waste-to-energy conversion, and synthetic fuels investigations.

5.2 EERC Mercury Sampling Background

The OH mercury speciation sampling method was developed at the EERC in conjunction with Dr. Keith Curtis of Ontario Hydro under a contract funded by EPRI and DOE. The exact OH method procedure required by the ICR was written by the EERC. It is clear that this sampling method is difficult and requires substantial experience to get consistent high-quality data. The EERC personnel have done more sampling with this method than any other group in the world. The EERC is considered by the scientific community to be the leader in mercury measurement from coal flue gas streams.

The EERC has been involved in mercury speciation sampling at a number of power plants across the country. Last summer, for example, the EERC sampled two power plants in North Dakota (Milton R. Young Unit 2 and Coal Creek Unit 2) in essentially the same manner which is being proposed. From discussion with DOE and the EPA, it is expected that the data from these two power plants will be accepted by EPA as part of the ICR. The data from these two plants were of very high quality based on the extensive QA/QC procedures that were established for these tests. All field blanks were below detection limits, and field-spiked samples were found to be with 15% of what was expected. Included in the work at these two power plants was the successful use of a mercury CEM. The EERC is considered a leader in the testing of mercury CEMs at the bench-, pilot-, and field scale.

The EERC is the only group that routinely does mercury analyses in the field. We feel very strongly that this adds a lot to the credibility of the data because corrective actions can take place quickly if problems occur. For example, if the analyses are done off-site and there is a problem with

sources and pathways that contribute to elevated mercury levels in streams and lakes rather than assuming that one industry is primarily responsible. By better understanding mercury pathways, we can apply common-sense solutions to mercury contamination issues and potentially reduce mercury levels without negative economic impacts.

7.0 SCHEDULE

The work schedule will be very dependent on the power plant that will be tested; however, based on conversations with plant personnel, the following test plan is proposed. The first milestone date will be June 1, 1999. A detailed test plan and QA/QC plan must be submitted to EPA by then. The actual testing, however, does not have to be completed until March 2000. However, it is our recommendation to complete the testing during the summer or early fall of this year. Because of the need to produce an EPA-approved test plan by June 1, the project will need to begin prior to NDIC's commitment. As discussed in Sections 8.1 the matching funds should be available to begin the project on May 1, 1999. A tentative schedule is shown in Table 2.

Table 2. Suggested Project Schedule*

Month	1	2	3	4	5	6	7	8	9
Develop Test and QA/QC Plans	█								
Prepare for Test at Stanton	█	█	█						
Test at the Stanton Station			█	█					
Complete All Analyses				█	█	█			
Complete All Reports						█	█	█	█

* This suggested test plan assumes a start date of May 1, 1999.

10.0 REFERENCES

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MERCURY SPECIATION SAMPLING FOR GREAT RIVER ENERGY'S STANTON STATION

PROPOSED START DATE: 01-Jul-99

EERC PROPOSAL #99-0096

28-Apr-99

	TOTAL		NDIC SHARE		EPRI SHARE		EERC JSRP SHARE	
	HOURS	\$ COST	HOURS	\$ COST	HOURS	\$ COST	HOURS	\$ COST
TOTAL DIRECT LABOR	1898	\$41,802	609	\$13,556	609	\$13,556	680	\$14,690
FRINGE BENEFITS - % OF DIRECT LABOR	52%	\$21,737		\$7,049		\$7,049		\$7,639
TOTAL LABOR		\$63,539		\$20,605		\$20,605		\$22,329
OTHER DIRECT COSTS								
TRAVEL		\$6,909		\$2,573		\$2,573		\$1,763
SUPPLIES		\$1,250		\$380		\$380		\$490
EQUIPMENT > \$750		\$4,250		\$0		\$0		\$4,250
COMMUNICATIONS - PHONES & POSTAGE		\$300		\$100		\$100		\$100
OFFICE (PROJECT SPECIFIC SUPPLIES)		\$300		\$100		\$100		\$100
REPAIRS		\$250		\$81		\$81		\$88
FEES		\$14,560		\$4,732		\$4,732		\$5,096
TOTAL OTHER DIRECT COST		\$27,819		\$7,966		\$7,966		\$11,887
TOTAL DIRECT COST		\$91,358		\$28,571		\$28,571		\$34,216
INDIRECT COST - % OF MTDC	VAR	\$44,640	54%	\$15,429	54%	\$15,429	46%	\$13,782
TOTAL ESTIMATED COST		\$135,998		\$44,000		\$44,000		\$47,998

Communications (Phones and Postage)

Monthly telephone services and fax telephone lines are included in indirect cost. Direct project cost includes long-distance telephone including fax-related long-distance calls; postage for regular, air, and express mail; and other data or document transportation costs.

Office (Project Specific Supplies)

General purpose office supplies (pencils, pens, paper clips, staples, Post-it notes, etc.) are provided through a central storeroom at no cost to individual projects. Budgeted project office supplies include items specifically related to the project: special research notebooks, binders, and other project organizational materials; duplicating, printing, special covers or paper, and binding of reports; project data forms, transparencies or other presentation materials; literature searches and technical information procurement, including subscriptions; manuals, computer diskettes, memory chips, laser printer paper, and toner cartridges; and other miscellaneous supplies required to complete the project.

Data Processing

Data processing includes items such as site licenses and computer software.

Supplies

Supplies in this category include scientific supply items such as chemicals, gases, and glassware and/or other project items such as: nuts, bolts, and piping necessary for pilot plant operations.

Fees

Laboratory and analytical fees are established and approved at the beginning of each fiscal year and are charged based on a per sample or hourly charge depending on the analytical services performed. Additionally, laboratory analyses may be performed outside the University when necessary.

Engineering support fees are based on an established per hour rate for drafting services related to the production of drawings as part of EERC's quality assurance/quality control program for complying with piping and pressure vessel codes.

Graphic services fees are based on an established per hour rate for overall graphics production such as report figures, poster sessions, standard word or table slides, simple maps, schematic slides, desktop publishing, photographs, and printing or copying.

Shop and operation fees are for expenses directly associated with the operation of the pilot plant facility. These fees cover such items as training, safety (protective eye glasses, boots, gloves), and physicals for pilot plant and shop personnel.