Energy &
Environmental
Research
Center

MERCURY FORMATION AND FATE

Submitted to:

Ms. Karlene Fine

Executive Director
Industrial Commission of North Dakota
600 East Boulevard Avenue
Bismarck, ND 58505

Prepared by:

Steven A. Benson
Dennis L. Laudal
Jim A. Sorensen
Marc D. Kurz

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

Steven A. Benson, Project Manager

Dr. Carl A. Fox, Director
Office of Research and Program Development

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ABSTRACT

This project provides information that will assist in determining the potential impact of mercury emissions from North Dakota lignite-fired power plants on the bioavailability of mercury to humans. The specific objectives of this work conducted at Energy & Environmental Research Center are to determine the abundance and forms of mercury in flue gases emitted from lignite-fired power plants and to determine the source of mercury in Devils Lake in North Dakota. The first objective is focused on determining the forms of mercury emitted from North Dakota lignite-fired power plants, since the chemical form of mercury affects its transport through air, land, and water as well as its chemical and biological behavior. The second objective of the project will address discrepancies noted in the literature regarding the source of mercury in lakes. Some investigators indicate that the source of all the Hg bioaccumulated in fish is from atmospheric deposition, while others indicate that much of the Hg is from natural sources or nonatmospheric anthropogenic sources. The degree of natural enrichment of mercury can be documented in the watersheds and sediments of various North American surface waters. These natural enrichment data can be used along with the potential for atmospheric deposition to assess the source of mercury in lakes. The major source of high levels of methylmercury that can be bioaccumulated in fish may not be from atmospheric deposition of mercury derived from coal-fired power plants. This work will be coordinated with Dr. Jan Hulla's, who is proposing a project to study to determine the bioavailability of mercury in Devils Lake fish to humans.

MERCURY FORMATION AND FATE

PROJECT SUMMARY

The goal of this project is to provide information that will assist in determining the potential impact of mercury emissions from North Dakota lignite-fired power plants on the bioavailability of mercury to humans. This work will be coordinated with the work conducted by Dr. Jan Hulla, Department of Pharmacology and Toxicology, University of North Dakota, who is proposing a project to determine the bioavailability of mercury in fish to humans. The specific objectives of this work conducted at the Energy & Environmental Research Center (EERC) are to determine the abundance and forms of mercury in flue gases emitted from two North Dakota lignite-fired power plants and to determine the source of mercury in Devils Lake in North Dakota.

Task 1 of the project is focused on determining the abundance and forms of mercury emitted, since the chemical form of mercury affects its transport through air, land, and water as well as its chemical and biological behavior. The most important forms in the environment include elemental mercury (Hg^0), inorganic, oxidized mercury (Hg^{2+}), and monomethylmercury. Power plants emit elemental and oxidized mercury. Elemental mercury is known to circulate in the atmosphere for about 1 to 2 years before it deposits. Oxidized mercury in the atmosphere can deposit directly onto water bodies or enter them indirectly after depositing on land or surface through runoff. In addition, the form of Hg influences the effectiveness of control technologies. Sampling will be conducted at the inlet and outlet of the air pollution control systems, as well as at the stack. A modified Environmental Protection Agency (EPA) Method 29 mercury speciation method will be used at the inlet and outlet of the air pollution control system. In addition, a continuous mercury emission monitor will be used at the stack location.

Task 2 of the project will address discrepancies noted in the literature regarding the source of mercury in lakes. Some investigators indicate that the source of all the Hg bioaccumulated in fish is from atmospheric deposition, while others indicate that much of the Hg is from natural sources or other onthropogenic sources. The degree of natural enrichment of mercury can be documented in the watersheds and sediments of various North American surface waters and, subsequently, correlated to lakes that have particularly high levels of methylmercury in fish; these results suggest that atmospheric deposition from coal-fired power plants may not be the most significant source of mercury in these lakes. Sediments will be collected and characterized to determine natural mercury contribution and be used to determine the extent of anthropogenic mercury enrichment. The lake sediment data in conjunction with data derived from Task 1 can be used to provide insight into the contribution of naturally derived mercury to mercury accumulation in fish.

PROJECT DESCRIPTION

The specific objectives of the project are to determine the abundance and forms of mercury in flue gases emitted from lignite-fired power plants and to determine the source of mercury in Devils Lake in North Dakota. In order to meet the objectives of the project, a two-task approach is proposed.

Task 1 – Mercury Emissions from North Dakota Lignite-Fired Power Plants

This task consists of determining the abundance and forms of mercury in flue gases before and after the air pollution control system and at the stack. The mercury determination will be made using a validated mercury speciation sampling method (currently two methods are undergoing validation tests at the EERC and at various utility host sites). Two utilities are proposed to be sampled for this program.

The sampling plan proposed by the EERC is designed to produce data that will provide the following benefits:

- If mercury control becomes necessary, the data will be useful in developing the most cost-effective control strategy.

- Be able to compare data derived from lignite-fired power plant existing databases (EPRI, [Electric Power Research Institute], EPA) to other coals and power plants. These databases are being used to generate statistical correlations that allow the determination of mercury emissions based on easily measured input data such as coal type, plant configuration, and coal analysis.

- The data will be used to provide input to receptor and deposition models which may help prove that mercury emission from North Dakota lignite-fired plants do not contribute to a significant degree to the mercury levels in lakes and streams.

Proposed Sampling/Analytical Strategy

The proposed sampling and analytical strategy is based on previous field application of wet chemical mercury speciation conducted by the EERC.

Some of the features of the sampling plan proposed include:

- Sampling locations as follows: inlet and outlet to air pollution control devices and at the stack.
- Six test replicates at each sampling location spread over a 3-day period.
- Flue gas measurements of HCl levels.
- Documentation of flue gas SO_2, NO_x, and O_2 levels.
- A complete characterization of daily coal and fly ash samples.

The mercury speciation sampling method that will be chosen for this program will depend on the results from the Mercury Speciation Methods Evaluation project currently under way at the EERC. It is expected that validation tests will be completed early this summer (June 1997). A description of the two proposed methods, the Ontario-Hydro and tris-buffer mercury speciation techniques, is provided in Appendix A. Both of these methods are modifications of EPA Method 29. To supplement the chemical data and provide a quality assurance (QA) check, a continuous emission monitor (Semtech and/or PS Analytical) will be used at the stack location. The Semtech has been successfully used in the field in previous tests conducted by the EERC.

Sampling will be conducted at the inlet and outlet of the particulate control device (ESP [electrostatic precipitator] or baghouse) and at the stack. For plants with spray dryers and baghouses, sampling will be done at the inlet to the spray dryer and outlet of the baghouse. For plants with an ESP and wet scrubbers, sampling will be completed at the ESP inlet and outlet and the scrubber outlet.

As mentioned earlier, six test replicates will be completed at each sampling location spread over a 3-day period. From previous experience at the EERC, multiple samples are needed at each sampling to ensure the quality of the data and to allow the precision of the data to be determined. Sampling will be conducted over a 3-day period, with two samples collected at each location per day. The sampling times will be 1–2 hours, which will be enough sample volume to meet a target detection limit of 0.1 $\mu g/Nm^3$, without jeopardizing the integrity of the wet chemical solutions.

All mercury analyses of the impinger solutions will be completed on-site by EERC personnel using a cold-vapor atomic absorption (CVAA) analyzer. This instrument has been used successfully in previous field tests for mercury analysis and is compact and relatively simple to set up. The primary advantage of on-site analysis is that questionable mercury results can be repeated before the measurement crew leaves the host site. Also, it eliminates the need to store and ship mercury samples, which can be a significant source of contamination, sample loss, and other factors that lead to more uncertainty.

Daily representative coal samples will be taken and analyzed for mercury and other targeted parameters. If representative fly ash samples are available, they will also be taken on a daily basis for characterization. Other elements such as arsenic and/or selenium may be measured. Selection of additional elements will be made based on discussion with sponsors at the initiation of the project. Filter, fly ash, and coal samples will be taken back to the EERC for analysis. Ash samples are digested using a mixed acid technique and then analyzed using the CVAA instrument. Coal samples are digested using a microwave digestion process and also analyzed using CVAA.

The sampling and measurement team will consist of seven people. The field team leader, a chemist to do the analysis and make up the solutions, four sampling people, and a person to help set up and break down impinger trains and probes. All the setup and breakdown of impinger trains and the analysis of the solutions will be done in a large, 40-foot trailer that will be rented and placed either on-site or, if the selected plants are close enough, in a central location.

The results of the analysis will be interpreted in terms of collection efficiency and form and quantity of Hg emitted. The ability of the control technology to capture Hg will be assessed and recommendations on various types of control technologies and sorbents will be made. The form and quantity of Hg emitted will be evaluated relative to its potential to be transported and deposited in lakes.

Task 2 – Sources of Hg in Devils Lake

This task is focused on determining the source of Hg in Devils Lake. In order to identify the source of Hg, lake sediments will be collected and analyzed. A locality within Devils Lake where the presence of water has been relatively constant will be selected for analysis of lake bottom sediments, based on a review of historical data and descriptions. These sediment samples are expected to provide "natural background" data for the lake. The results of the sediment analyses from the lake will provide data regarding the contribution of natural mercury to the lake sediments, which, in turn, will provide insight into the extent of anthropogenic mercury enrichment. These data in conjunction with data on the mercury methylation process and bioavailability may ultimately be useful in determining the contribution of naturally derived mercury to the levels of mercury in fish.

The data generated by the proposed project will also provide information regarding the vertical distribution of mercury in the Devils Lake sediment. Such information would be of great value to any future efforts to determine the bioavailability of mercury in lake sediments. The baseline data obtained by the proposed project activities below will provide a foundation for future research efforts that may be aimed at examining the relationship between geologic setting and natural mercury contributions to lake ecosystems.

The work plan has been divided into three specific subtasks as outlined below.

Task 2.1 – Site Selection

Several coal-fired power plants are operated in North Dakota, Montana, and Minnesota, and numerous lakes in those states have undergone extensive aquatic and ecological characterization with respect to mercury. Devils Lake in central North Dakota is one such lake and has been selected for detailed evaluation under this task of the proposed research. The selection of the specific sampling area within the lake will be based on an evaluation of information from a variety of sources. Data for mercury concentrations in the lake water and fish will also be evaluated as part of the specific site selection process.

Task 2.2 – Sample Collection, Preparation, and Analysis

Devils Lake sediments will be collected by coring at three main areas within the basin. Within these areas, localities will be selected and documented using a global positioning system (GPS). At each locality, a set of four cores will be obtained, resulting in a total of 35 cores. Cores will be taken with a Livingston coring tool. At each locality, one core will be used to determine the rate of sedimentation for the immediate area to establish a chronometry for mercury measurement. Thus there will be three cores sacrificed to provide a good understanding of the rate of sediment deposition throughout Devils Lake. Sedimentation rates will be determined through ^{210}Pb radiometric analysis (1). Carbon samples will be taken at the base of these core sections for ^{14}C analysis, which will provide corroboration of extrapolated ^{210}Pb results. The derived core chronometry will provide a rigorous basis upon which to compare selected, chronometrically equivalent, core intervals or horizons throughout the lake. Three preindustrial sediment intervals will be selected from the remaining cores at each locality. Under this procedure, preindustrial mercury values will be known from 27 analyses (three intervals per core × three cores per location × three locations). In addition, random duplicate samples will be taken at 10% of the horizons for statistical validation of analytical procedures. All coring and sampling performed will use an ultraclean technique (2).

Sediment samples to be used in mercury analyses will be taken from each core and separated by centrifugation, air-dried, and then processed with stainless steel sieves under clean conditions to obtain the <63-micron fraction. The fine-grained fraction of the samples will be analyzed for mercury using the cold-vapor atomic absorption spectroscopy (CVAAS) technique.

The approach described above will provide data for the evaluation of changes in mercury concentrations in Devils Lake bottom sediments over time, particularly with respect to preindustrial age versus industrial age.

Task 2.3 – Statistical Analysis of Data

Analytical data will be processed to provide representative statistical parameters to be used as comparative criteria for respective sampling locations. Simple parameters (sample variation, averages, and standard deviation) coupled with advanced statistical methods (ANOVA, cluster, factor analysis) addressing a wider variety of environmental background data will be employed to correlate the analytical data obtained in Task 2. After comparison with respective geochemical background concentrations, the results are expected to provide information on the natural occurrence of mercury within preindustrial-age lake bottom sediments. Ultimately these data may be used to provide insight regarding the potential geochemical relation between mercury in fine-grained sediments and its corresponding lake water and, thus, mercury bioavailability for fish.

The results of the data collection and statistical analysis will be used to prepare a final report and possibly a peer-reviewed publication for an appropriate journal.

STANDARDS OF SUCCESS

Quality Assurance/Quality Control (QA/QC) for Task 1

The EERC recognizes the imperative of producing high-quality measurement results. As such, a comprehensive QA/QC program is in place at the EERC which is designed to maintain overall data integrity. Additional procedures, however, will be instituted specific to this project. The project's QA officer will ensure that the following QA/QC program is strictly adhered to at each test site. Important features of this plan include:

- On-site wet chemical mercury analysis (which will help eliminate outliers since they can identified in the field and repeated).
- Operation of mercury speciation sampling trains at probe/filter temperatures of 350°F to eliminate $HgCl_2$ deposition on front-half glassware.
- Daily field blanks (which will be used for blank corrections) and daily field spikes.
- A "one-use" impinger glassware system designed to minimize contamination problems.
- The use of a Semtech and/or PS Analytical mercury analyzer as a supplement to outlet wet chemical data that can provide a quality assurance cross-check.

Instrument Setup and Calibration

The instrument to be used in the field for mercury determination is a Leeman Labs PS200 CVAA. The instrument is set up for absorption at 253.7 nm, with a carrier gas of nitrogen and 10%

stannous chloride in 10% HCl as the reductant. Each day, the drying tube and acetate trap are replaced and the tubing checked and replaced if necessary. The rinse container is cleaned and filled with fresh solution of 10% HCl. After the pump and lamp are turned on and warmed up for 45 minutes, the aperture is set to the manufacturer specifications. A four-point calibration curve is completed using matrix-matched standards. The detector response for a given standard is logged and compared to specifications to ensure that the instrument has been properly set up. A QC standard of a known analyte concentration is analyzed immediately after an instrument is standardized in order to verify the calibration. This QC standard is prepared from a different stock than the calibration standards. The values obtained must read within 5% of the true value. A QC chart is maintained to monitor the long-term precision of the instrument. After the initial QC standardization has been completed, standards are run every five samples to check the slope of the calibration curve. The check standards must read within 5% of the expected value. All samples are then run in duplicate, and one in every ten samples is spiked to verify analyte recovery.

Flue Gas-Sampling Equipment

Prior to the testing, all gas-sampling equipment will be calibrated according to the *Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III. Stationary Source Specific Methods*. The uncertainty of the individual measurements will be determined using the performance test codes in ANSI/ASME PTC 19.1-1985, Part 1, Measurement Uncertainty, as a guideline (3).

All flue gas-sampling equipment including pitot tubes and temperature meters will be calibrated according to EPA QA/QC specifications for Method 5 sampling prior to and following each host site test program.

Presampling Preparation

All data sheets, volumetric flasks, and petri dishes used for sample recovery will be marked with preprinted labels. The liquid samples will be recovered into premarked volumetric flasks and logged. The filter samples will be placed in premarked petri dishes. The labels will contain identifying data to include date, time, run number, sample port location, and sampler.

Glassware and Plasticware Cleaning and Storage

All glass volumetric flasks and transfer pipets used in the preparation of analytical reagents and calibration standards are designated as Class A to meet federal specifications. Special cleaning procedures are required for all laboratory glassware and plasticware related to mercury analysis. This procedure includes washing with hot, soapy water, several rinses with tap water, and several rinses with distilled deionized water. All vessels are then soaked in 5% bromine monochloride (BrCl) solution (see reagent preparation) for a minimum of 30 minutes, followed by several rinses with distilled deionized water.

Prior to being used for sampling, all glassware is washed with hot, soapy water, rinsed with deionized water three times, soaked in 10% (V/V) nitric acid for a minimum of 4 hours, then rinsed an additional 3 times with deionized water and dried. The glassware is then stored in closed containers until it is used.

Analytical Reagents

All acids used for the analytical methods that pertain to trace metal analysis including mercury are trace metal-grade. Other chemicals used in the preparation of analytical reagents are analytical reagent-grade. The calibration standards used for instrument calibration and the QC standards used for calibration verification are purchased commercially, certified to be accurate within ±0.5%, and traceable to National Institute of Standards and Technology (NIST) standard reference materials.

Blanks

As discussed earlier, sampling at each site will be conducted over a 3-day period, giving 6 replicate samples for each site at each location. As part of the QA/QC, a field blank will associated at each location every day. A field blank is defined as a complete impinger train, including all glassware and solutions that are taken out to the field during sampling and exposed to ambient conditions. This train is then taken apart and the solutions recovered and analyzed the same as those used for sampling. If the field blank shows contamination above instrument background, steps must be taken to eliminate or reduce the contamination to below background levels. This is another advantage of doing the bulk of the mercury analyses in the field. If the contamination cannot be eliminated, the magnitude of the contamination must be considered when calculating the concentration of mercury in the samples.

All acids, chemical reagents and deionized water used for mercury determination are analyzed for background levels of mercury. Each time a new batch of reagents is prepared, an aliquot will be immediately taken and analyzed for mercury.

Spiked Sample Analysis

In order to ensure that adequate levels of accuracy are maintained, spiked samples will also be submitted for analysis. These samples will be made up independently of the chemist doing the analyses. These spikes must be within 10% of the true value. Accuracy is reported as percent recovery of the spike added. Recoveries are plotted on an accuracy control chart.

$$\%\text{Recovery} = \frac{(\text{Sample} + \text{Spike}) - (\text{Sample})}{(\text{Spike})} \times 100\%$$

It is recommended that on a mass basis, the spike added should be approximately equal to the mass of the constituent sought in the sample or sample aliquot. Spike volume relative to the sample aliquot volume should be as small as possible, but not so small that it cannot be dispensed accurately. The solution used for spiking is from a separate stock then the calibration standards.

External Quality Control

The Analytical Research Laboratory at the EERC has ~~U.S~~. EPA certification through the state of North Dakota by participating annually in its water pollution study. An on-site evaluation is conducted every three years by the state in order to maintain full certification. The EERC laboratories have also participated in a number of round-robin studies during the past three years.

An external audit of the mercury speciation sampling and QA/QC procedures at the EERC was conducted by Advanced Technology Systems and International Technology Corporation. This audit was conducted as part of the "Formal Evaluation of Flue Gas Chemical Measurement Methods" project (funded by EPRI and DOE) that has been ongoing at the EERC for the past three years, Their report (available upon request) rates the mercury work being done at the EERC as excellent.

Quality Assurance/Quality Control for Task 2

Presampling Preparation

Lake sediment core samples will be collected using a stainless steel Livingston coring device. Within the coring device will be a dedicated stainless steel core liner where the sediment core will be stored until analysis. The dedicated core liners will be cleaned in a solution of deionized water and Citrinox detergent, air-dried, and wrapped in cellophane prior to transportation to the sampling location. All core liners will be appropriately labeled prior to sample collection. To minimize inadvertant contamination of the samples caused by the collection process, the coring device and all dedicated core liners will be handled according to the ultraclean technique, which calls for the wearing of Class 100 vinyl gloves at all times during washing, packing, and shipping activities (2).

Sample Collection

The Livingston coring device will be dropped or pushed into the sediment to a depth of approximately 1 meter. The intact sediment core will be contained in the dedicated core liner and brought to the surface of the lake. Once at the surface, the dedicated core liner will be removed and capped at both ends using Teflon caps. Ultraclean techniques will be employed throughout the collection process.

Sample Storage and Transportation

The capped core liners will be wrapped in plastic and placed in a cooler for storage at 10°C. Samples will be transported to the EERC facility in Grand Forks, ND, the same day they are collected and placed into a refrigerated storage unit to be stored at 10°C until analysis.

Duplicates and Standards

Duplicate samples will be collected at 10% of the sampling locations in a random selection process. The analysis of these samples for mercury will provide QA/QC data for the selected analytical and sampling procedures. QA/QC data for the CVAAS mercury analyses will also be collected by analyzing samples of a NIST soil at the beginning and end of the analytical work. All QA/QC activities will be approved and supervised by the EERC QA/QC coordinator.

BACKGROUND

The 1990 Clean Air Act Amendments (CAAA) require 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 (4). EPA's conclusions and recommendations will be presented in two reports: "Utility Air Toxics Report to Congress" and "Mercury Study Report to Congress." Potential regulation of HAP emissions from electric utilities will be delayed until the reports are completed. The formal release of these reports, originally scheduled for 1993–1994, is being delayed pending additional review and data (5). The mercury report has been reviewed and is currently being scheduled for release (6). The National Institute of Environmental Health Sciences is also required by the CAAA to investigate mercury and to determine a safe threshold level of exposure. Mercury is of considerable environmental concern because it is a mobile and persistent pollutant that becomes more concentrated as it proceeds through the food chain (7).

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 (Hg^0), inorganic, oxidized mercury (Hg^{2+}), 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 (8). Oxidized mercury in the atmosphere can deposit directly onto water bodies or enter them indirectly after depositing on land or surface 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 emitted from power plants. The concentration of mercury emitted in the flue gas from coal combustion is often very low compared with other processes such waste incineration and metal smelters. In addition, there appears to be contradictory data as to the level of deposition, particularly from North Dakota power plants.

The form and quantity of trace elements emitted from a fuel energy conversion system are a function of the trace metal concentrations, forms, and associations in the fuel; the conversion process; and the operating conditions (9–11). Trace elements have a wide range of associations in coals that depends primarily on coal rank and the depositional environment of the coal (12). System conditions such as initial combustion or gasification temperature and excess air or oxygen-to-carbon ratios, influence the release of the trace element from the coal or mineral components. The trace elements are released from the fuel in the form of inorganic gases, liquids, and solids. These species are transported through the system with the bulk gas flow where reaction occurs between the inorganic species and combustion products. Many of the trace species condense to form particulate material upon gas cooling the conversion and air pollution control system. Some elements such as mercury, selenium, halogens, and minor amounts of other species have the potential to be released from the system in the form of gas-phase species. The quantity of the elements released from the coal conversion and air pollution control system depends on the ability to prevent the trace elements from entering the system, to convert to solid particles, to capture particulate matter, and to sorb vapor-phase components.

Knowledge of the various physicochemical forms (i.e., species) of mercury that may exist in combustion flue gas is crucial for addressing questions concerning mercury emission control, toxicity, mobility, bioaccumulation, and atmospheric fate and transport, because each has distinctive physical, chemical, and biological properties. Until recently, only total mercury concentration was 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 (g) and solid (s) particulate phases. The three oxidation states of Hg, elemental (Hg^0), mercurous (Hg_2^{2+}), and mercuric (Hg^{2+}), 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 Hg 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.

Many research and development organizations, including the EERC, are striving to develop an effective and economical mercury control technology for electric utility power plants. The development of mercury control technologies is being spurred, as summarized above, by environmental and human health concerns and the resulting potential for mercury emission regulations. Mercury exists primarily as gaseous elemental mercury, $Hg^0(g)$, and as gaseous or solid inorganic mercuric compounds, $Hg^{2+}X$ (where X is $Cl_2[g]$, $SO_4[s]$, O[s,g], etc.), in coal combustion flue gas (12). Lindqvist and coworkers (14) proposed that $Hg^{2+}X(s,g)$ compounds are collected more efficiently in air pollution control systems relative to $Hg^0(g)$ because of their greater water solubilities and particulate affinities; whereas, $Hg^0(g)$ is difficult to collect because of its volatility and low water solubility. In accordance with this hypothesis, pilot-scale testing by Hargrove and coworkers (15) demonstrated that SO_2 and particulate scrubber systems are relatively effective in removing soluble $Hg^{2+}X(s,g)$ forms but not $Hg^0(g)$. The identification of a catalyst for converting $Hg^0(g)$ to soluble $Hg^{2+}X(s,g)$ forms could potentially improve the mercury control efficiency of wet scrubber systems. According to EPRI, the use of sorbents to capture mercury is the most promising and cost-effective approach for utility boilers without a scrubber (approximately two-thirds of existing coal-fired capacity) (16). Sorbents can be injected directly into the flue gas stream or used in a bed through which the flue gas flows. Although various sorbents including activated carbon, diatomaceous earth, and zeolite have been evaluated, a reliable and cost-effective mercury control method has not been identified.

Research at the EERC and elsewhere indicates that certain fly ashes are potential catalysts for converting $Hg^0(g)$ to soluble $Hg^{2+}X(s,g)$ forms and/or sorbents for capturing mercury (15,17–19). Measurements by Otani and coworkers (20), Schager and coworkers (21), and Hall and coworkers (22) indicate that some fly ashes adsorb mercury at rates greater than various sorbents, including activated carbon. The catalytic potential and adsorption capacity of a fly ash are probably dependent on a large number of factors, including ash physical properties (e.g., morphology, particle-size distribution, and surface area), ash chemical and mineralogical composition, mercury concentration and speciation, flue gas temperature and chemical composition, and fly ash residence time in the flue gas. Knowledge of the relative importance of these factors in controlling mercury–ash interactions is required to effectively utilize fly ash in a mercury control technology .

Estimates of the relative proportions of $Hg^0(g)$, $Hg^{2+}X(g)$, $Hg^{2+}X(s)$, and $CH_3Hg(g)$ have been made for numerous coals in various coal combustion pilot- and full-scale systems, and gaseous and particulate Hg compounds, $Hg^{2+}X(s, g)$, generally make up greater than one-half of the total Hg present in combustion flue gas (10). The other dominant form of Hg in combustion flue gas is $Hg^0(g)$.

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. The available information relevant to the speciation and transformations of mercury in fossil fuel combustion flue gas was reviewed (10). Focused coal combustion testing was then performed with a view to noting impacts of fly ash, Cl_2, NO_x , SO_2, and HF components of combustion flue gas for transforming gaseous elemental mercury into other solid- or gas-phase species at typical flue duct temperatures. The mercury in fossil fuels is initially transformed to gaseous elemental mercury during the combustion process. Kinetic data and speciation analysis results indicate that not all of the gaseous elemental mercury is oxidized. The transformation of mercury in coal to oxidized species is important because the oxidized form is generally water-soluble and is, therefore, more effectively captured by wet scrubber pollution control systems and is more likely to deposit locally or regionally. Conversely, gaseous elemental mercury is difficult to capture and is apt to enter the global atmospheric cycle because of its high vapor pressure and low water solubility.

An investigation of mercury partitioning indicates, as shown in Figure 1, that greater than 90% of the mercury emitted from the Falkirk North Dakota lignite coal is associated with relatively large ($d_{50} \geq 2\ \mu m$) ash particles. The association of mercury with relatively large ash particulate from the Falkirk coal results in the efficient collection of mercury by the baghouse. Apparently, the Falkirk fly ash possesses a much greater mercury sorption capacity relative to the other coal fly ashes tested. These preliminary testing results warrant an investigation of the applicability of Falkirk coal and fly ash as mercury control commodities. Assuming that additional research verifies the mercury sorption properties of Falkirk fly ash and mercury emission regulations are promulgated, potential marketing opportunities include utilizing Falkirk coal as a baseline or fuel supplement and the duct injection of Falkirk fly ash to mitigate mercury emissions.

Coal-fired power plants are considered to be significant contributors to the global atmospheric mercury budget (23). However, this has recently been misconstrued to the point that coal-fired power plants are perhaps erroneously perceived by the public as the only significant contributors of methylmercury in fish. If significant relative natural enrichment of mercury can be documented in the watersheds and sediments of various North American surface waters and, subsequently, correlated to lakes that have particularly high levels of methylmercury in fish, then the results would suggest that atmospheric deposition from coal-fired power plants is not the most significant source of mercury in these lakes. Previous research suggests that small variations in the supply of mercury to a lake or watershed can induce large variations in the observed mercury concentrations in biota of the respective lake or watershed (24).

Swain and coworkers (25) concluded that mercury accumulation in lake sediment can be correlated with the ratio of catchment to lake area. This conclusion is based on simple mass-balance data from seven lakes in Minnesota and Wisconsin that have no stream outflow and makes several assumptions (e.g., that all mercury is a result of atmospheric deposition and that mercury is immobile in the sediment column). However, Bonham-Carter and coworkers (26) applied the Swain and coworkers (25) approach to data from 21 lakes in Ontario and found that the simple mass balance model did not fit the data for either the modern or preindustrial sediments. This suggests that not

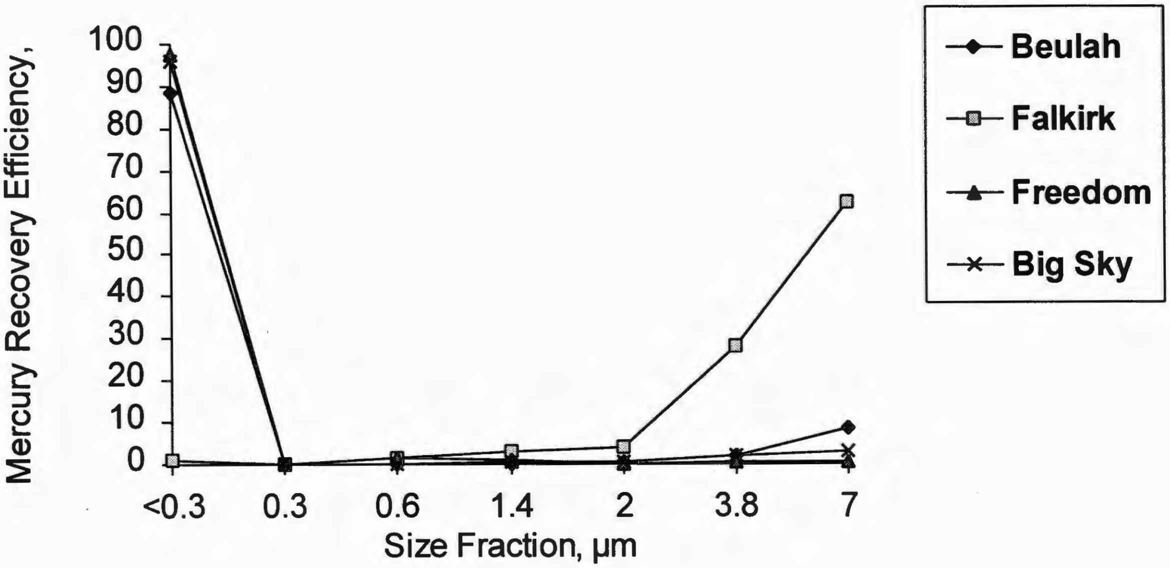

Figure 1. Comparison of mercury recovery efficiency as a function of fly ash particle size for the Beulah, Falkirk, Freedom, and Big Sky coals.

enough reliable information exists to distinguish sources of natural occurrence in the surficial materials of the geological/geochemical environment from sources of anthropogenic pollution. However, extensive research performed by the Geological Survey of Canada (27–29) has shown that based on various inorganic mercury concentrations in small-fraction (fine-grained) analyses of bedrock materials and glacial dispersal trains, there is significant spatial variation of mercury due to differences in geological setting. The Canadian work indicates that geological setting may have a significant influence on mercury concentrations in lake sediments and water and that the analysis of small-fraction portions of sediment samples is a more statistically valid method for such determinations. Small fractions tend to be more geochemically active because of a high total surface area and cation exchange capacity, resulting in preferential adsorption of representative portions of trace metals during weathering of primary minerals. A detailed evaluation of mercury concentrations in the small-fraction portion of lake sediments whose age can be accurately determined may provide data regarding the contribution of mercury from geological sources. Fractions of <2 microns are considered the best to analyze for metal enrichment; however, because of material availability and cost of sample recovery, often the <63-micron fraction is analyzed (30). The research conducted under this task will focus on the <63-micron fraction. Data regarding the natural enrichment of mercury in lake sediment can be useful in determining the anthropogenic contribution of mercury to areas that have elevated levels of mercury in fish.

QUALIFICATIONS

The EERC of the University of North Dakota is one of the world's major energy and environmental research organizations. Since its founding in 1949, the EERC has conducted research, testing, and evaluation of fuels, combustion and gasification technologies, emissions control technologies, ash use and disposal, analytical methods, groundwater, waste-to-energy systems, and advanced environmental control systems. The main EERC facilities—with 169,000 square feet of laboratory, pilot plant, and office space—are located on the southeast corner of the University of North Dakota campus. High-severity processes can be developed from conceptual ideas through proof-of-concept demonstration in the flexible EERC reactor systems. Laboratory- and pilot-scale combustors and gasifiers with capacities of up to 4.0 million Btu/hr, as well as diesel and gas turbine simulators, are available for evaluating new fuels and assessing new emission control technologies. Testing equipment is also available for full-scale sampling and measuring of system flow and temperature. Analytical techniques and instrumentation are available for the characterization of solid, liquid, and gaseous materials.

The EERC has conducted extensive research on the engineering aspects and environmental effects of carbon-based fuels combustion and gasification. Specific program areas include ash and slag chemistry, trace metals in fuels, inorganic transformations, ash deposition, coal combustion chemistry, corrosion/erosion mechanisms, fuels evaluation, fluidized-bed combustion, gas turbines, diesels, slurry combustion, SO_2 control, NO_X control, particulate control, hot-gas cleanup, clean coal technologies, advanced power systems, process development, gasification/combined cycle systems research, waste-to-energy conversion, and synthetic fuels investigations.

The project will be managed by Dr. Steve Benson. Dr. Benson has nearly 20 years of experience in coal combustion and the behavior of major, minor, and trace species in coal conversion and environmental control systems. The principal investigator for Task 1 is Dennis Laudal. Mr. Laudal has extensive experience in sampling and analysis of Hg and in environmental control technologies. Marc Kurz and James Sorensen will be coprincipal investigators for Task 2. Mr. Kurz has knowledge in environmental science, with an emphasis on contaminated groundwater and soil remediation. Mr. Sorensen performs hydrogeology-related fieldwork, hydrogeologic data reduction and interpretation, and computer database construction and maintenance. Resumes of key personnel are found in the Appendix B.

VALUE TO NORTH DAKOTA

The benefits of the proposed work to North Dakota are critical to the state's economic base and to ensure a safe and clean environment for generations to come. Information produced by this work will allow for more efficient mercury control measures. The cost-effective control of mercury emissions may be necessary for the long-term economic viability of lignite-fired power plants. Further, in order to best protect our environment and human health, we need to understand all the 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.

TIMETABLE

Task 1 – Mercury Emissions from North Dakota Lignite-Fired Power Plants

Sampling activities for Task 1 will include sampling at two sites for both total and speciated mercury. However, prior to beginning the project, probes will need to be assembled, equipment calibrated, and any necessary supplies such as glassware purchased. In addition, it will be necessary to lease a trailer which will serve as a mobile laboratory. Following all preliminary activities, the trailer equipment will be moved on-site. It is hoped that a location will be found close enough to the two selected plants such that it will not be necessary to move the trailer. A minimum of 2 weeks will be necessary to have the trailer completely operational. Once the trailer is in place, it will take 2 days to set up the equipment, 3 days to sample, and a day to get ready to move to the next site, if necessary. A tentative schedule is shown in Figure 2 and explained in Table 1.

	Feb					Project Months								March
Activities	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Task 1 – Mercury Emission from North Dakota Lignite-Fired Power Plants	A		B C	D E		F								
Task 2 – Sources of Mercury in Devils Lake	A		B				C		D					
Meetings and Reporting	A						B			C	D		E	
							August			Nov	Dec			

Figure 2. Project schedule and milestones.

Task 2 – Sources of Mercury in Devils Lake

The research activities that focus on the bottom sediments of Devils Lake have been designed to be performed over the course of 12 months. Activities during the first quarter will include literature review activities for the purpose of selecting appropriate sampling localities and arranging other logistical considerations that may be required for sampling. Second-quarter activities will include the cleaning and preparation of equipment, the collection of sediment samples, and the submission of samples for radiometric dating and mercury concentration analyses. The results of the radiometric dating and mercury concentration analyses will be available late in the second quarter or early in the third quarter. The statistical analyses of the data, and subsequent interpretation, will be conducted during the third quarter of the project. The final 3 months of the project will be spent preparing a final report or paper suitable for journal publication that will describe the research activities, present the results of those activities, and discuss possible implications.

Meetings with project sponsors will be conducted at the project initiation, after plant sampling, and at the end of the project. A final report will be written that will include all data, interpretations, and conclusions gained from the work.

TABLE 1

Description of Activities Shown in Figure 2

	Activity
Task 1 Schedule	
A	Begin preliminary phase of the sampling effort.
B	Move trailer and equipment to site.
C	Begin sampling activities at Site 1.
D	Begin sampling activities at Site 2.
E	Remove trailer from site.
F	Complete site reports.
Task 2 Schedule	
A	Initiate selection of sampling sites.
B	Prepare sampling equipment and identify of sites.
C	Complete sampling.
D	Complete analysis of samples.
E	Complete interim report on lake sediment sampling.
Meetings and Reporting	
A	Kick-off meeting with project sponsors.
B	Interim progress meeting to discuss preliminary results.
C	Final report submitted for review.
D	Reviewer's comments due.
E	Final meeting.

BUDGET

This request is for $120,000 from NDIC in support of a program with a total cost of $400,000. The sources of matching funds are discussed in the next section. The cost breakdown for this project is as shown in the following detailed budget.

Matching Funds

The total cost for this effort is $400,000. Of this amount, we will seek support from four sponsors that will likely include utilities and coal companies for $120,000. We will also seek funding from EPRI. Project cosponsors will be asked to contribute $30,000 each for a total of $120,000. The remaining $160,000 required to fully fund this program will be requested from DOE through the EERC–DOE Jointly Sponsored Research Program (JSRP). A detailed budget follows showing how these dollars will be utilized in support of the proposed program.

CONFIDENTIAL INFORMATION

None.

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MERCURY FORMATION AND FATE
NDIC/INDUSTRY/EERC JSRP SHARE
PROPOSED START DATE: 7/1/97
EERC PROPOSAL #97-6271 30-May-97

LABOR	LABOR CATEGORY	HOURLY RATE	TASK 1 HOURS	TASK 1 $ COST	TASK 2 HOURS	TASK 2 $ COST	TOTAL HOURS	TOTAL $ COST	NDIC SHARE HOURS	NDIC SHARE $ COST	INDUSTRY SHARE HOURS	INDUSTRY SHARE $ COST	EERC JSRP SHARE HOURS	EERC JSRP SHARE $ COST
S. BENSON	PROJECT MANAGER	$39.52	100	$3,952	50	$1,976	150	$5,928	50	$1,976	50	$1,976	50	$1,976
D. LAUDAL	PRINCIPAL INVESTIGATOR	$28.07	215	$6,035	0	$0	215	$6,035	50	$1,404	50	$1,404	115	$3,227
M. KURZ	PRINCIPAL INVESTIGATOR	$12.99	0	$0	1000	$12,990	1000	$12,990	350	$4,547	350	$4,547	300	$3,896
J. SORENSEN	PRINCIPAL INVESTIGATOR	$14.90	0	$0	1000	$14,900	1000	$14,900	350	$5,215	350	$5,215	300	$4,470
---------------	SENIOR MANAGEMENT	$38.74	90	$3,487	78	$3,022	168	$6,509	50	$1,937	50	$1,937	68	$2,635
---------------	QUALITY CONTROL MANAGER	$21.40	25	$535	19	$407	44	$942	10	$214	10	$214	24	$514
---------------	RESEARCH SCIENTIST/ENGINEER	$21.40	2075	$44,405	821	$17,569	2896	$61,974	850	$18,190	850	$18,190	1196	$25,594
---------------	CHEMIST II	$12.85	400	$5,140	0	$0	400	$5,140	150	$1,928	150	$1,928	100	$1,284
---------------	RESEARCH TECHNICIAN	$13.91	200	$2,782	150	$2,087	350	$4,869	80	$1,113	80	$1,113	190	$2,643
---------------	STUDENT ASSISTANTS	$6.27	20	$125	700	$4,389	720	$4,514	200	$1,254	200	$1,254	320	$2,006
---------------	TECHNICAL SUPPORT SERVICES	$9.70	60	$582	120	$1,164	180	$1,746	50	$485	50	$485	80	$776
			3185	$67,043	3938	$58,504	7123	$125,547	2190	$38,263	2190	$38,263	2743	$49,0[illegible]
ESCALATION ABOVE CURRENT BASE		5%		$3,352		$2,925		$6,277		$1,913		$1,913		$2,451
TOTAL DIRECT LABOR				$70,395		$61,429		$131,824		$40,176		$40,176		$51,472
FRINGE BENEFITS - % OF DIRECT LABOR		47%		$33,086		$28,872		$61,958		$18,883		$18,883		$24,192
TOTAL LABOR				$103,481		$90,301		$193,782		$59,059		$59,059		$75,664
OTHER DIRECT COSTS														
TRAVEL				$5,797		$6,836		$12,633		$4,000		$4,000		$4,633
SUPPLIES				$1,938		$2,025		$3,963		$1,500		$1,500		$963
TRAILER RENTAL				$1,875		$0		$1,875		$750		$750		$375
EQUIPMENT > $750				$4,375		$0		$4,375		$0		$0		$4,375
COMMUNICATIONS - PHONES & POSTAGE				$375		$500		$875		$113		$113		$649
PROJECT OFFICE SUPPLIES				$375		$884		$1,259		$400		$400		$459
REPAIR AND REPLACEMENT PARTS				$625		$0		$625		$200		$200		$225
GRAPHICS				$1,470		$1,323		$2,793		$950		$950		$893
NATURAL MATERIALS ANALYTICAL RES. LAB.				$823		$0		$823		$250		$250		$323
COAL LAB				$2,234		$0		$2,234		$700		$700		$[illegible]
ANALYTICAL RESEARCH LAB.				$6,011		$12,758		$18,769		$4,500		$4,500		$9,7[illegible]
PARTICULATE LAB				$14,805		$0		$14,805		$3,500		$3,500		$7,805
OUTSIDE LABS				$0		$8,000		$8,000		$2,000		$2,000		$4,000
TOTAL OTHER DIRECT COST				$40,703		$32,326		$73,029		$18,863		$18,863		$35,303
TOTAL DIRECT COST				$144,184		$122,627		$266,811		$77,922		$77,922		$110,967
INDIRECT COST - % OF MTDC							VAR	$133,189	54%	$42,078	54%	$42,078	46%	$49,033
TOTAL ESTIMATED COST								$400,000		$120,000		$120,000		$160,000

DETAIL OF FEES
EERC PROPOSAL #97-6271

		TASK 1		TASK 2		TOTAL	
NATURAL MAT. ANALYTICAL RES. LAB.	**RATE**	**#**	**$ COST**	**#**	**$ COST**	**#**	**$ COST**
XRFA	$98	0	$0	8	$784	8	$784
SUBTOTAL			$0		$784		$784
ESCALATION	5%		$0		$39		$39
TOTAL NATURAL MATERIALS ANALYTICAL RES. LAB			$0		$823		$823
COAL LAB.	**RATE**	**#**	**$ COST**	**#**	**$ COST**	**#**	**$ COST**
BTU	$35	0	$0	8	$280	8	$280
CHLORINE PREP.	$43	0	$0	8	$344	8	$344
DRY SIEVE	$39	0	$0	8	$312	8	$312
LOSS ON IGNITION (LOI)	$23	0	$0	8	$184	8	$184
PROXIMATE/ULTIMATE	$107	0	$0	8	$856	8	$856
XRF PREP	$19	0	$0	8	$152	8	$152
SUBTOTAL			$0		$2,128		$2,128
ESCALATION	5%		$0		$106		$106
TOTAL COAL LAB			$0		$2,234		$2,234
ANALYTICAL RESEARCH LAB	**RATE**	**#**	**$ COST**	**#**	**$ COST**	**#**	**$ COST**
CVGAA	$33	150	$4,950	60	$1,980	210	$6,930
Hg PREP	$37	0	$0	53	$1,961	53	$1,961
FILTERING	$10	150	$1,500	60	$600	210	$2,100
IC PREP	$10	0	$0	8	$80	8	$80
COAL DIGESTION	$138	0	$0	8	$1,104	8	$1,104
MIXED ACID DIGESTION	$38	150	$5,700	0	$0	150	$5,700
SUBTOTAL			$12,150		$5,725		$17,875
ESCALATION	5%		$608		$286		$894
TOTAL ANALYTICAL RESEARCH LABORATORY			$12,758		$6,011		$18,769
PARTICULATE LAB	**RATE**	**#**	**$ COST**	**#**	**$ COST**	**#**	**$ COST**
EPA METHOD 29	$235	0	$0	60	$14,100	60	$14,100
SUBTOTAL			$0		$14,100		$14,100
ESCALATION	5%		$0		$705		$705
TOTAL PARTICULATE LAB			$0		$14,805		$14,805
GRAPHICS SUPPORT COST CENTER	**RATE**	**#**	**$ COST**	**#**	**$ COST**	**#**	**$ COST**
GRAPHICS(HOURLY)	$35	36	$1,260	40	$1,400	76	$2,660
SUBTOTAL			$1,260		$1,400		$2,660
ESCALATION	5%		$63		$70		$133
TOTAL GRAPHICS SUPPORT COST CENTER			$1,323		$1,470		$2,793

EERC PROPOSAL #97-6271

Summary of Equipment

Cold Vapor AA	$55,000

*Note: EERC is purchasing a $55,000 cold vapor AA with a contribution from this program of $4,375.

BUDGET NOTES

ENERGY & ENVIRONMENTAL RESEARCH CENTER (EERC)

Background

The EERC is an independently organized multidisciplinary research center within the University of North Dakota. The EERC receives no appropriated funding from the state of North Dakota and is funded through federal and nonfederal grants, contracts, or other agreements. Although the EERC is not affiliated with any one academic department, university academic faculty may participate in a project based on the scope of work and expertise required to perform the project.

The proposed work will be done on a cost-reimbursable basis. The distribution of costs between budget categories (labor, travel, supplies, equipment, subcontracts) is for planning purposes only. The principal investigator may, as dictated by the needs of the work, reallocate the budget among approved items or use the funds for other items directly related to the project, subject only to staying within the total dollars authorized for the overall program. The budget for this proposal has been prepared based on a specific start date; this start date is indicated at the top of the EERC detail budget or identified in the body of the proposal. Please be aware that any delay in the start of this project may result in an increase in the budget. Financial reporting will be at the total project level.

Salaries and Fringe Benefits

As an interdisciplinary, multiprogram, and multiproject research center, the EERC employs an administrative staff to provide required services for various direct and indirect support functions. Direct project salaries are estimated based on the scope of work and prior experience on projects of similar scope. Technical and administrative salaries are charged based on direct hourly effort on the project. Costs for general support services, such as grants and contracts administration, accounting, personnel, purchasing and receiving, as well as clerical support of these functions, are included in the indirect cost of the EERC.

Fringe benefits are estimated based on historical data. The fringe benefits actually charged consist of two components. The first component covers average vacation, holiday, and sick leave (VSL) for the EERC. This component is approved by the UND cognizant audit agency and charged as a percentage of direct labor on permanent staff employees eligible for VSL benefits. The second component covers actual expenses for items such as health, life, and unemployment insurance; social security matching; worker's compensation; and UND retirement contributions.

Travel

Travel is estimated based on UND travel policies, which include estimated GSA daily meal rates. Travel includes scheduled meetings and conference participation as indicated in the scope of work.

Communications

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.

Project Office 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 computer use charges and computer software.

Supplies

Supplies in this category include scientific supply items such as chemicals, gases, and glassware supplies and/or 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.

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.

General

Membership fees (if included) are for memberships in technical areas directly related to work on this project. Technical journals and newsletters received as a result of a membership are used throughout development and execution of the project as well as by the research team directly involved in project activity.

General expenditures for workshops and conferences may include such items as food (some of which may exceed the institutional established limits), room amenities (e.g., place cards, music, banners, floral arrangements), speaker gifts, security, interpreters, technical tour transportation, and room and equipment rental necessary to conduct workshops and conferences.

Indirect Cost

The indirect cost rate included in this proposal is the rate which became effective July 1, 1995. Indirect cost is calculated on modified total direct costs (MTDC). MTDC is defined as total direct costs less individual items of equipment in excess of $750 and subcontracts/subgrants in excess of the first $25,000 of each award.