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## MERCURY AND AIR TOXIC ELEMENT IMPACTS OF COAL COMBUSTION BY-PRODUCT DISPOSAL AND UTILIZATION

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### ***Project Description***

This effort is focused on the evaluation of coal combustion by-products (CCBs) for their potential to release mercury and other air toxic elements under different controlled laboratory conditions and will investigate the release of these same air toxic elements in select disposal and utilization field settings to understand the impact of various emission control technologies. Information collected through Year 2 was evaluated and interpreted together with past EERC data and similar data from other studies. Results were used to determine if mercury release from CCBs, both as currently produced and as produced with mercury and other emission controls in place, will potentially impact CCB management practices.

The 3-year project was designed to develop baseline information on release mechanisms of select elements in both conventional CCBs and modified or experimental CCBs. Through Year 2, the modified or experimental CCBs were selected to represent CCBs from systems that have improved emission controls. Controlling these emissions has a high potential to change the chemical characteristics and environmental performance of CCBs.

Development of reliable methods to determine the release of mercury from CCBs provided a means of evaluating the environmental risk associated with CCB management practices. Using appropriate methods to develop a data set of currently produced CCBs and those produced under experimental or simulated conditions provided a baseline for the CCB industry to understand the impact of various emission control technologies.

The effort is sponsored by the U.S. Department of Energy National Energy Technology Laboratory (DOE NETL), EERC Center for Air Toxic Metals<sup>®</sup> Program Affiliates Program, Cinergy, EPRI, Great River Energy, North Dakota Lignite Research Council, and the Utility Solid Waste Activities Group (USWAG).

### ***Goal***

The overall goal of this project is to evaluate the impact of mercury and other air toxic elements on the management of CCBs. Specific objectives to accomplish this goal are to 1) determine the release potential of selected air toxic elements, including mercury and arsenic, from CCBs under specific environmental conditions; 2) increase the database of information on mercury and other air toxic element

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releases for CCBs; 3) develop comparative laboratory and field data; and 4) develop appropriate laboratory and field protocols. The specific mechanisms of air toxic element releases to be evaluated will be leaching releases, vapor releases to the atmosphere, and biologically induced leaching and vapor releases.

### ***Rationale***

Mercury and other air toxic elements can be present in fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) material. Emission control technologies have a significant potential to impact the mercury and other air toxic element concentrations present in fly ash and FGD materials. Significant changes in the chemical composition, physical properties, and morphology of by-products may occur as a result of the application of new emission controls. This EERC project was designed to evaluate CCBs from all coal types (bituminous, subbituminous, and lignite) and a limited number of coal blends.

The presence of mercury, arsenic, and other air toxic elements in CCBs poses a potential environmental problem depending on the stability of these elements under disposal and utilization conditions, a concern raised by state regulatory agencies (1) and citizen groups. Anticipated changes in emission regulations may impact the elements and concentrations of elements incorporated into or sorbed onto CCBs, and it is important to understand the fundamental behavior of these elements in CCBs in order to manage them in an environmentally sound manner. Data also need to be developed on by-products from advanced emission control technologies, such as those under development for mercury emission control. This effort is focused on increasing the database of elemental releases from conventional fly ash samples and ash produced from systems with various existing and potential emission controls in place.

Laboratory tasks addressed the following three areas: 1) direct leachability of air toxic constituents from CCBs, 2) vapor release of mercury from CCBs at ambient and elevated temperatures, and 3) biologically induced leachability and vapor release of mercury and other air toxic elements from CCBs. These tasks address fundamental issues critical to determining the release of these constituents over the life cycle of CCBs in a variety of management scenarios. A field task was also conducted to address the same release mechanisms at CCB management sites.

Leaching is the most likely mechanism of transport of constituents from disposed or utilized CCBs contacted by water. Leaching is typically performed on CCBs to characterize them for management purposes. Several issues have been raised by EPA's Office of Research and Development (ORD) and Office of Solid Waste (OSW) related to the best means of evaluating the leaching potential of CCBs. In this project, leaching methodologies were reviewed. In Year 3 of this effort, recommendations will be made and coordinated with EPA, based on the appropriateness of existing methodologies.

Vapor phase release, particularly of mercury, is important from the perspective of long-term use, storage, or disposal of CCBs. Although the concentration of mercury in CCBs is relatively low, the large volumes of CCBs produced annually cause concern about potential mercury releases. Ambient, near-ambient, and elevated-temperature studies of mercury release resulted in the development of an apparatus to determine mercury release in real time from CCBs.

Previous EERC experiments (2) indicate that mercury can be released from CCBs at ambient and near-ambient temperature. These preliminary laboratory data warrant further investigation. Vapor transport experiments evaluated mercury release from a bed of CCBs at ambient and near-ambient

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temperatures and constant airflow through the bed. The design of these experiments is critical to give laboratory results that can be compared to field experiments at CCB management sites.

The wide distribution and variety of microorganisms in the environment indicate that microbiological release of mercury and other air toxic elements needs to be investigated. A wide variety of specific microbe interactions can affect key elements associated with CCBs, including oxidation/reduction and alkylation/dealkylation reactions. The microbial cycling of other air toxic metals follows a similar pattern to that seen with mercury. In order for microbes to be metabolically active, a few constraints must be satisfied. In some CCB management options, these criteria are unlikely to be met, but for options where they can be met, laboratory experiments simulated appropriate scenarios.

## ***Approach***

### **Literature Search**

Publications related to mercury, air toxic elements, and CCBs continued to be collected. A database was developed as an electronic forum to house the documents collected.

### **Analytical Methods Selection**

This task was completed in Year 1 of the project; however, in Year 2, the task was expanded to include participation in a DOE NETL informal interlaboratory round-robin experiment aimed at providing the industry with appropriate leaching procedures for CCBs.

### **Sample Identification and Selection**

Samples were identified through government, industry, and marketing contacts. CCBs were selected from systems with conventional emission control technologies and advanced emission control technologies. Examples of samples from conventional technologies are wet and dry FGD materials, ammoniated ash from systems using selective catalytic reduction, selective noncatalytic reduction, and “high”-mercury fly ash.

Early in the project, samples were received with incomplete sample identification information. Incomplete information made it difficult to categorize and analyze project results. A sample identification form was developed that allowed each sample submitter to easily identify system and sample information. Previous sample submitters were asked to complete the forms, and all new sample submitters are given the sample identification form.

### **Chemical and Physical Characterization**

The bulk chemical and physical characterization task focused on determining trace element composition, moisture content, loss on ignition (LOI), pH, and carbon forms. Samples received during Years 1 and 2 were analyzed for total arsenic, cadmium, chromium, lead, mercury, nickel, and selenium concentrations.

The pH of samples was determined using distilled water and/or 1 M KCl. The method employing 1 M KCl is required for many types of solid samples that exhibit a double electric layer that impacts the determination of pH. For this task, a slurry of 25 mL of 1 M KCl solution was mixed with 10 grams of

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CCB, and the resulting pH was measured and recorded. As already noted, the pH of many of the project samples was also determined in a slurry of distilled, deionized water.

Moisture content and LOI were determined on project samples using standard American Society for Testing and Materials (ASTM) gravimetric techniques. LOI provides an estimate amount of carbon present in the sample.

Dominant carbon forms were identified in a select group of project samples. The samples on which carbon forms were determined were prepared by mounting the sample in epoxy resin. The sample was dispersed in the bottom of a rubber cup mold of approximately 1 inch in diameter. The epoxy was stained using Sudan Black, which results in a high contrast between the particles of interest and the mounting medium. The surfaces to be analyzed were polished with incrementally smaller grits, with  $\frac{1}{4}$   $\mu\text{m}$  being the final polishing grit used. The samples were then examined using a reflected light microscope.

### **Laboratory Evaluation of Air Toxic Element Releases**

Assembled samples were used in laboratory experiments focusing on specific release mechanisms of mercury and other air toxic elements. Primary release mechanisms are leaching, vaporization, and biologically stimulated leaching and vaporization. Air toxic elements were evaluated including mercury, arsenic, and selenium for release through leaching. Vapor release experiments focused on mercury, based on previous research and a fundamental understanding of mercury chemistry.

#### **Leaching**

Project samples were evaluated through the continued use of the synthetic groundwater leaching procedure (SGLP), toxicity characteristic leaching procedure (TCLP), and 30- and 60-day long-term leaching (LTL) procedure in Year 2. The SGLP was selected as the primary leaching procedure applied to characterize release of mercury and other air toxic elements from CCBs. TCLP was applied to some samples at the request of the sample submitter. Samples with  $\text{pH} > 10$  were also leached using LTL because CCBs with  $\text{pH} > 10$  are typically reactive, and the leaching profile may change over time, hence requiring the longer duration leaching data to assess the leaching characteristics of those samples.

#### **Vapor Transport**

The vapor transport experiments continued to focus on mercury. The release of mercury from CCB samples was investigated at ambient and elevated temperatures in an effort to simulate temperature conditions typical of various types of CCB management and disposal options.

##### *Ambient Temperature Release Experiments*

The ambient temperature release of mercury was evaluated by capturing the mercury released from 100–200 grams of sample placed in a closed system designed for this subtask. The apparatus and protocol are detailed elsewhere (3). The mercury released from a sample was captured on an individual gold-coated quartz analytical trap, which was analyzed with double-gold amalgamation and atomic fluorescence (AF) detection after one 7-day period and two 90-day periods. Twelve CCBs were evaluated in duplicate (see Table 1).

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**Table 1. Samples Included in Long-Term Ambient Temperature Mercury Release Experiment**

ID No.	Sample Type	Hg Control	Project Sample
99-188	Fly ash + FGD		Yes
99-456	Fly ash		No
00-048	Fly ash + FGD		No
01-002	Fly ash		No
01-008	Fly ash		No
01-011	Fly ash + FGD		No
03-006	Fly ash		Yes
03-017	Fly ash + FGD	√	Yes
03-018	Fly ash + FGD	√	Yes
03-060	Fly ash	√	Yes
03-061	Fly ash		Yes
03-062	Fly ash + FGD	√	Yes

*Elevated Temperature Release Experiments*

The release of mercury at elevated temperatures was evaluated by heating a sample in a temperature-controlled tube furnace and detecting the emitted mercury or mercury compounds with atomic absorption in a t-cell heated to 800°C. Over the duration of the project, the apparatus for elevated temperature release experiments has been modified to increase the achievable maximum temperature from 700° to 750°C. The higher temperature of 750°C provides adequate heat to break the bonds of mercury compounds that may be present on the CCBs under investigation. Additionally, during Year 2, a mass flow controller was added to the apparatus to improve reproducibility. After the mass flow controller was installed on the thermal desorption apparatus, the flow rate was optimized to 10 mL/min when samples were heated from ambient to 750°C at a rate of 25°C/min.

**Microbiological Releases**

The microbiological release subtask focused on improving the protocol developed for these experiments and performing analytical procedures following the new protocol. The original methodology described elsewhere (4) did not yield adequate liquid sample to determine all mercury forms plus other trace elements, and it was determined that the buffer solution was not being thoroughly mixed and, therefore, not maintaining contact with the complete sample. In Year 2, a new method was developed using a higher ratio of buffer solution to solid sample and a stir bar to facilitate complete mixing. Additionally, the overall buffer system was changed in an attempt to eliminate interferences noted for SPME (solid-phase microextraction) analysis by the old buffer system. The new buffer system consists of L-glutamic acid, potassium phosphate monobasic, and D-(+)-glucose. The new buffer system significantly reduced the previously noted analytical interferences to the SPME analysis. When alkaline CCBs were evaluated, dilute sulfuric acid was added to neutralize the sample prior to introducing the microbes.

**Field Investigations**

This task focused on developing information to facilitate an understanding of how laboratory results can be used effectively to determine potential releases of air toxic elements from CCBs in real-world management settings.

The Year 2 field investigation task was performed at CCB management facilities associated with a lignite-fired power plant during the third quarter of 2004. The field task consisted of three key activities: 1) mercury flux measurements taken at near surface locations, 2) collection of mercury samples from ambient air at near surface locations, and 3) collection of near-surface solid samples and water samples where available. The EERC contracted with the University of Nevada – Reno (UNR) to perform the mercury flux measurements using a mercury flux chamber as reported previously by UNR (5). Ambient mercury was sampled by drawing air through gold-coated quartz traps and tubes containing Supelco Carbotrap™. The combination of collection on these two types of analytical traps allows assessment of inorganic mercury (gold trap) and organomercury species (Supelco Carbotrap™). Air sampling was performed at a variety of locations at the CCB management facilities. The sampling locations included a fly ash disposal site, a site where FGD material and mill rejects were codisposed, a reclaimed fly ash landfill site, near a disposal pond containing FGD material and bottom ash, and near a disposal pond containing FGD material stabilized with fly ash.

Water samples and replicate (EERC and UNR) solid samples were obtained for laboratory testing. Solid composite samples were taken of the substrate on which the mercury air sampling was conducted. Composite samples included a fly ash sample from a disposal site, an FGD scrubber material mixed with mill rejects from a disposal site, a soil sample from a reclaimed fly ash landfill, bottom ash and FGD samples from a wet disposal pond, and FGD stabilized with fly ash from a wet disposal pond. Liquid samples were collected at disposal ponds where possible.

Laboratory analysis of samples collected at the field site was initiated at the EERC. Gold-coated quartz traps and traps containing Supelco Carbotrap™ were analyzed utilizing double-gold amalgamation with AF (atomic fluorescence) detection. The liquid samples were evaluated using SPME with GC separation and AF detection of organomercury compounds.

### **Data Reduction and Interpretation**

All data collected to date in this project were compiled into a database. Preliminary interpretative efforts were initiated in Year 2 with comparisons of results from various leaching procedures, comparisons of the total mercury content and leachable mercury, comparisons of the total mercury content, and dominant carbon form present in the sample source. Data were presented to project sponsors in regular reports throughout the year and at several conferences.

### ***Progress***

#### **Literature Search**

Citations and abstracts to documents assembled were added to the Mercury and Air Toxic Element document database. The database was modeled after the EERC's FIRST SEARCH database. The database can be quickly searched using the "Quick Search" tool or by using the "Advanced Search" tool; it can be searched for a specific title, author, source/publisher, or abstract text. Users may also browse all publications in alphabetical order by title. The majority of publications contain abstract text, and a method is provided to acquire the full text. In several instances, full text is provided free of charge by following the full-text instructions. As of December 31, 2004, 415 documents were contained in the database.

The database is located on the Coal Ash Resource Center Web site at [www.undeerc.org/carrc/mercury](http://www.undeerc.org/carrc/mercury). A username and password are required to access the database, which allows only project sponsors and researchers to access the database.

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### **Analytical Methods Selection**

NETL sent a sample to all participating laboratories for evaluation. Samples were requested by EERC from various utilities burning subbituminous or lignite coal to provide an additional fly ash sample for evaluation. Samples received were evaluated, and one reactive sample was selected for the experiments. Leaching was initiated on the sample from NETL and the sample selected by the EERC.

### **Sample Identification and Selection**

Approximately 39 samples were obtained for use in the laboratory experiments. Samples collected included 1) currently produced fly ash from a variety of coal sources and system configurations; 2) wet and dry FGD materials, focusing on processes with a higher probability for future installation; and 3) CCBs from pilot-scale or experimental emission control technologies with a high potential to be implemented under existing or expected regulations. The sample identification form helped to categorize and analyze project results.

### **Chemical and Physical Characterization**

The total trace element concentrations of arsenic, cadmium, chromium, lead, nickel, and selenium were determined on 42 samples, and total mercury was determined in replicate on 74 samples. Replicate trace element concentrations were obtained for five samples. The ranges of total trace element concentrations were <1.00–492 µg/g arsenic, <1.00–8.59 µg/g cadmium, 2.90–160 µg/g chromium, <1.00–272 µg/g lead, <0.100–120 µg/g mercury, <1.00–277 µg/g nickel, and <1.00–36.6 µg/g selenium. The samples from mercury control tests were within the ranges of those without mercury control except for mercury, which ranged from 0.147–120 µg/g and <0.100–2.03 µg/g, respectively, and selenium, which had maximum values of 36.6 µg/g and 26.8 µg/g, respectively.

The pH of 67 samples was determined. Samples of fly ash, both with and without mercury control, ranged in pH from approximately 3.5 to 12.5. FGD material pH values ranged from ~7 to 12.5. Where both methods (distilled water and 1 M KCl) were employed, the pH values were similar. A comparison of these data for a relatively broad range of CCB types led researchers to conclude that it is not necessary to use 1 M KCl in determining the pH of CCB, so remaining samples were evaluated using distilled, deionized water slurries. It is likely that the high concentration of total dissolved solids generated in the pH determination eliminated the double electric-layer effect that requires the use of KCl solution in the determination of pH in other types of solid samples.

Moisture content and LOI were determined on 58 samples. The moisture content of the samples ranged from 0.05%–65.7%, and the LOI ranged from 0.34%–34.5%. Fly ash with activated carbon present had LOIs ranging from 0.64% to 24.4%. Fly ash with no activated carbon present had LOIs ranging from ~0.5% to 34.5%. FGD LOIs ranged from ~1% to ~6.5%.

Samples with high mercury content and activated carbon present generally had isotropic coke or anisotropic coke as the dominant carbon form.

### **Laboratory Evaluation of Air Toxic Element Releases**

This task consists of three subtasks including leaching, vapor transport, and microbiological releases.

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## Leaching

A wide range of leachate concentrations were reported. Leaching has been performed on 58 samples. The ranges of concentrations for the elements included in this leaching subtask were <2.0–1500 µg/L arsenic, <0.20–27 µg/L cadmium, <2.0–680 µg/L chromium, <2.0–37 µg/L lead, <0.010–1.0 µg/L mercury, <2.0–280 µg/L nickel, and <2.0–8600 µg/L selenium, which were also the ranges of concentrations for the mercury control test samples. One sample had the highest levels of arsenic and selenium noted, and a series of three samples from the same power plant had the highest chromium leachate concentrations. However, the samples without mercury control had lower upper range limits, which were 340 µg/L arsenic, 8.3 µg/L cadmium, 280 µg/L chromium, 14 µg/L lead, 0.40 µg/L mercury, 140 µg/L nickel, and 780 µg/L selenium.

Leachate mercury concentrations have been found to be extremely low regardless of the total mercury content of the sample. Most leachates exhibited mercury concentrations less than the reporting limit of 0.01 µg/L. All leachate concentrations fell well below the PDW (primary drinking water) limit of 2.0 µg/L for mercury as well as the limit at 30X PDW (60 µg/L) and 100X PDW (200 µg/L). Even the highest leachate concentration reported (1.0 µg/L) is more than an order of magnitude less than the PDW limit for mercury. A comparison of total and leachate mercury concentrations is presented graphically in Figure 1. The figure clearly indicates that the leachable mercury cannot be correlated to the total mercury content of a CCB. Assembled leaching results for other trace elements are under review.

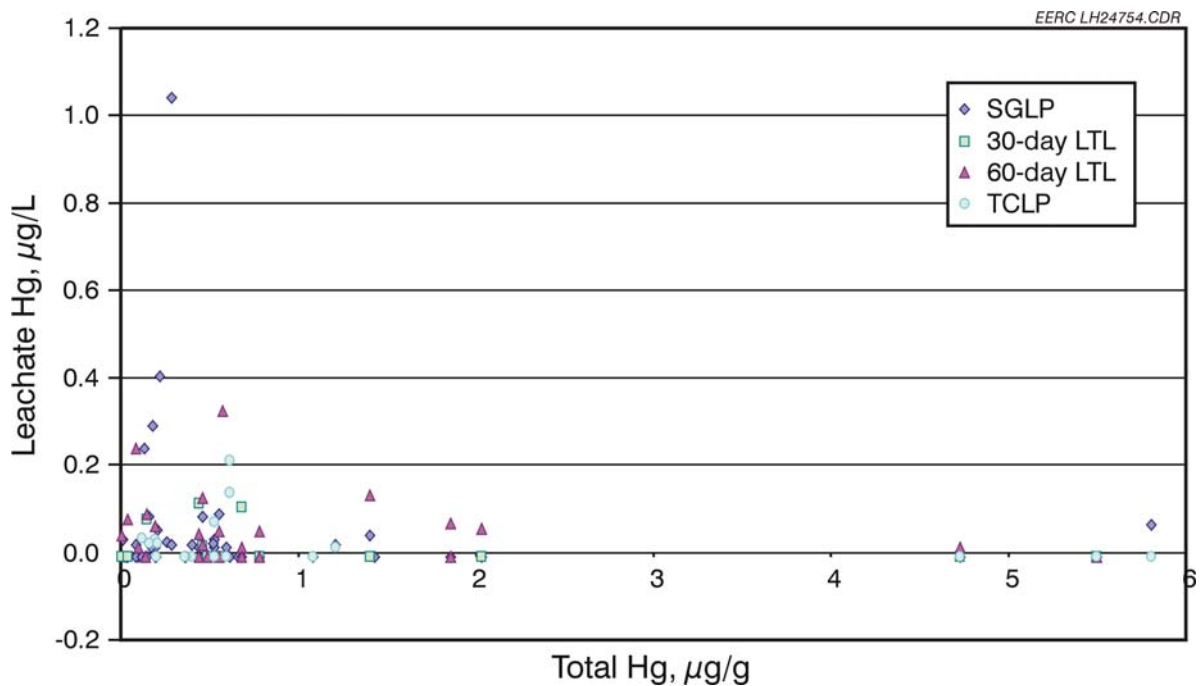


Figure 4. Comparison of total mercury concentrations and leachate concentrations. Negative values indicate less than the reporting limit.

**Vapor Transport**

Two methods were used to determine mercury vapor transport.

*Ambient Temperature Release Experiments*

The mercury release measurements obtained from individual sample containers for the Year 2 sample set are shown in Figure 2. Over the duration of the entire 187 days of the experiment, five samples showed overall mercury release, and seven samples showed overall mercury sorption. The release of mercury, expressed as pg/g/day, was less for most samples in the final 90-day collection period than for the previous 90-day collection period. As evident in Figure 2, the variability of the data is relatively high, averaging -0.0002 pg/g/day. In part, the variability can be attributed to the variability inherent in the analysis of the extremely low concentrations of mercury captured by and desorbed from the gold-coated analytical traps.

**Elevated Temperature Release Experiments**

Mercury thermal desorption curves were generated for 57 CCBs, including 33 samples without and 24 samples with mercury control. The samples were primarily fly ash but also included various types of FGD materials and a dust collector ash. Most samples generated either one or two mercury peaks with a range of 0–4 peaks. The temperature of the primary mercury peak ranged from 145° to 747°C with an average of 411°C. Some samples actually continued to show increasing mercury release at 750°C, so the peak temperature at which the mercury was released could not be determined.

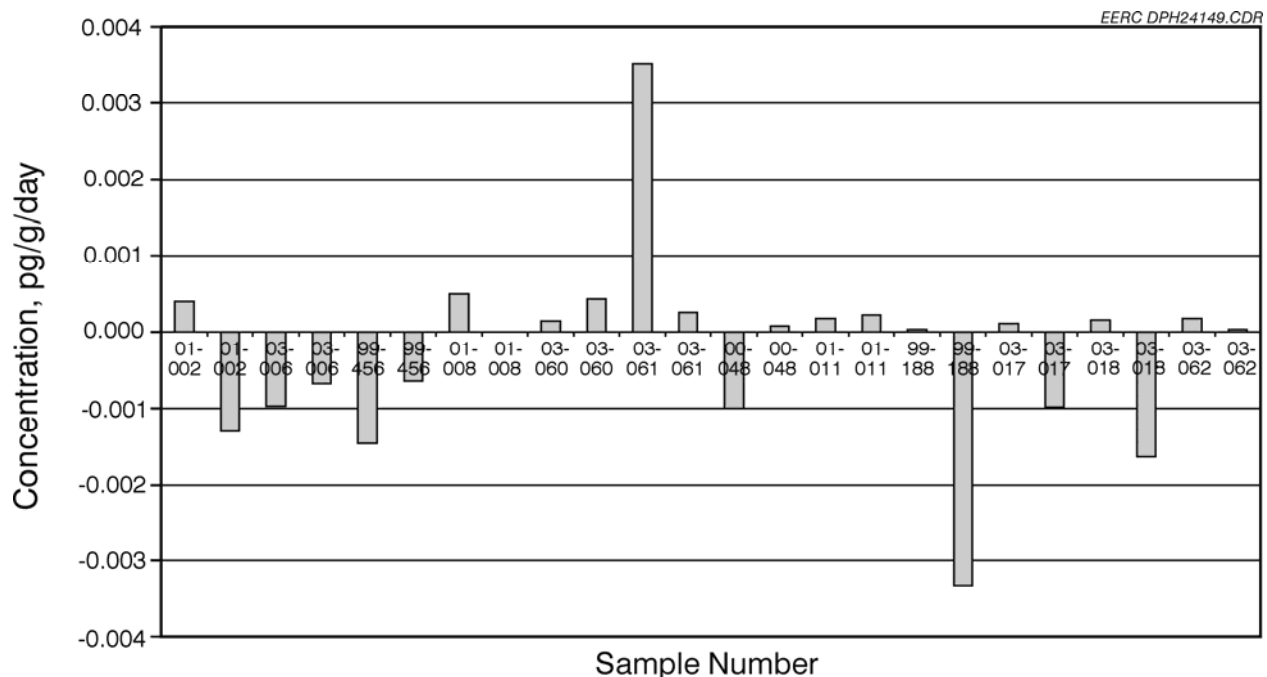


Figure 2. Average total long-term ambient-temperature mercury release or sorption as related to blank values, pg/g/day. Positive values indicate release and negative values indicate sorption of mercury.

Table 2 breaks down the information on the mercury thermal desorption curves by samples with and without mercury control testing. Samples consisting of or containing FGD material released mercury at a lower temperature than fly ash samples. The lowest mercury release peak temperature for a fly ash sample was 287°C. More samples from mercury control testing continued to release mercury at 750°C than those without mercury control testing. Most samples have not been duplicated but will be in order to confirm initial results.

**Table 2. Mercury Release at Elevated Temperatures**

Sample Type	No. of Samples	No. of Peaks	Peak Temperature, °C		
			Average	Minimum	Maximum
Without Hg Control	33	0–4	382	145	747
With Hg Control	24	1–3	456	302	740

It has been hypothesized that the mercury species associated with fly ash, FGD material, or carbon can be identified using thermal desorption techniques. Under this subtask, EERC researchers performed several experiments in an effort to confirm or refute this hypothesis. The experimental design focused on the use of analytical spikes using mercuric chloride and elemental mercury. The base samples for spike additions were CCB samples, quartz sand, or quartz powder. Mercuric chloride was dissolved in ether and then added to the base samples. Elemental mercury was added in a gaseous form to CCB samples.

In the mercuric chloride experiments, a single sharp peak with an average peak temperature of 266°C was recorded when the mercuric chloride was added to the quartz sand. When mercuric chloride was spiked onto the quartz powder, a double peak with an average peak temperature of 218°C was noted.

Additional elevated temperature release experiments were also performed on five CCB samples spiked with mercury. All samples used in this experiment were fly ash, and three of the samples contained activated carbon from mercury emission control demonstrations. The addition of mercury chloride or elemental mercury to the CCBs resulted in a shift of the mercury release peak(s) noted previously from the samples without any added mercury. The peak temperatures measured for spiked CCB samples shifted to higher temperatures for some samples and to lower temperatures for other samples. In one case, the release of mercuric chloride occurred at 260°C, but in all other cases, the release of mercury from mercury spiking was above 300° or 400°C. These data are under continued review, and additional experiments may be performed in Year 3.

Preliminary research was performed to evaluate the elevated temperature release of air toxic elements using the same apparatus as was used for the mercury experiments. The thermal desorption profiles for arsenic and selenium showed a gradual continuous release with respect to time and temperature. Initial arsenic and selenium thermal curves generated were inconclusive, and these experiments will continue in Year 3.

### **Microbiological Releases**

Early in Year 2, the release experimentation on one sample initiated in Year 1 was completed. Results indicated that the glucose-fed flasks released more vapor-phase elemental and organomercury compared to the starved flasks, with the aerobic glucose-fed flasks showing the highest mercury releases.

Three samples, see Table 3, were evaluated in aerobic and anaerobic glucose-fed conditions in triplicate using the new method. Sample 03-082 was a moist FGD sample, whereas the other two samples

and all previous samples were dry. A 20-gram sample, 150-mL buffer solution, a sample dependent amount of sulfuric acid, and a 100- $\mu$ L aliquot of a sulfate-reducing bacteria culture were used for evaluation. The bacteria were added 4 days after the addition of the buffer and acid to allow the systems to neutralize. The system was stirred intermittently over the duration of the experiment. Vapor-phase organomercury released from the system was captured in tubes containing Supelco Carbotrap™, and elemental mercury releases were captured on gold-coated quartz traps.

**Table 3. Samples Included in New Method of Microbiological Release of Mercury**

ID No.	Sample Type
03-079	Fly ash
03-082	FGD filter cake
04-043	Fly ash

In this experiment, 3 weeks elapsed before the addition of the buffer solution; therefore, the gold-coated quartz traps were analyzed to determine the amount of elemental mercury released from the samples in the interim period. Sample and blank flasks generally released similar low quantities of mercury, but Sample 03-082 under aerobic conditions released significantly more elemental mercury than the other samples. It should be noted that this was a wet FGD sample that was determined to contain a significant population of sulfate-reducing bacteria. The gold-coated quartz traps were then replaced on the flasks for collection of elemental mercury over the duration of the experiment.

After only 3 days of having bacteria present, Sample 03-082 under anaerobic conditions exhibited noticeable changes. The CCB changed from a cream to a gray color, and a hydrogen sulfide smell was emitting from the flasks. The gas from these flasks was directed to flasks containing zinc acetate to capture the hydrogen sulfide being produced. Fifteen days after the addition of bacteria, crystal-like formations were noted on the liquid surface layer from Sample 04-043, two flasks under anaerobic and one under aerobic conditions.

Upon completion of the experiment, evaluations included pH and Eh measurement, elemental and organomercury vapor releases, and solution organomercury content. Additional evaluations will include a bacterial count, solution elemental concentrations, solid elemental concentrations, and particle-size distribution.

After the liquid was filtered from the solid, pH and Eh values were determined. For Samples 03-079 and 03-082, the pH was higher under anaerobic conditions than aerobic; the opposite was true for Sample 04-043. Mold was noted in the Sample 04-043 aerobic flasks.

Vapor-phase mercury releases were analyzed as described elsewhere (4). In some instances, the results were highly variable for the replicate flasks. The highest release of both elemental and organomercury was from Sample 03-082 under aerobic conditions. Analysis of the gold-coated quartz traps from Sample 03-082 under anaerobic conditions resulted in a white, sulfur-smelling deposit on the gold trap. Analyzing the tubes containing Supelco Carbotrap™ from Sample 03-082 aerobic condition caused a sulfur smell to be released with no deposit formed. Analyzing the tubes containing Supelco Carbotrap from Sample 03-082 anaerobic condition resulted in a noticeable sulfur-smelling smoke to be released, and a subsequent formation of a white to yellow-colored deposit on both the Carbotrap and pyrolysis tubes. The amount of vapor-phase elemental mercury released coincided with the amount of mold present in the Sample 04-043 aerobic flasks at the completion of the experiment.

SPME was used to determine organomercury compounds in the liquid remaining in the flasks after the experimental collection period. Five mL of the liquid plus an aliquot of ethylmercuric chloride as an internal standard was placed into a 15-mL septum-capped non-actinic vial containing a Teflon-coated stir bar. 500  $\mu$ L of a pH 4.5 acetate buffer was added followed by 200  $\mu$ L of a 1% solution of sodium tetrapropylborate. SPME sampling was accomplished using a 100- $\mu$ m polydimethylsiloxane-coated fiber and sampler from Supelco. The headspace was sampled for 20 minutes after which the SPME fiber was directly introduced into the gas chromatograph (GC).

A GC coupled to an atomic fluorescence detector was used for the separation and detection of mercury compounds captured onto the SPME fiber. The GC temperature program began at 50°C, was held at that temperature for 2 minutes, ramped at 10°C/min to 250°C, and held there for several minutes. Inlet temperature was held at 200°C. Nonpolar megabore (0.53-mm ID) columns coated with either nonpolar methylsilicone or methylsilicone with 5% phenyl content worked well for this application. Adequate separations could be achieved using 15-meter columns. Helium gas flow was optimized for each column used. The gas exiting the GC through a heated length of uncoated 0.53-mm ID fused silica capillary tubing was directed to a thermal converter held at 800°C. Just before the gas entered the thermal converter, makeup helium was added for a total gas flow of approximately 25 mL/min. These chromatographic conditions allowed separation of elemental, dimethyl-, and diethylmercury as well as methylmercuric chloride. The results were highly variable.

Results of the microbiologically mediated release experiments are under continuing review.

### Field Investigations

Results from the mercury vapor measurements were not immediately available in the field. The gold-coated quartz traps were analyzed, and results are currently under interpretation. SPME determinations of organomercury species in liquid samples taken in the field indicated the presence of methylmercury. The amounts were small, but the high concentrations of solids in these samples made quantitation challenging.

### Data Reduction and Interpretation

A summary of the project data assembled is shown in Table 4.

**Table 4. Summary of Year 1 and 2 Accomplishments\***

Task	Proposed through Year 2 (without/with Hg Control)	Actual Accomplished to Date (without/with Hg Control)
Leaching	25/40	34/24
Vapor Transport 1 (elevated temperature)	25/40	33/24
Vapor Transport 2 (ambient temperature)	9/12	3/4
Microbiological Sample Analysis	6/6	4/1
Total Hg	NA**	47/27
Total As, Cd, Cr, Pb, Ni, and Se	NA	31/11
Carbon Forms	NA	17/9
LOI	NA	35/23

\* Total number of samples was 47 without mercury control and 28 with mercury control.

\*\* Not applicable.

### ***Quality Assurance/Quality Control***

The quality objectives of this effort support continued environmentally responsible management of CCBs and appropriate federal regulation of CCBs. Results of the 3-year project will provide an indication of appropriate utilization guidelines and disposal requirements. If the environmental performance of CCBs from conventional and advanced emission control systems is similar, it will facilitate the maintenance of current CCB markets and minimize the potential for an additional barrier to utilization of CCBs. If the environmental performance changes, the project will facilitate an understanding of appropriate management options and provide direction for any future regulatory assessment of CCBs.

Because this was a laboratory project to evaluate mercury stability in CCBs, most of the analyses of the samples were done using standard EPA-approved laboratory methods. Other laboratory techniques that did not have specific EPA-approved methods were performed in accordance with standard EERC laboratory practice.

The standard analysis techniques used in the project indicate acceptable performance criteria. The repeatability of the data was within the expected  $\pm 20\%$  with the exception of the data produced in the microbiological experiments. In this case, the experiments are still a work in progress with much improvement yet needed on the technique. This is nearing completion. Despite more variability than had been hoped for, the data still proved useful.

The thermal desorption curves of HgO and HgCl<sub>2</sub> released peaks at temperatures repeatable to within 10%. Again this is a technique in development and further improvements are expected.

In Year 2, leaching quality assurance/quality control (QA/QC) activities were performed including the inclusion of a leaching container (distilled water for SGLP) blank and a solution blank. Replicate leaching procedures were also performed on 17% of the samples evaluated. Both blank analyses yielded values below reporting limits except the solution blank nickel, which was slightly above the reporting limit. Replicate leaching evaluations indicated a typical RSD of 19%.

### ***Status***

The project is entering the third year of a 3-year effort. The following is a list of tasks to be completed during Year 3.

#### **Literature Search**

During Year 3, efforts to expand the existing EERC document database on the effects of mercury and other air toxic elements on CCBs, the mobility of those elements from CCBs, and new control technologies will be limited to adding appropriate documents through the end of the project. The document database was established as an online resource with links to obtain the full text.

#### **Analytical Methods Selection**

The methods selected for use in this project were identified early in the project with methods development continuing into Year 2. Method selection will be finalized at the conclusion of Year 2.

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### **Sample Identification and Selection**

Sample identification was completed during Year 2. While an adequate number of samples were identified and obtained, several sample types are underrepresented in the project sample set. Key samples of interest that are underrepresented are samples of subbituminous fly ash with activated carbon from mercury emission control demonstrations, samples of FGD liquids and solids both normal and with modifications to improve mercury capture in FGD systems, and fly ash samples both with and without added activated carbon that have been collected by fabric filters. Additional samples will be sought during the first two quarters of Year 3 to fill the sample gaps. In the event samples meeting the selection criteria cannot be accessed, alternate samples may be obtained from the EERC sample archives and from project sponsors.

### **Chemical and Physical Characterization**

The bulk chemical and physical characterization of project samples included total trace elements content, moisture content, loss on ignition, pH, and carbon forms for select samples. Select characterization will continue on remaining samples and samples collected in Year 3. The characterization data generated in Year 3 will be incorporated into the sample database and reports and will be used in data interpretation.

### **Laboratory Evaluation of Air Toxic Element Releases**

Task 5 will be a key task in Year 3. Subtasks will evaluate the potential for release of mercury by various mechanisms.

#### **Leaching**

During Year 3, research will continue to complete the SGLP–LTL leaching on all samples selected for this subtask. Also during Year 3, the effort to compare data from a variety of leaching procedures will continue in conjunction with a study led by DOE NETL. The EERC will complete a series of leaching tests (SGLP–LTL, serial batch leaching procedure [SBLP] (6), and the 3-Tier Method (7)) on two fly ash samples. These tests were initiated in Year 2.

#### **Vapor Transport**

The vapor transport experiments include the elevated and ambient-temperature vapor release experiments that have been ongoing through the duration of the project. In Year 3, the elevated temperature experiments will include the evaluation of the release of mercury. The apparatus used to profile elevated temperature releases may also be coupled with alternate detection systems in an alternate attempt to identify the species of mercury and other air toxic elements present on CCBs. The ambient temperature experiments, which are long-term experiments of up to 180 days, will continue to develop that type of data for mercury only.

#### **Microbiological Releases**

During Year 3, the evaluation of microbiologically mediated release of mercury from CCBs will continue. This task was modified to include not only the microbiologically mediated vapor-phase releases but also the microbiologically mediated leaching releases. This subtask will continue to evaluate these releases under aerobic and anaerobic conditions. An attempt will be made to correlate vapor-phase and leaching releases of organomercury compounds.

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### **Field Investigations**

The specific activities for Year 3 field investigations will need to be determined early in Year 3. The options for the Year 3 activity are as follows.

*Option 1* – At the same lignite CCB disposal site used in Year 2 investigations, it is proposed that fly ash with added activated carbon may be generated under a mercury emission control demonstration. If this demonstration is scheduled early enough in project Year 3, it is anticipated that the fly ash with activated carbon can be disposed in a discreet cell at the site. The Year 3 activity then will consist of evaluating the mercury flux associated with the disposed fly ash with activated carbon. Some replicate mercury flux evaluations will also be measured at the site to compare with those taken during Year 2.

*Option 2* – A similar mercury flux evaluation will be performed at an alternate CCB management site. The alternate CCB site will be selected based on the following prioritization: 1) presence of fly ash with activated carbon, 2) presence of high-mercury FGD material, 3) FGD gypsum land application, or 4) near-surface CCB use (stabilized soils or agricultural land application).

### **Data Reduction and Interpretation**

This task will be a major effort during Year 3 in order to prepare the final project report. During Year 2, laboratory data comparisons were initiated and preliminary conclusions drawn. With the set of data to be assembled with results of Year 2 and 3 efforts, these comparisons will be updated and preliminary conclusions reevaluated. Data reduction will include statistical evaluation of data, correlations between elemental content and various types of release data, and comparison and correlation (if appropriate) of laboratory data with field data. EERC data will be interpreted using the results of these data reduction techniques and incorporating appropriate available data from similar studies.

The culmination of this task will be the preparation of a comprehensive final project report which will include descriptions of the data reduction and interpretation process and the conclusions that will be drawn from these activities.

### **Potential Users/Technology Transfer**

The preliminary information generated in this project was used to prepare two reports for potential users. The first report was prepared for USWAG, which is a trade association serving utilities. The report generated under separate funding was made available to USWAG members who need to understand the impact of mercury emission controls on by-product management. Another report focusing on leaching data generated in this project was prepared for Cinergy, which provided the report to state environmental agency representatives. The information will facilitate decisions on revisions to Cinergy disposal permits. Utility by-product managers and environmental specialists are expected to be the users of the information generated in this project.

The following technology transfer activities were completed during Year 2:

- Loreal Heebink presented “Evaluation of Coal Combustion By-Product Mercury Rerelease Potential” at the 227th American Chemical Society National Meeting on March 29, 2004, in Anaheim, California.
  - The Year 1 DOE Final Report was completed and distributed to sponsors in April 2004.
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- The project's annual meeting was held on April 15, 2004, at the EERC in Grand Forks, North Dakota. Attendees/participants included Lynn Brickett, DOE NETL; Ken Ladwig, EPRI; Diane Stockdill, Great River Energy; and Tera Buckley, Kurt Eylands, John Gallagher, Gerald Groenewold, David Hassett, Loreal Heebink, John Pavlish, Debra Pflughoeft-Hassett, and Erick Zacher, EERC. James Roewer, USWAG, and R. James Meiers, Cinergy Corporation, participated via conference call.
- David Hassett gave a presentation entitled "HOT TOPIC – Mercury and Its Impact on CCBs" at the Coal Ash Professionals Training Course held May 10–13, 2004, in Bloomington, Minnesota.
- Debra Pflughoeft-Hassett gave a presentation entitled "Mercury Impacts on By-Products" at the DOE NETL Mercury Project Review July 14–15, 2004, in Pittsburgh, Pennsylvania.
- Debra Pflughoeft-Hassett presented "The Current State of the Science Related to the Rerelease of Mercury from Coal Combustion Products" at the 2nd Annual Sciencetech Stack Emissions Symposium, July 28–30, 2004, in Clearwater Beach, Florida.
- David Hassett and Erick Zacher attended the EPRI/EPA/DOE/Air & Waste Management Association Power Plant Air Pollutant Control "MEGA" Symposium held August 30–September 2, 2004, in Washington, D.C. Mr. Hassett presented a paper entitled "Determination of Organomercury Compounds from Microbiologically Mediated Mercury Release Experiments Using Gas Chromatography with SPME Sample Introduction after Boroethylation, Boropropylation, or Borophenylation," and Mr. Zacher presented a poster entitled "Long-Term Storage of Mercury Sampled from Ambient Air."
- Three abstracts, "A Method for Determining Microbiologically Mediated Release of Elemental and Organomercury Compounds from CCBs Using SPME, Gas Chromatography, and Atomic Fluorescence," "Long-Term Storage of Air-Sampled Mercury on Gold-Coated Quartz Tubes," and "Real-Time Thermal Devolatilization of Mercury and Mercury Compounds from CCBs Detected with Atomic Absorption Spectrometry," were submitted for consideration at PITTCON® 2005, February 27–March 4, 2005, in Orlando, Florida.
- Five abstracts were submitted for consideration and accepted to the 2005 World of Coal Ash Symposium, April 11–15, 2005, Lexington, Kentucky. The following two abstracts submitted pertain to ongoing mercury research: "Organomercury Compound Determination from Microbiologically Mediated CUB Samples," and "Quantitation and Interpretation of Release of Mercury from Coal Utilization By-Products." Ms. Pflughoeft-Hassett presented "Mercury, Coal Combustion By-Products, and the Potential for Rerelease" at the EERC Western Fuels Symposium, October 12–14, 2004, in Billings, Montana.

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