

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

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INTRODUCTION

A multiyear effort entitled “Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization” was undertaken by the Energy & Environmental Research Center (EERC) to evaluate coal combustion by-products (CCBs) for their potential to release mercury and other air toxic elements. Controlled laboratory experiments were used to perform these evaluations for the three primary release mechanisms:

- Direct leachability of air toxic constituents from CCBs
- Vapor release of mercury from CCBs at ambient and elevated temperatures
- Biologically induced leachability and vapor release of mercury and other air toxic elements from CCBs

A limited number of field measurements were also performed in an effort to compare laboratory and field data.

Selection and development of reliable experimental protocols to determine the releases of mercury and air toxic elements was a key project task. A large number of fly ash samples were selected for inclusion in the laboratory evaluations, and a limited number of flue gas desulfurization (FGD) materials were evaluated on the laboratory scale. This paper presents laboratory data on a specific subset of fly ash samples produced at a single facility and includes a true baseline sample and multiple test samples with varying levels and sources of activated carbon. Complete laboratory and field data will be included in the project final report.

BACKGROUND

The reduction of emissions at coal-fired power plants has historically impacted the quantity and character of resulting CCBs. The recently mandated removal or reduction of mercury emissions at coal-fired power plants has high potential to result in changes to both the quantity and character of fly ash because several proposed mercury emission control technologies involve the use of solid sorbents that will likely be introduced in the flue gas and collected with the fly ash. Other candidate emission control technologies focus on increasing the mercury sorbed on FGD materials. These mercury emission control technologies will impact the mercury content of these two CCB types. The question that this project was designed to answer is, “Will the changes in

CCBs associated with mercury emission controls change the management options for those CCBs as they relate to the potential release of mercury?”

Since the large volumes of CCBs produced annually in the United States are managed either by disposal or utilization, the design of various tasks in this project focused on simulating potential behavior of CCBs in environments where they are typically managed.

In order to adequately address the potential for release of mercury from CCBs, sorbents, and combinations, release mechanisms that must be evaluated include leaching, elevated- and ambient-temperature vapor-phase releases, and microbiologically mediated releases. The EERC initiated research on the potential release of mercury from CCBs in 1999 and found that methods for evaluating the release of mercury from CCBs using these mechanisms were not documented in the scientific literature, with the exception of leaching. As a result, the EERC initiated a program under the U.S. Environmental Protection Agency’s (EPA’s) Center for Air Toxic Metals[®] and the Coal Ash Resources Research Consortium[®] to develop laboratory methods that would provide information on the potential for CCBs to release mercury and other air toxic elements under conditions associated with the proposed release mechanisms of direct leaching, direct ambient- and elevated-temperature vapor-phase release, and microbiologically mediated leaching and vapor-phase release.

EXPERIMENTAL METHODS

Preliminary characterization of the CCB samples included moisture content, loss-on-ignition (LOI), pH, and total elemental concentrations. Laboratory experiments conducted to assess potential mercury and air toxic element release included direct leaching, elevated-temperature mercury release, long-term ambient-temperature mercury release, and microbiologically mediated mercury release. Detailed descriptions of the methods utilized were published in earlier project reports (1) and presented at the 2004 and 2005 U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) Mercury R&D Contractors meetings (2, 3). The data presented here for microbiologically mediated releases were obtained using a slightly modified apparatus that used a fly ash–soil mixture. Using this experimental apparatus and protocol, no solution was added to the system, so only vapor-phase releases were measured. A schematic of the apparatus is shown in Figure 1.

RESULTS AND DISCUSSION

A specific sample set was selected for use in presenting examples of data obtained in the project entitled “Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization.” The project sample set included 90 samples of fly ash and FGD materials. A summary of the samples evaluated in laboratory experiments is included in Table 1. The sample descriptions for the samples used in this paper are presented in Table 2.

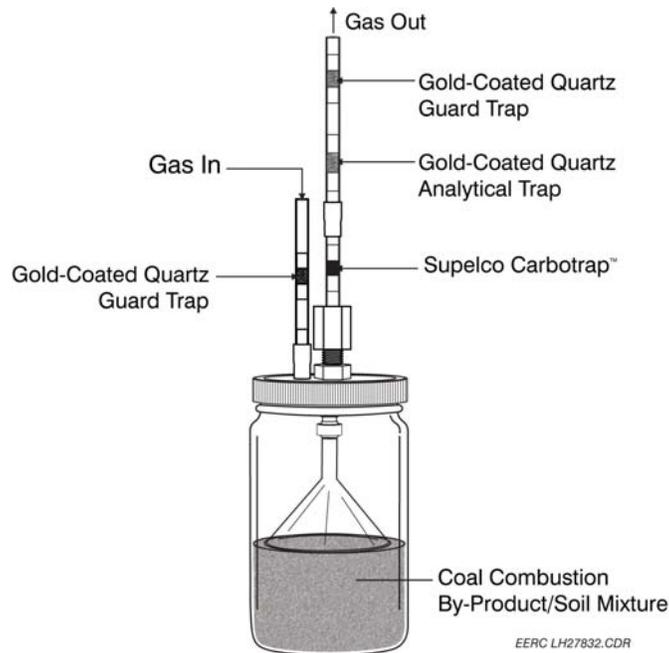


Figure 1. CCB–soil mercury vapor release collection apparatus.

The sample subset used to present results and discussion here includes a true baseline and samples from a variety of activated carbon injection (ACI) mercury emission control tests. The fuel was Fort Union (Canadian) lignite, and tests included both high-ash- and low-ash-content samples as can be identified by the measured LOI values. Moisture (not included in the table) was <0.5% in all cases. The pH of all samples was >10, indicating that long-term leaching was required in order to assess the impact of reactivity of the material on the leaching profile of the sample. The ratio of total mercury content to %LOI is also included in Table 2. The Hg/LOI ratio ranges from six to ten times higher in test samples as compared to the baseline sample.

Total elemental concentrations of the sample subset are shown in Table 3. Sample Low Ash-4 was analyzed in duplicate. As expected, the mercury concentrations increased markedly in samples from ACI as compared to the baseline sample. The high-ash-load samples exhibited lower mercury and selenium concentrations than the other ACI fly ash samples. This indicates that the mercury and selenium are associated with the carbon in the sample, yielding a lower total concentration in the high-ash-loading ACI fly ash samples. The other air toxic elements concentrations were similar for the samples from ACI and the baseline tests.

Leaching results for the sample subset are shown in Table 4. All leachate mercury values were below the 0.01- $\mu\text{g/L}$ detection limit. This is consistent with previous results indicating that the total mercury content does not correlate with the leachable mercury. CCBs with a high pH have the potential to undergo hydration reactions that can change the leaching profile with time. Elements most likely to be incorporated into the ettringite structure, a secondary hydrated phase, and exhibit a change in leaching profile with time are those that are present as oxyanions at high pH. Indirect ettringite formation is noted in some samples in the decreasing concentrations over time in the As, Cr, and Se leachate values.

Table 1. Summary of Solid Samples Evaluated Using Laboratory Experiments

Sample Type	Coal Type	Total of Samples	No. of Samples by Hg Control	24-hour pH Range	LOI Range, %	Total Hg Concentration Range, µg/g
Fly Ash	Eastern bituminous	26	9, with ACI	3.99–9.20	12.6–24.4	0.742–120
			17, no Hg control	5.52–12.44	0.47–12.7	<0.01–0.685
Fly Ash	Western bituminous	2	2, no Hg control	10.38–12.65	1.42–2.46	0.144–0.521
Fly Ash	Subbituminous	7	5 with ACI	10.95–12.60	2.11–4.14	0.640–5.81
			2, no Hg control	12.27–12.56	0.48–1.08	0.261–0.578
Fly Ash	Lignite	30	17, with ACI	10.52–12.77	0.59–13.2	0.147–64.5
			13, no Hg control	10.50–12.74	0.22–7.48	<0.01–0.878
Fly Ash	Lignite–subbituminous blend	5	5, no Hg control	10.98–11.51	NT ^a	0.287–0.802
Fly Ash	Unknown	5	5, unknown	8.69–9.65	10.5–12.8	0.362–1.21
Fly Ash + FGD–SDA ^b	Lignite	2	1, with ACI	12.50	1.12	0.332
			1, no Hg control	12.54	0.95	<0.01
Fly Ash + FGD–SDA FGD Material	Subbituminous	1	1, no Hg control	12.22	2.07	0.122
– Wet Mg-Enhanced Lime	Eastern bituminous	3	3, no Hg control	7.75–8.86	1.22–6.06	0.0323–1.80
– Wet Limestone (nonoxidized)	Eastern bituminous	6	6, no Hg control	7.70–12.43	3.11–6.19	0.136–0.305
– Wet Limestone (forced oxidation)	Eastern bituminous	3	3, no Hg control	7.72–7.95	1.60–2.26	0.0427–0.103

^a Not tested.^b Spray dryer absorber.

Table 2. Sample Subset Descriptions and Basic Characterization

ID No.	AC Type	AC Injection Rate, lb/Macf	Ash Loading, lb/Macf	LOI, %	24-hr pH	Total Hg, $\mu\text{g/g}$	Total Hg ($\mu\text{g/g}$)/% LOI
Baseline	NA ^a	NA	4.7	0.22	11.73	0.104	0.47
Low Ash-1	Luscar 4	2.5	4.7	13.2	11.33	39.0	2.95
High Ash-1	Luscar 4	2.1	34	3.84	12.00	12.7	3.31
Low Ash-2	DARCO [®]	2.0	4.7	9.45	11.41	35.9	3.80
High Ash-2	DARCO [®]	1.8	34	3.18	11.99	12.6	3.96
Low Ash-3	DARCO [®]	2.0	4.7	9.68	11.36	44.5	4.60
Low Ash-4	DARCO [®]	2.0	4.7	11.7	11.37	64.5	5.51

^a Not applicable.

Table 3. Sample Subset Total Elemental Concentrations, $\mu\text{g/g}$

ID No.	As	Cd	Cr	Pb	Hg	Ni	Se
Baseline	43.4	0.864	43.4	90.1	0.104	21.1	23.4
Low Ash-1	38.6	0.682	36.5	73.2	39.0	15.4	60.3
High Ash-1	48.3	0.865	42.6	87.1	12.7	18.6	22.5
Low ash-2	42.5	0.848	35.5	82.2	35.9	17.6	87.3
High ash-2	46.8	0.971	39.1	84.7	12.6	20.4	30.1
Low ash-3	38.4	0.776	42.2	74.5	44.5	22.0	42.2
Low ash-4	35.3	0.781	40.5	71.2	64.5	20.6	38.9
Low ash-4	35.6	0.635	39.0	72.7	NA	20.5	38.8

Determination of the vapor-phase release of mercury at elevated temperature was complicated by the high total mercury content of the ACI fly ash samples in this sample subset. As noted previously (4), the determination of elevated-temperature vapor-phase mercury releases was dependent on the total mercury present and, in most cases, 100% of the mercury present on a samples was released before the maximum temperature of the apparatus (750°C) was attained. For the sample subset being presented, sample size varied from 1.2 to 55.5 mg for the ACI fly ash samples, whereas 800–950 mg was needed for the baseline fly ash sample. The samples generally produced one to three separate mercury peaks. As already noted, reproducibility was affected by the need to use a small analytical sample.

Table 5 lists the temperature at which the first mercury peak was noted for each sample. The baseline fly ash sample behaved similarly to other lignite fly ash samples that have been tested at the EERC. In the ACI fly ash samples, the mercury was generally released at a temperature higher than what has been observed in other ACI fly ash samples. These data are consistent with the EERC's early conclusion (4) that mercury is not expected to be released at temperatures below 250°C.

Table 4. Sample Subset Leachate Results, µg/L

ID No.	Test	As	Cd	Cr	Pb	Hg	Ni	Se	Leachate pH
Baseline	SGLP ^a	8.1	1.1	169	<2	<0.01	18.9	60.5	11.85
Baseline	30-day LTL ^b	2.4	0.58	92	<2	<0.01	5.3	20.1	12.00
Baseline	60-day LTL	<2.0	0.67	88.6	<2	<0.01	5.2	26.8	12.09
Low Ash-1	SGLP	30.4	1.29	112	<2	<0.01	15.8	498	11.45
Low Ash-1	30-day LTL	30.4	1.08	159	<2	<0.01	5.9	312	11.66
Low Ash-1	60-day LTL	27.3	1.14	156	<2	<0.01	4.1	199	11.61
High Ash-1	SGLP	14.5	1.01	168	<2	<0.01	11.8	145	11.85
High Ash-1	30-day LTL	8.1	0.75	134	<2	<0.01	4.9	65.1	12.05
High Ash-1	60-day LTL	9.1	0.72	138	<2	<0.01	5	72.2	12.09
Low Ash-2	SGLP	24.6	1.5	141	<2	<0.01	20.3	343	11.51
Low Ash-2	30-day LTL	17.9	1.13	173	<2	<0.01	5.2	75.9	11.67
Low Ash-2	60-day LTL	14	1.16	167	<2	<0.01	4	73.2	11.68
High Ash-2	SGLP	16.3	1.49	153	<2	<0.01	12.2	147	11.88
High Ash-2	30-day LTL	9.9	1.06	147	<2	<0.01	5.4	100	12.04
High Ash-2	60-day LTL	11.7	0.9	133	<2	<0.01	5.3	114	12.07
Low Ash-3	SGLP	20.9	1.35	112	<2	<0.01	19.4	161	11.47
Low Ash-3	30-day LTL	17	0.96	152	<2	<0.01	5.6	47.7	11.55
Low Ash-3	60-day LTL	15.6	1.08	155	<2	<0.01	3.9	45.2	11.54
Low Ash-4	SGLP	20.2	0.99	119	<2	<0.01	23.4	99.3	11.38
Low Ash-4	SGLP	21.3	1.01	120	<2	<0.01	22.8	101	11.39
Low Ash-4	30-day LTL	18.6	0.85	166	<2	<0.01	7.1	66.4	11.52
Low Ash-4	60-day LTL	17.7	0.85	157	<2	<0.01	4.9	49.9	11.45
Low Ash-4	60-day LTL	17.5	0.89	160	<2	<0.01	5.1	46.1	11.49

^a Synthetic groundwater leaching procedure (5).

^b Long-term leaching.

Table 5. Sample Subset General Temperature of First Mercury Peak in Elevated-Temperature Mercury Release Experiments

ID No.	First Mercury Peak Temperature
Baseline	>330°C
Low Ash-1	>420°C
High Ash-1	>450°C
Low Ash-2	>430°C
High Ash-2	>430°C
Low Ash-3	>420°C
Low Ash-4	>380°C

Ambient-temperature vapor-phase release tests were performed on the sample subset described, and results are shown in Figure 2, expressed as rate of release in units of pg Hg/g sample/day. As shown in Figure 2, the rate of release is higher for each sample in the first period. It is hypothesized that the first reading (7 days of mercury vapor collection) is elevated in all cases

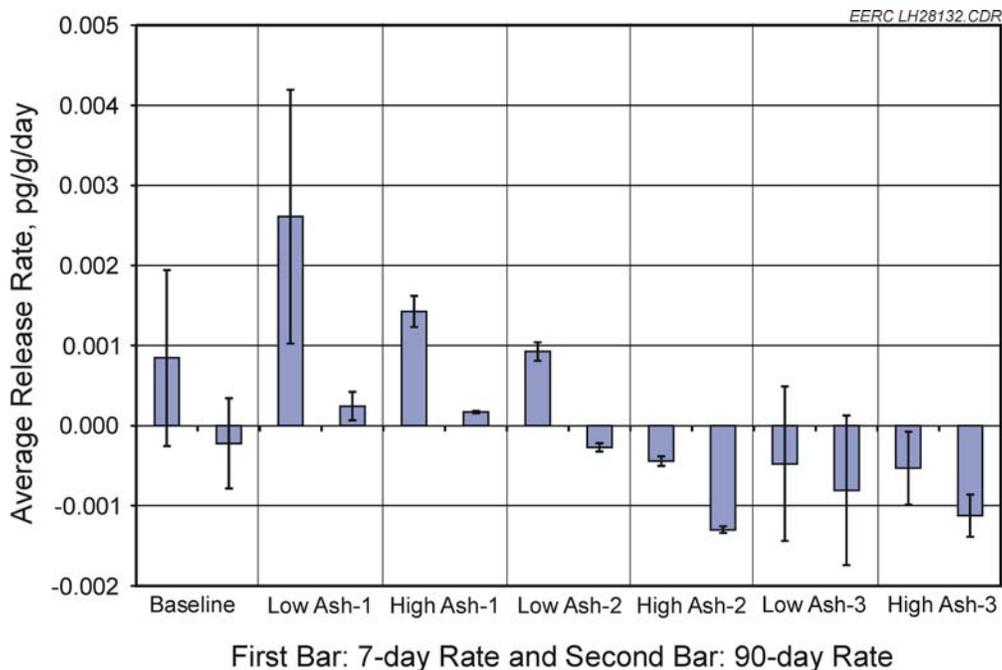


Figure 2. Sample subset long-term ambient-temperature mercury vapor release rate, pg/g/day. Positive values indicate mercury release, and negative values indicate mercury sorption.

because the sample is disturbed in the handling to introduce the sample to the experimental apparatus. A compilation of the data shown in Figure 2 is presented in tabular form in Table 6. Table 6 includes a column with the total mercury released over 97 days of the experiment and the percentage of the total mercury content released during that period. For the two samples that exhibited a net release over the 97 days, the number of years for 100% of the mercury to be released at the noted rate was calculated and presented in Table 6. The results indicated that the release or sorption of mercury from these samples is low, which is consistent with previous results from experiments performed on other fly ash samples from other sources. Example ambient-temperature vapor-phase release results from a variety of other samples from the larger project sample set are shown in Figure 3. Sample identification information is shown in Table 7. The FGD material sample represented in Figure 3 is one example of several FGD materials that were evaluated under this project. The data shown indicated that higher levels of mercury were released in ambient-temperature vapor-phase experiments, and this example is consistent with the limited data generated under this project. Based on observations of the ambient-temperature vapor-phase release of mercury from FGD materials, it is hypothesized that the mercury release, measured as Hg^0 , is likely due to chemical reduction via sulfite present in many FGD materials. It is also hypothesized that the chemical reduction is facilitated by the presence of water, which may explain the reduction in mercury releases from FGD materials with time and associated drying.

Table 6. Long-Term Ambient-Temperature Mercury Experiment Results

ID No.	Total Hg, $\mu\text{g/g}$	Average Total Sorbed or Released Hg over 97 Days, $\mu\text{g/g}$	Average % Sorption or Release over 97 Days	Average Years to Release 100% of Hg
Baseline	0.104	-0.000000139	-0.0000134	NA ^a
Low Ash-1	39.0	0.000000402	0.00000103	259,393,862
High Ash-1	12.7	0.000000253	0.000000199	134,078,921
Low Ash-2	35.9	-0.000000179	-0.000000498	NA
High Ash-2	12.6	-0.000000120	-0.000000950	NA
Low Ash-3	44.5	-0.000000759	-0.000000170	NA
Low Ash-4	64.5	-0.000000105	-0.000000162	NA

^a Not applicable.

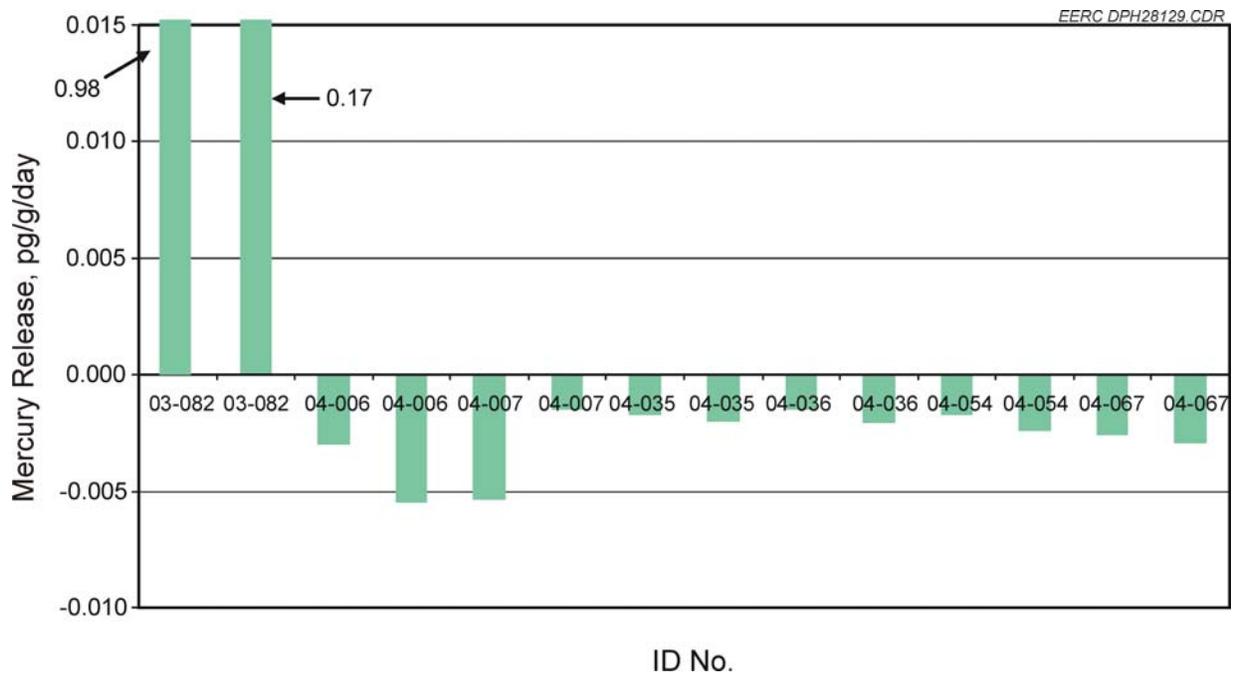


Figure 3. Long-term ambient-temperature mercury vapor release rate for various project samples, pg/g/day. Positive values indicate mercury release and negative values indicate mercury sorption.

The release experiments that presented the most experimental and analytical challenges under this project were the microbiologically mediated mercury releases. Initial experiments were designed to evaluate both the microbiologically mediated leaching and vapor-phase releases of inorganic and organomercury. These experiments and results were reported in detail in a project topical report (6). The experiments that were originally designed were successful for fly ash samples with low to moderate alkalinity. The experimental protocol was not well suited for making similar measurements on FGD materials or highly alkaline fly ash including those in the sample subset described in Table 2.

Table 7. Identification of Samples in Figure 3

ID No.	Sample Type	Coal Type	System	Hg Control	LOI, %	Total Hg, $\mu\text{g/g}$
03-082	FGD Filtercake (wet limestone – nonoxidized)	Bituminous	pc ^a – SCR ^b	None	4.20	0.218
04-006	Fly Ash	Bituminous	pc – FF ^c	None	1.42	0.144
04-007	Fly ash	Bituminous	pc – FF	None	2.46	0.52
04-035	Fly ash	Lignite	pc – ESP– CS ^d	None	2.24	0.159
04-036	Fly ash	Lignite	pc – ESP– CS	ACI & SEA1 ^e	2.16	0.287
04-054	COHPAC TM ash/sorbent	Bituminous	pc – ESP– HS ^f COHPAC	ACI	18.60	17.73
04-067	Fly ash	Subbituminous	pc – ESP– CS	ACI and SEA2	2.11	0.640

^a Pulverized coal.

^b Selective catalytic reduction.

^c Fabric filter.

^d Electrostatic precipitator–cold side.

^e Sorbent enhancing agent.

^f Electrostatic precipitator–hot side.

As noted in the Experimental section, a modified apparatus was used to evaluate the microbiologically mediated vapor-phase mercury release from fly ash–soil mixtures. A 20% addition of fly ash was made to the soil. Data collected for selected samples are shown in Figure 4. Additional samples are currently being evaluated using this alternate methodology including samples of FGD material. The rate of mercury release is higher than that for the ambient-temperature vapor-phase mercury releases noted in Figure 4, but final data presentation will be made in the project final report.

CONCLUSIONS

Based on the results of the laboratory experiments conducted in the project entitled “Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization,” the following conclusions were drawn:

- For comparative baseline and test samples containing activated carbon, elevated concentrations of selenium were noted in some samples containing activated carbon.
- Mercury is not readily leached from fly ash or FGD materials, and mercury leachate concentrations do not correlate to total mercury concentrations.

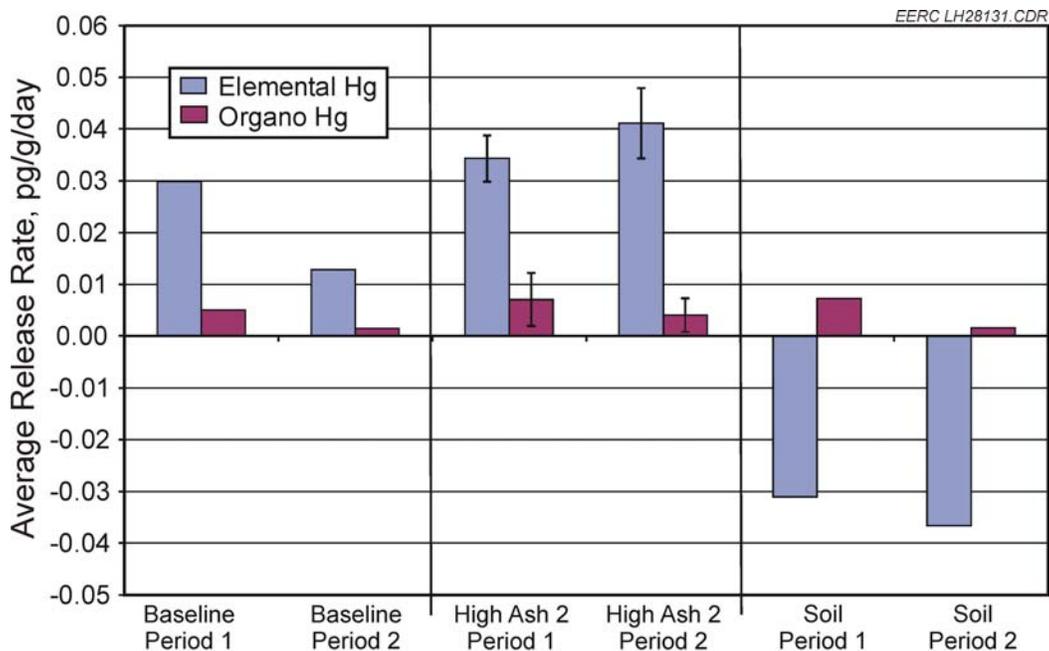


Figure 4. Sample subset microbiologically mediated mercury vapor release rate, pg/g/day. Positive values indicate mercury release and negative values indicate mercury sorption.

- The presence of activated carbon with fly ash may increase the temperature at which mercury is released when exposed to elevated temperature. Mercury is not readily released at temperatures below 250°C.
- Many fly ash samples, and especially those with unburned or activated carbon present, sorb mercury in ambient-temperature vapor-phase experiments. When releases were noted, they were extremely low both in total released over extended laboratory tests and in rate released. Laboratory data indicated that the potential for ambient-temperature vapor-phase mercury releases are unlikely to impact atmospheric mercury loading.
- Microbiologically mediated vapor-phase mercury releases were most challenging to carry out. Limited data indicated the potential for increased elemental mercury and organomercury release when fly ash was mixed with soil when compared to releases from fly ash alone.

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