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MERCURY STACK EMISSIONS FROM U.S. ELECTRIC UTILITY POWER PLANTS

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Abstract. Literature estimates for worldwide anthropogenic mercury (Hg) emissions range from 900 to 6200 t/yr. EPA recently estimated that U.S. electric utilities emit about 93 t/yr. EPRI, DOE, and others have recently conducted field measurements to better quantify electric utility emissions of Hg and other trace substances. Hg emissions inventories based on these recent measurements indicate that total electric utility Hg emissions are about 40 t/yr - about half of these previous estimates. Furthermore, the results have indicated that Hg emissions are quite variable and are not consistently captured by conventional air pollution control technologies - electrostatic precipitators, fabric filters, and flue gas desulfurization systems.

1. Introduction

Title III of the 1990 Clean Air Act Amendments (CAAA) mandated that the U.S. Environmental Protection Agency (EPA) evaluate emissions and health risks associated with 189 hazardous air pollutants from electric utility steam generating stations. Hg was singled out for two separate studies that will examine emissions from utilities and other sources and define the thresholds at which Hg affects health and ecology. In anticipation of the CAAA, the Electric Power Research Institute (EPRI) initiated the Power Plant Integrated Systems: Chemical Emission Studies (PISCES) research program in 1988 (Chow 1991).

As part of the PISCES program, the Field Chemical Emission Monitoring (FCEM) program was undertaken to fill critical data gaps in the literature. To date, the EPRI FCEM program has sampled at 35 utility sites - encompassing a range of fuels, boiler configurations, particulate control technologies, flue gas desulfurization systems, and NOx control technologies. Parallel to EPRI's efforts, the Department of Energy (DOE) has conducted field measurements as part of two DOE studies - the Clean Coal Technology program and the Comprehensive Assessment of Air Toxic Emissions from Coal-Fired Power Plants (Schmidt and Brown 1994). The combined studies provide the most extensive quality-controlled data set extant for estimating Hg (as well as other trace substances) emissions from electric utilities.

Parallel to the FCEM program, EPRI's work in Hg cycling highlighted the need to characterize the various species of Hg in stack emissions. EPRI sponsored development of a technique to speciate Hg, and at select sites, Hg speciation measurements were conducted. This paper summarizes recent Hg field results and quantifies total Hg emissions from electric utility power plants.

2. Literature

Various authors have estimated global anthropogenic Hg emissions. Using the geometric mean of the range of Hg emissions compiled by Nriagu and Pacyna (1988), present day worldwide fossil-fuel combustion was estimated to produce about 1500 t (1000kg)/yr (290 from electricity generation and 1210 from other industrial use). The U.S. EPA has compiled information about present day estimates of Hg emissions from many sources to the atmosphere in the U.S. that amount to about 300 t/yr in 1990 (MRI 1993). This study estimated that coal-fired power plants emit 89 t/yr, with total power plant Hg emissions of 93 t/yr. This estimate was based largely on Hg in coal data from the U.S. Geological Survey (USGS). The USGS analyzed thousands of channel and core samples of coal for various coal quality

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parameters, including Hg content. These data represent "in-the-ground" coals which are often different in Hg content from "as-fired" coals. After the coal is mined, the coal may be washed before it is pulverized and burned.

3. Recent Field Studies

The PISCES program was initiated in 1988, and the initial phase involved a compilation of an interim chemical emissions database based on literature information. EPRI and the Utility Air Regulatory Group (UARG) concluded that the literature data (1) contained significant gaps -- especially with regard to internal plant streams, (2) were highly variable for a given plant characteristic, and (3) were conducted using inconsistent sampling and analytical procedures (Radian 1992). The limitations in the database became the impetus for EPRI and DOE's intensive field data acquisition efforts. To date, 48 fossil fuel-fired power plants have been sampled by EPRI and DOE. Because some sites were tested under different configurations (i.e. pilot facilities, pre- and post-low NO_x burners, upstream and downstream of an flue gas desulfurization (FGD) system), more than one data set was obtained at some sites. The combined field studies include every significant coal type, boiler configuration, and particulate, SO₂, and NO_x control technology. The two sampling programs followed generally consistent sampling and analytical protocols. Triplicate samples were collected at each field site over a period of about 3 to 5 days. The results of these field studies provide a reasonable estimate of expected Hg emissions from utility power plants. However, because of the low concentrations of Hg and the nature of Hg, sampling and analysis have generally been difficult and significant uncertainty exists in the data.

3.1 HG IN FOSSIL-FUELS

The U.S. electric utility industry burns three major classifications of fossil fuels - coal, fuel oil, and natural gas. Figure 1 compares the measured Hg concentrations from the recent field sites with those in the literature for the three fossil fuels - coal, oil, and gas. The recent measurements have indicated Hg levels in U.S. coal range from 0.02 to 0.25 µg/g (emissions in the range: 0.5 to 10 µg/MJ; multiply µg/MJ by 2.3 to obtain lb/10¹² Btu). Hg levels in coal tend to be 1 to 4 orders of magnitude greater than in fuel oil and natural gas; thus it makes sense to discuss Hg emissions by these different fuel types.

3.1.1 Coal

The more recent measurements tend to be within the data range of the literature values, but do not include some of the high literature results. Because of the limited sample size from EPRI's field studies and in order to better quantify Hg concentrations in coal, EPRI and UARG sponsored a study to analyze 123 different "as fired" coals (Baker, Bloom). At select power plants, multiple samples were taken at different time intervals in order to evaluate variability. A total of 154 samples (106 bituminous, 37 sub-bituminous, and 11-lignite) were analyzed. These coal samples represent a significant portion of the current and anticipated future coal supplies for the U.S. utility industry. These include samples of coal from a total of 76 counties in all 18 major coal-producing states in the U.S. In aggregate, this study provides a broad-based representation of the Hg content in U.S. coals. The results are summarized in Table I. The overall mean Hg concentration in the 154 samples was 0.085 µg/g (standard deviation of 0.074 µg/g). The multiple samples from the select plants varied within 10 percent but did not significantly affect the mean. The mean of the 123 different coals was 0.088 µg/g.

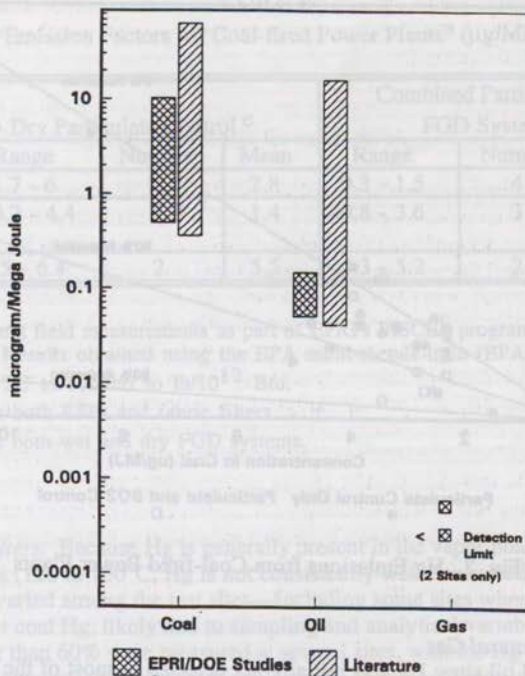


Fig. 1. Hg Levels in Fossil Fuels

TABLE I
Summary of Hg Concentrations by Coal Rank (Baker 1994)

Coal Type	Number of Samples	Arithmetic Mean ($\mu\text{g/g}$)	Standard Deviation ($\mu\text{g/g}$)
Bituminous	87	0.087	0.070
Sub-bituminous	37	0.053	0.027
Lignite	11	0.177	0.118
All Ranks	154	0.085	0.074

The results showed lower levels of Hg in the coal than the revised USGS coal database. The mean Hg concentration for bituminous coals from the EPRI/UARG study was $0.087 \mu\text{g/g}$. This compares with an average of 0.21 for bituminous coals based on the USGS database. As noted earlier, the USGS database represents as-mined core samples, while the EPRI study represents as-fired coal samples. Thus process steps such as coal washing remove some Hg and are not accounted for in the USGS analyses.

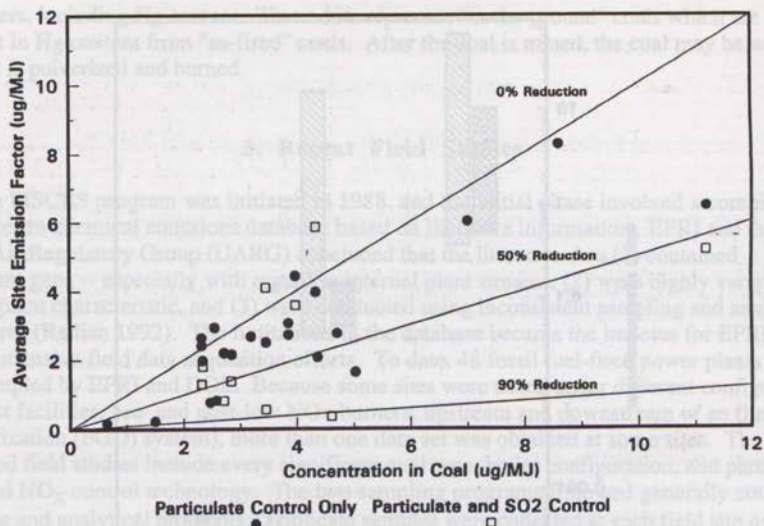


Fig. 2. Hg Emissions from Coal-fired Power Plants

3.1.2 Fuel Oil and Natural Gas

In the EPRI fuel oil sites, Hg was initially not detected in most of the fuel oil samples. To obtain lower detection limits, INAA (instrument neutron activation analysis) was used instead of CVAAS (cold vapor atomic absorption spectrophotometry). Using INAA with standards and blanks to ensure no loss of Hg, Hg was measured in the 0.002 to 0.008 $\mu\text{g/g}$ range (0.04 to 0.13 $\mu\text{g/MJ}$). This is 1 to 2 orders of magnitude less than in coal. Natural gas samples were analyzed for Hg at only two sites. Hg was detected at 0.02 $\mu\text{g/m}^3$ (0.00056 $\mu\text{g/MJ}$) at one site and below the detection limit of 0.01 $\mu\text{g/m}^3$ (0.00028 $\mu\text{g/MJ}$) at the other site.

3.2 FLUE GAS STACK EMISSIONS

All coal-fired plants employ some type of particulate control technology and some plants also include an FGD system. This is significant because particulate and SO_2 control systems may remove Hg. Only a fraction of the oil-fired plants have a particulate control device, and no commercial oil-fired plants use an FGD system. Gas-fired power plants are generally uncontrolled.

3.2.1 Coal-fired Power Plants

Figure 2 compares the Hg specific emission factors with the inlet coal feed for coal-fired units. Both the individual Hg emission rates and the inlet coal concentration are normalized to mass of Hg per unit of heat input ($\mu\text{g/MJ}$) to calculate Hg removals for each site. Hg removal is defined as the reduction in total Hg stack emissions relative to potential Hg emissions based on the Hg in coal concentrations. The results are presented for the two general air pollution control technologies - dry particulate control (ESP and fabric filters) and FGD systems (spray dryer absorbers and wet FGD systems).

TABLE II
Hg Emission Factors for Coal-fired Power Plants^a ($\mu\text{g}/\text{MJ}$)^b

Coal Type	Dry Particulate Control ^c			Combined Particulate and FGD Systems ^d		
	Range	Number	Mean	Range	Number	Mean
Bituminous	1.7 - 6	15	2.8	0.3 - 1.5	4	0.6
Sub-bituminous	< 0.2 - 4.4	7	1.4	0.8 - 3.6	3	2.1
Lignite	4.5 - 6.4	2	5.5	4.3 - 5.2	2	4.7

^a Based on recent field measurements as part of EPRI's PISCES program and DOE's field test efforts. Results obtained using the EPA multi-metals train (EPA Method 29).

^b Multiply by 2.3 to convert to $\text{lb}/10^{12}$ Btu.

^c This includes both ESPs and fabric filters.

^d This includes both wet and dry FGD systems.

ESPs and Fabric Filters. Because Hg is generally present in the vapor phase at particulate control temperatures (120 to 150°C, Hg is not consistently well controlled by an ESP or fabric filter. Hg removal varied among the test sites—including some sites where the outlet Hg was greater than the inlet coal Hg, likely due to sampling and analytical variability. By contrast, Hg removals greater than 60% were measured at several sites, with the Hg accounted for in the collected fly ash. However, an explanation could not be found why certain plants or coals yield more particulate phase Hg. The mean removal efficiency for all coal-fired plants with dry particulate controls was about 30%.

Wet FGD Systems. Hg removal efficiencies for a combined ESP (or fabric filter) and wet FGD systems were highly variable and gave poor correlation with the FGD design, coal composition, or measured Hg valence (oxidation) state. The Hg removal efficiencies for ESP/FGD systems ranged from as low as 0% to as high as 90%. Research has shown that oxidized Hg appears to be removed to a greater degree than elemental Hg (Peterson et al. 1994). However, only poor correlation was obtained with oxidized Hg or with Hg removal efficiency by FGD systems. The mean Hg removal efficiency for the combined ESP/FGD system was about 45%. EPRI, DOE, and other organizations are continuing work in this area to better understand Hg chemistry.

Emission Factors - The Hg emission results for coal-fired plants are presented for the three major coal classifications as well as the two general air pollution control technologies - dry particulate control (ESP and fabric filters) and FGD systems (spray dryer absorbers and wet FGD systems). The database is quite small for most of the categories, and this should be considered when applying the results in Table II. For example, the average Hg emission factor for units burning sub-bituminous coals with only particulate controls was actually less than the average Hg emission factor for the combination of the particulate and FGD system. This artifact was due to the small number of units studied. Two of the FGD systems had less than 25% Hg removal, while four of the dry particulate control sites achieved greater than 65% removal. Only two sites were tested that burn lignite coal; thus the confidence interval around the average emissions for these units is broad. The sites tested include both North Dakota and Texas lignite coals.

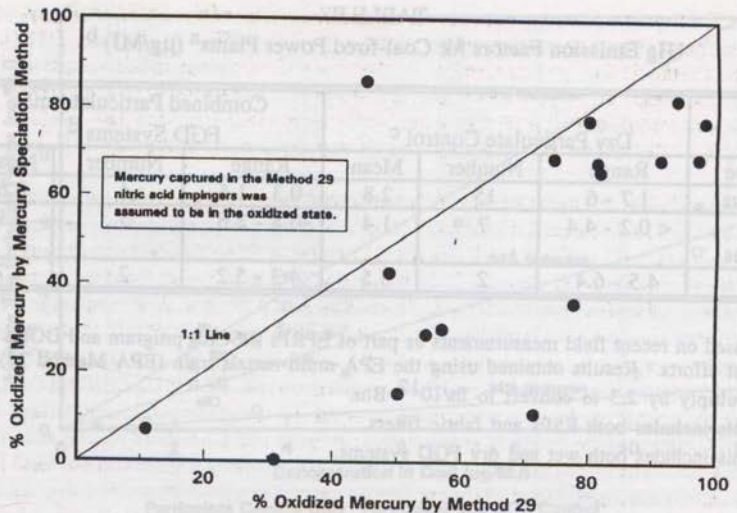


Fig. 3. Comparison of Hg Speciation Methods

Hg Speciation. Hg emissions may be present in several valence states - elemental (Hg^0) and oxidized (Hg^{+2}). This has significance for several reasons. The chemical form of the Hg may affect the degree of removal, as well as atmospheric fate, health effects, and risk assessment. EPRI has applied two sampling methods to quantify Hg emissions - the EPA multi-metals train (EPA draft Method 29) and the mercury speciation adsorption (MESA) method (Prestbo and Bloom 1995). EPRI has used both methods to provide some estimate of oxidized and elemental Hg. Neither method has been validated for Hg speciation. At some sites, the flue gas was sampled downstream of the ESP and some oxidation/reduction of Hg may occur before exiting the stack. In addition, oxidation/reduction of Hg may occur in the sampling system as well. Both methods are still experimental for Hg speciation, and further validation studies are planned. The multi-metals train uses two sets of impingers to capture the vaporous Hg. The first set of impingers consists of $\text{HNO}_3/\text{H}_2\text{O}_2$ and the second set consists of KMnO_4 . Method 29 was not designed to speciate Hg, but it has been suggested that only oxidized Hg is captured in the $\text{HNO}_3/\text{H}_2\text{O}_2$ impingers, thus all remaining Hg (which should be elemental Hg) is captured in the KMnO_4 impingers. The MESA method, designed to speciate flue gas Hg, follows a similar approach except it uses a different medium to capture the Hg. This method employs solid sorbent traps - consisting of soda lime and iodated carbon - to capture the oxidized and elemental Hg, respectively.

The oxidized Hg concentrations from Method 29 (this assumes that the Hg captured in the $\text{HNO}_3/\text{H}_2\text{O}_2$ impingers is oxidized Hg) generally appear to be higher than the oxidized Hg concentrations from the MESA method. Figure 3 compares the measured levels of oxidized Hg based upon these two methods. Because the two methods generally agree for total Hg (some sites having large discrepancies), it would appear that one or both methods does not accurately quantify oxidized Hg. The purpose of the $\text{HNO}_3/\text{H}_2\text{O}_2$ impingers in Method 29 was to capture the volatile trace metals (such as arsenic, chromium, and nickel) and was not intended to selectively capture oxidized Hg. Thus, some elemental Hg may be captured in the $\text{HNO}_3/\text{H}_2\text{O}_2$ impingers. The other possibility is that the MESA method does not efficiently capture all the oxidized Hg. Recent research has shown that the oxidized Hg capture efficiency in the soda lime traps is a function of the sampling temperature. Some of the early runs were

not conducted at optimum temperatures and it is possible some of the oxidized Hg was not captured in the soda lime traps—thus underestimating oxidized Hg. In addition, the MESA was not designed to sample flue gas isokinetically, thus the train may not obtain a representative sample of particulates. However, when detected, the particulate phase Hg has generally been a small fraction (<1%) of the total Hg. In addition to being present at very low levels in the particulate phase, the ESP or fabric filter would be expected to capture most of the particulate phase Hg.

For dry particulate controls (ESPs and fabric filters), the mean percentage of oxidized Hg levels based on the sorbent speciation and Method 29 trains were 55 and 70%, respectively. The mean percentage of oxidized Hg for FGD systems were 25 and 45%, respectively.

The ratio of oxidized and elemental Hg is potentially a function of the coal type and composition as well as flue gas conditions. Data were insufficient to determine any definitive correlations to predict levels of oxidized and elemental Hg—other than by direct measurement. Figures 4 and 5 compare the concentration of oxidized Hg (in $\mu\text{g}/\text{Nm}^3$ - normal [25°C , 1 atm]) as a function of Cl in the coal for the multi-metals and sorbent speciation methods. The results from the MESA method show a trend toward higher oxidized Hg concentrations with increasing Cl content in the coal. This trend was not apparent with the Hg speciation results from Method 29. It is important to note that some results appear to be "outliers" and there is significant scatter among the data. This may be due to other factors that affect Hg speciation and that have not been completely considered. In addition, some of this scatter may be due to process variability as well as sampling and analytical methods.

3.2.2 Fuel Oil-fired Power Plants

As part of the State of California AB2588 study, utilities attempted to measure Hg (as well as other trace substances) emissions from oil-fired power plants. The method detection limits were not sufficient to quantify the concentrations of Hg in either the fuel oil or the stack. In EPRI field sites, more sensitive analytical methods were used to achieve lower detection limits in both the fuel oil and stack measurements. INAA was used to analyze the fuel oil - instead of CVAAS. Using INAA, Hg in fuel oil was measured in the 0.002 to 0.008 $\mu\text{g}/\text{g}$ (0.04 to 0.13 $\mu\text{g}/\text{MJ}$) range. Assuming that all the Hg in the fuel oil is emitted in the stack, the Hg concentration in the flue gas would be approximately 0.1 to 0.4 $\mu\text{g}/\text{Nm}^3$. Because the Hg method detection limit (flue gas measurements) have ranged from 0.1 to 0.5 $\mu\text{g}/\text{Nm}^3$, these low levels of Hg have led to difficulties in quantifying the Hg concentration in flue gas for oil-fired power plants. Measured Hg stack emissions have ranged from 0.2 to 1.7 $\mu\text{g}/\text{Nm}^3$ (0.07 to 0.6 $\mu\text{g}/\text{MJ}$). The measured emission levels have been highly variable and have sometimes been much greater than the inlet fuel levels. Trace metals emissions data from fuel oil plant appear to be log normal, thus a geometric mean for Hg appears to be more appropriate than an arithmetic mean. A geometric mean reduces the emphasis on the very high measurements which are likely due to sampling and analytical difficulties. The geometric mean is 0.2 $\mu\text{g}/\text{MJ}$ (Table III); this emission factor is conservative since this is higher than the Hg levels in the fuel oil.

3.2.3 Gas-fired Power Plants

Field tests were conducted at two electric utility gas boiler sites. Hg was not detected at the stack at either site. The detection limit was about 0.5 $\mu\text{g}/\text{Nm}^3$ (0.17 $\mu\text{g}/\text{MJ}$) which was three orders of magnitude higher than the expected levels based on the natural gas analyses. The Hg concentration in the natural gas was measured at 0.00056 $\mu\text{g}/\text{MJ}$ (near the detection limit) at one boiler and less than the detection limit of 0.00027 $\mu\text{g}/\text{MJ}$ at the other. This yields an average of 0.00034 $\mu\text{g}/\text{MJ}$ (assumes half of the detection limit for the not detected value). The best estimate for Hg emissions would be to use the natural gas analyses and assume all the Hg is emitted in the stack (Table III).

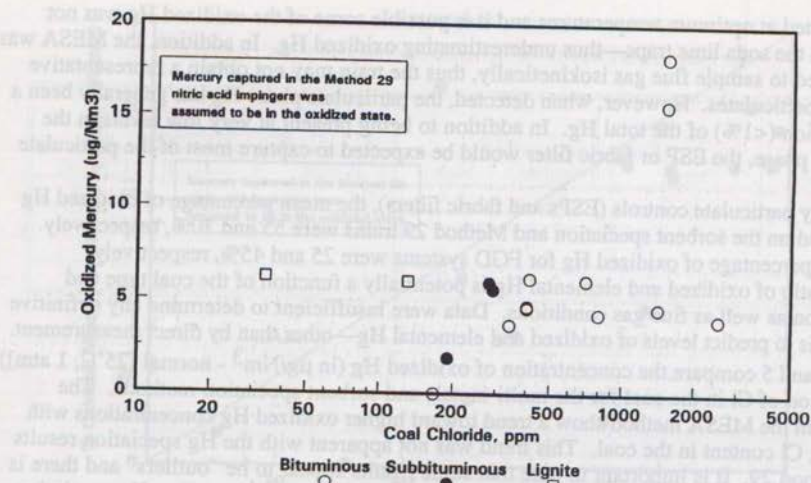


Fig. 4. ESP Outlet Oxidized Hg Concentration (Method 29) as a Function of Chloride Level

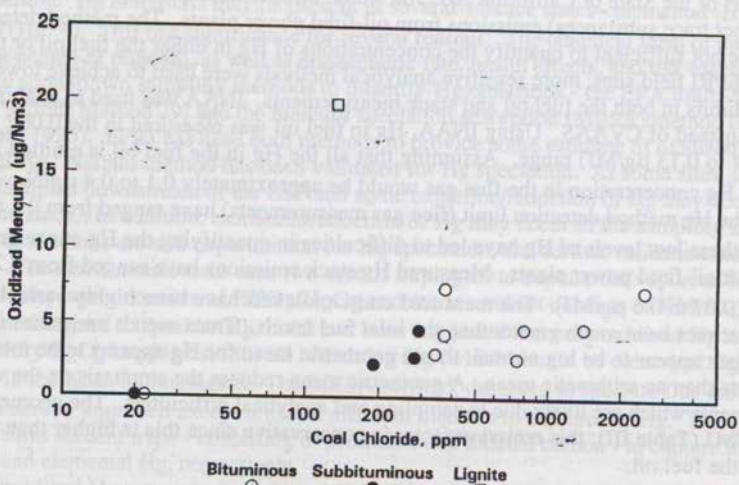


Fig. 5. ESP Outlet Oxidized Hg Concentration (MESA) as a Function of Chloride Level

TABLE III
Hg Emission Factors for Oil and Gas-fired Power Plants ($\mu\text{g}/\text{MJ}$)^a

Fuel Type	Range	Number	Mean
Fuel Oil	0.07 - 0.6	5	0.20 ^b
Natural Gas	<0.00026 - 0.00056	2	0.00034 ^c

^a Multiply by 2.3 to convert to $\text{lb}/10^{12}$ Btu.

^b Hg stack emission results for oil plants were assumed log normally distributed. This emission factor is a conservative estimate for oil-fired plants with ESPs.

^c Natural gas emission factors are based upon Hg in the inlet natural gas analyses, assuming that all Hg was emitted in the flue gas.

4. Total Electric Utility Emissions

Based on these recent and relatively extensive fuel and stack measurements, two approaches additional to MRI (1993) were employed to estimate total electric utility emissions from fossil-fuel fired power plants.

1. The more detailed approach incorporated the coal purchases for each individual power plant (EIA/DOE 1993) and average Hg concentrations based on the Hg coal analyses study (Baker, Bloom 1994) to estimate input Hg. Average removal efficiencies as calculated from the recent EPRI/DOE studies were then applied to estimate Hg emissions at each power plant. The individual Hg emissions were then summed to yield about 39 t/yr for the U.S. electric utility coal fired plants. Hg emissions from oil- and gas-fired utility plants estimated based on heat input data (MRI 1993) and average emission factors (Table III) were less than 0.3 t/yr.

2. An alternative approach applied the average emission factors for each category of fuel type and control technology from Tables II and III and the total heat input data for the U.S. utility industry. The UDI Power Statistics Database (1989) was used to calculate a weighted emission factor based on each of the categories of fuel type and control technology. This simplistic approach is similar to the methods used by other surveys such as MRI (1993), and yields a similar Hg emissions estimate as the detailed approach (described above) of 41 t/yr for the coal-fired power plants.

The estimated Hg emissions from these two approaches are compared with MRI's estimates in Table IV. Both approaches provide estimates of utility Hg inventory on the order of 40 t/yr for the 1990 period - less than half of MRI's estimate. Thus the revised U.S. total for Hg from all sources would likely be on the order of 250 t/yr (MRI 1993) - assuming the Hg emissions data for all other sources were correct. Power plants would amount to about 15 to 20% of the U.S. total, a number likely to decrease as newer generation technologies coming on-line.

TABLE IV
Total Hg Emission from Fossil Fuel-fired Power Plants (t/yr - in 1990)

Fuel Type	MRI ^a	EPRI Estimates	
		Fuel/Removal Efficiencies Methodology ^b	Emission Factors Methodology ^c
Coal	89	39	41
Oil	3.8	0.3 ^d	0.3
Natural gas	not estimated	0.001 ^d	0.001
Total	93	39.3	41.3

^a Midwest Research Institute (1993).

^b This methodology employs recent data on Hg in fuels and average removal efficiencies for ESP/fabric filters and ESP/FGD systems for coal fired power plants.

^c This methodology employs average emission factors and heat inputs. The emission factors were based on actual measured Hg concentrations in flue gases. This calculation is the same approach as MRI (1993), but uses the recent emission factors in Table II.

^d Based on recent emission factors in Table III.

5. Conclusions

Recent field measurements by EPRI and DOE better quantify Hg levels in fossil fuels and in flue gas emissions from electric utility power plants. These measurements show total Hg emissions from electric utility fossil-fuel fired power plants are about half of previous estimates. Hg is relatively volatile at nominal power plant stack temperatures, and is not consistently captured in conventional particulate and SO₂ control devices. The factors that affect Hg removal efficiencies could not be determined from the limited results available. Further, experiments on Hg speciation show the need for additional development work to develop reliable methods.

References

- Baker, S.S., EPRI Mercury in Coal Study: A Summary Report for Utilities That Submitted Samples, May 1994.
- Bloom, N.S. and E. M. Prestbo. In press. A New Survey of Mercury in U.S. Fossil Fuels. Pittsburgh Coal Conference. Pittsburgh PA 1993.
- Prestbo, E. M. and N. S. Bloom. Mercury Speciation Adsorption (MESA) method for Combustion Flue Gas : Methodology, Intercomparison and Atmospheric Implications. Accepted. WASP. This Volume/
- Chow, W., et al., Managing Air Toxics: Status of EPRI's PISCES Project, Proceedings of the Conference on Managing Air Toxics: State of the Art, November 4-6, 1991, Washington, D.C.
- Energy Information Administration, U.S. Department of Energy, Cost and Quality of Fuels for Electric Utility plants 1992, August 1993.
- Midwest Research Institute (MRI). Locating and Estimating From Sources of Mercury and Mercury Compounds. EPA-454/R-93-023, September 1993.
- Nriagu, J.O. and J.M. Pacyna, Quantitative Assessment of Worldwide Contamination of Air, Water, and Soils by Trace Metals, Nature 356:389, 1988.
- Peterson et al. "Mercury Removal By Wet Limestone Fgd Systems. EPRI HSTC Results." Proceedings of the 87th Annual Meeting and Exhibition of the Air & Waste Management Association, Paper 94-RP114B.01, June 19-24, 1994.
- Public Law 101-549, November 15, 1990.
- Radian Corporation, Evaluation of Emissions Information in the PISCES Database, Report DCN 92-213-161-02, March 1992.
- Schmidt, C.R. and T.D. Brown, Comprehensive Assessment of Air Toxic Emissions from Coal-Fired Power Plants, Proceedings of the 87th Annual Meeting and Exhibition of the Air & Waste Management Association, Paper 94-WA-68A.03, June 19-24, 1994.
- Utility Data Institute Power Statistics Directory Database, 1989.