Reports

Mercury Emissions from Coal Combustion

Abstract. Mercury liberated during coal combustion can be either discharged as vapor in the flue as or retained in the furnace ash. About 90 percent (by weight) of the mercury released from a furnace fired with pulverized coal appears to be in the vapor phase, and 10 percent remains with the furnace residual ash. For a 700-megawatt unit, approximately 2.5 kilograms of mercury per day are released.

The global amount of Hg mobilized from coal combustion has been estimated to be 3000 metric tons per year (1). Reported concentrations of Hg in coals range from 0.012 part per million (ppm) (2) to 33 ppm (1) with an average value of about 1 ppm (1) for certain U.S. coals. The total annual U.S. coal consumption is estimated at 10^{15} g (2). The authors of these studies cite the need for data on the Hg content in fuels, in the ash retained in the furnace and dust collectors, and in the flue-gas constituents emitted to the atmosphere. Such information is also of value for comparison with proposed federal Hg emission standards (3). We present here data on Hg concentrations and flow

rates in samples of coal, ash, water, fly ash, and flue gas from a large steam generator fired with pulverized coal.

The furnace tested serves a single 755-Mw (net) steam turbine-driven, electricity-generating set. During the period of test, the electrical output was maintained nearly constant at 660 Mw (net). Coal obtained from a nearby seam contains approximately 21 percent ash (< 1 percent S) and averages 9000 Btu (2270 kcal) per pound. Electricity is distributed to networks serving customers in four states. The total electrical capacity at the station is greater than 2000 Mw (net), or approximately 1 percent of the installed U.S. electrical capacity (4).

Table 1. Mercury balance in a furnace fired with pulverized coal. All samples were initially screened by anodic stripping voltammetry (ASV) with a modified electrode (δ); subsequently, samples were analyzed by radio-frequency helium plasma emission spectrophotometry (PE) (7) or neutron activation analysis (NAA) (δ). The value reported in each case is the average of the results of all techniques used.

Material	Method of analysis	Average flow rate (metric tons per day)	Average Hg concentration (µg of Hg per gram of material)	Average Hg flow rate (g/day)
Coal	ASV } NAA }	7,750	0.3	2,580
Furnace bottom ash	ASV } NAA }	330	.2	66
Recirculation duct and econo- mizer hopper ash	ASV } NAA	330	.2	66
Electrostatic precipitator hopper ash	ASV } NAA }	970	.2	97
Water return to river	ASV PE }	12,700	.001	13
Suspended fly ash	ASV } NAA}	2	.2	< 1
Flue gas	ASV } PE }	81,000	.033	2,500

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Samples of coal were obtained on each of 3 days from collections (averaged over 24 hours) taken for routine combustion analysis. Ash samples were taken directly from appropriate hoppers, including samples from the receiver bin for the slurry from the bottom ash, from beneath the economizer section, from the inlet duct leading to the gas recirculation fan, and from the hopper ash silos of the electrostatic precipitator. Water samples were taken from the adjacent river and from effluent returns for the slurry from the bottom ash. We sampled the suspended fly ash isokinetically at several locations across the outlet duct of the electrostatic precipitator using the Harvard in-stack filter thimble method (5). Samples of the effluent gas containing Hg vapor were obtained at the same location with apparatus suggested by the Environmental Protection Agency (Office of Air Programs) (3).

The vapor sampling train consisted of a condensate collection flask (dip tube in 100 ml of water) followed by four gas washing bottles (Corning 31760-125 EC), each containing 50 ml of an absorbing solution consisting of a mixture of 10 percent (by volume) H_2SO_4 and 1 percent (by weight) $KMnO_4$. Gas sample volumes ranged from 0.15 to 1.5 m³ during sampling periods of 24 to 390 minutes.

Three analytical methods of high sensitivity for trace metals were used to determine the Hg content of the samples: anodic stripping voltammetry (ASV) (6), radio-frequency helium plasma emission spectrophotometry (PE) (7), and neutron activation analysis (NAA) (6, 8). All samples received were initially screened by ASV to obtain an estimate of the more significant sample types involved in the Hg balance. The samples containing the highest concentrations of Hg were then selected for comparative analysis by NAA or PE. Methods of analysis used for each type of sample are indicated in Table 1.

Table 1 presents the concentrations of Hg found in each of the sample materials and the estimated or calculated flow rate of raw material and waste product streams from the furnace. The average Hg concentration in the coal was found to be 0.3 ppm for three consecutive 24-hour composite samples. Using this average Hg concentration and an average daily flow rate of coal, we calculated an average daily Hg input to the furnace of 2580 g/day. All collected ash, fly ash, and water samples

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were found to contain less than 0.5 ppm of Hg, with average values as indicated in Table 1. The total Hg loss in the ash and water streams from the furnace totaled approximately 250 g/day. About 10 percent of the Hg input is disposed of in these waste products.

The average Hg vapor concentration in the flue-gas discharge was 31 μ g/m³ (range, 6 to 82 μ g/m³ on four samples). On the basis of data on the flow rates of furnace flue gas, the average Hg discharge rate is approximately 2500 g/day. Most of the Hg appears to be discharged from the plant as vapor in the flue gas, as hypothesized by Bertine and Goldberg (2). The total Hg flow rate from the entire plant (three stacks, 2100 Mw) is estimated to be approximately 7.5 kg/day. The annual plant load factor, based on previous operating experience, is 0.72. The total amount of Hg emitted annually into the U.S. atmosphere from this source $(10^{15} \text{ g of coal per year, } 0.3)$ ppm of Hg) is estimated to be of the order of 10^3 metric tons.

Because of the small number of samples obtained in this preliminary study, the differing analytical methods used, and the range of the data used in averages, the overall average Hg balance (input versus output) does not check exactly. Apart from further extended sampling and analysis of fuels and emissions, there are several aspects of the problem of environmental Hg from fossil fuels that require further consideration. The fate of the vapor in the stack plume and its partitioning characteristics with respect to chemical constituents and attachment to aerosol particle during cooling will affect downwind Hg deposition and inhalation patterns. Atmospheric concentrations of Hg associated with suspended particulate matter have been reported to range from 1 to 5 ng per cubic meter of air (9). The biological consequences of the transport of airborne Hg are unknown. Technology for the control of Hg emissions from these large sources has not been developed, although Hg has been observed in effluent liquid from a fluegas scrubber for sulfur oxides.

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Oceanic Electric Fields: Perception by American Eels?

Abstract. American eels, long-distance migrating fish, consistently exhibited conditioned cardiac deceleration responses to electric fields as small as $0.167 \times$ 10-2 microampere per square centimeter in water of resistivity 4000 ohm centimeters (6.7 microvolts per centimeter) and 400 ohm centimeters (0.67 microvolt per centimeter). Fewer responses were shown at this current density (0.167×10^{-2}) microampere per square centimeter) in more saline water (40 ohm centimeters, 0.067 microvolt per centimeter) and at a lower current density (0.167×10^{-3}) microampere per square centimeter) in fresh water. Thus, eels have sufficient sensitivity to utilize geoelectric information for orientation.

Royce, Smith, and Hartt (1) have revived the suggestion that aquatic animals might use the weak electric fields generated in the ocean by water currents moving through the geomagnetic field for orientation or navigation. They suggested that Pacific salmon (Oncorhynchus), which migrate along ocean currents, may determine the direction of the water currents by means of this geoelectric field. Others have made similar hypotheses (2, 3); Deelder (4)offered electric field detection as one possible means by which migrating elvers of the European eel (Anguilla

anguilla) orient themselves in tidal streams.

Several groups of essentially nonmigratory fish have been shown to have sensitivity to very weak electric fields, for example, the weakly electric fish (Gymnotidae, Mormyridae) to 0.03 $\mu v/cm$ (3, 5), sharks (Scyliorhinus canicula) and skates (Raja clavata) to 0.01 μ v/cm (6), and bullheads (Ictalurus nebulosus) to 30 μ v/cm (7). However, determination of the electric current density to which the fish were exposed is not possible, since a nonuniform field was applied to known re-

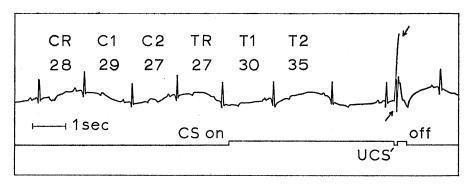


Fig. 1. Electrocardiogram of an American eel (number 73 in Table 2) during one training trial, showing apparent conditioned cardiac deceleration, presentation of weak electric field (CS) (0.167 \times 10⁻² μ amp/cm²), unconditioned stimulus (UCS), and designation of test and control heartbeats. CR, control reference beat; CI and C2, control beats; TR, test reference beat; TI and T2, test beats. The numbers are interbeat intervals in millimeters from the original EKG record. The arrows mark artifacts caused by UCS interference in the recording system. The EKG electrodes were disconnected from the recording circuit during UCS presentation.