Investigation of Mercury and Methyl Mercury Discharges from Flue Gas Desulfurization Systems at Four Coal-Fired Power Generation Facilities on the Ohio River

Ohio River Valley Water Sanitation Commission

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Abstract

Flue Gas Desulfurization (FGD) systems have become standard equipment for modernizing coal-fired power generation facilities. Most of the FGD system capacity based on the Ohio River was been installed between 2000 and 2009. Concern was held by ORSANCO that FGD systems could increase mercury discharges to the Ohio River as the systems removed the pollutant from air emissions with sulfur controls. Furthermore this project investigated concentrations of methyl mercury in power plant wastestreams for comparisons with methyl mercury concentrations in the Ohio River. This project consisted of quarterly monitoring at four power generation facilities for one year. Samples were collected from raw water intakes, FGD system wastewaters, and final discharges to the Ohio River that contained the FGD system waste stream. Sample data indicates the FGD Systems remove mercury along with sulfur but the removed mercury is captured by wastewater controls prior to discharge to the Ohio River. Methyl mercury results showed no increase in methyl mercury concentration or percentages of total mercury relative to raw Ohio River water power facility discharges. Finally, results indicate that wet transport of fly ash, independent of FGD systems operation, is a contributor to mercury discharges on the Ohio River.

Introduction

This monitoring project was planned to investigate total and methyl mercury concentrations, and other constituents, in Flue Gas Desulfurization (FGD) wastewater and power utility final effluent due to concerns that improved mercury capture from stack emissions could result in increased mercury loads to the Ohio River through wastewater discharges. The study also aims to determine if in-plant processes increase the formation of methyl mercury relative to ambient Ohio River water. To address that goal samples were collected in paired methyl mercury and total mercury sets from raw water intakes, FGD wastewater, and final effluents for each monitoring event. Monitoring was scheduled on a quarterly basis for one year although some events occurred outside the one-year period.

Background

ORSANCO has found, since aqueous low-level mercury testing began in 2001, common exceedences of the total mercury instream criteria of 12ng/L, with greater frequency in the lower Ohio River. The water quality criterion for total mercury in the water column is established to protect against undesirable accumulation of methyl mercury in fish tissue in excess of 0.3 mg/kg using a consumption-weighted approach. Data from the 2012 Ohio River 305b Assessment was not of a sufficient distribution of trophic levels to allow determination of support of the 0.3mg/Kg methyl mercury in fish tissue criteria (ORSANCO, 2012). ORSANCO has not assessed the Ohio River for support of the Fish Consumption use for mercury since the wider range of trophic levels was deemed necessary.

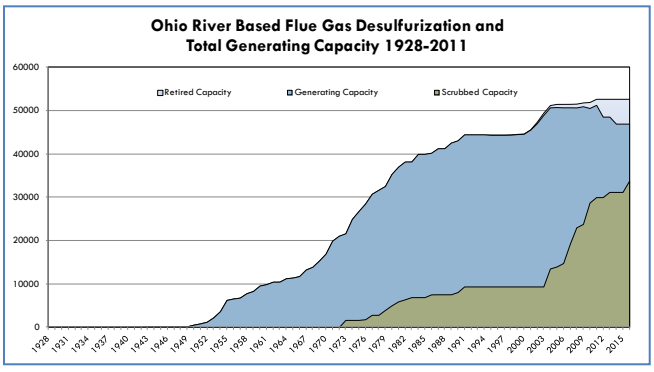
Coal-fired power generation is the largest source of anthropogenic mercury in the United States, however anthropogenic emissions of mercury in Asia, Africam and Europe exceed that in this country (USEPA, 1997; EPRI, 2000).

Of the nation's 317,619 megawatt hours (MWh) of coal-fired electric energy production capacity 31% is located in the Ohio River basin. A large portion of that, 43%, mostly from 28 large utilities, is located directly on the banks of the Ohio River, using it for cooling and other processes of power generation (EIA, 2011). Gaseous emission from the combustion of coal is the primary release pathway for mercury at these utilities. Implementation of acid controls for stack emissions has captured some of the mercury lost in the past. An impetus for this study was the concern that some captured mercury would be carried in the wastewater stream and discharged to the Ohio River.

Air Pollution Controls Effect on Mercury Emissions to Air

Flue Gas Desulfurization systems, though in use at utility scale in the U.S. and Ohio basin since the early 1970's (JAPCA, 1977), became widespread in response to the Clean Air Act Amendments of 1990 and by 2013 are now nearly ubiquitous on the Ohio River (See figure 1). Recent Implementation of Mercury and Air Toxics Standards (MATS) has caused intense interest in optimization of acid and particulate matter emission control systems to increase capture of mercury vapor in flue gas.

Figure 1: FGD Scrubber Installation for Ohio River Facilities 1928-2015 (projected)



Wet and dry FGD systems have been shown in the past to be only partially effective in capture

of elemental mercury (USEPA, 1997). However, more recent studies by industry groups and also summarized by USEPA show that operational changes can greatly increase the removal of mercury in existing FGD systems. Most importantly, maximum oxidation of elemental mercury prior to entering the FGD system, for example by Selective Catalytic Reduction (SCR) catalysts for NOx control, allow for greater mercury capture efficiency for the FGD system (USEPA, 2005). One report (EPRI, 2006) documented a coal-to-stack total mercury removal rate of between 65-97% at coal-fired power plants equipped with both wet FGD and SCR systems.

Oxidation of vaporized elemental mercury (Hg^0) to oxidized mercury species (Hg^{2+}) or particulate mercury occurs in homogeneous gas phase by chlorine and heterogeneously between particulates and mercury vapor in adsorption to unburned carbon, fly ash particulates, or on SCR catalysts (Niksa, 2004). Once the mercury vapor is oxidized and bound to particulates it is more easily captured by wet FGD systems and electrostatic precipitators (ESP) or fabric filtering systems. Once captured from the vapor state in the flue gas, most of the particulate bound mercury is partitioned to FGD or fabric filter solid waste byproducts (filter cake or gypsum). A portion of the mercury in the FGD reactor modules is partitioned to an aqueous wastestream as chloride purge stream (CPS), which must be discharged once the concentration of chloride exceeds about 10,000 mg/L.

The effectiveness of mercury removal in SO2 control systems is dependent on factors including coal feedstock, FGD oxidant type, flue gas temperature at particulate matter controls, availability of halides for oxidation, and availability of unburned carbon as available adsorbent. The level of chlorine in the flue gas is limiting to the oxidation process so subituminous coals, with lower chloride levels than bituminous, require mixing of bituminous coal or pretreatment with addition of other reducing agents (i.e. bromine). Injection of sorbent, most often powder activated carbon (PAC) or halogenated PAC to the flue gas, have been shown to increase mercury capture by subsequent wet FGD systems (USEPA, 2005). In addition, proprietary additives to the FGD recirculation fluid have been tested successfully in some systems (Renniger et. al., 2004)

Treatment of FGD wastewater

As shown by the attached inventory of power utilities on the Ohio River (Appendix A) the most common FGD systems on the Ohio River are wet systems. Wet FGD systems produce acidic wastewater that contains high concentrations of suspended solids including chloride, nitrogen, sulfur, and mercury (Riffe, et.al., 2008). Wet FGD wastewater is often treated within the plant and cycled back to the FGD system or discharged internally to fly and bottom ash pond systems, clear water pond treatment systems, or mixed with large volumes of cooling water prior to discharge, or discharged directly to the Ohio River.

Wastewater treatment and processing options include physical/chemical treatment and biological treatment via constructed wetlands or engineered contact with biological substrates. Basic physical/chemical treatment of FGD water involves pH adjustment by addition of an alkali and sulfate desaturation. Next, the wastestream passess through clarifiers (primary and secondary, in most cases), with particulate trace elements removed in this step. Further precipitation of metal sulfides is achieved by addition of an organo-sulfide and finally an iron salt increases flocculation for more metal precipitation and better clarifier performance. After coagulation, the slurry is dewatered using hydroclones or filter presses and the solids are removed and disposed in a dry landfill. (Heimbigner, 2007).

Monitoring plan

The project was planned for a one-year period of monitoring on a quarterly basis at four coal-

fired power plants. Three participating plants were to have online FGD units while one was to have no FGD system or a planned FGD system not yet in operation.

Samples were collected from the raw water intake for assessment of incoming mercury concentrations and the partition of methyl mercury in the process and cooling water. Internal outfall samples were collected from the FGD wastewater (CPS) at three FGD facilities. Finally, samples were collected from each utility's final outfall that included the input of the FGD wastewater. Although these target sample points were available at each utility, the underlying structure of air pollution controls, fly and bottom ash transport, and FGD wastewater treatment differed at each of the four facilities who participated in the monitoring project.

Project analytes included mercury and methyl mercury among other parameters representative of wet FGD-equipped coal-fired power plants. Most of these parameters have numeric water quality criteria applicable to the Ohio River. Mercury, methyl mercury, and selenium were analyzed by Brooks Rand Laboratories of Seattle, Washington. All non-metal parameters were analyzed by Pace Analytical Laboratories of Indianapolis, Indiana and Ormond Beach, Florida. The complete list of parameters analyzed is below:

- Filtered total Hg
- Unfiltered total Hg
- Filtered methyl Hg
- Unfiltered methyl Hg
- Total Selenium
- Bromide
- Dissolved Organic Carbon
- Dissolved Sulfate
- Ammonia*
- pH/Specific Conductance

*Late addition included in final events only

Participating Utilities

The four participating utilities are similar in size, with nominal generating capacities between 1200 and 1800MW and using the Ohio River as a cooling and process water source. One is located in Ohio, two in West Virginia, and one in Indiana. Each utility is between 30 and 50 years old. A plant summary from the US Energy Information Administration (USEIA, 2011) detailing environmental controls is show in Table 1.

Table 1: Plant Characteristics

Plant ID	Plant 1	Plant 2	Plant 3	Plant 4
Online Year	1967, 1977	1971	1980	1955
Generating Capacity	1800 MW	1560 MW	1300 MW	1200 MW
Number of Boilers	3 Units	2 Units	1 Unit	6 Units
Particulate Matter Online Year	1977-1980	1977-1978	1980	1979
Particulate Matter Unit	Electrostatic precipitator, cold side, without flue gas conditioning (One hot side also without conditioning)	Electrostatic precipitator, cold side, without flue gas conditioning	Electrostatic precipitator, cold side, without flue gas conditioning	Electrostatic precipitator, cold side, with flue gas conditioning (one hot side with conditioning)
Bottom Ash Transport	wet	wet	wet	wet
Fly Ash Transport	wet	Part dry (vacuum)	dry	dry
NOX Control Online Year	2000	2000	2000	2009
NOX Control	Low NOX burner Selective Catalytic Reduction	Low NOX burner Selective Catalytic Reduction	Low NOX burner Selective Catalytic Reduction	Overfire Air Selective Catalytic Reduction
FGD Scrubber Online Year	2007-2010	2007	2007	2013
FGD Scrubber Type	Jet Bubbling	Spray Type	Spray Type	Jet Bubbling
Scrubber Catalyst	Limestone	Limestone	Limestone	Limestone
Generative FGD	no recovery	gypsum recovery	no recovery	gypsum recovery
FGD WW (CPS) Volume	0.32 MGD	0.73 MGD	0.48 MGD	NA
FGD WW Treatment	Physical/chemical	Physical/chemical	Physical/chemical with bioreactor	Physical/chemical with wetland
Final Effluent (w/ CPS) Discharge Point	12.58 MGD (Non-cooling)	5.79 MGD (Non-cooling)	4.31 MGD (Non-cooling	20.5 MGD (Non-cooling)
Fuel Type	Bituminous	Bituminous	Bituminous	Mix Bituminous/Subitu minous

Monitoring Data

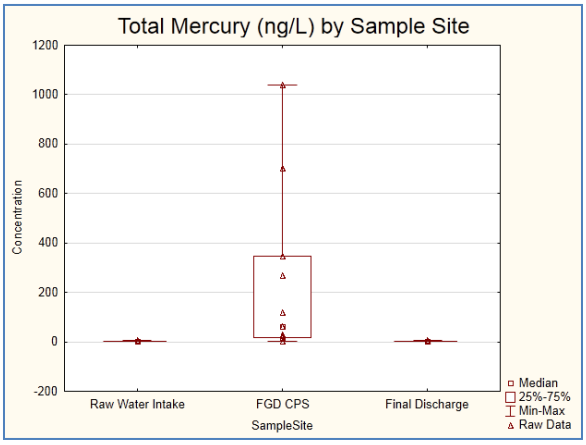
Samples were collected at the four plants from March 2012 through December 2012. Sampling was performed quarterly to capture conditions under summer power and winter production demands and the lower demand spring and fall power generation period. Sample results are presented in full detail in Appendix B. Findings specific to each pollutant in Ohio River raw intake water, FGD wastewater, and final effluents are discussed here.

Total Mercury

Mercury was analyzed by Brooks Rand Laboratories (BRL). The method detection limit (MDL) achieved for this project was 0.15 ng/L with an associated reporting limit (RL) of 0.41 ng/L. At those very low detection limits all samples generated detections above the detection limit with 20% qualified as estimates due to concentrations greater than the MDL but less than the RL. The highest concentrations observed came from the unofficial FGD wastewater sample points with a maximum over 1000 ng/L but a most of the data less than 100ng/L and a median value of 8.4 ng/L.

Each of the three FGD systems showed higher concentrations of mercury in the treated FGD wastewater than in the raw water intake or final discharges (Figure 2). During the monitoring period no sample of raw water intakes from the Ohio River or final discharges to the Ohio River exceeded the instream human health water quality criterion of 0.012ug/L (12.0 ng/L) total mercury. All raw water intake concentrations were in the range normally observed in the Ohio River with a maximum of 5.5 ng/L. The maximum observed concentration in a final discharge sample was slightly lower at 4.9 ng/L.

Figure 2



The average mass loading of total mercury in grams per day was calculated for each sample location (Table 2) using design flow volumes for FGD wastewater and final effluent including the FGD wastewater (Table 1). Raw water intake mass shown in Table 2 does not include the volume discharged without the FGD wastewater. It should be noted that the actual discharge flow at the time of collection could have been less than the design flow. These calculations show that the two plants where final effluent is discharged from bottom ash impoundments without additional clearwater ponds show a net increase in total mercury loads from intake to final effluent. The two plants discharging from a final clearwater pond show a net decrease in total loading. The total mercury increases from those systems averaged 0.06 grams per day.

Table 2: Total Mercury Net Increase/Decrease from Intake to Effluent (g/day Averages)

Plant	Raw Water Intake	FGD CPS	Final Effluent	Net Inc/Dec
Plant 1	0.139	0.111	0.144	0.005
Plant 2	0.069	1.522	0.040	-0.029
Plant 3	0.053	0.020	0.048	-0.006
Plant 4	0.122	NA	0.233	0.111
Average	0.096	0.551	0.116	0.020

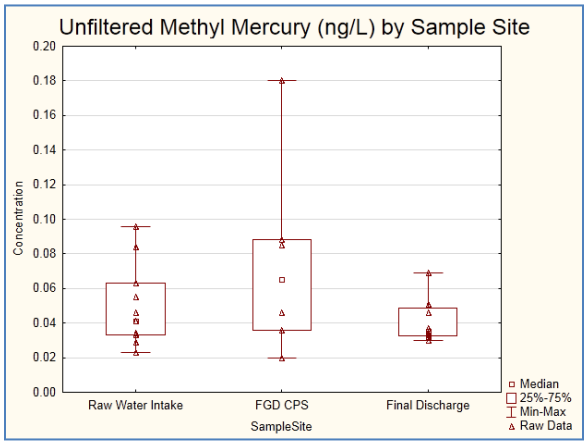
Methyl mercury (MeHg)

Concentrations of methyl mercury, also analyzed by Brooks Rand Laboratories with an

extremely low detection level, were very low. The reporting limit achieved by BRL was 0.002 ng/L. Methyl mercury, however, is present in such low concentrations and percentages of the total mercury present in the Ohio River, tested FGD wastewaters, and facility final effluents that only 9 of 41 samples yielded an unqualified result. Median values reported below include the qualified "estimated" values that fall between the method detection limit and the laboratory reporting limit.

The median unfiltered methyl mercury concentration of Ohio River raw intake water to the participating plants was 0.041 ng/L; an estimated value below the reporting limit and shown in Figure 3. The median concentration of all plants final discharges to the Ohio River was lower, 0.034 ng/L while samples of the chloride purge stream showed a slightly higher median of 0.046 ng/L.

Figure 3

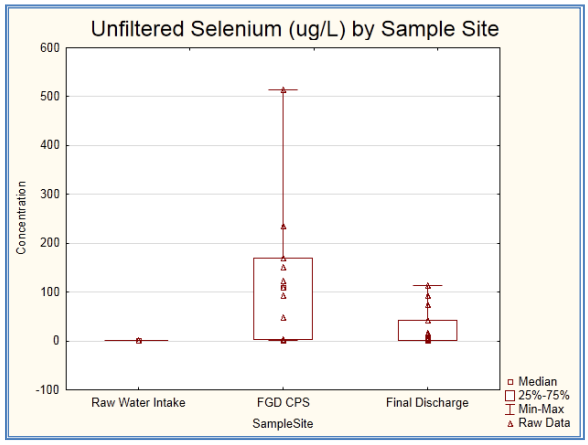


The maximum methyl mercury concentration observed was 0.18 ng/L in an FGD system chloride purge stream. During that event the MeHg concentration in raw intake water and final discharge effluent were equal. As a whole final discharges to the Ohio River revealed less MeHg relative to Ohio River intake water, including one facility which showed no detectable methyl mercury from its discharge in all four events. This finding is not surprising as all of the FGD systems studied are forced oxidation types. Thus, the FGD wastestream has a high redox potential, indicating oxidizing conditions. The formation of methyl mercury, at least in the environment, only occurs under reducing conditions such as that in anoxic sediments.

Selenium

Selenium analysis was done at BRL with a method reporting limit of 0.072 ug/L. About two-thirds of raw Ohio River water samples were above the MDL, with all concentrations being less than 1.0 ug/L (Figure 4). In CPS water the detection rate was 100% with a median concentration of 100ug/L.

Figure 4



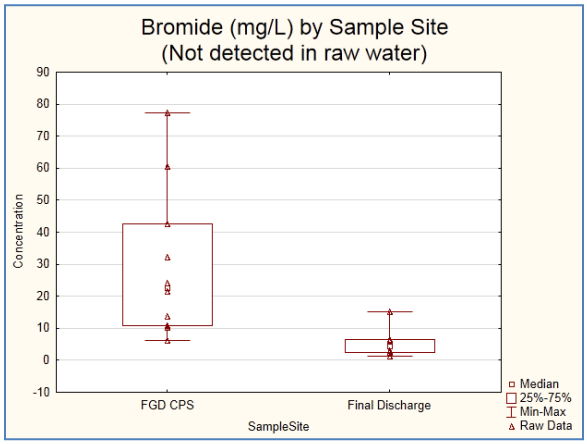
Final discharges contained selenium concentrations significantly higher than in raw intake water but with median concentration of 5ug/L. This concentration is equal to the chronic aquatic life criterion value.

Bromide

Bromide was analyzed by Pace Analytical Laboratories with a method reporting limit of 1mg/L. This reporting level did not allow detections of bromide in raw Ohio River intake water. A separate ORSANCO study has found that bromide levels in the Ohio River rarely are above 0.1 mg/L. Bromide concentrations were high in all CPS waters and detected in half of the final discharge samples (Figure 5). The plant

without a FGD online showed no detections of bromide in final discharge waters.

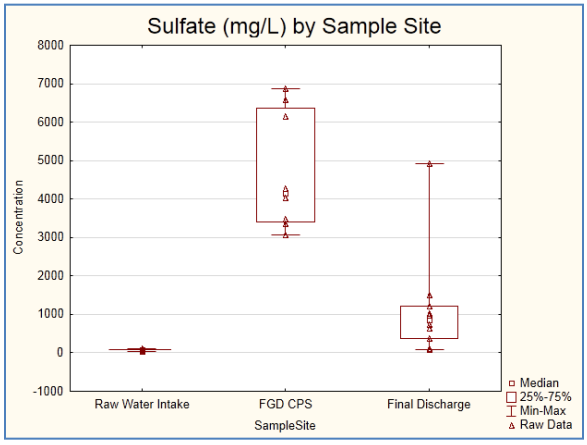
Figure 5



Sulfate

Sulfate is nearly always present n Ohio River waters. In this study it was detected in all raw water intake, CPS, and final discharge samples. The final discharges contained sulfate levels more than 100 times that of the Ohio River and commonly above the 250mg/L secondary drinking water criterion for sulfate (Figure 6).

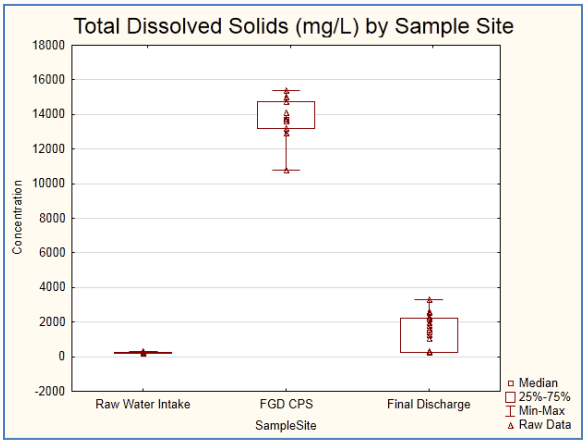
Figure 6



Total Dissolved Solids

ORSANCO implemented a 500 mg/L secondary water quality criterion for total dissolved solids in the 2012 Pollution Control Standards. The secondary standard applies only at drinking water intakes and is in place to protect those intakes from adverse taste and odor. That protective criterion does not apply to discharge waters though it is a useful benchmark for the quality of those discharges. During this study the maximum and median TDS concentrations in Ohio River raw intake water samples were 278 mg/L and 213 mg/L, respectively, while the final discharges showed a median of 1417 mg/L with a maximum of 3280 mg/L (Figure 7).

Figure 7



Conclusions

The study was conceived as a characterization of FGD discharges for the Ohio River though it was known from the start that a comprehensive evaluation of all FGD-equipped power plants on the Ohio River would not be possible. On the Ohio River there are no two FGD systems that are alike when pre- and post- treatments are considered. In spite of that, this study's quantification of methyl mercury in some FGD wastewater has provided useful information. Most importantly it was found that in these four systems there were no increases of methyl mercury concentrations from the raw intake water to the final discharge water. Other conclusions relating to mercury discharges from FGD systems follow:

- No violations of the 12ng/L total mercury criterion were observed in final effluent.

- Concentrations of total mercury in final effluents containing FGD wastewater are consistent with concentrations found in Ohio River intake water.
- Methyl mercury concentrations were consistent across raw intake, FGD wastewater, and Final Effluent.
- Bioreactor treatment is effective for mercury, selenium, and bromide
- Study average mass discharge:
    - FGD wastewater mercury mass averages ranged from 1.5 to 0.02 g/day total mercury.
    - Final effluents when separate from ash transport water release less total mercury per day than taken in from the Ohio River.
    - Results indicate mercury sequestered by FGD systems is effectively captured in solids and later secondary clear water ponds and not discharged to the Ohio River.
    - At two plants net decreases in mercury mass are shown in the effluent containing FGD wastewater than is taken in at the intakes.
    - Total mercury mass contributed to the Ohio River by the two plants with net mass increases would result in increases to Ohio River concentration several orders of magnitude less than the water quality criterion.

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