The Behavior of Mercury Emissions from a Commercial Coal-Fired Power Plant: The Relationship Between Stack Speciation and Near-Field Plume Measurements

4 AUTHORS, INCLUDING:

Matthew S Landis
United States Environmental Protection Agency
91 PUBLICATIONS **2,439** CITATIONS

Arnout ter schure
Electric Power Research Institute
17 PUBLICATIONS **524** CITATIONS

Behavior of Mercury Emissions from a Commercial Coal-Fired Power Plant: The Relationship between Stack Speciation and Near-Field Plume Measurements

Matthew S. Landis* and Jeffrey V. Ryan

U.S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, North Carolina 27709, United States

Arnout F. H. ter Schure

Electric Power Research Institute, Palo Alto, California 94304, United States

Dennis Laudal

Energy & Environmental Research Center, Grand Forks, North Dakota 58202, United States

Ⓢ *Supporting Information*

ABSTRACT: The reduction of divalent gaseous mercury (Hg^{II}) to elemental gaseous mercury (Hg^0) in a commercial coal-fired power plant (CFPP) exhaust plume was investigated by simultaneous measurement in-stack and in-plume as part of a collaborative study among the U.S. EPA, EPRI, EERC, and Southern Company. In-stack continuous emission monitoring data were used to establish the CFPP's real-time mercury speciation and plume dilution tracer species (SO_2, NO_X) emission rates, and an airship was utilized as an airborne sampling platform to maintain static position with respect to the exhaust plume centerline for semicontinuous measurement of target species. Varying levels of Hg^{II} concentration (2.39−3.90 $\mu g\ m^{-3}$) and percent abundance (~87−99%) in flue gas and in-plume reduction were observed. The existence and magnitude of Hg^{II} reduction to Hg^0 (0−55%) observed varied with respect to the types and relative amounts of coals combusted, suggesting that exhaust plume reduction occurring downwind of the CFPP is influenced by coal chemical composition and characteristics.
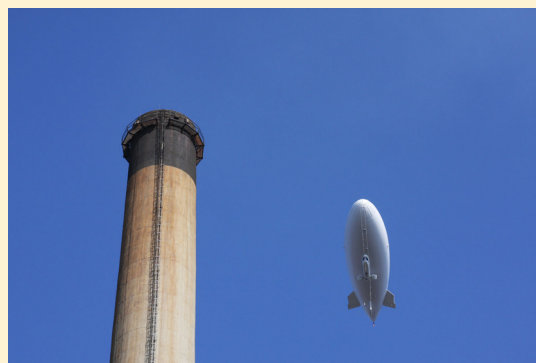
■ INTRODUCTION

Anthropogenic sources of mercury (Hg) to the atmosphere have been extensively studied,[1−5] with the most recent global estimate established as 1960 tonnes being emitted in 2010.[6] About 16% of these global anthropogenic emissions were attributed to commercial coal-fired power plants (CFPPs). In North America, coal combustion was the largest Hg source category, contributing an estimated 43.4 tonnes (71%) of the estimated 60.7 tonnes emitted in 2010.[7] Mercury in the exhaust plume of a CFPP typically consists of three main fractions: elemental gaseous mercury (Hg^0), divalent gaseous mercury (Hg^{II}), and particulate-bound mercury (Hg(p)). It is important to ascertain the relative distribution of Hg fractions emitted since each has different physicochemical properties that strongly determine its environmental fate.[8] Theoretically, Hg^{II} and Hg(p) fractions deposit on local or regional scales via wet and dry atmospheric deposition processes because of their solubility, reactivity, and higher deposition velocities; while Hg^0 is more likely to be transported long distances and contribute

to the global atmospheric burden.[8−11] Field measurements have demonstrated that Hg emissions from CFPPs can have near-source impacts, and contribute to enhanced wet and dry atmospheric deposition on local and regional scales in regions with significant coal-burning sources.[12−14]

Several recent studies hypothesized the reduction of Hg^{II} to Hg^0 in CFPP plumes after emission from the stack, which if parametrized and incorporated into deterministic model runs would partially mitigate the near-field impact of atmospheric Hg deposition currently estimated using contemporary in-stack speciation estimates.[15−18] Briefly, Hg^0, Hg^{II}, and Hg(p) measured at three sites in the southeastern U.S. for 21 plume-impact events showed that total gaseous mercury (TGM; $Hg^0 + Hg^{II}$) was essentially conserved from the point

of emission to the sites, and that Hg^0 was the dominant form (84%). However, emission estimates indicated that Hg^0 should represent approximately 42% of the TGM. Results showed that observed Hg^{II}/SO_2 ratios were lower by a factor of 2−4 compared to expected ratios. In-plume reduction of Hg^{II} to Hg^0 was postulated as one of several possible explanations.[15] Nine of the aforementioned plume-events were simulated with the Reactive & Optics Model of Emissions (ROME) in a separate study.[18] The simulations first failed to reproduce the measured depletion in Hg^{II}, but when two possible reduction pathways for Hg^{II} (a pseudo-first-order decay and an empirical reaction with SO_2) resulted in better agreement with the observations.

In 2002, a study was conducted to investigate in-plume Hg behavior at the Plant Bowen (GA, U.S.A.) CFPP using a fixed-wing aircraft as an airborne sampling platform.[19] The investigators flew repeated crosswind transects through the plume to collect sufficient mass for integrated manual Hg speciation analysis. The researchers found that Hg^{II} concentrations appeared to decrease slightly in samples taken approximately 20 km downwind of the stack, as compared to levels in integrated stack samples. The Hg^0/Hg^{II} ratio was 84% of the estimated in-stack ratio suggesting reduction of Hg^{II} to Hg^0 as the plume was advected. A combination of deposition and/or chemical changes in the plume was suggested to explain these results.[19] In 2003, a second CFPP in-plume study was conducted at the Pleasant Prairie Power Plant (WI, U.S.A.). The study also used a fixed-wing aircraft and a similar sampling design. The researchers estimated a 44% reduction in the fraction of RGM between the stack exit and the first sampling location (0.5 km downwind), and a 66% reduction from the stack to 8 km downwind, with no additional reduction between 8 and 16 km downwind.[20,21] While both of these studies were suggestive of in-plume Hg^{II} reduction to Hg^0, the lack of concurrent time-resolved stack and plume data, and the small number of measurements precluded robust statistical conclusions.

A recently published multiseason experiment was conducted in 2000 to study the mercury speciation in the plume of the 3640 MW Nanticoke coal-fired power plant in Southern Ontario.[22] A fixed-wing aircraft equipped with semicontinuous instrumentation for Hg^0 and manual sampling systems for Hg^{II} was used. While the authors observed significant discrepancies between dilution-corrected estimated and measured in-plume Hg^{II} concentrations, they concluded the lower in plume Hg^{II} concentrations could be explained by potential bias between in-stack and in-plume measurement techniques.

Projecting the effectiveness of planned controls in reducing mercury emissions from CFPPs depends on an accurate understanding of the reduction/oxidation chemistry of Hg species in the atmosphere and associated changes to deposition phenomena. Since contemporary air quality models use emission rates and speciation estimates based on in-stack measurements, any near field in-plume reactions that significantly alters Hg speciation will affect the accuracy of the model dispersion and deposition estimates. Although the in-plume Hg reduction reactions hypothesized by surface ambient observations[15] and some initial in-plume measurements[20,21] may alter the source attribution of CFPPs to local and regional Hg deposition, the existence of a significant reduction is still open to debate,[22] and our understanding of a plausible reduction/oxidation chemical mechanism remains limited.[23,24]

This paper presents results from a study designed to provide data for a statistically robust analysis of the plume reduction hypothesis, using simultaneous high temporal resolution measurements of Hg fractions (TGM, Hg^0) and tracer gases (SO_2, NO_y) in-stack and in-plume conducted at a CFPP located in the southeastern U.S.A. In-stack continuous emission monitoring (CEM) data were used to establish the CFPP's real time Hg and tracer species emission rates, and an airship was utilized as an airborne sampling platform to maintain position in the exhaust plume for semicontinuous measurement of target species. The relationship between observed and expected in-stack versus in-plume Hg fraction concentrations based on observed dilution ratios (DRs), and the implications for in-plume Hg^{II} reduction to Hg^0 are presented and discussed.

■ MATERIALS AND METHODS

Study Design. This study tested the null hypothesis that Hg^{II} is not significantly reduced to Hg^0 in the emissions plume of a CFPP. Simultaneous high-resolution (2.5 min) speciated Hg measurements were made in a CFPP stack and in the resulting exhaust plume using an airship. The novel aspects of this study included (i) utilizing the same automated continuous measurement techniques in the stack and in the plume, thereby reducing the potential for measurement bias, and (ii) the use of an airship to maintain constant position with respect to the exhaust plume centerline (Supporting Information (SI) Figure S1) at various dilution ratios (distances) rather than traversing back and forth across the plume with fixed-wing aircraft, resulting in a larger number of independent observations on which to test the null hypothesis relative to the SO_2 and NO_Y dilution tracer species.

Selection of CFPP. After a thorough review of candidate facilities (see SI), the Crist Plant located in Pensacola, Florida was selected for this study. The facility is owned by Gulf Power Company (Pensacola, FL), a subsidiary of Southern Company (Atlanta, GA). The Crist Plant consists of four coal-fired units sharing two stacks. During the selected sampling period of February 18 to March 1, 2008 units #4 and #5 that feed one of the stacks were both shut down for maintenance. The remaining boilers, unit #6 (320 MW) and unit #7 (500 MW) shared a common 138 m tall stack. Both units had cold-side electrostatic precipitators (ESPs) for particulate control and Unit # 7 had selective catalytic reduction (SCR) that operates year round for NO_x control. Both units were burning a blend (nominally 50%) of Illinois (high in sulfur and high in halogens) and South American (Columbian) bituminous coal (low in sulfur and low in halogens). The coal was manually "blended" by a front end loader alternately dumping loads of coal from two separate storage piles onto a conveyor belt. The terrain surrounding the plant is essentially flat, and no other significant near-field Hg emission sources were identified.

Crist Plant Stack Emissions Measurements. As the stack serving the two active boilers during this study did not have integrated sampling ports for emissions monitoring access, all continuous emissions monitoring systems (CEMs) were installed in the exhaust ducts of each boiler unit prior to discharge into the common stack collocated with the facility's CEM systems. As a result, overall reported stack emissions are calculated as the proportional average of each exhaust duct normalized to its flow rate. As a function of the Crist Plant's participation in EPA's Acid Rain Program, the plant staff measured sulfur dioxide (SO_2), oxides of nitrogen (NO_x), and

volumetric exhaust gas flow in each boiler exhaust duct in accordance with 40 CFR Part 75 (see SI).

Total and speciated Hg emission measurements were made by EPA in each of the two boiler unit ducts using EPA's Tekran Instruments Corporation (Knoxville, TN) model 3300 series speciated Hg CEM systems (SI Figure S2 and associated description). In the standard Tekran 3300 configuration as deployed during this study, TGM and Hg^0 measurements are made sequentially using a single Tekran Model 2537A cold vapor atomic fluorescence spectrometer (CVAFS) that switches between and alternately samples each channel (SI Figure S3). The Tekran 3300 systems were programmed to measure TGM and Hg^0 semicontinuously over a 2.5 min collection/analysis cycle. The reported Hg^{II} fraction is calculated as the difference between sequentially measured TGM and Hg^0 concentrations. An initial multipoint calibration was performed with Hg^0 on each Tekran CEM following installation and conditioning. Continued measurement performance of each Hg CEM was verified through daily System Integrity/Drift Tests using Hg^0 and $HgCl_2$ gas standards as described in EPA Method 30A.[25] The Hg CEM stack sampling systems were continuously monitored by on-site personnel during the plume sampling periods to ensure data were available during all airship flight sorties.

Additional Speciated Hg Measurements. The reliable measurement of Hg^0 and Hg^{II} was a critical component of this study. Many variables contribute to the quality and reliability of speciated Hg measurements, including the effects from particulate matter which can not only capture gaseous Hg, but can also oxidize Hg^0.[26] Verifying the quality of the Hg CEMs speciated Hg measurements is difficult and is primarily accomplished by comparison to other speciated Hg measurement techniques, including the Ontario-Hydro (OH) method. For this study, the quality of the speciated Hg CEMs measurements was assessed through comparison to three independent speciated Hg measurement approaches (see SI).

Crist Plant Coal Measurements. The coal burned as fuel during the study was sampled at each of the two active unit feeders once a day during each flight-day using a grab sample technique. The coal's composition was then analyzed on an "as-received" wet and dry weight basis. The coal was analyzed for a suite of constituents including halogens and trace metals.

Airship Operations. EPA contracted with Integrated Systems Solutions, Inc. (ISSI; California, Maryland) to provide an airborne sampling platform for this study. ISSI provided an Airship Management Services (AMS; Greenwich, CT) Skyship 600B and flight crew. The AMS Skyship 600B is 61 m long, 19 m wide, 20 m high, and holds approximately 7,200 m^3 of helium. The airship was powered by two engines with vectorable propellers which allowed for vertical launch, three-dimensional maneuverability, and the ability to maintain a fixed position in winds up to 11 m s^{-1}. The airship met our specifications to accommodate a 2300 kg instrument payload, three scientists, and provide 40 A of 120 VAC power. In addition, the airship had a 650 km range and an endurance of 8 h at a cruising speed of 65 km h^{-1}. The airship was equipped with a state-of-the-art avionics package including an encoding altimeter, air temperature sensor, and redundant global positioning systems.

The operational flight window for this study was from February 18 to March 1, 2008. Conducting the study in the winter was advantageous in that (i) the plume thermal buoyancy was maximized and in general kept the plume at a safer sampling altitude, and (ii) lower atmospheric turbulence minimized initial emission plume dispersion. Each sampling day consisted of approximately 7−8 h of airship flight time (depending on wind speed and the resultant fuel burn required to maintain airship positioning). The first hour of each flight was used to establish the upwind background concentrations at the estimated sampling altitude (n = 24 discrete 2.5 min integrated semicontinuous Hg measurements). The airship was then maneuvered downwind of the exhaust stack as close to the stack emission point as safely possible, approximately 200−800 m. The subsequent downwind sampling locations were determined based on the airship crew's ability to identify and maintain the airships position in the dissipated exhaust plume.

Airship Measurements. The automated Hg speciation and criteria gas measurements in the stack and in the airship were made using similar instrumentation manufactured by Tekran and Thermo Electron, respectively. Two minor differences in the configuration of the Tekran speciation systems were (i) the stack system used an inertial sampling probe to extract sample gas from the stack exhaust stream while the airship configuration did not require this component, and (ii) the stack measurement system utilized one 2537A cold vapor atomic fluorescence spectrometer (CVAFS) instrument that was switched between the Hg^0 and TGM channels while the airship system utilized two 2537A CVAFS instruments to continuously sample both channels. The criteria gas measurements were made using Thermo Electron model 43i pulsed fluorescence (SO_2) and model 42i chemiluminescence (NO_Y) dual-range federal reference equivalent method certified instruments (see SI for calibration information). All instruments were kept energized on ground power while the airship was moored to keep analytical bench temperatures stable.

Each Tekran 2537A used during this study was thoroughly evaluated and calibrated[27] prior to and after each flight day (see SI). The raw Hg^0 data generated by the Tekran 2537A instrument in the airship was corrected to account for the effect of atmospheric pressure changes with altitude and reported in units of mass per standard m^{-3} (see SI). Despite rigorous laboratory testing of the modified Tekran 3320 conditioner deployed in the airship and application on a previous motor vehicle study, the motion of the equipment during air operations caused substantial migration of mist chamber water into the heated catalyst reaction chamber invalidating all TGM measurements (SI Figure S3). The Hg^0 channel measurements were not affected and were deemed to be valid.

During sampling, a 20 meter heated sampling umbilical line was lowered from the airship gondola to project the sampling inlets into the plume while minimizing the impact of the airship on the measurements. A heated (120 °C) Teflon particulate matter filter (Hg, SO_2) and heated (350 °C) molybdenum converter (NO_Y) enclosure was attached to the inlet of the umbilical line. The umbilical line encapsulated three Teflon sampling lines and was heated to 120 °C. It was used for continuous Hg, SO_2, and NO_Y sample transport into the gondola. One of the lines was used to introduce ultracarrier grade N_2 gas (99.9995%) to the inlet to purge lines and provide zero air value confirmation between in-plume sample points. Supplemental sample line flow was provided using a vacuum pump to maintain a sample line retention time of less than five seconds and ensure synchronous sampling through the two sampling lines.

Data provided by Gulf Power estimated that (i) Hg^{II} would constitute approximately 84% of the total Hg emission from the

Table 1. Daily (10:00−18:00) Summary of CEM Stack Measurements, Shaded Samples Indicate Associated Airship Flight Days

| | NO_x | SO_2 | CO_2 | Flow | Load | Hg Concentrations $\mu g\ m^{-3}$ wet | | | Hg^{II} |
	ppm wet	ppm wet	% wet	kcfm	MW	Hg^T	Hg^0	Hg^{II}	%
02/23/2008	68.2 ± 1.9	439.1 ± 14.4	11.05 ± 0.08	2288 ± 36	804 ± 3	3.37 ± 0.18	0.14 ± 0.06	3.23 ± 0.15	96.0 ± 1.6
02/24/2008	67.4 ± 2.1	409.4 ± 25.7	10.93 ± 0.13	2317 ± 56	795 ± 7	3.39 ± 0.09	0.09 ± 0.08	3.30 ± 0.13	97.2 ± 2.5
02/25/2008	61.5 ± 2.1	470.1 ± 18.6	10.96 ± 0.07	2114 ± 33	720 ± 8	3.68 ± 0.42	0.03 ± 0.01	3.65 ± 0.42	99.2 ± 0.4
02/26/2008	72.1 ± 1.8	566.5 ± 13.3	11.03 ± 0.08	2271 ± 43	793 ± 4	3.93 ± 0.38	0.03 ± 0.01	3.90 ± 0.39	99.2 ± 1.4
02/27/2008	69.9 ± 1.9	393.5 ± 10.9	11.12 ± 0.10	2173 ± 37	816 ± 3	2.93 ± 0.13	0.06 ± 0.03	2.87 ± 0.13	98.1 ± 1.1
02/28/2008	68.3 ± 2.3	319.2 ± 4.3	11.27 ± 0.09	2135 ± 56	795 ± 22	2.95 ± 0.17	0.39 ± 0.08	2.56 ± 0.12	86.8 ± 2.1
02/29/2008	69.5 ± 2.3	356.8 ± 22.9	11.27 ± 0.80	2190 ± 30	804 ± 8	2.58 ± 0.13	0.19 ± 0.13	2.39 ± 0.10	92.9 ± 4.7
03/01/2008	67.1 ± 3.1	438.1 ± 7.7	10.95 ± 0.23	2234 ± 98	776 ± 41	2.93 ± 0.26	0.08 ± 0.03	2.85 ± 0.27	97.3 ± 1.3

Crist Plant, (ii) Hg^{II} stack emission concentration would be approximately 0.47 ppb or 3.94 $\mu g\ m^{-3}$ (as Hg^0) at full load, and (iii) Hg^0 stack emission concentration would be 0.09 ppb or 0.75 $\mu g\ m^{-3}$ at full load. On the basis of historical data, Gulf Power indicated that it was expected that the Crist Plant units #6 and #7 would be operating at between 80 and 95% full load. For planning purposes, an 80% total combined load on the two units was anticipated. Estimated stack exhaust concentrations of Hg and tracer species for 80% total combined load were calculated and are presented in SI Table S1.

On the basis of the dilution rates from the Plant Bowen experiment,[19] our ability to quantify Hg^{II} using the Tekran speciation system was calculated to be of the same magnitude as our ability to quantify NO_Y and SO_2 (SI Table S2) and effectively ranged between DR of 100 and 25 000 or approximately 0 to 32 km. Even with a limiting case scenario for Hg^{II} reduction equating to TGM/Hg^{II} ratio of 10, we anticipated still being able to quantify our key tracers (SO_2, NO_Y) as well as Hg^{II} up to a DR of 25 000.

Airship Data Screening and Validation. Identifying the location of the plume boundaries and maintaining airship position with respect to the stack exhaust plume proved challenging during the study. While a portion of the plume was visible from the ground due to the associated condensed water vapor, it was not visible while in flight. In addition, when close to the stack exhaust the resulting turbulence and thermal impact on the airship helium envelope challenged the pilots to maintain position with respect to the plume. We utilized a combination of approaches to identify the plume location including: a FLIR (Boston, MA) infrared camera, radio contact with ground observers, use of a Thermo Electron model 43i SO_2 instrument, and a personal exposure SO_2 monitor in the cockpit. Ultimately, the cockpit SO_2 monitor was the most successful tool as the pilots had direct feedback from the monitor's audible signal without radio direction from the scientific flight crew. To screen the airship data for periods that it was successfully positioned "in-plume", the ratio of the measured in-stack SO_2/NO_X to the airship measured SO_2/NO_Y and Hg^0 concentrations were utilized. In the hypothetical ideal case, the ratio of the in-stack SO_2/NO_X divided by the in-plume SO_2/NO_Y ratio should equal 1 and the measured Hg^0 concentration should be greater than background. In this case, a SO_2/NO_X criterion of 1 ± 0.35 and background corrected Hg^0 value >0.1 ng m^{-3} was used to characterize 2.5 min integrated data points as being "in-plume"; data points that did not meet this criterion were invalidated.

Although we were unable to measure TGM in-plume and therefore directly calculate in-plume Hg^{II} concentrations due to

the malfunction of the Tekran model 3320 gas conditioner TGM channel in the airship, we were able to test the null hypothesis that Hg^{II} was not reduced to Hg^0 in the Crist Plant exhaust plume using the difference in the expected versus observed Hg^0 concentrations. For each in-plume run the airship Hg^0, SO_2, and NO_Y concentrations were first corrected for their corresponding average levels measured during the upwind background runs of that same day. The effective DR, in-stack SO_2/NO_X /in-plume SO_2/NO_Y ratios, and the percent Hg^0 of total Hg in-stack were then calculated for each 2.5 min integrated data point.

Due to the plume's thermal buoyancy, loss of Hg from the plume due to depositional processes is unlikely to occur over the short distances measured downwind of the stack exit. Therefore, TGM is expected to be conserved in-plume, with concentrations depending on the plume's DR. In addition, if no reduction or oxidation of Hg species occurs in the plume, the percent of Hg^0 in-stack: ($Hg^0_{\text{in-stack}}/TGM_{\text{in-stack}}$) × 100%; is the same as the percent Hg^0 in-plume. On the basis of these assumptions, the % $Hg^0_{\text{in-plume}}$ was calculated using eq 1.

$$\%Hg^0_{\text{in-plume}} = \left(\frac{\text{measured } Hg^0_{\text{in-plume}}}{\text{expected } TGM_{\text{in-plume}}} \right) \times 100 \tag{1}$$

where:

$$\text{expected } TGM_{\text{in-plume}} = TGM_{\text{in-stack}}/\text{plume DR}$$

$$\text{plume DR} = SO_2(\text{in stack})/SO_2(\text{in plume})$$

The %Hg^{II} reduction was then calculated by subtracting the % $Hg^0_{\text{in-plume}}$ from the measured %$Hg^0_{\text{in-stack}}$.

Meteorological Measurements. An EPA Remtech (St. James, NY) phased array Doppler SODAR system was deployed at the University of West Florida campus to determine local meteorological conditions aloft such as vector wind speeds, wind direction, and mixing layer height. Data from the SODAR system was used to support airship operations and estimate plume aging time (SI eq S3).

Statistical Analysis. Data processing and all statistical analyses were performed using SAS v.9.4 (SAS Institute, Cary, NC). The assumptions of the parametric procedures were examined using residual plots, skewness and kurtosis coefficients, Shapiro-Wilk test, and the Brown-Forsythe test. The t test for independent samples parametric procedure was applied where appropriate. If data seriously violated the assumptions of the parametric procedure, then a Wilcoxon test was utilized. A level of significance of α = 0.05 was used for all statistical procedures.

Table 2. Summary of Coal Grab Sample Composition, Shaded Samples are Most Indicative of Unblended Columbian (February 22-24) and Illinois (February 27–28) Bituminous Coals

| Unit | Date | As Received (Wet Basis) | | | | | Dry Weight Basis | | | | | Br/Cl Ratio | Iron Oxide* % |
		Carbon %	Sulfur %	Mercury mg kg⁻¹	Chlorine mg kg⁻¹	Bromine mg kg⁻¹	Carbon %	Sulfur %	Mercury mg kg⁻¹	Chlorine mg kg⁻¹	Bromine mg kg⁻¹		
6	02/20/08	64.3	0.8	0.08	1301	4.6	74.6	0.9	0.09	1510	5.3	0.004	10.8
6	02/21/08	64.1	0.7	0.07	1281	5.5	74.6	0.9	0.08	1490	6.4	0.004	11.1
6	02/22/08	63.0	0.5	0.07	66	7.3	74.3	0.6	0.08	78	8.6	0.110	8.2
6	02/23/08	65.3	0.8	0.07	83	3.4	75.6	0.9	0.08	93	-	0.041	12.7
6	02/24/08	66.0	0.6	0.09	55	2.8	73.8	0.7	0.10	62	3.1	0.051	8.6
6	02/25/08	64.6	0.9	0.08	1769	7.3	75.3	1.0	0.09	2062	8.5	0.004	13.9
6	02/26/08	64.7	0.7	0.07	1198	4.6	74.8	0.8	0.08	1386	5.3	0.004	11.6
6	02/27/08	66.3	1.0	0.09	1909	6.6	75.0	1.2	0.10	2158	7.4	0.003	12.9
6	02/28/08	64.8	0.9	0.07	1939	4.6	75.1	1.1	0.09	2247	5.3	0.002	13.7
6	02/29/08	63.5	0.7	0.07	891	3.6	74.2	0.8	0.08	1042	4.2	0.004	10.3
6	03/01/08	64.4	0.5	0.06	150	-	74.6	0.6	0.07	174	-	-	8.7
6	03/02/08	66.8	1.0	0.09	1763	3.7	75.0	1.1	0.10	1979	4.2	0.002	12.7
7	02/20/08	64.2	0.7	0.07	1286	4.7	74.8	0.9	0.08	1500	5.5	0.004	11.0
7	02/21/08	63.9	0.7	0.09	1051	3.7	74.0	0.8	0.10	1217	4.3	0.004	10.6
7	02/22/08	62.7	0.5	0.08	87	3.6	74.4	0.6	0.10	103	4.3	0.042	8.0
7	02/23/08	64.1	0.4	0.06	74	6.4	74.2	0.5	0.07	86	7.4	0.087	7.7
7	02/24/08	65.2	0.6	0.07	52	1.9	73.8	0.7	0.08	59	2.1	0.035	8.3
7	02/25/08	64.1	0.9	0.07	1669	7.2	75.3	1.0	0.09	1960	8.4	0.004	13.3
7	02/26/08	64.6	1.0	0.08	1850	14.5	75.1	1.1	0.09	2150	16.8	0.008	13.9
7	02/27/08	66.8	1.1	0.09	2052	5.7	75.1	1.2	0.10	2307	6.4	0.003	14.3
7	02/28/08	65.6	1.0	0.08	2222	3.7	75.0	1.2	0.10	2538	4.2	0.002	13.8
7	02/29/08	63.9	0.7	0.06	910	0.9	74.7	0.8	0.07	1065	1.1	0.001	10.3
7	03/01/08	65.1	0.5	0.07	124	-	75.0	0.5	0.08	143	-	-	9.0
7	03/02/08	66.8	0.9	0.08	1601	9.4	74.5	1.1	0.09	1786	10.5	0.006	11.8

a Coal ash basis.

Table 3. Characteristics of Columbian and Illinois Categorized Coal Samples

coal	sulfur %	mercury mg kg⁻¹	chlorine mg kg⁻¹	bromine mg kg⁻¹	Br/Cl ratio	iron oxide*a* %
Columbian	0.6 ± 0.1	0.07 ± 0.01	70 ± 16	3.6 ± 1.7	0.051 ± 0.021	9.1 ± 2.1
Illinois	1.0 ± 0.1	0.08 ± 0.01	2031 ± 142	5.2 ± 1.3	0.003 ± 0.001	13.7 ± 0.6

*a* Coal ash basis.

■ RESULTS AND DISCUSSION

Stack Emissions. A summary of the plant's daily operational process parameters (electrical load and stack flow) and combustion emissions (SO_2, NO_x, and Hg) are presented in Table 1. The average values represent the period of time each day when valid Hg CEM measurements data were collected (typically 10:00−18:00). While plant emissions measurement data are routinely available 24 h/day, Hg CEM data are not, due to automated quality control checks performed at the beginning and end of each test day. Subsets of these same data are presented in SI Table S3 summarizing the emission measurements for the actual flight time periods that airship sampling was conducted. The gaseous emissions for these same time frames are graphically depicted in SI Figure S4a,b to illustrate the stability as well as temporal variability of the process emissions. While the CFPP stack emissions are relatively stable over the nominal 8 h test day, it can be seen that day-to-day emissions were highly variable. This variability is attributed to variations in coal blend. During the study, the plant experienced a malfunction to the primary coal feeding system that resulted in additional variation to the coal charged into the boilers from February 25−29, 2008 as coal was directly fed from the bulk storage piles into the boilers. The reported nominal 50/50 blend of Illinois and Colombian bituminous coal became highly variable. This variability is evidenced in the

daily coal analyses presented in Table 2 as well the daily stack emissions averages presented in Table 1.

A significant shift in stack emissions was observed on 2/28 as evidenced by the lower SO_2 emissions as well as the significant decrease in $\%Hg^{II}$ distribution. A closer examination of the daily coal analyses and the daily stack emissions indicates that there is not consistent agreement between measured coal elemental levels (e.g., sulfur) and stack emissions (SO_2). This is likely due to the "inexact" manual blending approach combined with the single point-in-time coal sampling. The six coal samples collected between 02/22−02/24 are clearly representative of the Columbian coal with lower sulfur (0.6 ± 0.1; mean ± standard deviation), lower chlorine (70 ± 16), and higher bromine/chlorine ratio (0.051 ± 0.021), while the four samples collected between 02/28−02/29 are clearly representative of Illinois coal with higher sulfur (1.0 ± 0.1), higher chlorine (2031 ± 142), and lower bromine/chlorine ratio (0.003 ± 0.001; Table 3). The resulting stack emissions are clearly the definitive basis for assessing coal blend characteristics.

The coal blend changes resulted in a highly variable net chlorine content (ranging from <100 ppm to >2000 ppm) as well as moderate variations in sulfur and Hg content. The chloride content in coal is known to be an important component in determining Hg speciation in CFPP flue gas.[28,29] So the increase in the relative proportion of Columbian

coal should result in a moderate decrease in SO_2 and a major decrease in chlorine in the combustion flue gas, reducing the overall Hg^0 oxidation potential. The relationship between measured daily integrated stack Hg^{II} and SO_2 concentration is presented in Figure 1a, and the relationship between $%Hg^{II}$ and
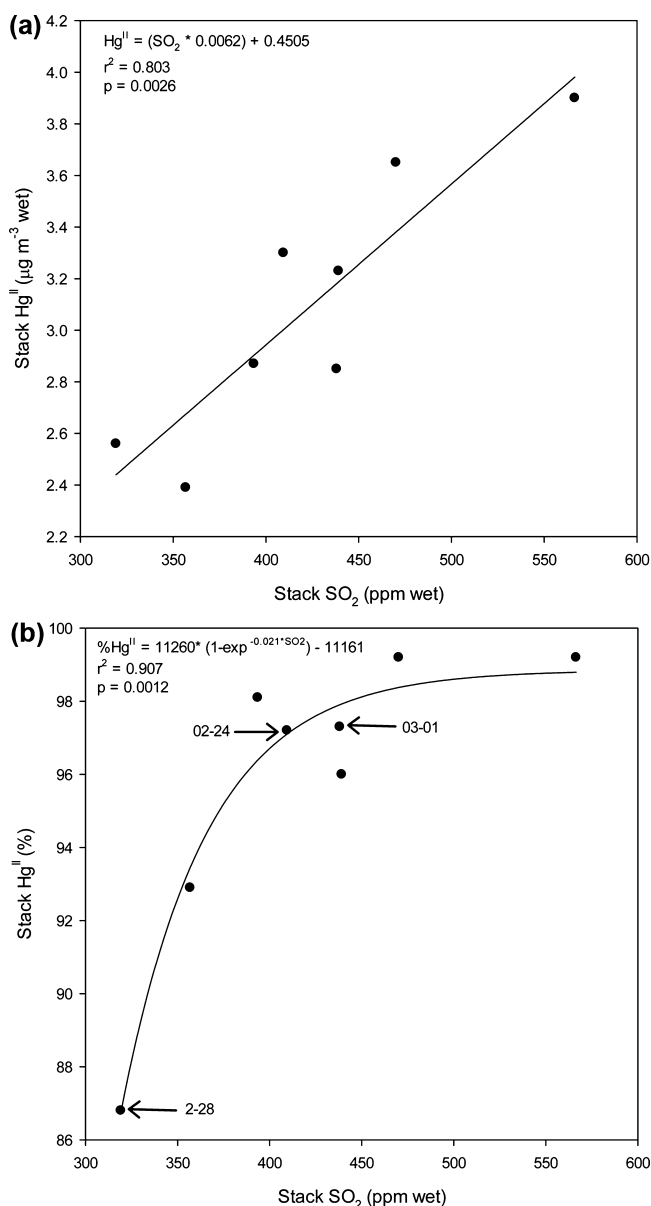
Figure 1. Relationship between daily (10:00−18:00) integrated in-stack CEM (a) Hg^{II} and SO_2 concentration, and (b) percent Hg^{II} and SO_2 concentration (February 23 to March 1, 2008).

SO_2 concentration is presented in Figure 1b. The result of the significant relationship ($p = 0.0026$) between in-stack SO_2 and Hg^{II} concentration is consistent with varying blends of Columbian and Illinois coal. The significant ($p = 0.0012$) exponential relationship between in-stack SO_2 concentration and $%Hg^{II}$ suggests that once SO_2 concentration reaches approximately 450 ppm, the formation of Hg^{II} levels off and is no longer sensitive to shifts in coal blend. But when the increase in the Columbian coal fraction results in SO_2 concentrations lower than approximately 450 ppm the production of Hg^{II} is reduced, similar to what we believe

occurred on 02/28−02/29 when there was a 3−4 fold increase in Hg^0 in the flue gas on the 2/28 with the mean $% Hg^{II}$ in-stack decreasing ∼13% compared to the previous day (Table 1). While the short-term variability of in-stack SO_2 and Hg speciation observed by CEMs over the course of the individual 1-h airship sampling periods was low, day-to-day variability was substantially higher in response to the changing blend of coal being charged into the boilers (Table 1, SI Figure S4a,b).

Characterizing the Quality of the Speciated Hg Stack Measurements. The ability to characterize the quality of the speciated Hg stack measurements is integral to the interpretation of the speciated in-plume Hg measurements. As a result, emphasis was placed on obtaining speciated Hg measurements by multiple techniques as the primary means for characterizing the quality of the Hg CEM speciated Hg stack measurements. In addition to the CEM and OH measurements, speciated Hg measurements were also made using the sorbent traps and FUME approaches.

A summary of the Unit 7 speciated Hg measurements by all available techniques is presented in SI Table S4. These results show that not only are Unit 7 Hg^{II} emissions consistently greater than 90% (with the exception of those made on 2/28), but that all the speciated Hg measurements techniques reported consistent results. The Hg CEMs speciated Hg^{II} measurements were slightly higher relative to the other techniques, with the OH speciated measurements consistently measuring the lowest relative Hg^{II} ($−7.1 \pm 2.9\%$). The speciated trap and FUME Hg^{II} speciated Hg measurements also agree well with those observed by the Hg CEMs measurements ($−0.3 \pm 0.7\%$ and $−3.3 \pm 2.2\%$, respectively). As a result of the excellent agreement between the Hg CEMs, the OH speciated Hg measurements as well as the alternative speciated Hg measurements, the speciated Hg data reported in this study are based solely on the Hg CEMs.

The Unit 7 Hg^{II} emissions are also relatively consistent over the duration of the test program, averaging ∼96% ± 5% Hg^{II} for the Hg CEMs Hg^{II} measurements. However, a significant drop in Hg^{II} emissions is observed on 2/28 and 2/29 for all speciated Hg measurement techniques due to a significant shift in coal blend (as discussed in the previous section).

In-Plume Measurements. A summary of each valid in-plume measurement run is presented in Table 4 and an integrated study average compared to other published data is presented in Table 5. The average 2.5 min integrated $% Hg^0_{in-stack}$ during the valid in-plume measurement periods was $6.2 \pm 5.8\%$ and ranged from 0.0 to 16.1%. The calculated $% Hg^0_{in-plume}$ during the same periods was $11.1 \pm 9.9\%$ and ranged from 1.4 to 58.8%. The unexpected malfunction of the Crist Plant coal blending system provided a unique opportunity to observe the facility Hg emission rate, in-stack speciation, and resulting in-plume dynamic response to changing sulfur, chloride, and Hg concentrations in the feed coal. In-stack and concurrent in-plume measurements conducted on February 24, 2008 during typical coal blending operations showed a relatively small but significant in-plume reduction of Hg^{II} to Hg^0 ($3.2 \pm 1.5\%$) that was not significantly related to plume aging time (Table 4; Figure 2a).

On February 28, 2008 following the malfunction of the automated coal charging system and during the manual charging of mostly Colombian coal (low sulfur and halide content), we observed no significant reduction of Hg^{II} to Hg^0. On March 1, 2008 after the automated coal charging system was back online and the coal blend was transitioning back to

Table 4. Summary of All Valid In-Plume Measurements

run	date	n^a	%Hg^0 In-stack^b	%Hg^0 In-plume^{b,c}	%Hg^{II} reduction^b	distance^d	wind speed^{b,e}
5	02/24/08	18	1.58 ± 0.74	4.57 ± 1.64	2.99 ± 1.72	0.56 ± 0.11	8.2 ± 0.8
6	02/24/08	8	0.22 ± 0.24	3.90 ± 0.69	3.68 ± 0.71	1.20 ± 0.23	6.5 ± 0.5
15	02/28/08	12	14.13 ± 0.68	14.42 ± 7.37	0.29 ± 7.43	0.57 ± 0.21	7.3 ± 1.2
17	02/28/08	14	14.20 ± 0.94	14.54 ± 5.06	0.34 ± 5.32	0.69 ± 0.34	7.5 ± 0.2
22	03/01/08	13	2.25 ± 0.67	7.22 ± 3.75	4.97 ± 4.03	0.80 ± 0.20	8.9 ± 2.8
23	03/01/08	4	3.24 ± 0.22	39.17 ± 16.70	35.93 ± 16.54	1.31 ± 0.18	7.6 ± 0.8
24	03/01/08	9	4.71 ± 0.34	13.95 ± 9.98	9.24 ± 9.89	1.09 ± 0.08	9.1 ± 0.3
Total		78					

^{a}Number of valid 2.5 min samples within each run. ^{b}Values are mean ± standard deviations. ^{c}Calculated by dividing the measured Hg^0 levels in-plume by the calculated TGM levels in-plume. ^{d}Effective three-dimensional distance downwind from stack exit (km). ^{e}Remtech SODAR (m s^{-1}) at airship altitude.

Table 5. Comparison of Independent Coal-Fired Power Plant Mercury Plume Studies

	Plant Crist*	Plant Bowen[19]	Pleasant Prairie[20]	OLF ambient site[15]
	Pensacola, FL	Atlanta, GA	Kenosha, WI	Pensacola, FL
Hg^{II} reduction to Hg^0	0–36%	~12%	~44–54%	37–74%
plume reaction time	<1–5 min			2–5 h
stack distance (km)	0.4–1.6	~10–12	0.6–16	14.6

*This Study—stack distance is minimum—maximum.

normal, we observed a larger significant in-plume reduction of Hg^{II} to Hg^0 (11.2 ± 13.8%) that was significantly related to plume aging time (Table 4; Figure 2b). The highest Hg^{II} to Hg^0 reduction rate of 58.8% was observed at the furthest point away from the exhaust stack (1.5 km), and was well within the range of Edgerton et al.[15] estimated Hg^{II} to Hg^0 reduction based on surface observations downwind of the Crist Plant.

It has been generally assumed[30−32] and was later confirmed[12−14] that Hg^{II} present in CFPP plumes deposits, on average, closer to its emission source then Hg^0, causing near field deposition enhancement due to its chemical/physical properties. However, this study and recent field/modeling studies suggest that in-plume reduction of Hg^{II} to Hg^0 can also occur depending on coal composition that may moderate the near field impact.[15,16,19−21] However, as these results demonstrate, coal characteristics can play a major role in determining in-stack and in-plume Hg concentration and speciation when all other plant variables remain equal.

It is assumed that Hg^{II} in the atmosphere exists primarily as mercuric chloride (HgCl$_2$). However, the mechanisms of interaction between Hg in flue gas, fly ash, chlorine-containing species, SO$_2$, NO, water vapor, and trace elements from different coal types and sources remain ambiguous.[17,28,29,33−35] In bench reactor tests using simulated flue gas, it has been shown that Hg oxidation rates decreased in the presence of SO$_2$, NO, and water vapor, while Hg reduction rates increased. In addition, Hg reduction rates increased as flue gas temperature rose, while reduction rates declined as dichloride (Cl$_2$) concentrations increased.[17] Hence, SO$_2$, NO, and H$_2$O may affect the concentrations of chloride ions and free chlorine in flue gas and determine how effectively chlorine will form the chlorinated sites on unburned carbon needed to oxidize Hg^0.[17,28,29] The effect of Cl$_2$, SO$_2$, and NO on the formation of Hg^{II} in simulated flue gas has also been predicted.[33] In the presence of Cl$_2$, about 80% of the Hg^0 was oxidized to Hg^{II}. Adding SO$_2$ to the flue gas mixture lowered the oxidation rate to 30%. NO had little to no effect on the mercury oxidation rate.[33] Tong et al.[34,35] tested variables that potentially affect heterogeneous photoreduction of HgCl$_2$. It was found that

sulfur in fly ash possibly enhanced photoreduction, while chlorine, carbon, and iron inhibited photoreduction. The reduction of Hg^{II} to Hg^0 was only observed in the presence of light, with average reduction rates of 20−30% per hour when normalized to real-world clear sky atmospheric intensities.[34,35]

The flue gas SO$_2$ concentrations on February 28, when we observed no significant Hg^{II} reduction in the plume, were the lowest of all our measurement days ranging from 315 to 321 ppm (Table 1; SI Table S3) suggesting our field observations were consistent with the laboratory observations of Zhao et al.[17] On March 1 when we observed the highest degree of Hg^{II} reduction to Hg^0 of up to 55.3%, SO$_2$ flue gas concentrations were higher (ranging from 430 to 450 ppm; SI Table S3) indicating a higher proportion of Illinois coal with correspondingly higher chlorine, bromine, and iron (Table 3) consistent with conditions favoring more reduction of Hg^{II} in the flue gas.[17,33−35] Also on February 24, when significant mercury reduction was observed, SO$_2$ flue gas and %Hg^{II} conditions were similar to that of March 1, again suggesting a higher proportion of Illinois coal with correspondingly higher chlorine and iron (Table 3).

Our results (i) are generally in agreement with those from previous in-plume studies (Table 5) demonstrating instances of significant Hg^{II} to Hg^0 reduction,[15−16,19-21] as well as instances of no significant plume speciation change[22] and (ii) highlight the importance of coal composition in driving in-stack and in-plume Hg species dynamics. The results of this study further confirm that in-plume reactions exist that result in the reduction of Hg^{II}. Moreover, variable levels of Hg^{II} reduction were observed. As a result of the significant variation in the relative amounts in the coals blended during this study and their diverse chemical composition, the data suggest that coal chemical composition are a major influence on Hg^{II} production and in-plume reduction chemistry. Therefore, measurements made under specific conditions at CFPPs cannot be generalized to other facilities or operating conditions.
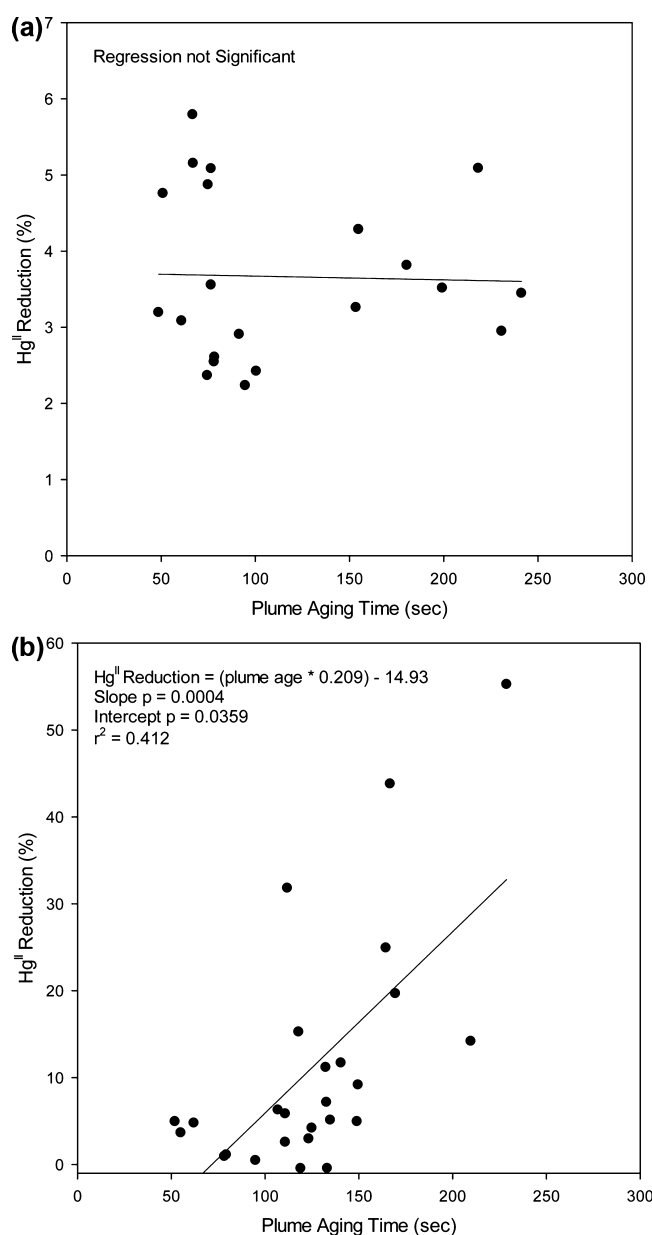
Figure 2. Relationship between calculated Hg^{II} to Hg^0 reduction and plume aging time for sorties flown on (a) February 24, 2008 and (b) March 1, 2008 when individual sample periods were categorized as plume impacted.

ASSOCIATED CONTENT

S **Supporting Information**

Figure S1: Airship sampling Crist Plant stack emission plume exhaust; Figure S2: schematic of Tekran Model 3300 CEM system; Figure S3: schematic of standard Tekran 3320 conditioner; Figure S4: time series plot of in-stack (a) NO_x and SO_2 (b) total mercury concentrations; Figure S5: relationship between 2.5-min integrated CEM in-stack (a) Hg^{II} and SO_2 concentrations, and (b) percent Hg^{II} and SO_2 concentration; Table S1: estimated stack parameters and exhaust concentrations for Crist Plant unit #6 and unit #7 at combined 80% load based upon linear interpolation of data provided by Gulf Power for 50% and 100% total combined load; Table S2: estimated concentrations of target compounds emitted from Crist Plant combined units #6 and #7 at 80% load

from 100 to 75 000 dilution ratios (Hg^{II} expressed as Hg^0); Table S3: flight time summary of CEM stack measurements; Table S4: comparison of in-stack speciation method results; Table S5: summary of airship in-plume measurements (mean ± standard deviation); and Methods, selection of coal-fired power plant, Crist Plant stack emission measurements, additional speciated Hg measurements, airship criteria gas instrument calibration, Airship Tekran evaluation and calibration, and meteorological measurements. This material is available free of charge via the Internet at http://pubs.acs.org/.

AUTHOR INFORMATION

Corresponding Author

*Phone: (919) 541-4841; fax: (919) 541-0960; e-mail: landis.matthew@epa.gov.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Pacyna, E. G.; Pacyna, J. M. Global emissions of mercury from anthropogenic sources in 1995. *Water Air Soil Pollut.* **2002**, 137, 149−165.

(2) Pacyna, J. M.; Pacyna, E. G.; Steenhuisen, F.; Wilson, S. Mapping 1995 global anthropogenic emissions of mercury. *Atmos. Environ.* **2003**, 37, 109−117.

(3) Pacyna, E. G.; Pacyna, J. M.; Steenhuisen, F.; Wilson, S. Global anthropogenic mercury emission inventory for 2000. *Atmos. Environ.* **2006**, 40, 4048−4063.

(4) Wilson, S. J.; Steenhuisen, F.; Pacyna, J. M.; Pacyna, E. G. Mapping the spatial distribution of global anthropogenic mercury atmospheric emission inventories. *Atmos. Environ.* **2006**, 40, 4621−4632.

(5) Streets, D. G.; Zhang, Q.; Wu, Y. Projections of global mercury emissions in 2050. *Environ. Sci. Technol.* **2009**, 43, 2983−2988.

(6) United Nations Environment Programe, 2013. Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport. UNEP Chemicals Branch, Geneva, Switzerland. http://www.unep.org/PDF/PressReleases/GlobalMercuryAssessment2013.pdf. Last accessed October 15, 2014.

(7) Arctic Monitoring and Assessment Programme/United Nations Environment Programe, 2013. Technical Background Report for the Global Mercury Assessment 2013. AMAP, Oslo, Norway/UNEP Chemicals Branch, Geneva, Switzerland. http://www.amap.no/

documents/doc/Technical-Background-Report-for-the-Global-Mercury-Assessment-2013/848. Last accessed October 15, 2014.

(8) Schroeder, W. H.; Munthe, J. Atmospheric mercury—An overview. *Atmos. Environ.* **1998**, *32*, 809−822.

(9) US Environmental Protection Agency, 1997. Mercury Study Report to Congress, Vol. 3, EPA-452/R-97-003; Office or Air Quality Planning and Standards, Office of Research and Development: Washington, DC. (Chapter 4).

(10) Lindberg, S. E.; Stratton, W. J. Atmospheric mercury speciation: Concentrations and behavior of reactive gaseous mercury in ambient air. *Environ. Sci. Technol.* **1998**, *32*, 49−57.

(11) Pehkonen, S. O.; Lin, C. J. Aqueous photochemistry of mercury with organic acids. *J. Air Waste Manage. Assoc.* **1998**, *48*, 144−150.

(12) Keeler, G. J.; Landis, M. S.; Norris, G. A.; Christianson, E. M.; Dvonch, J. T. Sources of mercury wet deposition in eastern Ohio, USA. *Environ. Sci. Technol.* **2006**, *40*, 5874−5881.

(13) White, E. M.; Keeler, G. J.; Landis, M. S. Spatial variability of mercury wet deposition in eastern Ohio: Summertime meteorological case study analysis of local source influences. *Environ. Sci. Technol.* **2009**, *43*, 4946−4953.

(14) Pancras, J. P.; Vedantham, R.; Landis, M. S.; Norris, G. A.; Ondov, J. M. Application of EPA UNMIX and non-parametric wind regression on high time resolution trace elements and speciated mercury in Tampa, Florida aerosol. *Environ. Sci. Technol.* **2011**, *45*, 3511−3518.

(15) Edgerton, E. S.; Hartsell, B. E.; Jansen, J. J. Mercury speciation in coal-fired power plant plumes observed at three surface sites in the southeastern US. *Environ. Sci. Technol.* **2006**, *40*, 4563−4570.

(16) Lohman, K.; Seigneur, C.; Edgerton, E.; Jansen, J. Modeling mercury in power plant plumes. *Environ. Sci. Technol.* **2006**, *40*, 3848−3854.

(17) Zhao, Y.; Mann, M. D.; Olson, E. S.; Pavlish, J. H.; Dunham, G. E. Effects of sulfur dioxide and nitric oxide on mercury oxidation and reduction under homogeneous conditions. *J. Air Waste Manage. Assoc.* **2006**, *56*, 628−635.

(18) Vijayaraghavan, K.; Karamchandani, P.; Seigneur, C.; Balmori, R.; Chen, S.-Y. Plume-in-grid modeling of atmospheric mercury. *J. Geophys. Res.* **2008**, *113*, D24305 DOI: 10.1029/2008JD010580.

(19) Prestbo, E.; Levin, L.; Jansen, J. J.; Monroe, L.; Laudal, D.; Schulz, R.; Dunham, G.; Aljoe, W.; Valente, R. J.; Michaud D.; Swartzendruber, P.; 2004. "Interconversion of emitted atmospheric mercury species in coal-fired power plant plumes." Presented at the 7th International Conference on Mercury as a Global Pollutant, Ljubljana, Slovenia; *RMZ-Materiali in Geookolje*, 2004, *51*, 1732−1733.

(20) EPRI, 2005. Evaluation of Mercury Speciation in a Power Plant Plume. Palo Alto, CA: 1011113.

(21) EPRI, 2006. *Mercury Chemistry in Power Plant Plumes*. Palo Alto, CA: 1010142.

(22) Deeds, D. A.; Banic, C. M.; Lu, J.; Daggupaty, S. Mercury speciation in a coal-fired power plant plume: An aircraft-based study of emissions from the 3640 MW Nanticoke Generating Station, Ontario, Canada. *J. Geophys. Res.-Atmos.* **2013**, *118*, 4919−4935 DOI: 10.1002/jgrd.50349.

(23) Gardfeldt, K.; Jonsson, M. Is Bimolecular reduction of Hg(II) complexes possible in aqueous systems of environmental importance. *J. Phys. Chem. A* **2003**, *107*, 4478−4482.

(24) Seigneur, C.; Vijayaraghavan, K.; Lohman, K. Atmospheric mercury chemistry: Sensitivity of global model simulations to chemical reactions. *J. Geophys. Res.-Atmos.*, **2006**, *111* (D22306).

(25) U.S. Environmental Protection Agency. "Method 30A − DETERMINATION OF TOTAL VAPOR PHASE MERCURY EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)." *Code of Federal Regulations*, Title 40, Part 60, Appendix A. http://www.epa.gov/ttn/emc/promgate/Meth30A.pdf.

(26) Ryan, J. V., and R. Keeney *The Ontario Hydro Method for Speciated Mercury Measurements: Issues and Considerations* in Proceedings of 2004 Symposium on Air Quality Measurement

Methods and Technology, April 19−22, 2004, Research Triangle Park, North Carolina.

(27) Landis, M. S.; Stevens, R. K.; Schaedlich, F.; Prestbo, E. M. Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air. *Environ. Sci. Technol.* **2002**, *36*, 3000−3009.

(28) Cao, Y.; Duan, Y.; Kellie, S.; Lingchuan, L.; Xu, W.; Riley, J. T.; Pan, W.; Chu, P.; Mehta, A. K.; Carty, R. Impact of coal chlorine on mercury speciation and emission from a 100-MW utility boiler with cold-side electrostatic precipitators and low-NO$_x$ burners. *Energy Fuels* **2005**, *19*, 842−854.

(29) Effect of Selective Catalytic Reduction (SCR) and Ammonia on Mercury Speciation and Removal: 2003 Summary Report, EPRI, Palo Alto, CA, U.S. Department of Energy, Pittsburgh, PA, and U.S. Environmental Protection Agency: Research Triangle Park, NC, 2004, 1008494.

(30) Schroeder, W.; Munthe, J. Atmospheric mercury—An overview. *Atmos. Environ.* **1998**, *32*, 809−822.

(31) Mason, R. P.; Sheu, G. R. Role of ocean in the global mercury cycle. *Global Biogeochem. Cycl.* **2002**, *16*, 1093 DOI: 10.1029/2001GB001440.

(32) Pehkonen, S. O.; Lin, C.-J. Two-phase model of mercury chemistry in the atmosphere. *Atmos. Environ.* **1998**, *32*, 2543−2558.

(33) Krishnakumar, B.; Helble, J. J. Understanding mercury transformations in coal-fired power plants: Evaluation of homogeneous hg oxidation mechanisms. *Environ. Sci. Technol.* **2007**, *41*, 7870−7875.

(34) Tong, Y.; Eichhorst, T.; Olson, M. R.; McGinnis, J. E.; Turner, I.; Rutter, A. P.; Shafer, M. M.; Wang, X.; Schauer, J. J. Atmospheric photolytic reduction of mercury(II) in dry aerosols. *Environ. Sci.: Proc. Impacts* **2013**, *15*, 1883−1888.

(35) Tong, Y.; Eichhorst, T.; Olson, M. R.; Turner, I.; Rutter, A. P.; Shafer, M. M.; Wang, X.; Schauer, J. J. Comparison of heterogeneous photolytic reduction of Hg(II) in the coal fly ashes and synthetic aerosols. *Atmos. Res.* **2014**, *138*, 324−329.