

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

3
4
5 Matthew S. Landis* and Jeffrey V. Ryan
6 US EPA, Office of Research and Development, Research Triangle Park, NC 27709

7
8 Arnout ter Schure
9 Electric Power Research Institute, Palo Alto, CA 94304

10
11 Dennis Laudal
12 Energy & Environmental Research Center, Grand Forks, ND 58202

13
14
15 *Corresponding author; phone: (919) 541-4841; fax: (919) 541-0960; landis.matthew@epa.gov

16
17
18 **Abstract**

19 The reduction of divalent gaseous mercury (Hg^{II}) to elemental gaseous mercury (Hg^0) in a
20 commercial coal-fired power plant (CFPP) exhaust plume was investigated by simultaneous
21 measurement in-stack and in-plume as part of a collaborative study among the U.S. EPA, EPRI,
22 EERC, and Southern Company. In-stack continuous emission monitoring data were used to
23 establish the CFPP's real-time mercury speciation and plume dilution tracer species (SO_2 , NO_x)
24 emission rates, and an airship was utilized as an airborne sampling platform to maintain static
25 position with respect to the exhaust plume centerline for semi-continuous measurement of target
26 species. Varying levels of Hg^{II} concentration ($2.39\text{-}3.90 \mu\text{g m}^{-3}$) and percent abundance (~87-
27 99%) in flue gas and in-plume reduction were observed over the multi-day test program. The
28 existence and magnitude of Hg^{II} reduction to Hg^0 (0-55%) observed varied with respect to the
29 types and relative amounts of coals combusted, suggesting that exhaust plume reduction
30 occurring downwind of the CFPP is influenced by coal chemical composition and characteristics.

31
32
33 **Keywords:** mercury emissions, mercury speciation, redox chemistry, coal fired power plants

34 **Introduction**

35 Anthropogenic sources of mercury (Hg) to the atmosphere have been extensively studied (1, 2, 3,
36 4, 5), with the most recent global estimate established as 1960 tonnes being emitted in 2010 (6).
37 About 16% of these global anthropogenic emissions were attributed to commercial coal-fired
38 power plants (CFPPs). In North America, coal combustion was the largest Hg source category,
39 contributing an estimated 43.4 tonnes (71%) of the estimated 60.7 tonnes emitted in 2010 (7).
40 Mercury in the exhaust plume of a CFPP typically consists of three main fractions: elemental
41 gaseous mercury (Hg^0), divalent gaseous mercury (Hg^{II}), and particulate-bound mercury ($\text{Hg}(\text{p})$).
42 It is important to ascertain the relative distribution of Hg fractions emitted since each has
43 different physicochemical properties that strongly determine its environmental fate (8).
44 Theoretically, Hg^{II} and $\text{Hg}(\text{p})$ fractions should deposit on local or regional scales via wet and dry
45 atmospheric deposition processes because of their solubility, reactivity, and higher deposition
46 velocities; while Hg^0 is more likely to be transported long distances and contribute to the global
47 atmospheric burden (8, 9, 10, 11). Field measurements have demonstrated that Hg emissions
48 from CFPPs have near-source impacts, and contribute to enhanced wet and dry atmospheric
49 deposition on local and regional scales in regions with significant coal-burning sources (12, 13,
50 14).

51
52 Several recent studies hypothesized the reduction of Hg^{II} to Hg^0 in CFPP plumes after emission
53 from the stack, which if parameterized and incorporated into deterministic model runs would
54 partially mitigate the near-field impact of atmospheric Hg deposition currently estimated using
55 contemporary in-stack speciation estimates (15, 16, 17, 18). Briefly, Hg^0 , Hg^{II} , and $\text{Hg}(\text{p})$
56 measured at three sites in the southeastern U.S. for 21 plume-impact events showed that total
57 gaseous mercury (TGM; $\text{Hg}^0 + \text{Hg}^{\text{II}}$) was essentially conserved from the point of emission to the
58 sites, and that Hg^0 was the dominant form (84%). However, emission estimates indicated that
59 Hg^0 should represent approximately 42% of the TGM. Results showed that observed $\text{Hg}^{\text{II}}:\text{SO}_2$
60 ratios were lower by a factor of 2-4 compared to expected ratios. In-plume reduction of Hg^{II} to
61 Hg^0 was postulated as one of several possible explanations (15). Nine of the aforementioned
62 plume-events were simulated with the Reactive & Optics Model of Emissions (ROME) in a
63 separate study (18). The simulations first failed to reproduce the measured depletion in Hg^{II} , but
64 when two possible reduction pathways for Hg^{II} (a pseudo-first-order decay and an empirical

65 reaction with SO₂) resulted in better agreement with the observations.

66

67 In 2002 a study was conducted to investigate in plume Hg behavior at the Plant Bowen (GA,
68 USA) CFPP using a fixed-wing aircraft as an airborne sampling platform (19). The investigators
69 flew repeated crosswind transects through the plume to collect sufficient mass for integrated
70 manual Hg speciation analysis. The researchers found that Hg^{II} concentrations appeared to
71 decrease slightly in samples taken approximately 20 km downwind of the stack, as compared to
72 levels in integrated stack samples. The Hg⁰/Hg^{II} ratio was 84% of the estimated in-stack ratio
73 suggesting reduction of Hg^{II} to Hg⁰ as the plume was advected. A combination of deposition
74 and/or chemical changes in the plume was suggested to explain these results (19). In 2003, a
75 second CFPP in-plume study was conducted at the Pleasant Prairie Power Plant (WI, USA). The
76 study also used a fixed-wing aircraft and a similar sampling design. The researchers estimated a
77 44% reduction in the fraction of RGM between the stack exit and the first sampling location (0.5
78 km downwind), and a 66% reduction from the stack to 8 km downwind, with no additional
79 reduction between 8 and 16 km downwind (20, 21). While both of these studies were suggestive
80 of in-plume Hg^{II} reduction to Hg⁰, the lack of concurrent time-resolved stack and plume data,
81 and the small number of measurements precluded robust statistical conclusions.

82

83 A recently published multi-season experiment was conducted in 2000 to study the mercury
84 speciation in the plume of the 3640 MW Nanticoke coal-fired power plant in Southern Ontario
85 (22). A fixed-wing aircraft equipped with semi-continuous instrumentation for Hg⁰ and manual
86 sampling systems for Hg^{II} was used. While the authors observed significant discrepancies
87 between dilution-corrected estimated and measured in-plume Hg^{II} concentrations, they
88 concluded the lower in plume Hg^{II} concentrations could be explained by potential bias between
89 in-stack and in-plume measurement techniques.

90

91 Projecting the effectiveness of planned controls in reducing mercury emissions from CFPPs
92 depends on an accurate understanding of the reduction/oxidation chemistry of Hg species in the
93 atmosphere and associated changes to deposition phenomena. Since contemporary air quality
94 models use emission rates and speciation estimates based on in-stack measurements, any near
95 field in-plume reactions that significantly alters Hg speciation will affect the accuracy of the

96 model dispersion and deposition estimates. Although the in plume Hg reduction reactions
97 hypothesized by surface ambient observations (15) and some initial in-plume measurements (20,
98 21) may alter the source attribution of CFPPs to local and regional Hg deposition, the existence
99 of a significant reduction is still open to debate (22) and our understanding of a plausible
100 reduction/oxidation chemical mechanism remains limited (23, 24).

101
102 This paper presents results from a new study designed to provide data for a statistically robust
103 analysis of the plume reduction hypothesis, using simultaneous high temporal resolution
104 measurements of Hg fractions (TGM, Hg⁰) and tracer gases (SO₂, NO_y) in-stack and in-plume
105 conducted at a CFPP located in the southeastern USA. In-stack continuous emission monitoring
106 (CEM) data were used to establish the CFPP's real time Hg and tracer species emission rates,
107 and an airship was utilized as an airborne sampling platform to maintain position in the exhaust
108 plume for semi-continuous measurement of target species. The relationship between observed
109 and expected in-stack *versus* in-plume Hg fraction concentrations based on observed dilution
110 ratios (DRs) and the implications for in-plume Hg^{II} reduction to Hg⁰ are presented and discussed.

111

112 **Methods**

113 *Study Design*

114 This study tested the null hypothesis that Hg^{II} is not significantly reduced to Hg⁰ in the emissions
115 plumes of CFPPs. Simultaneous high-resolution (2.5 min) speciated Hg measurements were
116 made in a CFPP stack and in the resulting exhaust plume using an airship. The novel aspects of
117 this study included (i) utilizing the same automated continuous measurement techniques in the
118 stack and in the plume, thereby reducing the potential for measurement bias, and (ii) the use of
119 an airship to maintain constant position with respect to the exhaust plume centerline (Supporting
120 Information (SI) Figure 1) at various dilution ratios (distances) rather than traversing back and
121 forth across the plume with fixed-wing aircraft, resulting in a larger number of independent
122 observations on which to test the null hypothesis relative to the SO₂ and NO_y dilution tracer
123 species.

124

125 *Selection of CFPP*

126 After a thorough review of candidate facilities (see SI), the Crist Plant located in Pensacola,

127 Florida was selected for this study. The facility is owned by Gulf Power Company (Pensacola,
128 FL), a subsidiary of Southern Company (Atlanta, GA). The Crist Plant consists of four coal-
129 fired units sharing two stacks. During the selected sampling period of February 18 – March 1,
130 2008 units #4 and #5 that feed one of the stacks were both shut down for maintenance. The
131 remaining boilers, unit # 6 (320 MW) and unit #7 (500 MW) shared a common 138 meter tall
132 stack. Both units had cold-side electrostatic precipitators (ESPs) for particulate control and Unit
133 # 7 had selective catalytic reduction (SCR) that operates year round for NO_x control. Both units
134 were burning a blend (nominally 50%) of Illinois (high in sulfur and high in halogens) and
135 South American (Columbian) bituminous coal (low in sulfur and low in halogens). The coal was
136 manually “blended” by a front end loader alternately dumping loads of coal from two separate
137 storage piles onto a conveyor belt. The terrain surrounding the plant is essentially flat, and no
138 other significant near-field Hg emission sources were identified.

139

140 *Crist Plant Stack Emissions Measurements*

141 As the stack serving the two active boilers during this study did not have integrated sampling
142 ports for emissions monitoring access, all continuous emissions monitoring systems (CEMs)
143 were installed in the exhaust ducts of each boiler unit prior to discharge into the common stack
144 collocated with the facility’s CEM systems. As a result, overall reported stack emissions are
145 calculated as the proportional average of each exhaust duct normalized to its flow rate. As a
146 function of the Crist Plant’s participation in EPA’s Acid Rain Program, the plant staff measured
147 sulfur dioxide (SO₂), oxides of nitrogen (NO_x), and volumetric exhaust gas flow in each boiler
148 exhaust duct in accordance with 40 CFR Part 75 (see SI).

149

150 Total and speciated Hg emission measurements were made by EPA in each of the two boiler unit
151 ducts using EPA’s Tekran Instruments Corporation (Knoxville, TN) model 3300 series speciated
152 Hg CEM systems (SI Figure 2 and associated description). In the standard Tekran 3300
153 configuration as deployed during this study, TGM and Hg⁰ measurements are made sequentially
154 using a single Tekran Model 2537A cold vapor atomic fluorescence spectrometer (CVAFS) that
155 switches between and alternately samples each channel (SI Figure 3). The Tekran 3300 systems
156 were programmed to measure TGM and Hg⁰ semi-continuously over a 2.5 min
157 collection/analysis cycle. The reported Hg^{II} fraction is calculated as the difference between

158 sequentially measured TGM and Hg⁰ concentrations. An initial multipoint calibration was
159 performed with Hg⁰ on each Tekran CEM following installation and conditioning. Continued
160 measurement performance of each Hg CEM was verified through daily System Integrity/Drift
161 Tests using Hg⁰ and HgCl₂ gas standards as described in EPA Method 30A (25). The Hg CEM
162 stack sampling systems were continuously monitored by on-site personnel during the plume
163 sampling periods to ensure data were available during all airship flight sorties.

164

165 *Additional Speciated Hg Measurements*

166 The reliable measurement of Hg⁰ and Hg^{II} was a critical component of this study. Many
167 variables contribute to the quality and reliability of speciated Hg measurements, including the
168 effects from particulate matter which can not only capture gaseous Hg, but can also oxidize Hg⁰
169 (26). Verifying the quality of the Hg CEMs speciated Hg measurements is difficult and is
170 primarily accomplished by comparison to other speciated Hg measurement techniques, including
171 the Ontario-Hydro (OH) method. For this study, the quality of the speciated Hg CEMs
172 measurements was assessed through comparison to three independent speciated Hg measurement
173 approaches (See SI).

174

175 *Crist Plant Coal Measurements*

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

180

181 *Airship Operations*

182 EPA contracted with Integrated Systems Solutions, Inc. (ISSI; California, Maryland) to provide
183 an airborne sampling platform for this study. ISSI provided an Airship Management Services
184 (AMS; Greenwich, CT) Skyship 600B and flight crew. The AMS Skyship 600B is 61 m long,
185 19 m wide, 20 m high, and holds approximately 7,200 m³ of helium. The airship was powered by
186 two engines with vectorable propellers which allowed for vertical launch, three-dimensional
187 maneuverability, and the ability to maintain a fixed position in winds up to 11 m s⁻¹. The airship
188 met our specifications to accommodate a 2300 kg instrument payload, three scientists, and

189 provide 40 amps of 120 VAC power. In addition, the airship had a 650 km range and an
190 endurance of 8 h at a cruising speed of 65 km h⁻¹. The airship was equipped with a state-of-the-
191 art avionics package including an encoding altimeter, air temperature sensor, and redundant
192 global positioning systems.

193
194 The operational flight window for this study was from February 18-March 1, 2008. Conducting
195 the study in the winter was advantageous in that (i) the plume thermal buoyancy was maximized
196 and in general kept the plume at a safer sampling altitude, and (ii) lower atmospheric turbulence
197 minimized initial emission plume dispersion. Each sampling day consisted of approximately 7-8
198 hours of airship flight time (depending on wind speed and the resultant fuel burn required to
199 maintain airship positioning). The first hour of each flight was used to establish the upwind
200 background concentrations at the estimated sampling altitude (n = 24 discrete 2.5 min integrated
201 semi-continuous Hg measurements). The airship was then maneuvered downwind of the exhaust
202 stack as close to the stack emission point as safely possible, approximately 200 - 800 m. The
203 subsequent downwind sampling locations were determined based on the airship crew's ability to
204 identify and maintain the airships position in the dissipated exhaust plume.

205 206 *Airship Measurements*

207 The automated Hg speciation and criteria gas measurements in the stack and in the airship were
208 made using similar instrumentation manufactured by Tekran and Thermo Electron, respectively.
209 Two minor differences in the configuration of the Tekran speciation systems were (i) the stack
210 system used an inertial sampling probe to extract sample gas from the stack exhaust stream while
211 the airship configuration did not require this component, and (ii) the stack measurement system
212 utilized one 2537A cold vapor atomic fluorescence spectrometer (CVAFS) instrument that was
213 switched between the Hg⁰ and TGM channels while the airship system utilized two 2537A
214 CVAFS instruments to continuously sample both channels. The criteria gas measurements were
215 made using Thermo Electron model 43i pulsed fluorescence (SO₂) and model 42i
216 chemiluminescence (NO_x) dual-range federal reference equivalent method certified instruments
217 (See SI for calibration information). All instruments were kept energized on ground power while
218 the airship was moored to keep analytical bench temperatures stable.

219

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

229
230 During sampling, a twenty meter heated sampling umbilical line was lowered from the airship
231 gondola to project the sampling inlets into the plume while minimizing the impact of the airship
232 on the measurements. A heated ($120\text{ }^\circ\text{C}$) Teflon particulate matter filter (Hg , SO_2) and heated
233 ($350\text{ }^\circ\text{C}$) molybdenum converter (NO_Y) enclosure was attached to the inlet of the umbilical line.
234 The umbilical line encapsulated three Teflon sampling lines and was heated to $120\text{ }^\circ\text{C}$. It was
235 used for continuous Hg , SO_2 , and NO_Y sample transport into the gondola. One of the lines was
236 used to introduce ultra-carrier grade N_2 gas (99.9995%) to the inlet to purge lines and provide
237 zero air value confirmation between in-plume sample points. Supplemental sample line flow
238 was provided using a vacuum pump to maintain a sample line retention time of less than five
239 seconds and ensure synchronous sampling through the two sampling lines.

240
241 Data provided by Gulf Power estimated that (i) Hg^{II} would constitute approximately 84% of the
242 total Hg emission from the Crist Plant, (ii) Hg^{II} stack emission concentration would be
243 approximately 0.47 ppb or $3.94\text{ }\mu\text{g m}^{-3}$ (as Hg^0) at full load, and (iii) Hg^0 stack emission
244 concentration would be 0.09 ppb or $0.75\text{ }\mu\text{g m}^{-3}$ at full load. Based on historical data, Gulf
245 Power indicated that it was expected that the Crist Plant units #6 and #7 would be operating at
246 between 80-95% full load. For planning purposes, an 80% total combined load on the two units
247 was anticipated. Estimated stack exhaust concentrations of Hg and tracer species for 80% total
248 combined load were calculated and are presented in SI Table 1.

249
250 Based on the dilution rates from the Plant Bowen experiment (19), our ability to quantify Hg^{II}

251 using the Tekran speciation system was calculated to be of the same magnitude as our ability to
252 quantify NO_Y and SO_2 (SI Table 2) and effectively ranged between DR of 100 and 25,000 or
253 approximately 0 to 32 km. Even with a limiting case scenario for Hg^{II} reduction equating to
254 TGM/ Hg^{II} ratio of 10, we anticipated still being able to quantify our key tracers (SO_2 , NO_Y) as
255 well as Hg^{II} up to a DR of 25,000.

256

257 *Airship Data Screening and Validation*

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

275

276 Although we were unable to measure TGM in-plume and therefore directly calculate in-plume
277 Hg^{II} concentrations due to the malfunction of the Tekran model 3320 gas conditioner TGM
278 channel in the airship, we were able to test the null hypothesis that Hg^{II} was not reduced to Hg^0
279 in the Crist Plant exhaust plume using the difference in the expected versus observed Hg^0
280 concentrations. For each in-plume run the airship Hg^0 , SO_2 and NO_Y concentrations were first
281 corrected for their corresponding average levels measured during the upwind background runs of

282 that same day. The effective DR, in-stack SO_2/NO_x /in-plume SO_2/NO_y ratios, and the percent
283 Hg^0 of total Hg in-stack were then calculated for each 2.5-min integrated data point.

284
285 Due to the plume's thermal buoyancy, loss of Hg from the plume due to depositional processes is
286 unlikely to occur over the short distances measured downwind of the stack exit. Therefore,
287 TGM is expected to be conserved in-plume, with concentrations depending on the plume's DR.
288 In addition, if no reduction or oxidation of Hg species occurs in the plume, the percent of Hg^0 in-
289 stack: $(\text{Hg}^0_{\text{in-stack}}/\text{TGM}_{\text{in-stack}})*100\%$; is the same as the percent Hg^0 in-plume. Based on these
290 assumptions, the % $\text{Hg}^0_{\text{in-plume}}$ was calculated using equation 1.

291

$$292 \quad \% \text{Hg}^0_{\text{in-plume}} = \left(\frac{\text{Measured } \text{Hg}^0_{\text{in-plume}}}{\text{Expected TGM}_{\text{in-plume}}} \right) * 100 \quad (1)$$

293

294 Where: $\text{Expected TGM}_{\text{in-plume}} = \text{TGM}_{\text{in-stack}}/\text{Plume DR}$
295 $\text{Plume DR} = \text{SO}_2 \text{ (in stack)}/\text{SO}_2 \text{ (in plume)}$

296
297 The % Hg^{II} reduction was then calculated by subtracting the % $\text{Hg}^0_{\text{in-plume}}$ from the measured
298 % $\text{Hg}^0_{\text{in-stack}}$.

300 *Meteorological Measurements*

301 An EPA Remtech (St. James, NY) phased array Doppler SODAR system was deployed at the
302 University of West Florida campus to determine local meteorological conditions aloft such as
303 vector wind speeds, wind direction, and mixing layer height. Data from the SODAR system was
304 used to support airship operations and estimate plume aging time (SI Equation 3).

306 *Statistical Analysis*

307 Data processing and all statistical analyses were performed using SAS v.9.3 (SAS Institute,
308 Cary, NC). The assumptions of the parametric procedures were examined using residual plots,
309 skewness and kurtosis coefficients, Shapiro-Wilk test, and the Brown-Forsythe test. The t-test
310 for independent samples parametric procedure was applied where appropriate. If data seriously
311 violated the assumptions of the parametric procedure, then a Wilcoxon test was utilized. A level
312 of significance of $\alpha=0.05$ was used for all statistical procedures.

313

314 **Results and Discussion**

315 *Stack Emissions*

316 A summary of the plant's daily operational process parameters (electrical load and stack flow)
317 and combustion emissions (SO₂, NO_x, and Hg) are presented in Table 1. The average values
318 represent the period of time each day when valid Hg CEM measurements data were collected
319 (typically 10:00-18:00). While plant emissions measurement data are routinely available 24
320 hours/day, Hg CEM data are not, due to automated quality control checks performed at the
321 beginning and end of each test day. Subsets of these same data are presented in SI Table 3
322 summarizing the emission measurements for the actual flight time periods that airship sampling
323 was conducted. The gaseous emissions for these same time frames are graphically depicted in SI
324 Figures 4a and 4b to illustrate the stability as well as temporal variability of the process
325 emissions. While the CFPP stack emissions are relatively stable over the nominal 8h test day, it
326 can be seen that day-to-day emissions were highly variable. This variability is attributed to
327 variations in coal blend. During the study, the plant experienced a malfunction to the primary
328 coal feeding system that resulted in additional variation to the coal charged into the boilers from
329 February 25-29, 2008 as coal was directly fed from the bulk storage piles into the boilers. The
330 reported nominal 50/50 blend of Illinois and Colombian bituminous coal became highly variable.
331 This variability is evidenced in the daily coal analyses presented in Table 2 as well the daily
332 stack emissions averages presented in Table 1.

333

334 A significant shift in stack emissions was observed on 2/28 as evidenced by the lower SO₂
335 emissions as well as the significant decrease in %Hg^{II} distribution. A closer examination of the
336 daily coal analyses and the daily stack emissions indicates that there is not consistent agreement
337 between measured coal elemental levels (e.g., sulfur) and stack emissions (SO₂). This is likely
338 due to the "inexact" manual blending approach combined with the single point-in-time coal
339 sampling. The six coal samples collected between 02/22-02/24 are clearly representative of the
340 Columbian coal with low lower sulfur (0.6±0.1; mean ± standard deviation), lower chlorine
341 (70±16), and higher bromine/chlorine ratio (0.051±0.021), while the four samples collected
342 between 02/28-02/29 are clearly representative of Illinois coal with higher sulfur (1.0±0.1),

343 chlorine (2031 ± 142), and lower bromine/chlorine ratio (0.003 ± 0.001 ; Table 3). The resulting
344 stack emissions are clearly the definitive basis for assessing coal blend characteristics.

345
346 The coal blend changes resulted in a highly variable net chlorine content (ranging from <100
347 ppm to >2000 ppm) as well as moderate variations in sulfur and Hg content. The chloride
348 content in coal is known to be an important component in determining Hg speciation in CFPP
349 flue gas (28, 29). So the increase in the relative proportion of Columbian coal should result in a
350 moderate decrease in SO_2 and a major decrease in chlorine in the combustion flue gas, reducing
351 the overall Hg^0 oxidation potential. The relationship between measured daily integrated stack
352 Hg^{II} and SO_2 concentrations is presented in Figure 1a, and the relationship between % Hg^{II} and
353 SO_2 is presented in Figure 1b. The result of the significant relationship ($p=0.0026$) between in-
354 stack SO_2 and Hg^{II} concentration is consistent with varying blends of Columbian and Illinois
355 coal. The significant ($p=0.0012$) exponential relationship between in-stack SO_2 concentration
356 and % Hg^{II} suggests that once SO_2 concentration reaches approximately 450ppm, the formation
357 of Hg^{II} levels off and is no longer sensitive to shifts in coal blend. But when the increase in the
358 Columbian coal fraction results in SO_2 concentrations lower than approximately 450ppm the
359 production of Hg^{II} is reduced, similar to what we believe occurred on 02/28-02/29 when there
360 was a 3-4 fold increase in Hg^0 in the flue gas on the 2/28 with the mean % Hg^{II} in-stack
361 decreasing ~13% compared to the previous day (Table 1). While the short term variability of in-
362 stack SO_2 and Hg speciation observed by CEMs over the course of the individual 1-h airship
363 sampling periods was low, day-to-day variability was substantially higher in response to the
364 changing blend of coal being charged into the boilers (Table 1, SI Figures 4a-4b).

365 366 *Characterizing the Quality of the Speciated Hg Stack Measurements*

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

373

374 A summary of the Unit 7 speciated Hg measurements by all available techniques is presented in
375 SI Table 4. These results show that not only are Unit 7 Hg^{II} emissions consistently greater than
376 90% (with the exception of those made on 2/28), but that all the speciated Hg measurements
377 techniques reported consistent results. The Hg CEMs speciated Hg^{II} measurements were slightly
378 higher relative to the other techniques, with the OH speciated measurements consistently
379 measuring the lowest relative Hg^{II} (-7.1±2.9%). The speciated trap and FUME Hg^{II} speciated Hg
380 measurements also agree well with those observed by the Hg CEMs measurements (-0.3±0.7%
381 and -3.3±2.2%, respectively). As a result of the excellent agreement between the Hg CEMs, the
382 OH speciated Hg measurements as well as the alternative speciated Hg measurements, the
383 speciated Hg data reported in this study are based solely on the Hg CEMs.

384
385 The Unit 7 Hg^{II} emissions are also relatively consistent over the duration of the test program,
386 averaging ~96% ± 5% Hg^{II} for the Hg CEMs Hg^{II} measurements. However, a significant drop in
387 Hg^{II} emissions is observed on 2/28 and 2/29 for all speciated Hg measurement techniques due to
388 a significant shift in coal blend (as discussed in the previous section).

389

390 *In-plume Measurements*

391 A summary of each valid in-plume measurement run is presented in Table 4 and an integrated
392 study average compared to other published data is presented in Table 5. The average 2.5-min
393 integrated %Hg⁰_{in-stack} during the valid in-plume measurement periods was 6.2 ± 5.8% and
394 ranged from 0.0 to 16.1%. The calculated %Hg⁰_{in-plume} during the same periods was 11.1 ± 9.9%
395 and ranged from 1.4 to 58.8%. The unexpected malfunction of the Crist Plant coal blending
396 system provided a unique opportunity to observe the facility Hg emission rate, in-stack
397 speciation, and resulting in-plume dynamic response to changing sulfur, chloride, and Hg
398 concentrations in the feed coal. In-stack and concurrent in-plume measurements conducted on
399 February 24, 2008 during typical coal blending operations showed a relatively small but
400 significant in-plume reduction of Hg^{II} to Hg⁰ (3.2 ± 1.5%) that was not significantly related to
401 plume aging time (Table 4; Figure 2a).

402

403 On February 28, 2008 following the malfunction of the automated coal charging system and
404 during the manual charging of mostly Colombian coal (low sulfur and halide content), we
405 observed no significant reduction of Hg^{II} to Hg^0 . On March 1, 2008 after the automated coal
406 charging system was back on-line and the coal blend was transitioning back to normal, we
407 observed a larger significant in-plume reduction of Hg^{II} to Hg^0 ($11.2 \pm 13.8\%$) that was
408 significantly related to plume aging time (Table 4; Figure 2b). The highest Hg^{II} to Hg^0 reduction
409 rate of 58.8% was observed at the furthest point away from the exhaust stack (1.5 km), and was
410 well within the range of Edgerton et al. (15) estimated Hg^{II} to Hg^0 reduction based on surface
411 observations downwind of the Crist Plant.

412

413 It has been generally assumed (30, 31, 32) and was later confirmed (12, 13, 14) that Hg^{II} present
414 in CFPP plumes deposits, on average, closer to its emission source than Hg^0 , causing near field
415 deposition enhancement due to its chemical/physical properties. However this study and recent
416 field/modeling studies suggest that in-plume reduction of Hg^{II} to Hg^0 can also occur depending
417 on coal composition that may moderate the near field impact (15, 16, 17). But as these results
418 demonstrate, coal characteristics can play a major role in determining in-stack and in-plume Hg
419 concentration and speciation when all other plant variables remain equal.

420

421 It is assumed that Hg^{II} in the atmosphere exists primarily as mercuric chloride (HgCl_2). However,
422 the mechanisms of interaction between Hg in flue gas, fly ash, chlorine-containing species, SO_2 ,
423 NO, water vapor, and trace elements from different coal types and sources remain ambiguous
424 (17, 28, 29, 33, 34, 35). In bench reactor tests using simulated flue gas, it has been shown that
425 Hg oxidation rates decreased in the presence of SO_2 , NO, and water vapor, while Hg reduction
426 rates increased. In addition, Hg reduction rates increased as flue gas temperature rose, while
427 reduction rates declined as dichloride (Cl_2) concentrations increased (15). Hence, SO_2 , NO, and
428 H_2O may affect the concentrations of chloride ions and free chlorine in flue gas and determine
429 how effectively chlorine will form the chlorinated sites on unburned carbon needed to oxidize
430 Hg^0 (17, 28, 29). The effect of Cl_2 , SO_2 , and NO on the formation of Hg^{II} in simulated flue gas
431 has also been predicted (33). In the presence of Cl_2 , about 80% of the Hg^0 was oxidized to Hg^{II} .
432 Adding SO_2 to the flue gas mixture lowered the oxidation rate to 30%. NO had little to no effect
433 on the mercury oxidation rate (33). Tong et al. (34, 35) tested variables that potentially affect

434 heterogeneous photoreduction of HgCl_2 . It was found that sulfur in fly ash possibly enhanced
435 photoreduction, while chlorine, carbon, and iron inhibited photoreduction. The reduction of Hg^{II}
436 to Hg^0 was only observed in the presence of light, with average reduction rates of 20–30% per
437 hour when normalized to real-world clear sky atmospheric intensities (34, 35).

438
439 The flue gas SO_2 concentrations on February 28, when we observed no significant Hg^{II} reduction
440 in the plume, were the lowest of all our measurement days ranging from 315–321 ppm (Table 1;
441 SI Table 3) suggesting our field observations were consistent with the laboratory observations of
442 Zhao et al. (17). On March 1 when we observed the highest degree of Hg^{II} reduction to Hg^0 of
443 up to 55.3%, SO_2 flue gas concentrations were higher (ranging from 430–450 ppm; SI Table 3)
444 indicating a higher proportion of Illinois coal with correspondingly higher chlorine, bromine, and
445 iron (Table 3) consistent with conditions favoring more reduction of Hg^{II} in the flue gas (17, 33,
446 34, 35). Also on February 24, when significant mercury reduction was observed, SO_2 flue gas
447 and $\% \text{Hg}^{\text{II}}$ conditions were similar to that of March 1 again suggesting a higher proportion of
448 Illinois coal with correspondingly higher chlorine and iron (Table 3).

449
450 Our results are (i) generally in agreement with those from previous in-plume studies (Table 5)
451 demonstrating instances of significant Hg^{II} to Hg^0 reduction (15, 16, 17, 18), as well as instances
452 of no significant plume speciation change (22), and (ii) highlight the importance of coal
453 composition in driving in-stack and in-plume Hg species dynamics. The results of this study
454 further confirm that in-plume reactions exist that result in the reduction of Hg^{II} . Moreover,
455 variable levels of Hg^{II} reduction were observed. As a result of the significant variation in the
456 relative amounts in the coals blended during this study and their diverse chemical composition,
457 the data suggest that coal chemical composition and characteristics are a major influence on Hg^{II}
458 production and in-plume reduction chemistry. Therefore, measurements made under specific
459 conditions at CFPPs cannot be generalized to other facilities or operating conditions.

460
461 **Acknowledgements:** The United States Environmental Protection Agency through its Office of
462 Research and Development funded this research partially through an Advanced Monitoring
463 Initiative Grant. It has been subjected to Agency review and approved for publication. Mention
464 of trade names or commercial products do not constitute an endorsement or recommendation for

465 use. We thank John Jansen and Justin Walters (Southern Company), and Dwain Waters (Gulf
466 Power) in particular for access to the Crist Plant and collaboration with the project; Airship
467 Management Services (AMS) and Integrated Systems Solutions Incorporated (ISSI) for airship
468 operations and logistical support; Ed Brown (EPA) for Hg measurement support; Mike Wheeler
469 (Alion) and Chris Winterrowd (ARCADIS) for instrument calibration support; and Jane Caffery
470 (University of West Florida) for providing laboratory space and hosting our Sodar system. We
471 also thank Eric Edgerton from Atmospheric Research and Analysis, and Leonard Levin from
472 EPRI for their contributions to this project.

473

474 **Supporting Information Available:** This information is available free of charge via the
475 Internet at <http://pubs.acs.org/>.

476

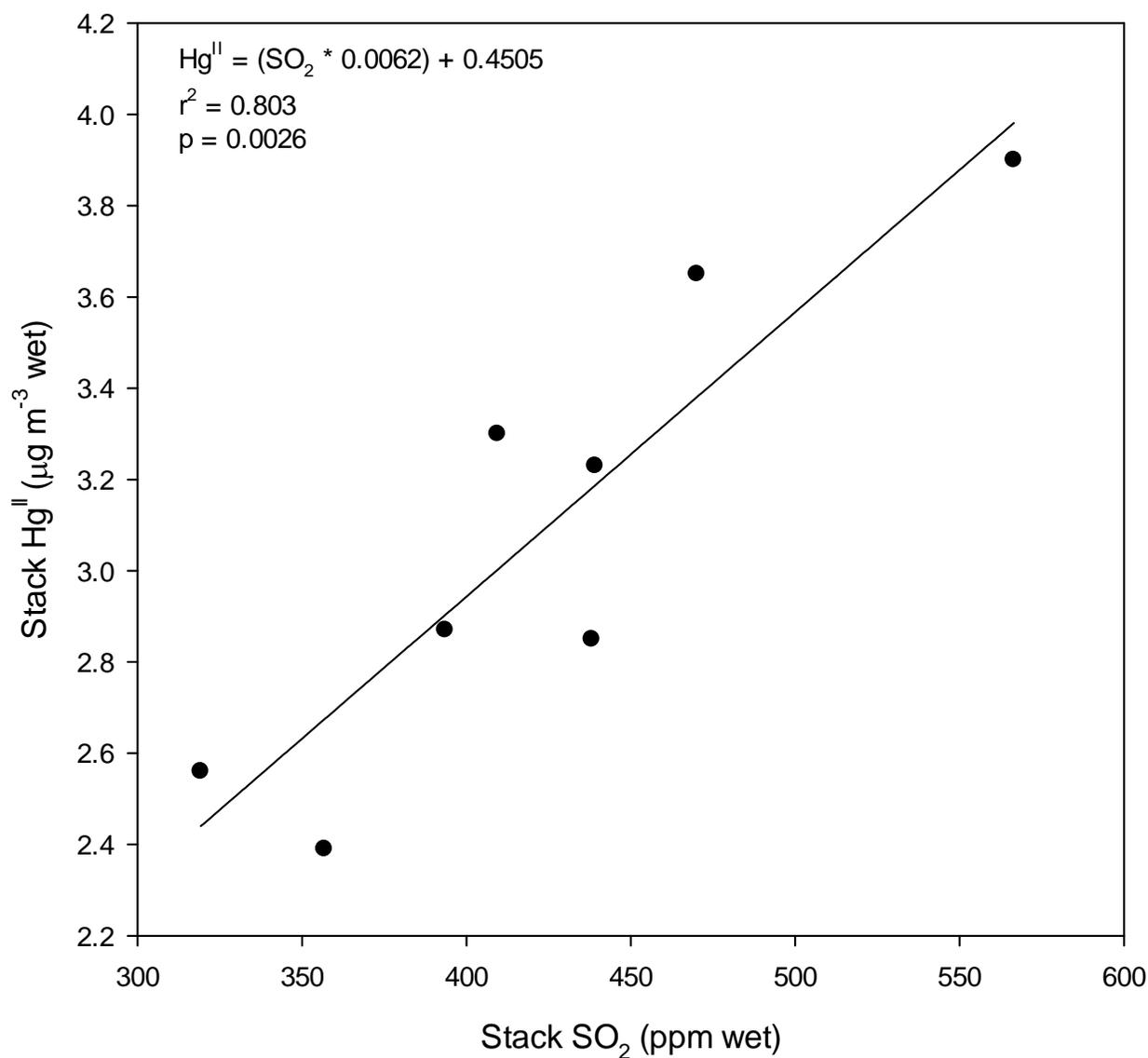
477 **List of Figures**

478 Figure 1. Relationship between daily (10:00 – 18:00) integrated in-stack CEM (a) Hg^{II} and SO₂
479 concentration, and (b) percent Hg^{II} and SO₂ concentration (February 23 – March 1,
480 2008).

481 Figure 2. Relationship between calculated Hg^{II} to Hg⁰ reduction and plume aging time for sorties
482 flown on (a) February 24, 2008, and (b) March 1, 2008 when individual sample periods
483 were categorized as plume impacted.

484

485 Figure 1a.

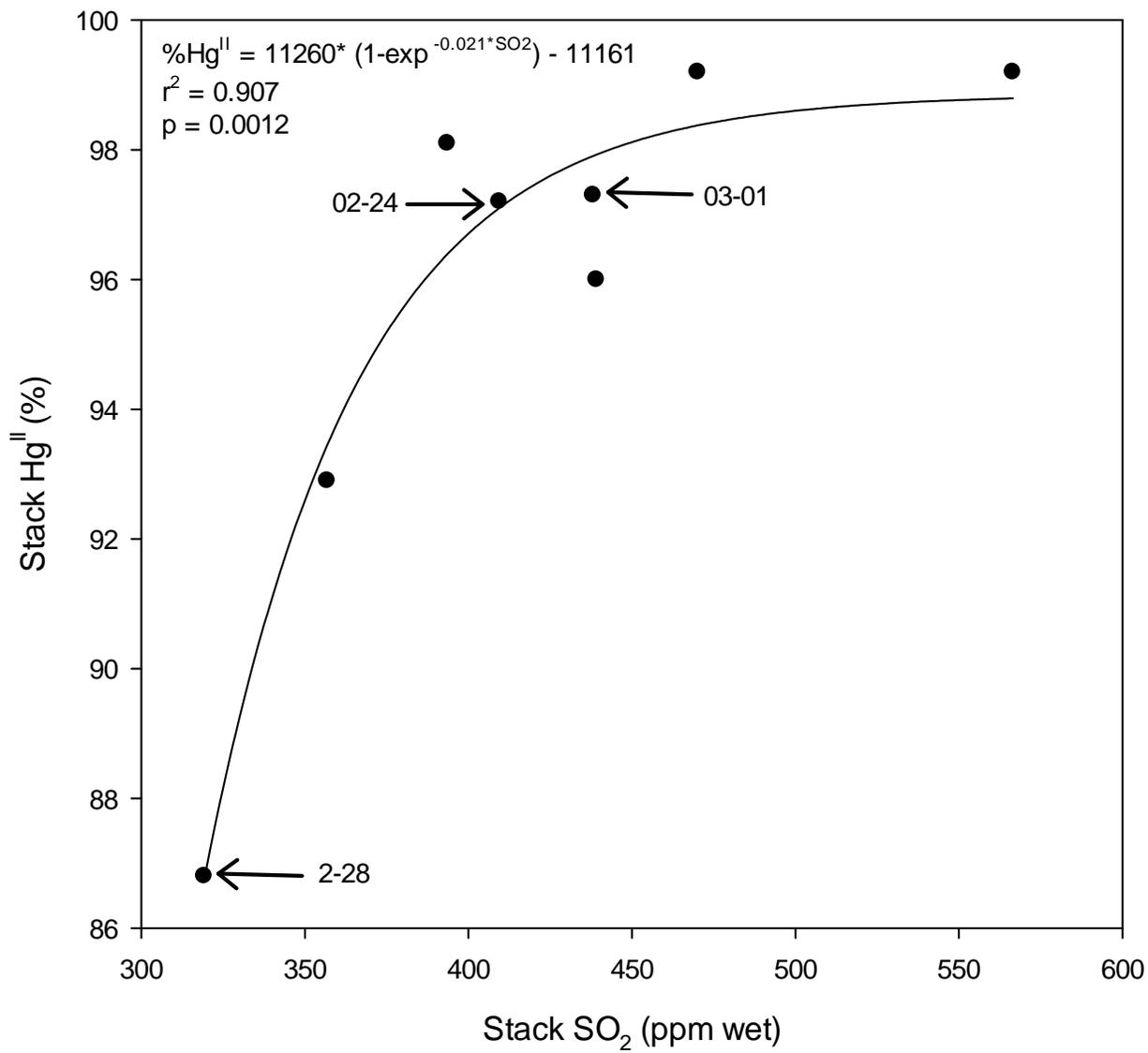


486

487

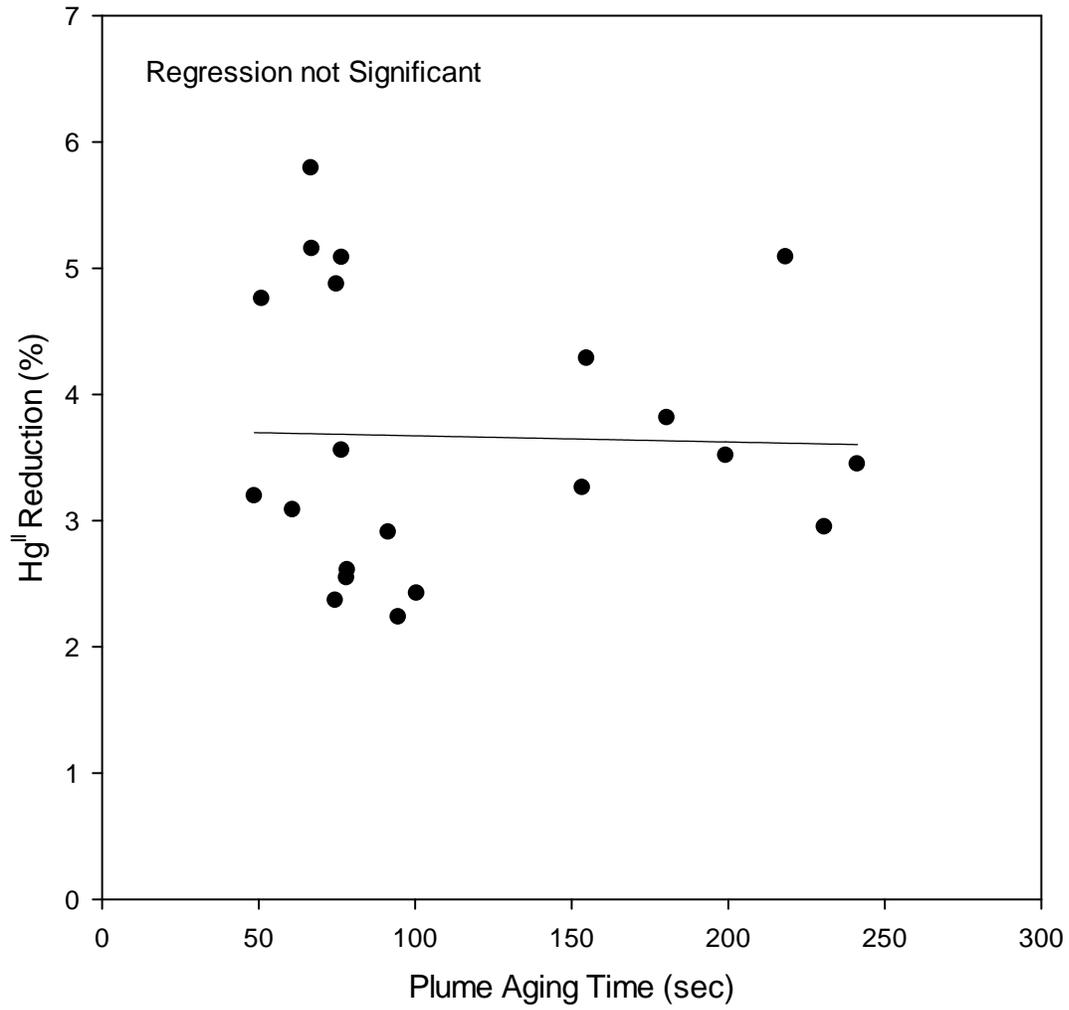
488

489 Figure 1b.



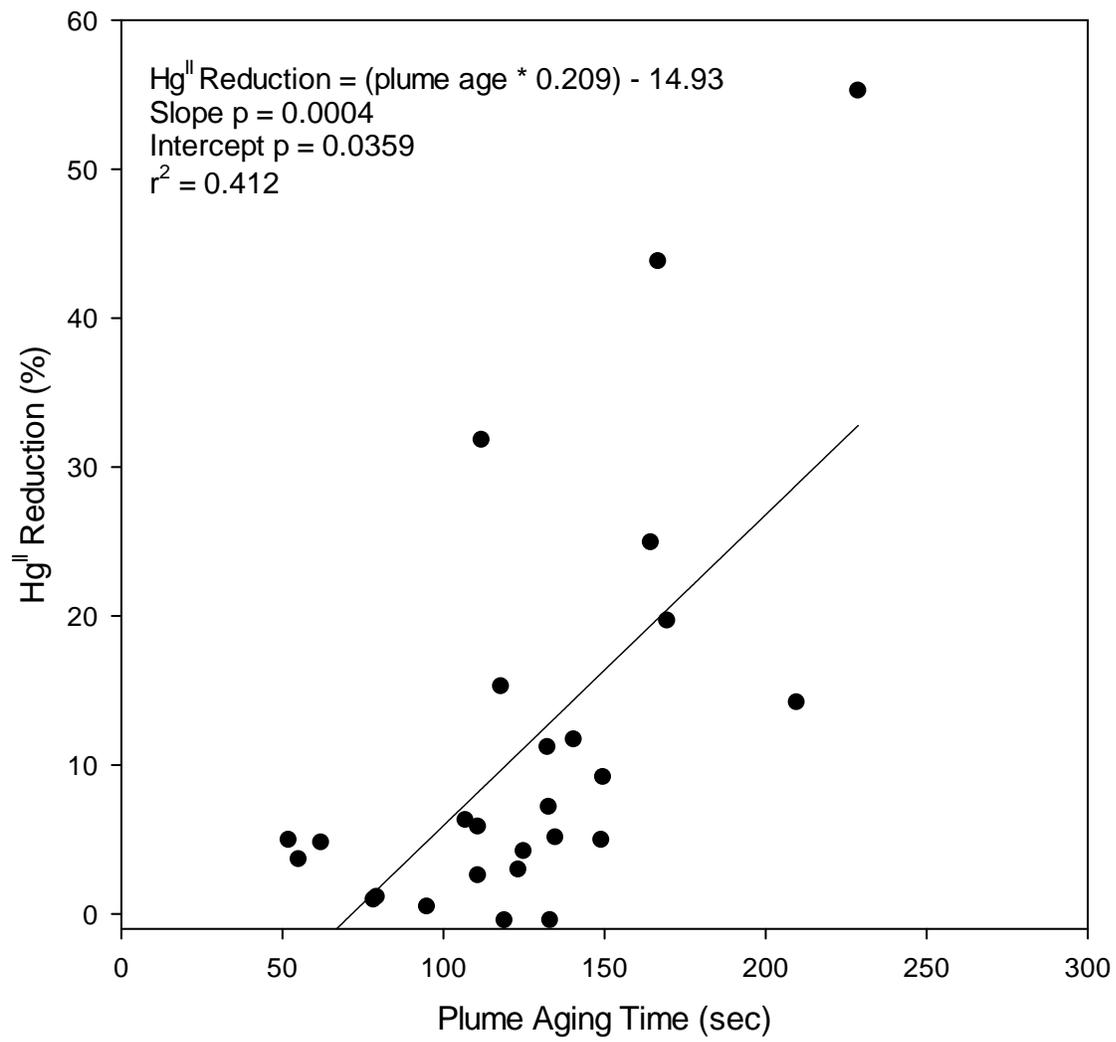
490
491

492 Figure 2a.



493
494

495 Figure 2b.
496



497
498

499 **List of Tables**

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

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

503 Table 3. Characteristics of Columbian and Illinois Categorized Coal Samples

504 Table 4. Summary of All Valid In-plume Measurements

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

506

507

508 Table 1.

509

	NO _x ppm wet	SO ₂ ppm wet	CO ₂ % wet	Flow kefm	Load MW	Hg Concentrations $\mu\text{g m}^{-3}$ wet			Hg ^{II} %
						Hg ^I	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

510

511

512

513 Table 2.

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

514 *Coal ash basis

515

516

517 Table 3.

518

Coal	Sulfur %	Mercury mg kg ⁻¹	Chlorine mg kg ⁻¹	Bromine mg kg ⁻¹	Br/Cl Ratio	Iron Oxide* %
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

519 *Coal ash basis

520

521 Table 4.

522

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					

523 ^A Number of valid 2.5 min samples within each run

524 ^B Values are mean ± standard deviations

525 ^C Calculated by dividing the measured Hg⁰ levels in-plume by the calculated TGM levels in-plume

526 ^D Effective three dimensional distance downwind from stack exit (km)

527 ^E Remtech SODAR (m s⁻¹) at airship altitude

528

529 Table 5.

	Plant Crist*	Plant Bowen (19)	Pleasant Prairie (20)	OLF Ambient Site (15)
	Pensacola, FL	Atlanta, GA	Kenosha, WI	Pensacola, FL
Hg^{II} Reduction to Hg⁰	0 - 36%	~12%	~44 - 54%	37 - 74%
Plume Reaction Time	< 1 - 5 min	---	---	2 - 5 hours
Stack Distance (km)	0.4 - 1.6	~10 - 12	0.6 - 16	14.6

530 *This Study – stack distance is minimum - maximum

531

- (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 Programme, 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 Programme, 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 of 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 Geokolje*, 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. *Journal of Geophysical Research-Atmospheres*, **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. *Journal of Physical Chemistry A*, **2003**, 107, 4478-4482.
- (24) Seigneur, C.; Vijayaraghavan, K.; Lohman, K. Atmospheric Mercury Chemistry: Sensitivity of Global Model Simulations to Chemical Reactions. *Journal of Geophysical Research-Atmospheres*, **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 proceeding 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-NOx 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., 1998. Atmospheric Mercury - An Overview, *Atmospheric*

Environment, 32, 809–822.

- (31) Mason R.P., Sheu G.R., 2002. Role of Ocean in the Global Mercury Cycle, *Global Biogeochemical Cycles*, 16, 1093, doi:10.1029/2001GB001440.
- (32) Pehkonen S.O., Lin C.-J., 1998. Two-phase Model of Mercury Chemistry in the Atmosphere, *Atmospheric Environment*, 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. *Environmental Science: Processes & 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. *Atmospheric Research.* **2014**, 138, 324-329.

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

Matthew S. Landis,*Jeffrey V. Ryan, Arnout ter Schure, Dennis Laudal

Supporting Information Figures

Figure 1: Airship sampling Crist Plant stack emission plume exhaust

Figure 2: Schematic of Tekran Model 3300 CEM system

Figure 3: Schematic of standard Tekran 3320 conditioner showing the Hg⁰ (A) and TGM (B) sampling channels. NOTE: Airship version did not have selector valve as both channels had associated Tekran Model 2537A CFAFS instruments

Figure 4: Time series plot of in-stack (a) NO_x and SO₂ (b) total mercury concentrations

Figure 5: Relationship between 2.5-min integrated CEM in-stack (a) Hg^{II} and SO₂ concentrations, and (b) percent Hg^{II} and SO₂ concentration (February 23 – March 1, 2008; n = 1333).

Supporting Information Tables

Table 1: 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 2: 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 Hg⁰)

Table 3: Flight time summary of CEM stack measurements

Table 4: Comparison of in-stack speciation method results

Table 5. Summary of airship in-plume measurements (mean ± standard deviation)

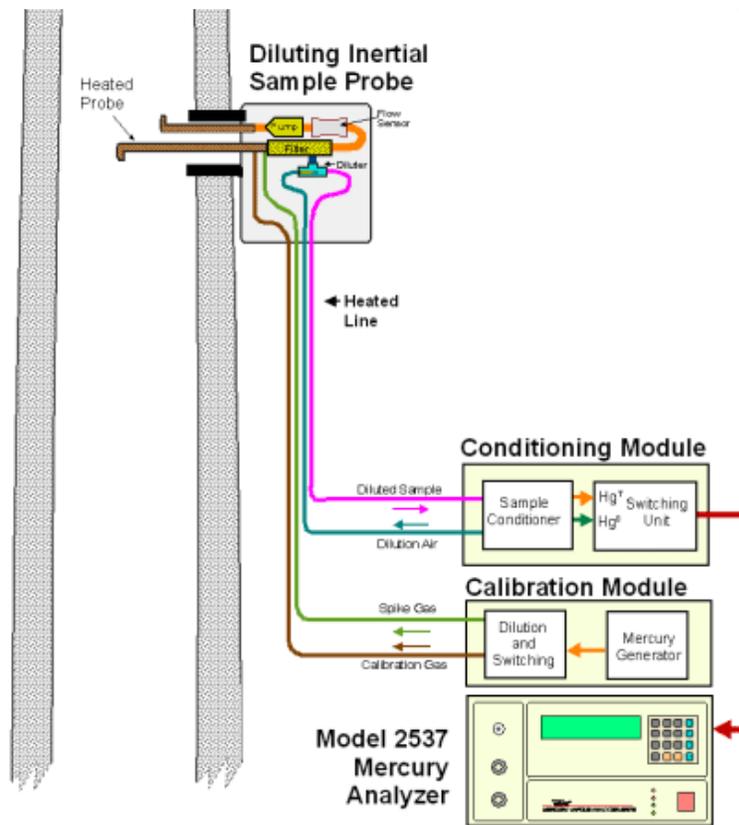
Supporting Information Methods

- 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
- Meteorological measurements

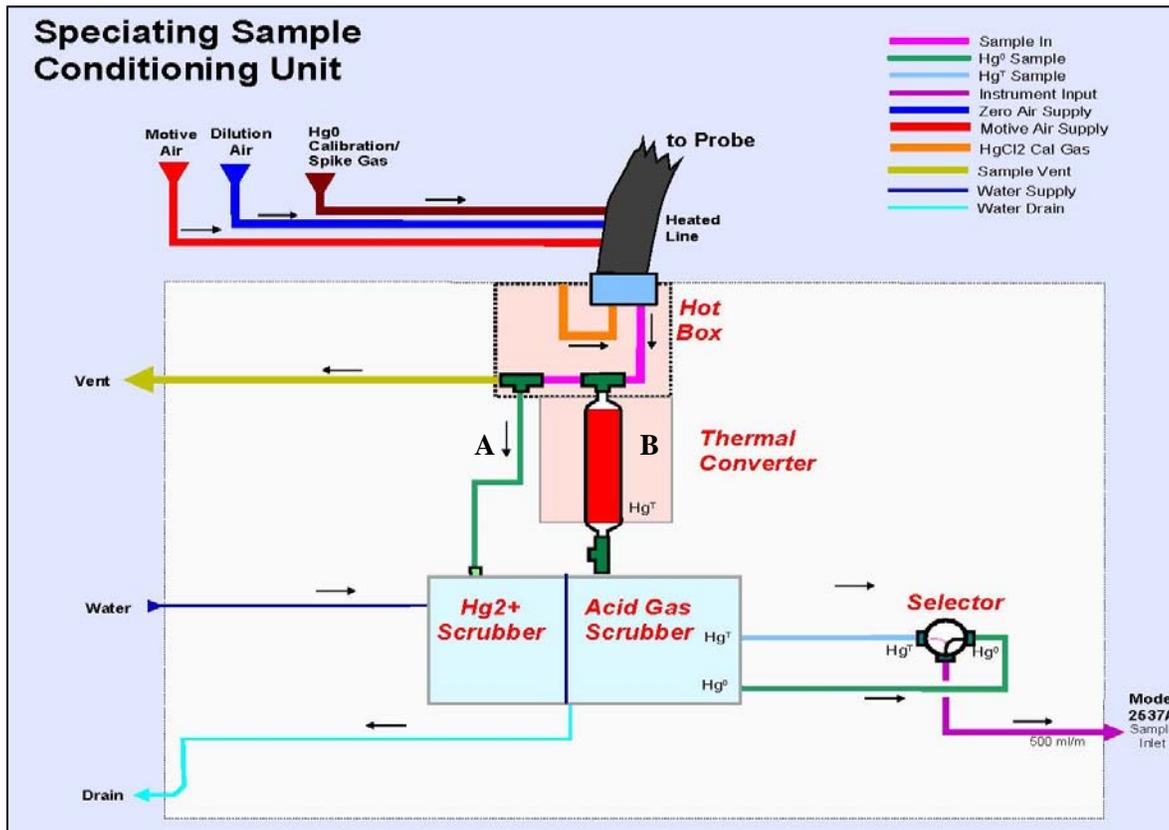
SI Figure 1. Airship sampling Crist Plant stack emission plume exhaust



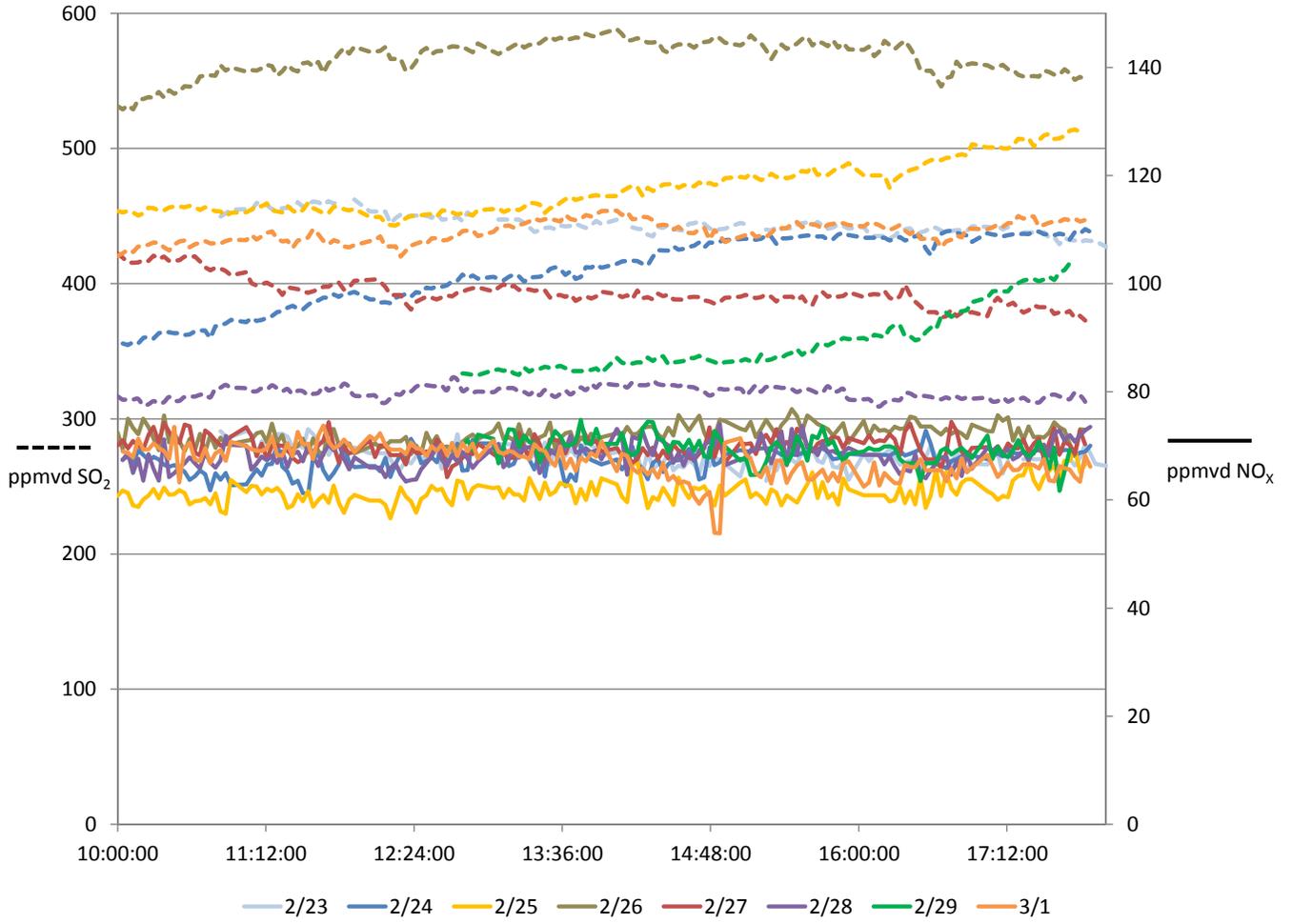
SI Figure 2. Schematic of Tekran Model 3300 CEM system.



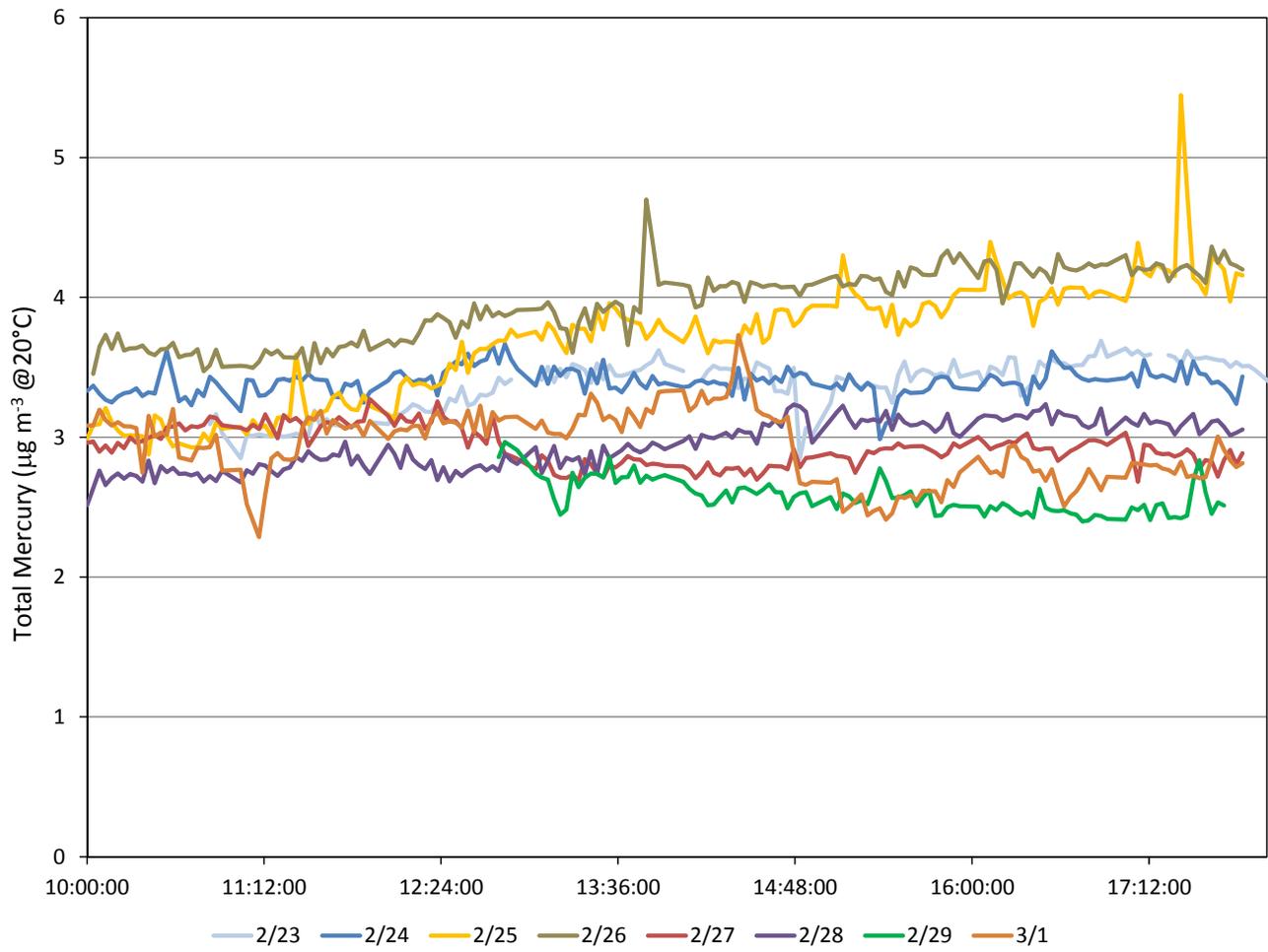
SI Figure 3. Schematic of standard Tekran 3320 conditioner showing the Hg⁰ (A) and TGM (B) sampling channels. **NOTE:** Airship version did not have selector valve as both channels had associated Tekran Model 2537A CVAFS instruments.



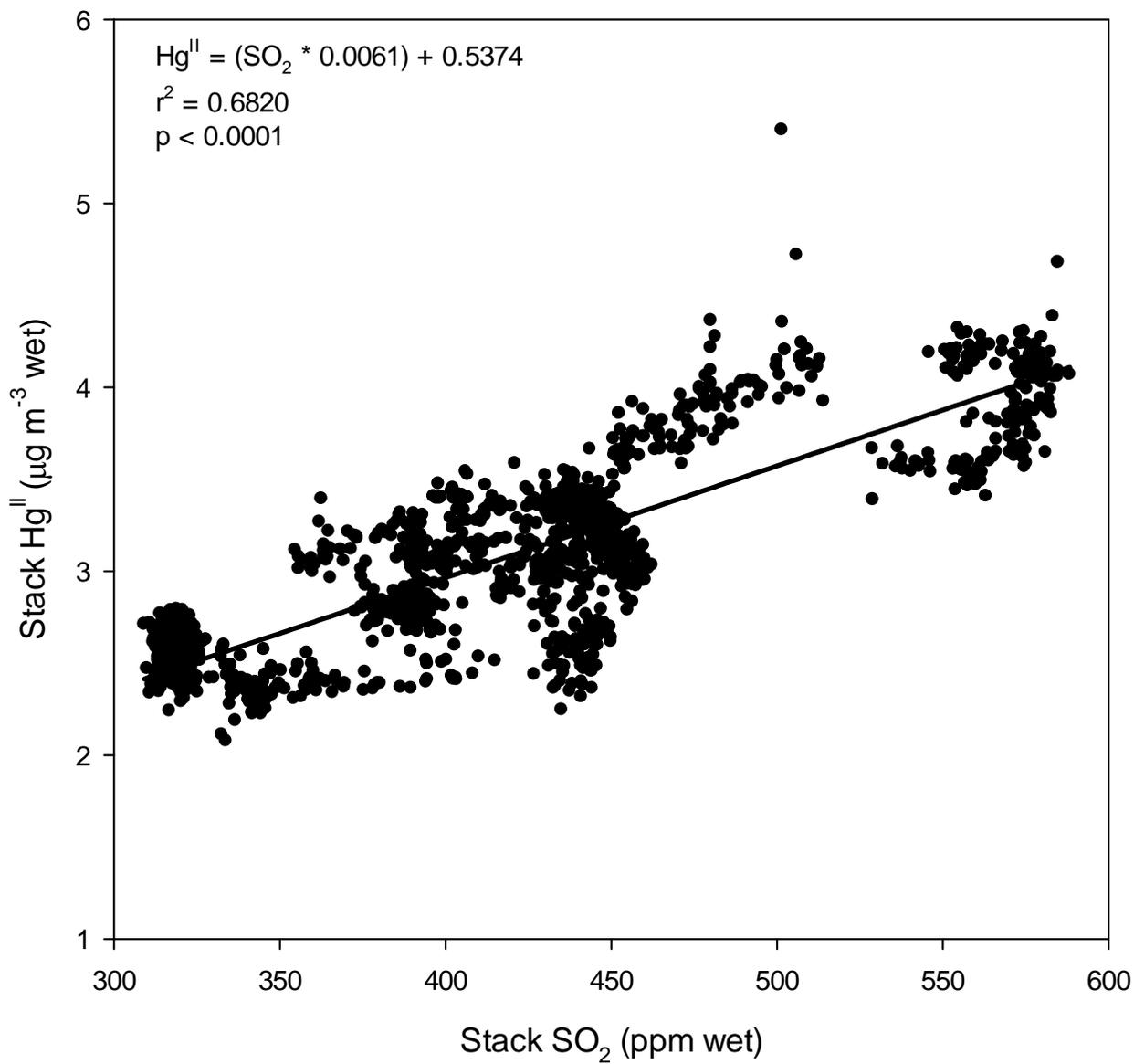
SI Figure 4a. Time series of NO_x and SO₂ stack emissions.



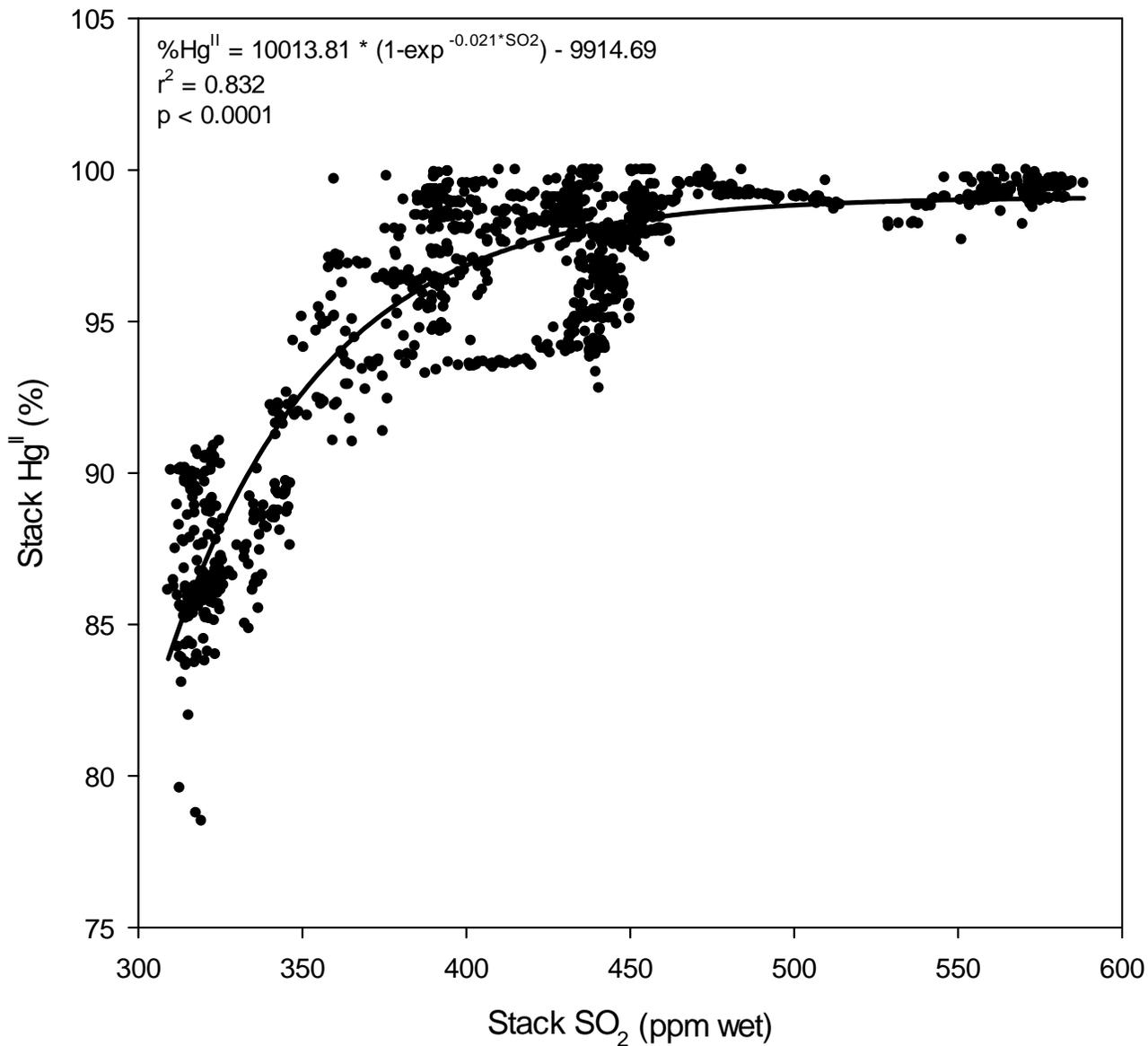
SI Figure 4b. Time series of total mercury stack emissions.



SI Figure 5a. Relationship between 2.5-min integrated in-stack CEM Hg^{II} and SO₂ concentrations (February 23 – March 1, 2008; n = 1333).



SI Figure 5b. Relationship between 2.5-min integrated in-stack CEM percent Hg^{II} and SO₂ concentration (February 23 – March 1, 2008; n = 1333).



SI Table 1. 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.

Load	MW	Stack Parameters			Estimated Concentrations				
		Flow (ACFM)	Temp (°C)	Velocity (m s ⁻¹)	SO ₂ (ppm)	NO _x (ppm)	CO ₂ (%)	Hg ⁰ (ppb)	Hg ^{II} (ppb)
100	820	3,287,000	160	39.2	497	84	11.77	0.0877	0.4665
80	656	2,778,000	146	33.1	460	73	10.93	0.0812	0.4321
50	410	2,015,000	124	24.0	405	57	9.67	0.0715	0.3804

SI Table 2. 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 Hg⁰).

Dilution Ratio	Estimated Concentrations					With Background	
	SO ₂ (ppb)	NO _y (ppb)	CO ₂ (ppm)	Hg ⁰ (ng m ⁻³)	Hg ^{II} (ng m ⁻³)	Hg ⁰ (ng m ⁻³)	Hg ^{II} (ng m ⁻³)
100	4602	732	1093	7.55	39.41	9.05	39.42
200	2301	366	546	3.77	19.71	5.27	19.71
500	920	146	219	1.51	7.88	3.01	7.89
2000	230	37	55	0.38	1.97	1.88	1.98
5000	92	15	22	0.15	0.79	1.65	0.79
10,000	46	7	11	0.08	0.39	1.58	0.40
25,000	18	3	4	0.03	0.16	1.53	0.16
75,000	6	1	1	0.01	0.05	1.51	0.06

SI Table 3. Flight Time Summary of CEM Stack Measurements.

	Time On (Local)	Time Off (Local)	Mean Stack SO ₂	Mean Stack NO _x	Mean Stack Hg ^T	Mean Stack Hg ⁰	Mean Stack Hg ^{II}	
Date On			ppmw	ppmw	µg m ⁻³ @ 20°C	µg m ⁻³ @ 20°C	µg m ⁻³ @ 20°C	Mean Stack % Hg ^{II}
02/24/2008	12:30	13:30	403.3	68.1	3.50 ± 0.09	0.11±0.03	3.39 ± 0.08	96.7%
02/24/2008	13:58	15:33	427.2	67.7	3.36 ± 0.11	0.04±0.02	3.32 ± 0.11	98.8%
02/24/2008	16:12	17:59	435.2	68.6	3.42 ± 0.08	0.01±0.02	3.41 ± 0.08	99.6%
02/28/2008	11:11	12:11	320.5	67.7	2.83 ± 0.06	0.31±0.02	2.52 ± 0.06	89.1%
02/28/2008	12:41	13:54	321.1	68.6	2.85 ± 0.07	0.41±0.03	2.44 ± 0.07	85.8%
02/28/2008	16:23	17:23	315.4	67.3	3.13 ± 0.05	0.45±0.02	2.68 ± 0.06	85.7%
03/01/2008	11:33	12:33	429.9	70.1	3.08 ± 0.06	0.05±0.01	3.03 ± 0.06	98.3%
03/01/2008	12:56	13:55	448.1	67.7	3.18 ± 0.11	0.07±0.01	3.11 ± 0.11	97.9%
03/01/2008	14:23	15:27	439.6	64.6	2.63 ± 0.18	0.09±0.01	2.54 ± 0.19	96.7%
03/01/2008	16:03	17:01	440.6	65.7	2.73 ± 0.17	0.13±0.02	2.58 ± 0.09	95.1%

SI Table 4. Comparison of in-stack speciation method results

Percent Hg ^{II}							
Date	Hg CEM	OH	Absolute Difference	Traps	Absolute Difference	FUME	Absolute Difference
2-23-2008	93.8%	84.4%	-9.4%	<i>NM</i>	NA	<i>NM</i>	<i>NA</i>
2-24-2008	99.7%	92.1%	-7.6%	96.8%	-2.9%	<i>NM</i>	<i>NA</i>
2-25-2008	100.0%	93.8%	-6.2%	97.7%	-2.3%	<i>NM</i>	<i>NA</i>
2-27-2008	98.2%	89.2%	-9.0%	95.1%	-3.1%	<i>NM</i>	<i>NA</i>
2-28-2008	86.5%	82.4%	-4.1%	84.5%	-2.0%	<i>NM</i>	<i>NA</i>
2-29-2008	92.8%	<i>NM</i>	<i>NA</i>	<i>NM</i>	<i>NA</i>	88.0%	-4.8%
3-1-2008	99.7%	93.6%	-6.1%	98.4%	-1.3%	98.0%	-1.7%
Average	95.8%	89.3%	-7.1%	94.5%	-2.3%	93.0%	-3.3%
Std Dev	5.1%	4.9%	2.0%	5.7%	0.7%	7.1%	2.2%

NM = Not measured

NA = Not applicable

SI Table 5. Summary of airship in-plume measurements (mean ± standard deviation)

Run	Date	n ^A	Hg ⁰ ng m ⁻³	BC Hg ^{0B} ng m ⁻³	SO ₂ ppb	NO _y ppb	CO ₂ ppm	Airship Altitude (m)
5	02/24/2008	18	2.1 ± 0.3	0.4 ± 0.3	1154 ± 455	173 ± 75	608 ± 98	574 ± 73
6	02/24/2008	8	2.2 ± 0.3	0.5 ± 0.3	1465 ± 678	222 ± 97	702 ± 143	521 ± 39
15	02/28/2008	12	3.3 ± 1.4	1.7 ± 1.4	1225 ± 626	269 ± 121	709 ± 192	415 ± 47
17	02/28/2008	14	3.6 ± 1.4	2.0 ± 1.4	1306 ± 659	279 ± 110	701 ± 202	392 ± 46
22	03/01/2008	13	2.5 ± 0.6	0.9 ± 0.6	1781 ± 1126	276 ± 165	765 ± 222	781 ± 107
23	03/01/2008	4	2.0 ± 0.3	0.4 ± 0.3	195 ± 117	31 ± 21	436 ± 21	1101 ± 69
24	03/01/2008	9	1.9 ± 0.2	0.3 ± 0.2	373 ± 115	68 ± 28	475 ± 39	1155 ± 51
Total		78						

^A Number of valid 2.5 min samples within each run

^B Background corrected

Supporting Information Methods

Selection of Coal-Fired Utility Boiler

The ideal plant for this study was identified as one that emitted a high percentage of Hg^{II} to allow for downwind measurements above our method detection limits at dilution ratios ranging from 500 to 25,000. Plants that burn eastern bituminous coal and do not utilize a flue gas desulfurization wet scrubber control system were deemed most likely to meet this criterion. Stack dilution rates relative to distance downwind in a coal-fired power plant plume during a previous fixed-wing aircraft study conducted by the Tennessee Valley Authority (TVA) were found to be extremely variable and strongly dependent on meteorological conditions (1). The downwind dilution ratio of stack plume gas at 10 km and 20 km downwind varied from 3,600-11,000 and 9,000-25,000, respectively. In addition, the ideal plant would: (i) have a single stack at least 125 meters high, (ii) not be in an area of complex mountainous terrain, and (iii) not be in close proximity to other significant atmospheric mercury sources.

Crist Plant Stack Emissions Measurements

Sulfur dioxide (SO₂) and oxides of nitrogen (NO_x) continuous emissions monitoring (CEM) measurements were made using Thermo Electron (Franklin, MA) Model 43C pulsed fluorescence SO₂ monitors, Thermo Electron Model 42C chemiluminescence NO-NO₂-NO_x monitors, and United Science Inc. (Gibsonia, PA) Model Ultraflow100 real-time volumetric flow monitors. The CEMs were installed and operated following standardized EPA monitoring and reporting requirements detailed in 40 CFR Part 75.

Each Hg-CEM system included an inertial sampling probe (Tekran Model 3330), a conditioner (Tekran Model 3320), a mercury analyzer (Tekran Model 2537A); and Hg⁰ (Tekran Model 3310) and HgCl₂ (Tekran Model 3315) gaseous calibrators. Each Tekran CEM also included a computer system for controlling and monitoring system temperatures, flows, and pressures. The Tekran 3300 systems were configured to measure TGM and Hg⁰ semi-continuously over a 2.5 min collection/analysis cycle. The Tekran model 3320 sample conditioner contained two separate sample channels for TGM and Hg⁰ (SI Figure 2). The TGM channel ran the sample air stream through a heated (700°C) catalyst reaction chamber to thermally reduce all oxidized mercury fractions to Hg⁰, and then through a chilled single-pass refluxing mist chamber that was continuously supplied ASTM type II reagent grade water (18.2 MΩ·cm) to scrub out halide species and prevent their recombination to non-detectable Hg^{II} compounds. The Hg⁰ channel ran the sample air stream through a separate chilled refluxing

mist chamber to remove the soluble Hg^{II} fraction. The reported Hg^{II} fraction was calculated as the difference between TGM and Hg⁰.

Additional Speciated Hg Measurements

Many variables contribute to the quality and reliability of speciated mercury measurements, including the effects from particulate matter which can not only capture gaseous Hg, but can also oxidize Hg⁰ (2). Verifying the quality of the Hg CEMS speciated mercury measurements is difficult and is primarily accomplished by comparison to other speciated mercury measurement techniques, including the Ontario-Hydro (OH) method. The OH method is widely considered to be the primary accepted method for speciated Hg emissions measurements and was the primary speciating method employed during this study (3). The OH method has been well investigated for its speciated measurement performance (4, 5). OH measurements were performed on Unit 7 each day of testing. While Ontario-Hydro measurements were made on Unit 6, they were performed and completed prior to the initiation of mercury CEM and airship measurements, and as a result, are not directly suitable for comparative purposes.

Method 30B, EPA's Reference Method for measuring TGM from coal combustion sources, was expanded to include and evaluate commercially-available, Ohio Lumex Company (Twinsburg, OH) model OL-Spec speciating sorbent traps as a viable mercury speciating option during these tests (6). The speciating sorbent traps are similar to the TGM traps used for EPA Reference Method 30B testing, with the addition of two sequential beds of granular potassium chloride (KCl) positioned upstream of the iodated activated carbon for TGM capture. The KCl was intended to capture Hg^{II} only. A series of quad probe measurements was performed consisting of one TGM carbon trap, one TGM carbon trap spiked with a known amount of Hg⁰ (for the Method 30B recovery test), and two speciated traps. The speciating traps were sampled and analyzed following EPA Method 30B. Only a limited number of measurements were made during these tests and all measurements were made on Unit 7 to coincide with OH sampling.

A separate CEM system was employed as an independent assessment of speciated mercury measurement quality. The Fluegas Unfiltered Mercury Emissions (FUME) system is a prototype measurement approach, developed by EPA specifically for this study, intended to reliably measure Hg⁰. The key feature of this measurement system is that no stack temperature PM filtering is employed. The measurement system consists of a probe, a series of water-containing impingers, and a Tekran model 2537 mercury analyzer. The particulate-containing gas stream is routed directly to the impingers to mitigate the PM bias effects. The system was challenged with Hg⁰, introduced at the probe, before and after each measurement event as a means of calibration and data validation. The FUME Hg⁰ measurements are related to the Tekran Hg CEMS TGM measurements to derive an independent Hg^{II} measurement. FUME measurements were made on Unit 7 only on 2/29 and 3/1.

An ancillary outcome of this study is the successful use of the speciating sorbent traps with the application of Method 30B. What is unique to these tests and the overall approach is that the speciating traps can be used in conjunction with Method 30B and the 30B total Hg measurement approach. When paired with total Hg traps, speciated measurements can be made following the same procedures and performance criteria contained in 30B. Total Hg measurements can be made from the speciating sorbent traps without any deviation from Method 30B requirements. As a result, speciation estimates can be obtained without compromising Method 30B data quality. These tests afforded an opportunity to verify this tenet as well as provide for comparisons to the other speciated Hg measurements.

Airship criteria gas instrument calibration

Each Thermo Electron instrument used during this study was thoroughly evaluated and optimized prior to deployment by EPA, and included automated pressure compensation. Each unit's high- and low-range channels were calibrated using a four point calibration curve conducted to ensure a linear response over the anticipated dynamic range prior to flight. After each sampling sortie, a zero and span check was conducted to bracket each

sampling days measurements. A certified Advanced Pollution Instruments (San Diego, CA) model 700 dynamic dilution calibration and model 701 zero air generation systems were used to conduct the calibrations. Scott Specialty Gases (Plumsteadville, PA) Certified Interference Free™ multi component EPA Protocol Gas cylinders (EPA, 1997) were used to calibrate the criteria gas instruments.

Airship Tekran evaluation and calibration

Each Tekran 2537A used during this study was thoroughly evaluated and calibrated using its internal perm tube calibration system prior to flight. After each sampling sortie, another internal perm tube calibration was conducted to bracket each sampling days measurements. The permeation tube in each of the Tekran 2537A instruments was calibrated just prior to the study as described in Landis et al. (7) using a Tekran model 2505 primary calibration unit. Manual inlet Hg⁰ standard injections using a Tekran model 2505 primary calibration unit into a zero air stream (7) were routinely performed after sampling sorties to ensure quantitative transport of Hg⁰ through the entire airship sampling and analytical system, the acceptable performance criteria for Hg⁰ recovery was ±5%.

Tekran 2537A instruments are equipped with a mass flow controller to regulate argon analytical carrier gas flow through the CVAFS detection cell. As atmospheric pressure decreases with altitude, the volumetric flow rate increased through the cell reducing the residence time in the detector cell and the instrument overall sensitivity. The actual mean argon flow rate for each 2.5 min integrated sample was calculated using the ideal gas law as presented in SI Equation 1.

$$Flow_{Ar} = \left[\frac{(Temp_{Tek} + 273.15) \times 780}{294.26 \times Press_{Gon}} \right] * 80 \quad (SI 1)$$

Where: Temp_{Tek}=Tekran 2537A internal temperature; Press_{Gon}=atmospheric pressure in the gondola

Laboratory experiments characterized the Tekran 2537A instrument's non-linear response to argon carrier gas flow change and each 2.5 min integrated sample was corrected using SI Equation 2.

$$Hg_{Corrected}^0 = \left[\frac{\left(1 + \left(1 - \left(1441352.4 - (12514.5 \times Flow_{Ar}) + (35.3 \times Flow_{Ar}^2) \right) \right) \right)}{667485.5} \right] \times Hg_{Raw}^0 \quad (SI 2)$$

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 in combination with predictive meteorological models interpreted by personnel from the EPA Atmospheric Modeling Division was used to support airship operations.

SODAR wind speed data were used to estimate plume aging time using SI equation 3.

$$Plume_{Age} = \left[\left(\frac{A_{dist}}{WS_{sodar}} * 1000 \right) + \left(\frac{\frac{1}{3} * A_{hgt}}{Stack_{vel}} \right) \right] \quad (SI\ 3)$$

Where: A_{dist} = Airship three dimensional distance from stack exhaust (m)

WS_{sodar} = Wind speed at airship altitude (m s⁻¹)

A_{hgt} = Altitude of airship above stack exhaust (m)

$Stack_{vel}$ = Stack exhaust velocity (m s⁻¹)

References

- (1) 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 Geokolje*, 2004, 51, 1732–1733.
- (2) Ryan, J.V., and R. Keeney. *The Ontario Hydro Method for Speciated Mercury Measurements: Issues and Considerations* in proceeding of 2004 Symposium on Air Quality Measurement Methods and Technology, April 19-22, 2004, Research Triangle Park, North Carolina.
- (3) ASTM Method D 6784-02, "Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario-Hydro Method)."
- (4) Electric Power Research Institute. *Evaluation of Flue Gas Mercury Speciation Methods*, Final Report TR-108988, Palo Alto, CA, December 1997
- (5) Electric Power Research Institute. *Power Plant Validation of the Mercury Speciation Sampling Method*, Final Report TR-112588, Palo Alto, CA, March, 1999.
- (6) U.S. Environmental Protection Agency . "Method 30B – DETERMINATION OF TOTAL VAPOR PHASE MERCURY EMISSIONS FROM COAL-FIRED COMBUSTION SOURCES USING CARBON SORBENT TRAPS." *Code of Federal Regulations*, Title 40, Part 60, Appendix A. <http://www.epa.gov/ttn/emc/promgate/Meth30B.pdf>.
- (7) 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.