

Field Observations of Mercury Partitioning in Power Plant Plumes

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ABSTRACT

High temporal resolution measurements of atmospheric Hg and various tracer species were made at a rural site in north Georgia from June 2001 through January 2002. Data were used to identify 15 periods when observations were influenced by coal fired power plants (CFPPs). Emission signatures were then used to determine, with reasonable certainty, when individual power plants affected measurements, and to compare observed Hg speciation with expected speciation. Results indicate that total Hg (i.e., Hg(0) + RGM + particulate Hg) in CFPP plumes agrees reasonably well with emission estimates, but that observed partitioning is significantly different. Hg(0) is the dominant form of Hg observed in CFPP plumes (average 88% percent), whereas emission estimates suggest it should account for only 48% of total emissions. Total Hg observed at the research site agrees well with emission estimates, thus ruling out depositional losses of Hg in transit to the site. Possible explanations for the discrepancy include 1) errors in emission estimates (i.e., at the stack) for RGM; or 2) rapid conversion of RGM to Hg(0) after emission to the atmosphere (i.e., downstream of the stack).

INTRODUCTION

Recent inventories of atmospheric Hg emissions show that anthropogenic sources are important on local, regional and perhaps even global scales. As important as the magnitude of emissions is their chemical form. Elemental Hg has a long atmospheric lifetime (approx. 1 year) and is therefore broadly dispersed from the point of emission. Reactive gaseous Hg

(RGM), on the other hand, is removed from the atmosphere much more quickly (atmospheric lifetime several days) and thus has a more localized range of influence than elemental Hg. Coal fired power plants (CFPPs) are recognized as a major source of atmospheric Hg. The form of Hg in CFPP emissions is a complex function of fuel composition, combustion characteristics and pollution control technology, but is generally considered to be about two-thirds RGM, one-third elemental Hg and less than a few percent particulate Hg.

This paper presents results of from the first 6 months of an ongoing field campaign designed to collect high temporal resolution measurements of Hg and tracer species at a rural site in north Georgia, USA. The data are used to assess overall quality of speciated Hg measurements, and then to identify and analyze CFPP plumes as they are observed at the research site. Finally, ratios of ambient Hg species are compared with expected ratios, based on day and plant-specific emission information.

EXPERIMENTAL

Measurements of elemental Hg (Hg(0)), reactive gaseous Hg (RGM), total particulate Hg (TPM), SO₂, reactive odd nitrogen (NO_y), CO, surface meteorology and fine particle mass and composition were measured at the Yorkville, GA SEARCH site from June 2001 through January 2002. Yorkville (lat. 33.931, lat. 85.046) is a rural site located approximately 55 km west-northwest of Atlanta, GA and 40 km south-southwest of Rome, GA (see Figure 1). The area consists of rolling terrain covered predominantly with hardwood interspersed with tilled farmland and open pasture. The site is on a broad ridge (elev. 395 m) in a large (75 ha) pasture. Groundcover around the site is short to medium-height grass. Contiguous forest canopy (loblolly pine and mixed hardwood) is 100-300 m from equipment, in all directions.

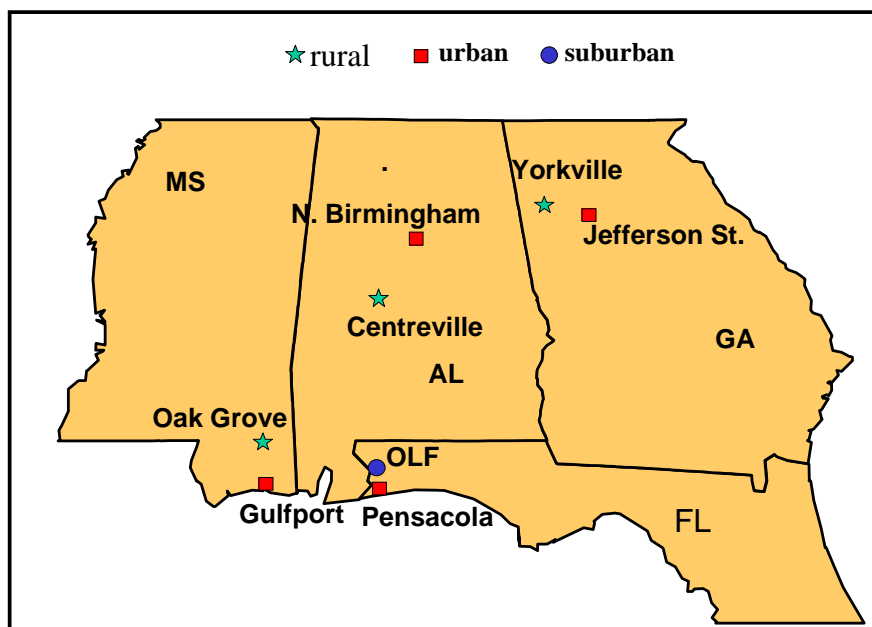


Figure 1. Map of SEARCH network, showing location of Yorkville, GA research site.

Speciated Hg measurements were made on the roof of an equipment shelter (4-5 m above ground level) with a Tekran Model 2537A Hg Analyzer equipped with a Model 1135 Particulate Hg Unit and a Model 1130 Speciation Unit. The measurement principle is as follows. Sample air is drawn at approximately 9 liters per minute (lpm) through a potassium chloride coated quartz annular denuder (1130) and a quartz particulate filter (1135), then into the Hg analyzer. In sample mode, RGM is trapped via diffusion on the denuder and TPM is trapped on the particulate filter. Hg(0) is transmitted quantitatively through the denuder and filter to the Hg analyzer, where it is trapped on a gold tube pre-concentrator, thermally desorbed and detected via cold vapor atomic fluorescence spectroscopy (CVAFS). In desorption mode, the particulate filter and a downstream pyrolyzer unit are heated to 650 C. TPM is converted to Hg(0), then transmitted in ultra-high purity argon to the 2537A for detection. Finally, the quartz denuder is heated to 650 C. RGM is converted to Hg(0), then transmitted to the 2537A for detection. The Hg analyzer was calibrated every 24 hours with an internal permeation source of Hg(0). The internal source calibration was verified against an external standard (Model 2025 calibration source) approximately once a month.

In routine operation, the Tekran was programmed to maximize temporal resolution of speciated Hg data. Sample mode was set to 25 minutes, during which 10 2.5-minute Hg(0) measurements were acquired. Desorption mode was set to 40 minutes with the following sequence: two 2.5 minutes purges, five 2.5 minute TPM measurements, five 2.5 minute RGM measurements, two 2.5 minute purges. Each measurement cycle thus produced 25-minute integrated measurements of RGM and TPM every 65 minutes. Although this approach yielded less than 50 percent data coverage, it was deemed necessary to analyze Hg behavior during short-lived plume events. Quartz denuders and particulate filters were replaced approximately every two weeks.

Independent confirmation of RGM and TPM measurements was accomplished by manual collection air samples using a quartz denuder/filter sampler provided by Frontier Geosciences, Inc (Frontier). Samples were collected over four hour time periods, then shipped overnight (on ice) to Frontier for analysis. Analysis was performed via thermal desorption followed by CVAFS. Each sample batch included four collectors, of which three were exposed and one was used as a field blank. Analytical results were corrected for field blank loadings. During these tests, the Tekran was programmed to sample for 4 hours and to desorb for 1 hour. This ensured identical sample exposure for the manual and automated analyses.

Trace gas data (i.e., SO₂, NO_y and CO) were used to screen for periods of influence from point and non-point sources, and to identify specific point sources. Measurements were made at a reference height of 10 m to avoid near surface gradients and contamination from surface activities. SO₂ was measured via UV-fluorescence using a Thermo-Environmental Model 43CTL trace level analyzer. NO_y was measured via Mo-reduction followed by NO-ozone chemiluminescence using a Thermo-Environmental Model 42CTL trace level NO/NO_x analyzer. CO was measured via non-dispersive IR absorption using a Thermo-Environmental 48CTL analyzer. Instrument calibration was performed automatically at least once a day by method of additions, using NIST-traceable compressed gas standards. NO_y converter efficiency was also checked daily via method of additions with n-propyl nitrate.

All analyzers were also zeroed at least once daily. Results of automated calibrations and zeros were used to adjust raw instrument response during the data validation process.

Air mass trajectory data were used to visualize atmospheric transport during plume events. Twenty-four hour backward trajectories were generated using the interactive version of the NOAA HYSPLIT4 model on the NOAA-ARL web site¹. Back trajectories were generated using the default vertical motion algorithm and with starting heights of 500 m and 250 m, for the time (hour) of peak SO₂ concentration during each plume event. The 500 m trajectory was used to assess the general direction of air mass transport, while the 250 m trajectory was used to estimate transit time from point source to the research site.

Coal data and continuous emission monitor (CEM) data for coal fired power plants in the vicinity of Yorkville were obtained from Southern Company for specific days when a plume event was observed at the site. Coal data included estimated emissions of total-Hg, Hg(0), RGM and TPM, while CEM data included measured emissions of SO₂ and NO_x. These data were used to calculate a variety of emission ratios, which were then compared with observed ratios at Yorkville. For example, SO₂ : NO_x was used for source identification, while total-Hg : SO₂ was used to verify conservation of mass between the point source and Yorkville.

RESULTS AND DISCUSSION

Continuous versus Manual Measurements

Results from the 4-hour integrated sampling experiments are shown for RGM and TPM in Figures 2 and 3, respectively. For RGM, only 4 of 9 samples exhibited concentrations above the nominal detection limit of both the manual and automated methods (roughly 3 pg/m³). Below 5 pg/m³, there was considerable scatter, but no evidence of strong bias between the two sets of measurements. Of more immediate interest, automated measurements above 10 pg/m³ showed reasonable agreement with manual data, but evidence of a slight positive bias. Linear least squares regression of automated versus manual data gave a slope of 1.18 and a highly significant correlation with an r-square of 0.98. Although based on limited samples, this suggests that the automated measurements overestimated RGM. Other things being equal, this suggests that subsequent estimates of RGM:SO₂ emission ratios might also be overestimates.

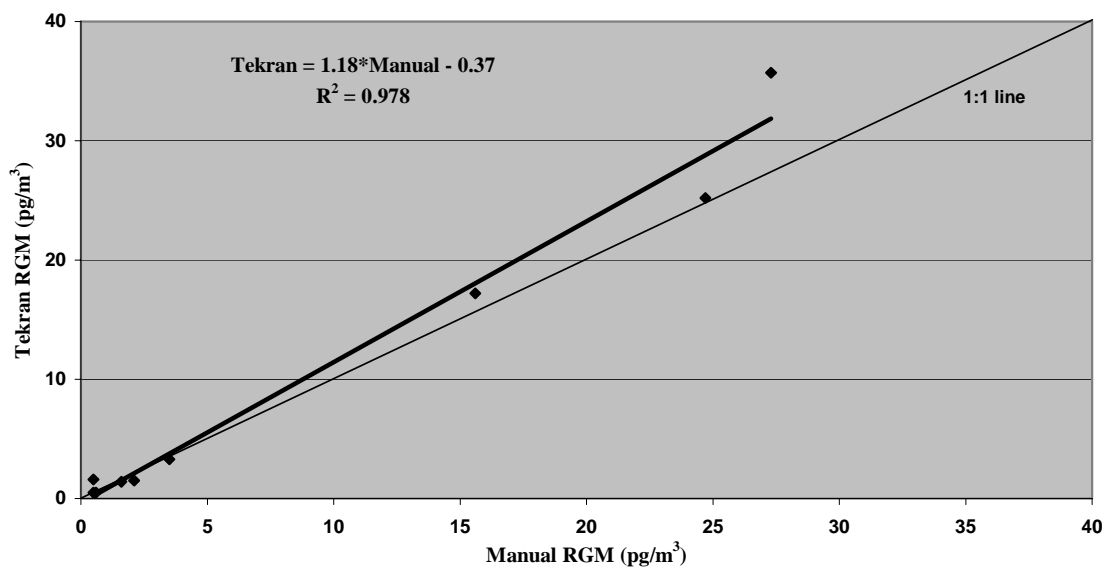


Figure 2. Scattergram of automated versus manual RGM measurements.

TPM data, in contrast, show that the automated method underestimated concentrations by a significant margin. Linear regression of automated versus manual data show a highly linear relationship, but with a slope of only 0.68 (without intercept) or 0.82 (with intercept). Recent discussions with the manufacturer and various researchers have suggested that the desorption temperature for TPM should be on the order of 750 C, rather than 650 C. Future experiments and comparison will be performed at the higher desorption temperature. As will be shown later, the underestimate of TPM has little bearing on Hg speciation in power plant plumes.

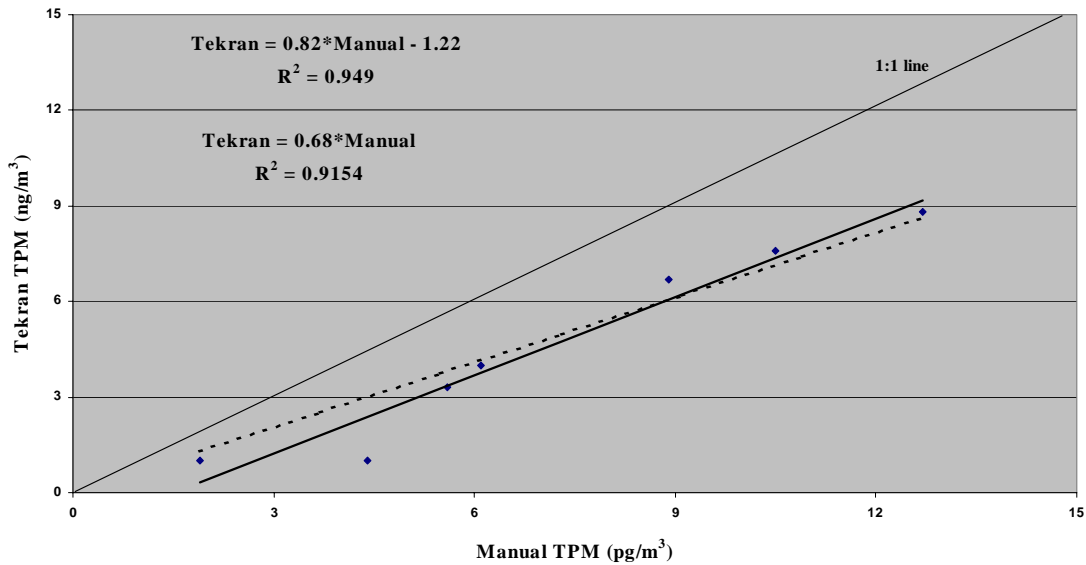
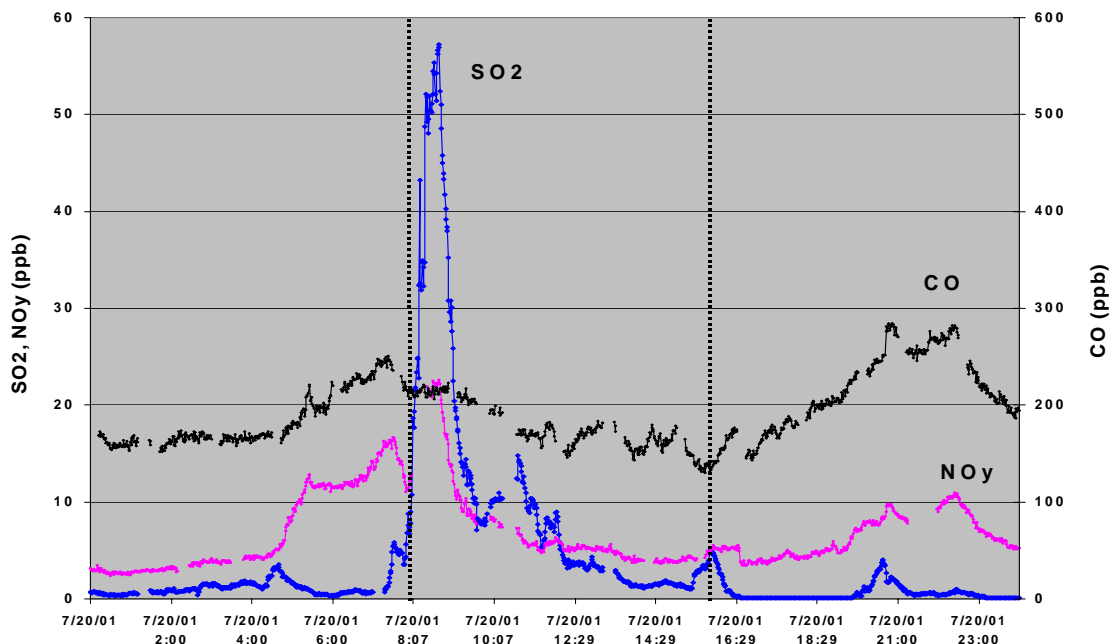


Figure 3. Scattergram of automated versus manual TPM measurements.

Figure 3 depicts a representative plume event observed at the research site on 7/20/01. Time series data for CO show morning and evening peaks indicative of surface emissions (probably mobile sources) and buildup under the nocturnal boundary layer (NBL). CO concentrations decline from mid-morning to late afternoon, as the NBL breaks up and

vertical mixing ensues. SO_2 data show a distinct peak between 0800 and 1000 (local standard time), with maximum 1-minute concentrations on the order of 57 parts per billion (ppb). This peak appears at the same time as CO begins to decline, suggesting that it is being mixed to the surface as the NBL breaks up. SO_2 remains above 20 ppb for about an hour,



then declines to near zero as the plume moves away from the site. NO_y exhibits a complex time series which reflects both mobile and point sources. Morning and afternoon peaks are apparent, and so, too, is a fairly sharp peak associated with the SO_2 maximum at approximately 0900. As shown in Figure 4, point source plume events are relatively short-lived phenomena, lasting from several tens of minutes to a few hours, and thus require high temporal resolution data for detection and analysis.

Figure 4. Time series of tracer species during 7/20/01. Vertical lines correspond to beginning and end times for event, as defined by Hg measurements.

Inspection of SO_2 and NO_y data from the 7/20/01 event shows there is a highly linear and statistically significant relationship between the two (see Figure 5). Regression analysis shows a slope of 3.18 ppb of SO_2 per ppb of NO_y , which is indicative of a coal-fired point source. The negative intercept in the linear regression equation simply reflects an elevated background of NO_y above that which can be accounted for by SO_2 alone.

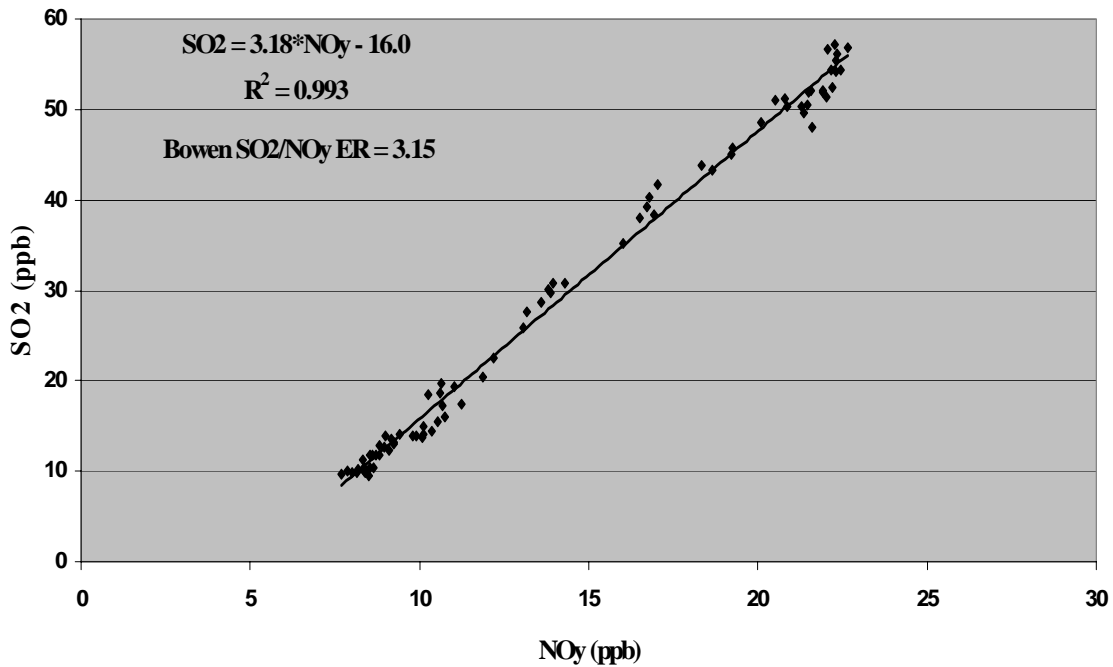


Figure 6. Scattergram of SO₂ versus NO_y during 7/20/01 event.

The above relationship between SO₂ and NO_y is suggestive of a coal-fired point source, but does not conclusively identify a particular source. Additional information is required to make the connection between field measurements and one of several possible point sources.

HYSPLIT trajectory calculations for the 7/20/01 event are shown in Figure 6. The two traces illustrate calculated paths traveled by an air parcel arriving at the site the same time as the observed plume. Results show slightly different paths for the 250 m and 500 m trajectories; however, both indicate a broad arc of atmospheric transport from the northwest, shifting to north or northeast as the parcel approached Yorkville. These results put the air parcel in close proximity to the Bowen steam plant (25 km NNE of Yorkville) roughly 4 hours prior to arrival at the site.

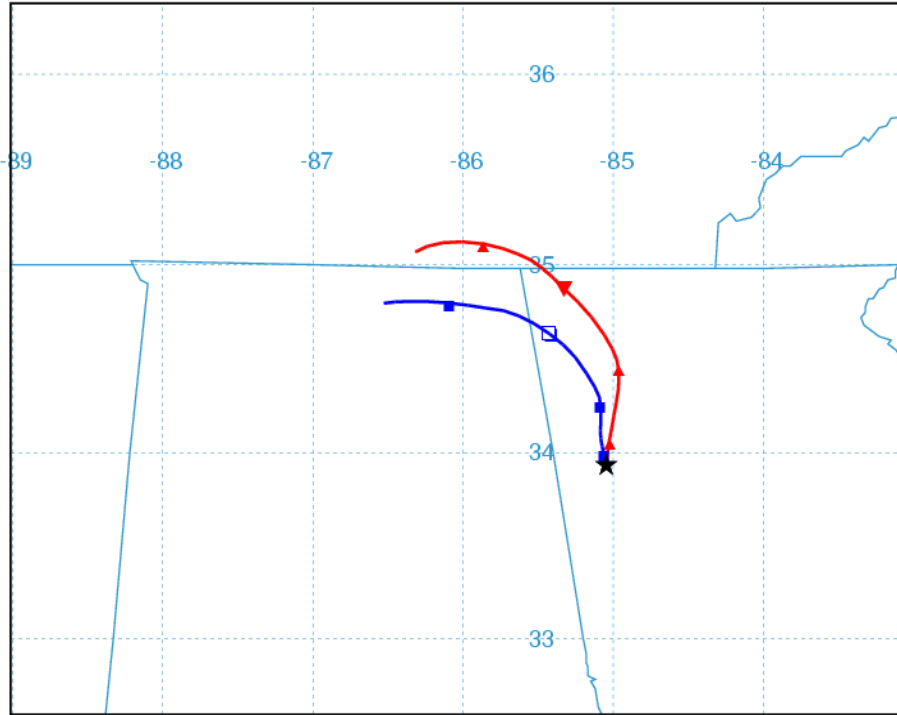


Figure 6. NOAA-HYSPLIT back trajectory for 7/20/01 event at Yorkville (star). Red and blue traces correspond to 500 m and 250 m trajectories, respectively.

Figure 7 shows emission data for the Bowen steam plant on 7/20/01. Each point represents an hourly average $\text{SO}_2:\text{NO}_y$ ratio (molar) from in-stack CEM measurements. Hourly ratios vary from about 3.1 at 0100 to about 3.8 between 1600 and 2000. Based on estimated transport time from trajectory calculations, the air parcel passed near Bowen steam plant at approximately 0500. Examination of emission ratios for the 3-hour period centered on 0500 yields an average value of 3.15 for the $\text{SO}_2:\text{NO}_y$ emission ratio. This matches the observed ratio at Yorkville and conclusively points to Bowen as the point source associated with the 7/20/01 plume event.

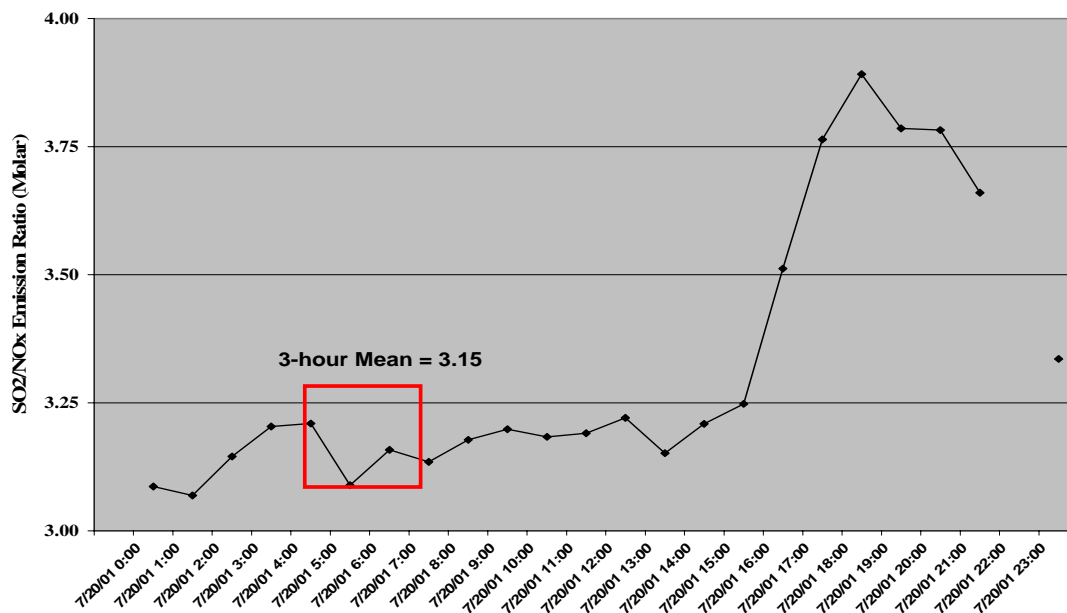


Figure 7. Hourly emission ratios for Plant Bowen, 7/20/01. Red box indicates estimated time of emission (+/- 1 hour) for plume observed at Yorkville.

Figure 8 shows results of speciated Hg measurements at Yorkville for 7/20/01. Like the other gases, there is considerable temporal variability in Hg(0) and RGM. TPM, in contrast, hovers near the analytical detection limit (3 pg/m^3) throughout the day. Hg(0) concentrations are on the order of 1.5 ng/m^3 early in the day, exhibit a sharp rise to about 1.7 ng/m^3 near 0900, then slowly decline through the afternoon. A sharp peak of unknown provenance also occurs late in the day. RGM values are at or below detection limit early and late, show a sharp peak near 0900, then decline through the afternoon. In other words, both Hg(0) and RGM show detectable changes in concentration during the plume event.

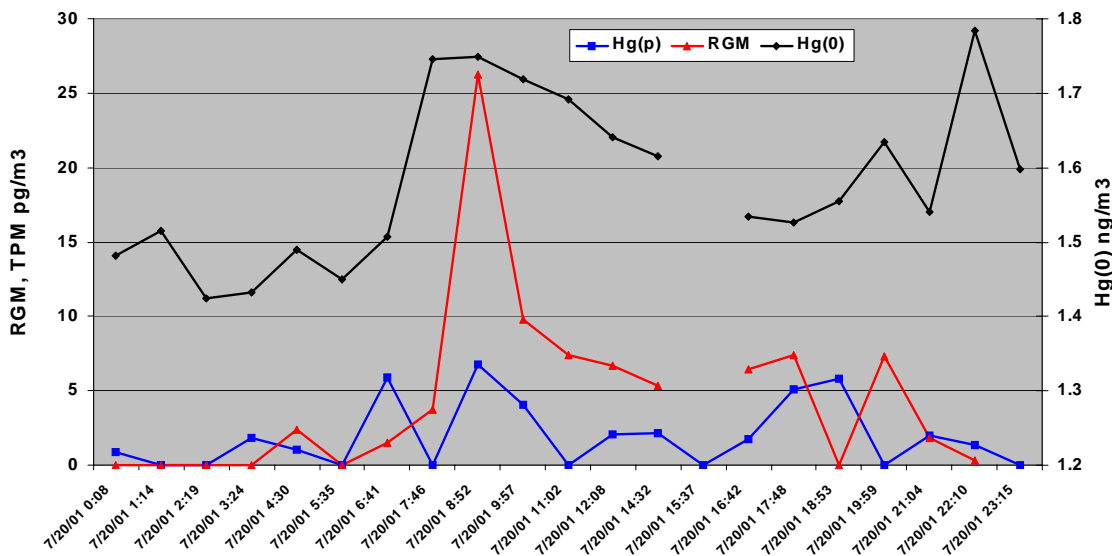


Figure 8. Time series of Hg species observed at Yorkville, 7/20/01.

The high resolution SO_2 and speciated Hg data can be used to estimate emission ratios in an analogous manner to what was done for SO_2 and NO_y . Figures 8 and 9 show scattergrams and associated linear regression statistics for RGM versus SO_2 and Hg(0) versus SO_2 , respectively, where 1-minute SO_2 concentrations have been aggregated to line up exactly with the Hg sample cycle. There is considerable scatter in the data, but linear relationships are clear and statistically significant for both species. For RGM, the slope of the regression line suggests an emission ratio of 0.74 pg/m^3 per ppb of SO_2 . For Hg(0), the slope of the regression line is considerably higher and suggests an emission ratio of 8.1 pg/m^3 per ppb of SO_2 . Results for TPM (not shown) indicate no statistically significant relationship with SO_2 . In other words, observed concentrations suggest that over 90 percent of the Hg associated with the plume event is in the form of Hg(0).

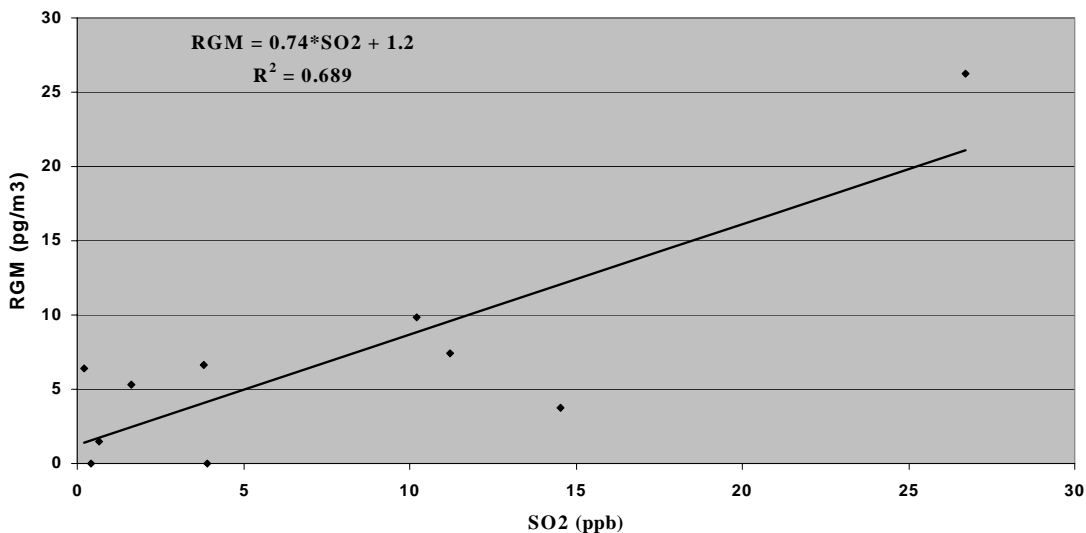


Figure 9. Scattergram of observed RGM versus SO_2 during 7/20/01 event.

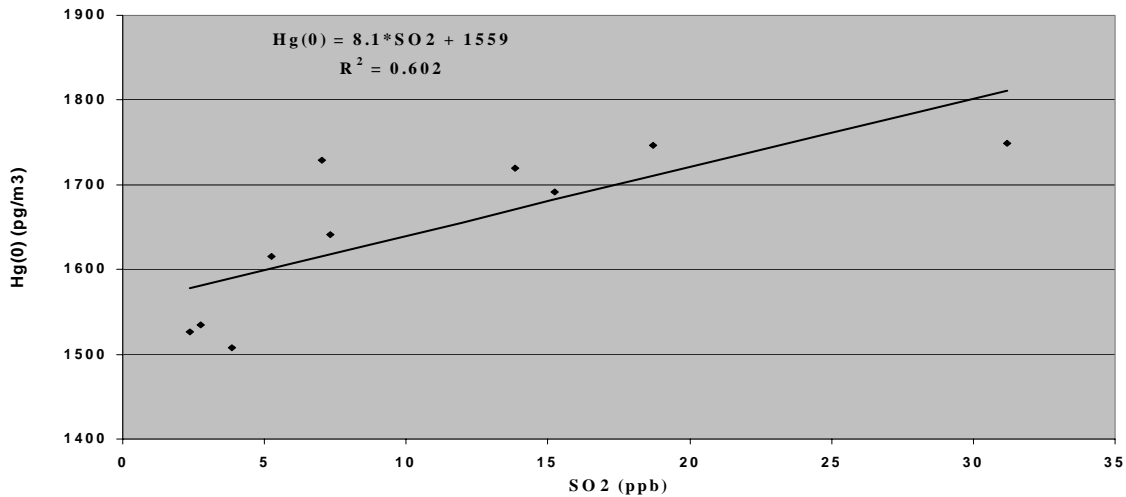


Figure 10. Scattergram of observed Hg(0) versus SO₂ during 7/20/01 event.

Observed and expected emission ratios (ER) of Hg(0), RGM and TPM for the 7/20/01 plume event are shown in Figure 11. Observed values were obtained as described above from linear regression of Hg species versus SO₂. Dashed lines indicate 95 percent confidence intervals for the regression slope. Expected values are based on analysis of contemporaneous coal samples from Bowen and CEM data. Dashed lines through expected ERs reflect combined uncertainties for the estimated speciation and CEM data.

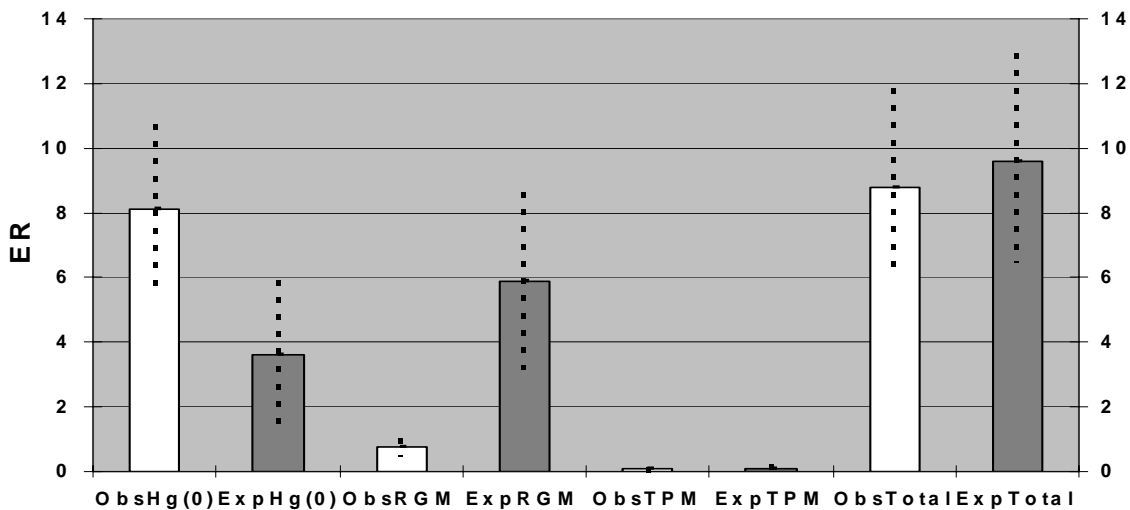


Figure 11. Observed (Obs) and expected (Exp) emission ratios for Hg species, 7/20/01 event. Units are pg/m³ per ppb of SO₂.

Inspection of Figure 11 shows sharp contrasts in the observed versus expected ERs. For Hg(0), observed and expected ERs are slightly below 4 and above 8 pg/m³ per ppb of SO₂, respectively. Differences for RGM are even larger, with observed and expected ERs of 0.8 and 5.9 pg/m³ per ppb of SO₂, respectively. In other words, observations show that the large

majority of Hg is in the form of Hg(0), whereas emissions estimates suggest the major form should be RGM. TPM ERs are essentially negligible for both observed and expected calculations. ERs for total-Hg (i.e., the sum of Hg(0), RGM and TPM) show remarkably good agreement, considering the large number of measurements and calculations involved. This finding demonstrates mass closure for Hg and rules out significant losses (e.g., dry deposition) of Hg in transit from Bowen to Yorkville.

The above techniques for analyzing plume events, identifying potential sources and estimating ERs were applied to measurements conducted between June 2001 and January 2002. Results showed a total of 15 events with available Hg and tracer data and identifiable point sources. It should be noted that more than 15 events occurred during this period; however, many of these were not analyzable due to confounding from CO (mobile sources) or other tracer species. Descriptive information for the 15 events is presented in Table 1. Most events occurred during the fall and early winter, when meteorological conditions bring fairly brisk and persistent winds, and the majority of transit times are between 3 and 5 hours. Included in the 15 events are 4 coal fired power plants: Bowen (7 events); Hammond (5 events); Gaston (2 events) and Wansley (1 event). Bowen and Hammond are located 25 km north-northeast and 46 km northwest of Yorkville, respectively. These are the plant in closest proximity to Yorkville, thus it is not surprising that they are involved in the preponderance of events. Wansley and especially Gaston are further from Yorkville (58 km south and 152 km south-southwest, respectively), and consequently are associated with fewer events. Inspection of SO₂/NO_y ratios shows astonishingly good agreement between CEM data (source) and field observations. Calculated ratios invariably agree within +/- 20 percent and often agree within +/- 10 percent. This not only facilitates identification of sources, but, as noted above, rules out significant losses of reactive gases between the point of emission and observation at Yorkville.

Table 1. Plume Events with Identified Sources, 6/01-1/02.

Date	Time	Max. SO ₂ (ppb)	Probable Source	Transit Time (hrs.)	SO ₂ /NO _y Source	SO ₂ /NO _y Obs.
6/27/01	1600	12.7	Bowen	6	3.58	3.76
7/20/01	0900	27.0	Bowen	4	3.15	3.18
10/20/01	2000	17.0	Wansley	8	2.31	1.96
10/22/01	1300	22.9	Bowen	4	2.66	2.69
11/16/01	1400	40.0	Bowen	4	3.01	2.39
11/17/01	1900	35.0	Bowen	5	2.79	2.85
12/7/01	1100	16.5	Gaston	9	3.22	2.92
12/13/01	1000	30.0	Bowen	3	2.51	2.59
12/15/01	1400	27.8	Bowen	4	2.84	2.89
12/19/01	0500	7.5	Hammond	5	1.29	1.14
12/26/01	1000	10.7	Hammond	5	1.48	1.33
12/28/01	1800	12.2	Gaston	8	3.46	2.98
12/29/01	1900	15.6	Hammond	4	2.08	1.79
12/31/01	1700	28.5	Hammond	3	1.54	1.39
1/3/02	1800	21.8	Hammond	4	1.26	1.17

Table 2 summarizes observed and expected Hg emissions information for the 15 point source plume events. Within the combined uncertainties of measurements and calculations, mass closure is observed for all events. Results are generally consistent with the 7/20/01 event. ERs for RGM exhibit an aggregate average of 2.0 (range 0.4-6.3), while those for Hg(0) average 10.1 (range 6.3-12.4). These data show that observed ERs are much for Hg(0) than for RGM, and that this difference is statistically significant. Comparison of observed and expected ERs for Hg(0) shows that the former is invariably greater than the latter. In aggregate, Hg(0) is expected to represent 48 percent of emissions. Observational data, in contrast, show that Hg(0) represents almost 90 percent of the increment above background during plume events.

The above results may point to an important gap in our understanding of Hg emissions from coal fired power plants. On the one hand, we can account for total Hg and see good agreement between field observations and estimated emissions. On the other hand, there is substantial disagreement in the partitioning between Hg(0) and RGM. Possible explanations include: 1) loss of RGM during transport from the point source to Yorkville; 2) errors in field measurements; and/or 3) chemical conversion of RGM during transport.

Loss of RGM cannot explain the observations, because we observe reasonable mass closure for plume events. In addition, most events occurred during dry periods, which would limit losses to dry deposition. Results of an allied modeling study show that dry deposition rates cannot account for apparent losses of RGM, even if deposition velocity is increased significantly above the generally accepted range of reasonable values². Gross error in field measurements is effectively ruled out by the comparison of manual and automated data for RGM. Beyond this, the excellent agreement for SO₂:NO_y ratios (observed vs. CEM) suggests that these species are conserved and well quantified. Chemical conversion of RGM following emission from the point source could account for the shift in partitioning; however, the mechanism for such a conversion, under plume conditions, is not readily apparent. Application of a reactive plume model for the 7/20/01 and 12/29/01 events shows that current chemical mechanisms can only account for a few percent conversion of RGM to Hg(0) over several hour transport times². Further research is therefore needed to explain unexpected Hg partitioning at Yorkville.

Table 2. Observed and Expected Emission Ratios for Plume Events.

Date	Probable Source	Observed RGM/SO₂*	Observed Hg(0)/SO₂*	Observed % Hg(0)	Expected % Hg(0)[#]
6/27/01	Bowen	1.2	9.7	89	46
7/20/01	Bowen	0.75	12.0	94	39
10/20/01	Wansley	0.85	6.3	88	48
10/22/01	Bowen	4.7	6.8	59	44
11/16/01	Bowen	4.6	nd	nd	43
11/17/01	Bowen	6.3	nd	nd	41
12/7/01	Gaston	0.59	12.4	94	61
12/13/01	Bowen	0.93	12.3	93	38
12/15/01	Bowen	3.5	nd	nd	42
12/19/01	Hammond	0.36	11.3	97	42

12/26/01	Hammond	1.6	9.2	85	40
12/28/01	Gaston	1.3	13.9	92	58
12/29/01	Hammond	1.0	6.4	87	63
12/31/01	Hammond	0.56	10.4	95	60
1/3/02	Hammond	2.9	9.9	78	58
Mean		2.1	10.1	88	48
Lower 95% CI		1.1	8.8	82	44
Upper 95% CI		3.0	11.3	93	53

* units are $\text{pg}/\text{m}^3/\text{ppb}$ # based on coal analysis for day of event

CONCLUSIONS

High temporal resolution measurements of Hg species and various gas phase tracers are extremely useful for developing insights into sources of atmospheric Hg. Data from a rural site in north Georgia demonstrate capabilities to detect Hg in CFPP plumes and to estimate partitioning between Hg(0), RGM and TPM. Results show that, for 15 individual events, Hg(0) is the dominant form of Hg (88%) in CFPP plumes, that RGM is a minor component (11%) and that TPM is virtually a negligible component (<1%). This partitioning is at odds with the current understanding of CFPP emissions, which indicate that over 50% of the Hg emitted should be in the form of RGM. The events analyzed included four different power plants at varying distances from the research site, three different seasons and transport times ranging from 3 to 9 hours. Findings thus cover a fairly broad range of atmospheric conditions and suggest that a common, but unidentified, mechanism for rapid reduction of RGM to Hg(0) is involved.

REFERENCES

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