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Sources of Mercury Wet Deposition in Eastern Ohio, USA

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In the fall of 2002, an enhanced air monitoring site was established in Steubenville, Ohio as part of a multi-year comprehensive mercury monitoring and source apportionment study to investigate the impact of local and regional coal combustion sources on atmospheric mercury deposition in the Ohio River Valley. This study deployed advanced monitoring instrumentation, utilized innovative analytical techniques, and applied state-of-the-art statistical receptor models. This paper presents wet deposition data and source apportionment modeling results from daily event precipitation samples collected during the calendar years 2003–2004. The volume-weighted mean mercury concentrations for 2003 and 2004 were 14.0 and 13.5 ng L⁻¹, respectively, and total annual mercury wet deposition was 13.5 and 19.7 $\mu\text{g m}^{-2}$, respectively. Two new EPA-implemented multivariate statistical models, positive matrix factorization (PMF) and Unmix, were applied to the data set and six sources were identified. The dominant contributor to the mercury wet deposition was found by both models to be coal combustion (~70%). Meteorological analysis also indicated that a majority of the mercury deposition found at the Steubenville site was due to local and regional sources.

Introduction

Mercury (Hg) is a persistent, bioaccumulative toxic pollutant. Once Hg is released into the environment, it can be converted to the organic form, methylmercury (MeHg) and then bioaccumulate in organisms within the food chain, such as fish, posing a consumption risk to wildlife and humans. In the Great Lakes Region, atmospheric deposition is widely considered to be the primary pathway for Hg into aquatic and terrestrial ecosystems (1, 2). Mercury is emitted into the atmosphere through both natural and anthropogenic processes with 50–75% of global emissions attributed to anthropogenic sources (3, 4). Major anthropogenic sources of mercury to the atmosphere include fossil fuel combustion, waste incineration, iron-steel production, coke and lime production, hazardous waste recycling, non-ferrous metal smelting, petroleum refining, and mercury cell chlor-alkali plants (5, 6).

While natural emissions of Hg are primarily in the gaseous elemental form (Hg⁰), combustion processes release Hg in

three major forms: Hg⁰, divalent reactive gaseous Hg (RGM), and particulate Hg (Hg(p)). RGM and Hg(p) are more efficiently deposited on local and regional scales near major sources because of their solubility and affinity for surface reactions, which results in much shorter atmospheric lifetimes (4). Researchers in both the U.S. and Europe have observed significant mercury deposition gradients with maximums found near urban and industrial areas (6–9) highlighting the importance of near field deposition enhancement in proximity to large anthropogenic sources. Deposition of atmospheric Hg at any particular location is therefore a complex combination of local, regional, and global emissions as well as transport, transformation, and deposition processes (4).

In a 1998 report to Congress, the U.S. Environmental Protection Agency (EPA) identified coal-fired utility boilers as the largest source of domestic anthropogenic mercury emissions to the atmosphere and provided evidence of a causal link between such releases and the presence of methylmercury in fish tissue (9). At that time, EPA recognized that the Ohio River Valley contained a high density of coal-fired utility boilers and that monitoring of atmospheric mercury deposition was not being conducted in this area. In 1999, EPA initiated planning for a mercury monitoring and source apportionment study to investigate the impact of local and regional coal combustion sources on atmospheric mercury deposition in the Ohio River Valley.

The Clean Air Mercury Rule (CAMR) was subsequently promulgated by the EPA in 2005 and established the first U.S. regulation to control mercury emissions from coal-fired utility boilers (10). CAMR uses a cap and trade approach under which utilities can buy and sell allotments in a national emissions market. Under CAMR, an interim national cap of 38 tons y⁻¹ becomes effective in 2010 and a final cap of 15 tons y⁻¹ becomes effective in 2018. The 2010 interim cap is based on mercury reductions expected to be achieved as a co-benefit from the EPA Clean Air Interstate Rule, also promulgated by EPA in 2005, which requires utilities to install controls to reduce NO_x and SO₂.

The relative importance of domestic coal combustion sources to atmospheric Hg deposition in the U.S. and the efficacy of the CAMR cap and trade approach to decrease Hg in fish is the topic of ongoing debate in the scientific community. At the center of this debate is the question of the relative importance of Hg emissions from domestic coal-fired utility boilers to atmospheric deposition into sensitive aquatic and terrestrial ecosystems. As part of the CAMR development process, EPA used the Community Multi-Scale Air Quality model (CMAQ), an Eulerian dispersion model, to estimate the impact of domestic mercury sources on atmospheric deposition for CY2001. While extremely useful, all contemporary deterministic models (e.g., CMAQ) are currently limited by the substantial uncertainties in emission inventories, atmospheric Hg chemistry, and wet and dry deposition parametrizations. Receptor models differ from deterministic models in that they only rely upon speciated wet deposition samples collected at a monitoring location or receptor. Deterministic and receptor modeling source apportionment approaches are independent and complementary.

Multivariate statistical receptor models, such as principal component analysis (PCA), have been successfully used to apportion the sources of Hg deposited in South Florida (11) and the sources of other chemical compounds elsewhere (12). More recently, statistical approaches such as Unmix (13) and positive matrix factorization (PMF) have been

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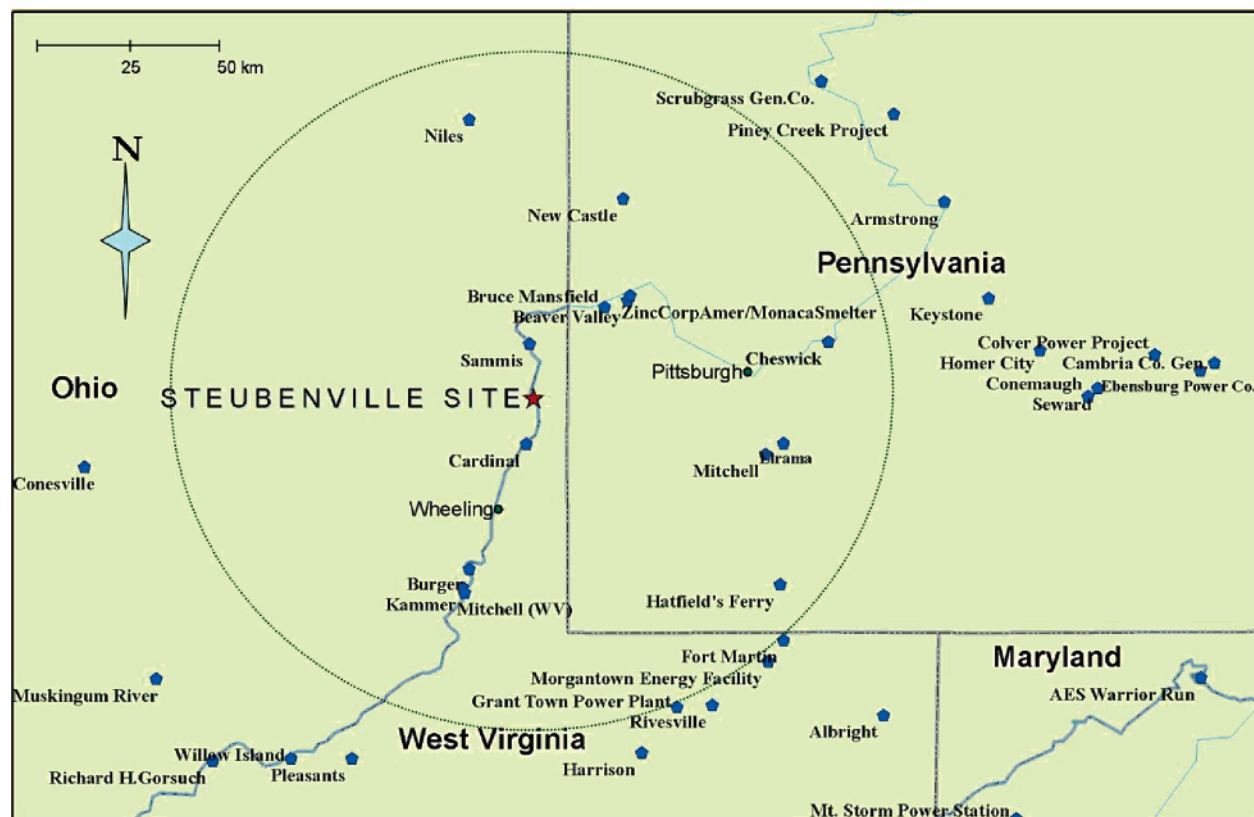


FIGURE 1. Location of the Steubenville, OH monitoring site and surrounding coal-fired utility boilers (circle with 100 km radius centered on site).

developed, improving upon the earlier techniques by using uncertainties in the data matrix (14, 15) as well as through constraining the solutions to non-negative values. Both techniques have the advantage of not requiring prior measurements of source profiles or emission inventories. In this study, PMF and Unmix are applied to the precipitation chemistry data collected at the Steubenville, Ohio site to determine the sources contributing to Hg in wet deposition. In addition, meteorological analysis is performed to provide insights into the probable sources of Hg deposition.

Methods

Measurement Site. An enhanced Hg monitoring site was established in October 2002, in Steubenville, OH on the campus of the Franciscan University (40.379 N, 80.620 W; 306 m above mean sea level) overlooking the Ohio River. This monitoring site was selected because of its proximity to numerous anthropogenic air pollution sources in the Ohio River Valley and because of the human health impacts shown to be caused by these sources during the Harvard Six-City study (16). There are five large coal-fired utility boilers within a 50 km radius of the site and seventeen within 100 km. Figure 1 shows the location of the site as well the location of coal-fired utility boilers in the area.

Event Deposition Sampling. Collection of wet deposition on a daily event basis rather than longer duration integrated sampling (e.g., weekly, monthly) is essential for receptor modeling and meteorological analysis (8, 11, 17, 18). The automatic wet-only event precipitation sampling system used for this study is described in detail by Landis and Keeler (19), and has been successfully deployed in the field for more than a decade (8, 20, 21). Precipitation sampling for this study began in October 2002 and will continue through December 2006. Results are reported here for samples collected in CY2003 and CY2004.

For this study, the volume of each precipitation sample was determined gravimetrically, the precipitation depth was

calculated by dividing the precipitation volume by the funnel area, and all events ≥ 0.1 cm provided sufficient volume for analysis. A heated tipping-bucket precipitation gauge provided a continuous record of the precipitation received at the site and was used to calculate precipitation depths when the 1 L sample bottles were insufficient for containing the entire event and sample overflow occurred (six events).

All field and analytical supplies used in the collection and analysis of Hg and trace element samples were prepared using an 11-day acid-cleaning procedure (18, 19). The Teflon sample bottles were further prepared by an internal 1% BrCl solution (v/v) soak for a minimum of 24-hours. Standard operating procedures included bottle blank determinations for each batch of cleaned bottles to ensure that sampling bottles were essentially Hg-free before they were deployed into the field (median < MDL; 5 ± 14 pg bottle⁻¹ (mean \pm std dev); $n = 151$).

Analytical Methods. Precipitation samples were sent back to the University of Michigan within 24-hours of collection and were processed and analyzed in a Class 100 clean room to avoid potential contamination. Clean room suits and particle-free gloves were worn at all times during preparation and analysis of samples.

Mercury. Mercury samples were oxidized with concentrated BrCl to a 1% solution (v/v) and stored in the dark in a cold room for at least 24 h (19). Mercury in precipitation was purged from solution in a Hg-free nitrogen stream after reduction of BrCl with NH₂OH and reduction of divalent Hg by SnCl₂ to Hg⁰, and concentrated onto a gold-coated bead trap. Total Hg was then quantified using a dual amalgamation technique followed by cold-vapor atomic fluorescence spectrometry (CVAFS) (19, 22). In a previous study, collocated total Hg samples collected using identical samplers and protocols as those used at Steubenville gave an absolute mean difference in the samples of 8.1% (19). The Method Detection Limit (MDL) for total Hg during this study was determined to be 0.23 ng L⁻¹; determined using EPA method 200.8 (23).

Analytical precision of laboratory replicate Hg analysis during this study was 97.3% ($n = 51$).

Trace Elements. Precipitation samples for trace element analysis were acidified with concentrated HNO_3 to a 0.2% solution (v/v) in the sample bottle and stored in a dark cold room for a minimum of 14 days before analysis to provide adequate time for optimal leaching (24). Precipitation samples were then analyzed for a suite of trace elements using a Finnigan MAT Element magnetic sector field high-resolution inductively coupled plasma mass spectrometer using a method similar to that previously described (25). Trace element isotopes were analyzed in low, medium, or high-resolution depending on the potential of impact of isobaric and/or polyatomic interferences (25). The sensitivity of the element decreases approximately by a factor of 10 with each successive increase in resolution so elements quantified in high-resolution had significantly higher MDLs (See Table S1, Supporting Information).

Ion Chromatography. Precipitation samples were analyzed for major anions using a Dionex (Sunnyvale, CA) model DX-600 ion chromatography system equipped with an IonPac AS14 Analytical and AG14 Guard and running a 1.8 mM Na_2CO_3 /1.7 mM NaHCO_3 eluent solution. Precision based on replicate analyses was 95.5 and 93.2%, for nitrate and chloride, respectively.

Multivariate Statistical Receptor Models. In this work, two fairly new multivariate receptor modeling approaches were employed: EPA PMF 1.1 (26) and EPA Unmix 5.0 (27). Both PMF and Unmix provide the source compositions, source composition uncertainties, and source contributions to each sample based only on the measured data. These two models use different algorithms and input data with PMF using a combination of concentration and uncertainty data and Unmix using only concentration data. For both models, the sample Hg source contributions were calculated by multiplying the Hg profile value by its source contribution estimate. All samples with sufficient volume from October 2002 through December 2004 were included in the PMF and Unmix analysis ($n = 162$).

EPA PMF couples a graphical user interface with analysis software that implements the PMF 2 model through the multilinear engine 2 (ME-2), and provides block bootstrap uncertainty estimates (26). All analyses were conducted using the default model specifications, and the results are reported for the run with the lowest Q robust value from 20 random starting points, with random seeds. One hundred bootstrap runs were used to calculate the uncertainty distribution.

EPA Unmix 5.0 includes both a graphical user interface and analysis tools. All analyses were run using the default model specifications and one hundred feasible solutions from a blocked bootstrap were used to calculate the uncertainty distribution (27).

One potential advantage of the PMF model is the ability to weight individual data points using measurement uncertainties and other analytical details such as the elemental MDLs. Here, an objective approach was used to calculate a total deposition uncertainty (U) associated with each data point (each analyte in every sample) for use in PMF by propagating the uncertainty of sample collection (SC), analytical measurement (AM), and precipitation depth (PD) measurement uncertainties (eq 1).

$$U_{Dep} = MDL + \sqrt{(SC)^2 + (AM)^2 + (PD)^2} \quad (1)$$

where, MDL = method detection limit; SC = 10%; AM = standard deviation of three replicate analysis; and PD = 5%.

Meteorological and Trajectory Analysis. Air mass transport to the Steubenville site was estimated using the hybrid single-particle lagrangian integrated trajectory (HYSPLIT) model version 4.6 (28). HYSPLIT 72-h back trajectories were

TABLE 1. Volume-weighted Mean (VWM) Hg Concentrations and Total Deposition Calculated from Event Samples Collected Using Identical U of M Samplers in 2003

site	N	precipitation depth (cm)	VWM Hg (ng L ⁻¹)	deposition (μg m ⁻² y ⁻¹)
Eagle Harbor, MI ^a	58	64.5	8.3	5.2
Pellston, MI ^a	43	78.7	9.4	7.4
Dexter, MI ^a	60	89.6	11.9	10.7
Steubenville, OH	77	94.8	14.0	13.5

^a Keeler and Dvorch (21).

calculated using input data from the National Weather Service. The hour of maximum precipitation intensity from each event was used as the start time for the trajectory calculation, and the starting height for each trajectory was calculated as one-half the mixing height, as determined from upper-air soundings. Surface and upper air meteorological maps obtained from the National Weather Service were used to explore the validity of the calculated trajectories and to better understand the type of precipitation and meteorological patterns that influenced the deposition events.

Results and Discussion

Concentrations and Deposition. The 2-year record of Hg in event precipitation at Steubenville is the only such record collected in Ohio to date. The volume-weighted mean (VWM) Hg concentration was 13.7 ng L⁻¹ for the 2-year period, with little difference between the years (14.0 and 13.5 ng L⁻¹ for 2003 and 2004, respectively). The range in the event Hg concentrations recorded over the 2-year period in Steubenville was 4.0–78.9 ng L⁻¹, similar to the range of Hg concentrations observed in a highly industrialized area in southeast Michigan during the same time period (21). However, the distribution of the Hg concentrations observed in Steubenville was quite different than those measured at rural sites in Michigan and Vermont using identical samplers (20, 21). The minimum or baseline Hg concentration observed at Steubenville was ~4 ng L⁻¹; about 4 times higher than the baseline concentrations recorded during the same period at rural sites in Michigan and at Underhill, VT.

The Hg wet deposition recorded at the Steubenville site was 13.5 and 19.7 μg m⁻² y⁻¹ in 2003 and 2004, respectively. Table 1 shows a comparison of the 2003 VWM concentrations and the annual deposition reported for three sites in Michigan with that at Steubenville (21). The Hg wet deposition observed at Steubenville in 2003 was ~25% greater than that received at Dexter, MI and ~2.5 times that recorded at the northern most site located in Eagle Harbor, MI. The pattern observed in 2003, with a south to north Hg deposition gradient across Michigan, has been observed consistently over the past decade through collection of event precipitation samples at several sites in Michigan (8, 18, 21). The higher Hg deposition observed at the Steubenville site was not unexpected, because of the density of Hg sources in the upwind region such as coal-fired utility boilers, iron-steel manufacturing, incinerators, and other non-ferrous metal processing industries (9). The Hg deposition recorded at the Steubenville site in 2004 was 19.7 μg m⁻² year⁻¹, 46% greater than the previous year. The VWM concentrations for the 2003–2004 period for the trace elements used for source apportionment are provided in the Supporting Information (Table S1).

PMF Model Results. PMF solutions with six and seven sources were evaluated, and species contributions to sources were considered significant if the fifth percentile of the bootstrap uncertainty distribution was greater than 0. The results from the six-source solution are presented based on

TABLE 2. PMF Source Profiles for Steubenville Event Precipitation Data^a

analyte	source 1 iron/steel production	source 2 oil and incineration	source 3 crustal	source 4 coal combustion	source 5 phosphorous	source 6 molybdenum
Mg	187	*	558	*	101	*
Al	51	80	355	37	*	52
P	7.8	*	*	*	63.8	*
S	*	*	642	11299	197	*
Cl	267	20480	*	584	*	771
V	2.9	1.1	*	*	*	*
Cr	2.5	*	*	*	*	*
Mn	54.4	*	34.1	*	15.4	*
Fe	344	102	17	37	27	*
Ni	*	3.19	*	*	0.68	*
Cu	1.8	14.0	*	18.4	2.7	7.0
Zn	4.0	44.1	6.1	10.7	5.3	15.6
As	*	0.81	0.10	0.49	0.05	0.27
Se	*	0.97	*	1.73	*	1.30
Rb	*	0.25	0.15	0.20	0.29	0.08
Sr	0.48	3.30	5.64	0.95	1.61	*
Mo	*	*	*	*	*	4.02
Cd	0.09	0.27	*	0.31	0.02	0.23
La	*	0.13	0.63	*	*	0.04
Ce	0.02	*	1.23	*	*	*
Hg	0.01	*	*	0.15	< 0.01	*
Pb	1.10	6.59	0.59	3.62	0.36	1.13
NO ₃ ⁻	*	8639	1501	4532	314	*
% Hg	6	*	*	73	2	*

^a * means not significant at 95% confidence interval.

the ability to identify the sources and the bootstrap uncertainty results. The six-source solution was composed of iron/steel production (V, Cr, Mn, Fe), oil and incineration (V, Ni, Zn, Cd, Pb), crustal (Mg, Al, Sr, La, Ce), coal combustion (S, Se, NO₃⁻), phosphorus (P, Mg, Mn, Fe, Sr), and molybdenum (Mo, Cu). The seven-source solution separated out one additional crustal source (La, Ce, Mg), and the Hg contributions from coal for the six- and seven-source solutions were similar with 73 and 70%, respectively. Three sources contributed significant amounts of Hg: iron/steel production (6%), coal combustion (73%), and phosphorus (2%). The results determined from the six-source solution are presented in Table 2.

While PMF was able to separate out six sources, the source identified as coal combustion was clearly dominant in terms of explaining the Hg deposition. Atmospheric Se is often associated with the burning of fossil fuels such as coal (29, 30), and Se in the absence of significant Ni and V was determined to be an appropriate tracer of coal combustion in Steubenville (31). There are several large steel manufacturing facilities in the Steubenville, OH–Wheeling, WV area as well as plants to the east in Pittsburgh, and iron-steel production was found to be a minor contributor to Hg deposition in this study. An unidentified phosphorus source was also found to be significant small contributors to Hg deposition. The elements Zn, Pb, Cu, and Cl have been used to identify municipal waste incinerator emissions (11, 32), and the elements Ni and V are commonly used tracers to identify oil combustion (33, 34). Two other sources of trace elements were identified in the event deposition data using PMF: a crustal source (24, 35) and a molybdenum source. The molybdenum source may be production of Mo which is used in the steel industry. However, neither was found to be a significant contributor to Hg wet deposition during the study period.

The model (sum of the calculated source contributions) does an excellent job of reproducing the observations except for several of the top deposition events over the 2 years of record. The regression results of the PMF predicted versus measured Hg had a slope of 0.70, an intercept of 0.05, and a coefficient of determination of 0.85 ($n = 162$). Figure 2a

depicts the time series of the predicted deposition from coal combustion versus observed Hg wet deposition at Steubenville using the PMF six-source model solution, showing the clearly dominant impact of coal combustion.

Unmix Results. Unmix identified one influential Ni data point and its value was replaced using the missing data algorithm (Ni on 04-07-2003, measured = 364.15 ng m⁻², replaced = 8.44 ng m⁻²). A reduced number of species was used in the Unmix run: Hg, Cd, La, Ce, Mg, Al, P, S, V, Cr, Mn, Fe, Ni, Se, and NO₃⁻ because using less species improved the stability of the uncertainty estimate. The source profiles for a feasible six source solution produced by Unmix are given in Table 3, and species contributions to each source were considered significant if the fifth percentile of the bootstrap uncertainty distribution was greater than 0. Identification of the sources was performed in a similar way to that with the PMF solutions. The Unmix model found six sources which were identified as phosphorus, incinerator, nickel, iron/steel production, crustal, and coal combustion sources. Only three sources contributed significant amounts of Hg including incinerator (12%), nickel (12%), and coal combustion (69%). The regression results of the Unmix predicted versus measured Hg had a slope of 1.00, an intercept of -0.02, and a coefficient of determination of 0.86 ($n = 162$).

Comparison of Unmix and PMF. Both models tracked the measured values closely but under-predicted the peak depositions. Two high deposition Hg events occurred on 08/29/2004 (1.53 μg m⁻²) and 09/08/2004 (1.69 μg m⁻²) shown in Figures 2a and b as events 146 and 147 in the time series. The Unmix and PMF Hg results for these two events were 1.08 and 1.40 μg m⁻², and 0.85 and 1.08 μg m⁻² respectively. Table 4 shows that Unmix over-predicted the total measured Hg deposition by 13 and 5%, while PMF under-predicted by 7 and 11% in 2003 and 2004, respectively.

Confidence intervals (CI) were calculated for those sources identified by Unmix and PMF as a measure of the uncertainty associated with their contribution to Hg deposition. The 95% confidence interval (CI) was calculated using the fifth and 95th percentiles of the source profile uncertainty distributions. Total coal Hg contributions were 23.7 μg m⁻², with a CI of 16.7–38.4 μg m⁻² for PMF, and 26.8 μg m⁻², with a CI

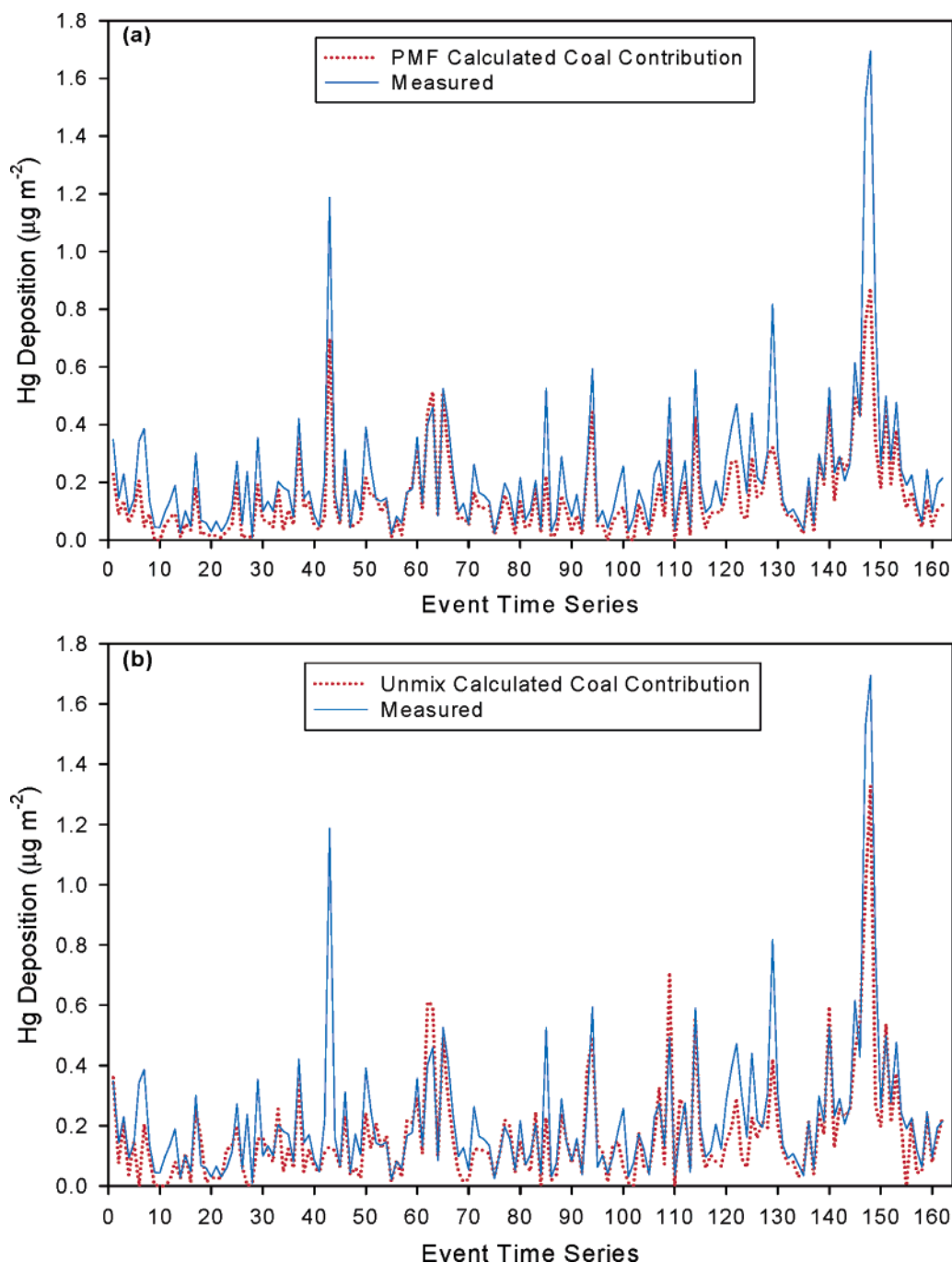


FIGURE 2. (a) PMF predicted deposition from coal combustion versus measured deposition of Hg at Steubenville, OH (2003–2004). (2b) Unmix predicted deposition from coal combustion versus measured deposition of Hg at Steubenville, OH (2003–2004).

of 16.4–39.1 $\mu\text{g m}^{-2}$ for Unmix during the study period. Two additional PMF sources had significant Hg contributions: phosphorus total of 0.6 $\mu\text{g m}^{-2}$ with a CI 0.3–1.5 $\mu\text{g m}^{-2}$, iron/steel production total of 1.9 $\mu\text{g m}^{-2}$ with a CI 0.1–3.4 $\mu\text{g m}^{-2}$. Unmix also had two additional sources with significant Hg contributions: incinerator total of 4.6 $\mu\text{g m}^{-2}$ with a CI 0.1–10.2; and nickel total of 4.5 $\mu\text{g m}^{-2}$ with a CI 0.4–7.1. The lack of agreement between Unmix and PMF for these small Hg sources may indicate that these sources contribute too little to be accurately quantified. Average results from both PMF and Unmix are well within the confidence intervals stated for both model estimates, and this wide range of uncertainties will be reduced as additional samples are included in the analysis at the conclusion of this study (CY2006).

As clearly stated in Poirot et al. (35), receptor models, such as PMF and Unmix, start with the assumption that the source compositions are constant and unique, and that source contributions vary over time. These assumptions may not be well met when attempting to apportion sources that emit species that undergo atmospheric transformations and form secondary species such as sulfate aerosols. Mercury chemistry may be even more complicated than that of sulfur as a larger fraction of the emissions are emitted in the oxidized forms that deposits more quickly than the Hg^0 form that is emitted concurrently. While this limitation is also acknowledged here, the use of multiple receptor models together with the meteorological analysis provided below offer independently consistent results and findings.

TABLE 3. Unmix Source Profiles for Steubenville Precipitation Data^a

analyte	source 1 phosphorous	source 2 incinerator	source 3 Ni	source 4 iron/steel production	source 5 crustal	source 6 coal combustion
Mg	103	*	*	120	869	*
Al	*	*	37	*	482	*
P	73.0	*	*	5.4	*	*
S	*	1069	1754	*	*	10494
V	*	*	0.85	3.16	*	1.35
Cr	*	*	*	3.2	*	0.4
Mn	18.5	*	*	50.9	50.3	*
Fe	33	*	55	356	70	93
Ni	*	*	11.75	0.74	*	*
Se	*	*	*	0.87	*	4.26
Cd	*	0.93	0.08	*	*	0.23
La	*	*	0.07	*	0.76	*
Ce	*	*	0.15	*	1.44	*
Hg	*	0.03	0.03	*	*	0.16
NO ₃	*	*	*	*	1860	7518
% Hg	*	12	12	*	*	69

^a * means not significant at 95% confidence interval

TABLE 4. Comparison of Measured Total Hg Wet Deposition ($\mu\text{g m}^{-2}$) at Steubenville, OH Site to PMF and Unmix Coal Combustion Contribution Estimates

year	total measured Hg wet deposition	PMF estimated Hg		Unmix estimated Hg	
		coal	total	coal	total
2003	13.5	9.1	12.2	9.9	14.8
2004	19.7	13.1	17.6	15.5	21.1

Climatology, Meteorology, and Sample Variability.

Investigations using relatively short meteorological records, e.g., 2-years, need to place the shorter record into a larger climatologically relevant context. While significant differences in the Steubenville wind speed and direction were not expected nor observed, for the CY2003–2004 period from the long-term norm, differences in temperature and precipitation were thought to be more likely. In fact, while the CY 2003 rainfall total was representative of the Steubenville climatological norm, significantly more rain than normal fell in CY 2004, with 10 of 12 months above average and the majority of the excess rainfall occurring in September. CY 2003 was a unique year for eastern Ohio in terms of frozen precipitation; snowfall totals were well over twice the climatologically expected amount. These facts help explain the large deviation between the annual deposition totals (13.5 and 19.7 g m^{-2}) despite annual VWA Hg concentration similarities, because snow in temperate latitudes appears to be much less efficient at capturing Hg via wet deposition (8). In addition, the long-term study of event precipitation collected in Vermont over 11-years found average surface temperatures were highly correlated with the monthly total deposition at that site (20). However, the average surface temperatures for CY 2003 and 2004, did not significantly deviate from the climatological norm.

Individual precipitation events can contribute significantly to the annual Hg deposition total at individual sites (20, 21). This was clearly seen in the Steubenville record as the top five Hg deposition events (1.69, 1.53, 1.19, 0.82, and 0.77 $\mu\text{g m}^{-2}$ seen in Figures 2a and b as events 147, 146, 42, 128, and 148, respectively) all had above average Hg concentrations as well as precipitation depths. While one of these (sample 43) contained precipitation from more than one distinct event and, therefore, cannot be clearly categorized meteorologically, the other four samples corresponded to discrete summer-time events. Two of the discrete events were associated with remnants of September hurricanes (Frances

and Ivan; samples 147 and 148), one was associated with a warm sector squall line (sample 47) and the fourth (sample 148) occurred in a series of intense precipitation events associated with outflow boundary cells preceding a stationary front. The origin of feed air for these types of precipitating systems is fairly unique; the vertical structure of a strong mid-latitude cyclone dynamically allows exceptional local entrainment and wet deposition, cleaning out the atmospheric boundary layer as the storm sweeps through. Sample 128 was associated with a squall line that formed in the warm sector of a low-pressure system only hours before it reached Steubenville, indicating that the entrained air was from within a relatively short distance of the site, as outflow boundaries force lift and condensation on a local scale. Surface winds associated with the two hurricane events were primarily from the northeast, while the other events experienced weak surface winds primarily from the south–southwest which are both areas that contain a high density of coal-fired utility boilers. Three-day back trajectories also indicated air masses with origins northeast or south–southwest of the Steubenville site for these four events (See Figures S3a–e, Supporting Information). The observation of local stagnation prior to large Hg deposition events in Steubenville was also observed at a site in Chicago, IL during the Lake Michigan Mass Balance Study (8). Weak surface winds prior to the precipitation events in Chicago lead to higher observed Hg deposition at that site, but at rural sites in South Haven and Sleeping Bear Dunes, MI, local stagnation did not lead to elevated deposition. At these rural sites, the highest Hg concentrations and wet deposition, were observed after relatively fast transport from the Chicago/Gary area.

The average rainfall rates for these high deposition events were approximately three times the 2-year average (5.7 and 1.7 mm h^{-1} , respectively) and four of the top five events had maximum rainfall occurring in late night/early morning hours when the boundary layer is relatively shallow. Maximum rainfall times for the 2-year period did not, on average, show a preference to any particular time of day.

The influence of local and regional sources is also evident when comparing the Hg concentrations of event samples collected at different sites following the path of hurricane Frances, Steubenville's highest deposition event of the 2-year record. The center of the low for this system moved northward into the Mid-Atlantic states and then toward the northeast, while winds prior to and during the precipitation period at Steubenville were out of the northeast. The Hg concentration at Steubenville for this event was 18.7 ng L^{-1} , the concentration found in samples with similar volume collected during

Hurricane Frances at a site in Underhill, Vermont was less than half that at Steubenville (9.1 ng L^{-1}) and that collected at a site in Tampa where the feed air was primarily of oceanic origin was 4.1 ng L^{-1} .

The large temporal variability and range of concentrations among the event samples in Steubenville during this study ($4.0\text{--}78.9 \text{ ng L}^{-1}$) also indicates a strong local and regional source influence. Only 9.5% of the variability in concentration could be accounted for by precipitation amount alone. In addition, a large range was found in Hg concentrations among samples with a similar precipitation depth: $4.3\text{--}78.9 \text{ ng L}^{-1}$ for low precipitation depth samples ($<1 \text{ cm}$) and $4.2\text{--}22.1 \text{ ng L}^{-1}$ for high precipitation depth samples ($>5 \text{ cm}$). Previous studies have shown that a large range in concentration for similar rainfall amounts can be attributed to variability in impacts by local sources and to the variation in distance between the sources and the receptor site (8, 36, 37).

The results of the multivariate statistical analysis ($\sim 70\%$ of the Hg in the wet deposition at Steubenville coal combustion sources), and meteorological analysis (highlighting the importance of local regional sources), consistently point toward the dominant influence by local and regional coal-burning sources.

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Supporting Information Available

MDLs and volume-weighted mean concentrations for all of the trace elements in Table S1. Scatter plots of PMF and Unmix modeled versus observed Hg deposition in Figures S2a-b. Three day back trajectory plots for high deposition events in Figures S3a-d. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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