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Extensive exploration of event precipitation data in the Ohio River Valley indicates that coal combustion emissions play an important role in mercury (Hg) wet deposition. During July–September 2006, an intensive study was undertaken to discern the degree of local source influence. Source–receptor relationships were explored by establishing a set of wet deposition sites in and around Steubenville, Ohio. For the three month period of study, volume-weighted mean Hg concentrations observed at the eight sites ranged from 10.2 to 22.3 ng L^{-1}, but this range increased drastically on an event basis with a maximum concentration of 89.4 ng L^{-1} and a minimum concentration of 4.1 ng L^{-1}. A subset of events was explored in depth, and the degree of variability in Hg concentrations between sites was linked to the degree of local source enhancement. Samples collected at sites less than 1 km from coal-fired utility stacks (near-field) exhibited up to 72% enhancement in Hg concentrations over regionally representative samples on an event basis. Air mass transport and precipitating cell histories were traced in order to evaluate relationships between local point sources and receptor sites. It was found that the interaction of several dynamic atmospheric parameters combined to favor local Hg concentration enhancement over the more regional contribution. When significant meteorological factors (wind speed at time of maximum rain rate, wind speed 24 h prior to precipitation, mixing height, and observed ceiling) were explored, it was estimated that during summertime precipitation, 42% of Hg concentration in near-field samples could be attributed to the adjacent coal-fired utility source.

Introduction

Mercury (Hg) is a persistent heavy metal that bioaccumulates in organisms and biomagnifies through aquatic food chains. Inorganic Hg is transformed into highly toxic, organic methylmercury (MeHg) by aqueous biota and is subsequently consumed by fish. Recent studies have shown that even low exposure may be associated with neurological and cardio-

vascular effects (*1*). Reproductive changes associated with Hg blood levels in the North American common loon have been found to have adverse effects on this species, while individual piscivorous mammals such as mink and otter demonstrate reduced avoidance behavior even at low Hg blood levels (*2*). Although the major concern to the general public is MeHg concentrations in top predatory fish and the subsequent consumption of such species, understanding the means by which the contaminant enters the food chain is pivotal in designing strategies for reduction efforts.

Atmospheric transport is widely recognized as the primary method of Hg distribution in the environment. Direct atmospheric deposition of Hg can often be the most significant source of this contaminant to large lakes as was found during the Lake Michigan Mass Balance Study (*3, 4*). The form of Hg emissions and synoptic scale meteorological patterns strongly influence the amount of Hg that is deposited nearby the source versus transported long distances. Mercury is emitted in three forms (gaseous elemental Hg—Hg^0, gaseous oxidized Hg—Hg^{2+}, and particulate bound Hg—Hg$_P$) from anthropogenic sources, including medical and municipal waste incinerators, cement plants, crematoriums, fluorescent light production, coke ovens, metal refineries, mining facilities, and fossil fuel-burning power plants. Mercury is also emitted naturally into the atmosphere, primarily as Hg^0; however, anthropogenic emissions account for between 50% and 75% of total global emissions (*5, 6*). The spatial scale on which Hg is deposited is also a complex function of the concentrations of copollutants, chemical transformations, gas—particle interactions (*7*), stack height, and other local-scale meteorological parameters. Hg^{2+} and Hg$_P$ are relatively soluble and readily undergo heterogeneous reactions, resulting in much shorter atmospheric residence times than Hg^0 (*4, 8, 9*). Speciated stack measurements of anthropogenic Hg emissions [incineration, cement kilns, and coal-fired utility boilers (CFUB)] have shown a significant percentage of total Hg to be in the Hg^{2+} and Hg$_P$ forms (*10, 11*), and because of their short atmospheric life times, this suggests these emissions may result in enhanced local and regional deposition gradients near anthropogenic sources.

Recent studies have linked MeHg concentrations in biota to atmospheric deposition of inorganic Hg (*12, 13*). In a 2006 study, 70% of the variability in smallmouth bass MeHg concentration (EPA and individual state environmental program publications) was accounted for by differences in Hg wet deposition (state averages of National Atmospheric Deposition Program Mercury Deposition Network (MDN) results) alone, with little to no correlation between fish concentration and MeHg production physiochemical factors (*14*). It is important to note that two of the 25 states analyzed were not fit well by the linear regression model as MeHg concentrations in fish caught in New Hampshire and Maine exceeded that predicted by the Hg wet deposition. It was suggested that the deposition sites, located in rural areas of the two states, were not representative of the more industrially influenced areas of the states, where a large number of the smallmouth bass were caught and subsequently analyzed. The inaccurate characterization of atmospheric inputs due to collection at background precipitation sites caused an underprediction of Hg fish tissue concentrations and therefore suggests a regional or local impact of wet deposition on Hg concentrations in the tissue of the sampled fish. The MDN requires monitoring site locations to be regionally representative; "and minimizes the impact of local point or area sources" (*15*). Although these criteria may allow for adequate representation of a regional loading, the near-field

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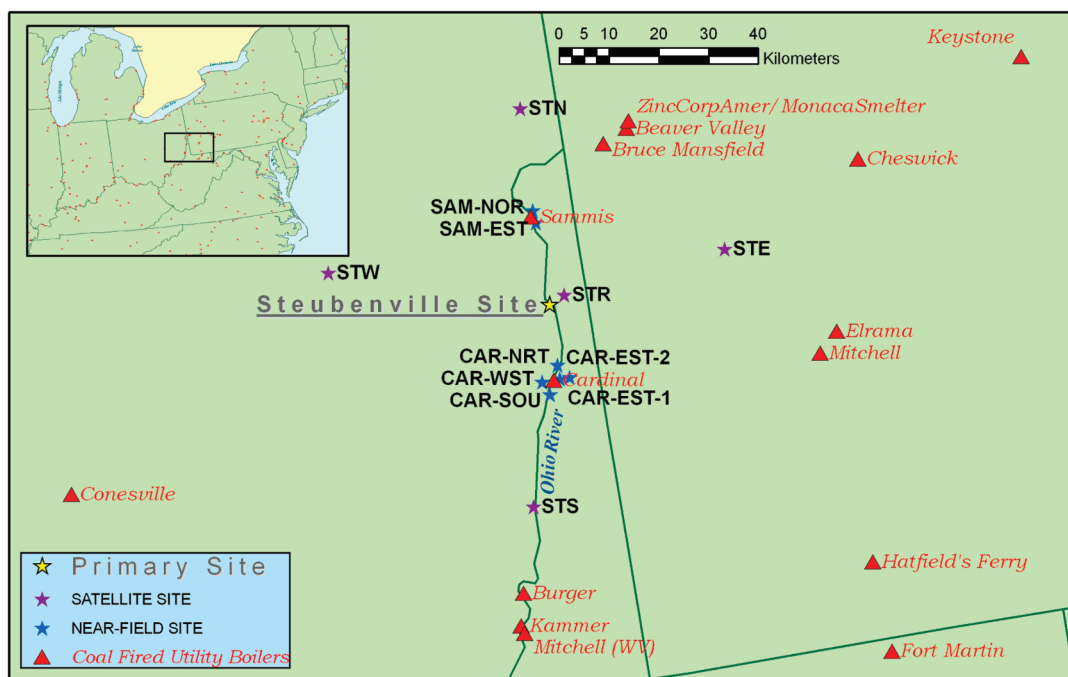‡ United States Environmental Protection Agency.

FIGURE 1. Locations of precipitation collection sites and coal-fired utility boilers in the Steubenville vicinity.

impact of large point sources and urban and industrial areas cannot be evaluated. Large-scale interpolation maps created by MDN do not depict local gradations or deposition "hotspots" because the siting criteria preclude data collection in areas that could potentially be impacted by large anthropogenic sources.

The importance of local and regional influences on near-field wet deposition has been previously reported with significant Hg deposition gradients near industrial and urbanized areas (*7, 8, 16*). Wet deposition data collected throughout the Great Lakes over the past decade has demonstrated distinct regional variability and a robust north–south gradient in Hg concentration and deposition (*17, 18*). In south Florida the spatial and temporal patterns of wet-deposited mercury were strongly influenced by local anthropogenic sources (*19, 20*). The Chicago/Gary urban area has been shown to have substantial influence over Hg concentrations in precipitation when multiple wet deposition sites were examined concurrently; sites less than 100 km apart differed in yearly volume-weighted mean (VWM) Hg concentration by over 30% (*6*). Precipitation samples collected in southeastern Michigan revealed 25–35% enhancement in the VWM Hg concentration between urban sites in Detroit and a rural site (Dexter, MI) ~60 km east (*21, 22*).

In November 2002, an enhanced air monitoring site was established in Steubenville, OH, to investigate source–receptor relationships for Hg deposition in eastern Ohio. The site overlooking the Ohio River was in close proximity to several anthropogenic point sources, including numerous CFUBs (Figure 1). It was determined that ~70% of the Hg in wet deposition was due to CFUBs, and it was suggested that local sources played a significant role (*23*). The relative contribution of local sources to the elevated Hg concentrations observed in eastern Ohio is the main focus of this paper.

Experimental Methods

Measurement Sites. Event wet deposition samples were collected at the primary monitoring site in Steubenville, OH (STB) and at four satellite sites for the period from July through September 2006, using a wet only precipitation sampling system (*24*). These systems were placed at the four satellite sites located ~40 km north (STN), south (STS), east (STE),

and west (STW) of the STB site (Figure 1 and Table S1 of the Supporting Information). In addition, wet deposition collectors were manually deployed at several locations, including along the Ohio River (STR, minimal lateral displacement from the primary site but approximately 300 m below STB) and within 1 km of Cardinal (CAR-EST1, CAR-EST2, CAR-NRT, CAR-WST, and CAR-SOU) and Sammis (SAM-EST, SAM-NOR) CFUBs, hereby referred to as near-field sites. The manually deployed samplers utilized identical sample trains as the automated collectors but were deployed just prior to forecasted precipitation events, and samples were collected immediately following the termination of the events to reduce any potential dry deposition to the collector. When operated in this manner, the manual and automated wet only methods were equivalent (*24*). Samples at all sites were collected on an event basis, with "event" defined as the abatement of rain for 3 h. Event sampling was essential for receptor modeling as well as meteorological analysis because integrating more than one event would preclude tracking the history of the precipitating air mass and would obscure the source chemical signature.

Event Deposition Sampling and Analysis. All precipitation collectors were configured with two sample trains: one for total Hg analysis and the other for trace element and ion analysis. The collection of all precipitation samples for Hg and trace elements followed the procedures previously described by Landis and Keeler (*24*). The only deviation from the procedure was the addition of an internal 1% v/v BrCl polishing soak of the 1 L Teflon sample bottles to ensure that every bottle was Hg-free prior to sampling.

Hg samples were returned to the University of Michigan, Air Quality Laboratory (UMAQL), where each sample was oxidized with a concentrated BrCl solution to 1% v/v and stored in a dark cold room. Analysis of total Hg was performed in a clean room using a Tekran Instruments Corporation (Knoxville, TN) Series 2600 Automated Water Analysis System with cold vapor atomic fluorescence spectroscopy (CVAFS). Trace element samples were acidified to a 0.2% HNO_3, 0.1% HCl v/v solution and stored in a dark cold room for over 14 days to provide adequate time for optimal leaching (*25*). A suite of 48 trace elements were quantified using a ThermoFinnigan Element2 high-resolution magnetic sector

TABLE 1. Sample Site Summary Statistics[a]

	site	N	minimum event [Hg] (ng L^{-1})	maximum event [Hg] (ng L^{-1})	VWM[b] [Hg] (ng L^{-1})	three month Hg deposition (μg m^{-2})	three month precipitation depth (cm)	meteorlogical station precipitation depth (cm)
automatic	STB	23	4.8	34.2	11.8	2.9	27.4	29.3
	STN	20	4.8	45.9	10.2	2.8	29.6	27.5
	STE	17	4.4	49.2	12.8	2.5	21.5	22.2
	STS	21	5.8	30.1	12.9	2.1	18.0	21.7
	STW	24	5.1	29.4	10.6	2.9	28.3	32.4
manual	STR	13	5.0	41.7	10.9			
	CAR	15	4.8	89.4	22.3			
	SAM	4	4.1	18.5	13.8			

[a] STB−STW are primary and satellite sites. CAR and SAM represent Cardinal and Sammis coal-fired utility boiler near-field sample collection, respectively. Although samples <1 mm were included in the VWM calculations, these were not considered when determining maximum sample concentrations. [b] Volume weighted mean.

field inductively coupled plasma mass spectrometer (HR-ICPMS). Major ion concentrations were determined using a Dionex model DX-600 ion chromatograph.

Meteorological Data and Analysis. The main Steubenville site was equipped with an anemometer and thermocouple; meteorological data was integrated and recorded at 5 min intervals. Two collocated RM Young tipping buckets, measuring 0.1 mm precipitation depth increments, were used to determine event initiation, duration, intensity, total event accumulations, and time of maximum precipitation. A tipping bucket was also deployed at STW. Cloud base heights were obtained from hourly surface observations in Wheeling, WV (40 km south of STB), and soundings were obtained from Pittsburgh, PA for determination of atmospheric stability.

National Climatic Data Center (NCDC) archived Doppler radar (WSR-88D) data from Pittsburgh, PA (KPBZ) was used to identify the path history of precipitating cells impacting the wet deposition sites as well as to determine the spatial scales of transport for air feeding these precipitating cells. Tracking the precipitation cells as they moved through the study area allowed us to infer which sources likely contributed to the mercury burden within a given precipitating cell. Precipitation cell history was tracked using Level II NEXRAD radar data in GRLevelX Analyst (Gibson Ridge Software, LLC), a volumetric visualization tool. Events depicted in the figures of the following sections show a Level III NEXRAD radar storm total precipitation product overlay from the Pittsburgh radar. Visual representations and shape files shown were created using the NCDC's Java NEXRAD viewer and ArcGIS.

Hg Concentration and Deposition Summary Results

Table 1 provides a summary of the data collected from July to September 2006. All samples collected at a particular near-field location were used to calculate a single volume-weighted mean (VWM), e.g., all samples collected near the Cardinal CFUB, CAR-EST1, CAR-EST2, CAR-WST, CAR-NRT, and CAR-SOU were averaged as "CAR". Manual sample collection trains were deployed only under conditions when the probability of precipitation was >70%, and approaching systems were observed on PBZ radar, so small or unpredicted events were not collected. Therefore, total deposition and precipitation depth for manually collected samples could not be calculated and compared to totals collected at the sites with automated collectors.

Minimum Hg concentrations ranged from 4.1 to 5.8 ng L^{-1} across the sampling sites. The maximum concentration at a satellite site was 49.2 ng L^{-1}, much lower than the maximum concentration sampled at a near-field site (89.4 ng L^{-1}). The VWM concentrations across the sites ranged from 10.2 to 22.3 ng L^{-1}. Because the precipitation depth varied among the sites for the study period, a comparison between measured sample precipitation depth and that

observed at the nearest meteorological station provided confidence in the variability of the amount of precipitation impacting a given site (Table 1).

Comparison between the samples collected during the intensive study and those from the five year study at the STB site revealed that the intensive study period reported here was not atypical of Hg data collected during the other summertime periods of record. The baseline precipitation Hg concentration at STB during the multiyear study was found to be 6.1 ng L^{-1} (baseline operationally defined as fifth percentile), and the 95th percentile Hg concentration was 42.0 ng L^{-1}. Overall, the STB Hg concentration baseline was twice the baseline observed at our other sites in the Great Lakes Region during the four year period. The contrast in Hg wet deposition across the Great Lakes region can be seen in Figure S1 of the Supporting Information via illustrations of the total deposition and volume-weighted mean (VWM) concentrations for the last four years at sites in Michigan and Ohio.

The influence of the precipitation amount on the concentration of Hg was determined for samples collected during the intensive study, and only 7% of the variability ($p = 0.001$) in Hg concentration could be explained by precipitation depth (Figure S2 of the Supporting Information), indicating that dilution of large rainfall amounts or enhancement of Hg in lower precipitation depths did not account for the large range of Hg concentrations.

Individual Event Case Study Results

Twenty-three distinct events were collected during the three month study. Nine of the 23 events were concurrently observed with sufficient precipitation depth (all samples ≥ 1 mm) to deposit substantial precipitation volume at (i) four of the five primary and satellite sites and (ii) two or more manually deployed near-field collection sites. The meteorological conditions and resultant Hg deposition were investigated in-depth for the nine events. The degree of spatial variability in rainfall Hg concentrations between concurrently collected samples was not uniform and differed by precipitation event. The Hg concentrations measured in the samples during the nine major events were classified by calculating the event coefficient of variation (c_v), which is a normalized measure of the dispersion of the data distribution, as standard deviation of Hg concentrations divided by the mean Hg concentration for the event. The events fell into three distinct categories: (1) low-spatial variability, with low- and high-concentrations ($c_v < 0.2$), (2) moderate-spatial variability ($0.3 < c_v < 0.5$), and (3) high-spatial variability ($c_v > 0.5$). Table 2 contains statistics for each of the nine events as well as the meteorological parameters that were found to be statistically significant in relation to individual event coefficient of variability. Other meteorological parameters associated with

TABLE 2. Individual Statistics on the Variability of Hg Concentration and Significant Meteorological Parameters for Nine Precipitation Events Studied during the Summer of 2006[a]

	date	coeff of variation	% near-field enhancement	range (ng L^{-1})	event VWM[b] [Hg] (ng L^{-1})			windspeed (m sec^{-1})		mixing height (m)	ceiling (m)
					all sites	satellite sites	near-field sites	during maximum rain rate	24 h prior		
low variability	9/1 (low conc.)	0.12	0	0.4	4.9 ± 0.4	5.0 ± 0.4	4.8 ± 0.4	5.6	2.5	806	3658
	8/3 (high conc.)	0.19	20	19.1	35.5 ± 2.8	33.7 ± 2.7	42.2 ± 3.3	4.6	3.8	2070	2134
moderate variability	7/12	0.31	48	6.7	6.5 ± 0.5	5.9 ± 0.5	11.5 ± 0.9	4.1	1.8	602	884
	7/28	0.44	45	20.5	18.3 ± 1.5	12.6 ± 1	22.9 ± 1.8	4.0	2.5	702	518
	8/19	0.28	28	13.2	15.0 ± 1.1	13.9 ± 1.1	19.4 ± 1.6	3.9	1.6	1119	1494
	9/18	0.35[c]	66	9.5	13.3 ± 1.1	8.5 ± 0.7	25.3 ± 2.0	2.8	1.2	493	1463
high variability	7/22	0.69	72	50.6	24.3 ± 1.9	12.9 ± 1.0	46.96 ± 3.8	1.6	0.9	250	274
	8/14	0.58	55	27.3	21.0 ± 1.7	12.7 ± 1.0	28.3 ± 2.3	1.2	0.6	593	457
	9/28	0.58	43	21.1	12.9 ± 1.0	8.0 ± 0.6	14.1 ± 1.1	1.9	2.3	497	1128

[a] See Table S2 of the Supporting Information for additional event statistics. [b] Volume weighted mean. [c] In this calculation, one sample has been removed because of exceptionally high concentration as explained by direct plume hit; coefficient of variation equals 1.44 if this sample is included.

these events can be found in Table S2 of the Supporting Information. Individual events from the low- and high-variability categories are discussed in the following sections, while those from the moderately-variable category are in Figure S3 and the text of the Supporting Information.

Our analyses suggest that the variability of Hg concentration in samples collected during a single event can generally be attributed to the fact that there were sources present between two receptor sites along the precipitation path and that Hg was fed into the precipitating cloud on a local, rather than regional scale. A local deposition gradient due to near-field point sources was observed on several occasions during the three month collection period as indicated by the high-variability category. Low variability among the samples collected during a given event was associated with occurrences of either a lesser influence by local sources and/or increased atmospheric mixing. Even samples collected at sampling sites very close to each other, e.g., samples collected near the Cardinal facility with ∼0.5 km spacing, exhibited sample variability to 62% (CAR-NOR and CAR-SOU on 8/14). Variability of this magnitude exceeded the variability observed in collocated precipitation samplers of 8.1% (5).

Another measure used to define the variability among Hg concentrations for a given event was percent attribution to near-field samples calculated using eq 1

$$\% \text{ near-field attribution} = 1 - VWM_{\text{satellite}}/VWM_{\text{near-field}} \times 100 \qquad (1)$$

The % near-field attribution is the percentage of the Hg concentration collected at the near-field sites attributed to the adjacent coal-fired utility. The calculated values ranged from 0% to 72% for the nine cases examined, with an average of 41% attribution to adjacent source.

Another approach used to determine source proximity was the sample Hg concentration and the sulfur/selenium (S/Se) ratio relationship. In the absence of coal-type differentiation and without prior knowledge of pollution control technology, S/Se variability can be used as a proxy for the distance from the coal source influence. S and Se are copollutants, but there is an important difference in the chemical conversion properties of the two elements. S is emitted from CFUBs as SO_2 and is converted to sulfuric acid droplets and particles relatively slowly, over distances on the order of hundreds of kilometers (26, 27). Se is emitted in the gaseous and particulate form, but the gas condenses on particulates much more rapidly than conversion of SO_2 to particulate sulfate. Therefore, concentration of Se drops off more quickly because of deposition with transport distance. The S measured in rain is primarily SO_4^{2-}, and therefore, as one samples at progressive distances away from large coal-fired sources, the S/Se ratio typically increases, gradually reaching steady state until another large point source is encountered along the trajectory of the air parcel. Regional steady state has been previously defined as S/Se > 3000 (28).

Low Hg Variability: August 3, 2006. This event, although low in relative variability, exhibited high concentrations at every site (VWM = 35.5 ng L^{-1}, Figure 2a). In this case, precipitation depths influenced the concentration differences as the lowest depth corresponded to the highest concentrations (Figure S4a of the Supporting Information). Severe thunderstorms occurred in the warm sector ahead of a cold front for this event, with severe precipitation cells approaching from the west. The mixing height was 2070 m, allowing for a large volume to mix boundary layer air. Surface observations indicated a ceiling of 2100 m, consistent with the mixing height. All S/Se ratios were well above the steady state values of 3000, indicating a regionally representative boundary layer. Surface winds were moderate to high from
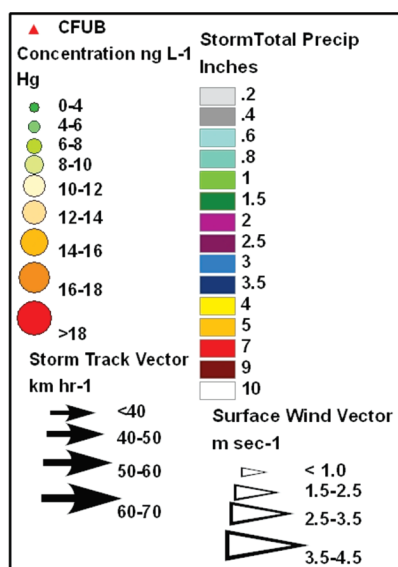
Legend for Figures 2, 3 and S3.

(a) 8/03/06 12:54 - 8/04/06 04:01 GMT

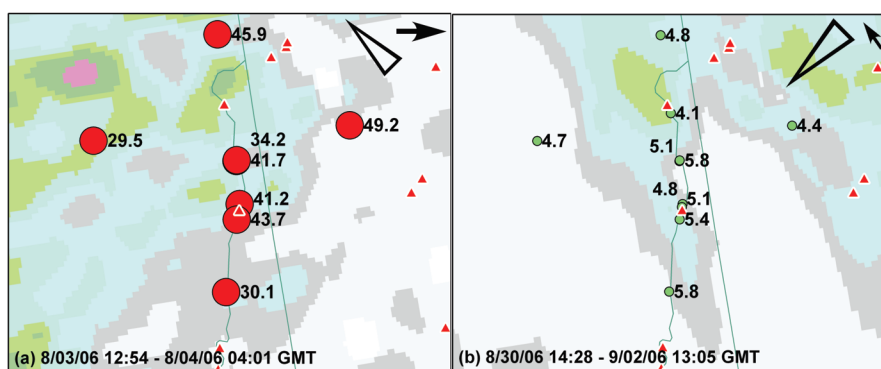(b) 8/30/06 14:28 - 9/02/06 13:05 GMT

FIGURE 2. Low variability Hg concentration. Hg concentrations are depicted atop NEXRAD storm total precipitation, with storm track and surface wind vectors at the top right. (a) August 3, 2006: high concentrations. (b) September 1, 2006: low concentrations.

the southwest throughout the event, with 5 min sustained gusts of 6 m s^{-1}, the highest winds of the 2006 summer. The 6 h average wind speed 24 h prior to the event was 3.8 m s^{-1}. This observed strong southwesterly flow would provide the environment for the transport of pollutants up the Ohio River Valley, resulting in high rainfall mercury concentrations. Regional transport likely resulted in significant mixing of the airmass and thus the subsequent low variability.

Low Hg Variability: September 1, 2006. Unlike the August 3 low variability event, all samples collected during the September 1 event were close to that considered baseline for the Steubenville area, with an event VWM of 4.9 (Figure 2b). In fact, the small variability among the sample concentrations was not much higher than our collocated sample precision. Variability among the concentrations can be accounted for by sample depth; there is a significant negative relationship between concentration and depth when the STE sample is removed as it contained 0.5 cm more rain than other samples collected during the event ($r^2 = 0.4858$, $p = 0.037$; Figure S4b of the Supporting Information). All Se values were below the method detection limit (MDL) (0.012 ppb). Using 5 times the Se MDL yields, we found that all S/Se ratios greater than or equal to 3000, indicating a regional background signature for all samples collected. The northeasterly surface winds were sustained prior to and during rain, an event associated with the remnants of the western edge of Hurricane Ernesto, and winds averaged 5.6 m sec^{-1} during maximum rain. The rapid air parcel transport helped to explain the regional, well-mixed background characteristic of the sample concentrations. The ceiling was reported at 3658 m.

High Hg Variability: July 22, 2006. This event lasted from approximately 03:45 to 05:00 EST, with an average rain fall rate of 7.8 mm h^{-1}. The convective event was associated with a large low-pressure system, and although precipitating cell movement was from the southwest, measured surface winds indicated air transport in the boundary layer from the south−southwest during maximum precipitation intensity. Maximum Hg concentrations were collected adjacent to the Cardinal facility (58.5, 47.0, and 32.7 ng L^{-1} for CAR-EST2, CAR-WST, and CAR-SOU, respectively) with the lowest concentration found at STN (7.9 ng L^{-1}, Figure 3a). For this highly variable event, the mixing height was only 250 m, and the observed cloud ceiling was reported at 274 m. Surface winds were particularly stagnant, averaging 1.5 m s^{-1} during the event, with a 24 h average prior to the event of 1.2 m s^{-1}.

Precipitation depth varied from 1−5 cm, but this did not explain the difference in Hg concentration as sites with similar depths exhibited a large range in Hg concentration and, therefore, wet deposition (Figure S5a of the Supporting Information). For the July 22 event, the S/Se to Hg concentration relationship is particularly significant ($r^2 = 0.957$, $p < 0.001$; Figure S6 of the Supporting Information), indicating that distance from source is a prime driver for the Hg concentration differences.

High Hg Variability: August 14, 2006. Convection occurred along a distinct cold front late in the evening of August 14, with precipitation lasting 45 min. Although all precipitation occurred along the frontal boundary, two distinct cells seemed to contribute to the rain, with all but the northern most site receiving rain from a southern cell (Figure 3b). The
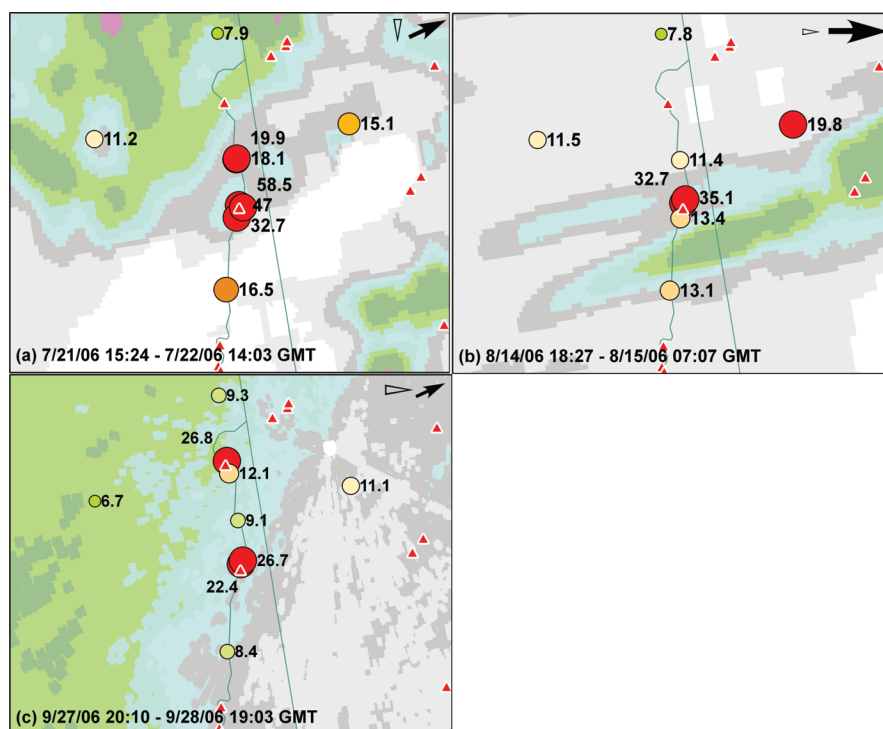
FIGURE 3. Highly variable Hg concentration. Hg concentrations are depicted atop NEXRAD storm total precipitation, with storm track and surface wind vectors an the top right. (a) July 22, 2006, (b) August 14, 2006, and (c) September 28, 2006.

observed rainfall depth was not correlated to Hg concentrations (Figure S5b of the Supporting Information). For example, identical rainfall depths were observed at STN and STE, with concentrations of 7.8 and 19.8 ng L^{-1}, respectively. On an even smaller spatial displacement (<0.5 km), samples collected at sites CAR-EST2 and CAR-SOU (depths of 0.67 and 0.64 cm, respectively) differed by 21.7 ng L^{-1}. The large difference between these near-field collected sample concentrations was likely due to the combination of surface winds and sample collection placement. Namely, with surface winds from the south shifting to west, the stack plume from the Cardinal facility was observed directly overhead of the CAR-EST2 and CAR-NOR sample sites during the rain event, with the plume directed *away* from the CAR-SOU site. It appears the rain "scrubbed" the plumes of the CFUBs in two of the three cases, possibly scavenging the reactive gases and some particles. Of the nine samples collected during this event, four contained S/Se ratios below steady state, indicating that a coal combustion point source had influenced the precipitation chemistry between the receptor sites, and these corresponded to the samples with the four highest Hg concentrations (STE, CAR-SOU, CAR-NOR, and CAR-EST2).

The boundary layer mixing height was 593 m, while the observed ceiling was 457 m during thundershowers with fog. Severe weather cells moved through the Ohio River Valley along a southwest to northeast trajectory. Relatively calm (1.9 m s^{-1}) southerly surface winds prior to the event shifted to westerly during the course of the storm, with wind speeds at 1.2 m s^{-1} during maximum rain intensity. It is of importance to note the degree of local stagnation as surface winds measured at Steubenville averaged 0.6 m s^{-1} 24 h prior to rainfall, and with all things remaining equal, post release ambient concentration of pollutants emitted from a stack will be higher if emitted into slow wind conditions.

High Hg Variability: September 28, 2006. High variability during this event is accentuated once again by the large difference between near-field samples; with westerly surface winds dominating during the rain event, the sample collected just east (SAM-EST) of the Sammis facility contained precipitation with Hg concentrations more than twice that

collected to the north (SAM-NOR) of the stacks (26.8 and 12.0 ng L^{-1}, respectively), suggesting that rain had fallen through the plume, resulting in a washout of pollutants. Samples collected near the Cardinal facility did not exhibit a similar level of variability, but it can be seen in Figure 3c that the large variability in Hg concentration during this event is enhanced by these near-field samples. Only three samples exhibited S/Se ratios below background (three of the four near-field samples, with the exception of SAM-NOR), indicating that wind direction can have a distinct effect on the degree to which a collection site might be locally enhanced by point sources.

Rain occurred along a distinct cold front that was moving west to east across the northeastern United States. The most intense portion of the precipitation field passed through the Ohio River Valley in late morning on September 28. The cloud base was reported at 1128 m during the heaviest rain, with a mixing height of 500 m. The majority of the rain fell in 4 h, from 07:00 to 11:00 EST, with the most intense rain observed at 10:00 with winds at 1.9 m s^{-1}. There was no significant relationship between precipitation depth and concentration (Figure S5c of the Supporting Information).

Case Study Implications. Overall, precipitation depth was found to account for only 7% of the concentration variability, and a strong depth−concentration relationship was observed only during events that exhibited regionally well-mixed characteristics and low between site variability. Therefore, it was concluded that for the period studied local source emissions had a greater impact on concentrations than precipitation depth differences for near-field sites within the Steubenville area. Unlike larger scale regionally representative Hg deposition collection, concentrations could not be spatially interpolated because of exceptionally tight gradients, which invalidated the basic assumptions of spatial interpolation.

The coefficient of variance and near-field attribution of the Hg concentrations observed concurrently at the sites were somewhat correlated ($r^2 = 0.62$, $p = 0.012$). Differences between the two descriptive parameters were due to spatial anisotropy in the events. Directionality of winds, airmass

transport, and precipitating cell movement cause satellite sites that are downwind of point sources to be higher in Hg concentration, while the near-field attribution calculation was determined only by the absolute distance from coal combustion point sources and not direction.

The nine case studies highlighted four distinct meteorological conditions that influenced the degree to which Hg concentration is enhanced on a local scale during a particular precipitation event. The most significant factor in determining the degree of spatial variability and near-field attribution of Hg concentrations was surface wind speed during the period of maximum rain rate. When relatively low wind speeds were observed during these periods of maximum rain rates, we suggest that boundary layer mixing was reduced, resulting in tight deposition gradients. A linear regression analysis exhibits these relationships in Figure S7a of the Supporting Information (both significant at $p < 0.05$). It was also found that low boundary layer heights coincided with reduced vertical dispersion and consequently local deposition patterns, although higher boundary layer coincides with lower variability among concentrations collected as indicative of regional influence. The nine events studied are compared in Figure S7b of the Supporting Information, and a relationship can be seen among the mixed layer height, coefficient of variability in Hg concentration, and percent attribution to the near-field site concentrations. The other two meteorological factors that demonstrated relationships were the 6 h average of wind speeds 24 h prior to precipitation and the lowest observed ceiling during precipitation; these relationships can be seen in graphs c and d of Figure S7 of the Supporting Information. When the four meteorological factors are examined in aggregate using multivariate linear regression (MLR), the significance of the relationship increases, with 95% of the variability in coefficient of variance explained by meteorological parameters ($p = 0.008$). The MLR was slightly less statistically significant when the four meteorological parameters were regressed against percent attribution ($r^2 = 0.826$, $p = 0.08$), most likely due to the lack of segregation between upwind and downwind Hg concentrations in the percent attribution calculation.

One of the major goals of this work was to determine the overall degree of individual source influence at near-field locations, as current wet deposition collection networks do not include near-field source sampling sites. Using the statistical model for the MLR, we estimated percent attribution and coefficient of variability for an additional 14 events during the three month period. It was found that for July, August, and September 2006, there was a predicted average near-field source attribution to Hg concentration of 42%, and that 19 of the 23 events were moderately or highly spatially variable (coefficient of variation >0.3) in Hg concentration for the region studied. Of all of precipitation from CY2003 through CY2006 at Steubenville, Ohio, 29% fell during the summer months of July, August, and September. Although we cannot use the equations of fit to extrapolate to cold weather months because of the difference in atmospheric chemistry, meteorology, and cloud properties (i.e., ice, mixed, or water only), the results from the summer evaluation indicate that coal-fired utility boiler near-field contribution to Hg concentration is significant and greater than previously estimated. Given that our study results suggest that meteorological parameters explain greater than 80% of the variability in local Hg deposition gradients during the study period, it is evident that local sources play a significant role. This work, therefore, establishes the need for longer-term multiseasonal near-field wet deposition collection for discernment of an accurate local-scale gradient of Hg wet deposition in the vicinity of point sources.

Supporting Information Available

Great Lakes region Hg in wet deposition (Figure S1), concentration versus depth for all collected samples (Figure S2), latitudes and longitudes of collection sites (Table S1), additional event meteorological parameters (Table S2), a moderately variable event meteorological discussion, moderate variability event radar and Hg concentration depiction (Figure S3), low variability event Hg concentrations versus sample depth (Figure S4), high variability event Hg concentrations versus sample depth (Figure S5), and S/Se ratio versus Hg concentration on July 22, 2006 (Figure S4). This information is available free of charge via the Internet at http://pubs.acs.org.

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