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Assessing the emission sources of atmospheric mercury in wet deposition across Illinois

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HIGHLIGHTS

- We collected event-based wet-only precipitation at four sites in Illinois, USA.
- All four sites appeared to be impacted by local and regional emission sources.
- PMF model results attributed Hg wet deposition predominantly to coal combustion.
- The QTBA model associated Hg wet deposition with known industrial source areas.

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ABSTRACT

From August 4, 2007 to August 31, 2009, we collected event-based precipitation samples for mercury (Hg) and trace element analyses at four sites in Illinois (IL), USA. The objectives of these measurements were to quantify Hg wet deposition across the state, and to assess the contributions to Hg in precipitation from major local and regional emission sources. Monitoring sites were located, from north to south, in Chicago, Peoria, Nilwood, and Carbondale, IL. Measurements from these four sites demonstrated that a clear spatial gradient in Hg wet deposition was not evident across the state. Each site received > 10 μg m^{-2} of Hg wet deposition annually, and these observed values were comparable to annual Hg wet deposition measurements from other event-based precipitation monitoring sites in source-impacted areas of the Midwestern U.S. We applied the multivariate statistical receptor model, Positive Matrix Factorization (EPA PMF v3.0), to the measured Hg and trace element wet deposition amounts at the four sites. Results suggested that 50% to 74% of total Hg wet deposition at each site could be attributed to coal combustion emissions. The other source signatures identified in the precipitation compositions included cement manufacturing, mixed metal smelting/waste incineration, iron–steel production, and a phosphorus source. We also applied a hybrid receptor model, Quantitative Transport Bias Analysis (QTBA), to the Hg wet deposition datasets to identify the major source regions associated with the measured values. The calculated QTBA probability fields suggested that transport from urban/industrial areas, such as Chicago/Gary, St. Louis, and the Ohio River Valley, resulted in some of the highest estimated event-based Hg wet deposition amounts at the four sites (potential mass transfer of up to 0.32 μg m^{-2}). The combined application of PMF and QTBA supported the hypothesis that local and regional coal combustion was the largest source of Hg wet deposition in Illinois.

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1. Introduction

Mercury (Hg) is a hazardous air pollutant released to the atmosphere through natural and anthropogenic activities. Atmospheric deposition is widely recognized as the primary mechanism by which Hg enters terrestrial and aquatic ecosystems (U.S. EPA, 1997; Landis and Keeler, 2002; Landis et al., 2002; Hammerschmidt and Fitzgerald, 2006), where it can be converted to the organic, bioaccumulative form, methyl mercury (U.S. EPA, 1997; Schroeder and Munthe, 1998). Investigation of atmospheric source emissions and transport patterns on varying spatial scales is essential for effectively mitigating the impact of Hg on the environment.

The U.S. Midwest has for many years been a region of particular interest for studying atmospheric Hg due to the density of anthropogenic sources (Fig. 1) and elevated Hg concentrations in fish from the region's lakes and waterways (U.S. EPA, 1994, 1997). To begin investigating Hg deposition to the Lake Michigan Basin, the University of Michigan Air Quality Laboratory established five Hg wet deposition monitoring sites as part of the Lake Michigan Mass Balance Study (LMMBS, July 1994–October 1995) (Landis and Keeler, 2002; Landis et al., 2002; Vette et al., 2002). Results from the LMMBS indicated that the concentration of Hg in precipitation in the Chicago/Gary urban

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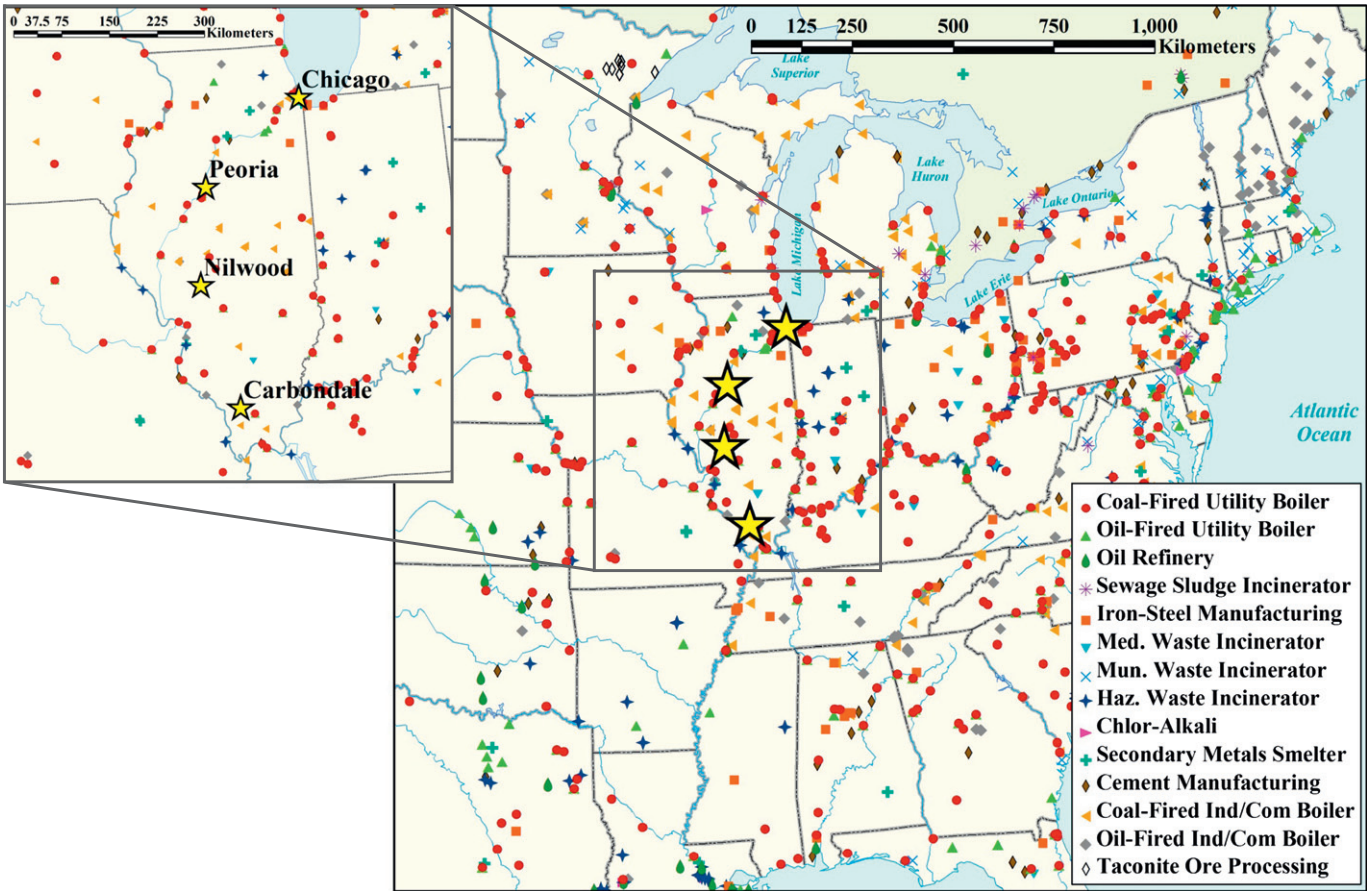

Fig. 1. Location of the Illinois monitoring sites with respect to major regional mercury point sources emitting ≥0.1 kg (≥0.0001 tons) Hg/yr (U.S. EPA, 2005; Environment Canada, 2007).

area (volume weighted mean (VWM) concentration = 21.5 ng L^{-1}) was a factor of two larger than the surrounding sites (Landis et al., 2002). At all five sites, air mass transport from urban and/or industrial areas led to enhanced Hg concentrations in precipitation (Landis et al., 2002). Precipitation at the upwind background Bondville site in central Illinois (40.03°N, 88.22°W) showed the greatest enhancement under southwest transport from St. Louis and northeast transport from Chicago/Gary (Landis et al., 2002). In contrast, precipitation events in Chicago associated with northerly flow had a much lower VWM concentration compared to events with either stagnant conditions or southeasterly transport from Chicago/Gary (Landis et al., 2002).

Building upon this earlier work, from August 4, 2007 to August 31, 2009 we measured Hg and a suite of trace elements (Mg, Al, P, S, K, Ca, V, Cr, Mn, Fe, Ni, Zn, As, Se, Sr, Cd, Ba, La, Ce, Pb) in wet deposition at four sites in Illinois. This statewide network offered a quantitative spatial assessment of Hg deposition, and provided the necessary information to quantify the contributions from major local and regional atmospheric Hg sources on Hg wet deposition in Illinois.

Event-based wet-only precipitation samples were collected using the measurement techniques developed and employed by the University of Michigan Air Quality Laboratory (Hoyer et al., 1995; Landis and Keeler, 1997; Keeler and Dvonch, 2005; Keeler et al., 2005, 2006; Gratz et al., 2009; White et al., 2009; Gratz and Keeler, 2011). Event-based measurements are essential for applying meteorological and receptor models, as the path of a precipitating system relative to major sources has a significant and observable impact on Hg and trace element deposition (Dvonch et al., 2005; White et al., 2009). The frequency and form of precipitation, the origin of air masses that feed precipitating systems, and the source mixture and density in the upwind areas for each storm system can importantly influence precipitation chemistry and the amount of Hg that is wet deposited during precipitation events.

Furthermore, the contribution from a source depends not only on the total Hg emitted, but also on the relative amounts of the chemical forms emitted. Mercury is emitted to the atmosphere in three main forms: gaseous elemental Hg (Hg^0), fine particulate-bound Hg (Hg_p), and divalent reactive gaseous Hg (RGM). RGM and Hg_p are relatively soluble and readily undergo heterogeneous reactions, resulting in much shorter atmospheric residence times than Hg^0 (Lindberg et al., 2007). Variability in the quantity and speciation of Hg emissions by source type consequently influences the relative amounts of emitted Hg that can be deposited nearby sources or transported downwind. In the U.S., annual total Hg point source emissions are approximately 55 tons, of which 54% are from fossil fuel and electric power generation, with 53% coming specifically from coal-fired electric generating units (EGUs) (U.S. EPA, 2008). These percentages do not include additional contributions from coal-fired industrial/commercial boilers. In the state of Illinois, 56% of total Hg emissions come from fossil fuel power generation, with 49% from coal-fired EGUs and 7% from other fossil fuel power generation (U.S. EPA, 2008). Given that a large fraction (50 to 80%; Carpi, 1997; Seigneur et al., 2006) of total Hg emissions from coal combustion are in the oxidized form, near-field Hg deposition can be significantly enhanced at local receptors (White et al., 2009). Examples of other major Hg emission source categories in Illinois include: iron–steel mills (3%), petroleum refining (3%), cement manufacturing (2%), and non-ferrous metal smelting (<1%) (U.S. EPA, 2008).

To quantify the relative contributions from emission sources to Hg wet deposition at the four sites, we applied the multivariate statistical receptor model Positive Matrix Factorization (U.S. EPA PMF v3.0) to the Hg and trace element wet deposition datasets. We also calculated air mass back-trajectories for each event and combined them with the sample chemical compositions using the hybrid receptor model Quantitative Transport Bias Analysis (QTBA). While the PMF method

looks for similar covariance structure in the Hg and trace element datasets to calculate the contributions of major sources, QTBA looks for covariance between the deposition measurements and the meteorological transport pathway associated with each precipitation event to determine the region(s) where the sources are located. Together, these two techniques provide useful information for estimating the emission source contributions to Hg wet deposition.

2. Materials and methods

2.1. Study sites

The Illinois network sites were located in Chicago (41.791 N, 87.602 W), Peoria (40.697 N, 89.584 W), Nilwood (39.396 N, 89.810 W), and Carbondale (37.722 N, 89.209 W) (Fig. 1). The Chicago site was located on the roof of the University of Chicago's Kersten Physics building in southern downtown Chicago, approximately 2 km west of Lake Michigan. The Peoria site was located at an Illinois EPA air quality monitoring station, on the roof of a city office building. The Nilwood site, positioned at the local Illinois EPA monitoring trailer, was in a rural location downwind of the greater St. Louis metropolitan area. The Carbondale site was located near the campus of Southern Illinois University near both the Ohio and Mississippi Rivers.

2.2. Event wet deposition sampling

We collected event-based precipitation samples using the modified University of Michigan MIC-B (MIC, Thornhill, Ontario) wet-only precipitation collector with separate sampling trains for Hg and trace elements (Landis and Keeler, 1997). The Hg sampling train consisted of a borosilicate glass funnel (average collection area 191 ± 9 cm^2) and 1-L Teflon® bottle. The trace element sampling train consisted of a polypropylene funnel (average collection area 167 ± 7 cm^2) and a 1-L polypropylene bottle.

In Peoria, Nilwood, and Carbondale, the Teflon® and polypropylene bottles were attached to their corresponding funnels through Teflon® and polypropylene adapters, respectively. The Teflon® adapter contained a glass vapor lock to prevent loss of vapor phase Hg from the samples (Landis and Keeler, 1997). Full-time operators collected daily-event precipitation samples on the morning after an event and installed a clean sampling train. Weekly samples were collected in Peoria in August 2007 ($n = 3$) due to the lack of a full-time operator during that time. While we included these samples in the event record (Fig. 2, SI-1) and in calculations of VWM concentration, total precipitation amount, and total deposition (Tables 1, SI-2–SI-5; Fig. 4), we excluded them from any event-based statistics and from the statistical receptor analyses.

In Chicago, the MIC-B precipitation collector was equipped with the Automated Sequential Precipitation Sampler (ASPS-II). This collector is identical to the standard MIC-B automatic wet-only collector, with the exception that, instead of the single bottle-funnel sampling trains described by Landis and Keeler (1997), the ASPS-II is deployed with multiple sample bottles that are individually and sequentially activated by an internal control module to collect event samples without the need for a local field operator after each event. Eight 1-L bottles of each type (Teflon® and polypropylene) were placed in separate racks inside the MIC-B where the bottles were attached to their corresponding funnels through acid-cleaned silicone tubing that passed through solenoid pinch valves. The valves remained closed at all times, except when an individual bottle was activated by the control module. An onsite tipping bucket rain gauge was used to determine when a precipitation event had concluded (defined as a 3-hour period without precipitation), at which point the valve to the current bottle closed and the subsequent sample bottle was activated. The operator visited the site weekly to collect sample bottles and replace funnels and tubing. In part as a result of employing this true-event collection scheme, slightly more samples were collected in Chicago ($n = 225$) relative to the other locations ($n = 139$ (Peoria), 148 (Nilwood), 138 (Carbondale); Table 1). These values may also reflect differences in the meteorological conditions and storm patterns experienced at each site over the two-year study.

All field and analytical supplies were prepared using an eleven-day acid-cleaning procedure (Landis and Keeler, 1997). Additionally, Teflon® bottles were soaked in an internal 1% BrCl solution (v/v) for a minimum of 24-hours followed by a thorough rise with ultrapure Milli-Q water. Teflon® bottles were deployed with 20 mL of 0.8% HCl to preserve samples in the field. Site operators sent precipitation samples to the University of Michigan Air Quality Laboratory to be processed and analyzed in a Class 100 clean room.

The volume of each precipitation sample was determined gravimetrically. Events ≥ 0.1 cm in depth provided sufficient volume for analysis. Precipitation depths were calculated as the sample volume divided by the measured funnel area. VWM concentrations were calculated as the measured sample concentrations multiplied by the sample precipitation depth, and the sum of those values divided by the sum of precipitation depth for the period of interest. Sample deposition amounts were calculated as the measured concentration multiplied by the calculated precipitation depth.

2.3. Precipitation sample analysis

2.3.1. Total mercury analysis

Hg samples were oxidized with concentrated BrCl to a 1% solution (v/v) in the sample bottle and stored in a dark cold room for at least 24-hours prior to analysis. Total Hg concentration was measured using dual amalgamation and cold-vapor atomic fluorescence spectrometry (CVAFS) (Landis and Keeler, 1997). The Method Detection Limit (MDL) for total Hg in the present study was 0.11 ng/L, determined using EPA method 200.8 (U.S. EPA, 1994). The analytical precision of laboratory replicate Hg analysis was 3.0% ($\pm 2.2\%$) ($n = 151$). Bottle blank determinations resulted in a mean value of 0.4 (± 1.6) pg bottle^{-1} ($n = 159$). Field blanks and funnel rinses for materials prepared according to the previously described procedures were shown to contain Hg concentrations below the reported MDL (Landis and Keeler, 1997). Collocated total Hg samples collected using identical samplers and protocols as those used here gave an absolute mean difference in the sample concentrations of 8.1% (Landis and Keeler, 1997).

2.3.2. Trace element analysis

Trace element samples were acidified with concentrated Optima Grade HNO_3 (Fisher Chemical) to a 1% solution (v/v) in the sample bottle. Samples were stored for a minimum of 14 days before analysis to provide adequate time for trace element desorption off particles and the walls of the sample bottle (Landis and Keeler, 1997). Samples were analyzed using a Finnigan MAT Element 2 magnetic sector field high-resolution inductively coupled plasma mass spectrometer (ICP-MS). Calibration curves were generated using multi-element Spex standards (SPEX CertiPrep) in a 1% HNO_3 Optima Grade (Fisher Chemical) solution. The standard matrix was matched to the expected sample composition. NIST Standard Reference Material 1604a was analyzed for quality control of the instrument calibration. All samples were analyzed in triplicate, and the resulting concentration was determined from the mean of the replicate analyses.

We determined MDLs for the 20 trace elements according to EPA Method 200.8. Analyses of bottle blanks and funnel rinses prepared following the cleaning and analytical methods described here were shown to contain trace element concentrations below the MDLs (Landis and Keeler, 1997). Table SI-1 reports the trace element MDLs for this study, the percentage of samples above the MDL, and the average analytical uncertainties (determined as the average relative standard deviation (RSD) for each element; RSD is the standard deviation of the triplicate analysis of each sample).

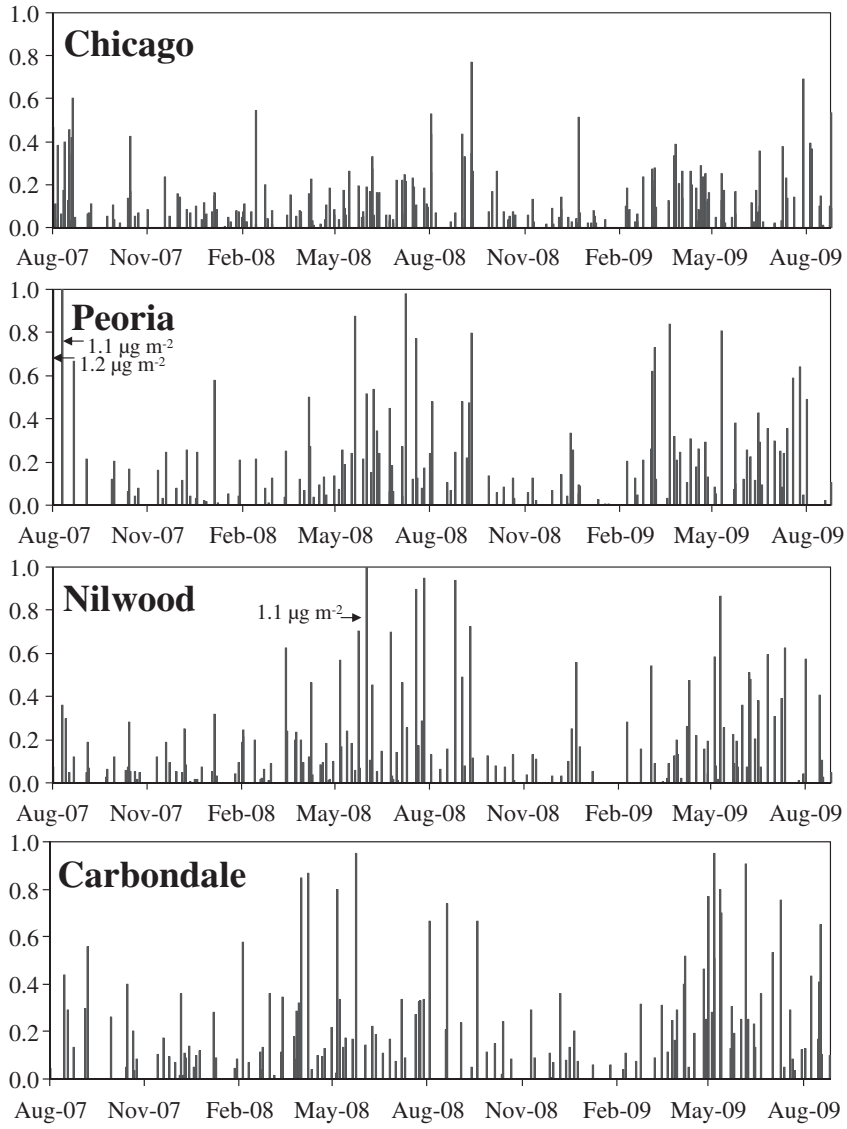

Fig. 2. Event-based mercury deposition (μg m^{-2}) measured in precipitation samples from Chicago, Peoria, Nilwood, and Carbondale, IL from August 4, 2007 to August 31, 2009.

2.4. Meteorological analysis and back trajectory calculations

We modeled air mass transport to each site using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model, Version 4.8 (Draxler and Hess, 1997). Three-day (72-hour) back-trajectories were calculated using the National Weather Service's National Center for Environmental Prediction (NCEP) Eta Data Assimilation System (EDAS) gridded meteorological data, provided by the National Oceanic and Atmospheric Administration's Air Resources Laboratory (NOAA-ARL). Three-day back trajectories are reasonable for adequately representing regional-scale transport within acceptable limits of uncertainty considering that, due to the available spatial resolution of gridded meteorological data, there is increasing uncertainty in computed back-trajectories with distance from the starting location that is particularly enhanced beyond 72 h (Kahl and Samson, 1986). The hybrid receptor model applied in this study (QTBA; Section 2.5) accounts for uncertainty in the computed trajectories with distance from the starting location when calculating the probability fields.

A single trajectory was computed for each precipitation event. The trajectory start times were assigned as the hour of maximum precipitation determined from the onsite heated tipping bucket rain gauges. The trajectory start heights were set to one-half of the mixed layer height, as determined by HYSPLIT.

Table 1
Summary statistics for event-based Hg concentration and wet deposition measurements at the Chicago (UOC), Peoria (PEO), Nilwood (NLW), and Carbondale (CBD), Illinois precipitation monitoring sites from August 4, 2007 to August 31, 2009.

Site	N	Total precipitation depth (cm)	Volume-weighted mean concentration (ng L^{-1})	Concentration range (ng L^{-1})	Total deposition (μg m^{-2})	Mean event deposition (μg m^{-2}) [a]	Maximum event deposition (μg m^{-2}) [a]
UOC	225	258	12.0	0.9 – 243.9	31.1	0.14	0.77
PEO	139	221	14.4	3.1 – 143.7	31.9	0.21	0.98
NLW	148	227	13.2	1.6 – 50.3	30.1	0.20	1.08
CBD	138	260	13.1	2.7 – 60.1	34.0	0.25	0.95

[a] Samples from Peoria in August 2007 (N = 3) excluded from calculation due to weekly sample collection during that period.

2.5. Multivariate statistical receptor analysis

Multivariate statistical methods, such as factor analysis, are widely used to identify source signatures and explore source–receptor relationships using the trace element compositions of atmospheric aerosols (Polissar et al., 2001; Liu et al., 2003; Morishita et al., 2006; Pekney et al., 2006) and precipitation (Dvonch et al., 1999; Keeler et al., 2006; Gratz and Keeler, 2011). Since many sources emit characteristic amounts of certain trace elements, relationships may be established by linking emissions with receptor measurements through signature elements and elemental ratios (Dvonch et al., 1998). With an understanding of these signatures, source–receptor techniques can be used to identify the major sources influencing a given receptor site.

We applied Positive Matrix Factorization (PMF) to the event-based precipitation measurements at each Illinois site. PMF is a multivariate statistical technique that uses weighted least-squares factor analysis to decouple the matrix of observed values (**X**) into two matrices representing the factor scores (**G**) and factor loadings (**F**), as represented by the equation $\mathbf{X}=\mathbf{GF}+\mathbf{E}$,where **E** is the residual matrix representing the difference between observed and predicted values (Paatero and Tapper, 1994; Paatero, 1997). As it applies here, the measured precipitation sample compositions were decoupled into an estimated factor profile (representing the mean quantity of each analyte apportioned to each factor) and the factor contributions to each sample (Paatero and Tapper, 1994; Paatero, 1997). The residuals are weighted by the measurement uncertainties, and PMF uses these weighted residuals to determine a goodness-of-fit parameter (Q) (Paatero, 1997). The objective is to minimize Q with respect to the factor matrices, while imposing non-negativity constraints on the modeled source contributions due to the physical reality of the source–receptor problem (Paatero and Tapper, 1994; Paatero, 1997).

The U.S. EPA has developed a publicly available PMF model that couples a graphical user interface with the PMF statistical approach and provides the user with block bootstrap uncertainty estimates (Norris et al., 2008). We applied EPA PMF v3.0 (Norris et al., 2008) to the matrices of event-based Hg and trace element wet deposition measurements from each site. Prior to applying PMF, we converted the sample concentrations to deposition amounts and we replaced concentrations reported as less than zero with one half of the MDL (Gratz and Keeler, 2011). We determined the uncertainties (U) for each sample analyte using the MDL, and propagating the uncertainties in sample collection ($SC=10\%$), analytical measurement (AM = standard deviation of three replicate analysis for each sample; Table SI-1), and precipitation depth measurement ($PD=5\%$) according to Eq. (1) (Keeler et al., 2006)

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

We approached this analysis from a network perspective by examining the results across all sites and applying PMF to the same set of 20 trace elements, plus Hg, for each site. We included all valid samples for each site, excluding a small number of samples that we identified as extreme outliers (<3% of samples for each site). We also excluded these outlier samples from QTBA. We evaluated PMF solutions with four to five factors, and we identified source signatures based on the combination of elements within each factor and the elemental ratios for known source tracers.

We applied PMF using the default model specifications (Norris et al., 2008). To improve the model output, achieve a Q value that was closer to the theoretical Q, and account for sources of uncertainty in the measurements not represented in our uncertainty calculation (Norris et al., 2008), we applied 10% extra modeling uncertainty to each site. For each site, we examined the input data statistics and the regression diagnostics provided by PMF. Elements with a signal-to-noise (S/N) ratio<2 (e.g. comparable values of signal and noise) were down-weighted so that the user-provided uncertainty was increased by a factor of three (Paatero and Hopke, 2003; Norris et al., 2008). We similarly down-weighted any element with an r^2 value<0.4 in the regression of predicted-versus-observed values.

The variability in the PMF solution was estimated using a block bootstrap technique, which calculates the stability of the model solution by randomly re-sampling blocks of the input dataset and computing the variability between model solutions (Norris et al., 2008). Bootstrap factors are mapped against base model factors to demonstrate the reproducibility of the solution, and uncertainty statistics are provided in the PMF output (Norris et al., 2008). We applied 100 bootstrap runs to the PMF base run with the lowest Q value (Keeler et al., 2006). We determined the final factor profiles based on our ability to identify all the factors, the robustness of Q values, the ability of the model to replicate measured results, and the bootstrap results.

2.6. Hybrid receptor model analysis

Quantitative Transport Bias Analysis (QTBA) is a hybrid receptor model that combines air mass back-trajectories with measured amounts of analytes at the receptor site to determine the most probable source regions of those species. This approach was described in detail by Keeler and Samson (1989), and applied here in the same manner as Gratz and Keeler (2011).

QTBA defines the probability of a species arriving at the receptor location (x,y) at time (t) as:

$$A(x,t)=\int_{t-\tau}^{t}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}T(x,y,t|x',y',t')dx'dy'dt'. \quad (2)$$

The potential mass transfer function, $T(x,y,t|x',y',t')$, is defined by:

$$T(x,y,t|x',y',t') = Q(x,y,t|x',y',t')R(x,y,t|x',y',t')D(x,y,t|x',y',t')\Lambda(x,y,t|x',y',t'). \quad (3)$$

$Q(x,y,t|x',y',t')$ is the transition probability density function of an air parcel arriving at the site at a given time. Q is assumed to be normally distributed about the trajectory axis with a standard deviation that increases linearly upwind (Keeler and Samson, 1989). $R(x,y,t|x',y',t')$ is the probability that the species will not react to form another species during transport. We assumed this to be 100%, which is a suitable approximation for Hg^0, Hg_p (Burke, 1998; Liu, 2007) and trace elements (Keeler and Samson, 1989). Although this may not be suitable for the more chemically reactive RGM, we maintained this assumption due to the limited available knowledge about atmospheric Hg physicochemistry (Liu, 2007). This is an area for further investigation in the future. $D(x,y,t|x',y',t')$ and $\Lambda(x,y,t|x',y',t')$ are the probabilities that the species will not be dry or wet deposited during transport. We assumed that they were linearly proportional to the measured deposition amounts (Keeler and Samson, 1989; Liu, 2007). We estimated the dry deposition rate coefficient as a ratio between the dry deposition velocity (which was allowed to vary diurnally and seasonally; Keeler and Samson, 1989; Burke, 1998; Liu, 2007), and the mixing height along each trajectory (determined by HYSPLIT). The wet deposition rate coefficient was approximated using the power law $Precipitation^{0.6}$ (Keeler and Samson, 1989). Precipitation amounts along the trajectory path were obtained from HYSPLIT.

Integration of $T(x,y,t|x',y',t')$ generates a transport probability field for each trajectory that is then weighted by the associated deposition amount (Keeler and Samson, 1989). The QTBA field is defined as the ratio of weighted to un-weighted potential mass transfer fields multiplied by the average deposition amount for the study period (Liu, 2007). The QTBA field has units of deposition ($\mu g\ m^{-2}$) and is viewed as 2-dimensional contours, which provide an estimate of local

and regional source contributions to event-wet deposition. Thus, QTBA uses the calculated transport pathways to spatially locate the most probable source regions contributing to wet deposition at the receptor (Keeler and Samson, 1989).

3. Results and discussion

3.1. Site characterization — temporal and spatial variability of Hg in precipitation

The Hg wet deposition data distributions provided some initial insight into the characteristics of the monitoring locations in this study (Table 1; Fig. 2, SI-1). The range in Hg concentrations observed at the four sites was greatest in Chicago, where the maximum event concentration was 243 ng L^{-1}, and two other events had concentrations > 100 ng L^{-1} (Table 1, Figs. SI-1). The minimum Hg concentrations (0.9 to 3.1 ng L^{-1}; Table 1) were typical of other Great Lakes event precipitation sampling sites (Keeler and Dvonch, 2005). The 5th percentile Hg concentrations (ng L^{-1}), which provide an approximation of the regional baseline, were similar at all four sites: Carbondale (3.7), Peoria (4.1), Chicago (4.3), and Nilwood (4.5). The 95th percentile concentrations (ng L^{-1}) were also comparable: Peoria (40.8), Nilwood (40.4), Chicago (37.9), and Carbondale (35.1). These 5th and 95th percentiles are slightly less than those reported for event-based precipitation measurements at the highly industrialized Steubenville, OH site (6.1 ng L^{-1} and 42.0 ng L^{-1}, respectively) (White et al., 2009).

Regressions between event Hg concentration and event precipitation depth at each site were used to examine the degree of concentration dilution during precipitation events (Fig. 3) (Landis et al., 2002; White et al., 2009). Precipitation depth explained 5% and 6% of the variability in Hg concentration at the Nilwood and Peoria sites, respectively. For Chicago and Carbondale, precipitation depth explained 12% of the variability in Hg concentration (Fig. 3). These values appear slightly lower than those reported for the LMMBS sites (8 to 20%; Landis et al., 2002). In Steubenville, precipitation depth accounted for only 7% of the variability in event-based Hg concentration measurements (White et al., 2009). The similarly weak relationships observed at the IL sites demonstrated that the dilution of Hg concentrations during high volume precipitation events, or the enhancement of concentrations during smaller events, could not account for the large observed ranges in Hg concentrations (White et al., 2009). These large concentration ranges must be more fully explained by other factors, such as atmospheric transport, chemical cycling, and/or inputs from nearby emission sources.

All four sites accumulated more than 10 μg m^{-2} of Hg wet deposition per year, and the range in annual deposition amounts across the four sites was 11.8 μg m^{-2} to 17.6 μg m^{-2} (Fig. 4). These values are generally greater than annual Hg wet deposition measurements (collected using the same event-based sampling method) at remote locations in northern Vermont (8.7 μg m^{-2} to 13.3 μg m^{-2},1995 to 2006; Gratz et al., 2009), and in northern Michigan (<12 μg m^{-2}, 1994 to 2003; Keeler and Dvonch, 2005). However, they are comparable to annual Hg wet deposition amounts from the source-impacted Steubenville site (13.5 μg m^{-2} and 19.7 μg m^{-2} in 2003 and 2004, respectively; Keeler et al., 2006).

Carbondale received the highest amount of total Hg wet deposition annually while the lowest annual Hg wet deposition occurred in Chicago (Fig. 4). Considering the uncertainties in total annual deposition (calculated using 8.1% uncertainty in total Hg concentration measurements (Landis and Keeler, 1997), and 5% uncertainty in the measured precipitation amount (Keeler et al., 2006)), the annual deposition amounts recorded at the sites were not detectably different from one another during each year, with two exceptions. In September 2007 to August 2008, Chicago received less Hg deposition than Nilwood or Carbondale, and in September 2008 August 2009 the annual deposition at Nilwood was less than Carbondale. The lack of a clear spatial gradient in annual Hg deposition, such as that reported for sites in Michigan and Ohio (White et al., 2009), can be partially explained by the distribution of major Hg sources in Illinois and the surrounding states and their proximity to the measurement sites (Fig. 1).

We compared the event-based Hg wet deposition measurements during CY2008 at the four sites in this study with weekly Hg deposition amounts reported by the Mercury Deposition Network (MDN) for 2008 (http://nadp.sws.uiuc.edu/mdn/) (Table 2). The MDN Indiana Dunes site on Lake Michigan was closest to our Chicago site. Both the VWM Hg concentration and the Hg deposition were lower at Indiana Dunes (8.9 ng L^{-1} and 12.1 μg m^{-2}, respectively) than in Chicago (11.1 ng L^{-1} and 13.9 μg m^{-2}, respectively) in 2008, even though the total precipitation amount was greater at Indiana Dunes (136 cm) compared to Chicago (125 cm). The Bondville, IL MDN site reported similar statistics for 2008 as those seen at Nilwood for the same period. Nilwood and Bondville received the same precipitation amount in 2008 (131 cm) but Nilwood observed 1.0 μg m^{-2} more total Hg deposition; however, single precipitation events can deposit more than 1.0 μg m^{-2} in a single day with the concurrence of available source emissions and meteorological conditions that produce large volume samples. The Southeastern Missouri MDN site was the closest to Carbondale and observed 29 cm more precipitation in 2008 than Carbondale, which appears largely responsible for the 6.7 μg m^{-2} greater deposition reported at the MDN site.

3.2. PMF results and interpretation

The PMF analyses for Chicago and Peoria (Tables 3 and 4) resulted in four factors, which we identified, based upon elevated loadings of the elements listed in parentheses, as: cement production (Mg, K, Ca, Mn), iron–steel manufacturing (Mg, Al, Cr, Mn, Fe, Sr, La, Ce), mixed non-ferrous metal smelting and waste incineration (Cr, Ni, Zn, As, Cd, Pb), and coal combustion (S, As, Se). When these PMF solutions were expanded to include five factors, the fifth factor contained elevated loadings of P and K. For both sites, the five-factor solution appeared less stable, based upon the mapping of bootstrapping factors to base model factors, and therefore the four-factor solutions more successfully reproduced the measurements.

We obtained a five-factor solution for Nilwood (Table 5), which we identified as cement production (Mg, Ca, Mn), phosphorus (P, K), iron–steel manufacturing (Mg, Al, Cr, Mn, Fe, La, Ce,), non-ferrous metal smelting/waste incineration (Cr, As, Cd, Pb), and coal combustion (S, Se). We obtained a four-factor solution for Carbondale (Table 6), which we identified as phosphorus (P, K), iron–steel manufacturing (Mg, Al, Cr, Mn, Fe, La, Ce), non-ferrous metal smelting/waste incineration (Zn, As, Cd, Pb), and coal combustion (S,V, As, Se).

Table 7 displays the percentages of the total measured Hg wet deposition input to PMF that was accounted for by the model, regression statistics for predicted-versus-measured Hg wet deposition, and the Hg wet deposition (μg m^{-2}) attributed to each PMF factor. For each site, the sums of the calculated factor contributions suggested that PMF was highly successful in reproducing the observed Hg wet deposition amounts that were input to the model (84% to 89% by site). The regressions of predicted-versus-observed values yielded slopes ranging from 0.67 to 0.87, with r^2 values of 0.67 to 0.83. The fraction of measured Hg wet deposition unaccounted for by the model (11% to 16% by site) is hypothesized to be associated with sources unidentified in the PMF factors, which may include contributions from the global atmospheric background. Based upon our knowledge of point sources in the region (Fig. 1), other sources that might have contributed to Hg wet deposition, but were not distinctly identified in the PMF factor profiles, include oil combustion (identified by V and Ni loadings (Pacyna and Pacyna, 2001)) and oil refining (identified by La loadings (Morishita et al., 2006)). It is evident from the PMF profiles that each site was uniquely influenced by emission source contributions, resulting in some variability in the trace element deposition and factor loadings at

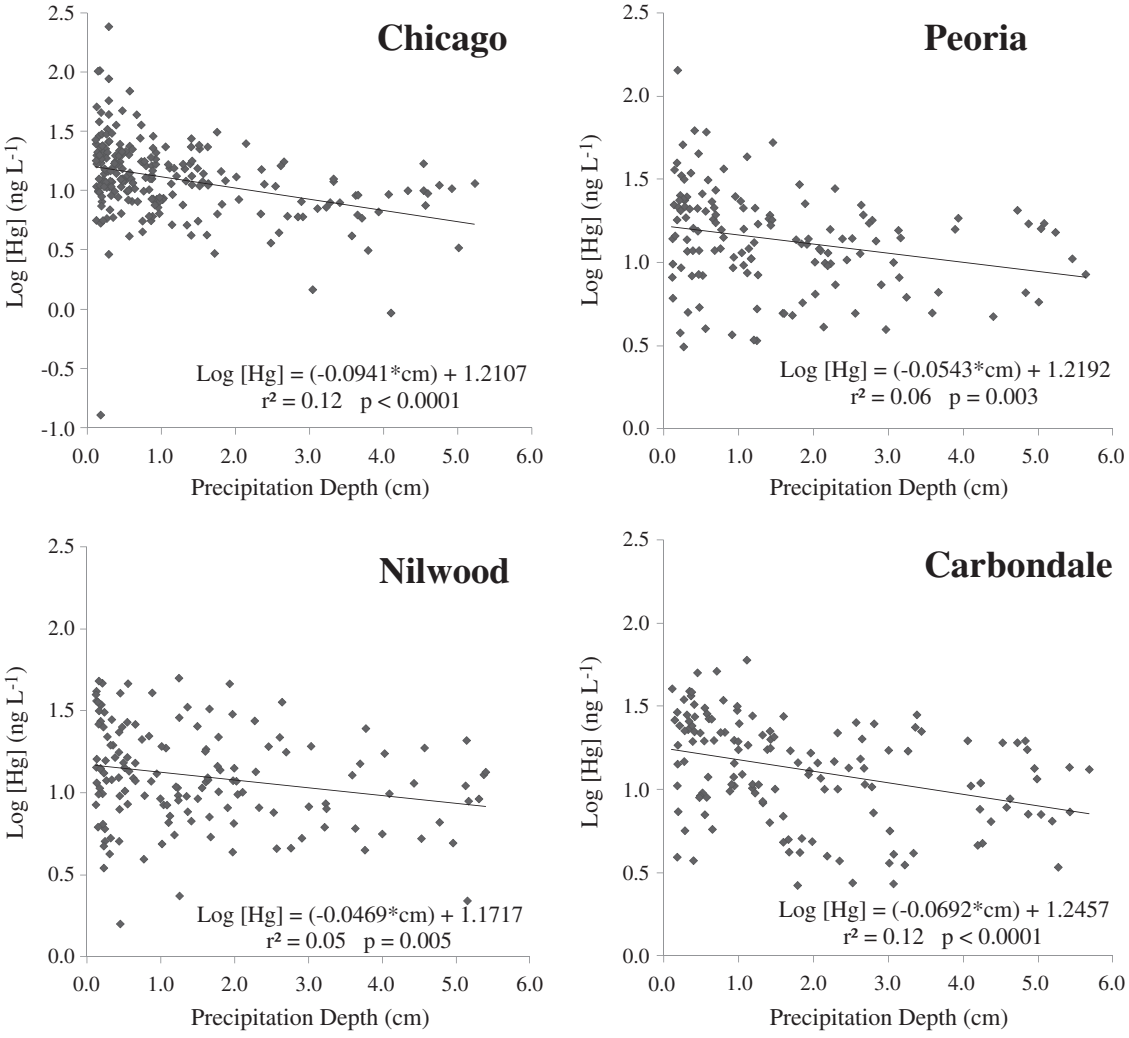

Fig. 3. Regression of event Hg concentration versus event precipitation depth at the Chicago, Peoria, Nilwood, and Carbondale sites from August 4, 2007 to August 31, 2009.

each site. This was to be expected given the geographical distribution of the four sites; yet, the covariance between the trace elements allowed for identifying several similar source signatures.

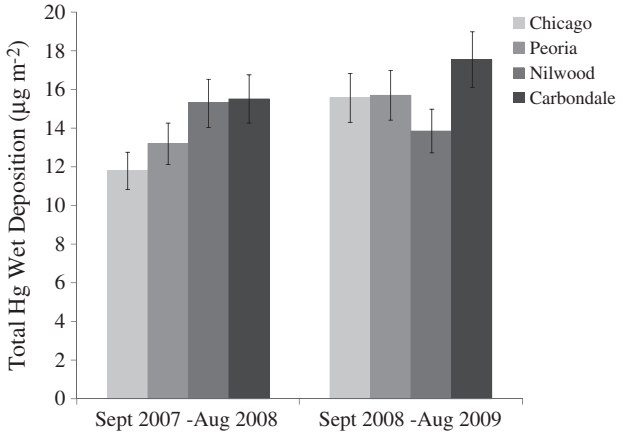

Fig. 4. Annual total Hg wet deposition at the Illinois study sites. Due to the time frame of the 2-year study, annual periods were defined as September 1 to August 31. Uncertainties in the total annual deposition amounts were calculated using 8.1% uncertainty in the total Hg concentration measurements (Landis and Keeler, 1997), and 5% uncertainty in the measured precipitation amount (Keeler et al., 2006).

The identification of the cement signature is consistent with the location of facilities in northern Illinois, eastern Kansas, and Oklahoma (Fig. 1). Mercury wet deposition was significantly attributed to this factor only for Peoria (29%). This may be related to cement and building manufacturers located between Peoria and Chicago and northwest of Peoria along the Iowa border (Fig. 1). Given that those sources are also upwind of Chicago, it was somewhat surprising that cement manufacturing did not significantly influence Hg wet deposition in Chicago. This could be due to the relatively low stack heights for cement facilities, which may not facilitate long-distance transport

Table 2
Summary of event-based Hg wet deposition measurements at the four Illinois sites in this study and nearby Mercury Deposition Network (MDN) weekly sampling sites in CY 2008.

Site	Network	Precipitation depth (cm)	VWM Hg concentration (ng L^{-1})	Total Hg deposition (µg m^{-2})
Chicago, IL	This study	125	11.1	13.9
Peoria, IL	This study	102	14.5	14.8
Nilwood, IL	This study	131	12.6	16.5
Carbondale, IL	This study	118	12.9	15.2
Indiana Dunes, IN	MDN	136	8.9	12.1
Bondville, IL	MDN	131	11.9	15.5
Southeastern, MO	MDN	147	12.1	21.9

Table 3
PMF factor profiles (μg m^{-2}) for Chicago precipitation samples. Elemental contributions not significant at the 95% confidence interval, based upon the bootstrapping distributions, are displayed in italic. The last row displays the percentage of the total measured Hg wet deposition input to PMF that was attributed to each factor.

	Cement	Iron–steel	Smelter/incinerator	Coal combustion
Mg	707	*178*	*0*	134
Al	36.3	435	105	*14.4*
P	*43.8*	23.4	*0.19*	*10.3*
S	*1195*	*119*	1778	3249
K	107	227	46.5	109
Ca	3024	1162	364	415
V	*0.19*	1.06	0.51	0.55
Cr	0.32	0.46	0.46	*0.02*
Mn	21.0	15.4	*2.36*	*0.88*
Fe	78.7	358	67.6	*8.01*
Ni	0.41	0.43	0.83	0.65
Zn	9.76	*0*	66.1	*6.99*
As	0.13	0.17	0.30	0.27
Se	*0.11*	0.09	0.39	0.32
Sr	2.25	6.18	3.88	0.86
Cd	*0*	0.04	0.26	0.10
Ba	1.99	9.52	*9.25*	*0*
La	*0.01*	0.53	0.14	0.03
Ce	0.05	0.84	*0.13*	0.05
Hg	*0.01*	*0*	*0.01*	0.09
Pb	*0.07*	1.91	6.38	*0.55*
% Hg	11%	0%	9%	65%

Table 5
PMF factor profiles (μg m^{-2}) for Nilwood precipitation samples. Elemental contributions not significant at the 95% confidence interval, based upon the bootstrapping distributions, are displayed in italic. The last row displays the percentage of the total measured Hg wet deposition input to PMF that was attributed to each factor.

	Cement	Phosphorus	Iron–steel	Smelter/incinerator	Coal combustion
Mg	346	107	197	43.7	115
Al	*199*	*0.69*	743	*59.8*	*126*
P	*50.2*	167	*14.4*	*1.12*	*0*
S	*655*	377	*0*	2496	3503
K	*193*	399	270	93.5	200
Ca	3291	294	*51.4*	*98.6*	*927*
V	*0*	*0.11*	1.73	0.78	0.63
Cr	*0.23*	*0.03*	0.51	0.46	*0.48*
Mn	19.9	1.94	13.9	*0*	*4.23*
Fe	183	6.7	457	*22.7*	94.2
Ni	0.41	0.17	0.46	0.69	1.16
Zn	*5.25*	4.99	*2.12*	*27.5*	*22.2*
As	0.24	0.05	0.13	0.57	*0.31*
Se	*0.16*	*0.04*	*0*	0.43	0.46
Sr	5.94	0.40	5.23	1.55	2.17
Cd	*0*	0.06	*0.02*	0.35	*0.22*
Ba	8.40	*0*	6.05	*5.21*	*0*
La	0.22	0.02	0.71	0.09	0.14
Ce	0.45	*0*	1.27	*0.04*	0.23
Hg	*0*	*0.01*	*0.04*	*0*	0.13
Pb	*0.19*	*0.06*	*1.02*	4.37	*1.98*
% Hg	0%	3%	19%	0%	65%

of emissions, or may suggest seasonal differences in transport patterns between the two sites that did not facilitate the transport of cement emissions to the Chicago site. Cement manufacturing also did not strongly contribute to Hg wet deposition in Nilwood or Carbondale, sites which are located at a greater distance from the region's cement manufacturers (Fig. 1), supporting the idea that Hg emissions from cement manufacturing may have a more measurable impact on local receptors.

The iron–steel factor was identified based on loadings of Fe, Al, Mg, Mn and Cr commonly found in airborne particles from iron–steel facilities (Machemer, 2004). Despite the proximity of iron–steel mills to the monitoring sites, particularly Chicago and Peoria, as well as the fraction of total Hg emissions from this source category in Illinois (U.S. EPA NEI, 2008), this factor did not contribute significantly to Hg wet deposition at the sites. It is possible that the form of Hg emitted from iron–steel mills is predominantly RGM, which, together with the large fugitive dust concentrations typical of these plants (Sweet et al., 1993), may lead to efficient local removal of emitted Hg. At all four sites, the highest loadings of crustal elements (La, Ce) on the iron–steel factor may also represent a contribution from windblown dust (Gratz and Keeler, 2011). In Chicago, V and Ni loadings on this factor may also suggest a contribution from oil combustion, while at Nilwood and Carbondale, this factor may suggest a contribution from oil refining (La) and/or combustion (V) emissions, given the locations of oil refineries and oil-fired utility boilers south of Illinois (Fig. 1) (Olmez et al., 1988; Kitto et al., 1992). The V:Ni ratios on this factor in Chicago (2.5), Nilwood (3.8), and Carbondale (2.1) are similar to the V:Ni ratio in $PM_{2.5}$ at sites impacted by fuel oil combustion (V:Ni = 2.6; Laden et al., 2000) and in average emission factors for oil combustion

Table 4
PMF factor profiles (μg m^{-2}) for Peoria precipitation samples. Elemental contributions not significant at the 95% confidence interval, based upon the bootstrapping distributions, are displayed in italic. The last row displays the percentage of the total measured Hg wet deposition input to PMF that was attributed to each factor.

	Cement	Iron–steel	Smelter/incinerator	Coal combustion
Mg	376	449	80.8	62.7
Al	*80.8*	741	40.1	174
P	54.0	*37.5*	*13.6*	*12.4*
S	*80.6*	*0*	*2299*	5757
K	117	345	72.9	215
Ca	2050	2612	412	*0.86*
V	*0*	*1.58*	*0.31*	1.50
Cr	0.54	0.53	0.22	0.25
Mn	14.8	27.7	*0.87*	*0*
Fe	157	492	19.4	83.2
Ni	0.76	0.65	0.32	0.91
Zn	10.9	*0.17*	28.4	18.3
As	0.09	0.19	0.34	0.40
Se	*0*	*0*	0.46	0.48
Sr	1.87	9.97	1.78	2.83
Cd	*0.01*	*0*	0.20	0.16
Ba	*2.59*	14.7	4.01	*0.19*
La	0.08	0.71	0.05	0.18
Ce	0.22	1.36	*0*	0.25
Hg	0.06	*0.01*	*0*	0.11
Pb	*0.52*	*0.67*	4.25	*1.88*
% Hg	29%	4%	0%	50%

Table 6
PMF factor profiles (μg m^{-2}) for Carbondale precipitation samples. Elemental contributions not significant at the 95% confidence interval, based upon the bootstrapping distributions, are displayed in italic. The last row displays the percentage of the total measured Hg wet deposition input to PMF that was attributed to each factor.

	Phosphorus	Iron–steel	Smelter/incinerator	Coal combustion
Mg	173	490	186	146
Al	*64.0*	848	71.1	191
P	249	*0.24*	*60.3*	*5.1*
S	269	*0*	3751	3837
K	561	379	211	217
Ca	403	3057	2150	*0*
V	*0.46*	1.56	*0.09*	2.11
Cr	0.09	0.67	0.48	0.39
Mn	11.3	37.3	*7.24*	*4.97*
Fe	*65.6*	625	68.9	150
Ni	0.28	0.76	1.04	1.72
Zn	7.78	*1.66*	44.7	21.7
As	*0.02*	0.20	0.55	0.55
Se	*0.01*	*0.09*	0.60	0.87
Sr	1.21	11.6	4.62	2.06
Cd	0.03	*0.02*	0.21	*0.13*
Ba	2.30	16.4	7.16	5.38
La	0.11	0.91	0.06	0.23
Ce	0.21	1.79	*0.07*	*0.35*
Hg	*0.03*	*0*	*0*	0.18
Pb	*0*	1.83	3.91	3.15
% Hg	14%	1%	0%	74%

Table 7
PMF results for Hg wet deposition at the Chicago (UOC), Peoria (PEO), Nilwood (NLW), and Carbondale (CBD) monitoring sites, including the percentage of the measured Hg wet deposition input to PMF that was accounted for by the model; regression statistics for predicted-versus-measured Hg wet deposition; and the amount of Hg wet deposition (μg m^{-2}) input to PMF that was attributed to each modeled factor.

Site	% of measured Hg wet deposition explained by PMF factors	PMF predicted-versus-measured regression for Hg wet deposition			Hg wet deposition (μg m^{-2}) attributed to each PMF factor					
		Slope	Intercept	r^2	Cement	Phosphorus	Iron–steel	Smelter/incinerator	Coal combustion	Unexplained
UOC	84%	0.67	0.02	0.67	3.3	–	0.0	2.7	19.9	4.9
PEO	84%	0.71	0.03	0.82	8.3	–	1.2	0.0	14.1	4.6
NLW	87%	0.73	0.03	0.83	0.0	1.0	5.8	0.0	19.4	3.8
CBD	89%	0.87	0.004	0.83	–	4.7	0.3	0.0	24.4	3.6

(V:Ni = 3; Pacyna and Pacyna, 2001), perhaps supporting the idea of this as a mixed factor.

It was difficult to separate the source signatures for non-ferrous metal smelting and waste incineration, due to common elements in their emissions (e.g. Pb, Zn) (Polissar et al., 2001; Gratz and Keeler, 2011). Globally, non-ferrous metal production is reportedly the largest source of As, Cd, and Zn and a major source of Pb and Se (Pacyna and Pacyna, 2001). The metal smelting signature was previously identified in particulate matter measurements downwind of East St. Louis (Sweet et al., 1993). The waste incinerator signature has also been identified in Chicago soils enriched with Pb, S, and Zn (Cannon and Horton, 2009) and is consistent with the location of municipal and hazardous waste incinerators along the Mississippi and Ohio River Valleys (Fig. 1). The observation that waste incineration did not significantly contribute to Hg wet deposition can be explained by the more than 90% reduction in municipal and medical waste incinerator Hg emissions that occurred in the U.S. in the late 1990s (U.S. EPA, 1997; Cohen et al., 2007). However, while this may not be a major source of Hg, the PMF profiles do suggest that metal smelting and/or waste incineration contributed significantly to the presence of other potentially toxic trace elements (e.g. Cd, As, Cr, and Pb) in precipitation at the measurement sites (Tables 2 through 5).

Recent source apportionment studies have identified a phosphorus source in precipitation with elevated loadings of P and K, and suggested that it was a minor source of Hg in Steubenville, OH and Underhill, VT (Keeler et al., 2006; Gratz and Keeler, 2011). For Underhill, the phosphorus source was hypothesized to represent biomass burning or fertilizer application (Gratz and Keeler, 2011). It is interesting that in Chicago and Peoria the phosphorus source could not be identified within acceptable limits of the PMF model uncertainty (based upon the bootstrap uncertainty analyses), whereas for Nilwood and Carbondale, the phosphorus source was clearly a stand-alone factor. QTBA of P deposition at Nilwood pointed to a major source region southeast of the sites near the Kentucky–Tennessee border, with additional contributions from the southwest. These areas are consistent with the locations of phosphate fertilizer facilities in central Tennessee and eastern Missouri, suggesting that fertilizer production may also be a source of atmospheric P to southern Illinois.

At all four sites, the PMF results suggest that the highest contribution to Hg deposition (50% to 74% by site) was from a factor containing high loadings of S and Se, which are common tracer elements for coal combustion emissions (Pacyna and Pacyna, 2001; Keeler et al., 2006; Gratz and Keeler, 2011). Although S and Se were also somewhat elevated on the smelter/incinerator factor for most sites, the coal combustion factor typically did not display similarly high loadings of signature smelter/incinerator elements (Zn, Pb, Cd, Cr). The coal combustion factor also contained elevated loadings of V, typically indicative of oil combustion; however, the V:Ni ratio on this factor was <2 at all four sites, suggesting that emissions from oil combustion were not strongly reflected in this factor (Laden et al., 2000; Pacyna and Pacyna, 2001). Furthermore, if the elevated loadings of V did represent a contribution from oil combustion on this factor, we expect that it would not strongly contribute to Hg wet deposition given that much lower Hg concentrations are found in residual oil than in coal burned in utility boilers (Olmez et al., 1988; Pacyna and Pacyna, 2001; Gratz and Keeler, 2011). The attribution of 50 to 74% of Hg wet deposition to coal combustion is consistent with total Hg emissions from coal combustion reported in the national (U.S. EPA, 2008) and global Hg emission inventories (Pacyna and Pacyna, 2001), especially given the demonstrated local-scale impacts of coal combustion emissions (White et al., 2009) and the known locations of facilities near the measurement sites (Fig. 1).

3.3. Spatial variability in Hg source contributions

The calculated QTBA spatial contribution fields for Hg wet deposition at the four sites are shown in Fig. 5. In Chicago, the highest contributions to event Hg wet deposition (0.22 to 0.28 μg m^{-2}) coincide with several large local and regional Hg emission source regions. There was a large predicted contribution from emission sources in southwestern Chicago/Gary, a region where coal-fired EGUs contribute >75% of the total Hg point source emissions (Gratz et al., 2013), as well as the area encompassing an industrial/commercial boiler in central Illinois (0.09 tons per year (tpy) of Hg; U.S. EPA, 2008). This contour extended through Springfield, IL and into the St. Louis urban area, where in each location the two largest point sources are coal-fired EGUs whose combined total Hg emissions are 0.07 tpy (Springfield) and 0.38 tpy (St. Louis). Another large predicted contribution to Hg wet deposition came from an area in northern Missouri surrounding a coal-fired EGU (0.12 tpy of total Hg; U.S. EPA, 2008), and extending toward Kansas City, MO where the largest emission point sources (>0.01 tpy of Hg) include several coal-fired EGUs and industrial/commercial boilers (U.S. EPA, 2008). There was also a large predicted contribution to event Hg wet deposition from northern Michigan (0.24 to 0.26 μg m^{-2}), where two large Portland cement manufacturers collectively emit 0.27 tpy of Hg, suggesting that perhaps cement manufacturing did contribute more to Hg wet deposition in Chicago than calculated by PMF. Finally, the large estimated contribution (0.22 to 0.26 μg m^{-2}) from southeastern Indiana and the Ohio River Valley was consistent with QTBA analysis of S and Se wet deposition for Chicago, which demonstrated that the highest contributions to these elements were associated with easterly transport from Chicago/Gary, southeast Michigan, and eastern Ohio River Valley, where Hg emissions from coal-fired EGUs are known to be substantial (U.S. EPA, 2005, 2008; Gratz et al., 2013; Keeler et al., 2006).

In Peoria, there was a clear influence on event Hg wet deposition (0.24 to 0.28 μg m^{-2}) from sources in and around the Chicago/Gary urban area. Within the contour that extends toward the Milwaukee metropolitan area, the two largest point sources are coal-fired EGUs, emitting a combined 0.28 tpy of Hg (U.S. EPA, 2008). QTBA also suggested a comparable contribution to Hg wet deposition from sources in Iowa and along the Mississippi River, where there are several cement manufacturers, and the largest Hg emission point source is a coal-fired EGU (0.17 tpy; U.S. EPA, 2008). Here, the QTBA contours for Peoria and Chicago are more consistent with the finding from PMF, that Hg wet deposition at Peoria was significantly influenced by cement manufacturers north and west of the site, whereas in Chicago westerly

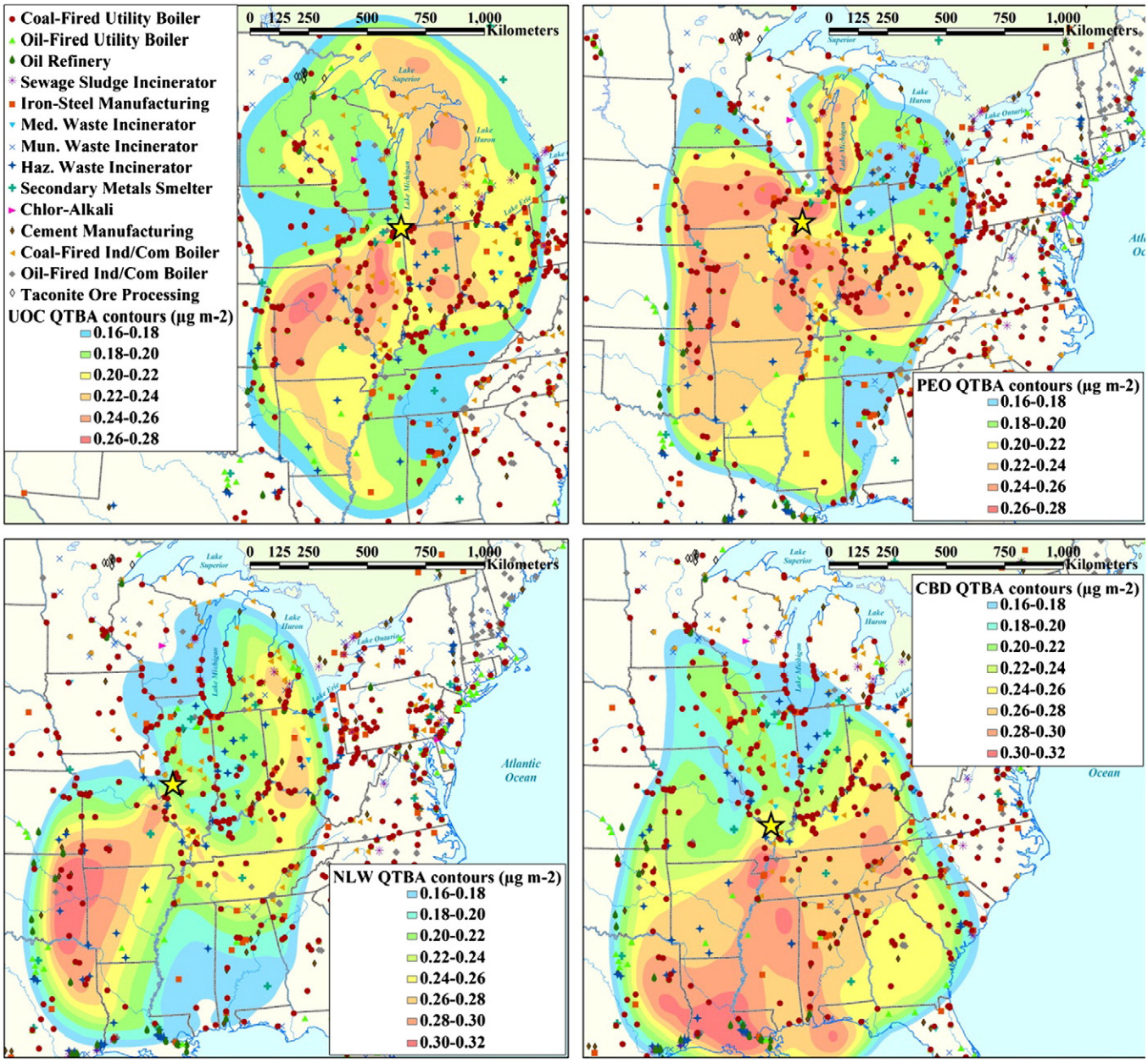

Fig. 5. Calculated spatial contribution field for measured event-based Hg wet deposition from August 4, 2007 to August 31, 2009 at the Chicago (UOC), Peoria (PEO), Nilwood (NLW), and Carbondale (CBD), Illinois monitoring sites. Contours are in units of µg m^{-2}.

transport from the locations of those facilities had a lesser influence on Hg wet deposition. It is also evident that the coal-fired EGUs in and around nearby Springfield, IL substantially influenced the Peoria site (0.26 − 0.28 µg m^{-2}). Southwesterly flow also brought a contribution (0.24 to 0.26 µg m^{-2}) from the St. Louis area, while southeasterly flow produced a comparable contribution from emission sources in southern Indiana along the Ohio River.

The spatial contribution field at Nilwood was noticeably different from that calculated for Chicago and Peoria. Here, the largest contribution to event Hg wet deposition (0.28 to 0.32 µg m^{-2}) was associated with sources southwest of Illinois, including those in the St. Louis metropolitan area, eastern Oklahoma, and northeastern Texas, where the largest Hg emissions (>0.1 tpy) are from coal-fired EGUs (U.S. EPA, 2008). Other Hg emission point sources in this region include oil refineries, hazardous waste incinerators, iron–steel mills, cement manufacturers, and non-ferrous metal smelters; however, total Hg emissions from these sources are less (<0.1 tpy) than those from coal combustion in the region (U.S. EPA, 2008). Additional contributions to event Hg wet deposition in Nilwood (0.26 to 0.28 µg m^{-2}) were associated with flow through the Ohio River Valley and southeast Michigan.

The contribution from southern sources was even more evident in Carbondale. The location of this site, in the southernmost portion of Illinois, made it more susceptible to Hg deposition from out-of-state sources; however, sources in the southernmost regions of Illinois, including local sources in the Carbondale area, also contributed to Hg deposition. In the source region just south of Carbondale, where the estimated contribution to Hg wet deposition was 0.30 to 0.32 µg m^{-2}, the largest emission sources are a coal-fired EGU (0.12 tpy) and a steel mill (0.15 tpy), while two other nearby coal-fired EGUs collectively emit 0.12 tpy (U.S. EPA, 2008). Further south in the Louisiana gulf coast region, Hg point sources emitting >0.1 tpy include coal-fired EGUs, oil refineries, chlori-alkali plants, and iron–steel mills (U.S. EPA, 2008).

Despite the large total Hg emissions from these various facilities, the PMF results suggest that the emissions from coal combustion were the largest source of Hg wet deposition in Carbondale.

4. Conclusion

Two years of event-based precipitation measurements at four sites in Illinois have provided a spatial and temporal understanding of Hg wet deposition to source-impacted areas across the state. The results of multivariate and hybrid receptor modeling analyses applied in this study suggest that local and regional coal combustion was the dominant source of Hg in precipitation. The presented findings also demonstrate that, when used together, PMF and QTBA are extremely powerful tools for identifying source signatures and locations in environmental datasets. Following the conclusion of this study in 2009, the U.S. EPA has since issued the Mercury and Air Toxics Standards (MATS), which require the use of available control technologies for regulating emissions of Hg and other toxic elements from coal- and oil-fired power plants. In the future, as this new regulation is evaluated for its efficacy, source–receptor studies like the one presented here will be a useful benchmark for quantifying the progress made in the effort to reduce the levels of Hg deposition to the environment.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.11.011.

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