Assessing the Emission Sources of Atmospheric Mercury in Wet Deposition Across Illinois, USA

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Abstract. From August 2007 to August 2009, we collected event-based precipitation samples for mercury (Hg) and trace element analysis at four sites in Illinois, USA. The objectives of these measurements were to quantify the levels of Hg wet deposition across the state, and to assess the contributions to Hg in precipitation from major local and regional emission sources. The measurement sites were located in Chicago, Peoria, Nilwood, and Carbondale, IL. We were not able to identify a clear spatial gradient in Hg wet deposition among the sites. At all four locations we frequently observed Hg concentrations in precipitation > 25 ng/L, while each site received > 10 µg/m^2 of Hg wet deposition annually, suggesting a substantial impact from local and regional anthropogenic emission sources. We applied the multivariate statistical receptor model Positive Matrix Factorization (PMF) to the measured Hg and trace element wet deposition amounts at the four sites. The results suggested that 60-83% of total Hg deposition at each site could be attributed to coal combustion emissions. Although we identified other source signatures in the precipitation composition, including cement manufacturing, metal smelting / waste incineration, and iron-steel production, these sources contributed substantially less to the measured amounts of Hg wet deposition. We also applied the hybrid receptor model Quantitative Transport Bias Analysis (QTBA) to the Hg wet deposition data from each site to identify the major source regions associated with the measured values. Results suggested that sources in the Chicago/Gary, St. Louis, and Ohio River Valley urban/industrial areas had a substantial impact on Hg wet deposition, strongly supporting the conclusion that local and regional coal combustion was the largest source of Hg wet deposition in Illinois.

Key words: mercury, trace elements, precipitation, Illinois, source apportionment, receptor modeling

Introduction

Mercury (Hg) is a hazardous air pollutant and bioaccumulative neurotoxin released into the atmosphere through natural and anthropogenic activities. Atmospheric transport and deposition are widely recognized as the primary mechanisms by which Hg enters terrestrial and aquatic ecosystems (U.S. EPA, 1997; Landis and Keeler, 2002; Landis et al., 2002; Hammerschmidt and Fitzgerald, 2006). Therefore, it is essential to understand the contributions from various atmospheric Hg sources so that policymakers can effectively regulate Hg emissions and their effect on the environment.

To assess the impact of local and regional emission sources in the U.S. Midwest, we performed a study of Hg wet deposition in Illinois where elevated levels of Hg in many of the state's terrestrial and aquatic ecosystems have prompted concerns about Hg contamination from industrial emissions (U.S. EPA, 1997; Dreher and Follmer, 2004; Cannon and Horton, 2009). From August 2007 to August 2009, we established a statewide network

consisting of four precipitation monitoring sites, which offered a quantitative spatial assessment of Hg deposition in Illinois. This site network provided the necessary information to identify major local and regional atmospheric Hg sources and quantify their relative impacts on wet deposition in the state.

Materials and Methods

The Illinois network sites were located in Chicago, Peoria, Nilwood, and Carbondale, IL (Figure 1). We collected event-based precipitation samples from August 4, 2007 until August 31, 2009 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). All field and analytical supplies used in the collection and analysis of Hg and trace element samples were prepared using an eleven-day acid-cleaning procedure (Landis and Keeler, 1997). We quantified the total Hg concentration using a dual amalgamation technique followed by cold-vapor atomic fluorescence spectrometry (CVAFS), as described by Landis and Keeler (1997). We analyzed the trace element samples using a Finnigan MAT Element 2 magnetic sector field high-resolution inductively coupled plasma mass spectrometer (ICP-MS).
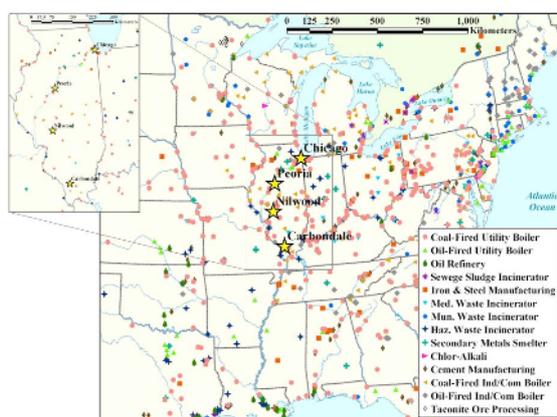
Figure 1. Location of the Illinois monitoring sites with respect to major regional mercury point sources emitting ≥ 0.1 kg Hg/yr (US EPA 2005 NEI; Environment Canada 2007 NPRI).

We applied the EPA PMF 3.0 model to the matrix of event-based Hg and trace element wet deposition measurements from each site. Positive Matrix Factorization (PMF) is a multivariate statistical receptor model that uses weighted least-squares analysis to decouple measured sample compositions into an estimated source profile and the source contributions to each sample (Paatero, 1997). We approached the PMF analysis from a network perspective, by examining the results across all sites and consistently applying PMF to the same set of 20 trace elements, plus Hg, for each site. We evaluated PMF solutions with four to five factors, and we identified the sources based on the combination of

elements within each factor and the elemental ratios for known source tracers.

We modeled air mass transport to the four sites for each precipitation event using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model, Version 4.8 (Draxler and Hess, 1997). We then applied the hybrid receptor model Quantitative Transport Bias Analysis (QTBA) to the measurement dataset. QTBA combines air mass back-trajectories with measured amounts of analytes at the receptor site to determine the most probable source regions of those species (Keeler and Samson, 1989; Gratz and Keeler, 2011). Together, PMF and QTBA allowed us to provide critical information about the impact of major sources on Hg wet deposition in the state of Illinois.

Results and Discussion

Event-Based Precipitation Measurements

The event Hg concentrations and annual deposition amounts suggested that all four sites were highly-impacted by regional Hg sources. Elevated Hg concentrations (defined here as [Hg] > 25 ng/L) were measured at all sites. Most often these events occurred during the warmer summer months; however, at all four sites we occasionally recorded concentrations > 25 ng/L during colder winter months, demonstrating the impact of local and regional source emissions on these locations throughout the year.
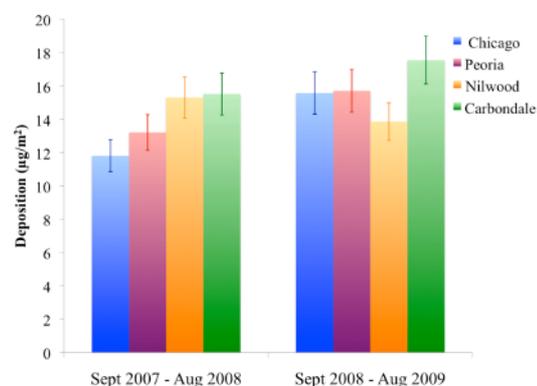

Figure 2. Annual total Hg wet deposition at Illinois study sites. Due to the time frame of the 2-year study, annual periods were defined as September 1 – August 31. Uncertainties in the total annual deposition amounts were calculated using 8.1% uncertainty in the total Hg concentration measurements (Landis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

All four sites accumulated more than 10 μg/m^2 of Hg wet deposition per year (Figure 2). Additionally, the total annual Hg wet deposition was not significantly different between the sites, with two exceptions: in the first year, Chicago received significantly less Hg deposition than Nilwood or Carbondale, and in the second year, the annual deposition at Nilwood was significantly less than

Carbondale. The lack of a clear north-south spatial gradient in annual Hg deposition can be partially explained by the location of major Hg sources in Illinois and the surrounding states, such as those in Chicago/Gary, St. Louis, and the Ohio River Valley, and their proximity to the measurement sites.

PMF and QTBA

We identified four common source factors in the PMF results for four the Illinois sites: cement manufacturing, iron-steel manufacturing, metal smelting / waste incineration, and coal combustion. Additionally, we identified a distinct phosphorus source in Nilwood and Carbondale that we could not clearly identify in Chicago or Peoria.

At all four sites, the PMF results suggested that the highest contribution to Hg deposition was from coal combustion emissions. This was supported by the consistent apportionment of Hg deposition to a factor containing the highest loadings of sulfur (S) and selenium (Se). At each site, 60-83% of Hg wet deposition was attributed to this factor. The finding that coal combustion was the largest contributer to Hg wet deposition at all four Illinois sites was consistent with previous source apportionment studies of event precipitation measurements, which demonstrated the significant local and regional impacts of coal combustion Hg emissions from sources in the Midwestern U.S. (Keeler et al., 2006; Gratz and Keeler, 2011).

The QTBA spatial contribution field for Hg wet deposition at all four sites was consistent with the known locations of major Hg emission sources in the state and the region. QTBA suggested important contributions to Hg wet deposition from sources in the Chicago/Gary urban area, along the Mississippi River and in the St. Louis metropolitan area, as well as in the Ohio River Valley. This was consistent with the locations of major regional coal-fired utility boilers as well as other anthropogenic emission sources identified in the PMF model results.

Conclusions

Multivariate and hybrid receptor modeling analyses conclusively indicate that coal combustion Hg emissions were the most significant source of Hg in precipitation in Illinois. In addition, our results demonstrate that, when used together, PMF and QTBA are extremely powerful tools for identifying source signatures and locations in environmental datasets. In conjunction with other studies performed throughout the U.S., our findings provide a framework for policymakers to understand the impact of local and regional atmospheric Hg emissions, and to determine an appropriate way to regulate Hg emissions to the atmosphere.

Acknowledgements

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