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Source apportionment of wet-deposited atmospheric mercury in Tampa, Florida

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ABSTRACT

In this paper, sources of mercury deposition to the Tampa area (Florida, USA) are investigated by analysis of one year (March 2000–March 2001) of daily wet deposition data. HYSPLIT back-trajectory modeling was performed to assess potential source locations for high versus low concentration events in data stratified by precipitation level. Positive matrix factorization (PMF) was also applied to apportion the elemental compositions from each event and to identify sources. Increased total mercury deposition was observed during summer months, corresponding to increased precipitation. However, mercury concentration in deposited samples was not strongly correlated with precipitation amount. Back-trajectories show air masses passing over Florida land in the short (12 h) and medium (24 h) term prior to deposition for high mercury concentration events. PMF results indicate that eleven factors contribute to the deposited elements in the event data. Diagnosed elemental profiles suggest the sources that contribute to mercury wet deposition at the study site are coal combustion (52% of the deposited mercury mass), municipal waste incineration (23%), medical waste incineration (19%), and crustal dust (6%). Overall, results suggest that sources local to the county and in Florida likely contributed substantially to mercury deposition at the study site, but distant sources may also contribute.

1. Introduction

Mercury is a persistent environmental contaminant whose most toxic form, methyl mercury, is found at high levels in fish in water bodies throughout the world (Sheehan et al., 2014). Methyl mercury strongly bioaccumulates and biomagnifies in aquatic ecosystems, making consumption of predatory fish the leading route to toxic human exposures (Tchounwou et al., 2003). Adverse effects on piscivorous birds and mammals have also been documented (Scheuhammer et al., 2015). To mitigate these effects, attribution of mercury in the environment to its sources is needed.

Sources of mercury released to the environment are numerous, but emission to the atmosphere and subsequent surface deposition is a primary pathway to levels currently observed in water bodies (Driscoll et al., 2013). Although mercury has both natural and anthropogenic sources, historical and current human activities are responsible for much of the current atmospheric levels (Amos et al., 2013; Streets et al., 2011). However, substantial uncertainties exist in connecting specific sources of emitted mercury to measured levels of deposited mercury (Lindberg et al., 2007). Attribution of the relative contributions of nearby primary emission sources versus distant sources or remissions is particularly elusive. Large-scale modeling suggests a substantial contribution due to photochemical conversion of elemental mercury (Hg^0) emitted from distant sources (Seigneur et al., 2004; Sillman et al., 2007; Selin and Jacob, 2008), with recent work indicating primary anthropogenic emissions contribute approximately 23% overall (Song et al., 2015). Deposition measurement studies in eastern Ohio and southeastern Florida suggest that local and regional sources dominate (Dvonch et al., 1999; Keeler et al., 2006; White, 2009), while Caffrey et al. (2010) found that the scale of variations in deposition in northwest Florida is inconsistent with local emissions. Overall, previous work suggests that the relative importance of local versus long-range sources may depend on location.

Here, we investigate deposition and sources of mercury in the Tampa region in the early 2000s. Levels of mercury in fish in the Tampa Bay watershed have been found to be some of the highest in Florida (Kannan et al., 1998), with mercury consumption advisories in place for many fish species in freshwater lakes and streams in the area (Florida Department of Health, 2015).

2. Methods

To investigate sources of atmospheric mercury, we analyzed available wet-deposition data using back trajectory modeling and statistical receptor analysis. Methods are detailed here.

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2.1. Description of the deposition data

The data used for this analysis were collected as part of the Bay Region Atmospheric Chemistry Experiment (BRACE) (Atkeson et al., 2007) and were provided to us by the Florida Department of Environmental Protection (Atkeson, 2007). The data are from precipitation samples collected between March 2000 and March 2001 at a monitoring site (AirMon FL18 at 27.85 N, 82.55 W) located on the Tampa side of the Gandy Bridge that connects the south Tampa peninsula with St. Petersburg. Landis and Keeler (1997) describe the wet-only event precipitation sampling system used to collect samples, with a detailed description of their collection and chemical analysis methods provided by Keeler et al. (2006). Data provided for our work included trace element concentrations and precipitation amounts for each (24 h) day when precipitation occurred, for a total of 48 event day samples during the period of study. Trace elements measured include a few alkali and alkaline earth metals (Na, Cs, Mg, Sr, Ba), lanthanoids (La, Ce), transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Hg), poor metals and metalloids (Al, As, Pb, Sb), and non-metals (P, S).

2.2. Modeling of meteorological back trajectories

To investigate potential source influences on the Tampa special site data, we performed back trajectory modeling to determine air mass trajectories corresponding to specific mercury wet deposition event days. Prior to modeling, we compared temporal trends in precipitation depth, mercury deposition amount, and mercury concentration from the event data. Because the deposition amount was highly correlated with precipitation depth, the event day data were stratified by similar precipitation level (using natural divisions in the rain depth distribution). The groups with high precipitation (and generally higher mercury deposition) were selected for back trajectory analysis. A total of 23 event days were analyzed. Within each precipitation group, back trajectory characteristics for event days that had comparatively higher mercury concentrations in the deposited water were compared with those with lower concentrations. Locations of the trajectories and the amount of previous precipitation along the trajectory in the short-term (6 h), intermediate term (24 h), and long-term (72 h) were compared. Thus, potential source influences that led to comparatively high mercury concentrations at similar rain levels were identified.

For back trajectory modeling of each event day, we used the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 1998). The hour with the highest precipitation amount for each event day was selected to initialize the back trajectory, based on hourly precipitation from the Tampa International Airport (station GHCND:USW00012842 at 27.96 N, 82.54 W). Back trajectories were initiated at three heights, 250, 500, and 1000 m. To drive the HYSPLIT model, we primarily used EDAS model meteorological data from the National Centers for Environmental Prediction; these data have 80 km horizontal resolution, 23 vertical levels, and 3 h temporal resolution. GDAS FNL archive data were used for two events (June 25 and March 27, 2000) because the EDAS data were incomplete. FNL data have a 190 km grid resolution, 13 vertical layers, and 6 h temporal resolution.

2.3. Source apportionment modeling

To apportion the deposited mercury to sources, we applied multivariate statistical receptor analysis, using the Positive Matrix Factorization (PMF) package, Version 3.0 (Norris et al., 2008). PMF uses time series data on simultaneously measured concentrations of multiple chemical species to determine composition profiles of independent factors (whose component species vary together). In PMF, a $n \times m$ data matrix, consisting of m species measured over n sampling events, is factored to generate a $n \times p$ matrix of fractional factor contributions to each sample, and a $p \times m$ matrix of factor composition profiles, where p is the number of independent factors (Paatero and Tapper, 1994; Hopke, 2000). Model-generated factor contributions and profiles are then compared with known emission profiles in order to determine the likely source identity of each factor (Hopke, 2000; Reff et al., 2007).

Prior to running PMF, we examined statistical correlations between species pairs and we calculated crustal enrichment factors (cEF) for each element. Both methods help to elucidate and constrain the interpretation of PMF results. Calculation of cEF, the ratio of the normalized concentration of an element in a sample to that in natural crustal material (Chester and Stoner, 1973), is particularly useful for identifying elements of anthropogenic origin (Kolker et al., 2013). When cEF is large, the element is considered enriched in the atmosphere, suggesting anthropogenic contributions (Galloway et al., 1982). We used aluminum as the reference element for normalization, and used the average upper crust elemental compositions from McLennan (2001).

To perform PMF analysis, data on uncertainties in the measurement data are needed. We used an uncertainty matrix for model runs with the uncertainty specific to each sample and element. Uncertainties were calculated using the standard method (Norris et al., 2008; Polissar et al., 1998) for species with available analytical method detection limits (MDLs). The element-specific MDL and analytical measurement precision reported by Keeler et al. (2006) and its Supplemental information was used for all elements listed there. For Sb and Ba, we used the MDLs reported by Landis and Keeler (1997) and an analytical method uncertainty of 10%. For Na, Ag, and Cs, no MDL was available so we used the method of Chueinta et al. (2000) and Reff et al. (2007). For all uncertainty calculations, we used a sample collection uncertainty of 10% and precipitation depth measurement uncertainty of 5% for all elements and samples. All reported concentrations were used as is, with no replacement of values below the MDL. One measurement of Hg was missing for one sample date; it was replaced by the arithmetic mean of its measurements from the other sample dates.

The number of independent factors, p, influencing the variability in the deposited concentration profiles must also be selected. We performed initial sensitivity runs with p ranging from 5 to 15, and assessed differences between the theoretical and model generated Q-value (sum of the squared weighted residuals) (Hopke, 2000), and in the maximum values of the individual element means and standard deviations (Lee et al., 1999). Ultimately, we chose a p value of 11, as it gave a local minimum in each trend plot.

To ensure a global minimum solution was achieved by the PMF results, we used 20 random starting points with a random seed for generation of base factors, and a pre-defined seed for analysis of the selected base run. For posterior analyses of PMF results, we assessed the model fit for individual elements by examining the distributions of scaled residuals. To assess uncertainty in the solution, bootstrapping was performed on the selected base solution. We used 100 runs, with a minimum correlation coefficient of 0.6, and a block size of 2. A 95% confidence cutoff was applied to determine the significance of each contribution. We assessed rotational ambiguity in model solutions by use of the FPEAK parameter. The sensitivity of Q values, G-space plots, factor contributions, and factor profiles to FPEAK values in the range of −0.5 to 0.5 (in increments of 0.1) were examined (Paatero and Tapper, 1994; Paatero and Hopke, 2003).

3. Results and discussion

3.1. Insights from the deposition data

Mercury concentrations in the wet deposition data studied here ranged from 5.4 to 75.5 ng L^{-1}. Although the maximum observed value is high, the other values were in the range of those observed at other comparable sites. For example, Scherbatskoy et al. (1994) found values in the range of 1.5–44 ng L^{-1} in the Lake Champlain basin, while Mason et al. (2000) and Tsai and Hoenicke (2001) found values