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## Mercury Deposition to the Tampa Bay Area: Source Influences from the 2012 USF Deposition Experiment

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# Mercury deposition to the Tampa Bay area: Source influences from the 2012 USF deposition experiment

Extended Abstract #497

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## INTRODUCTION

Mercury is a persistent environmental contaminant whose most toxic form, methyl mercury, strongly bioaccumulates and biomagnifies in aquatic ecosystems, making consumption of predatory fish the leading route to toxic human exposures<sup>1</sup>. Mitigation of mercury exposure requires attribution of observed levels of mercury (Hg) in the environment to emission sources. Of particular interest is identifying the relative contributions to deposition to sensitive watersheds of local anthropogenic sources versus distant sources. Existing uncertainties in the scientific literature on the point is detrimental to adequate control at all management levels, from international to local. Previous research specifically addressing the relative contributions is somewhat contradictory.

Here, we investigate the deposition and sources of mercury in the Tampa region utilizing mercury and trace metals measurements collected at one site in 2012. We conducted a 6-month campaign for the collection of event-based precipitation samples. We quantified total mercury, and the trace metals concentration in the deposition samples. Rain depth and mercury concentration measurements informed deposition trends for the local domain. Trace metal data were used as input for source apportionment modeling. We also performed meteorological trajectory simulations to elucidate the influences of sources on deposition events in the domain. Identification of emission sources were informed by querying the EPA's National Emissions Inventory (NEI). Sample collection and analysis methods, deposition, back-trajectory, and receptor modeling results, and potential implications for source influences are discussed below.

## METHODS

- *Event wet deposition sampling and analysis*

We conducted a 6-month campaign, covering the period July 2012 to December 2012, for the collection of wet-only deposition samples at a site located on the grounds of the University of South Florida campus (28.056N, 82.422W). We collected event-based precipitation samples using an automated precipitation sampler (MDN Mercury Deposition Sampler sourced from N-CON Systems Company, Inc.). The collector samples continuously by opening automatically during precipitation events, as determined by a sensor. Within two minutes of the end of the event, the sampler closes to minimize exposure to dry deposition. The sampling train consisted of a high density polyethylene (HDPE) funnel (average collection area 126 cm<sup>2</sup>), and a 1L HDPE

sample bottle. The stem of the funnel was molded to the cap of the sample bottle allowing for maintenance of sample integrity during sample collection. We subjected all field and analytical supplies to an eleven-day acid-cleaning procedure <sup>2</sup>. This included standard laboratory glassware, HDPE sampling trains, Teflon<sup>®</sup> bottles for trace metal samples, and borosilicate glass bottles for mercury samples. We calculated precipitation depth as the captured sample volume divided by the measured funnel area. We calculated mercury deposition amounts as the measured concentration multiplied by the calculated precipitation depth. We reserved and preserved separate aliquots for the determination of total mercury, and trace metal concentrations. Trace metal samples were preserved in 5% HNO<sub>3</sub> and stored in pre-cleaned Teflon sample bottles at 4 ± 2 °C. Samples for determination of total mercury were placed in pre-cleaned borosilicate glass bottles with Teflon<sup>®</sup>-lined caps, and preserved with 5% KBr/KBrO<sub>3</sub>. Samples were stored in a cleanroom at ± 2 °C. We assessed the integrity of sampling supplies by systematic sampling of bottle blanks and field blanks. We collected a bottle blank every three samples by filling a sample bottle with a 5% BrCl solution for 24 hr and assessing the total mercury content of the solution. At any three day interval without a sample, we captured a field blank by rinsing the sampling train with ultrapure water, and retaining this sample for analysis of total mercury concentrations. We measured total mercury concentration in deposition samples using EPA's Method 1631, Revision E <sup>3</sup>, for the determination of mercury (Hg) in filtered and unfiltered water by oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS). We used Standard Reference Material 3133 (NIST) for quality control and instrument calibration. To quantify the trace metals concentration in the deposition samples we applied EPA Method 200.8 <sup>4</sup>. Samples were analyzed using a quadrupole inductively coupled plasma mass spectrometer (ICP-MS) [Perkin Elmer Elan II DRC]. The data consisted of 23 trace metal species, collected over 30 event days.

- *Back trajectory modeling*

We investigated potential source influences on event mercury concentrations observed at the USF site by performing back trajectory modeling simulations. We applied the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT, Version 4) model developed by the National Oceanic and Atmospheric Administration (NOAA) <sup>5</sup>. We used EDAS (Eta Data Assimilation model) data (with 80 km horizontal resolution, 23 vertical levels, and 3 hr temporal resolution) for time frames that coincided with event precipitation data. Back trajectories were initiated from the hour that coincided with the hour of maximum precipitation throughout the duration of each event, and were initiated at three heights, 250m, 500m, and 1000m, in order to span the vertical space through which precipitation may have fallen. Specific deposition event time was recorded by USF Botanical gardens meteorological station, located about 300m from the sampling site (ID:KFLTAMPA78, [28.057, -82.425], Elevation:40ft). Back trajectory characteristics for event days that had comparatively higher mercury concentrations in the deposited water were compared with those having lower mercury concentrations. Specifically, short-term (6 hr), intermediate term (24 hr), and long-term (72 hr) back trajectory locations and previous precipitation amounts (along the trajectory) were compared to identify potential source influences that led to comparatively high mercury concentrations.

- *Source - receptor modeling*

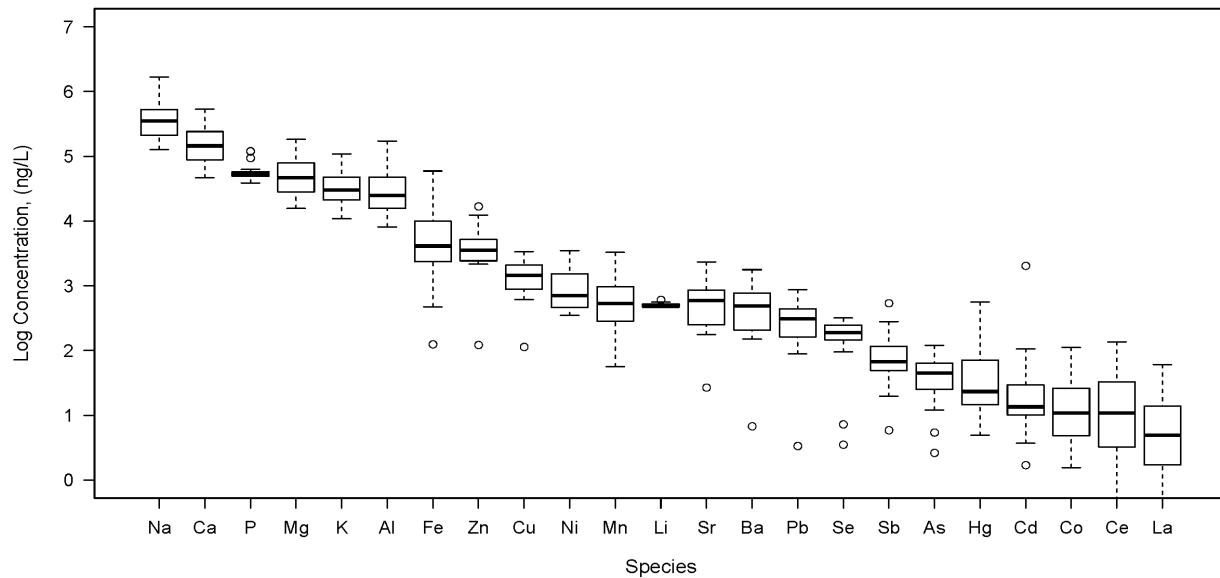
To apportion mercury deposited in Tampa to sources, we applied multivariate statistical receptor analysis on the BRACE deposition data, using the Positive Matrix Factorization (PMF) package, Version 3.0<sup>6</sup>. Trace metal data measured at the USF site was used as input to derive potential source profiles with PMF. Twenty random starting points with non-random seeds were used for our analyses, to ensure a reproducible global minimum solution was achieved. We resolved the data for 7 independent factors based on the minimum difference between the model-calculated value of Q (the sum of the squared residuals between modeled and measured species concentrations) and the number of degrees of freedom in the data set (the theoretical  $Q_{th}$ ). Generated profiles for 7 factors were also resolved to sources with the least uncertainty. To assess sources of uncertainty and characterize variability in model solutions, boot-strapping was performed on the selected base solution. Uncertainty analyses consisted of 100 runs of the bootstrapped factor, with a minimum correlation coefficient of 0.6, and a block size of 2. A 95% confidence cutoff was applied to determine significance of each contribution. Initial explorations of relative contributions of biogenic and anthropogenic emission sources on species concentrations was achieved by calculating crustal Enrichment Factors (cEF) for each species.

## RESULTS AND DISCUSSION

- *Mercury concentration and deposition*

Chemical elements measured at the USF monitoring site for each event day were Li, P, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Sb, Ba, La, Ce, Hg, Pb, Na, Mg, Al, K, Ca, Mn, and Fe. Average species concentrations ranged from a high of  $1.7 \times 10^6$  ng L<sup>-1</sup> (Na) to a low of  $1.1 \times 10^1$  ng L<sup>-1</sup> (La) (Figure 1). Mean species concentrations are comparable to measurements performed within the region during a shorter campaign with fewer elements<sup>7</sup>, and data from the Bay Regional Atmospheric Chemistry Experiment (BRACE) from 2000 - 2001<sup>8</sup>. Lower mean concentrations were observed in this study. Estimated uncertainties for each data point included the sample collection uncertainty (SC, 10%), precipitation depth measurement uncertainty (PD, 5%), the element-specific analytical method detection limits (MDL), and analytical measurement precision uncertainties (AM). Precipitation depth ranged from 0.7 - 6.6 cm. High precipitation depth events coincided with usual precipitation trends for the region, occurring over the initial two months (summer) of the campaign before tapering off for the fall/winter period. Mercury concentration ranged from 5 - 562 ng L<sup>-1</sup>, with a median concentration of 23 ng L<sup>-1</sup>. Several high mercury concentration events were observed over the period. Higher mercury concentration events occurred over the period 07/22/2012 to 08/13/2012. Event mercury concentration did not correspond with precipitation depth. Event precipitation depth explained less than 1% of the variation observed in event mercury concentration. Similarly, we observed high mercury deposition events occurring with both low and high precipitation depth events. Event deposition ranged from 0.1 - 11.4  $\mu\text{gm}^{-2}$ , with a median of 0.4  $\mu\text{gm}^{-2}$ .

**Figure 1. Summary statistics for 2012 USF deposition study.**



- *Event back trajectories*

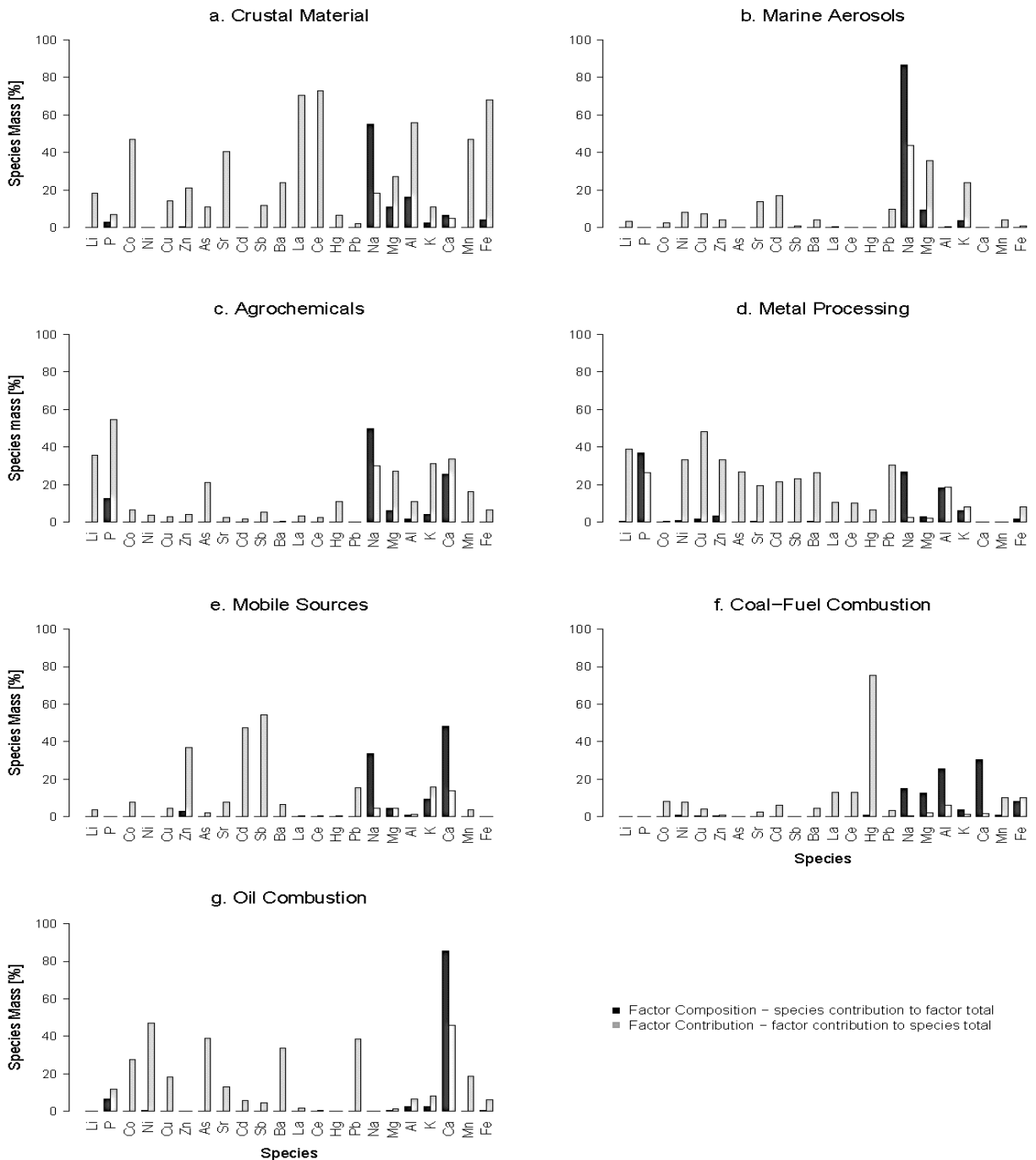
Results from back-trajectory modeling indicate high mercury concentration events had trajectories that originated predominantly over Florida land in the 6 hr and 24 hr prior to the precipitation event at the receptor. Long term trajectories for high mercury concentration events showed some variation, originating over the Atlantic, Caribbean Sea, and the Gulf of Mexico. Low mercury concentration events had a strong trend of trajectories originating over the Gulf of Mexico in the short-term. Some variations were observed in the intermediate term. The longer-term trajectories showed fewer variations, with origins occurring over the Caribbean and Atlantic. Overall, the trajectories observed here compared well to those from the BRACE analysis<sup>8</sup>, and suggests that the air mass reaching the receptor during these high mercury concentration events may be influenced by emission sources local to Florida and the receptor.

- *Statistical factors and contributions to mercury from PMF modeling*

Figure 2 shows the model resolved factors contributing to mercury species mass observed in the dataset. The regression results of the PMF predicted versus measured Hg concentrations had slope of 1.01, an intercept of 0.97, and a coefficient of determination ( $r^2$ ) of 0.99, indicating an excellent fit to the data. Four sources were identified as the major contributors to mercury species mass. Coal fuel combustion was identified as the largest mercury contributing factor, accounting for approximately 75% of mercury species in the dataset. The fractional allocation of mercury species to coal combustion sources here is approximately 20% higher than that reported for the BRACE data analysis<sup>8</sup>, but consistent with changes in the local emissions inventory. Agrochemical sources were identified as the second largest mercury-contributing source, accounting for approximately 11% of mercury species in the dataset. This result differs from the results of the BRACE data, where this source was not resolved as a mercury emission source.

Agrochemical industries (especially phosphate mining) are major part of the industrial landscape in the Tampa Bay area. Metal processing was identified as the third highest mercury contributing factor, accounting for 7% of Hg species mass. Finally, the crustal material source also contributed about 7% of the mercury species observed in the deposition data.

**Figure 2. Source identification for 7-factor PMF simulation for USF deposition data.**



## SUMMARY

We performed wet deposition sampling at a site on the USF campus for 6 months to capture mercury and trace metals data. The data was used to drive receptor modeling to understand the influence of local emission sources on mercury deposition in the Tampa Bay area, and compare with similar studies previously conducted in the area. Results from mercury event sampling indicates an extremely weak relationship between event precipitation depth and event mercury concentration. Event precipitation depth explained less than 1% of the variation observed in event mercury concentration. Event mercury deposition mirrored this trend. Results from back-trajectory modeling indicated that high mercury concentration events coincided with air mass trajectories that consistently tracked over Florida landmass in the short and intermediate term. Additionally, PMF results indicate that coal-fired power generation, agrochemical and metal processing facilities may be influencing mercury deposition in the region.

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