

Atmospheric Mercury Deposition and Source Attribution for Tampa

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Ryan Michael, Amy L. Stuart, Pakornkit Borisuth, Maya A. Trotz, Fenda Akiwuma
University of South Florida, 13201 Bruce B. Downs Blvd, MDC-56, Tampa, FL 33612

INTRODUCTION

Mercury is a persistent environmental contaminant whose most toxic form, methyl mercury, is found at high levels in fish present in water bodies throughout the world.¹ Fish consumption is therefore a leading route to human mercury exposure for vulnerable populations such as women of child-bearing age, the developing fetus and young children, nursing mothers, and those consuming large amounts of piscivorous fish in their diet.² Deleterious human health effects include impaired mental function, neurological disorders, cardiovascular effects, and kidney damage.³ Adverse effects on other species, including piscivorous birds and mammals, have also been documented.^{4,5} In order to mitigate these effects, attribution of observed levels of mercury (Hg) in the environment to Hg sources is needed.

Anthropogenic mercury releases have been shown to contribute significantly to the global biogeochemical cycling of mercury, and the resultant increases in ecosystem mercury concentrations.^{6,7} Anthropogenic emissions sources include combustion of fossil fuels (largely at coal- and oil-fired power plants), incineration (largely at medical and municipal waste facilities and crematoriums), and volatilization during production and use of mercury-containing products (fluorescent light bulbs, measurement instruments, and switches).^{6,8} Volatilization of Hg used for gold and silver mining is also an important source globally.^{9,10}

While environmental mercury sources may be numerous, it has been demonstrated that emission to the atmosphere and subsequent surface deposition is a primary source pathway leading to levels currently observed in water bodies.¹¹ Once emitted, Hg can be transported long distances or be deposited locally, depending on chemical speciation and meteorological phenomena.¹²⁻¹⁴ Oxidized mercury in gaseous species (categorized as reactive gaseous mercury, RGM) and mercury in particulate matter (categorized as particulate mercury, Hg_p) are readily deposited near to sources, through collection during rain events. Gaseous elemental mercury (Hg⁰) is much less soluble and can persist over long distances and timescales before oxidizing to more soluble forms.¹⁴⁻¹⁶ Due to limited characterization of speciated source emissions profiles, and limitations in our understandings of dry deposition and aqueous Hg chemistry, substantial uncertainties exist in connecting specific sources of Hg emissions to measured levels of mercury deposition.¹⁷

Specifically, uncertainties exist in the identification of the relative contributions to deposition to sensitive watersheds of local anthropogenic sources versus distant sources. Large-scale photochemical modeling studies suggest a substantial contribution to mercury wet deposition is

due to photochemical conversion of Hg^0 from distant sources.¹⁸ Conversely, deposition measurement analysis case studies in eastern Ohio and southeastern Florida suggest a dominant role for contributions of local and regional sources.¹⁹⁻²¹ The level of uncertainty in the scientific literature on the point is detrimental to adequate control at all management levels, from international to local.

Here, we investigate deposition and sources of mercury in the Tampa Bay region. Levels of mercury found in fish in the Tampa Bay watershed have been found to be some of the highest in Florida,²² with mercury consumption advisories in place for many fish species in bay area freshwater lakes and streams. Methods, results, and potential implications for local versus long-range source influences are discussed in the following sections.

METHODS

To investigate atmospheric mercury sources contributing to deposition phenomena in the Tampa region, we analyzed trends in mercury deposition data, performed back trajectory modeling, and applied statistical receptor modeling based on Tampa special-site metals deposition data.

Data from the Mercury Deposition Network,²³ a network of more than 100 active sites throughout the United States, Canada and Mexico, were queried to assess trends and cycles in measurement data potentially relevant to mercury deposition in the Tampa Bay area. These sites measure long-term trends in wet deposition of total mercury through automated collectors and precipitation gauges. Specifically, data from the Mercury Deposition Network sites in Florida were plotted and compared for discussion of implications for Tampa area deposition.

One year of special precipitation event data (from March 2000 – March 2001) measured through the Bay Regional Atmospheric Chemistry Experiment²⁴ for a monitoring site in Tampa, was obtained and used to diagnose source influences. The dataset included individual sample data on trace metals and precipitation amounts for each day when precipitation occurred over the sampling period. The data were used to compare temporal trends in precipitation depths and mercury concentrations.

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. Precipitation event data were first categorized by precipitation depth. We used the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model²⁵ to compare air mass transport paths contributing to events with comparatively high versus low mercury concentrations for similar precipitation levels. Back trajectories were initiated at three heights, 250, 500, and 1000 m, in order to span the vertical space through which precipitation may have fallen. To drive the HYSPLIT model, meteorological data from the National Centers for Environmental Prediction (NCEP) model output were used. 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 apportion deposited mercury to sources, we applied multivariate statistical receptor analysis using the Positive Matrix Factorization (PMF) package, (EPA PMF v3.0).²⁶ Metals

concentrations from the 48 wet event day samples measured at the special study Tampa site were used as input to derive potential source profiles with PMF. Chemical species measured at the Tampa monitoring site for each event day were Hg, Mg, Al, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Cd, Sb, Ba, La, Ce, and Pb. Overall uncertainties of measurement for each species were derived using the approach described by Keeler et al.²⁰ The uncertainties applied in the input dataset were first examined utilizing the signal-to-noise ratio method described by Paarero and Hopke.²⁷ A sensitivity analysis, in which the number of factors was varied, indicated that the variability in the dataset was best characterized when 10 factors are used to account for source contributions. This was determined by minimizing the absolute difference between the model calculated Q_{robust} (goodness of fit parameter) and the theoretical Q_{true} . The model was initiated from 20 randomly generated starting points since it has been demonstrated that this is adequate to produce stable Q -values.²⁸ All runs converged, and the model run with the smallest minimum was selected for further analysis. Bootstrapping, with 100 runs, was performed on this solution to estimate stability and uncertainty. Derived source profiles will be compared and evaluated against available profiles for specific source types in order to identify likely sources of mercury to the Tampa Bay.

RESULTS

Multi-year monthly averages indicate that mercury wet deposition is highest during the summer months, from about June to September, at all sites in all years (Figure 1b). This is likely due in part to increased precipitation amounts during the summer as precipitation depth (Figure 1d) displays a similar annual cycle. Measured mercury concentration (Figure 1e and f), appears to exhibit less similarity to mercury deposition (or precipitation amount).

Back trajectory results (not shown) indicate that the high mercury concentration events predominantly had short-term (6 hr) air mass backward trajectories coming from the south and east of the monitoring site, primarily over nearby land. The low mercury concentration events predominantly had short term trajectories from a more southerly and westerly origin, primarily passing over the Gulf of Mexico. For the intermediate (24 hr) trajectories, the high mercury concentration event air masses traveled primarily over Florida land, while the low mercury concentration event air masses traveled mainly over Gulf and Caribbean waters. The longer-term (72 hr) trajectory locations show fewer origin differences, with event trajectories traveling primarily over water (in the Caribbean, Gulf, and Atlantic Ocean) during their initial 48 hrs.

PMF analysis indicates that two factors contribute to a significant portion of mercury species observed at the receptor, accounting for ~75% of total mercury mass. Factor A accounted for the largest fraction of total mercury mass (52%), while Factor B accounted for the second largest fraction (~25%) (Figure 2). The remaining mercury mass was distributed among 5 factors at fractions of 8%, 7%, 3%, 3%, and 2%. Factor A also contributed the largest fraction of sulphur species (28%) to the total species mass, while Factor B was the largest contributor to zinc (51%), copper (41%), and cadmium (31%) species masses. Examination of the species contribution to factor profiles reveals that Factor A consists primarily of sulphur species (94%), with smaller contributions from magnesium, aluminum, phosphorus, and iron species (Figure 3). The species profile for Factor B indicates majority contributions from zinc species (66%), with smaller contributions from iron (10%), copper (8%), phosphorus (8%), and aluminum (3%) species.

Figure 1. Annual cycles and multi-year trends in mercury deposition (a, b), mercury concentration (c,d), and precipitation depth (e, f) for each Mercury Deposition Network site. (Site IDs are provided in the legend).

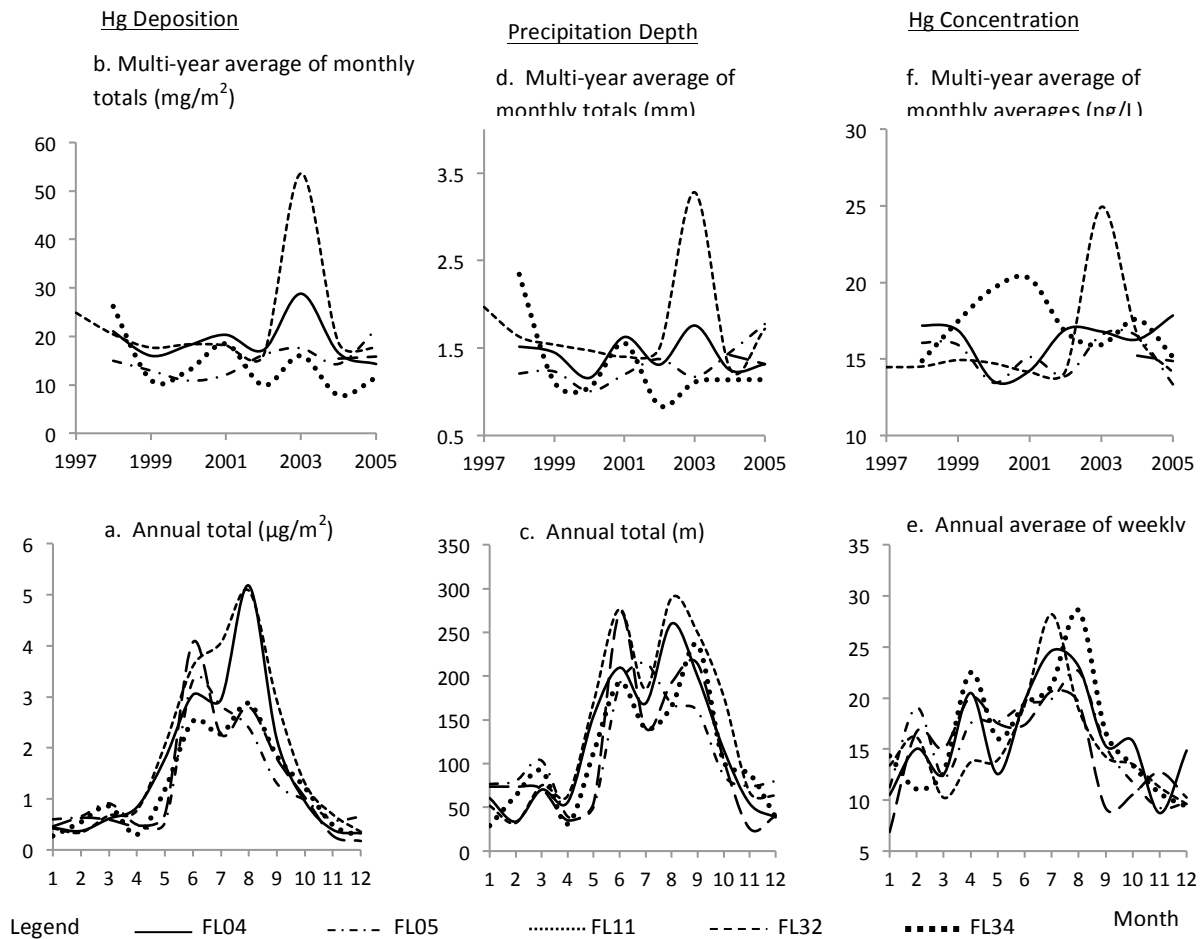
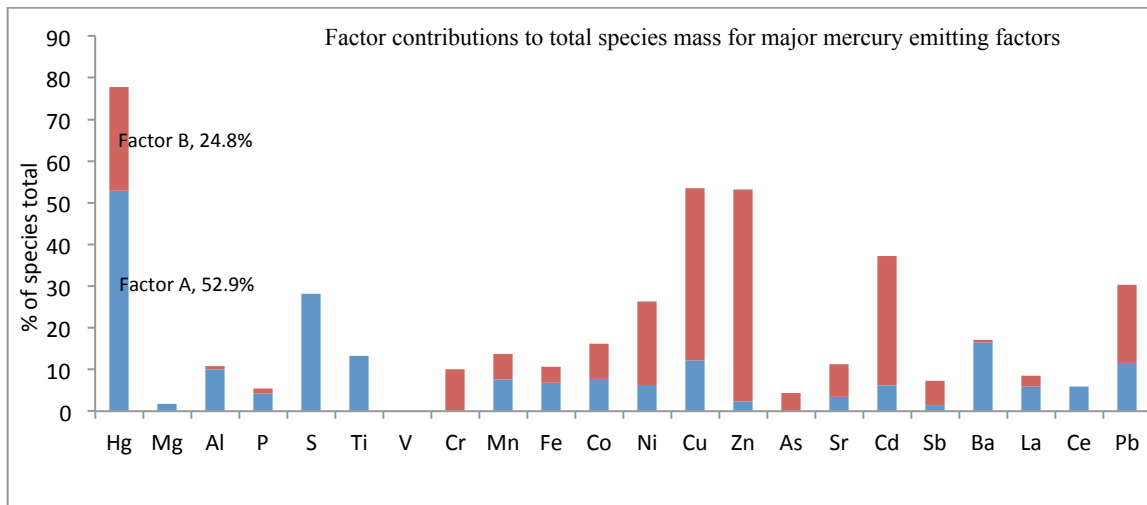
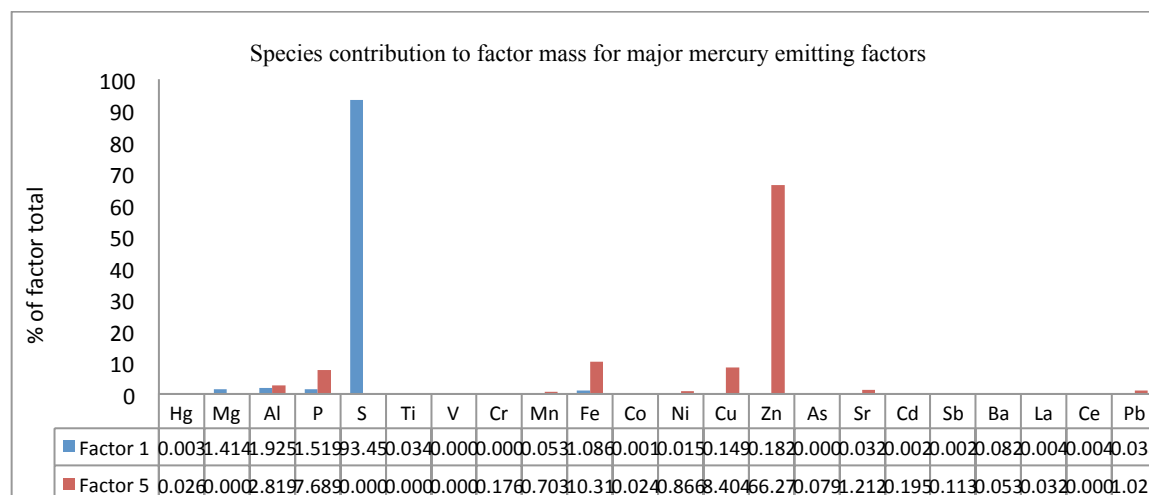


Figure 2. PMF factorization of special site precipitation event data showing factor contributions to total species mass for the two major mercury emitting factors.





DISCUSSIONS AND CONCLUSION

Results from analysis of the network data indicate no long-term trend in wet deposition of mercury in Florida over the decade of available data. Additionally, the annual cycle of wet deposition shows that mercury deposition amount closely follows precipitation amount (with abruptly higher amounts in summer months), but mercury concentration in deposited rain exhibits different peaks and smaller relative differences between seasons.

Results from backward trajectory modeling of the event data suggest the likely influence of Florida sources on high mercury concentration events studied here, while the PMF analysis indicates that mercury deposition may be originating from sources with significant sulphur influences (likely fossil fuel burning facilities) and heavy metals (e.g. consumer or medical waste incineration). Taken in the context of area emission inventories, the analysis results here suggest potential contributions to Tampa mercury deposition from local and regional sources. However, contributions from distant sources cannot be precluded since coal-fired power plants and incinerators have large mercury emissions globally. Further work is needed, combining modeling and event data, for quantitative attribution to local versus distant sources of mercury deposition.

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