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Assessing the Sources of Atmospheric Mercury Wet Deposited in Florida, USA

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Abstract. From October 2008 through August 2010, event-based precipitation samples for mercury (Hg), trace elements, and major ions analysis were collected at six monitoring sites in Florida, 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 in support of a Hg Total Maximum Daily Load (TMDL) project. The measurement sites were located in Pensacola, Jacksonville, Orlando, Tampa, Davie, and Everglades National Park. For the period April 2009 through August 2010, Hg wet deposition rates ranged from 26.8 to 38.7 μg/m^2 across the six sites. We observed a strong seasonal pattern, with increases in measured Hg concentrations and Hg wet deposition occurring during the summer months, which was further pronounced at the southern sites. We also observed a clear overall spatial gradient in Hg wet deposition, increasing across sites from north to south.

Key words: Mercury, trace elements, wet deposition, Florida, TMDL

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. Therefore, it is essential to understand the local, regional, and global scale contributions from atmospheric Hg sources so that policymakers can effectively regulate Hg emissions and their effect on the environment.

The state of Florida, USA is a region of particular interest for studying atmospheric Hg deposition, due to the current fish consumption advisories for fresh waters due to elevated methylmercury concentrations in fish taken from these waters. In support of a Hg Total Maximum Daily Load (TMDL) project, the University of Michigan Air Quality Laboratory (UMAQL) established six Hg wet deposition monitoring sites in order to investigate the impact of Hg deposition across the state of Florida.

Materials and Methods

Using the measurement techniques that the UMAQL has employed for the last 20 years (Hoyer et al. 1995; Landis and Keeler, 1997; Keeler and Dvonch, 2005; Keeler et al. 2005; Keeler et al. 2006; Gratz et al. 2009; Gratz and Keeler, 2011), we collected event-based wet-only precipitation samples at the six Florida sites. Event-based measurements are essential for applying meteorological and source-receptor models to the precipitation dataset, as the path of a precipitating system relative to major emission 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 the air masses that feed the precipitating system, and the source mixture and source density in the upwind areas for each storm system can significantly impact the observed precipitation chemistry and the amount of Hg that is wet deposited during precipitation events. Therefore, event-based Hg wet deposition monitoring offers the ability to effectively quantify individual source impacts.

For the period October 2008 through August 2010, event-based precipitation samples for Hg, trace elements, and major ions were collected at Pensacola (30.550,

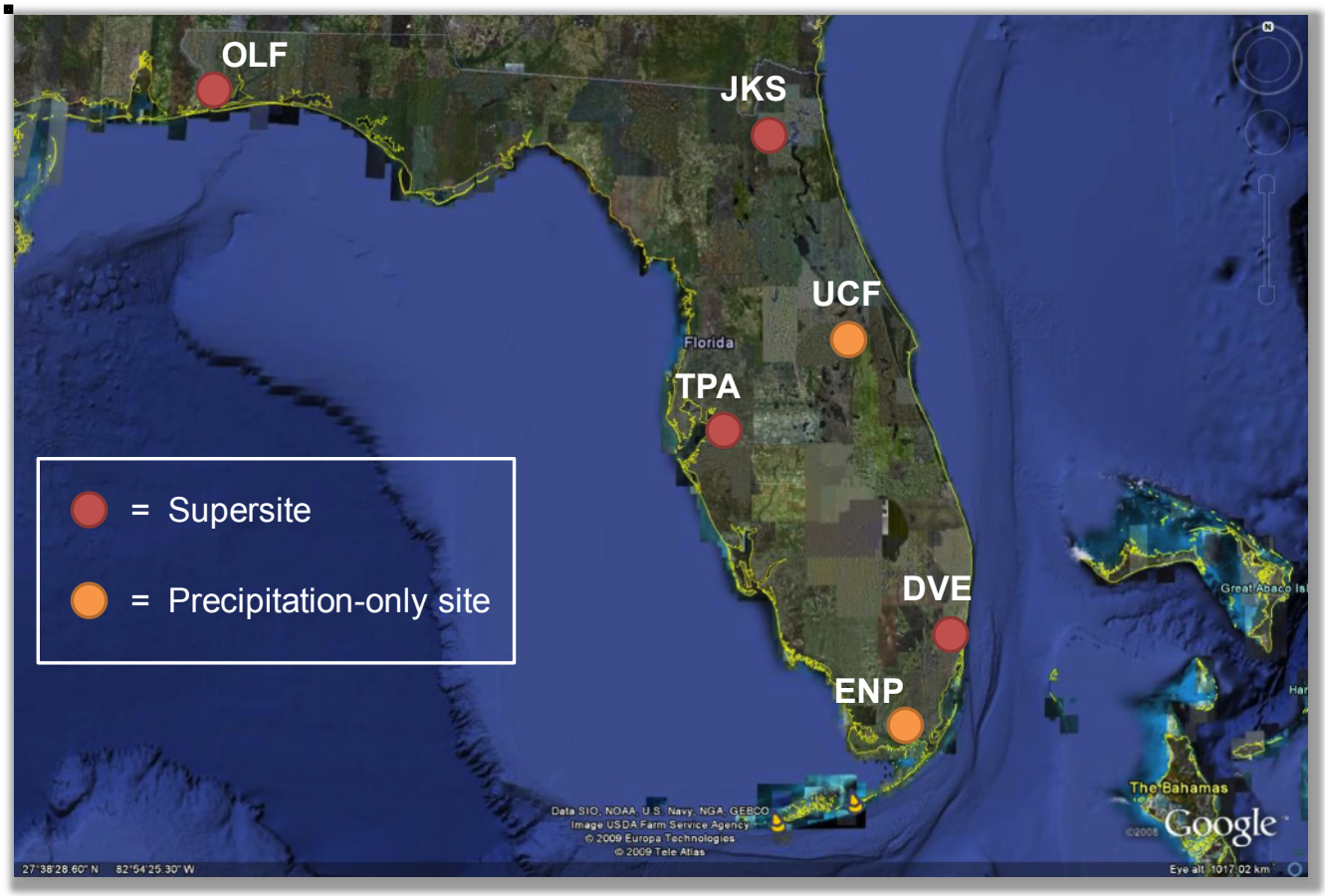

Fig. 1. Location of wet deposition monitoring sites in Florida

-87.375), Jacksonville (30.248, -81.952), Orlando (28.592, -81.190), Tampa (27.914, -82.375), Davie (26.085, -80.241), and Everglades National Park (25.390, -80.680), as illustrated in Figure 1. Wet deposition was collected using the UMAQL Automated Sequential Precipitation Sampler (ASPS). This sampler is a computer-controlled precipitation sampling system designed and built by the UMAQL that allows unattended wet-only event-precipitation collection. The ASPS allows for the concurrent automated collection of up to four different samples using independent sampling trains. The Hg sampling train was composed of glass funnels and fluorinated polyethylene bottles. A separate sampling train (all polypropylene) was used for trace elements and major ions. The ASPS utilizes sampling racks that hold eight individual bottles connected to discrete sampling trains, and automatically sequences to a new sampling bottle each day to allow for discrete precipitation events to be characterized on a daily basis. Each bottle is sealed before and after the precipitation sample is collected using the computer controlled rack module and valves. The sample racks are housed in the base of the sampler in a temperature-controlled chamber that is kept between 5-8^{o}C.

Laboratory determinations for total Hg in precipitation were conducted at the Florida Department of Environmental Protection (FDEP) Central Laboratory. After oxidation with BrCl, total Hg in precipitation was purged from solution in a Hg-free argon stream after reduction with NH_2OH and reduction of divalent Hg by $SnCl_2$ to Hg^0, and concentrated onto a gold trap. Total Hg was then quantified using a dual amalgamation technique followed by cold-vapor atomic fluorescence spectrometry (CVAFS). Laboratory analyses of trace elements in precipitation were carried out at the UMAQL. Samples were acidified with concentrated HNO_3 to a 1% solution (v/v) in the sample bottle and stored in a dark cold room for a minimum of 14 days before analysis to provide adequate time for optimal leaching (Graney et al 2004). Precipitation samples were analyzed for a suite of trace elements using a Finnigan MAT Element magnetic sector field high resolution ICP-MS using a method similar to that previously described (Keeler et al. 2006). Laboratory analyses for major ions were completed at the UMAQL, using a Dionex (Sunnyvale, CA) ion chromatography system.

Results and Discussion

Monthly volume-weighted mean (VWM) Hg concentrations across the sites ranged from a minimum of 3.0 ng/L (Pensacola site, December 2008) to a maximum of 39.7 ng/L (Jacksonville site, July 2010). This range in VWM Hg concentrations is similar to those measured in a previous study in south Florida during 1995-1996 (Dvonch et al. 1998, Dvonch et al. 1999,

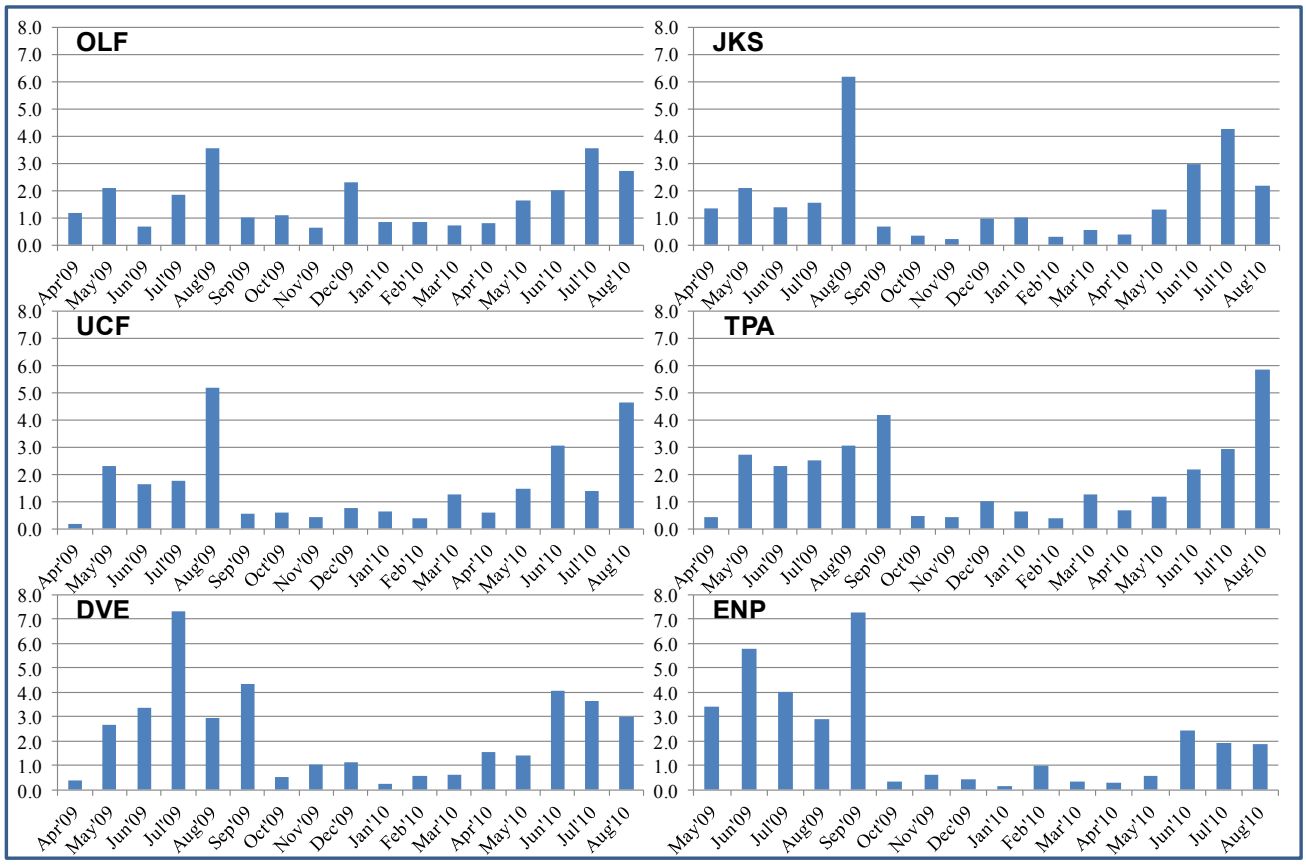

Fig. 2. Monthly mercury wet deposition (μg/m^2) at Florida monitoring sites (Apr 2009 – Aug 2010).

Dvonch et al. 2005).

Since the monitoring sites for the current project came online over a staggered start(October 2008 to March 2009), data for monthly Hg wet deposition observed at each of the sites are plotted in Figure 2 for the period April 2009 through August 2010, to allow direct spatial comparisons across sites. Mercury wet deposition rates for this period ranged from 26.8 to 38.7 μg/m^2 across the six sites. We observed a clear overall spatial gradient in Hg wet deposition, increasing across sites from north to south. North to south increases were also observed in ambient reactive gaseous Hg (RGM) across sites using measurements collected with a Tekran Hg speciation system (data not presented here). RGM species are known to have increased water solubility and to be more easily incorporated into precipitating systems. We also observed a strong seasonal pattern in the measurements, with increases in Hg concentrations and Hg wet deposition occurring during the summer months (May through September), as seen in Figure 2. This strong seasonal impact was most enhanced at the southern monitoring sites.

Conclusion

Significant amounts of Hg wet deposition were observed at all six monitoring sites across Florida. In particular, we observed a clear overall spatial gradient in Hg wet deposition, increasing across sites from north to south. We also observed a strong seasonal pattern in the measurements, with increases in Hg concentrations and Hg wet deposition occurring during the summer months, with this strong seasonal impact most enhanced at the southern monitoring sites.

Future analyses applying the receptor models USEPA-PMF and USEPA-Unmix to the Hg, trace element and major ion wet deposition datasets will allow a quantitative apportionment of the emission sources contributing to the observed Hg deposition loads across the state.

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