ATMOSPHERIC DEPOSITION OF MERCURY IN FLORIDA: 

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Abstract. The primary goal of the Florida Atmospheric Mercury Study (FAMS) is to quantify the seasonal and geographical variability in the atmospheric deposition of Hg and other trace elements in central and south Florida. Precipitation, aerosol, and gaseous Hg samples have been collected at seven sites in Florida for periods ranging from 3 to 24 months. The summertime wet season in south Florida accounts for 80 to 90% of the annual rainfall Hg deposition. Depositional rates in south Florida are 30 to 50% higher than those from central Florida. Particle phase measurements range from 2 to 18 pg/m³ Hg at all sites. Measurements of monomethylmercury in precipitation range from <0.005 to 0.020 ng/L.

1. Introduction

A 5-year study focusing on the atmospheric deposition of Hg and other trace elements in central and south Florida has been initiated. The organization and rationale for the FAMS project are described by Pollman et al. (this volume). One of the primary objectives of the Florida Atmospheric Mercury Study (FAMS) is to quantify geographical and seasonal variations in atmospheric mercury deposition and to subsequently determine if subregional differences in Hg deposition occur in Florida. Other objectives include quantifying the marine background contribution for Florida, determining the partitioning between wet and dry deposition, investigating the speciation of Hg in precipitation and gaseous Hg, and identifying possible sources of Hg using multiple chemical tracers (Pollman et al., this volume).

The FAMS project presently encompasses the tower-based collection of weekly integrated total gaseous and aerosol mercury samples and monthly integrated bulk and wet deposition samples at seven field locations in north-central and south Florida. The use of ultra-clean protocols during the manual collection of event rain samples for Hg have proven to be extremely successful (Gill and Fitzgerald 1987; Fitzgerald et al., 1991). The establishment of the FAMS monitoring network has been contingent upon the adaptation of these clean collection protocols to automated, tower-based, precipitation sampling. Quantifying the atmospheric deposition of Hg to Florida is a necessary precursor to understanding the mechanisms that govern the partitioning of Hg in Florida's aquatic environments.

2. Materials and Methods

2.1 Site preparation

The FAMS monitoring network presently includes seven sites within Florida (Figure 1). Lake Barco (LB) represents our north-central Florida site. Additional sites are located in

Ft. Myers (FM), Fakahatchee Strand State Preserve (FS), Tamiami Trail Ranger Station (TT), and Everglades National Park (EG). The marine background; Little Crawl Key (CK) and urban; Andytown (AT) sites were established in April, 1994 (Pollman et al., this volume). The data sets from these two sites are limited, so they will not be discussed in detail. Two new stations will be added in November 1994, at the Everglades nutrient removal project and near Caryville in north Florida. Each station is equipped with a 48' aluminum tower with outboard sampling platforms. The towers are outfitted with a full array of meteorological equipment. A shed at the base of each tower houses pumps, mass-flow systems, meteorological data loggers, and telecommunications equipment. The shed can also serve as a class 100 clean area when necessary (Landing et al., 1993).

Fig. 1. Locations of FAMS monitoring sites.
2.2 Sample Collection

Monthly integrated bulk deposition samples are collected using a modified version of the collectors used by Iverfeldt (1991) and Lindqvist et al. (1991). The FAMS sampler consists of a polycarbonate funnel threaded into a PTFE Teflon collar connected to a 90 cm length of 0.64 cm OD FEP Teflon tubing. The tubing is connected to a 2L FEP Teflon receiving bottle threaded into another PTFE Teflon collar. The bottle is precharged with 15 mL 6M triple distilled (3xQ) HCL and is shielded to reduce photochemical reactions. The bulk deposition samplers are deployed in duplicate at each site. Immediately prior to recovery, the walls of the funnels are rinsed into the receiving bottle with two 70 mL aliquots of ultrapure acidified water (0.045M 3xQ-HCI). One of the funnels at one of the sites is turned down for the monthly sampling interval to serve as a field blank.

Wet deposition is collected using a modified version of the Aerochem Metrics wet/dry deposition sampler. The aluminum arms of the sampler are replaced with Teflon-coated arms. The aluminum roof is replaced with a polycarbonate roof equipped with a 6-inch-high Plexiglas rain splash guard. The polyethylene-enclosed foam seal is placed in a FEP Teflon bag. Three 1L teflon receiving bottles are nested inside the wet bucket. The 1-liter bottles are threaded into PTFE Teflon dual collars which also connect to 1L polycarbonate funnels. Two of the Teflon bottles are precharged with 7.5 mL 6M 3xQ-HCl and one is deployed without preservative. The precharged bottles are specifically for mercury, nutrients, and other trace metals, while the unacidified bottle is used to obtain sub-samples for major ions and pH (Landing et al., 1993). The excellent agreement between rain sample and rain gauge volumes (98 ± 2%, n = 130) indicates that the rain events are quantitatively collected with both types of samplers.

Weekly integrated aerosol samples are collected on 47mm 0.4 μm polypropylene membranes (Micron Separations, Inc.) held in open-faced polypropylene filter housings with PTFE Teflon O-rings. Polypropylene membranes were chosen because they can be successfully cleaned for Hg and all of the other trace elements measured in this project. The aerosol filter holders are placed in vented Plexiglas rain shrouds mounted on the outboard platform. Field blanks are placed in identical filter holders within the rain shrouds. The air flow rate through the filters is 50 LPM yielding a 50 cm/s face velocity (Landing et al., 1993). Tests conducted on these filters indicate that they are > 99% efficient at collecting particles > 0.4 μm and 96-98% efficient at collecting particles ranging from 0.015 to 0.8 μm (Hal Maring, pers. comm.).

We have determined that a minimum sampling interval of 3-6 days is required to collect a sufficient aerosol sample. The collection of a 24 hour integrated sample does not yield enough particulate Hg to detect accurately. While the possibility of sampling artifacts cannot be ignored during extended sampling periods, several researchers have demonstrated successful collection of weekly integrated aerosol samples, for Hg and trace metals, using 0.4 μm filters in open-faced 47 mm filter holders (Arimoto and Duce 1987; Lindberg et al., 1991). One question to address is loss or gain of Hg from the filters during their deployment. If there were significant loss or gain of Hg during a four week deployment period, then we would expect the filter from the first week to be consistently and significantly lower or higher than the sample from the fourth week. This trend is not observable in the data that we have accumulated thus far.
For cleaning, all Teflonware is rinsed with acetone, cleaned with Micro detergent (Cole-Parmer), leached in conc. reagent grade nitric acid at 55 °C for 7 days, followed by 7 day leaches in 3M HCl, 0.5M HCl, and 0.5M quartz distilled HCl (1xQ-HCl). Teflon bottles are rinsed with ultrapure water, filled with acidified water (0.045 M 3xQ-HCl), hermetically sealed, double bagged in polyethylene bags and stored in the clean lab until use. Other Teflonware is rinsed with ultrapure water, double bagged in polyethylene bags, and stored in the clean lab. Polycarbonate equipment is Micro washed, leached for 7 days in 3M HCl, 0.5M HCl, 0.5M 1xQ-HCl, rinsed with ultrapure water, double bagged, and stored in the clean lab. Polypropylene aerosol filter holders are washed in Micro after use and are stored in 0.5M 1xQ-HCl between uses. The polypropylene filters are cleaned prior to deployment using sequential 7 day 3M and 0.5M 3xQ-HCL leaches and ultrapure water rinses.

2.3 SAMPLE ANALYSIS

Mercury is measured by dual amalgamation (Fitzgerald and Gill, 1979) using a Brooks-Rand (model 2) cold vapor atomic fluorescence detector. With our instrumental settings, the detector response is linear from 100 to 10,000 pg Hg with a relative standard deviation of ±2% for replicate injections of Hg (yielding an instrumental detection limit of 30 pg Hg). Detector calibration is accomplished using vapor phase additions of a Hg-saturated air standard. The standard is calculated to contain 10.0 ng Hg/cm³ at 16.7°C (Fitzgerald and Gill, 1979).

Measurements for total mercury are made using a method similar to that described by Gill and Bruland, (1990). The samples are predigested with dilute aqua regia (7.5mL 6M 3xQ-HCl/L and 6mL 7.5M Q-HNO₃/L) and exposed to low wattage UV (730 µW/cm²; 254 nm) for 48 hours. A solution of 20% hydroxylamine hydrochloride is added to the sample (400 µL/300 mL sample) to quench the free chlorine and the sample is reduced with 25 ml 4% NaBH₄ (GFS Chemicals). The analytical detection limit for this procedure, based on three times the standard deviation of the purge blank, is 0.05 ng/L (n=75). Aqueous Hg standards are prepared and analyzed in the HCl/HNO₃ matrix. Standard additions of 1000 pg Hg typically give results of 100 ±5%. Analytical variability within samples ranges from 0.05 to 1.0 ng/L. Variability between colocated samples ranges from 1 to 5%. An interlaboratory comparison between the FSU (Florida State University) and TAMUG (Texas A&M University at Galveston) labs demonstrates excellent analytical reproducibility. Replicate samples were analyzed in a "blind" intercomparison by Jane Guentzel at FSU and Mary Stordal at TAMUG. The sample concentrations ranged between 0.5 to 2.1 ng/L Hg-total (n=12), with the average absolute deviation between the labs equal to 0.2 ng/L.

The BrCl method (Bloom and Crecelius,1983) and the dilute aqua regia digestion method were compared for their ability to solubilize total Hg in precipitation samples. Duplicate bulk deposition samples were collected, digested with either BrCl or aqua regia, photo-oxidized for 48 hour, neutralized with hydroxylamine HCl, and then analyzed under the same set of conditions, using NaBH₄ as the reductant. The average of the aqua regia-to-BrCl ratios was 98 ±4% (n=14). This is not significantly different from the routine analytical error (±5%). The comparison between the two methods has been further tested by the participation of FSU in the international intercomparison
exercise (Bloom and Horvat, this volume). The result obtained by Guentzel (1.39 ± 0.06 ng/L; n=2) is not significantly different from the overall result obtained by the primary reference lab (1.27 ± 0.14 ng/L; n=30), and the result obtained by the reference lab using the BrCl/photo-oxidation treatment (1.33 ± 0.12 ng/L; n=6) (Bloom and Horvat, this volume).

Aerosol samples are digested for total mercury and other trace metals using PTFE Teflon digestion bombs (Eggimann and Betzer, 1976). The filters are digested using a mixture of 6M 3xQ-HCl/conc. Q-HNO₃/conc.HF (Ultrex, J.T. Baker). The digest is analyzed for total Hg using SnCl₂ reduction (Gill and Fitzgerald, 1987). The procedural detection limit, based on three times the standard deviation of the total (deployment, handling, digestion, and analysis) blank divided by a volume of 300m³, is 1.28pg/m³ (n=73). Digestions of NIST-2704 standard reference material (Buffalo River Sediment) yield 94±12% (n=43) for total Hg.

Results and Discussion

3.1 EQUIPMENT BLANKS

Sampling equipment is rotated on a quarterly basis for every station. If the equipment has been fouled by bird droppings or insects it is replaced regardless of the schedule. Equipment blanks for the deployment of new equipment and the recovery of old equipment are quite low relative to the samples. New and old equipment blanks are measured by pouring one-half of a 1000 mL bottle of ultrapure acidified water (0.045 M Q-HCl) through the sampling setup (the "B" solution). The remainder of the water is retained as the "A" solution. The equipment blank is reflected in any differences in Hg concentration between the A and B solutions. New equipment blanks are < 20 pg Hg and old equipment blanks are < 200 pg Hg. Field blanks for 30 day deployment of bulk and wet deposition are 350±110 pg Hg and 65±21 pg Hg respectively. These blanks are corrected for the initial acid contribution and are negligible relative to the total mass of Hg in the samples (5,000 to 30,000 pg Hg).

3.2 QUALITY ASSURANCE EXPERIMENTS

The integrity and validity of the samples is of paramount importance to this project. Quality assurance tests have been, and continue to be, an integral part of our project. As the project and sampling equipment evolves, so do the QA/QC experiments. The short nature of this paper makes it virtually impossible to address every QA/QC concern. The most important issue to focus on is gain or loss of Hg from the samples during month-long integrated collection periods. Schroeder et al., (1991) state that the principal form of oxidized Hg in the atmospheric environment is Hg²⁺ and at pH values less than 5.5, the aqueous phase oxidation of Hg⁰ to Hg²⁺ is the dominating reaction. Therefore, loss of Hg from a shielded, acidified sample should be negligible. Gain of Hg through elemental Hg diffusion and oxidation is minimized by the design of the sampling equipment and quantified by collecting field blanks and making the appropriate blank correction.
In addition to measuring blanks, we have attempted to quantify loss or gain of Hg from the samples using aqueous phase Hg standards and actual samples. A 5.0 ng/L Hg(II) standard, acidified to the same level as a bulk deposition sample, was deployed for 30 days. The total Hg measured after recovery of the bottle was not significantly different from the original standard solution: 5.07 vs. 5.04 ng/L respectively. In a 1990 comparison, Iverfeldt and Munthe (1993) demonstrated that there was no significant difference between weekly, biweekly, and monthly collections of bulk precipitation samples. We have also confirmed that there is no significant gain or loss of Hg from bulk deposition samples deployed for a 14 day period. Colocated 24 hour event rain samples and a continuous bulk precipitation sample were collected during a 14 day period. The total mass of Hg in the 14 day integrated sample was 5.1 ng and the volume weighted sum of the event samples was 4.6 ng. The difference between these values is not significantly different from the variability between monthly colocated samples. Similar tests have been successfully completed for the Aerochem Metrics sampler. However, the limited nature of this paper does not allow for a lengthy discussion of QA/QC procedures.

3.3 MERCURY IN PRECIPITATION

The bulk deposition samples contain 100% of the wet deposition and whatever dry deposition collects in the funnels and is rinsed into the receiving bottle. Although we have not fully investigated the aerodynamic behavior of the polycarbonate funnels, if we assume that the bulk deposition funnels collect the majority of any aerosol dry deposition, then we might expect to find differences between bulk and wet deposition proportional to dry deposition. Average volume weighted bulk and wet fluxes and concentrations have been calculated for each FAMS site (Table I). There are no significant differences between bulk and wet flux or concentration at each site. This is direct contrast to the other trace metals. Landing et al., (1994) report that elements such as Al, Cu, Zn, As, and Pb differ significantly between bulk and wet deposition. In Sweden, Iverfeldt and Munthe (1993) also report no significant differences between bulk and wet Hg concentrations or fluxes.

Preliminary calculations suggest that the atmospheric flux of Hg varies seasonally, with the highest fluxes occurring during the summer months (Apr. to Sept.). There does appear to be a slight geographic trend, with the annual volume weighted fluxes being lowest in north-central Florida and increasing towards the southern stations (Table 1). Currently, there does not appear to be a sub-geographical trend within south Florida. Tamiami Trail (TT) is presently the station with the highest annual flux and concentration. These values are accentuated by one month with normal rainfall concentrations and an abnormally high monthly rainfall volume (40 cm). If we substitute a more normal rainfall amount for this month (20 cm), the annual volume weighted flux and concentration would be 20 μg/m²/yr and 21 ng/L, respectively.
### Table I

<table>
<thead>
<tr>
<th>Site</th>
<th>n</th>
<th>Flux (Range)</th>
<th>Summer (%)</th>
<th>Winter (%)</th>
<th>Concentration (Range)</th>
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<tr>
<td></td>
<td></td>
<td>Bulk Wet</td>
<td></td>
<td></td>
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<tr>
<td>LB</td>
<td>30</td>
<td>15(11-20) 15(12-20) 64 36</td>
<td>13(9-15) 12(9-15)</td>
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<td></td>
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<tr>
<td>FM</td>
<td>24</td>
<td>23(21-25) 24(22-27) 77 23</td>
<td>17(15-20) 18(16-20)</td>
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<tr>
<td>TT</td>
<td>16</td>
<td>28(25-29) 30(27-31) 86 14</td>
<td>23(19-25) 24(23-26)</td>
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<tr>
<td>EG</td>
<td>16</td>
<td>20(19-23) 21(20-23) 86 14</td>
<td>16(15-17) 18(16-18)</td>
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<td></td>
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</table>

### 3.4 Aerosol Mercury

The average concentrations of particulate mercury at all five sites are given in Table II. These particulate concentrations are lower than previously reported values (Fitzgerald et al., 1991; Iverfeldt, 1991; Lamborg et al., this volume). One possible explanation for these differences is the difference in air mass sources. Florida is a peninsula which receives marine air, while the temperate and subpolar regions are impacted by continental air masses.

### Table II

<table>
<thead>
<tr>
<th>Site</th>
<th>n</th>
<th>Mean±1SD (Range)</th>
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<tbody>
<tr>
<td>LB</td>
<td>40</td>
<td>4.6±2.0 (1.8-9.1)</td>
</tr>
<tr>
<td>FM</td>
<td>32</td>
<td>7.9±3.5 (4-18)</td>
</tr>
<tr>
<td>FS</td>
<td>32</td>
<td>4.5±1.9 (2.4-12)</td>
</tr>
<tr>
<td>TT</td>
<td>32</td>
<td>5.0±1.9 (2.4-10.7)</td>
</tr>
<tr>
<td>EG</td>
<td>32</td>
<td>5.2±3.8 (1.5-12.8)</td>
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</table>

Event rain samples collected in northern temperate and sub-polar climates clearly show the affect of particle scavenging of aerosol Hg by rain (Bloom and Watras, 1989; Glass et al., this volume; Iverfeldt, 1991; Lamborg et al., this volume). The data for the monthly wintertime bulk concentrations vs. monthly rainfall volume, when only 14-36% of the annual deposition occurs, show some evidence of particle scavenging (Figure 2a). This graph is similar to the monthly integrated bulk concentration vs. monthly rainfall plot in the nordic regions (Munthe and Iverfeldt, pers. comm.), where particle scavenging is primarily responsible for the Hg found in precipitation year-round (Iverfeldt, 1991). In contrast to this, summertime plots of monthly concentration vs. monthly rainfall do not show evidence of aerosol scavenging (Figure 2b). The relationship between concentration and volume during the summertime is intriguing. High amounts of rainfall coincide with high Hg concentrations suggesting a large and "unlimited" source term for Hg rather than particle washout. For aerosol particles to represent the primary summertime source term for Hg in south Florida rain, a
mechanism which can replace all of the aerosol Hg in the troposphere over south Florida within a few hours would be required. Other elements, such as Al, Cu, Zn, As, and Pb, that do show a large difference between bulk and wet deposition also exhibit classical washout behavior, but correlations between Hg and these other elements are not significant (Landing et. al., this volume).

Another way to evaluate the importance of particulate Hg as a dominant source term is to calculate washout ratios. Washout ratios for the winter (October-March) and summer (April-September) have been calculated for all sites using the equation \( w = \frac{Hg_{\text{wet}} (\text{ng/L}) \times 1.2 \text{m}^3/\text{L}}{Hg_{\text{part}} (\text{ng/m}^3)} \) (Arimoto et al., 1985). Low values between 200 to 2000 are indicative of particle washout, while values above 2000 imply that processes other than aerosol washout contribute to the Hg found in precipitation (Table III).

![Figure 2](image-url)

**Fig. 2.** (a) Wintertime integrated Hg concentrations vs. monthly rainfall for 5 sites: October-April; 1992-1994; (b) Summertime integrated Hg concentrations vs. monthly rainfall for 5 sites: May-September; 1992 and 1993.

<table>
<thead>
<tr>
<th>TABLE III</th>
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<tr>
<td>Aerosol Washout Ratios-Monthly Integrated Samples (Mean ± 1SD)</td>
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<tr>
<td>Station Winter Summer</td>
</tr>
<tr>
<td>LB 2350±1100 4300±2250</td>
</tr>
<tr>
<td>FM 2000±1050 3000±1200</td>
</tr>
<tr>
<td>FS 2500±1110 4200±1800</td>
</tr>
<tr>
<td>TT 2900±1450 5900±1900</td>
</tr>
<tr>
<td>EG 2400±1200 3900±2500</td>
</tr>
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</table>

Wintertime washout ratios range from 2000 to 3000 and suggest that aerosol washout partially contributes to the wintertime deposition, (14-36% of the annual Hg deposition).
Summertime ratios range from 3000 to 6000 and suggest that processes other than particle washout govern summertime deposition, (64-86% of the annual Hg deposition). Washout ratios calculated for event rain samples collected during the summertime range from 5000 to 20000 (Table IV). Despite the large uncertainties, the ratios are 2 to 40 times greater than previously reported values for rainfall Hg (Lamborg et al., this volume; Fitzgerald et al., 1991).

<table>
<thead>
<tr>
<th>Station</th>
<th>Julian Date</th>
<th>Event Ratio (mean±1SD)</th>
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<tbody>
<tr>
<td>FS (1993)</td>
<td>193</td>
<td>4600±650</td>
</tr>
<tr>
<td>194</td>
<td>4950±700</td>
<td></td>
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<tr>
<td>195</td>
<td>3700±500</td>
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</tr>
<tr>
<td>EG (1994)</td>
<td>171</td>
<td>20000±3000</td>
</tr>
<tr>
<td>171</td>
<td>17000±2300</td>
<td></td>
</tr>
<tr>
<td>235</td>
<td>17040±1700</td>
<td></td>
</tr>
<tr>
<td>236</td>
<td>9945±1000</td>
<td></td>
</tr>
</tbody>
</table>

3.5 Monomethyl Mercury in Rain

Measurements of MMHg in summertime event rain samples from south Florida (EG and FS), performed by Frontier Geosciences (Horvat et al., 1993), range from 0.013 to 0.022 ng/L (n=4). Measurements of MMHg from summertime monthly integrated bulk deposition samples (EG, AT, CK) range from 0.020 to <0.005 ng/L (n=7). These measurements are near the analytical detection limit and are an order of magnitude lower than results reported for more temperate environments (Bloom and Watras, 1989; Fitzgerald et al., 1991; Glass et al., this volume). These preliminary values suggest that direct deposition of MMHg may not be a significant source for MMHg in south Florida’s aquatic environments.

4. Conclusions

Based on the data we have accumulated thus far, we can make some preliminary conclusions regarding the atmospheric deposition of Hg to Florida and it’s possible source terms:

1. The deposition in north-central Florida is 29% lower than in south Florida.
2. There does not appear to be a significant decrease in rainfall Hg deposition from east to west across south Florida.
3. There is generally good agreement between bulk and wet Hg collection, suggesting that dry deposition does not contribute significantly to the total Hg deposition.
4. The unusual concentration to volume relationship and high scavenging ratios suggest that aerosol washout does not appear to be a dominant source term for Hg in south Florida during the summertime.
5. Preliminary measurements of very low MMHg concentrations suggest that direct MMHg deposition may not be significant in south Florida.

6. The regional and seasonal trends in Hg deposition do not appear to be correlated with atmospheric total gaseous Hg concentrations. Future work needs to address the relationship between rainfall Hg deposition and reactive gaseous Hg species in the atmosphere (Gill et al., this volume).

Acknowledgements

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