

Dry Deposition of Mercury Measured with a Water Surface Sampler

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Mercury (Hg) is a toxic trace metal, it has been linked to human illness and environmental damage. Industrial activities have resulted in substantial emissions of Hg to the atmosphere and long distance transport. The primary environmental problem associated with mercury is its bioaccumulation in fish and subsequent human health effects on fish consumers. Long-range transport and atmospheric deposition play a major role in mercury contamination of many aquatic ecosystems. Deposition monitoring for mercury is needed to help identify atmospheric mercury sources, to better understand transport and deposition mechanisms, and to improve atmospheric deposition models.

There are three processes involved in the cycling of mercury through the atmosphere; wet deposition, dry deposition and air-water exchange. Wet deposition is the transfer of a substance from the atmosphere to the surface of the earth with precipitation, dry deposition is the transport of particulate contaminants from the atmosphere onto surfaces in the absence of precipitation, and air-surface exchange is the deposition and reemission of mercury between the earth surface and the atmosphere. Wet deposition may be the most important atmospheric input of mercury to water and soil surfaces at rural or remote sites. Dry deposition of mercury is an important input to water surfaces and is thought to be the dominant input to forested terrestrial surfaces. Both processes need to be monitored for quantitative estimation of atmospheric mercury deposition fluxes and a full understanding of mercury deposition and environmental cycling.

Mercury can be found in the atmosphere in three forms: elemental mercury (Hg^0), particle bound mercury (Hg^p) and reactive gaseous mercury (Hg^{2+}). Elemental mercury (Hg^0) is the predominant species in ambient air and its residence time is $\frac{1}{2}$ to 2 years due to its low solubility and chemical inertness⁴. Reactive gaseous mercury (Hg^{2+}) is highly water soluble, reactive, and rapidly deposited. The amount of reactive gaseous mercury (RGM) in the

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⁴ Schroeder et al., 1998

atmosphere is typically less than five percent of the total mercury concentration, but RGM is very important with respect to mercury deposition.

In the present project, dry deposition of Hg is being collected with a static Water Surface Sampler (WSS) which is a sampling instrument designed to quantify the flux of atmospheric pollutants to its surface (See Figure 1). There are four WSS being used for sampling on the Science Center Building at Clarkson University. Different experimental methods are being used to quantify dry deposition; the first one is a side-by-side comparison. For these experiments 0.08 M hydrochloric acid (HCl) solution is used in a clean Petri dish placed in the WSS to limit reemission of the deposited Hg to the atmosphere. The sampling time varies between 12 and 24 hours to compare how sampling time impacts the measured deposition. In the second type of experiment 0.08 M HCl solution is added to two side-by-side samplers. Five ng/L Hg solution in 0.08 M HCl is added to the other two side-by-side samplers. For the third experiment 0.08 M HCl solution is added to two side-by-side samplers and deionized water is added to the other two side-by-side samplers.

Total Hg is analyzed with a Tekran Series 2600 Mercury Analysis System and a Quality Assurance and Control (QA/QC) sampling protocol is used to maintain the high quality necessary for sampling and analysis of Hg. Two different QA/QC protocols are used. Duplicate samples are analyzed for every field blank and dry deposition sample; also the solution added to each Petri dish is analyzed to ensure that it is not contaminated. To confirm that dry deposition of Hg is being measured and the results are not being affected by other factors two side-by-side samplers were covered with a glass lid and two side-by-side samplers were left uncovered to compare the values obtained. In addition, statistical methods will be used to determine if the results of the static WSS are reproducible.



Figure 1: Static Water Surface Sampler

Two hypotheses are proposed for the present project; the first is that the amount of Hg deposited to the static Water Surface Sampler can be predicted from the concentration of Hg^{2+} , RGM, and particulate Hg in the air. To test this hypothesis the WSS is used following the methods specified above and the measured flux is compared to modeled Hg flux. The flux of Hg deposited by dry deposition will be calculated with equation 1 and reported in $\left[\frac{ng}{m^2} \cdot week \right]$.

$$F = \frac{m}{A \cdot t} \quad \text{Equation 1}$$

Where m is the mass of Hg deposited [ng], A is the surface area of the Petri dish [m^2] and t is the sampling period [week].

The Hg concentration in air will be obtained from an ongoing project at Clarkson University. The equipment used to measure the Hg^0 , Hg^{2+} , and $Hg^{(p)}$ in air is the Automatic Tekran Air Sampler. When all the necessary data is obtained models will be used to predict the amount of Hg deposited to the static WSS from measured air concentrations. Equation 2 is used to predict the Hg flux deposited to the WSS.

$$F = \left(C_{Hg^{2+}} \cdot V_d \right) + \left(C_{Hg^{(p)}} \cdot V_d \right) + k_w \left(DGM - \frac{Hg^0}{H'} \right) \quad \text{Equation 2}$$

Where $C_{Hg^{2+}}$ and $C_{Hg^{(p)}}$ are the concentration of RGM and particulate Hg in the air respectively [ng/L], V_d is the dry deposition velocity [cm/s], k_w is the mass transfer coefficient [cm/s], DGM is the dissolved gaseous mercury in water [ng/L], Hg^0 is the Hg concentration in air [ng/L] and H' is a dimensionless constant.

The second hypothesis of this project is that the amount of Hg deposited by gas and particle-phase Hg is less than the amount deposited by rain. To test this hypothesis the flux measured with the WSS will be compared to the value obtained for wet deposition. The wet deposition data will be obtained from an ongoing project at Clarkson University. This flux is obtained from an MIC-B Automatic Precipitation Collector. The total Hg for wet deposition is measured by using the Tekran Series 2600 Mercury Analysis System. The flux for wet deposition is calculated by equation 3 and reported in $\frac{ng}{m^2} \cdot week$. Appropriate unit conversion must be done.

$$F = C_{Hg} \cdot precipitation \ depth \quad \text{Equation 3}$$

Where C_{Hg} is the Hg concentration in water [ng/L] and the precipitation depth is the amount of rain divided by the cross-sectional area of the glass funnel collector [L/m^2] when the rain gauge is not available.

References

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