Contribution of Dry Deposited Mercury to Urban Run-Off

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Introduction

Atmospheric deposition is the primary source of mercury (Hg) for most landscapes[1], and occurs with and without precipitation, called wet and dry deposition respectively. Hg concentration in wet deposition is widely measured, notably by the National Atmospheric Deposition Program's Mercury Deposition Network (NADP MDN), using established, simple methodologies, such as funnel and bottle collectors[2].

In some landscapes dry deposition appears to provide the majority of deposited Hg[3,4,5] and research is ongoing into the standardization of such measurements. None of methodologies for quantifying Hg dry deposition is as simple and reproducible as those used to measure Hg in wet deposition. Hg dry deposition is often modeled using atmospheric concentrations and meteorological conditions, despite the associated high costs of equipment and maintenance. The complexity of urban meteorological conditions may limit this method in urban landscapes, surrogate surfaces may provide equally valid deposition measurements at reduced costs and complexity.

One such surrogate surface, ion exchange (IX) membranes, has been used to produce Hg deposition measurements that correlate well with modeled reactive gaseous mercury (RGM) deposition[6]. RGM is a soluble form of Hg, largely Hg(II), the primary substrate for methylation[7], which exhibits elevated atmospheric concentrations in urban areas and often has a higher modeled deposition velocity than other Hg forms[8]. This poster reports a preliminary use of IX membranes and static water surface samplers in an urban environment and compares the obtained values those from similar studies.

Hg dry deposited to "natural" surfaces, moss, leaves and soil, has been repeatedly studied[9,10,11]. The extent and fate of Hg dry deposited onto urban surfaces is less understood. Quantifying these values is important due to the elevated levels of Hg deposition in urban areas[12] and the presence of drainage systems that convey storm water directly into natural environments. Pavement is an effective sink of Hg with recorded deposition rates of up to 1.05ng Hg/m^2/hr[13]. Current RGM dry deposition models incorporate surface resistance, a variable unique to surfaces that must be determined in order to produce accurate deposition estimates[14]. For the work presented on this poster, measured total Hg and RGM dry deposition are compared to rainwater-labile dry deposited Hg on urban surfaces, providing an estimate of their relative contribution. This may elucidate relationships that allow urban Hg dry deposition to be estimated using surrogate surfaces.

Methods

In order to investigate the efficacy of surrogate surfaces and estimate urban Hg dry deposition, surrogate surface samplers were deployed at an industrial site in Seattle, WA. Total Hg dry deposition was measured using static water surface samplers and RGM deposition was determined using IX membranes. To quantify Hg dry deposition on road surfaces, sections of pavement and concrete were exposed and rinsed to determine dry deposited rain-water labile Hg. Measured deposition values obtained for pavement and cement were not significantly different and were. The measuring station was on the roof of a three-story building, within 100m of a major road, working ship canal and dry dock, multiple factories and a road surfacing materials distribution center. The 10 sampling periods averaged 6.8 days (5-11) from August 7th and October 16th, 2007. Blank correction of the results was determined by relative surface area and was performed weekly.

Chart 1. Various methods of measuring Hg dry deposition are in use. Presented here is a synopsis of the 10 most common methods. The three that were used in the surrounding poster were chosen because they were easy to perform, gave us unidirectional flux values, and provided limited speciation information.

Considerations

Method	Synopsis	Speciated Results	Bi-Directional Flux	Real-Time Results	Scale	Ease of Use	Source
Water Surface Sampler	A static or dynamic plane of (acidified) water is exposed for set amounts of time. The surface is protected from wet deposition and possibly cooled to limit evaporation. Acidification precludes speciated results but allows for the capture of GEM. Change in water concentration is used to determine deposition.	Yes/No	No	No	Site	Easy	Sakata et al. Regional variations in wet and dry deposition fluxes of trace elements in Japan. Atmos Env. 40 2006 521-531
Ion Exchange Membrane	Cation exchange membranes are exposed and digested in BrCl. They are only able to capture RGM.	Partial	No	No	Site	Easy	Caldwell et. al. Concentration and Dry Deposition of Mercury Species in Arid South Central New Mexico (2001-2002). Environ Sci Tech 40 (24) 2006 7535-7540
Surrogate Surface (general)	A surface such as a Teflon sheet or empty wet deposition bucket is exposed and then rinsed to determine deposited Hg.	No	No	No	Site	Easy	Ros. Et. Al.. Assessment of Dry Deposition and Foliar Leaching of Mercury and Selected Trace Elements Based on Washed Foliar and Surrogate Surfaces. Environ. Sci. Technol. 34 2000 2418-2425
Flux Chamber	Hg flux is determined by pulling a measured stream of air over a surface or object contained within the flux chamber. The difference in Hg concentration of air entering and leaving the chamberis used to determine flux.	Yes	Yes	Yes	Site	Medium	Gabriel et. Al. Diurnal and seasonal trends in total gaseous mercury flux from three urban ground surfaces. Atmos. Environ. 40 2006 4269-4284
Surface Washing	Surfaces of interest, typically foliar, are rinsed before and after environmental exposure. The concentration difference of rinsate is measured and used to quantify deposition.	No	No	No	Site	Easy	Lyman et al. Estimation of Dry Deposition of Atmospheric Mercury in Nevada by Direct and Indirect Methods. Environ. Sci. Tech. 41 2007 1970-1976
Bryophyte Analysis	Due to their unique physiology including a lack of vascular structure, and complex, frequently moist external structure, Hg levels in moss correspond more to atmospheric deposition than to substrate levels. Moss has been used to quantify Hg deposition both by measuring the amount of Hg in naturally occurring plants and by making moss bags which can be exposed in desired locations.	No	No	No	Site/ Landscape	Medium	Steines et al. Temporal and spatial trends in Hg deposition monitored by moss analysis. Science of the Total Environment. 304 2003 215-219 Tan et al. Atmospheric Mercury Deposition in Guizhou, China. Sci. Total. Env. 259 2000 223-230
Mathematical	In woodland settings, throughfall and litterfall are sumed, and corrected for wet deposition to determine total dry deposition.	No	No	No	Site/ Landscape	Medium	Munthe, et. Al. Mechanisms of deposition of methylmercury and mercury to coniferous forests. Earth and Environ. Sci. 80 1995 363-377
Inferential	Atmospheric Hg concentrations, either total or speciated, are measured at the site of Hg release or deposition, and this information is combined with meteorological measurements and chemistry models, which are themselves incorporated into deposition velocity and resistance models to calculate a deposition rate. Models of note include Eulerian Models to calculate deposition velocities coupled with deposition resistance calculation based on electrical resistance. Modifications of the acid deposition and oxidants model (ADOM) allow the incorporation of atmospheric chemistry, Hg species shifts, and wet deposition to large-scale dry deposition models. Munthe et. Al., incorporated tropospheric chemistry models (TCM) into an ADOM to predict deposition over the European continent.	Yes	Yes	Yes	Site/ Landscape	Medium/ Difficult	Lyman et al. Estimation of Dry Deposition of Atmospheric Mercury in Nevada by Direct and Indirect Methods. Environ. Sci. Tech. 41 2007 1970-1976 Miller et. Al. Estimation and Mapping of Wet and Dry Mercury Deposition Across Northeastern North America. Ecotoxicology. 14 2005 53-70
Gradient/Bown Ratio	Atmospheric Hg concentration is measured at various heights and an atmospheric Hg gradient is established. Accounting for heat gradients, the Modified Bowen Ratio provides a method for determining Hg flux from or to a surface.	Yes	Yes	Yes	Site/ Landscape	Medium/ Difficult	Lindberg et. Al. Micrometeorological gradient approach for quantifying air/surface exchange of mercury vapor: tests over contaminated soils. Environ. Sci. tech. 29 1995 126-135
Relaxed Eddy Accumulation	Anemometer controls two sampling trains, pointing in opposite directions along the desired axis of flux. Air flow direction determines which sampling train is active. By comparing the concentration of Hg in the airflows, flux can be determined.	Yes	Yes	Yes	Site/ Landscape	Medium/ Difficult	Skov et al. Fluxes of reactive gaseous mercury measured with a newly developed method using relaxed eddy accumulation. Atmos. Env. 40 2006 5452-5463

RGM dry deposition was determined using (IX) membranes, which have been shown to be a precise and reproducible method of quantifying RGM dry deposition. The IX membranes used were Pall Corporation ICE 450 supported medium hydrophilic membranes with cationic polysulfonic acid active sites on a non-woven polyester backing. Two or four replicates of approximately 70 cm^2 of IX membrane were deployed with each sampling. A section of membrane was cut from a common stock with a clean razor and attached to a cleaned PVC surface, face down to prevent particle deposition. For a section of IX membrane was cut free with a clean razor and digested in a .004M BrCl solution. After 45-60 minutes the Hg concentration was measured and deposition was determined relative to the surface area of the cut section of membrane. Blanks consisted of sections of membrane digested without deployment.

Total Hg dry deposition was determined using static water surfaces samplers, consisting of externally threaded 240m-Teflon jars containing a 0.004M BrCl solution to prevent re-volatilization or adsorption of deposited Hg. Two jars were filled to ~1 cm below the lip to maximize environmental exposure while protecting from wind. The samplers were covered such that they were open to the ambient environment and protected from direct sunlight and rainfall. For analysis, the jars were filled to a measured level and the Hg concentration determined. Blanks consisted of jars left capped during deployment.

Urban surface Hg deposition was measured on four sections of scavenged pavement and cement, which were cleaned with dilute HCl until blanks normalized. The sections were exposed and rinsed to determine rain-labile dry-deposited Hg. Surfaces were deployed under the same covering as the water surface samplers. Extraction fluid #1 from EPA Method 1311 (TCLP #1) was used as a rinse. TCLP #1 has a lower pH, 4.9, than that of average rainfall in Seattle, 5.2, yet consistent with average values for much of the Eastern United States[15]. Deposited Hg was calculated by rinsing the same surface area twice, with the second rinse used as a blank value. Reagent blanks were taken with each study period. The sections were rinsed to simulate a 10mm rain event, the average precipitation per sampling period was 13.3mm. The rinse solution was oxidized to 0.002M BrCl ~ 45 minutes prior to analysis.

High variability in the measured RGM deposition suggested the IX membrane digestion used might be incomplete. In order to determine an adequate digestion for IX membranes various acid strengths and digestion times were compared. A large section of membrane was exposed for 6 days then cut sections that were digested in duplicate in 1.12M HCl, 0.004M BrCl and 0.02M BrCl. An aliquot was taken of the digestion acid before the membrane was added and 0.25, 1, 4 and 24 hours after the start of digestion.

Analysis was performed on a Brooks Rand Model III CVAFS Mercury Analyzer or a CETAC M-8000 Mercury Autoanalyzer using a Brooks Rand Model III detector. Analysis protocols followed EPA Method 1631.

Results

All methods showed a positive correlation between Hg accumulation and sampling period duration (fig 1). The average total Hg deposition was 70.2 ± 27.6 μg/m^2/yr, the average urban surface Hg deposition was 1.36 ± 0.73 μg/m^2/yr, and RGM deposition averaged 8.6 ± 5.5μg/m^{2}yr (Fig 2). There was high variability within sampling periods; the average RSD for total deposition measurements was 20%, and ranged from 4 to 49%. The average RGM RSD was 24%, and ranged from 8 to 52%, though when 4 membranes were exposed instead of 2, the average RSD dropped to 13%. Urban surface deposition showed the highest variability with an average RSD of 44% and a range from 13 to 123%.

Fig 1. Exposure Duration and Accumulated Deposition

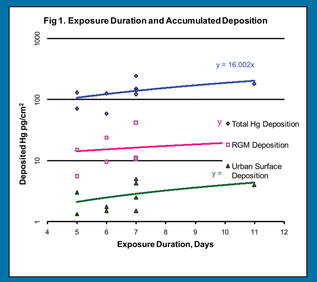
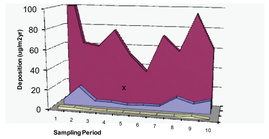


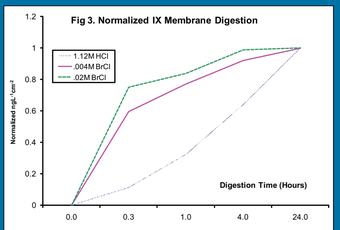
Fig 2. Deposition Rates



	1	2	3	4	5	6	7	8	9	10
Urban Surface Deposition	2.00	2.3	1.3	1.2	1.9	1.0	0.8	1.1	2.1	0.28
RGM Deposition	5.6	13.7	5.6	5.4	3.6	4.3	4.6	14.3	9.3	13.7
Total Hg Deposition	134.3	62.1	59.2	76.3	30.8	34.7	73.5	97.2	84.5	40.9

The comparative digestion of the IX membranes shows that only the 0.02M BrCl solution showed a leveling of Hg concentration, suggesting a complete digestion. The 0.004M BrCl digestion, as performed above did not show complete digestion at 4hours. This suggests that the actual RGM deposition is likely higher than suggested above. The 0.04M BrCl digestion for 0.75-1.0 hours appears to have removed ~80% of the deposited Hg, suggesting a true value closer to 10.8μg/m^2/yr.

Fig 3. Normalized IX Membrane Digestion



Values normalized to average 24 hr digestion concentration/ membrane surface area. The HCl digestion recorded a slightly lower recovery than the BrCl digestions. It appears that only the .02M BrCl achieved complete digestion.

RGM and total Hg deposition showed no correlation (fig 4). Urban surface deposition also did not correspond with RGM deposition but may correspond with total Hg deposition (fig 5, fig 6).

Fig 4. Total Hg and RGM Deposition

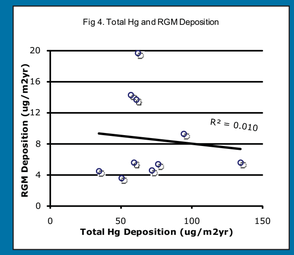


Figure 5. Total and Urban Surface Deposition

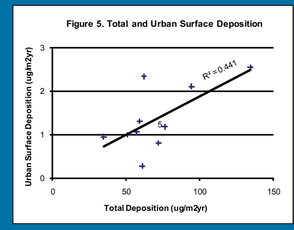
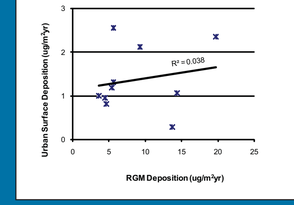
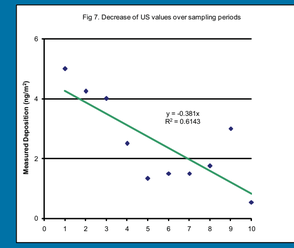


Figure 6. RGM and Urban Surface Deposition



It appears that urban surface deposition values decreased over the sampling period (fig 7). This may be an artifact of the sampling/rinsing methods used and would indicate that values obtained for urban surface deposition are underestimated.

Fig 7. Decrease of US values over sampling periods



Conclusion

All deposition fractions exhibited a high degree of variability; the standard deviation of total Hg deposition values was greater than 50% of the average recorded value. RGM deposition showed the highest variability. This could be due to the complex chemistry involved in determining RGM levels in urban environments and the subsequently high variability in atmospheric concentrations[16].

The value obtained here for average total Hg dry deposition is above the average value presented by many other studies. Sakata (2006)[17], using acidified water surface samplers recorded an average of 10.7μg/m^2/yr (vs. our measurement of 70.2 μg/m^{2}yr). However, 7 of the 10 sites sampled by Sakata (2006) were classified as "remote" or "background" thus, likely removed from Hg sources. Marsik (2007)[18] recorded an average value of 4.9μg/m^2/yr using a non-acidified water sampler, which is unable to capture Hg^0.

The values here may be an overestimate or may be atypically high due to the proximity of the sampling stand to sources of atmospheric Hg.

The average recorded value using the IX membranes to measure RGM is similar to previous studies. Lyman (2007) recorded an average IX membrane deposition of 9.0 ug/m^2/yr (vs. our measurement of 8.6 μg/m^2/yr) per deployment (0.9 to 400 μg/ m^2/yr), while Caldwell (2006) recorded an average value of 35.0 μg/ m^2/yr. Both of these deployments were in locations that are drier and receive more daily sunlight than the Pacific Northwest, factors that could lead to lower RGM scavenging and elevated RGM formation, respectively[19].

The average observed urban surface deposition value of 1.36 μg Hg/ m^2/yr (0.155ng/m^2/hr) is a fraction of the peak deposition level of 1.05 g/m^2/hr seen by Gabriel (2006). The values presented here are integrated over sampling periods of 5-11 days while Gabriel (2006) reported sampling periods of 10 minutes. The values presented here are unidirectional, accounting only for deposition. Gabriel (2006) recorded bi-directional flux including Hg^0 emissions, values that may underestimate gross Hg evasion as it fails to account for mercury deposition.

The measured urban surface deposition values may correlate with total deposition values, though there appears to be no correlation between urban surface deposition and RGM deposition. This suggests that other forms of Hg deposition, Hg^0 or particulate-bound Hg (HgP), dominate pavement deposition. This trend would not seem to be an artifact of the method presented, as RGM would be expected to be highly soluble in the TCLP solution. Considering the proximity to heavy industrial sites Hg(P) may be elevated.

There also appears to be no correlation between measured RGM deposition and total Hg deposition (Fig 4). This was not expected, as RGM values averaged 12% of the total Hg deposition, and RGM is often modeled to provide the majority of dry-deposited Hg[20]. This result could be due to the incomplete digestion performed for this study. In addition variability in the other forms of Hg deposition, specifically Hg(P), could have overwhelmed the RGM variability.

Based on this limited study it appears that dry deposition does significantly contribute to the amount of Hg in urban runoff. The city of Seattle has ~2.3x10^7 m^2 of roadway[21] and at the deposition rate of 1.36 μg/m^2/yr reported here, ~ 31.3g Hg would annually accumulate on city streets. If evenly distributed, the 0.96 m/yr, of rainwater that falls[22] on local roadways would experience an increase in Hg concentration of 1.31ng/L. This represents an increase of 19% over the local average rainfall concentration of 6.9ng/L[23]. The above values may be underestimated, as measured deposition consistently decreased over the study, perhaps due to the rinse/cleaning process altering the ability of the roadway surface to bind and release Hg.

Compared to the 7.9μg/ m^2/yr that wet deposition contributes to the Seattle area, this poster estimates that dry deposition accounts for an additional 15% of the total Hg deposition on concrete and asphalt surfaces.

Figure 8-10. Schematics of a device to allow for the clean handling and deployment of ion exchange membranes in the field. The first figure shows the two sheets between which the membrane will be placed in a clean environment. The holder is then slid into a drawer on a stand that allows for the membrane to be leveled and shielded from light and rain.

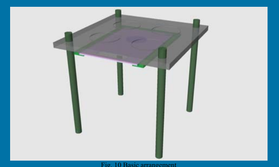


Fig. 10 Basic arrangement

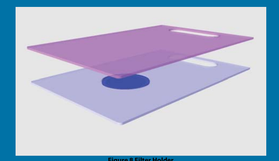


Figure 8 Filter Holder

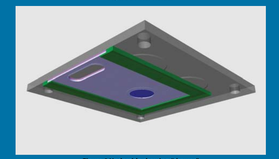


Figure 9 Underside showing "drawer"

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