Litterfall mercury dry deposition in the eastern USA

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ABSTRACT

Mercury (Hg) in autumn litterfall from predominately deciduous forests was measured in 3 years of samples from 23 Mercury Deposition Network sites in 15 states across the eastern USA. Annual litterfall Hg dry deposition was significantly higher (median 12.3 micrograms per square meter ($\mu g/m^2$), range 3.5–23.4 $\mu g/m^2$) than annual Hg wet deposition (median 9.6 $\mu g/m^2$, range 4.4–19.7 $\mu g/m^2$). The mean ratio of dry to wet Hg deposition was 1.3–1. The sum of dry and wet Hg deposition averaged 21 $\mu g/m^2$ per year and 55% was litterfall dry deposition. Methylmercury was a median 0.8% of Hg in litterfall and ranged from 0.6 to 1.5%. Annual litterfall Hg and wet Hg deposition rates differed significantly and were weakly correlated. Litterfall Hg dry deposition differed among forest-cover types. This study demonstrated how annual litterfall Hg dry deposition rates approximate the lower bound of annual Hg dry fluxes.

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1. Introduction

Most of the mercury (Hg) input to ecosystems is through atmospheric deposition. Atmospheric Hg comes from anthropogenic and natural sources and occurs in three species or fractions, in order of relative abundance – gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM, also called reactive gaseous Hg), and particulate-bound Hg (PBM), as summarized by Lindberg et al. (2007).

Atmospheric Hg can be transported to aquatic or terrestrial ecosystems through wet and dry deposition. Wet deposition is the transfer of atmospheric GOM and PBM to precipitation (rain, snow, sleet, hail, and fog). Large-scale monitoring of "open-field" Hg wet deposition in North America by the Mercury Deposition Network (MDN) has continued since 1996 (Prestbo and Gay, 2009); measurements of Hg dry deposition were not in the MDN as of 2011. More information about mercury-monitoring networks is in the Supplementary Data.

Dry deposition is the transfer of atmospheric Hg to vegetation, soil, water, and snow, controlled by the characteristics of the atmosphere, the surface, and the Hg species (Zhang et al., 2009). Although dry deposition occurs at a slower rate than that of wet deposition, it occurs continuously and at all times to all surfaces, unlike wet deposition, which is episodic. Hg dry deposition can be greater than Hg wet deposition in many ecosystems (Munthe et al., 2004; Sakata et al., 2006; Graydon et al., 2008). Forest canopies can uptake atmospheric Hg more rapidly than other landscapes due to their large leaf areas and rough surfaces. The dry-deposition velocity to forests for all three Hg species can be 2–5 times larger than to other vegetated or non-vegetated surfaces (Zhang et al., 2009).

Forest canopies are considered to be net sinks for atmospheric Hg (Grigal, 2002; Hartman et al., 2009). Translocation of Hg between tree roots and vegetation is virtually nonexistent (Lindberg et al., 1979; Cocking et al., 1995; Bishop et al., 1998; Cavallini et al., 1999). Thus, the Hg mass accumulated in forest canopies is believed to be largely atmospheric in origin (Mosbæk et al., 1988; Fleck et al., 1999; Ericksen et al., 2003; Frescholtz et al., 2003), from the interception of new Hg arriving above the canopy and from the uptake of reemitted and naturally emitted Hg from beneath the canopy. The Hg mass in litterfall represents a large portion of Hg dry deposition to forested landscapes of terrestrial ecosystems (Johnson and Lindberg, 1995; St. Louis et al., 2001; Grigal, 2002). More extensive reviews of Hg dry deposition are in the Supplementary Data.

Currently, Hg dry fluxes from the air can be estimated by three methods: litterfall/throughfall measurements, inferential modeling, and surrogate surface/passive samplers.

(1) Litterfall/throughfall measurements involve analysis of Hg concentrations in representative samples and determination of

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litterfall dry mass and throughfall volume. The Hg mass in litterfall and net throughfall constitute the Hg dry fluxes to forest landscapes measured in time scales from a few days for throughfall to a year for litterfall. Applications of this method were described by Demers et al. (2007), Grigal et al. (2000), Graydon et al. (2008), Rea et al. (1996, 2001, 2002), and St. Louis et al. (2001). Total litterfall consists of (a) leaves and needles, (b) woody material such as twigs and bark, and (c) reproductive bodies such as flowers, seeds, fruits, and nuts (Meier et al., 2006). In autumn, approximately 70–75% or more of total litterfall (called litterfall hereafter) consists of leaves in deciduous forests (Meier et al., 2006; Xiong and Nilsson, 1997). Throughfall includes Hg in precipitation, the Hg washed from foliage surfaces, plus Hg washed from tree branches and trunks (stemflow), which fall to the forest floor. Litterfall/throughfall measurements require relatively small investments in equipment, operation/maintenance, and data processing compared to the other two methods. Uncertainties are mostly associated with sample representativeness.

(2) Inferential modeling involves analysis of Hg species concentrations in air and determination of vertical deposition velocities with meteorological measurements. Hg dry fluxes can be inferred in time scales of the Hg species concentrations measurements (1–3 h), but longer time scales can be more practical. Applications of this method were described by Caldwell et al. (2006), Engle et al. (2010), Lyman et al. (2007), Marsik et al. (2007), Miller et al. (2005), and Seigneur et al. (2004). Uncertainties are associated with modeling natural processes.

(3) Surrogate surface/passive samplers are monitoring devices that capture dry fluxes of GOM and GEM, using ion-exchange membranes, static water surfaces, or other substrates. The devices typically integrate Hg dry fluxes in time scales of weeks or months. Applications of this method are described in Brumbaugh et al. (2000), Caldwell et al. (2006), Lai et al. (2011), and Lyman et al. (2007, 2010). Surrogate surface/passive sampler methods are still being developed and have not been used in large, long-term networks. Uncertainties include measurement interferences and simulation of natural surfaces and processes.

Previous investigations of litterfall Hg for estimating Hg dry deposition to compare with Hg wet deposition were spatially limited, single- and multi-year studies. Combined, they include locations in fewer than 10 sites in the USA, most of them in the Great Lakes region. Previous investigations of Hg in litterfall by Bushey et al. (2008), Demers et al. (2007), Ericksen et al. (2003), Grigal et al. (2000), Hall and St. Louis (2004), Hintelmann et al. (2002), Johnson and Lindberg (1995), Rea et al. (1996, 2002), Sheehan et al. (2006), and St. Louis et al. (2001) are summarized in the Supplementary Data. Broad agreement of the need for litterfall Hg monitoring outlined by Lindberg et al. (2007) and Mason et al. (2005) is documented in the Supplementary Data.

Our study of litterfall Hg dry deposition generated a multi-year set of autumn litterfall Hg data from a broader geographic area than the previous investigations combined. We used these data to compare litterfall Hg dry deposition to measurements and maps of Hg wet deposition, to maps of forest cover, and to models of Hg dry deposition.

2. Methods

Site selection for our study was a multi-step process that used land cover, land use, and site-specific information to find MDN sites with nearby forest for a study plot. More detail on site selection is in the Supplementary Data. Our study included 23 MDN sites in 15 states across a broad geographic area in the eastern USA (Supplementary Data

Table T1). Sites were in a wide variety of settings including the Great Lakes region, the Appalachian Highlands, the Atlantic Coastal Plain, and the Interior Plains. The study plots represented 6 forest-cover types and 3 forest-cover classes (Supplementary Data Table T2). The methods for identifying the forest-cover type and class are described in the Supplementary Data.

We obtained litterfall samples by sending sampling kits to MDN site operators who deployed and retrieved collectors, recorded field data, and shipped us the samples. We developed our methods with knowledge from previous investigations, but chose alternatives to the style and number of fixed collectors that are used in forest-ecology research to measure litterfall rates. Our study plots were 16 by 16 meters (m), representative of the forest type in the vicinity, and approximately 300 m or less from the MDN precipitation collector. MDN operators deployed 4 passive litterfall collectors at random locations in the study plot at the start of autumn leaf fall. The litterfall collector had a removable, plastic sample box, supported 3 centimeters (cm) off the ground by a wooden base. The sample box was 0.25 square meters (m^2) with a 0.6-μm nylon-mesh screen bottom to retain small particles while allowing water to drain. The side walls of the box could accumulate litterfall 15 cm deep to minimize losses during high winds.

The 4 collectors were deployed for approximately 6–8 weeks during September–December, depending on the latitude and altitude of the site, until the autumn litterfall at the site was determined by the operator to be complete. Operators allowed any frozen precipitation in the sample boxes to thaw and drain before they bagged each box and shipped them to us. Upon receipt, the 4 autumn litterfall samples per site were transferred to labeled bags, weighed, and frozen. Subsequently, these samples were freeze-dried, weighed, ground, and homogenized before subsamples were analyzed. The dry weight of each entire sample was recorded as the litterfall sample catch before subsampling and analysis. Sample catch is described further in the Results section, Total Sample Catch.

Trace-metal-free protocols were used to minimize sampling artifacts. Before a sample box was shipped to a site, it was pre-cleaned in a series of rinses with a detergent solution, deionized water, and diluted hydrochloric acid, dried in a HEPA work station, and placed in a new plastic bag. Personnel wore disposable gloves while processing the litterfall samples in a HEPA work station.

Sample analysis was done at the U.S. Geological Survey Hg Research Laboratory in Middleton, Wisconsin. Litterfall samples were analyzed by direct combustion, and Hg was quantified by cold-vapor atomic-absorbance detection comparable to EPA Method 7473 (U.S. Environmental Protection Agency, 2007). Composite samples for MeHg analysis were made by combining similar amounts of dried sample from the 4 collectors at a site. Composite samples for MeHg were digested with a potassium hydroxide–methanol mixture, using a standard operating procedure based on Xianchao et al. (2005) and analyzed by aqueous-phase ethylation and gas-chromatography separation with cold-vapor atomic-fluorescence detection (DeWild et al., 2002). Litterfall Hg and MeHg concentrations were reported on a sample dry weight basis with detection limits of 0.04 nanograms per gram (ng/g).

We report "annual litterfall Hg deposition at the study site" as mass per unit area, computed as the product of the mean Hg concentration in litterfall samples from the 4 collectors (called annual litterfall Hg concentration hereafter) and the sum of the autumn litterfall sample catch in the 4 collectors (in grams, called total sample catch hereafter). We converted annual litterfall Hg deposition units to micrograms per square meter (μg/m^2), the same as those for annual Hg wet deposition at an MDN site. Alternately, it is possible to compute the annual litterfall Hg mass in a single collector as the product of the litterfall Hg concentration and sample catch. The sum of the litterfall Hg mass in the 4 collectors can be in units of μg/m^2 because each collector had an area of 0.25 m^2. For most of the sites, the annual sum of the Hg mass in the 4 collectors was equal to or within 0.1 μg/m^2 of the annual litterfall Hg deposition computed as first stated, but this alternate method was not used for reasons explained in the Discussion section.

Nonparametric tests were used to compare data from different years, sites, and forest cover: the Wilcoxon rank-sum test (WRS), Kruskal–Wallis rank-sum (KWRS), and Tukey multiple comparison of medians (Tukey). A significance level of $\alpha = 0.05$ was used for the statistical tests, and a p-value less than 0.05 indicated a significant difference. Correlations were evaluated with the Spearman rank correlation coefficient (rho). Statistical methods are described in the Supplementary Data.

3. Results

3.1. Litterfall Hg concentrations

Hg concentrations in the litterfall samples were found to be reliable in several ways. Precision of the Hg analysis based on 40 laboratory replicate samples was a median 3.8% (relative percent difference (RPD), the absolute difference divided by the mean). Accuracy of the Hg analysis based on standard reference materials was a median 88% recovery of Hg and 119% recovery of MeHg. Measurement uncertainty for the Hg concentrations, based on the square root of the sum of squares for differences in pairs of