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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 (μg/m^2), range 3.5–23.4 μg/m^2) than annual Hg wet deposition (median 9.6 μg/m^2, range 4.4–19.7 μg/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 μg/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 ($\mu g/m^2$), 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 $\mu g/m^2$ 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 $\mu g/m^2$ 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

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laboratory duplicate samples was a factor of ±0.02 times the concentration. Variation in the Hg concentrations among the litterfall samples in the 4 collectors at each site was a median 7% (relative standard deviation (RSD), the standard deviation divided by the mean).

The annual litterfall Hg concentrations at the 23 study sites for 2007–2009 had a median of 41.1 ng/g and ranged from 21.4 to 62.7 ng/g (Supplementary Data Table T3). The highest (90th percentile) annual litterfall Hg concentrations, 53.4–62.7 ng/g, were recorded at 4 sites: IN21, IN34, MD08, and WI99. The precipitation-weighted annual Hg concentrations at the corresponding MDN sites for 2007–2009 had a median of 8.8 nanograms per liter (ng/L) and ranged from 4.9 to 15.6 ng/L (National Atmospheric Deposition Program, 2008, 2009, 2010). The highest (90th percentile) precipitation Hg concentrations, 11.1–15.6 ng/L, were recorded at 5 sites: IN21, IN26, MN16, MN98, and WI09. Correlations between annual litterfall Hg concentrations and annual Hg concentrations in precipitation for the study sites were not significant ($rho = -0.05$; $p = 0.729$).

MeHg was detected in all composite litterfall samples from 12 sites in 2007 (Supplementary Data Table T4). The median MeHg concentration was 0.35 ng/g and ranged from 0.24 to 0.70 ng/g. The same composite samples analyzed for MeHg were analyzed for Hg, and the percentage litterfall MeHg was a median 0.8% and ranged from 0.6 to 1.5%.

3.2. Total sample catch

Sample catch was more variable than Hg concentrations in the litterfall samples. Sample catch varied among the 4 collectors at a site by a median 14% RSD. Interannual variance of the total sample catch at a site was a median 43% RPD and was greater than 50% for 14 annual values.

We compared the total sample catch measured at our study sites with the autumn sample catch predicted for the latitude of our sites from equations by Lonsdale (1987) and Xiong and Nilsson (1997). The Xiong and Nilsson equation yields a predicted value on average 29% greater than the Lonsdale equation. We computed the predicted autumn sample catch as 70% of the annual value obtained from the equations (after Meier et al., 2006). The maximum total sample catch measured at our sites (Fig. 1) varied in agreement with the two predicted values for autumn litterfall sample catch. Our maximum total sample catch fell between the predicted values 35% of the time and was lower than the Xiong and Nilsson prediction twice as often as it was for the Lonsdale prediction.

We determined that 14 annual values for total sample catch were potentially incomplete because the interannual variance was more than 50% RPD, and each value was substantially less than the maximum measured catch and the predicted catch for the site. For some sites, the operator also reported deploying collectors after a storm that caused an unexpected early autumn leaf fall. For these 14 annual values, we substituted an adjusted total sample catch to compute litterfall Hg deposition. The adjusted total sample catch was either the maximum measured for the site or the value predicted with the Lonsdale equation, whichever was lowest (Fig. 1).

The total sample catch at the study sites for 2007–2009, including adjusted values, had a median of 280 g and ranged from 129 to 588 g (Supplementary Data Table T3). The highest (90th percentile) total sample catch amounts were 465–588 g, recorded at 6 sites: IN20, IN21, IN26, IN34, OH02, and TN11. Substitution of adjusted total sample catch reduced the interannual variance from a median 43 to 11% RPD and reduced the number of samples with interannual variance greater than 50% RPD from 14 to 2.

3.3. Litterfall Hg deposition

For the 3 years of the study, mean annual litterfall Hg deposition was significantly higher than mean annual Hg wet deposition ($p = 0.002$, WRS). Annual litterfall Hg deposition at the study sites for 2007–2009 had a median of 12.3 $\mu g/m^2$ and ranged from 3.5 to 23.4 $\mu g/m^2$ (Supplementary Data Table T3). The highest (90th percentile) annual litterfall Hg deposition rates, 19.7–23.4 $\mu g/m^2$, were recorded at 5 sites: IN20, IN26, IN34, OH02, and TN11. The annual Hg wet deposition at the corresponding MDN sites for 2007–2009 had a median of 9.6 $\mu g/m^2$ and ranged from 4.4 to 19.7 $\mu g/m^2$ (National Atmospheric Deposition Program, 2008, 2009, 2010). The highest (90th percentile) annual Hg-wet-deposition rates, 12.5–19.7 $\mu g/m^2$, were recorded at 4 sites: GA09, IN21, IN26, and WI31. Correlations were weak but significant between annual litterfall Hg deposition and annual Hg wet deposition for the sites ($rho = 0.38$; $p = 0.004$). The mean ratio of annual litterfall Hg deposition to Hg wet deposition was 1.3–1; the lowest ratio was 0.4–1 at GA09, MN16, and WI31 and the highest ratio was 2.6–1 at IN20. The sum of mean annual litterfall Hg (dry) deposition and mean annual Hg wet deposition (called total deposition hereafter) averaged 21.1 ($\mu g/m^2$)/yr, and 55% of this sum was dry deposition. The highest total deposition was 31 ($\mu g/m^2$)/yr at IN21, and the highest dry proportion of total deposition was 69% at OH02 (Fig. 2, Table 1).

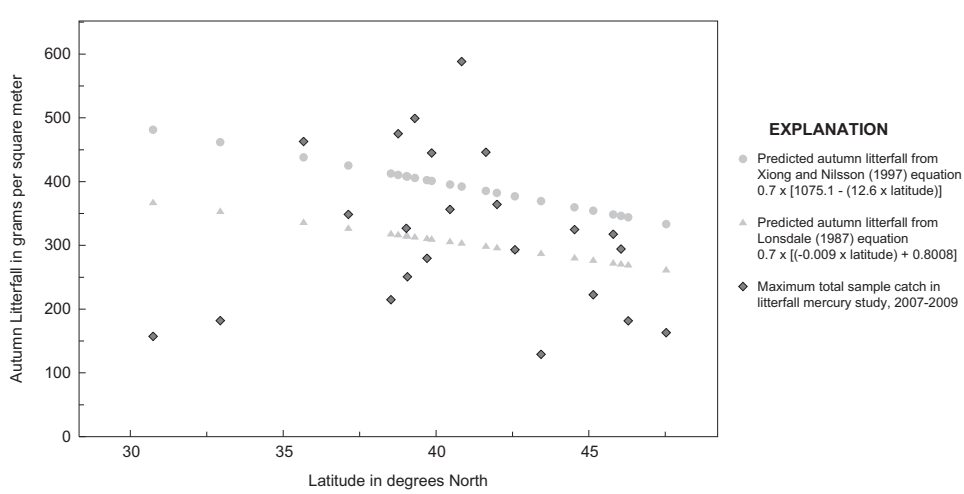

Fig. 1. Predicted and maximum measured autumn litterfall total sample catch for litterfall Hg study sites.

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3.4. Litterfall Hg, precipitation Hg, and forest cover

Study-site values of annual litterfall Hg concentrations, annual total sample catch, annual litterfall Hg deposition, annual Hg wet deposition, and annual total deposition differed significantly ($p < 0.01$, KWRS, Tukey) among forest-cover types and forest-cover classes (Supplementary Data Table T5). In all cases, values for the oak-hickory forest-cover type and deciduous forest class were higher than those for the aspen–birch type and the mixed and coniferous classes. Litterfall Hg deposition and total sample catch in the maple–beech–birch forest-cover type also were higher than those for the aspen–birch type.

Three-year mean litterfall dry deposition was 12.6–18.8 ($\mu g/m^2$)/yr for the 9 sites in the oak-hickory forest type and 9.9–15.3 ($\mu g/m^2$)/yr for the 4 nearby sites in the maple–beech–birch type (Supplementary Data Fig. F1). These 13 sites are located in an area extending from southern Wisconsin to Indiana, and Kentucky to Ohio, plus an area extending from Tennessee to through Pennsylvania to Vermont. Litterfall dry deposition was 3.8–7.8 ($\mu g/m^2$)/yr for 5 sites in the aspen–birch forest type where this forest type predominates in Wisconsin, Minnesota, and northern Michigan.

4. Discussion

4.1. Hg dry deposition

Our study found that sample catch had a greater influence on high litterfall Hg deposition than did litterfall Hg concentration, similar to the way precipitation depth can have a greater influence on high Hg wet deposition than Hg concentration (Risch et al., in this issue; Prestbo and Gay, 2009). For example, in the Results section, we listed the study sites with the highest (90th percentile) annual values of litterfall Hg concentration, total sample catch, and litterfall Hg deposition. Five sites – IN20, IN26, IN34, OH02, and TN1 – had the highest values of litterfall Hg deposition and total sample catch, while only IN34 also had the highest total Hg concentration.

Our results indicate that forest landscapes can have high Hg dry deposition even if Hg wet deposition is moderate. Annual litterfall Hg deposition and Hg-wet-deposition rates were statistically different and had a weak but significant correlation at our study sites. On average, annual litterfall Hg dry deposition exceeded Hg wet deposition. Of the study sites with the highest (90th percentile)

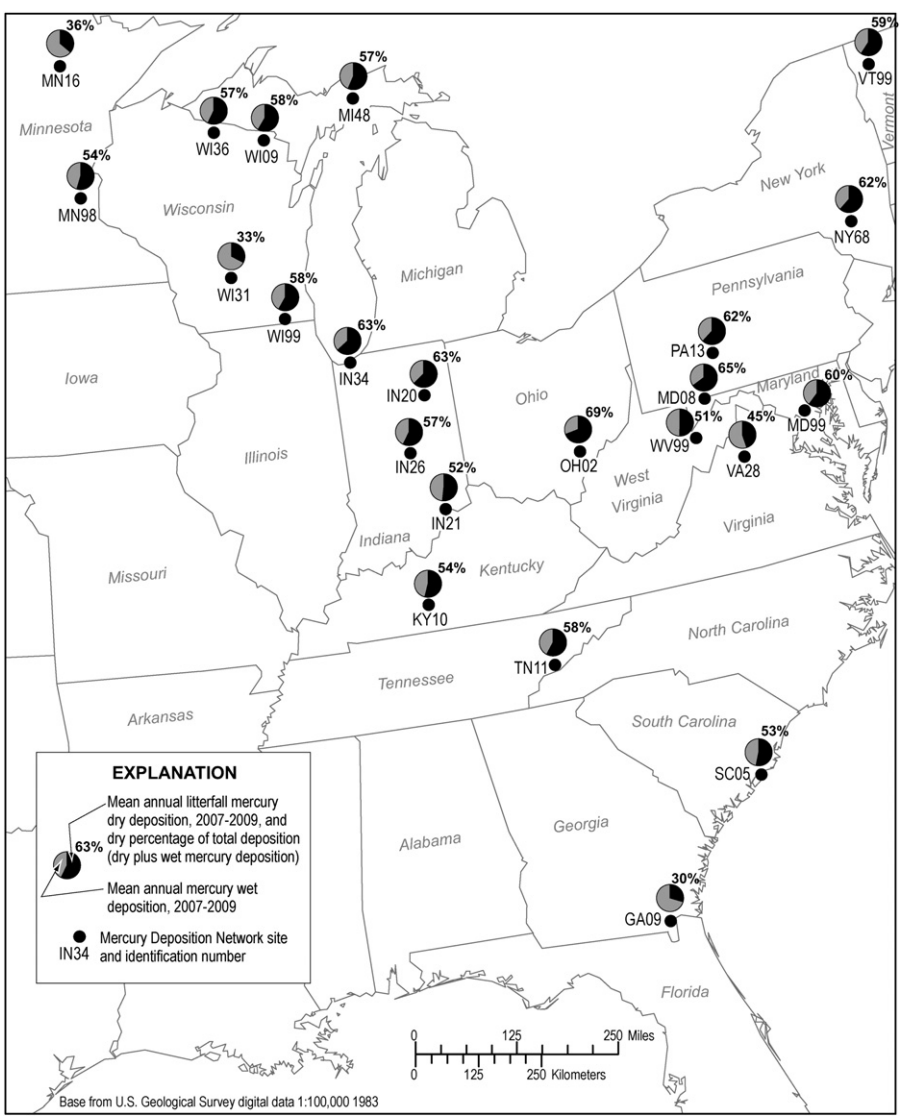

Fig. 2. Mean annual litterfall Hg dry and Hg wet deposition at litterfall Hg study sites, 2007–2009.

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Table 1
Mean annual litterfall Hg deposition and Hg wet deposition at litterfall study sites, 2007–2009. [MDN, Mercury Deposition Network (sites on Fig. 2); ($\mu g/m^2$)/yr, microgram per square meter per year, ± one standard deviation of the mean].

MDN site number	Litterfall Hg dry deposition [($\mu g/m^2$)/yr]	Hg wet deposition [($\mu g/m^2$)/yr]	Ratio of Hg dry to Hg wet deposition	Total dry plus wet Hg deposition[a] [($\mu g/m^2$)/yr]	Percent Hg dry deposition[b]
GA09	5.4 ± 0.1	12.9 ± 0.6	0.4	18.3	30
IN20	13.9 ± 5.2	8.3 ± 1.0	1.7	22.2	63
IN21	16.0 ± 1.2	15.0 ± 2.5	1.1	31.0	52
IN26	17.4 ± 5.5	13.0 ± 5.8	1.3	30.4	57
IN34	18.7 ± 5.7	10.9 ± 1.1	1.7	29.6	63
KY10	12.6 ± 0.1	10.8 ± 1.1	1.2	23.4	54
MD08	15.3 ± 2.1	8.3 ± 2.2	1.8	23.6	65
MD99	15.5 ± 1.0	10.3 ± 0.7	1.5	25.8	60
MI48	7.4 ± 0.4	5.7 ± 0.7	1.3	13.1	57
MN16	3.8 ± 0.4	6.7 ± 3.1	0.6	10.5	36
MN98	7.8 ± 0.3	6.5 ± 0.9	1.2	14.3	54
NY68	15.3 ± 1.0	9.6 ± 1.5	1.6	24.9	62
OH02	18.8 ± 2.8	8.4 ± 1.5	2.2	27.3	69
PA13	13.6 ± 4.0	8.4 ± 1.8	1.6	22.0	62
SC05	9.3 ± 0.2	8.2 ± 1.2	1.1	17.5	53
TN11	14.9 ± 4.7	10.9 ± 0.9	1.4	25.8	58
VA28	7.8 ± 0.8	9.6 ± 3.9	0.8	17.3	45
VT99	11.3 ± 1.8	7.8 ± 2.1	1.5	19.0	59
WI09	10.0 ± 1.1	7.1 ± 2.6	1.4	17.1	58
WI31	4.6 ± 1.0	9.5 ± 3.4	0.5	14.1	33
WI36	7.6 ± 1.4	5.7 ± 1.1	1.3	13.3	57
WI99	14.3 ± 1.3	10.3 ± 1.4	1.4	24.6	58
WV99	9.9 ± 0.3	9.7 ± 2.8	1.0	19.6	51

[a] Also called total deposition.
[b] Ratio of Hg dry to total deposition, as a percentage.

annual litterfall Hg deposition, only one site (IN26) also had the highest annual Hg wet deposition.

Annual litterfall Hg and Hg-wet-deposition rates showed a similarity in broad spatial patterns, even if they did not correlate closely at the study sites. Risch et al. (2011) mapped mean annual Hg wet deposition in the Great Lakes region for 2002–2008 using some of the same MDN sites in our study. Their maps showed a pattern of high Hg wet deposition in southern Wisconsin, Indiana, and Ohio, which coincides spatially with the area of high litterfall Hg deposition in our study. They also mapped low Hg wet deposition in northern Wisconsin, Minnesota, and northern Michigan, which coincides spatially with the area of low litterfall Hg deposition in our study. This comparison indicates that factors, such as Hg-emission sources, which affect Hg in precipitation, also may affect Hg in litterfall.

4.2. Variability in litterfall

Autumn intraseasonal differences in litterfall Hg concentrations and interannual differences in litterfall sample catch were observed. Autumn intraseasonal differences were found at all 9 sites where samples from two approximately equal sampling periods were collected in autumn 2007. The litterfall Hg concentrations were higher in the first half than the second half of autumn in 94% of the samples. The median difference for all samples was 22.0 ng/g. Autumn intraseasonal differences were not measured in 2008 and 2009. Although litterfall Hg concentrations did not differ year to year ($p = 0.887$, KWRS), significant interannual differences in total sample catch were identified ($p = 0.014$, KWRS, Tukey). Median total sample catch values were higher in 2007 (358 g) than in 2009 (255 g).

Our autumn intraseasonal differences in litterfall Hg concentrations and interannual differences in total sample catch were consistent with previous investigations. Tree species and vertical layers of the canopy and understory differ in their Hg content and in the rate and timing of when they drop their leaves (Bushey et al., 2008; Demers et al., 2007; and Grigal et al., 2000). Wind, precipitation, and temperature affect leaf mass and the rate and timing of leaf fall (Parker et al., 1989; Newman et al., 2006). In deciduous forest stands, a dominant species can account for nearly 70% of the leaf fall (Meier et al., 2006).

4.3. Method uncertainty

Our litterfall Hg study did not include a comparable study of throughfall Hg, Hg emitted from the soil, or Hg species concentrations in the air. Other investigators have used these measurements to quantify net Hg dry fluxes to the forest landscape (Demers et al., 2007; Engle et al., 2010; Graydon et al., 2008; Grigal et al., 2000; and Rea et al., 2001). Hg dry flux in net throughfall has been shown to be a minor but important part of the annual total for deciduous forests and at least equal to litterfall in mixed or coniferous forest classes. Therefore, the annual litterfall Hg dry deposition rates from our study approximate the lower bound of the annual Hg dry flux at a site.

The scope of our study was large-scale reconnaissance rather than an evaluation of method uncertainty, but our study was instructive for identifying factors to address in future litterfall Hg monitoring. By identifying the influence of total sample catch on litterfall Hg deposition estimates, we showed it is necessary to distinguish how natural factors and sample collection each affect sample catch. Aside from the absence of throughfall Hg data, the uncertainty of Hg dry deposition estimates based on litterfall Hg data from our study is tied to representativeness of the litterfall samples – how well our method provides unbiased quantification of a natural process. Method uncertainty in litterfall Hg concentration and sample catch is related to at least three factors: (1) sampling period and number of samples per site, (2) possible net Hg gains or losses between leaf fall and analysis, and (3) litterfall Hg deposition calculation.

(1) Our autumn sampling period probably represented the bulk of the atmospheric Hg accumulated in the deciduous forest canopy for the year, even though it did not include Hg in reproductive structures, leaves, needles, or woody debris that fell outside autumn. Adjusting the sampling period could increase the representative sample catch in at least two kinds of study plots. In mixed forest-class plots, the sample catch was lowest when the coniferous needle fall and deciduous leaf fall did not coincide. In deciduous forest-class plots dominated by oak species, the sample catch was lowest when the most of the oak leaf fall occurred after December. Our use of 4 collectors probably was adequate for our smaller study plots because Finotti et al. (2003) statistically determined a minimum of 5 litterfall collectors was needed for an 80 m by 80 m study plot. It is possible that more collectors could reduce the variability in the total sample catch at a site.
(2) We assumed that Hg gains and losses were not a substantial bias because the passive collectors we used separated the litterfall samples from the forest floor and allowed drainage after precipitation. Although we did not do it, an extensive experiment would provide a quantitative evaluation of any litterfall Hg concentration bias arising from net Hg gain or loss for samples in the passive collectors.
(3) Our method for computing annual litterfall Hg deposition reduced the effects of sample variance and minimized bias from adjusted values for sample catch. First, using mean litterfall Hg concentration compensated for high RSD values of 19–30% among the collectors at some sites. Second, using total

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sample catch compensated for high RSD values of 31–51% for unadjusted sample catch among the collectors at some sites. Third, adjusted total sample catch compensated for interannual RSD values greater than 50% at some sites. Bias was minimized by using adjusted sample catch based on the lower value of maximum measured or predicted sample catch. (If the predicted sample catch had been used instead of the measured total sample catch at all sites, the annual litterfall Hg deposition would have averaged 20% higher, increasing the mean for all sites combined from 12.2 to 12.8 $\mu g/m^2$. However, using all predicted values would cause an overall inconsistency because 56% of the annual values would have been between 0.3 and 8.9 $\mu g/m^2$ higher than what we measured and 39% would have been between 0.3 and 9.5 $\mu g/m^2$ lower.)

5. Conclusions

Our total deposition, in which dry deposition is based on litterfall Hg dry deposition, compares well to total deposition in two regional models. First, an assessment of modeled Hg dry deposition in the Great Lakes region by Zhang et al. (2011) showed that GOM plus PBM annual dry deposition rates are similar to those for GEM. They estimated net annual total deposition to the land surface south of the USA-Canada border was 5–40 $\mu g/m^2$, which matches the range for annual litterfall Hg deposition plus wet deposition at our study sites in this same area (8.6–39.2 $\mu g/m^2$, Supplementary Data Table T3). Notably, mean annual litterfall Hg deposition at nearly all our study sites closely match the GEM deposition (excluding reemission) in grid cells of the Zhang et al. model. Second, Miller et al. (2005) used estimates of Hg in autumn leaf fall to model net annual GEM dry deposition, and added calculated GOM plus PBM dry deposition with Hg wet deposition to map total deposition rates in rural areas of the northeastern USA. The mapped annual total deposition rates in their study (20–25 ($\mu g/m^2$)/yr) matched those from our sites in Pennsylvania, New York, and Vermont (19–24.9 ($\mu g/m^2$)/yr, Table 1).

Litterfall Hg data can be used to confirm Hg dry deposition rates obtained with inferential modeling. To inferentially model Hg dry deposition rates at a location, investigators multiply the atmospheric concentration of each Hg species times its vertical deposition velocity determined with high-resolution meteorological data collected nearby. Modeled dry deposition for GOM and PBM is relatively straightforward, but GEM dry deposition is either excluded or assigned high uncertainty because of the difficulty in modeling bi-directional fluxes that vary in different landscapes (Cohen et al., 2004; Engle et al., 2010; Lyman et al., 2007; Marsik et al., 2007; and Seigneur et al., 2004). For example, Engle et al. (2010) inferentially modeled annual dry deposition of GOM plus PBM at two sites they classified as rural inland (VA28) and coastal (SC05) that also were in our study. For a comparison of Hg dry deposition with Hg wet deposition, they estimated GEM deposition to be 3 times that for GOM plus PBM, and summed all species to get annual Hg dry deposition rates. Our mean annual litterfall Hg dry deposition rates generally confirmed their annual Hg dry deposition rates, although our values were higher – 7.8 compared to 6.0 $\mu g/m^2$ at VA28 and 9.3 compared to 7.6 $\mu g/m^2$ at SC05.

Litterfall Hg monitoring data may be helpful for understanding MeHg impacts on forest ecosystems. Others have stated the importance of whole-ecosystem measures of Hg deposition (Lindberg et al., 2007; Mason et al., 2005). Managers of public lands and forests need information about Hg inputs that impact water and wildlife (Sams, 2007). Regional assessments have expanded the inventories of MeHg-affected species and habitats beyond aquatic and piscivorous food webs, including relations to Hg in litterfall. For example, research has revealed songbirds and raptors with elevated MeHg exposure in terrestrial ecosystems (Evers, 2005; Rimmer et al., 2009). Our detections of MeHg in all litterfall samples are consistent with those of other investigators (Bushey et al., 2008; Ericksen et al., 2003; St. Louis et al., 2001) and may be related to MeHg exposure in some forest-wildlife species.

Our study provides a valuable reference for future litterfall monitoring in the MDN. Data for Hg in litterfall, such as the results from our study, may be used to constrain estimates of Hg dry deposition to forest landscapes, especially for large-scale atmospheric deposition models that include GEM. Routine litterfall monitoring at MDN sites could provide a long-term record with annual comparisons of dry and wet Hg deposition at a large number of locations.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.envpol.2011.06.005.

References

Bishop, K.H., Lee, Y.H., Munthe, J., Dambrine, E., 1998. Xylem sap as a pathway for total mercury and methylmercury transport from soils to tree canopy in the boreal forest. Biogeochemistry 40, 101–113.

Brumbaugh, W.G., Petty, J.D., May, T.W., Huckins, J.N., 2000. A passive integrative sampler for mercury vapor in air and neutral mercury species in water. Chemosphere Global Change Science 2, 1–9.

Bushey, J.T., Nallana, A.G., Montesdeoca, M.R., Driscoll, C.T., 2008. Mercury dynamics of a northern hardwood canopy. Atmospheric Environment 42, 6905–6914.

Caldwell, C.A., Swartzendruber, P., Prestbo, E., 2006. Concentration and dry deposition of mercury species in arid south central New Mexico (2001–2002). Environmental Science and Technology 40, 7535–7540.

Cavallini, A., Natali, L., Durante, M., Maserti, B., 1999. Mercury uptake, distribution and DNA affinity in durum wheat (*Triticum durum* Desf.) plants. Science of the Total Environment 243/244, 119–127.

Cocking, D., Rohrer, M., Thomas, R., Walker, J., Ward, D., 1995. Effects of root morphology and Hg concentration in the soil on uptake by terrestrial vascular plants. Water, Air, and Soil Pollution 80, 1113–1117.

Cohen, M., Artz, R., Draxler, R., Miller, P., Poissant, L., Niemi, D., Ratte, D., Deslauriers, M., Duval, R., Laurin, R., Slotnick, J., Nettesheim, T., McDonald, J., 2004. Modeling the atmospheric transport and deposition of mercury to the Great Lakes. Environmental Research 95, 247–265.

Demers, J.D., Driscoll, C.T., Fahey, T.J., Yavitt, J.B., 2007. Mercury cycling in litter and soil in different forest types in the Adirondack region, New York, USA. Ecological Applications 17 (5), 1341–1351.

DeWild, J.F., Olson, M.L., Olund, S.D., 2002. Determination of methylmercury by aqueous phase ethylation, followed by gas chromatographic separation with cold vapor atomic fluorescence detection. U.S. Geological Survey Open-File Report 01–445, 19.

Engle, M.A., Tate, M.T., Krabbenhoft, D.P., Schauer, J.J., Kolker, A., Shanley, J.B., Bothner, M.H., 2010. Comparison of atmospheric mercury speciation and deposition at nine sites across central and eastern North America. Journal of Geophysical Research 115, D18306. doi:10.1029/2010JD014064.

Ericksen, J.A., Gustin, M.S., Schorran, D.E., Johnson, D.W., Lindberg, S.E., Coleman, J.S., 2003. Accumulation of atmospheric mercury in forest foliage. Atmospheric Environment 37, 1613–1622.

Evers, D.C., 2005. Mercury Connections – The Extent and Effects of Mercury Pollution in Northeastern North America. In: Summary of 21 Papers in Ecotoxicology, vol. 14. Biodiversity Research Institute (1, 2).

Finotti, R., Freitas, S.R., Cerqueira, R., Vieira, M.V., 2003. A method to determine the minimum number of litter traps in litterfall studies. Biotropica 35 (3), 419–421.

Fleck, J.A., Grigal, D.F., Nater, E.A., 1999. Mercury uptake by trees – an observational experiment. Water, Air, and Soil Pollution 115, 513–523.

Frescholtz, T.F., Gustin, M.S., Schorran, D.E., Fernandez, G.C.J., 2003. Assessing the source of mercury in foliar tissue of quaking aspen. Environmental Toxicology and Chemistry 22, 2114–2119.

Graydon, J.A., St. Louis, V.L., Hintelmann, H., Lindberg, S.E., Sandilands, K.A., Rudd, J.W.M., Kelly, C.A., Hall, B.D., Mowat, L.D., 2008. Long-term wet and dry deposition of total and methyl mercury in the remote boreal ecoregion of Canada. Environmental Science and Technology 42, 8345–8351.

Grigal, D.F., Kolka, R.K., Fleck, J.A., Nater, E.A., 2000. Mercury budget of an upland-peatland watershed. Biogeochemistry 50, 95–109.

Grigal, D.F., 2002. Inputs and outputs of mercury from terrestrial watersheds – a review. National Research Council of Canada Environmental Reviews 10, 1–39.

Hall, B.D., St. Louis, V.L., 2004. Methylmercury and total mercury in plant litter decomposing in upland forests and flooded landscapes. Environmental Science and Technology 38, 5010–5021.

Hartman, J.S., Weisberg, P.J., Pillai, R., Ericksen, J.A., Kuiken, T., Lindberg, S.E., Zhang, H., Rytuba, J.J., Gustin, M.S., 2009. Application of a rule-based model to estimate mercury exchange for three background biomes in the continental United States. Environmental Science and Technology 43, 4989–4994.

Hintelmann, H., Harris, R., Heyes, A., Hurley, J.P., Kelly, C.A., Krabbenhoft, D.P., Lindberg, S., Rudd, J.W., Scott, K.J., St. Louis, V.L., 2002. Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the METAALICUS study. Environmental Science and Technology 36, 5034–5040.

Johnson, D.W., Lindberg, S.E., 1995. The biogeochemical cycling of Hg in forest – alternative methods for quantifying total deposition and soil emission. Water, Air, and Soil Pollution 80, 1069–1077.

Lai, S.O., Huang, J., Hopke, P.K., Holsen, T.M., 2011. An evaluation of direct measurement techniques for mercury dry deposition. Science of the Total Environment 409, 1320–1327.

Lindberg, S.E., Jackson, D.R., Huckabee, J.W., Janzen, S.A., Levin, M.J., Lund, J.R., 1979. Atmospheric emission and plant uptake of mercury from agricultural soils near the Almàden mercury mine. Journal of Environmental Quality 8, 572–578.

Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X., Fitzgerald, W., Pirrone, N., Prestbo, E., Seigneur, C., 2007. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. Ambio 36, 19–32.

Lonsdale, W.M., 1987. Predicting the amount of litterfall in forests of the world. Annals of Botany 61, 319–324.

Lyman, S.N., Gustin, M.A., Prestbo, E.M., Marsik, F.J., 2007. Estimation of dry deposition of atmospheric mercury in Nevada by direct and indirect methods. Environmental Science and Technology 41, 1970–1976.

Lyman, S.N., Gustin, M.S., Prestbo, E.M., 2010. A passive sampler for ambient gaseous oxidized mercury concentrations. Atmospheric Environment 44, 246–252.

Marsik, F.J., Keeler, G.J., Landis, M.S., 2007. The dry deposition of speciated mercury to the Florida Everglades – measurements and modeling. Atmospheric Environment 41, 136–149.

Mason, R.P., Abbott, M.L., Bodaly, R.A., Bullock, O.R., Driscoll, C.T., Evers, D., Lindberg, S.E., Murray, M., Swain, E.B., January 1, 2005. Monitoring the response to changing mercury deposition. Environmental Science and Technology, 14A–22A.

Meier, C.E., Stanturf, J.A., Gardiner, E.S., 2006. Litterfall in the hardwood forest of a minor alluvial floodplain. Forest Ecology and Management 234, 60–77.

Miller, E.K., Vanarsdale, A., Keeler, G.J., Chalmers, A., Poissant, L., Kamman, N.C., Brulotte, R., 2005. Estimation and mapping of wet and dry mercury deposition across northeastern North America. Ecotoxicology 14, 53–70.

Mosbæk, H., Tjell, J.C., Sevel, T., 1988. Plant uptake of airborne mercury in background areas. Chemosphere 17, 1227–1236.

Munthe, J., Bishop, K., Driscoll, C., Graydon, J., Hultberg, H., Lindberg, S., Matzner, E., Porvari, P., Rea, P., Schwesig, D., St Louis, V., Verta, M., 2004. Input–output of Hg in forested catchments in Europe and North America. RMZ-Materials and Geoenvironment 51, 1243–1246.

National Atmospheric Deposition Program, 2008. National Atmospheric Deposition Program 2007 Annual Summary. Illinois State Water Survey, Champaign, Ill., Data Report 2008–01.

National Atmospheric Deposition Program, 2009. National Atmospheric Deposition Program 2008 Annual Summary. Illinois State Water Survey, Champaign, Ill., Data Report 2009–01.

National Atmospheric Deposition Program, 2010. National Atmospheric Deposition Program 2009 Annual Summary. Illinois State Water Survey, Champaign, Ill, Data Report 2010–01.

Newman, G.S., Arthur, M.A., Muller, R.N., 2006. Above and below ground net primary production in a temperate mixed deciduous forest. Ecosystems 9 (3), 317–329.

Parker, G.G., O'Neill, J.P., Higman, D., 1989. Vertical profile and canopy organization in a mixed deciduous forest. Vegetatio 85 (1/2), 1–11.

Prestbo, E.M., Gay, D.A., 2009. Wet deposition of mercury in the U.S. and Canada, 1996–2005 – results and analysis of the NADP mercury deposition network (MDN). Atmospheric Environment 43, 4223–4233.

Rea, A.W., Keeler, G.J., Scherbatskoy, T., 1996. Litterfall in the Lake Champlain watershed – a short term study. Atmospheric Environment 30 (19), 3257–3263.

Rea, A.W., Lindberg, S.E., Keeler, G.J., 2001. Dry deposition and foliar leaching of mercury and selected trace elements in deciduous forest throughfall. Atmospheric Environment 36, 3453–3462.

Rea, A.W., Lindberg, S.E., Scherbatskoy, T., Keeler, G.J., 2002. Mercury accumulation in foliage over time in two northern mixed hardwood forests. Water, Air, and Soil Pollution 133, 49–67.

Rimmer, C.C., Miller, E.K., McFarland, K.P., Taylor, R.J., Faccio, S.D., 2009. Mercury bioaccumulation and trophic transfer in the terrestrial food web of a montane forest. Ecotoxicology. doi:10.1007/s10646-009-0443-x.

Risch, M.R., Gay, D.A., Fowler, K.K., Keeler, G.J., Backus, S.M., Blanchard, P., Barres, J.A., and Dvonch, J.T., 2011. Spatial pattern and temporal trends in mercury concentrations, precipitation depths, and mercury wet deposition in the North American Great Lakes Region, 2002–2008. Environmental Pollution, doi:10.1016/j.envpol.2011.05.030. in this issue.

Sakata, M., Marumoto, K., Narukawa, M., Asakura, K., 2006. Regional variations in wet and dry deposition fluxes of trace elements in Japan. Atmospheric Environment 40, 521–531.

Sams, C.E., 2007. Methylmercury contamination – impacts on aquatic systems and terrestrial species, and insights for abatement. In: Furniss, M., Clifton, C., Ronnenberg, K. (Eds.), Advancing the Fundamental Sciences – Proceedings of the Forest Service National Earth Sciences Conference. U.S.D.A. Forest Service Pacific Northwest Station, Portland, Oregon PNW-GTR-689.

Seigneur, C., Vijayaraghavan, K., Lohman, K., Karamchandani, P., Scott, C., 2004. Global source attribution for mercury deposition in the United States. Environmental Science and Technology 38, 555–569.

Sheehan, K.D., Fernandez, I.J., Kahl, J.S., Amirbahman, A., 2006. Litterfall mercury in two forested watersheds at Acadia National Park, Maine, USA. Water, Air, and Soil Pollution 170, 249–265.

St. Louis, V.L., Rudd, J.W., Kelly, C.A., Hall, B.D., Rolfhus, K.R., Scott, K.J., Lindberg, S.E., Dong, W., 2001. Importance of the forest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems. Environmental Science and Technology 35, 3089–3098.

U.S. Environmental Protection Agency, 2007. Method 7473 – Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry, Revision 0. http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/7473.pdf.

Xianchao, Yu, Chandrasekhar, T.M., Tate, K., 2005. Analysis of Methylmercury in Sediment and Tissue by KOH/CH3OH Digestion Followed by Aqueous Phase Ethylation. Florida Department of Environmental Protection (FDEP). HG-003–2.2.

Xiong, S., Nilsson, C., 1997. Dynamics of leaf litter accumulation and its effects on riparian vegetation – a review. Botanical Review 63 (3), 240–264.

Zhang, L., Wright, L.P., Blanchard, P., 2009. A review of current knowledge concerning dry deposition of atmospheric mercury. Atmospheric Environment 43, 5853–5864.

Zhang, L., Blanchard P., Johnson D., Dastoor, A., Ryzhkov, A., Lin, C.J., Vijayaraghavan, K., Gay, D., Holsen, T., Huang, J., Graydon, J., St. Louis, V.L., Castro, M.S., Miller, E.K., Marsik, F., Lu, J., Poissant, L., Pilote, M., Zhang, K.M., 2011. Assessment of modeled mercury deposition over the Great Lakes region. Environmental Pollution, doi:10.1016/j.envpol.2011.06.003. in this issue.

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