

Mercury Concentration and Deposition in Snow in Eastern Temperate North America

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ABSTRACT

Most published research evaluating total (wet+dry) mercury (Hg) deposition in eastern North America has been conducted during the growing season. However, recent research indicates that winter throughfall Hg deposition can be significant. We synthesized snow Hg concentration and deposition data collected at forested and open sites from 1989 - 2005 (14 studies) using various field methods. Mean snow Hg concentrations across years and locations ranged from 0.66 - 22.7 ng L⁻¹ (SD: 15 - 99%). Snow Hg deposition and concentration were consistently highest in conifer throughfall and lowest at open sites (no vegetation cover). These results suggest that the range of snow Hg deposition can be bracketed by sampling at two extremes: under conifer canopies and in open sites. Ratios of Hg under tree canopies versus open sites were 3:1 (conifers) and 2:1 (all forest types). Ratios of event throughfall to wet-only collections were 5:1 (conifers) and 4:1 (all forest types), exceeding the previously-reported overall average of throughfall to wet-only for the growing season. Future research should standardize snow Hg sampling methods to address volatilization and dry deposition. Mechanisms contributing to variability in snow Hg deposition could be assessed by measuring particulate Hg and examining interannual and spatial patterns.

Keywords: mercury; snow; throughfall; atmospheric deposition; forest type; Northeast

INTRODUCTION

Atmospheric deposition of mercury (Hg) is the largest input of this metal to rural, forested watersheds in temperate regions that are not influenced by natural geologic or point sources (Grigal, 2002). Total Hg deposition in forested landscapes is strongly influenced by dry deposition, which, in turn, is controlled by features such as vegetation type and topography (Nelson *et al.*, 2008, Johnson *et al.*, 2007, Miller *et al.*, 2005, Grigal, 2002, Kolka *et al.*, 1999, Lindberg *et al.*, 1994). The influence of landscape factors on Hg deposition has been the focus of research to improve spatially explicit models of Hg deposition to heterogeneous landscapes (e.g. Miller *et al.*, 2005).

Most published research evaluating the relationship between landscape factors and Hg deposition has been conducted during the growing season in temperate climates. Wet-only deposition of Hg typically is greater in the growing season than dormant season (Mast *et al.*, 2005, Guentzel *et al.*, 2001, Mason *et al.*, 2000, Glass and Sorenson, 1999, Scherbatskoy *et al.*, 1998).

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Also logistics and methods are more favorable during the growing season. However, in arctic sites (Ferrari *et al.*, 2005, Lahoutifard *et al.*, 2005, Schroeder *et al.*, 2005, Dommergue *et al.*, 2003, Lalonde *et al.*, 2003, 2002, Lindberg *et al.*, 2002) and temperate sites (Nelson *et al.*, 2008, Poulain *et al.*, 2007) the snowpack has been described as a dynamic system with respect to Hg. Hg can deposit to the snow surface from the atmosphere and re-emit from snowpack to the atmosphere. Depending on the study objective and methodology, snowfall and snowpack Hg burdens can represent 12-47% of annual total deposition of Hg (Nelson *et al.*, 2008) and 50% of Hg export in streamwater (Shanley *et al.*, 2002, Scherbatskoy *et al.*, 1998).

Though several studies in the region have sampled snow using varying methods, there are few citations in the literature on this subject, perhaps because the low snow Hg deposition is perceived as unimportant to mass balance studies. Snow Hg deposition and snowpack dynamics in North America have been studied in the Arctic in relation to Hg depletion events (e.g., Lindberg *et al.*, 2002) and in the Rocky Mountains at a transect of montane snowpack sites (Ingersoll *et al.*, 2005, Ingersoll *et al.*, 2002). These study regions have been well characterized with respect to Hg in snow. There is less information available about snow Hg deposition, and its subsequent transformations, in seasonally snow-covered areas in northeastern North America (Figure 1). Here we synthesize the available snow Hg concentration and deposition data from published research, theses, white papers, and unpublished data for temperate to sub-boreal, mixed deciduous and coniferous forested sites in eastern North America. We conclude by identifying information gaps about Hg deposition in snow for future research.

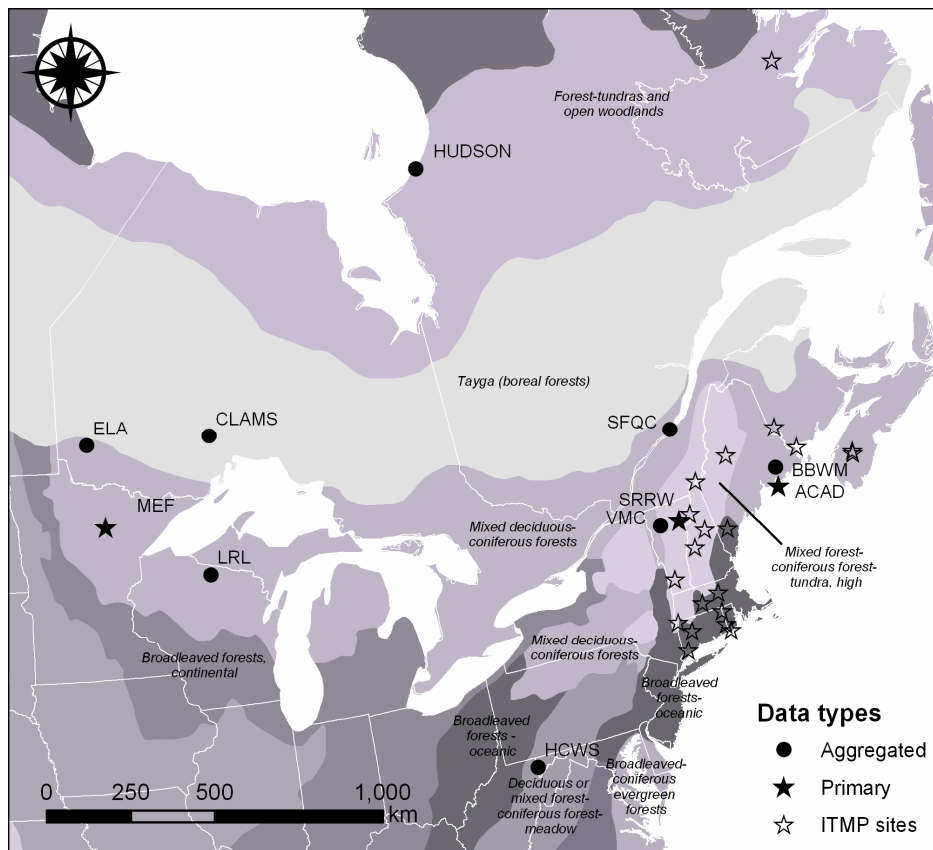


Figure 1. Map of snow Hg deposition research sites with published summary (aggregated) data and raw or unpublished (primary) data. Open stars show the locations of ITMP (International Toxics Monitoring Program, Haines 1994) transect survey sites. Sites are shown against a background of the Ecoregions of North America (Bailey 2001). Table 1 indicates full study names, references, and study details for each site abbreviation shown on this map.

MATERIALS AND METHODS

Rationale

Data from the Mercury Deposition Network (MDN), a rich data source that provides methodologically consistent Hg concentration and deposition data from across North America, are the basis of several studies on Hg deposition (e.g., Mason *et al.*, 2000, Miller *et al.*, 2005). MDN Hg data characterize wet-only deposition, because the instrumentation only collects samples of rain or snow during a precipitation event. The MDN network is currently the most comprehensive source of data publicly available to describe temporal variability in Hg deposition.

For this analysis, we were interested in characterizing total deposition of Hg via snow. Total atmospheric deposition is typically taken to represent wet plus dry deposition. At forested sites, dry deposition of Hg can equal or exceed wet-only deposition (Grigal, 2002). Many types of samples, each representing a different portion of total deposition, have been collected in atmospheric deposition research.

Throughfall and open sample collection with both bulk and wet-only sampling strategies are the focus of our analysis. The samples represent throughfall deposition if collected under full canopy for evergreen species and under twigs and branches for deciduous species, whereas the samples represent open deposition if collected in non-forested areas. Continuously collected samples represent bulk deposition, and samples collected only when it is actively raining or snowing represent wet-only deposition. We did not consider data from fog sampling (e.g., Ritchie *et al.*, 2006, Malcolm *et al.*, 2003), stemflow collection (e.g., Kolka *et al.*, 1999), or inferential studies that used measured air concentrations and deposition velocity (e.g., Caldwell *et al.*, 2006).

Data sources

Snow sampling methods: terminology

Snow sampling methodology varied among studies. Study characteristics, references, and site abbreviations are presented in Table 1. We identified three collection types in the data sources: open wet-only (not shown in Table 1, NADP/MDN 2006), open bulk (including lakeshore/lake center/clearing sampling), and bulk throughfall from below a forest canopy (Table 1). Within bulk throughfall, there were three sampling strategies: event sampling, cumulative snow buckets, and snowpack sampling (Table 1). Event samples were collected either in closed-bottom containers deployed before snowfall events and retrieved immediately following snowfall cessation (BBWM, ACAD) or were collected by scooping freshly-fallen snow from the snowpack surface (LRL, CLAMS, ELA, HCWS, SFQC). Though the methods differ slightly, the purpose of the sampling in each case was to characterize snow from a single storm during a short period of time. Cumulative snow bucket samples, collected only at ACAD to compare with other snow sampling methods, were collected in closed-bottom containers that were deployed for the entire snow-covered season and retrieved at the end of the winter. Snowpack samples represent an entire season's burden of Hg in snow and were collected by coring or excavating the entire, integrated snowpack overlying the soil surface, typically at the snowpack maximum (ITMP, VMC, MEF, ELA, HUDSON, and ACAD).

Primary Hg snow data: sources

We had the most detail from primary data sources that included forested watershed study sites in Maine (ACAD), Vermont (SRRW), and Minnesota (MEF) (Table 1). These primary data allowed: (1) an analysis of snow Hg data variability, and (2) an analysis of the relationship between site characteristics and Hg in snow, particularly as it relates to vegetation cover. We also analyzed wet-only Hg data reported for MDN collectors located near the research sites for the time periods that paralleled the watershed studies. We compared throughfall and open bulk Hg

Table 1. Characteristics, mean, and variability statistics for 14 studies that sampled snow Hg deposition or snowpack in northeastern temperate-sub-boreal forested areas in North America.

Site name	Site ID	State/ Province	Sample years	Site characterization	Collection type	Field procedure	Sampling strategy	Mean Hg (ng/L)	SD	Range	Number of		Sample period length (days)	Laboratory methods	Reference
											sites	obs.			
Little Rock Lake	LRL	WI	1989	Lake center	Open bulk	Lake surface snow	Event	6.00	0.9	~5-11	1	4	~14-21	Two stage gold amalg. w/AFS ^a	Fitzgerald et al. 1991
Bear Brook Watershed in Maine	BBWM	ME	1993	Clearing in mixed forest	Open bulk	Not given	Event	7.76	n/a	n/a	1	1	not given	Brooks-Rand model 2 CVAFS ^b	Abbott, 1994 ^e
Crab Lake	CLAMS	WI	1993	Lake center	Open bulk	Lake surface snow	Event	1.63	0.91	~0 - ~6	2	not given	not given	Two stage gold amalg. w/AFS ^a	Lamborg et al. 1995 ^f
International Toxics Monitoring Program	ITMP	CT RI MA VT NH ME NB NS NL	1994	Lakeshore	Open bulk	Teflon shovel- bag	Snowpack	4.78	4.22	1.30-20.4	21	21	not given	Brooks-Rand model 2 CVAFS	Haines, 1994 ^h
Experimental Lakes Area-Rawson Lake	ELA	ON	1994	Lake center	Open bulk	Lake surface snow	Event	2.61	1.26	0.95-4.60	1	7	7	CVAA ^b	St. Louis et al. 1995 ^g
Vermont Monitoring Cooperative	VMC	VT	1994	Clearing in mixed forest	Open bulk	10 cm x 10 cm column	Snowpack	1.8	n/a	n/a	1	1	110	CVAFS	Sherbatskoy et al. 1997
Marcell Experimental Forest	MEF	MN	1995	Mixed forest watersheds	Bulk throughfall	Snowpack pit	Snowpack	0.69	0.36	0.27-1.37	12	24	60	CVAFS ^b	Kolka 1996 ^h
Herrington Creek Watershed	HCWS	MD	1996-7	Hardwood forest watershed	Bulk throughfall	Snowpack pit	Event	22.7	11.4	not given	3	not given	7	CVAFS ^c	Castro et al. 2000
Sainte-Foy	SFQC	QC	2000	Lake center, suburban site	Open bulk	Lake surface snow	Event	3.05	3.02	0.20±0.2 - 12.4±1.0	1	135	1 (27 events)	Tekran CVAFS	Lalonde et al. 2002 ^{e,g}
Acadia Watersheds	ACAD	ME	2000	Mixed forest watersheds	Bulk throughfall	Bucket/bag	Cumulative	9.69	6.63	3.29-19.86	7	12	12-24 (mean=17)	Tekran CVAFS ^d	Johnson 2002 ^h
Sleepers River Research Watershed	SRRW	VT	2001	Mixed forest watershed	Bulk throughfall	Snowpack pit	Snowpack	10.6	5.59	4.45-20.6	7	7	107	CVAFS	Schuster et al. 2008 & Shanley pers. comm. ^h
Experimental Lakes Area-Lake 240	ELA	ON	2001	Lake center	Open bulk	Teflon Shovel- bottle	Event	1.42	0.52	0.72-2.84	1	30	1 (five events)	Tekran CVAFS	Lalonde et al. 2003 ^g
						Teflon Shovel- bottle	Snowpack	0.85	0.32	0.51-1.2	1	27	2 (four events)		
Hudson Bay	HUDSON	QC	2002	Open area	Open bulk	Snowpack pit	Snowpack	10.60	4.9	~4-15.4	1	4 depths	not given	CVAFS	Dommergue et al. 2003 ^e
Acadia Watersheds	ACAD	ME	2004-5	Mixed forest watersheds	Bulk throughfall	Teflon mini- cores	Snowpack	17.40	17.30	2.75-37.0	4	4	57	Tekran CVAFS ^d	Nelson et al. 2007 ^h
						Teflon-lined tube	Cumulative	4.73	2.63	2.49-10.0	7	7	91		
						Teflon-lined tube	Event	10.1	8.19	2.06-31.5	11	67	10-25 (mean=15)		

^aFitzgerald & Gill 1979; ^bBloom & Creelius 1983; ^cBloom & Fitzgerald 1988; ^dUS EPA 2002; ^e statistics calculated from data presented in a figure in paper; ^f the value 1.63 ng/L is “precipitation phase” or filtered, PHg for CLAMS was 6±4 pg m⁻³; ^g converted from pM as reported in publication; ^h statistics calculated from raw database, white paper, thesis/dissertation, or table in paper.

deposition to MDN wet-only Hg deposition at these sites to provide linkage to the well-established data base provided by the MDN international program. Primary data were also available from a transect of 21 open bulk deposition sites across the northeastern U.S. and eastern Canada (ITMP, Table 1). We calculated descriptive statistics from the raw data with SYSTAT statistical software (SYSTAT 2002).

Primary snow Hg data: methods

Open wet-only samples were collected by MDN at ACAD (NADP/MDN 2006), a VMC sampler at SRRW (Keeler *et al.*, 2005), or IVL-style collectors at MEF (Kolka *et al.*, 1999, Iverfeldt, 1991). Lakeshore sampling (ITMP) was performed in open areas by first removing the top 2 cm of snow, then excavating the snowpack to a depth 2 cm above the ground surface and placing the removed snow into Teflon bags. This ITMP sampling is similar to the methodology used for snowpack sampling at MEF, ACAD, and SRRW. The event sampling strategy at ACAD (Nelson *et al.*, 2008) involved snow collection in Teflon bag-lined cylinders within 24 hr of a snowfall event. Cumulative snow buckets at ACAD were lined with Teflon bags and collected once at the snowpack depth maximum (Nelson *et al.*, 2008) or twice, at the snow season midpoint and near snow season's end (Johnson, 2002). Snowpack was sampled with Teflon mini-corers at ACAD (Nelson *et al.*, 2008), snowpack pits sampled at the snowpack maximum at SRRW (Schuster *et al.*, 2008), or snowpack pits sampled twice during the snow season at MEF (Kolka, 1996).

Published summary snow Hg data

The published literature was searched for available summary data on snow Hg concentrations and deposition for northeastern North America. We were able to obtain data for 10 studies across the region of interest (Figure 1). Sampling methodology is described in detail in each original publication, and is summarized in Table 1 ("Field Procedure"). From published data sources, we extracted mean Hg concentration, standard deviation (SD) and range when available (Table 1).

Laboratory methods

Sample analysis methods for each published study are provided in the original references noted in Table 1. One study was unpublished at the time this manuscript was written: ITMP (Mower, pers. comm.). For ITMP, sampling materials and containers were prepared in a Class 100 clean bench, clean sampling protocols were followed, and samples were analyzed using a Brooks-Rand model 2 cold vapor atomic fluorescence spectrophotometer (Haines, 1994).

RESULTS AND DISCUSSION

Range of collection methods, frequencies, and snow sample volumes

The data used in this synthesis were drawn from 14 studies in the target region, and span a 16 year period from 1989 to 2005 (Table 1). All of the studies, except ITMP, represented a single, geographically localized research area or watershed. The ITMP sampled 21 sites across New England and eastern Canada. The data density was notably higher for New England (Figure 1), largely driven by the singular measurements of the ITMP program distributed across the region. Other locations represent observations that were replicated temporally and spatially.

Snow collection types and sampling strategies differed among the 14 studies we reviewed (Table 1). Samples were collected on lakeshores or lake centers in 6 studies, in clearings or open areas in 3 studies, and from forested sites in 5 studies. Snow samples taken on lakes or in clearings represent open bulk deposition, and samples collected under the forest canopy represent throughfall deposition. Of the 14 studies, 8 studies sampled one or more snow events, 7 studies sampled the snowpack, and 2 studies used the cumulative snow sampling strategy (ACAD). Two studies (ELA 2001, ACAD) used more than one sampling strategy. Field methods differed within collection types or sampling strategies. For example, at ACAD, event samples were collected with bag-lined tubes deployed between snow events (Nelson *et al.*, 2008), whereas in other studies

(e.g. CLAMS), event samples were collected by “scooping up newly fallen material into acid-cleaned wide-mouth jugs” (Lamborg *et al.*, 1995). More recently, Poulain *et al.* (2007) sampled snow under the forest canopy using automated wet-only collectors, another sampling strategy.

The number of sites and number of snow samples taken also varied widely among studies. Seven studies sampled one site only (LRL, BBWM, ELA 1994, VMC, SFQC, ELA 2001, HUDSON), 5 studies sampled 2-9 sites (CLAMS, HCWS, ACAD 2000, SRRW, ACAD 2004-2005 cumulative and snowpack), and 3 studies sampled 10 or more sites (ITMP, MEF, ACAD 2004-2005 event) (Table 1). At least 2 studies (BBWM, VMC) represented a single snow sample, but most studies replicated measurements either at the same site or by collecting at multiple sites. The length of time represented by the studies or the time that sampling equipment was deployed ranged from 1 day (some event samples) to a full winter season (110 days). Some studies did not report the date of equipment deployment or first permanent snowcover, so we were unable to calculate flux per unit time.

Snow Hg concentrations in the study region

Table 1 provides descriptive statistics on snow Hg concentrations for the northeastern U.S. and eastern Canada based on the data sources described above. Across all sites, the lowest mean snow Hg concentration was 0.69 ng L⁻¹ (MEF) and the highest mean snow Hg concentration was 22.7 ng L⁻¹ (HCWS). Snow Hg concentrations reported for all studies we summarized ranged 0.27-37.0 ng L⁻¹ (Table 1). Five of the six greatest mean values were collected in the eastern part of the study region, presumably downwind of major Hg emission sources (Driscoll *et al.*, 2006, VanArsdale *et al.*, 2005). Standard deviations of means averaged 59% and ranged from 15% to 99%.

Effects of collection type and sampling strategy on snow Hg concentration and deposition estimates

We focused on four studies (ITMP, MEF, SRRW, ACAD) to assess the effects of methodology and site characteristics on snow Hg concentration and deposition. Primary data were available for both Hg concentration and deposition for all studies, except ITMP, which did not report deposition, snow volumes, or water equivalent. ITMP was designed to examine spatial variability across a region and MEF, SRRW, and ACAD were designed to examine site-specific variability within a watershed. ACAD, SRRW, and MEF were true snow throughfall studies that sampled most sites under the forest canopy. ITMP gives a range of values for lakeshore samples. Sampling at ACAD occurred in two different years: 2000 and winter 2004-2005. Although reported independently, the sampling for both years was part of related research in small gauged watersheds (Nelson *et al.*, 2008, Johnson, 2002). The largest data ranges were reported for ACAD, SRRW, and ITMP.

Snow Hg concentration and deposition differed by collection type and sampling strategy (Figure 2). Median and ranges of Hg concentrations overlapped for open wet-only and lakeshore (ITMP) samples. Within the snow throughfall collection type, snowpack deposition (SRRW, MEF, ACAD) was less than event or cumulative deposition (ACAD 2000 and 2004-2005 data). Low vegetation may have contributed particles to one snowpack sample that contained a Hg concentration two times the mean for throughfall snowpack collections (Figure 2a). Other than this sample, the range of Hg concentrations was greatest for event sampling (ACAD 2004-2005). Snow Hg deposition estimates for cumulative and event sampling had similar ranges, perhaps influenced by the ACAD 2000 results, discussed below (Figure 2b).

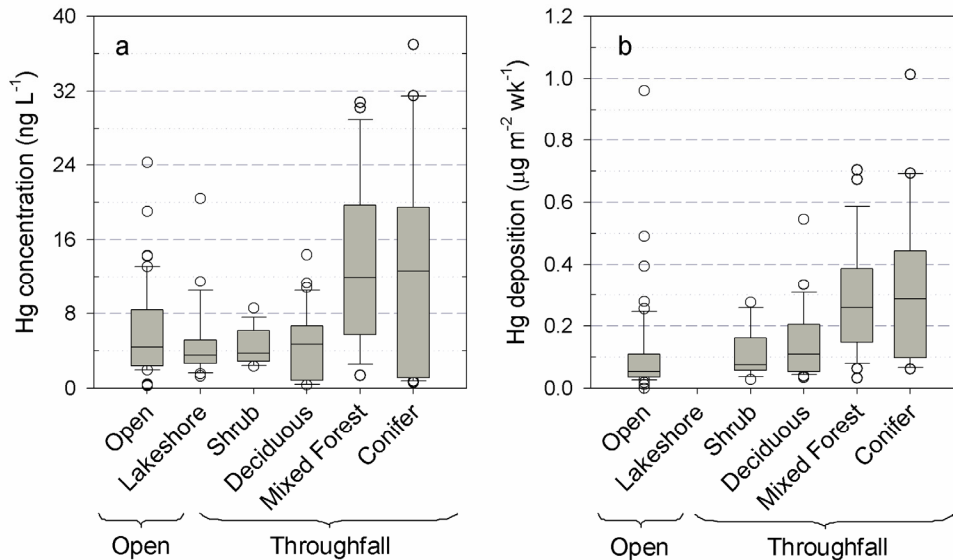


Figure 2. (a) Snow Hg concentration (ng L^{-1}) and (b) snow Hg deposition ($\mu\text{g m}^{-2} \text{wk}^{-1}$) at open sites and in throughfall, grouped by collection type, for SRRW, ACAD, MEF, and ITMP studies. Wet-only includes VMC (nearest MDN-type station to SRRW; Keeler *et al.*, 2005), MEF, ACAD 2000, ACAD 2004-2005; lakeshore includes ITMP; cumulative includes ACAD 2000, ACAD 2004-2005; snowpack includes SRRW, MEF, ACAD 2004-2005; event includes ACAD 2004-2005. See Table 1 for references and a description of collection methodology.

Only two studies – and only one primary data source - sampled snow Hg deposition in more than one year, and these studies used different collection methods. Cumulative snow Hg samples were collected at seven sites at ACAD in 2004-2005, and at seven sites in 2000 – some sites coincident with those sampled in 2004-2005. Concentrations of Hg in cumulative snow samples collected at these sites were greater in 2000 than in samples collected in 2004-2005 (Table 1). Concentrations may have been greater in 2000 because the shorter sampling period and more frequent sample collection would reduce loss of Hg through volatilization. Also, the 2004 study used dark-colored collection tubes that could have influenced snow characteristics and Hg volatilization. In addition, snowfall amount can vary annually. Differences in annual snowfall totals also could affect Hg concentrations in cumulative snow samples. Total snowfall reported at ACAD was 101 mm of precipitation during the 2000 snow Hg throughfall collection, whereas during the 2004-2005 snow throughfall collection study at ACAD, 322 mm of precipitation was reported (NADP/MDN 2006).

Though the limited data do not allow for mechanistic analysis of interannual variability, several factors could contribute to these different results between years sampled at ACAD: (1) more concentrated Hg with a lower snowfall amount; (2) changing atmospheric reservoirs of Hg; (3) changes in site-specific factors, such as vegetation type, or positioning of collectors; (4) differences in weather, such as higher temperatures that can affect volatilization; and (5) differences in sampling methodology. More research is necessary to fully understand mechanisms of interannual variability in snow Hg, though this analysis and Nelson *et al.* (2008) suggest that sampling methodology plays an important role in determination of snow Hg deposition. Comparison of three snow sampling methods throughout a single winter reveals that cumulative samples and snowpack emit Hg to the atmosphere, and snowpack can gain Hg from underlying soil and litter (Nelson *et al.*, 2008). Snow Hg burdens were two-thirds lower when snow was allowed more time to emit Hg to the atmosphere (Nelson *et al.*, 2008). Emission has been reported elsewhere (e.g., Lalonde *et al.*, 2002) emphasizing the influence of method selection on Hg snow deposition measurements.

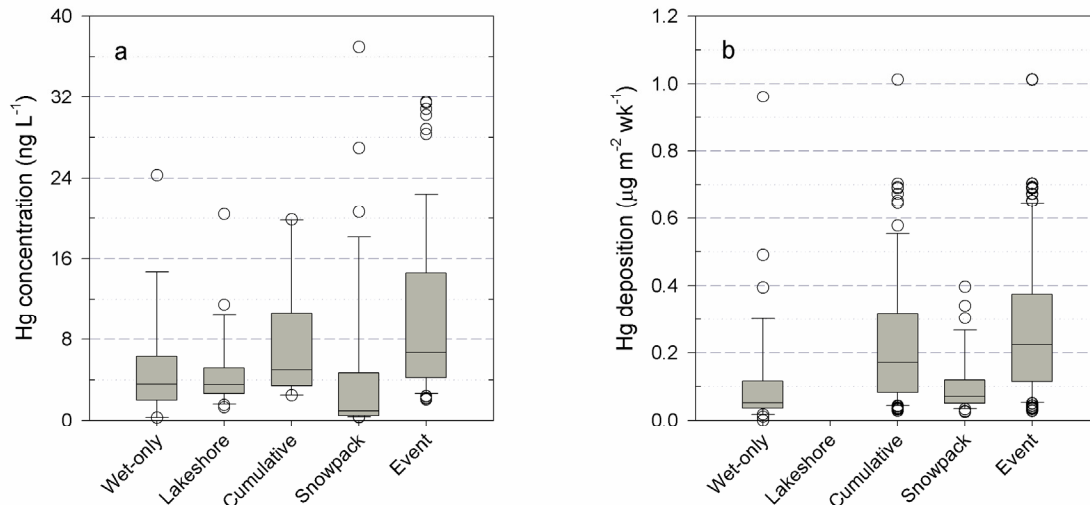


Figure 3. (a) Snow Hg concentration (ng L^{-1}) and (b) snow Hg deposition ($\mu\text{g m}^{-2} \text{wk}^{-1}$) at open sites and in throughfall, grouped by cover type, for SRRW, ACAD, MEF, and ITMP studies. For each site type, boxes include the following data: open - MEF, SRRW, VMC (nearest MDN-type station to SRRW; Keeler *et al.*, 2005), ACAD 2000, ACAD 2004-2005; lakeshore - ITMP; shrub - ACAD 2000, ACAD 2004-2005; deciduous - SRRW, MEF, ACAD 2000, ACAD 2004-2005; mixed forest - MEF, ACAD 2000, ACAD 2004-2005; and coniferous forest - SRRW, MEF, ACAD 2000, ACAD 2004-2005. See Table 1 for references and a description of collection methodology.

Effects of vegetation on Hg deposition and concentration estimates

It is possible to draw inferences about the effects of vegetation on snow Hg deposition by categorizing these data according to broad vegetation types (e.g., shrub, deciduous, mixed forest or coniferous) or site conditions (e.g., lakeshore or open). Three studies (ACAD, SRRW, MEF) considered vegetation type in their design. Hg concentrations and deposition (means, ranges) were similar among open, lakeshore, shrub, and deciduous sites. The greatest median and range of snow Hg concentrations and depositions were associated with coniferous and mixed forest sites (Figure 3). This finding is supported by more recent work at the Station de Biologie of the Université de Montréal, where snow Hg collected under mixed canopies was significantly greater than that collected under deciduous canopies or in the open (Poulain *et al.*, 2007). The ratio of bulk throughfall: open bulk (MEF, SRRW) or bulk throughfall: wet-only (ACAD) in snowpack samples at conifer sites was 3.4; at all forested sites (deciduous, mixed, and conifer), this ratio was 2.1. Using event deposition data for conifer sites (ACAD), bulk throughfall: wet only was 5.0 for conifer sites and 3.8 for all forested sites. These ratios exceed the previously reported overall average throughfall: wet deposition ratio of 1.8 for studies during the growing season in North America and Europe (Grigal, 2002), indicating that even during winter, Hg in snow throughfall is enhanced to the same or greater degree as during the growing season.

Throughfall flux of Hg during the growing season is affected by vegetation type (Nelson *et al.*, 2008, Johnson *et al.*, 2007, Poulain *et al.*, 2007, Grigal, 2002, Kolka *et al.*, 1999) because forests act as filters, scavenging dry particles and gases, including dry Hg, from the atmosphere (e.g., Weathers *et al.*, 2006, 2001, 1995, Grigal, 2002, Lovett *et al.*, 1999). This dry-deposited Hg is washed from the trees to the forest floor in subsequent rain events. Open, non-forested sites lack this additional enhancement mechanism for dry deposition. Deciduous forest canopies lose their leaves after the growing season, and only bare branches and leaves remain as accumulation surfaces. Canopy cover, estimated at ACAD with digital photos captured with a fisheye lens (ter Steege 1996) declined from 52% in summer to 23% in winter at deciduous sites, whereas canopy coverage at coniferous sites was 49% in summer and 40% in winter. Open and shrub sites at ACAD ranged 0-15% canopy cover throughout the year (Nelson, unpubl. data). Foliage is dramatically reduced and deciduous sites approach the coverage of open and shrub sites in winter. Our analysis suggests that investigators seeking to characterize snow Hg deposition in winter in

small watersheds need to sample only two types of sites: those with leaf cover in winter, and those without.

Special considerations for snow Hg sampling

Sample preservation

A consideration for sample preparation for Hg analysis is whether or not to preserve samples in the container in which they were collected. Hg has a tendency to adhere to container walls until preserved, so if aliquots were poured off prior to preservation, Hg concentrations could be artificially low (Lalonde *et al.*, 2001). Based on available documentation, six studies preserved samples in the collection container prior to decanting (ACAD 2004-2005, MEF, ELA 2001, VMC, SRRW, LRL), whereas three studies did not preserve prior to decanting (ACAD 2000, ITMP, ELA 1994), and five studies did not specify sample preparation method (HCWS, HUDSON, SFQC, CLAMS, BBWM). Low Hg concentrations in samples decanted prior to preservation at ACAD 2000, ITMP and ELA 1994 may be low due to sample handling rather than low deposition rates.

To filter or not to filter?

Snow samples were filtered to separate particulate Hg (PHg) from dissolved Hg in three studies (CLAMS, VMC, and SRRW). Poissant *et al.*, (2004) used a 0.1-2.5 μm pore size to represent PHg, whereas PHg mass median diameters of 0.61 μm (Milford and Davidson 1985) and 0.80 μm (Keeler *et al.*, 1995) also have been reported. CLAMS and VMC isolated PHg with 0.22 μm filters, and SRRW used 0.4 μm polycarbonate filters. PHg in snow sampled at CLAMS, which we calculated as the difference between unfiltered and filtered samples, was 0.70 ng/L, or 49% of the total Hg flux in throughfall (Lamborg *et al.*, 1995). Dissolved Hg in snowmelt lysimeters at VMC averaged 4.8 ng/L, representing 50% of total Hg (Scherbatskoy *et al.*, 1997). PHg estimated at SRRW ranged from 2.44 – 17.8 ng/L, or 54%-89% of the total Hg flux in throughfall. These studies indicate that at least half of the Hg in snow is ‘particulate’, although the proportion is affected by researcher’s choice of filter size.

The form of Hg deposited in winter could vary as compared to other seasons. PHg in ambient air was greater in winter than in other seasons in Michigan (Keeler *et al.*, 1995) and in Vermont (Scherbatskoy *et al.*, 1998). Hg speciation and its transformations in the atmosphere are complex processes, and are not the subject of this analysis. However, a brief discussion follows to highlight the need for more research on Hg speciation in winter deposition.

Although most of the Hg emitted and in the atmosphere is in the form of gaseous elemental Hg (GEM), most of the Hg that is washed out by precipitation and deposited in wet or dry deposition is generally thought to be reactive gaseous Hg (RGM) or PHg (Keeler *et al.*, 1995, Lindberg *et al.*, 1998, Mason and Sheu 2002, Swartendruher *et al.*, 2006). Once deposited, GEM re-emits rapidly (Poissant *et al.*, 2004). Although RGM and PHg have been thought to be deposited primarily near point sources, recent research has found these forms in remote areas (Lindberg *et al.*, 2002) and in higher than expected concentrations in the free troposphere (Swartendruher *et al.*, 2006). Data from this synthesis suggest that Hg in snow throughfall could be dominated by PHg, and that total deposition of Hg under forest canopies is greater than at open sites. It is unknown whether binding to particulates, especially to organic carbon in snow, can inhibit evasion of Hg from the snowpack, and could therefore determine whether this particulate form of Hg is the source of Hg in snowmelt events (Shanley *et al.*, 2002).

CONCLUSIONS

Across a broad geographic region and in temporally discontinuous studies during 1989-2005, median snow Hg deposition and concentration were consistently greatest in bulk throughfall at conifer sites and least at open bulk sites without vegetation cover, consistent across differences in field and laboratory methods. These results suggest that sampling at conifer and open sites will

capture the range of snow Hg deposition and concentrations expected at a site. Standardizing sample collection and analysis methods, coordinating sampling across a broad geographic range and in forested and non-forested settings, and extending sampling to capture intra- and inter-annual variability and long-term trends will reveal temporal and spatial variability in snow Hg deposition and concentration estimates. Preserving samples in the original collection container is essential to minimize loss of Hg to the sample container. Three studies suggest that PHg may comprise the largest fraction of Hg in snowpack samples; further research to speciate Hg in snow at temperate sites would complement studies of Hg dynamics in snow at Arctic and sub-Arctic sites. Given that the ratios of Hg in throughfall to open deposition in snowpack (ratio=2.1) and throughfall to wet-only deposition in snow events (ratio=3.8) were greater than the overall average growing season throughfall to wet deposition ratio (1.8) (Grigal, 2002), we conclude that enhancement by forest canopies is at least as important during winter months as during the growing season. Although some of the Hg literature explains low winter deposition by suggesting that snow could be a poorer scavenger of Hg than rain, snow has a higher surface area to volume ratio and a lower settling velocity than rain (Schemenauer *et al.*, 1981) that likely makes it a more efficient scavenger. Snow Hg deposition contributions to total annual Hg deposition often are estimated to be relatively low. It is plausible that these low estimates reflect re-emission of deposited Hg from the snowpack resulting from the selected sampling method rather than truly low Hg deposition.

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REFERENCES

- Abbott CC. 1994. The effects of watershed acidification on mercury uptake in brook trout (*Salvelinus fontinalis*). M.S. Thesis, University of Maine, Orono, ME, 55 pp.
- Bailey RG. 2001. Ecoregions of North America. Available online at [http://www.fs.fed.us/institute/ecoregions/eco_download.html] from the U.S. Forest Service, Inventory and Monitoring Institute, Ecoregions Center, Fort Collins, Colorado, USA.
- Bloom NS, Creelius EA. 1983. Determination of mercury in seawater at subnanogram per liter levels. *Marine Chemistry* 14: 49-59.
- Bloom NS, Fitzgerald WF. 1988. Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold vapour atomic fluorescence detection. *Analytica Chimica Acta* 208: 151-161.
- Caldwell CA, 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 (24): 7535 -7540.
- Castro MS, Scudlark JR, Church TM, Mason RP. 2000. Input-Output Budgets of Major Ions, Trace Elements and Mercury for a Forested Watershed in Western Maryland. Report to Maryland Department of Natural Resources, Power Plant Research Program, Annapolis, MD 21401, Report number PPAD-AD-1, July 2000, 72 pp.
- Dommergue A, Ferrari CP, Gauchard P-A, Boutron CF, Poissant L, Pilote M, Jitaru P, Adams FC. 2003. The fate of mercury species in a sub-arctic snowpack during snowmelt. *Geophysical Research Letters* 30: 1621-1624.
- Driscoll CT, Han Y-J, Chen CY, Evers DC, Lambert KF, Holsen TM, Kamman NC, Munson RK. 2007. Mercury contamination in forest and freshwater ecosystems in the Northeastern United States. *BioScience* 57 (1): 17-28.
- Ferrari CP, Gauchard P-A, Aspino K, Dommergue A, Magand O, Bahlmann E, Nagorski S, Temme C, Ebinghaus R, Steffen R, Steffen A, Banic C, Berg T, Planchon F, Barbante C,

- Cescon P, Boutron CF. 2005. Snow-to-air exchanges of mercury in an Arctic seasonal snow pack in Ny-Alesund, Svalbard. *Atmospheric Environment* 39: 7633-7645.
- Fitzgerald WF, Gill GA 1979. Subnanogram determination of mercury by two-stage gold amalgamation and gas phase detection applied to atmospheric analysis. *Analytical Chemistry* 51 (11): 1714-1720.
- Fitzgerald WF, Mason RP, Vandal GM. 1991. Atmospheric cycling and air-water exchange of mercury over mid-continental lacustrine regions. *Water, Air, and Soil Pollution* 56: 745-767.
- Glass GE, Sorenson JA. 1999. Six-year trend (1990-1995) of wet mercury deposition in the Upper Midwest, USA. *Environmental Science and Technology* 33: 3303-3312.
- Grigal DF. 2002. Inputs and outputs of mercury from terrestrial watersheds: a review. *Environmental Reviews* 10: 1-39.
- Guentzel JL, Landing WM, Gill GA, Pollman CD. 2001. Processes influencing rainfall deposition of mercury in Florida. *Environmental Science and Technology* 35: 863-873.
- Haines TA. 1994. Mercury in snow for the International Toxics Monitoring Program, 1994. Report to Maine Department of Environmental Protection, 3 pp. plus electronic data appendices.
- Ingersoll GP, Turk JT, Mast MA, Clow DW, Campbell DH, Bailey ZC. 2001. Rocky Mountain Snowpack Chemistry Network: History, Methods, and the Importance of Monitoring Mountain Ecosystems. USGS Open File Report 01-466, 14 pp.
- Ingersoll GP, Mast MA, Nanus L, Manthorne DJ, Handran HH, Hulstrand DM, Winterringer J. 2005. Rocky Mountain Snowpack Chemistry at Selected Sites, 2003. USGS Open File Report 2005-1332, 17 pp.
- Iverfeldt A. 1991. Mercury in forest canopy throughfall water and its relation to atmospheric deposition. *Water, Air, and Soil Pollution* 56: 553-564.
- Johnson KB. 2002. Fire and its effects on mercury and methylmercury dynamics for two watersheds in Acadia National Park, Maine. M.S. Thesis, University of Maine, Orono, ME, 72 pp.
- Johnson KB, Haines TA, Kahl JS, Norton SA, Amirbahman A, Sheehan KD. 2007. Controls on Mercury and Methylmercury Deposition for Two Watersheds in Acadia National Park, Maine. *Environmental Monitoring and Assessment* 126 (1-3): 55-67.
- Keeler G, Glinsorn G, Pirrone N. 1995. Particulate mercury in the atmosphere: Its significance, transport, transformation and sources. *Water, Air, and Soil Pollution* 80 (1-4): 159-168.
- Keeler GJ, Gratz L, Al-Wali K. 2005. Influences on the Long-term Atmospheric Mercury Wet Deposition at Underhill, Vermont. *Ecotoxicology* 14: 71-83.
- Kolka RK. 1996. Hydrologic transport of mercury through forested watersheds. Ph.D. Thesis, University of Minnesota, St. Paul, MN, 265 pp.
- Kolka RK, Nater EA, Grigal DF, Verry E.S. 1999. Atmospheric inputs of mercury and organic carbon into a forested upland/bog watershed. *Water, Air, and Soil Pollution* 113 (1-4): 273-294.
- Lahoutifard N, Sparling M, Lean D. 2005. Total and methyl mercury patterns in Arctic snow during springtime at Resolute, Nunavut, Canada. *Atmospheric Environment* 39: 7597-7606.
- Lalonde JD, Amyot M, Kraepiel AML, Morel FMM. 2001. Photooxidation of Hg(0) in artificial and natural waters. *Environmental Science and Technology* 35 (7): 1367-1372.
- Lalonde JD, Poulain AJ, Amyot M. 2002. The role of mercury redox reactions in snow-to-air mercury transfer. *Environmental Science and Technology* 36: 174-178.
- Lalonde JD, Amyot M, Doyon M-R, Auclair J-C. 2003. Photo-induced Hg(II) reduction in snow from the remote and temperate Experimental Lakes Area (Ontario, Canada). *Journal of Geophysical Research* 108: 4200-4207.
- Lamborg CH, Fitzgerald WF, Vandal GM, Rolfhus KR. 1995. Atmospheric mercury in northern Wisconsin: Sources and species. *Water, Air, and Soil Pollution* 80 (1-4): 189-198.
- Lindberg SE, Owens JG, Stratton WJ. 1994. Application of Throughfall Methods to Estimate Dry Deposition of Mercury. In *Mercury as a Global Pollutant: Integration and Synthesis*, Watras CJ, Huckabee JW (eds). Lewis Publishers: Boca Raton; 261-271.
- Lindberg SE, Stratton WJ. 1998. Atmospheric Mercury Speciation: Concentrations and Behavior of Reactive Gaseous Mercury in Ambient Air. *Environmental Science and Technology* 32: 49-57.

- Lindberg SE, Brooks S, Lin C-J, Scott KJ, Landis MS, Stevens RK, Goodsite M, Richter A. 2002. Dynamic oxidation of gaseous mercury in the Arctic troposphere at Polar sunrise. *Environmental Science and Technology* 36: 1245-1256.
- Lovett GM, Thompson AW, Anderson JB, Bowser JJ. 1999. Elevational patterns of sulfur deposition at a site in the Catskill Mountains, New York. *Atmospheric Environment* 33: 617-624.
- Malcolm EG, Keeler GJ, Lawson ST, Sherbatskoy TD. 2003. Mercury and trace elements in cloud water and precipitation collected on Mt. Mansfield Vermont. *Journal of Environmental Monitoring* 4: 584-90.
- Mason RP, Lawson NM, Sheu GR. 2000. Annual and seasonal trends in mercury deposition in Maryland. *Atmospheric Environment* 34: 1691-1701.
- Mason RP, Sheu G-R. 2002. Role of the ocean in the global mercury cycle, *Global Biogeochemical Cycles* 16 (4): 1093. DOI:10.1029/2001GB001440.
- Mast MA, Campbell DH, Krabbenhoft DP, Taylor HE. 2005. Mercury transport in a high-elevation watershed in Rocky Mountain National Park, Colorado. *Water, Air, and Soil Pollution* 164: 21-42.
- Milford JB, Davidson CI. 1985. The sizes of particulate trace elements in the atmosphere-a review. *Journal of the Air Pollution Control Association* 35 (12): 1249-60.
- Miller E, Vanarsdale A, Keeler G, Chalmers A, Poissant L, Kamman N, Brulotte R. 2005. Estimation and Mapping of Wet and Dry Mercury Deposition Across Northeastern North America. *Ecotoxicology* 14: 53-70.
- NADP/MDN. 2006, 2007. National Atmospheric Deposition Program (NRSP-3)/Mercury Deposition Network (2001). NADP Program Office, Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL 61820. Available: <http://nadp.sws.uiuc.edu/nadpdata>.
- Nelson SJ, Johnson KB, Weathers KC, Loftin CS, Fernandez IJ, Kahl JS, Krabbenhoft DP. 2008. A comparison of winter mercury accumulation at forested and no-canopy sites measured with different snow sampling techniques. *Applied Geochemistry* 23(3): 384-398.
- Poissant L, Pilote M, Xu X, Zhang H, Beauvais C. 2004. Atmospheric mercury speciation and deposition in the Bay St. François wetlands. *Journal of Geophysical Research* 109: D11301. DOI:10.1029/2003JD004364.
- Poulain AJ, Roy V, Amyot M. 2007. Influence of temperate mixed and deciduous tree covers on Hg concentrations and photoredox transformations in snow. *Geochimica et Cosmochimica Acta* 71:2448-2462. DOI: 10.1016/j.gca.2007.03.003.
- Ritchie CD, Richards W, Arp PA. 2006. Mercury in fog on the Bay of Fundy (Canada). *Atmospheric Environment* 40: 6321-6328.
- Schemenauer RS, Berry MO, Maxwell JB. 1981. Snowfall Formation. In *Handbook of Snow*, Gray DM, Male DH (eds). Pergamon Press Inc.: Elmsford, NY; 129-151.
- Scherbatskoy T, Burke JM, Rea AW, Keeler GJ. 1998. Atmospheric mercury deposition and cycling in the Lake Champlain basin of Vermont. In *Atmospheric deposition of contaminants to the Great Lakes and coastal waters*, Baker JE (ed). SETAC Press: Pensacola, FL; 245-258.
- Scherbatskoy T, Shanley JB, Keeler GJ. 1998. Factors controlling mercury transport in an upland forested catchment. *Water, Air, and Soil Pollution* 105: 427-438.
- Schroeder WH, Steffen A, Scott K, Bender T, Prestbo E, Ebinghaus R, Lu JY, Lindberg SE. 2003. Summary report: first international Arctic atmospheric mercury research workshop. *Atmospheric Environment* 37: 2551-2555.
- Schuster PF, Shanley JB, Marvin-Dipasquale M, Reddy MM, Aiken GR, Roth DA, Taylor HE, Krabbenhoft DP, DeWild JF. 2008. Mercury and organic carbon dynamics during runoff episodes from a northeastern USA watershed. *Water, Air, and Soil Pollution* 187: 89-108. DOI: 10.1007/s11270-007-9500-3.
- Shanley JB, Schuster PF, Reddy MM, Roth DA, Taylor HE, Aiken GR. 2002. Mercury on the move during snowmelt in Vermont. *EOS, Transactions, American Geophysical Union* 83 (5): 45, 47-48.
- St. Louis VL, Rudd JWM, Kelly CA, Barrie LA. 1995. Wet deposition of methyl mercury in northwestern Ontario compared to other geographic locations. *Water, Air, and Soil Pollution* 80 (1-4): 405-414.

- St. Louis VL, Sharp MJ, Steffen A, May A, Barker J, Kirk JL, Kelly DJA, Arnott SE, Keatley B, Smol JP. 2005. Some sources and sinks of monomethyl and inorganic mercury on Ellesmere Island in the Canadian High Arctic. *Environmental Science and Technology* 39: 2686-2701.
- Swartzendruber PC, Jaffe DA, Prestbo EM, Weiss-Penzias P, Selin NE, Park R, Jacob DJ, Strode S, Jaeglé L. 2006. Observations of reactive gaseous mercury in the free troposphere at the Mount Bachelor Observatory, *Journal of Geophysical Research* 111: D24301. DOI:10.1029/2006JD007415.
- SYSTAT. 2002. Version 11, SYSTAT Software Inc.: Richmond, CA.
- ter Steege H. 1996. WinPhot software, copyright 2/2/96. Available: http://www.bio.uu.nl/~herba/Guyana/winphot/wp_index.htm.
- US EPA. 2002. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, EPA-821-R-02-019, U.S. Environmental Protection Agency, Office of Water, August 2002.
- VanArsdale A, Weiss J, Keeler GJ, Miller EK, Boulet G, Brulotte R, Poissant L, Puckett K. 2005. Patterns of mercury deposition in northeastern North America (1996–2002). *Ecotoxicology* 14: 37-52.