



THE DEPOSITION OF MERCURY IN THROUGHFALL AND LITTERFALL IN THE LAKE CHAMPLAIN WATERSHED: A SHORT-TERM STUDY

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Abstract—As part of an ongoing study of the atmospheric deposition of Hg in the Lake Champlain watershed, event throughfall, event precipitation, ambient, green foliage, and litterfall samples were collected and analyzed for Hg from a mixed hardwood forest in Underhill Center, VT, for six weeks during the months of August and September 1994. During this time period, the volume-weighted mean Hg concentration in throughfall ($12.0 \pm 8.5 \text{ ng } \ell^{-1}$) was higher than in precipitation ($6.5 \pm 2.8 \text{ ng } \ell^{-1}$). In August and September 1994, the total deposition of Hg in throughfall was estimated to be $3.1 \mu\text{g m}^{-2}$ ($1.9 \mu\text{g m}^{-2}$ in precipitation) to the deciduous hardwood forests in the Lake Champlain basin. The mean Hg concentration in litterfall ($53.2 \pm 11.4 \text{ ng g}^{-1}$) was significantly greater than the mean concentration in green foliage ($34.2 \pm 7.2 \text{ ng g}^{-1}$), suggesting uptake of Hg from the atmosphere by foliage. Estimated annual litterfall deposition to the Lake Champlain basin was $13 \mu\text{g m}^{-2}$. This study suggests that throughfall and litterfall play a significant role in the cycling and deposition of Hg in the Lake Champlain watershed. Copyright © 1996 Elsevier Science Ltd

Key word index: Mercury, throughfall, litterfall, foliage, atmospheric deposition.

1. INTRODUCTION

In assessing ecosystem cycling of mercury (Hg) and regulatory concerns about Hg accumulation in lakes or forested watersheds, it is critical to understand the relative contributions of the various Hg flux pathways, including throughfall, litterfall, and precipitation. The interactions between the atmosphere and forest canopies are essential in developing an understanding of the cycling of Hg in forested watersheds. Atmospheric deposition (wet or dry) of Hg to forest canopies plays an important role in the chemistry of throughfall (precipitation after it falls through a forest canopy) (Lindberg *et al.*, 1994). Dry deposited Hg may be washed off plant surfaces, elevating concentrations of Hg in throughfall over the associated concentrations in precipitation (Iverfeldt, 1991a). Dry deposited Hg reaches plant surfaces through three processes: oxidation and adsorption of gaseous Hg (Hg^0) (Munthe *et al.*, 1995), uptake of Hg^0 by stomata (Lindberg *et al.*, 1992), or adsorption of particulate

Hg. This Hg may then be either washed off by precipitation in throughfall or held by the leaves and deposited as litterfall to the forest floor. Any of this Hg on the forest floor, either from throughfall or litterfall, may be absorbed in the roots of a tree along with Hg present in the soil. Various studies suggest, however, that this absorbed Hg is not translocated from the roots to the leaves in significant amounts relative to that available in the root zone (Lodenius, 1995; Godbold and Huttermann, 1988; Lindberg *et al.*, 1979; Gilmour and Miller, 1973).

Deposition of Hg in throughfall has been studied in two forests: a spruce (*Picea abies* (L.) Karst.) stand at Lake Gardsjon, Sweden (Munthe *et al.*, 1995; Iverfeldt, 1991b), and an oak (*Quercus* spp.) stand in the Walker Branch Watershed, TN (Lindberg *et al.*, 1994). Annual throughfall deposition of Hg at Lake Gardsjon was approximately $17\text{--}19 \mu\text{g m}^{-2}$ in 1989 (Iverfeldt, 1991b) and ranged from 15.4 to $16.5 \mu\text{g m}^{-2}$ during 1991–1994 (Munthe *et al.*, 1995). Annual throughfall deposition of Hg in the Walker Branch Watershed was approximately $20 \mu\text{g m}^{-2}$ in 1991 (Lindberg *et al.*, 1994) and averaged $14 \mu\text{g m}^{-2}$ during 1992–1994 (Lindberg, 1995).

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2. METHODOLOGY

2.1. Site characteristics

A suite of Hg samples were collected at a site in the Lake Champlain basin in an effort to better understand the processing of Hg in a mixed hardwood forest. An intensive six-week study was conducted during August and September 1994 at the Proctor Maple Research Center in Underhill Center, VT (44°31'N, 72°52'W; 400 m elev.) to estimate the deposition of Hg within the forested regions of the Lake Champlain watershed. The site is centrally located in the Lake Champlain basin, ~25 km east of Lake Champlain, and on the western, upland slopes of Mount Mansfield in an area of northern hardwood forest. The site is 31 km northwest from Burlington, VT, and 120 km south-southeast from Montreal. Ongoing Hg sampling at this site includes event, wet-only precipitation and every sixth day ambient sampling conducted by the University of Michigan Air Quality Laboratory (UMAQL) and the University of Vermont.

Throughfall and related sampling was conducted in the vicinity of a 24 m aluminum meteorological tower used for forest canopy research. Twenty-three rain gauges were randomly placed beneath the forest canopy to determine the spatial variability of each throughfall event. Two throughfall sites were established which consisted of two collectors in a young, mixed hardwood stand and two collectors in an older sugar maple stand. The mixed hardwood stand was 18 m in height and had a leaf area index (LAI, the ratio of one-sided leaf area per unit ground area) of 4.6. This stand was composed of 30–50 yr old American beech (*Fagus grandifolia* Ehrh.), hop-hornbeam (*Ostrya virginiana* (Mill.) K. Koch), yellow birch (*Betula alleghaniensis* Britt.), and white ash (*Fraxinus americana* L.) trees. The sugar maple (*Acer saccharum* Marsh.) stand was 28 m in height and had a LAI of 4.4.

2.2. Field sampling techniques

Ultraclean techniques were used in all phases of sample collection and handling. Throughfall samples were collected manually with the funnels covered during dry periods to prevent collection of dry deposition. To avoid contamination from the ground, the throughfall funnels were mounted at 1.5 m in a vertical section of opaque 6 cm PVC pipe. A precipitation collector (MIC-B) was fitted with a custom-designed plastic insert and was used to collect event, wet-only precipitation samples at the field site (0.5 km from the throughfall sites). Precipitation volume was determined by a Belfort recording rain gauge. Throughfall and precipitation samples were collected with a clean sampling train which consisted of a borosilicate glass funnel (15 cm) fitted with a Teflon adapter connected to a 1 l borosilicate glass bottle. The entire sampling train was acid-cleaned prior to use and replaced after each event. The total Hg concentration in six funnel rinses (in which the funnels were rinsed with deionized "Milli-Q" water) indicated that the funnels were neither absorbing nor introducing Hg during collection. A minimum

of 10% of all samples collected were blanks; field blanks and analytical precision are summarized in Table 1. Unless otherwise indicated, a significance level of $p < 0.05$ was used.

A small portion of throughfall was not sampled by the study's design for two reasons: (1) small rainfall events (less than 0.3 cm) were not sampled for throughfall; (2) during one large event (1.9 cm) on 11 September 1994, throughfall samples were not collected (although the associated precipitation was collected, as usual). The total volume of precipitation during periods for which throughfall was not collected was 3.1 cm or 16% of the total precipitation volume.

In an effort to quantify the ambient Hg levels in the mid-canopy and compare them to open-field ambient Hg levels, air sampling equipment was placed on the tower at a height of approximately 12 m. During an intensive two-week sampling period from 16–30 August 1994, vapor- and particulate-phase Hg samples were collected daily at the field site and on the tower, using mass flow controlled pumps (URG, Carboro, NC). Vapor-phase Hg was collected on gold-coated bead traps (using glass-fiber pre-filters) at a nominal flow rate of $300 \text{ cm}^3 \text{ min}^{-1}$ for 24 h. Total particulate Hg (no size segregation) was collected on glass-fiber filters using an open-face Teflon filter pack at a nominal flow rate of 30 l min^{-1} for 24 h (Burke *et al.*, 1995).

Green foliage and litterfall samples were collected to quantify the amount of Hg in canopy foliage and litterfall deposited on the forest floor. On 30 August 1994, three foliage samples were taken from three trees of each species influencing the throughfall collectors at a height of approximately 12 m. Foliage was collected by cutting small branches with a pole pruner, catching and stripping them of their leaves while wearing particle-free gloves. Twenty leaves were taken from each branch for Hg analysis; 20 others were used to determine leaf area and dry weight. Litterfall samples were collected twice per week in 0.25 m^2 litterfall collectors (Hughes *et al.*, 1987) and combined by species into early (20 September–7 October 1994) and late (8–21 October 1994) season samples.

2.3. Sample processing

From 15–31 August 1994, all throughfall and precipitation sample processing was performed in a portable Class 100 clean bench at the site. Throughfall and precipitation samples were processed using ultrapure reagents that were checked for purity both before use and during the course of analysis. These samples were oxidized with concentrated BrCl to a 1% solution for total Hg analysis. After 31 August, samples were shipped to the UMAQL and processed in a Class 100 clean room. All samples were allowed to react for at least 24 h before analysis.

The glass-fiber filters used for collecting particulate Hg were extracted in 20 ml of 1.6 M HNO_3 and microwave digested (CEM MDS-2000 Matthews, NC) at 160°C for 20 min (Keeler *et al.*, 1995). The extract was oxidized with concentrated BrCl to a 2.5% solution and allowed to react for at least 1 h before analysis.

Table 1. Summary of blanks and analytical precision of the Lake Champlain throughfall study

Sample type	Blanks	Mean analytical precision	Duplicate analyses performed
Throughfall and precipitation Hg	Avg. bottle blank: $20 \text{ pg bottle}^{-1}$	3%	25%
Vapor-phase Hg	Avg. field blank: 0.019 ng m^{-3}	na	na
Particulate-phase Hg	Avg. field blank: 0.4 pg m^{-3}	5%	50%
Green foliage and litterfall Hg	Vessel blank: $0.23 \text{ ng vessel}^{-1}$	Foliage 4% Litterfall 5%	100%

Before processing, foliage and litterfall samples were kept frozen until they were dried in a Class 100 clean bench at room temperature. The petiole (stem) from each leaf was manually removed while wearing particle-free gloves in order to prevent dilution of the sample (Rasmussen *et al.*, 1991). Samples were placed in an acid-cleaned Teflon bottle, ground to approximately 0.5–1 mm pieces using an acid-cleaned polyethylene spatula, Teflon-taped, and triple bagged. These samples were digested using an acid extraction/microwave digestion technique developed at the UMAQL. Recovery of a certified leaf standard (NIST SRM # 1515—apple leaves) for Hg was 89% ($39 \pm 3 \text{ ng g}^{-1}$) based on the reported NIST value of $44 \pm 4 \text{ ng g}^{-1}$. While the analytical precision for replicate foliage samples was greater than 95% ($< 2.2 \text{ ng g}^{-1}$), the variability between samples ranged from 13–28%. This variability is larger than the analytical error and is most likely due to the inhomogeneity of the sample material (Lindberg and Lovett, 1985).

2.4. Sample analysis

All Hg analysis was performed at the UMAQL in a Class 100 clean room using cold vapor atomic fluorescence spectrometry (CVAFS). Mercury forms in throughfall, precipitation, particulate, and leaf samples were removed from solution in a Hg-free nitrogen stream after reduction of BrCl with NH_2OH and reduction of Hg^{2+} by SnCl_2 to Hg^0 and concentrated onto a gold-coated bead trap. All traps were placed directly into the analytical train for analysis using dual amalgamation (Fitzgerald and Gill, 1979). Calibration curves covering the appropriate concentration levels were run each day of analysis with control standards checked after every sixth sample. The analyzer was recalibrated if the control standard was not within 10% of the expected value.

3. RESULTS AND DISCUSSION

3.1. Throughfall and precipitation

The mean volume-weighted throughfall and precipitation concentrations (\pm std. dev.) of Hg were $12.0 \pm 8.5 \text{ ng } \ell^{-1}$ (range 4.5–35.8 $\text{ng } \ell^{-1}$) and $6.5 \pm 2.8 \text{ ng } \ell^{-1}$ (2.1–12.4 $\text{ng } \ell^{-1}$), respectively. Munthe *et al.* (1995) found that differences in Hg concentrations in throughfall and precipitation were partially attributed to volume differences. However, the higher Hg concentrations in throughfall often coincided with dry periods of two or more days in the samples collected from the Lake Champlain watershed. Throughfall volume, based on the 23 rain gauges, was approximately 90% (81–98%) of precipitation volume, except for a light, steady event lasting for 24 h on 23 September 1994 in which throughfall volume was only 67% of precipitation volume. This difference in throughfall and precipitation sample volumes may have led to the higher throughfall Hg concentrations in this event (Fig. 1a), due to evaporation of water in the canopy.

Comparing the Hg concentrations and subsequent depositions (Fig. 1a and b), indicates that the high concentration/low volume events (8/26, 8/31, 9/6, and 9/23) result in less Hg deposition than the lower concentration/high volume events (8/17, 8/21, 8/25, and 9/13). The excess Hg between throughfall and precipitation cannot be explained by volume differences and may be attributed to either dry deposition or foliar leaching of Hg.

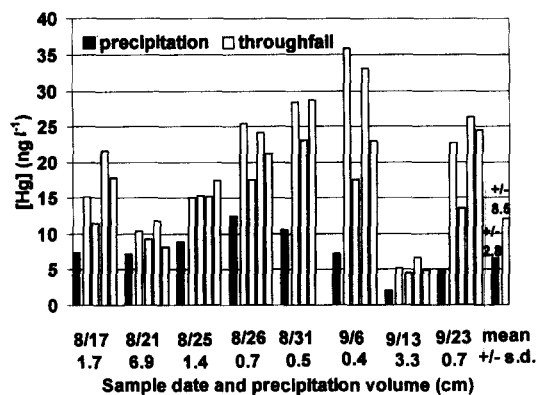


Fig. 1a. Total Hg concentration ($\text{ng } \ell^{-1}$) in precipitation and throughfall samples by collector and precipitation volume during each event for which throughfall was collected (last two bars indicate mean \pm std. dev. of precipitation and throughfall concentrations, respectively).

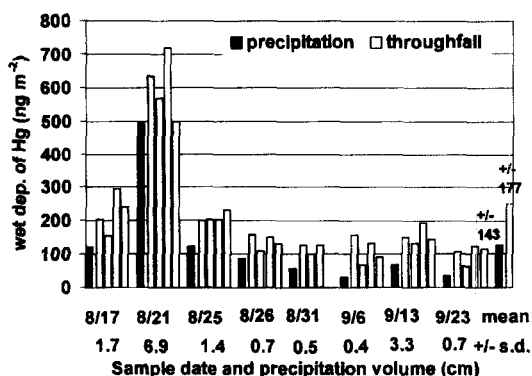


Fig. 1b. Total precipitation and total throughfall Hg deposition (ng m^{-2}) by collector and precipitation volume during each event for which throughfall was collected (last two bars indicate mean \pm std. dev. of precipitation and throughfall deposition, respectively).

The deposition of Hg in net throughfall (throughfall deposition minus precipitation deposition) was calculated for each event using the mean throughfall Hg concentration and mean throughfall volumes from the 23 rain gauges. The mean deposition of Hg in net throughfall (\pm std. dev.) was $70.5 \pm 21 \text{ ng m}^{-2}$ (range 46.8–109 ng m^{-2}) in the mixed hardwood stand and $89.9 \pm 37 \text{ ng m}^{-2}$ (54.5–148 ng m^{-2}) in the maple stand; the mean deposition of Hg in net throughfall for both stands was $80.2 \pm 25 \text{ ng m}^{-2}$ (50.7–113 ng m^{-2}). Although the deposition of Hg in net throughfall was consistently higher in the maple stand, the two stands were not statistically different. One explanation for this may be the physical differences in the canopy structure of these two stands. The surface area of each maple leaf is larger than the surface area of the other hardwood leaves sampled in this study. These influences provide larger retention times for both foliar leaching and wash-off of dry deposited Hg.

The largest storm (6.9 cm) occurred on 21 August 1994 which was characterized by heavy rain of over 6 cm in 4 h. At this time the sample bottles were replaced and the storm continued as a light, steady drizzle lasting over 9 h. In this storm, total throughfall deposition of Hg was 647 ng m^{-2} and total precipitation deposition of Hg was 492 ng m^{-2} . During the second part of the storm, the deposition of Hg in net throughfall was three to five times higher than in the first part of the storm. In the first and second parts of the storm, the average net throughfall deposition of Hg was 21.9 and 90.7 ng m^{-2} , respectively, for a total net throughfall deposition of Hg of 112 ng m^{-2} . There were no significant differences between either the concentration or deposition of Hg in either the maple or mixed hardwood stands.

The deposition of Hg in net throughfall during this storm may have been influenced by the residence time of water on the leaf surface as has been demonstrated for other ions (Scherbatskoy and Tyree, 1990). It was assumed that the water holding capacity of a typical maple leaf was 0.1 mm, and the rainfall rate was 1.5 and 0.096 cm h^{-1} during the first and second parts of the storm, respectively. The residence time of water on the leaf surface was estimated to be 24 s during the first part of the storm and estimated to be 6 min during the second part of the storm. Not only was the residence time longer during the second part of the event, but the lower rain volume may have also increased the concentration and, thus, the deposition of Hg.

3.2. Estimated throughfall deposition of Hg

The deposition of Hg to the Lake Champlain basin was estimated by extrapolating from the measurements taken at the sampling site. In August and September 1994, the total deposition of Hg in throughfall was estimated to be $3.1 \mu\text{g m}^{-2}$ or 41 kg ($1.9 \mu\text{g m}^{-2}$ or 25 kg in precipitation) to the total forested area of the Lake Champlain basin. In the few published studies available, the deposition of Hg in throughfall is between 2 and $6 \mu\text{g m}^{-2}$ during the months of August and September (Table 2). The deposition of Hg in throughfall ($9.4 \mu\text{g m}^{-2}$ or 124 kg) during the growing season

was estimated using 90% of the precipitation volume. Assuming this contribution is equal to the total for the year over the entire area of the Lake Champlain basin (2,133,719 ha), 62% of which is forested (Scherbatskoy *et al.*, 1996), net throughfall Hg deposition adds an estimated $4 \mu\text{g m}^{-2} \text{ yr}^{-1}$ (53 kg yr^{-1}) to the estimated $7.9 \mu\text{g m}^{-2} \text{ yr}^{-1}$ (169 kg yr^{-1}) of Hg deposited by precipitation in 1994. Notably, this net throughfall deposition is similar to the $4.9 \mu\text{g m}^{-2} \text{ yr}^{-1}$ reported for Lake Gardsjon (Munthe *et al.*, 1995) and the $4\text{--}6 \mu\text{g m}^{-2} \text{ yr}^{-1}$ reported for the Walker Branch Watershed (Lindberg, 1995; Lindberg *et al.*, 1994). Thus, an estimated total of $10.4 \mu\text{g m}^{-2} \text{ yr}^{-1}$ of Hg (222 kg) was deposited to the Lake Champlain basin (both forested and non-forested regions) in 1994 from deposition in both throughfall and precipitation.

3.3. Ambient mercury

During 16–30 August 1994, daily 24 h vapor-phase and particulate-phase Hg measurements were taken at both the field and canopy sites. The goal of this was to investigate the role of vapor- and particulate-phase Hg in the canopy processing of Hg. There were no statistical differences or trends between vapor-phase Hg concentrations between the field and canopy sites. Vapor-phase Hg levels averaged (\pm std. dev.) $1.6 \pm 0.3 \text{ ng m}^{-3}$ (range 1.2–2.3 ng m^{-3}) in the field and $1.6 \pm 0.5 \text{ ng m}^{-3}$ (1.3–3.1 ng m^{-3}) in the canopy. Particulate Hg concentrations were usually slightly higher in the canopy. Although it was not consistent, this pattern was usually seen during extended (3 d) dry periods and may be attributed to resuspension of particulate matter. Nonetheless, field and canopy concentrations of particulate-phase Hg were not statistically different. The mean (\pm std. dev.) particulate Hg concentration was $7 \pm 2 \text{ pg m}^{-3}$ (range 3–11 pg m^{-3}) in the field and $9 \pm 3 \text{ pg m}^{-3}$ (3–15 pg m^{-3}) in the canopy. These measurements were used to estimate the dry deposition of Hg.

3.4. Dry deposition estimates

The multiple resistance model developed by Hicks *et al.* (1987) and modified by Lindberg *et al.* (1992) for

Table 2. Summary of data from four studies on Hg in total throughfall deposition and precipitation deposition ($\mu\text{g m}^{-2}$) for the months of August and September

Location	Months and year	Forest type	Total throughfall deposition	Total precipitation deposition	Ref.
Lake Gardsjon, Sweden	Aug.–Sep. 1989	Spruce	5.0–6.0	2.4	(1)
Walker Branch Watershed, TN	Aug.–Sep. 1991	Oak	2.7	1.4	(2,3)
	Aug.–Sep. 1994	Oak	2.3	0.9	(3)
Lake Champlain; Underhill Center, VT	Aug.–Sep. 1994	Mixed hardwood	3.1	1.9	(4)

(1) Iverfeldt (1991b); (2) Lindberg *et al.* (1994); (3) Lindberg (personal communication); (4) this study.

Table 3. Mean ambient total Hg concentrations, modeled mean deposition velocities, calculated dry deposition rates, and estimated dry deposition rates from net throughfall deposition

Event date	Ant. dry per. (h)	Range of ambient Hg over dry period		Modeled mean V_d (cm s^{-1})		Dry dep. rates (using V_d) Hg(g)	Dry dep. rates (using V_d) Hg(p)	Estimated net throughfall dry dep. rates ($\text{ng m}^{-2} \text{h}^{-1}$)
		Vapor (ng m^{-3})	Particulate (ng m^{-3})	Hg(g)	Hg(p)	($\text{ng m}^{-2} \text{h}^{-1}$)	($\text{ng m}^{-2} \text{h}^{-1}$)	
8/17	48	1.7–2.0	0.006–0.012	0.071	0.118	4.35–5.11	0.025–0.051	2.16
8/21	62	1.3–3.1	0.003–0.011	0.081	0.122	3.79–9.04	0.013–0.048	1.82
8/25	95.5	1.2–1.8	0.006–0.015	0.051	0.095	2.20–3.30	0.021–0.051	1.03
8/26	24.5	1.6–1.8	0.007–0.010	0.065	0.176	3.74–4.21	0.044–0.063	2.07
8/31	90	1.4–1.8	0.005–0.010	0.063	0.062	3.18–4.08	0.011–0.022	0.70
9/6	91	1.5	0.006–0.009	0.041	0.083	2.21	0.018–0.027	0.86
9/13	10	2.0	0.013–0.014	0.020	0.029	1.44	0.014–0.015	8.57

estimating the dry deposition of Hg to forest canopies was used to determine the deposition velocity (V_d) for both vapor- and fine particulate-phase Hg forms during dry periods prior to rain events (Table 3). The modeled V_d was calculated using hourly on-site meteorological measurements. The model estimates (Table 3) indicate that if we assume particulate Hg was only in the fine fraction it would represent less than 10% (0.2–5.0%) of the Hg in net throughfall. Lindberg *et al.* (1994) also assumed Hg was only in the fine fraction and found it contributed from 4–23% of the Hg in net throughfall. This suggests that some Hg in net throughfall may be coarse particulate Hg, oxidized vapor forms (Hg-II compounds), and/or an Hg⁰ reaction with the wetted leaf surface. The importance of particulate Hg and Hg-II compounds will vary according to location and season.

An equation suggested by Lindberg *et al.* (1994) was also used to estimate the rate of Hg dry deposition. This straightforward approach assumes that the deposition of Hg in net throughfall consists only of washed off dry deposition, and that there is no sorption of Hg by the leaf. The dry deposition rate of Hg can then be estimated using the following equation (Lindberg *et al.*, 1994):

$$\text{est. mean dry dep. rate (ng m}^{-2} \text{h}^{-1}) = \frac{\text{net throughfall (ng m}^{-2})/\text{antecedent dry period (h)}}{\quad} \quad (1)$$

where the antecedent dry period is the time (h) between rain events. The Hg dry deposition rates calculated using equation (1) generally fall between the vapor and particulate Hg dry deposition rates calculated using the modeled V_d (Table 3). The exception is on 9/13 which had a relatively high net throughfall deposition (85.7 ng m^{-2}) and a short antecedent dry period (10 h).

3.5. Green foliage and litterfall

The mean Hg concentration in litterfall was 36% higher and significantly greater ($p < 0.0001$) than

the mean concentration in green foliage. The mean concentration (\pm std. dev.) in litterfall was $53.2 \pm 11.4 \text{ ng g}^{-1}$ (range 37.8–76.9) and the mean concentration in green foliage was $34.2 \pm 7.2 \text{ ng g}^{-1}$ (13.3–49.1). This difference may result from some dry deposited Hg remaining in the canopy after each throughfall event which is retained by the leaves and deposited as litterfall on the forest floor. The 36% increase of Hg in litterfall (50 kg or 19 ng g^{-1}) may be explained by an additional two months of processes acting on the leaves, such as absorption of atmospheric Hg⁰, dry deposition of aerosol Hg, and accumulation of Hg (either internal or external). This hypothesis was tested by considering the potential dry deposition, the net throughfall deposition, and the difference between them.

The estimated potential dry deposition from both vapor- and particle-phase Hg was $1.48 \mu\text{g m}^{-2}$ in September 1994 and $2.26 \mu\text{g m}^{-2}$ in October 1994. The potential dry deposition of Hg was estimated using (1) the modeled mean V_d for both vapor- and particle-phase Hg during the throughfall period as no meteorological data were available for October (0.056 and 0.098 cm s^{-1} , respectively), (2) the measured mean sixth day vapor (Hg(g)) and particle (Hg(p)) phase Hg concentrations (9/94, 1.4 ng m^{-3} Hg(g), 0.007 ng m^{-3} Hg(p); 10/94, 1.7 ng m^{-3} Hg(g), 0.006 ng m^{-3} Hg(p)), and (3) the number of dry hours per month (9/94, 519 h; 10/94, 655 h).

The estimated net throughfall deposition of Hg (throughfall deposition minus precipitation deposition) was $0.43 \mu\text{g m}^{-2}$ in September and $0.22 \mu\text{g m}^{-2}$ in October, assuming the elevated concentrations in throughfall are due solely to wash-off of dry deposited Hg. The net throughfall deposition of Hg was estimated using (1) the mean volume-weighted throughfall concentration (12 ng l^{-1}), (2) 90% of the total precipitation volume (total: 9/94, 9.6 cm; 10/94, 8.0 cm), and (3) the measured precipitation deposition of Hg (9/94, $0.60 \mu\text{g m}^{-2}$; 10/94, $0.64 \mu\text{g m}^{-2}$).

The estimated amount of dry deposited Hg remaining in the canopy is simply the potential dry deposition minus the net throughfall deposition. The result

is an estimated total of $3.09 \mu\text{g m}^{-2}$ of dry deposited Hg remaining in the canopy (9/94, $1.05 \mu\text{g m}^{-2}$; 10/94, $2.04 \mu\text{g m}^{-2}$). Converting this estimate to the total mass of dry deposited Hg accounts for 41 kg, or 82% of the 50 kg difference between green foliage and litterfall, in the forested regions of the Lake Champlain basin (1,322,506 ha). The estimated amount of dry deposited Hg remaining in the canopy can also be converted to a leaf concentration using the measured mean leaf area (49 cm^{-2} per leaf), dry weight (0.212 g per leaf), and LAI (4.6). This approach attributes approximately 80% of the difference in foliar Hg concentrations to dry deposition (15.3 ng g^{-1} of the 19 ng g^{-1} difference).

These estimates assume that there is no re-emission of Hg from the leaves (which has been observed in a study by Hanson *et al.* (1995)); that wash-off of Hg in throughfall is entirely dry deposition; and that the modeled V_d , estimated throughfall volume, and estimated throughfall deposition are reasonable. Under these assumptions, up to 82% of the increased Hg in litterfall measured in this study may be attributable to dry deposited Hg.

4. CONCLUSIONS

Ignoring the deposition of Hg in throughfall and litterfall may lead to considerable underestimates of Hg deposition to forested watersheds. In particular, through this study, we have found reason to be concerned with the significant contribution to Hg deposition from throughfall and litterfall. We estimate the annual deposition of Hg to the forested areas of the Lake Champlain basin in 1994 was $11.7 \mu\text{g m}^{-2}$ (155 kg) in throughfall and $13 \mu\text{g m}^{-2}$ (172 kg) in litterfall for a total below-canopy Hg deposition of $24.7 \mu\text{g m}^{-2}$ (327 kg). The deposition of Hg in precipitation only accounts for $7.9 \mu\text{g m}^{-2} \text{ yr}^{-1}$ (169 kg), or 32% of this 1994 below-canopy total.

Estimates of the potential dry deposition of Hg to the forest in September and October 1994 indicate that a significant amount (up to 82%) of the increased Hg in litterfall is due to the retention of atmospheric Hg in various forms by leaves followed by the deposition of this Hg in litterfall to the forest floor. To further understand these processes, we can quantify the relative contributions of both dry deposition and foliar leaching to foliar Hg concentrations. This is the focus of ongoing research.

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