MERCURY ACCUMULATION IN FOLIAGE OVER TIME IN TWO NORTHERN MIXED-HARDWOOD FORESTS

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Abstract. Concentrations of mercury (Hg) in live foliage increased ten-fold from spring bud break (mean $\pm$ std. dev. from both sites: 3.5 ± 1.3 ng g^{-1}) to autumn litterfall (36 ± 8 ng g^{-1}). Mercury in foliage did not behave similarly to eight other elements with known soil or aerosol sources (Aluminum (Al), Vanadium (V), Strontium (Sr), Rubidium (Rb), Copper (Cu), Zinc (Zn), Barium (Ba), and lead (Pb)), suggesting that Hg originated from a distinct pathway. Based on measured and modeled data, uptake of only 25% of the available ambient dry deposited Hg^0 could explain all of the Hg measured in foliage throughout the growing season. Estimates of gaseous elemental Hg (Hg^0) uptake from soil water accounted for 3–14% of the Hg in litterfall. Mercury deposition to forested sites in the Lake Champlain and Lake Huron basins was highest in litterfall (40%), followed by total throughfall (33%), and precipitation (27%). The Hg flux in litterfall was 15.8 ± 1.9 μg m^{-2} yr^{-1} to the Lake Champlain Watershed in 1995 and was 11.4 ± 2.8 μg m^{-2} yr^{-1} to the Lake Huron Watershed in 1996. In comparison, the Hg fluxes in precipitation and total throughfall were 9.0 ± 0.6 and 11.6 ± 0.7 μg m^{-2} yr^{-1} in the Lake Champlain Watershed (1995), and 8.7 ± 0.5 and 10.5 ± 1.0 μg m^{-2} yr^{-1} in the Lake Huron Watershed (1996).

Keywords: dry deposition, foliage, gaseous Hg^0, Lake Champlain Watershed, Lake Huron Watershed, litterfall, mercury, soil water, trace elements

1. Introduction

Mercury (Hg) in unimpacted deciduous forest foliage has been measured as high as 52.3 ± 25.9 ng g^{-1} (mean $\pm$ std. dev). (Lindberg, 1996), and from 20.0 to 65.5 ng g^{-1} in coniferous species (Rasmussen, 1994), while vegetation in contaminated areas may contain Hg at levels approaching 10^5-10^6 ng g^{-1} (Fischer *et al.*, 1995; Shaw and Panigrahi, 1986; Siegel *et al.*, 1984). The transfer of Hg to the forest floor in senescing foliage (litterfall) is the largest single flux of Hg in forested ecosystems (Iverfeldt, 1991; Lindberg, 1996; Rea *et al.*, 1996; Rea, 1998).

Mercury in plants may originate from several sources, including (1) uptake of ambient atmospheric Hg (usually in the elemental gaseous form, Hg^0) through stomata, (2) foliar accumulation of wet and dry deposited Hg (Hg^0, various Hg-II species, or aerosol-bound Hg) from the atmosphere, or (3) uptake of dissolved

Hg in soil water via the transpiration stream. Atmospheric Hg^0 is readily taken up by plants through the stomata (Browne and Fang, 1979; Mosbaek *et al.*, 1988), yet, being highly volatile, it may also be released (Siegel *et al.*, 1974; Iverfeldt, 1991; Hanson *et al.*, 1995; Lindberg, 1996). Mercury deposited to vegetation from either wet or dry atmospheric deposition may be irreversibly sorbed to the plant surface, or it may wash off during a precipitation event in throughfall (Iverfeldt, 1991; Lindberg *et al.*, 1994; Rea *et al.*, 1996; Rea, 1998, Rea *et al.*, 2001).

There are many potential sources of Hg in foliage. Although roots may contain high levels of Hg, little of this Hg is transported to aboveground tissues and this does not appear to be a significant pathway for plant accumulation (Beauford *et al.*, 1977; Lindberg *et al.*, 1979; Godbold and Huttermann, 1988). Foliar uptake of dissolved Hg in soil water may be another source of Hg in plant tissue (Bishop *et al.*, 1998). Dissolved Hg in soil water may enter the plant transpiration stream and become incorporated into leaf tissue or be released from the stomata with other gases. The direct uptake of dissolved Hg from soil water is estimated to account for less than 10% of the Hg in litterfall (Lindberg, 1996; Bishop *et al.*, 1998). It is not known if dissolved Hg^0 in soil water is accumulated in leaf tissue or released from the plant with other gases in the transpiration stream.

Measured Hg concentrations in living foliage (broadleaf and coniferous) ranges from 7.4 to 66 ng g^{-1} (Barghigiani *et al.*, 1990; Iverfeldt, 1991; Rasmussen *et al.*, 1991; Rasmussen, 1994; Moore *et al.*, 1995; Lindberg, 1996; Rea *et al.*, 1996). Studies have shown that Hg concentrations in both coniferous and deciduous litterfall were approximately 60% higher than in living foliage collected 4–6 weeks before litterfall (Iverfeldt, 1991; Rea *et al.*, 1996). Foliar Hg concentrations increased from 10.1 ± 7.5 ng g^{-1} in spring foliage to 105.0 ± 20.6 ng g^{-1} in litterfall from *Quercus* spp. (oak) and *Carya* spp. (hickory) collected from the Walker Branch Watershed (Lindberg, 1996). It was suggested that this increase in foliar Hg was due to atmospheric sources, but this hypothesis is difficult to prove.

Because litterfall comprises from 50–70% of the Hg budget in a forested watershed (Lindberg, 1996; Rea *et al.*, 1996; Rea, 1998), it is critical to identify its source as internal (from soil or 'recycled' Hg) or external (from the atmosphere or a new Hg input). We studied the biogeochemical cycle of Hg in deciduous forested ecosystems using foliage, litterfall, air, and soil samples and evaluated several potential uptake pathways for Hg. In addition, the behavior of Hg was compared to other trace elements (Al, V, Cu, Zn, Rb, Sr, Ba, and Pb) with known sources to determine the most likely source of Hg in litterfall.

2. Sampling and Analysis

2.1. SAMPLING SITES AND SAMPLE COLLECTION

The study sites were second growth, northern mixed-hardwood forests in the Lake Champlain Watershed (Underhill Center, Vermont; 44.53°N; 72.87°W) and in the Lake Huron Watershed (Pellston, Michigan; 45.57°N; 84.80°W). Both stands were 60–90 yr old and dominated by maple trees (*Acer* spp.). The focus of this research was on deciduous tree species as conifers were a minor component of each stand. The soil type at the Lake Champlain site was coarse, loamy Haplorthod and the soil at the Lake Huron site was sandy, well drained Haplorthod.

At the Lake Champlain site, foliage samples were collected in 1995 from three species: *Acer saccharum* Marsh. (sugar maple), *Betula alleghaniensis* Britt. (yellow birch), and *Fagus grandifolia* Ehrh. (American beech) at mid-canopy (9–12 m) from a meteorological tower on May 23, June 20, August 11, and September 29. At the Lake Huron site, foliage samples were collected in 1996 from five species: American beech, *Acer rubrum* L. (red maple), *Betula papyrifera* Marsh. (white birch), *Populus grandidentata* Michx. (bigtooth aspen), and *Quercus rubra* L. (red oak) at mid-canopy (7–12 m) using a hand held pole pruner on May 30, June 15, July 31, August 26, and September 20. Foliage was collected by carefully selecting fully developed, undamaged leaves directly into plastic bags while wearing gloves. All foliage and litterfall samples were triple bagged and frozen until processed (see Rea *et al*., 1996 and Rea and Keeler, 1998 for details). Litterfall from the Lake Champlain site was composited into early- (September 1–October 15) and late-season (October 16–November 15) samples; litterfall from the Lake Huron site was sorted and analyzed by species and then composited into early- and late-season samples.

Soil samples were collected at both sites using a soil corer at 3 depths (2, 30, and 50 cm). Particle-free gloves were worn during sample collection. Soil was collected directly into acid-cleaned Teflon or polypropylene vials, sealed with Teflon tape, triple bagged, and frozen until processed.

Ambient air samples were collected at both sites every sixth day throughout the growing seasons. Ambient total gaseous Hg was collected onto gold-coated bead traps for 24 hr at a nominal flow rate of 0.3 L min^{-1}. A second trap was placed behind the sample trap to monitor for breakthrough, which did not occur (i.e. the first sample trap was not saturated). Total suspended particulate (TSP) aerosols were collected onto pre-fired 47 mm glass-fiber filters (Hg) or 47 mm Teflon filters (trace elements) mounted ~3 m above the ground in open-face Teflon filter packs oriented vertically and facing downward for 24 hr at a nominal flow rate of 30 L min^{-1} (Keeler *et al*., 1995; Keeler and Landis, 1997).

Ambient aerosol and total gaseous Hg blanks were collected as described in Keeler *et al*. (1995). Blanks from aerosol samples contributed less than 2% (range 0.4–4%; n = 20) of the mean sample mass for all elements. Blanks from total

gaseous Hg samples contributed less than 2% (0.9 to 1.7%; n = 8) of the mean sample mass. All ambient sample concentrations have been corrected using air volumes expressed at standard temperature and pressure (0 °C; 1 atm). National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) #1643c (trace elements in water) and Certified Reference Material SLRS-3 (riverine water) were run to determine elemental recoveries for ambient samples. Recoveries were generally ±1% of expected values, and ranged from 99% (for Pb) to 105% (for Sr) (n = 15).

2.2. SAMPLE PROCESSING AND ANALYSIS

Foliage, litterfall, and soil samples were dried, ground with acid-cleaned ground-glass mortars and pestles, and microwave digested as described in Rea and Keeler (1998). Extraction recoveries were examined using NIST SRM #1515 (apple leaves) and, for most elements, were within ±5% of expected values, ranging from 90% (for Hg) to 101% (for Zn) (n = 23). Mean recoveries were low for Al and V (59 and 61%, respectively) using this procedure. The addition of hydrofluoric acid may have provided better recovery of Al and V, but was incompatible with the analytical systems. Mercury samples were analyzed by cold vapor atomic fluorescence spectroscopy using the dual amalgamation technique (Keeler and Landis, 1997). Particulate trace element samples from the Lake Champlain site were analyzed by X-ray fluorescence. Particulate Hg samples from both sites were microwave digested as described in Keeler *et al.* (1995), and particulate trace element samples from the Lake Huron site were microwave digested as described in Rea and Keeler (1998). Trace elements were analyzed using a Perkin Elmer 5000A Inductively Coupled Plasma-Mass Spectrometer equipped with a thin film electron multiplier. Details on the analytical procedures can be found elsewhere (Keeler *et al.*, 1995; Rea *et al.*, 1996; Rea and Keeler, 1998). Differences between species, month, and the interactions between species and month were tested using a multivariate analysis of variance under the general linear models procedure (SAS Institute, Inc., 1996). The bonferroni *t*-test was used to control for type 1 error ($\alpha = 0.0036$).

3. Results and Discussion

3.1. TRENDS IN ELEMENTAL CONCENTRATIONS IN FOLIAGE

Foliar Hg concentrations increased from 3.6±2.6 ng g^{-1} (mean ± std. dev.; n = 11; dry wt) immediately after bud break (May) to 47.1±5.6 ng g^{-1} (n = 4) in litterfall (October) at the Lake Champlain site in 1995 (Figure 1a). At the Lake Huron site in 1996, foliar Hg concentrations increased from 3.3±1.1 ng g^{-1} (n = 12) after bud break to 32.5±8.1 ng g^{-1} (n = 12) in litterfall (Figure 1b). This tenfold increase in foliar Hg concentrations occurred uniformly in all species sampled in both watersheds. Within any month, there were no significant differences in Hg
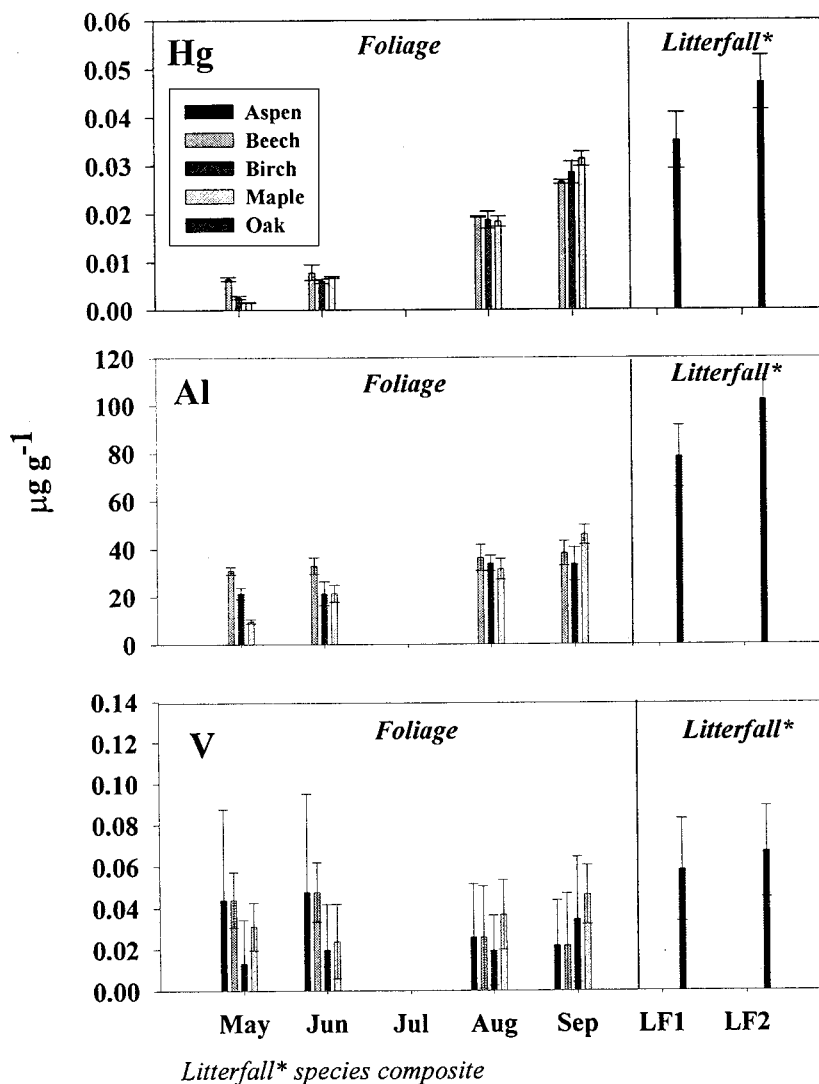
Lake Champlain Watershed:

Figure 1a. Concentrations of Hg, Al, and V (μg g^{-1} dry wt.; mean $\pm$ std. dev.) in foliage and litterfall measured in the Lake Champlain watersheds.

concentrations between species at either site, i.e. beech leaves were not significantly higher or lower in Hg than birch leaves, maple leaves, etc. During both the 1995 (Lake Champlain Watershed) and 1996 (Lake Huron Watershed) growing seasons, foliar Hg concentrations in all species were significantly higher during each successive month, except between May and June at the Lake Huron site. Most likely, this similarity in foliar Hg concentrations at the Lake Huron site in May
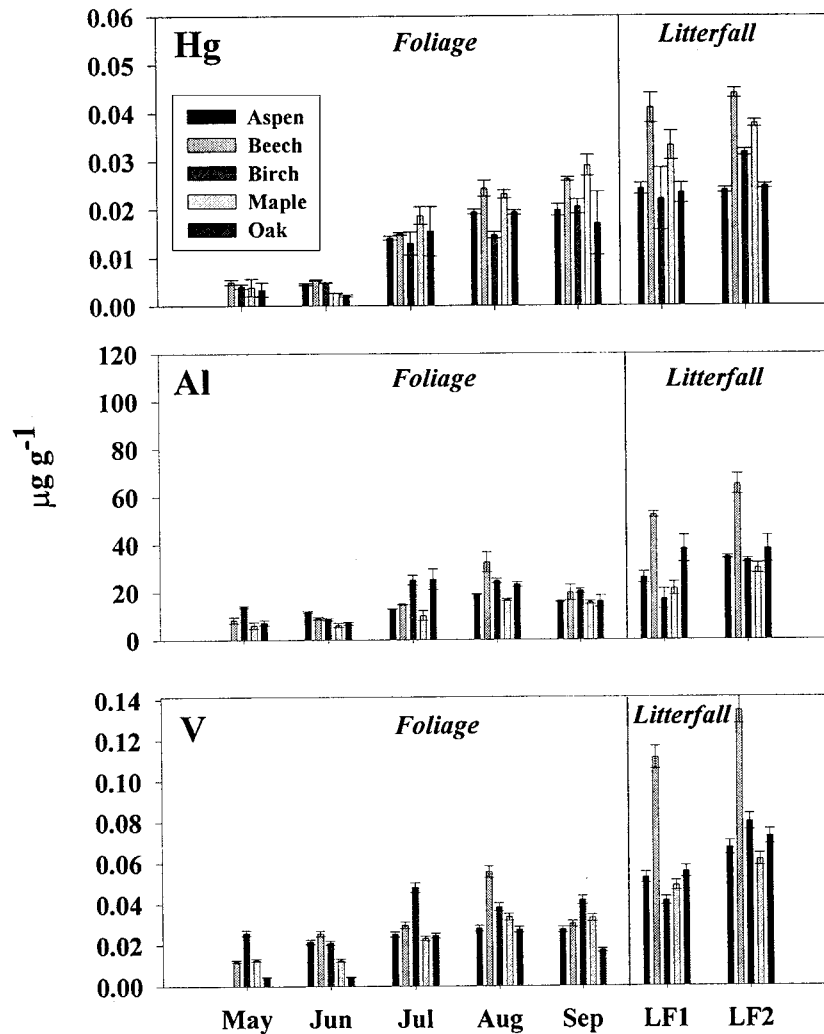
Lake Huron Watershed:

Figure 1b. Concentrations of Hg, Al, and V (μg g^{-1} dry wt.; mean ± std. dev.) in foliage and litterfall measured in the Lake Huron watersheds.

and June were due to the short interval between collections (16 days). The foliar collection interval was at least 27 days for the remainder of the growing season.

Following senescence, however, there were significant differences in Hg concentrations between species in litterfall samples collected at the Lake Huron site (the Lake Champlain litterfall samples were not sorted by species) (Figure 1b). Processes other than atmospheric uptake must explain the significant differences in litterfall Hg concentrations between tree species. This includes the length of
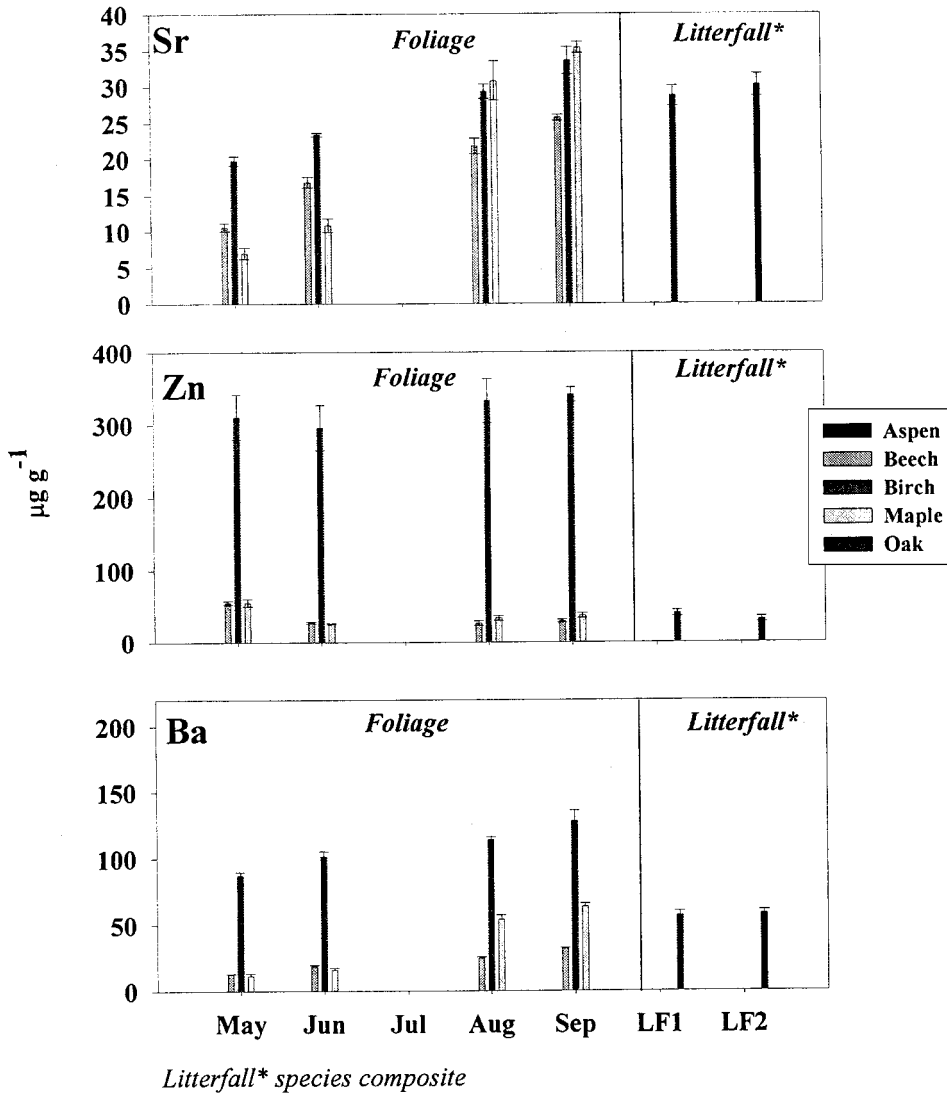
Lake Champlain Watershed:

Figure 2a. Concentrations of Sr, Zn, and Ba (μg g^{-1} dry wt.; mean $\pm$ std. dev.) in foliage and litterfall measured in the Lake Champlain watersheds.

time between leaf fall and collection (i.e. hours or days) in addition to the passive physiochemical absorption of Hg onto the senesced foliage during both wet and dry periods. Nutrient reabsorption prior to senescence may result in litterfall Hg concentrations that vary by species due to biochemical processes altering the concentration of other elements thereby affecting the total mass present in the leaf.
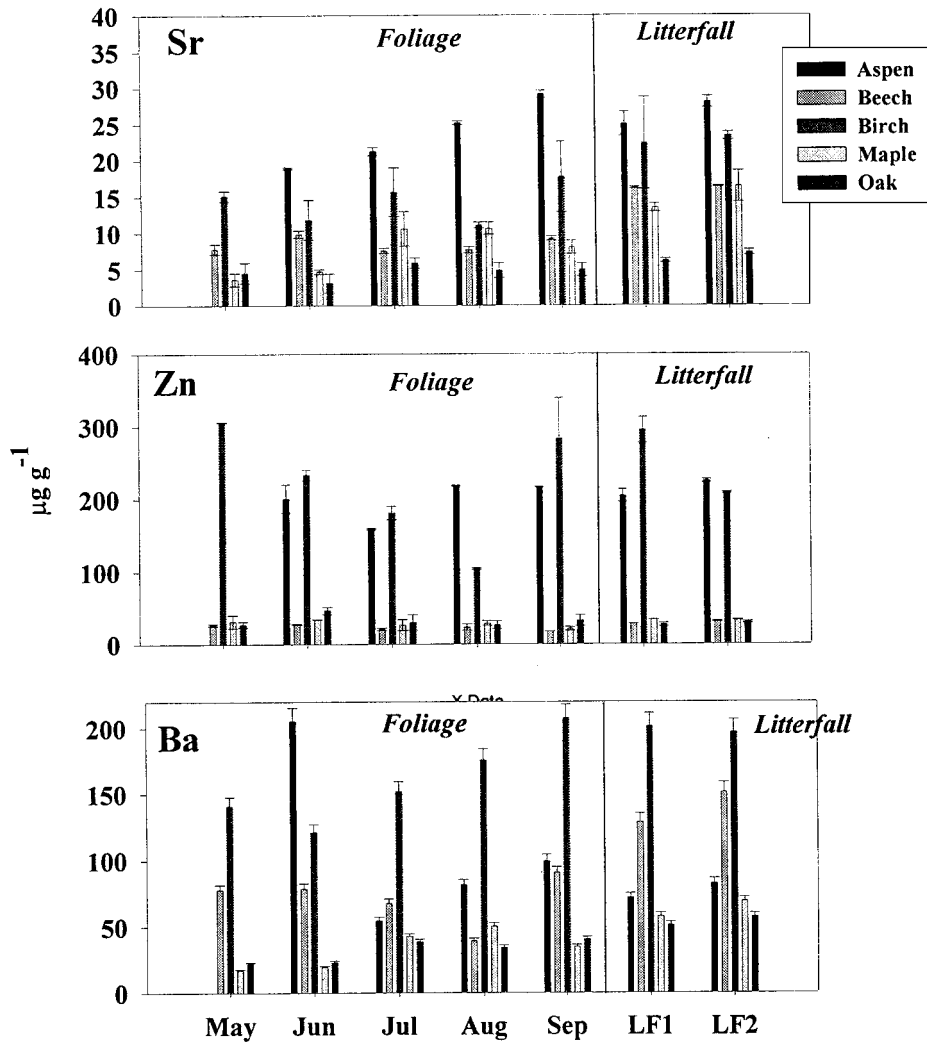
Lake Huron Watershed:

Figure 2b. Concentrations of Sr, Zn, and Ba (μg g^{-1} dry wt.; mean $\pm$ std. dev.) in foliage and litterfall measured in the Lake Huron watersheds.

Mercury was the only metal to show this large and uniformly significant increase in foliar concentrations (Figures 1–3) throughout the growing season. Foliar concentrations of Al, V, and Sr (Figures 1 and 2) also increased over the growing season, however, the increases were not statistically significant. A similar trend in foliar concentrations of Al, V, and Sr were observed for beech, horse chestnut, and sycamore leaves collected in Scotland in 1959 (Guha and Mitchell, 1966), however, the authors did not identify sources of elements in foliage.
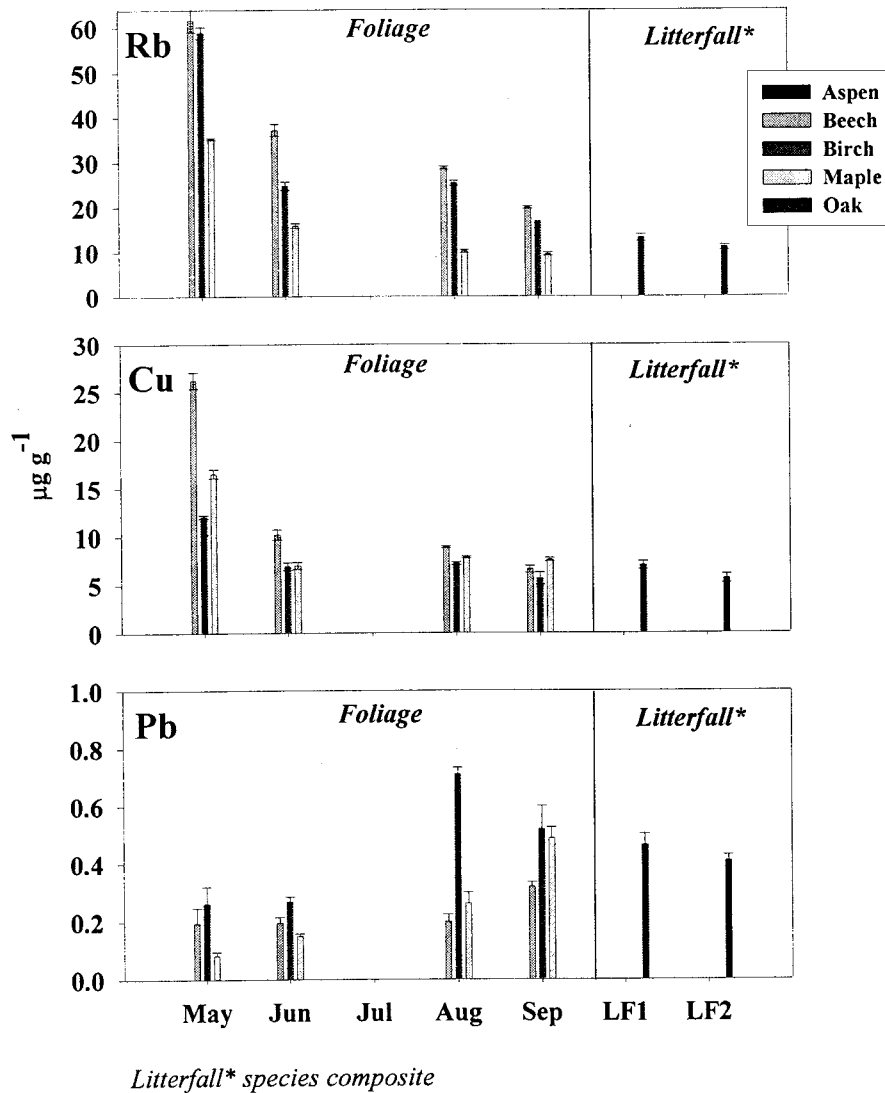
Lake Champlain Watershed:

Figure 3a. Concentrations of Rb, Cu, and Pb (μg g^{-1} dry wt.; mean ± std. dev.) in foliage and litterfall measured in the Lake Champlain watersheds.

Both the site and species differences for Al and V, which were not observed for Hg, suggest different processes were influencing the concentrations of these elements in foliage. Foliar concentrations of Al and V (Figures 1a and 1b) in May and June were two times higher in the Lake Champlain Watershed than in the Lake Huron Watershed. At both sites, total soil concentrations of Al (1974±602 μg g^{-1}, mean ± std. dev. at both sites) and V (3.6±0.8 μg g^{-1}) were similar at 30 cm, the
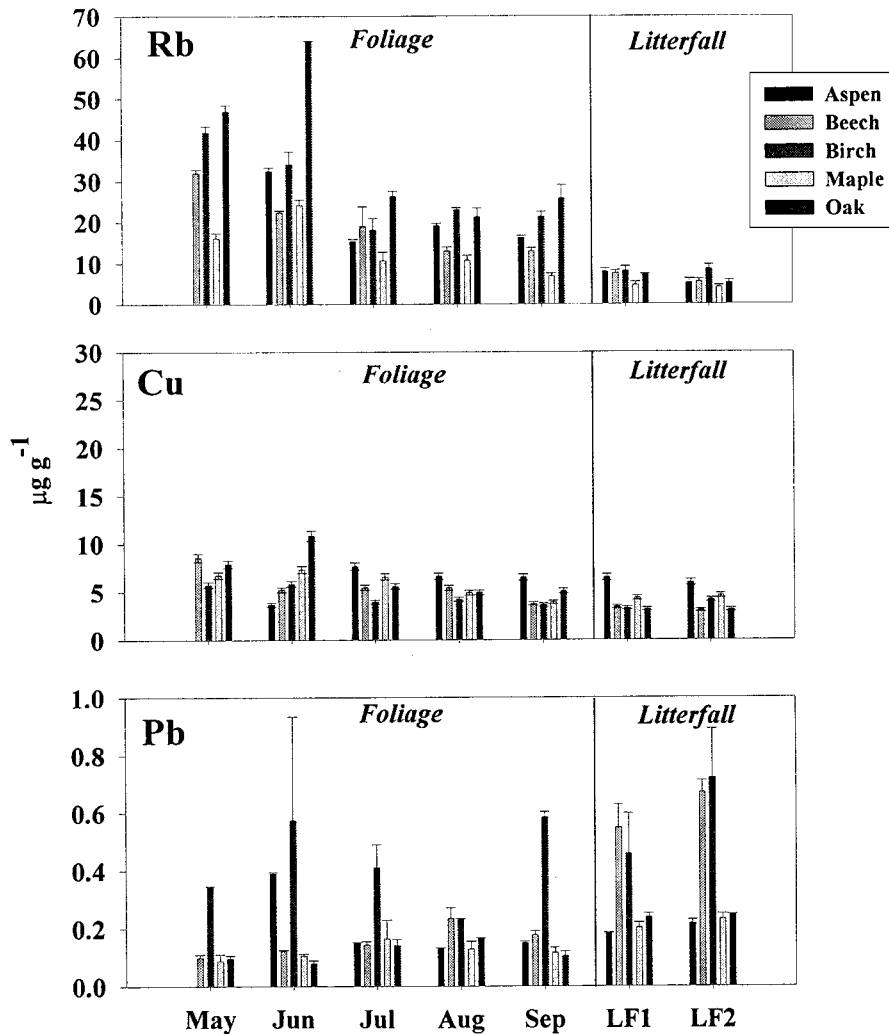
Lake Huron Watershed:

Figure 3b. Concentrations of Rb, Cu, and Pb (μg g^{-1} dry wt.; mean $\pm$ std. dev.) in foliage and litterfall measured in the Lake Huron watersheds.

approximate rooting depth, but varied at other depths (Table I). Aerosol concentrations of Al were more than three times higher at the Lake Champlain site (Table I), which may have influenced the higher foliar Al concentrations. Aerosol concentrations of V were similar at both sites (0.45$\pm$0.33 ng m^{-3}; Table I), suggesting that biochemical or metabolic processes may have influenced foliar V concentrations.

If Hg was replacing a nutrient and being taken up through the soil, significant differences would be expected in foliar concentrations between species due to biochemical or metabolic differences as shown by the micronutrient data (Sr, Zn, and

TABLE I

Elemental concentrations (mean ± std. dev.) in soil (μg g^{-1}) and total suspended particulate aerosol (ng m^{-3}) samples from monitoring sites in the Lake Champlain and Lake Huron watersheds

Element	2 cm soil		30 cm soil		50 cm soil		Ambient air	
	Champlain	Huron	Champlain	Huron	Champlain	Huron	Champlain	Huron
Hg	0.21±0.06	0.042±0.027	0.070±0.021	0.0037±0.0015	0.066±0.039	0.0086±0.0022	0.007±0.004	0.007±0.006
Al	1216±86	2362±672	2051±528	1896±676	1633±778	4472±850	137±112	42±40
V	3.3±0.5	3.1±0.3	3.9±0.5	3.2±1	4.0±0.3	6.3±1.4	0.49±0.34	0.40±0.31
Cu	2.2±0.5	3.6±1.8	3.3±1.6	0.64±0.16	3.6±0.7	1.5±0.2	0.81±0.37	1.3±1.3
Zn	6.8±2.0	35±21	9.4±2.9	4.4±1.6	9.1±2.2	9.4±2.5	5.5±3.4	4.8±4.7
Rb	3.4±0.3	5.0±2.1	3.8±0.4	2.8±0.5	3.0±1.6	3.9±0.9	0.34± 0.20	0.16±0.10
Sr	2.2±0.4	10±4	2.3±0.1	4.1±0.8	1.9±0.5	5.1±1.2	0.53±0.63	0.40±0.39
Ba	12±2	86±26	13±1	16±3	13±1	25±4	19±14	1.0±1.0
Pb	9.2±0.2	15±4	1.3±0.2	1.7±0.7	1.2±0.3	2.1±0.4	1.8±1.0	2.5±1.9
n	3	4	3	4	3	4	29	35

Ba in Figures 2a and 2b). Foliar levels of Sr increased at the Lake Champlain site over the growing season, but fluctuated over time at the Lake Huron site (Figures 1a and 1b). The faster growing species (birch and aspen) had higher concentrations of Sr, probably due to metabolic or biochemical differences between species. Uptake of Zn and Ba (Figures 2a and 2b) were also species-specific, with the highest concentrations measured in fast-growing birch and aspen trees. Within a species, levels of Zn and Ba remained fairly constant throughout the growing season. Species differences in foliar concentrations of Zn and Ba have been observed previously (Guha and Mitchell, 1966) and levels of Zn were much higher in aspen leaves than in oak leaves at both urban and rural sites in Indiana (Parker *et al.*, 1978).

Foliar concentrations of Rb decreased dramatically throughout the growing season (Figures 3a and 3b). Rubidium behaves similarly to phloem mobile K, which is needed in young, growing leaves and cycles rapidly through plants (Guha and Mitchell, 1966). Foliar concentrations of Cu (Figures 3a and 3b), another plant micronutrient, peaked early and then slowly declined and stabilized over the rest of the growing season. This trend was most apparent at the Lake Champlain site, but also occurred to a lesser extent at the Lake Huron site. Similar foliar trends for K and Cu were observed by Guha and Mitchell (1966). If Hg was being taken up from the mineral soil as a plant nutrient, behavior similar to Sr, Zn, Ba, Rb, or Cu would be expected. Mercury is the only element we studied which exhibits significant gas phase speciation, and may cause Hg to behave differently in foliage than the other elements. The role of gaseous Hg^0 uptake from soil water and the atmosphere is discussed below.

3.2. ESTIMATES OF FOLIAR Hg UPTAKE FROM SOIL WATER

The measured flux of Hg to the forest floor in litterfall was 15.8 ± 1.9 μg m^{-2} yr^{-1} in the Lake Champlain Watershed in 1995 (litter flux: 335 g m^{-2}; Leon, 1995) and 11.4 ± 2.8 μg m^{-2} yr^{-1} in the Lake Huron Watershed in 1996 (litter flux: 350 g m^{-2}). In an attempt to account for the Hg deposited in litterfall, we estimated foliar uptake of Hg from both soil water and the atmosphere. Soil water Hg was measured using lysimeters in 1997 at several locations in Underhill Center, VT, approximately 4 km from our sampling sites (Donlon, 1999). The volume-weighted mean ($\pm$ std. dev.) soil water Hg concentration was 11.4 ± 1.2 ng L^{-1} (n = 30) at a depth of 6–10 cm and 3.5 ± 3.1 ng L^{-1} (n = 9) at a depth of 22–28 cm. If we assume that this represents the range of Hg present in the rooting zone, and that 100% of the Hg measured in soil water is transported to foliage during evapotranspiration, then the product of the volume-weighted soil water Hg concentration and the evapotranspiration rate (55 cm yr^{-1}; MacDonald *et al.*, 1992) provides an estimated uptake rate of 1.9–6.3 μg m^{-2} yr^{-1}. This must be considered an upper limit on soil water uptake of Hg, because all of the Hg in soil water may not be in a form suitable for uptake. In addition, this estimate does not account for

any emission of soil water Hg^0 from leaves, which has been reported elsewhere (Siegel *et al*., 1974; Hanson *et al*., 1995; Lindberg, 1996).

Based on actual measurements of xylem sap and soil water, Bishop *et al*. (1998) concluded that approximately 25% of the Hg in soil water was taken up into xylem sap and that Hg in the xylem could account for 11% of the Hg in litterfall. Assuming that 25% of the Hg in the soil water is taken up into the xylem in this study, soil water accounts for 0.5–1.6 μg m^{-2} yr^{-1} or from 3–14% of the Hg deposited in litterfall. Similarly, soil water uptake of Hg was estimated to account for up to 10% of the Hg accumulated in litterfall at the Walker Branch Watershed (Lindberg, 1996). Another endpoint for the uptake of dissolved Hg in soil water is emission of Hg^0 from the plant along with water vapor. This may be one source of the measured Hg^0 emitted from plant canopies (Hanson *et al*., 1995; Lindberg, 1996; Lindberg *et al*., 1998).

If soil absorption was the primary route of Hg accumulation in foliage, then biochemical and metabolic influences such as transpiration rate would probably cause differences in uptake rates among species. In our study there were no significant differences in foliar Hg concentrations among tree species during a given sampling period, thus, it is unlikely that soil absorption is a major source of Hg in foliage and litterfall. Total Hg concentrations in soil were 5–18 times higher (depending on the sampling depth) at the Lake Champlain site than at the Lake Huron site (Table I). The enrichment of Hg in surface soils at the Lake Champlain site is probably influenced by both the humic and clay content of the soil which will bind Hg more effectively than the sandy soil at the Lake Huron site. If translocation of Hg from soil was a significant uptake pathway for Hg in foliage, foliar concentrations should reflect these differences, assuming that soil Hg levels reflect the Hg available for root uptake. Laboratory studies indicate that root uptake of Hg is minimal (Beauford *et al*., 1977; Godbold and Huttermann, 1988). Local sources of atmospheric Hg deposition are probably not significantly different at these sites because levels of Hg in aerosol (0.007±0.004 ng m^{-3} at the Lake Champlain site and 0.007±0.006 ng m^{-3} at the Lake Huron site), total gaseous Hg (1.7±0.5 ng m^{-3} and 1.3±0.3 ng m^{-3}), and precipitation Hg (10.2±4.4 ng L^{-1} and 14.3±8.3 ng L^{-1}) samples were similar (mean ± std. dev. May–November, 1995 at Lake Champlain and May-November, 1996 at Lake Huron).

3.3. ESTIMATES OF FOLIAR Hg ACCUMULATION FROM THE ATMOSPHERE

Mercury exists in the atmosphere primarily as gaseous Hg^0, with smaller (<5%) but important concentrations of reactive gaseous Hg (Lindberg and Stratton, 1998) and particulate Hg (Keeler *et al*., 1995). Since ambient Hg levels at both sites remain relatively constant throughout the year, continuous uptake of gaseous Hg^0 through the leaf stomata and surface absorption of both gaseous and particulate Hg might reasonably account for the Hg in foliage. These processes are a function of both meteorology (wind speed, turbulent mixing) and leaf surface characteristics, such

TABLE II

Measured Hg concentrations (mean ± std. dev.; ng g^{-1}) in live foliage. The estimated mean Hg^0 accumulation rate from the atmosphere is the accumulated Hg between foliage collections multiplied by the number of days between collections, assuming that all Hg has originated from atmospheric uptake. The mean ± std. dev. ambient Hg^0 concentration was measured at the sampling sites. The mean (± std. dev.) modeled Hg^0 V$_d$ was calculated using a multiple resistance dry deposition model (Hicks *et al.*, 1987; Lindberg *et al.*, 1992) based on local meteorological data and individual canopy characteristics. The mean (± std. dev.) modeled Hg^0 deposition flux was calculated by multiplying the mean modeled Hg^0 V$_d$ by the mean Hg^0 concentration

Site	Month	n	Mean foliar Hg conc. (ng g^{-1})	Day between collections	Mean Hg^0 accum. rate (ng m^{-2} d^{-1})	Mean ambient Hg^0 conc. (ng m^{-3})	Mean Hg^0 V$_d$ modeled (cm s^{-1})	Mean Hg^0 dry dep. modeled (ng m^{-2} d^{-1})
Lake Champlain Watershed 1995	May	11	3.6±2.6					
	June	9	6.9±0.9	28	8±2	1.3±0.1	0.056±0.041	63±46
	August	10	18.8±0.5	51	15±3	1.4±0.3	0.060±0.050	73±62
	September	11	28.8±2.4	50	13±2	1.1±0.2	0.041±0.031	39±30
Lake Huron Watershed 1996	May	12	3.3±1.1					
	June	9	4.9±0.4	16	14±5	1.2±0.1	0.071±0.024	74±26
	July	12	14.4±2.4	46	29±10	1.2±0.1	0.064±0.025	66±27
	August	7	21.0±2.4	27	34±11	1.5±0.3	0.083±0.024	108±38
	September	11	23.1±4.1	24	12±4	1.1±0.2	0.050±0.014	56±18

as leaf hairs, waxes, and roughness. It should be noted the following discussion focuses on the deciduous tree species sampled in this study and application to coniferous species remains speculative.

If foliar Hg concentrations were primarily due to aerosol deposition, then species differences should be expected based on leaf surface characteristics. It has been shown that Pb in foliage is primarily due to aerosol deposition to the leaf surface (Heinrichs and Mayer, 1980; Lindberg and Harriss, 1981), especially to pubescent leaf surfaces, such as birch. We also measured species differences for foliar Pb concentrations (Figures 3a and 3b) that indicated the most pubescent leaves (birch) also had the highest Pb concentrations. Aerosol absorption of Hg is likely to be minimal, since ambient total aerosol Hg concentrations were very low (mean $\pm$ std. dev. from both sites 0.007 ± 0.005 ng m^{-3}; n = 64) compared to total gaseous Hg (1.5 ± 0.4 ng m^{-3}; n = 64). Also, leaf washing experiments have demonstrated that particulate Hg readily washes off the leaf surface and may be less likely to be incorporated into leaf tissue (Rea *et al.*, 2000).

The steady increase in foliar Hg concentrations throughout the growing season suggests that the leaves accumulated gaseous Hg^0 from the atmosphere. To examine this source of Hg, foliar accumulation of atmospheric Hg was estimated using both measured and modeled data. Assuming that all of the Hg in foliage originated from atmospheric uptake, the actual Hg^0 uptake rate can be estimated based on the measured foliar Hg concentrations and leaf area data (63 ± 11 g m^{-2} at the Lake Champlain site and 141 ± 46 g m^{-2} at the Lake Huron site). The estimated mean daily Hg^0 uptake rate from the atmosphere (ng m^{-2} d^{-1}) was calculated based on the increased Hg accumulated in foliage between collections multiplied by the number of days between collections (Table II). The Hg^0 accumulation rate ranged from 8 ± 2 to 15 ± 3 ng m^{-2} d^{-1} at the Lake Champlain site and from 12 ± 4 to 34 ± 11 ng m^{-2} d^{-1} at the Lake Huron site (Table II). To determine if dry deposited Hg^0 could account for this accumulation rate, we compared these rates to the modeled dry deposition flux of Hg^0 to the canopy.

A multiple resistance model developed by Hicks *et al.* (1987) and modified by Lindberg *et al.* (1992) for Hg^0 was used to model the dry deposition flux of Hg^0 to these forests. The model estimated hourly dry deposition velocities (V_d) based on local meteorological data collected at both sites and individual canopy characteristics. The model was used to estimate the dry deposition of Hg^0, not Hg^{2+} or particulate Hg species because Hg^0 is the most likely form of Hg being taken up into foliage (Lindberg *et al.*, 1992). Water soluble reactive gaseous Hg (Hg^{+2}) and particulate Hg compounds will most likely wash-off the leaf surface in throughfall and are less likely to accumulate in the leaf interior (Lindberg *et al.*, 1994; Rea *et al.*, 2000; Rea *et al.*, 2001). Reactive gaseous Hg may also be photochemically reduced to Hg^0 and be re-emitted from the canopy surface.

The model does not take into account a compensation point for Hg, which has been observed for tree seedlings in a chamber study (Hanson *et al.*, 1995). The compensation point is the point at which net deposition and emission of Hg are

at equilibrium. For tree seedlings, the compensation point for Hg ranged from 9–20 ng m^{-3} (Hanson *et al.*, 1995). Deposition of Hg occurred above this range and emission of Hg^0 occurred below this range. The compensation point is dependent on the ambient air, soil, and soil water Hg concentrations, which will vary by site and forest type, and is beyond the current capability of this model.

The mean modeled gaseous Hg V_d ranged from 0.041±0.031 to 0.060±0.050 cm s^{-1} at the Lake Champlain site and from 0.050±0.014 to 0.083±0.024 cm s^{-1} at the Lake Huron site (Table II). The differences in mean V_d were due to differences in meteorology between years and canopy characteristics. The Lake Champlain site is located on Mt. Mansfield in the Green Mountains of Vermont, ∼400 m above sea level, while the Lake Huron site is located in the mid-west on rolling terrain between Lake Michigan and Lake Huron, ∼240 m above sea level. The modeled V_d for Hg^0 reported here are similar to the V_d (0.009–0.094 cm s^{-1} and 0.020–0.081 cm s^{-1}) reported for the Walker Branch Watershed and the Lake Champlain Watershed (Lindberg *et al.*, 1994; Rea *et al.*, 1996).

The dry deposition flux of Hg^0 to each canopy was calculated using the equation

$$F = V_d * [Hg^0_{air}] ,$$

where F is the dry deposition flux of Hg^0, V_d is the mean modeled dry deposition velocity between foliage collections, and [Hg$^0_{air}$] is the mean measured total gaseous Hg concentration during the time interval (Table II). The mean modeled dry deposition flux of Hg^0 ranged from 39 to 70 ng m^{-2} d^{-1} at the Lake Champlain site and from 49 to 107 ng m^{-2} d^{-1} at the Lake Huron site. At both sites, the modeled dry deposition flux of Hg^0 is much greater than the estimated foliar Hg accumulation rate (Table II). This indicates that Hg^0 dry deposition to the canopy is more than sufficient to account for the total Hg measured in foliage (Table II). These data show that, on average, only 25% of the Hg^0 dry deposited to the canopy needs to be accumulated by foliage to explain the measured foliar Hg concentrations. The remaining Hg^0 may be transformed into other Hg compounds that may be washed off the leaf surface in throughfall (Lindberg *et al.*, 1994; Rea *et al.*, 1996; Rea *et al.*, 2000; Rea *et al.*, 2001). Some of this Hg^0 may also be a source of Hg^0 emitted from plant canopies (Hanson *et al.*, 1995; Lindberg, 1996; Lindberg *et al.*, 1998).

4. Conclusions

Litterfall Hg deposition contributed an average of 40% of the total Hg flux in these watersheds, 15.8±1.9 μg m^{-2} yr^{-1} in the Lake Champlain Watershed and 11.4±2.8 μg m^{-2} yr^{-1} in the Lake Huron Watershed. Estimated annual total throughfall Hg deposition was 11.6±0.7 μg m^{-2} yr^{-1} in the Lake Champlain Watershed and 10.5±1.0 μg m^{-2} yr^{-1} in the Lake Huron Watershed, or ∼33% of the total Hg

flux. Measured Hg deposition in precipitation contributed $\sim$27% of the total Hg flux, 9.0$\pm$0.6 μg m^{-2} yr^{-1} and 8.7 μg m^{-2} yr^{-1} in the Lake Champlain and Lake Huron Watersheds, respectively (Rea, 1998; Rea et al., 2001; Keeler, unpublished data).

Identifying the source of the Hg deposited to the forest floor in litterfall is important because litterfall represents the largest deposition flux of Hg to forested watersheds. Determining the source of Hg in living foliage would also indicate the largest source of the Hg deposited in litterfall. Our measurements have shown that over the course of two growing seasons, foliar Hg concentrations increased steadily by an order of magnitude in all deciduous tree species sampled in these two northern mixed-hardwood forests. Foliar concentrations in both forests were similar despite differences in sampling years and soil Hg concentrations. Since Hg in foliage did not behave similarly to elements dominated by soil uptake or aerosol deposition, it appeared that gaseous Hg uptake from soil water or the atmosphere might be important. Estimates of the uptake of dissolved Hg in soil water accounted for 3–14% of the Hg in litterfall. Our measurements appear to indicate that other internal Hg sources (soil or 'recycled' Hg) were not significant contributors to foliar Hg concentrations. Based on Hg measurements and modeled deposition velocities, it is possible that all of the Hg in foliage represents atmospheric Hg accumulated throughout the growing season. Our atmospheric and foliar Hg measurements indicate that accumulation of ambient Hg appears to be the primary source of Hg in living foliage and, therefore, litterfall. An additional part of this research has been to identify the source of the Hg deposited in net throughfall. Wash-off of dry deposited Hg compounds from the leaf surface appears to be the most important source of Hg in throughfall (rather than foliar leaching) and has been reported elsewhere (Rea et al., 2000; Rea et al., 2001). These data suggest that the atmosphere plays a primary role in the biogeochemical cycle of Hg in forested ecosystems and that litterfall is a vehicle for atmospheric Hg deposition.

Acknowledgements

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