THE PROCESSING OF MERCURY IN FORESTED ECOSYSTEMS

by

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In memory of my brother

Daniel David Rea

(April 21, 1965-September 15, 1981)

Trees

I think that I shall never see
A poem lovely as a tree.

A tree whose hungry mouth is prest
Against the earth's sweet flowing breast;

A tree that looks at God all day,
And lifts her leafy arms to pray;

A tree that may in Summer wear
A nest of robins in her hair;

Upon whose bosom snow has lain;
Who intimately lives with rain.

Poems are made by fools like me,
But only God can make a tree.

--Joyce Kilmer

I see the light at the end of the tunnel now, someone please tell me it's not a train.

--David Lowery

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CHAPTER I

INTRODUCTION

The biogeochemical cycling of mercury (Hg) is both dynamic and complex, because Hg may be present in numerous physical and chemical forms which vary in toxicity. Mercury is a toxin which bioaccumulates in organisms and can be fatal. There are numerous sources of Hg in the environment, from both anthropogenic (power plants, waste incinerators, combustion) and natural (volcanoes, geothermal vents, soils, oceans) processes (Nriagu, 1979; Lindqvist and Rodhe, 1985; Lindqvist, 1994). In the atmosphere, Hg is present predominately in a gaseous form, but also may be present as an aerosol (Lindqvist and Rodhe, 1985; Brosset and Lord, 1991). Atmospheric deposition has been found to be a significant source of Hg to aquatic and terrestrial ecosystems (Iverfeldt, 1988; Lindqvist, 1994; Lindqvist and Schroeder, 1989; Lindqvist and Rodhe, 1985; Slemr and Langer, 1992; Iverfeldt, 1991a; Munthe *et al.,* 1995; Hultberg *et al.,* 1995; Lindberg, 1996).

Mercury can undergo numerous chemical transformations, and once deposited to a surface, gaseous Hg may be re-emitted (Iverfeldt and Lindqvist, 1986; Brosset and Lord, 1991; Iverfeldt, 1991a; Munthe, 1992; Hall, 1995; Lindberg, 1996; Lindberg *et al.,* 1998). Technological advances in recent years have made it possible to detect low levels of Hg in the environment using clean techniques for sample handling, collection, and analysis.

Run-off of Hg from forested ecosystems to aquatic ecosystems may be an important source of Hg in fish (Johansson and Iverfeldt, 1994; Lee *et al.,* 1994; Hultberg *et al.,* 1994; Hultberg *et al.,* 1995). In addition to the two forests studied in this project, Hg has been studied in two other forests world-wide: in the Lake Gardsjon Watershed, Sweden (Iverfeldt, 1991a; Munthe *et al.,* 1995) and the Walker Branch Watershed, Tennessee (Lindberg *et al.,* 1994).

Litterfall (i.e. senesced foliage) and throughfall (i.e. rain that passes through the forest canopy) represent the two largest deposition pathways for Hg in forested ecosystems (Iverfeldt, 1991; Lindberg, 1996; Rea *et al.,* 1996). Evaluating the biogeochemical cycling of Hg requires an understanding of the origin of the Hg annually deposited to the forest floor. There are many possible sources of Hg in living foliage, before it becomes litterfall, including soil uptake and translocation, evapotranspiration of gaseous Hg in soil water, and the uptake of gaseous Hg from the atmosphere. The sources of Hg in throughfall include foliar leaching from within the plant or wash-off of previously dry deposited Hg. While other studies have attributed the source of the Hg in litterfall and throughfall to dry deposition from the atmosphere, internal sources have not been discounted (Iverfeldt, 1991a; Lindberg *et al.,* 1994; Munthe *et al.,* 1995).

Identifying the source of the Hg in litterfall and throughfall is essential to proper assessment of the biogeochemical cycle of Hg in forested ecosystems. Forests may have a limited capacity for increased loading of Hg due to anthropogenic sources which may alter the natural Hg cycle. It is important to determine if the Hg deposited in litterfall and throughfall is anthropogenic or geologic in nature because increased Hg inputs due to anthropogenic atmospheric sources may disturb ecosystem dynamics. Understanding how forests process Hg at current background levels provides a foundation for studying forested ecosystems elevated in Hg.

This thesis will attempt to identify the origin of Hg deposited to forested ecosystems in litterfall and throughfall in order to understand how forested ecosystems process Hg. For the first time, a multi-element approach will be used to examine the origin of Hg in both litterfall and throughfall by comparing Hg to other trace elements (with both anthropogenic or geologic sources) which have been previously studied in detail. Although a suite of 27 trace elements were analyzed per sample, only selected trace elements have been reported together with the Hg data because the main focus of this thesis is identifying the source of Hg in litterfall and throughfall.

The chapters in this thesis are presented in a journal article format. All chapters have either been peer reviewed and published (chapters 2 and 3) or will be submitted (chapters 4, 5, and 6) manuscripts. The forested sites chosen for this study were removed from local source influences and did not have a history of extremely elevated Hg deposition (due to mining, for example). During the early phases of this work, samples were collected from a northern mixed-hardwood forest at the Proctor Maple Research Center in Underhill Center, Vermont. These data are reported in chapters 2, 3, and 4. Based on these data, a larger sampling campaign was conducted in a northern mixed-hardwood forest at the University of Michigan Biological Station in Pellston, Michigan. Precipitation, throughfall, foliage, litterfall, ambient air, and soil samples were collected at both locations. Following is a brief review of the major findings discussed in each chapter.

Chapter 2, "Microwave digestion and analysis of foliage for total mercury by cold vapor atomic fluorescence spectroscopy," describes a microwave digestion technique for foliage that was developed as part of this project. Foliage was ground by hand using glass mortars and pestles and digested in 1.6 M nitric acid. Using this method, recovery of Hg was 90 ± 6% from National Institute of Standards and Technology Standard Reference Material #1515 (apple leaves). This method also compared within 15% of Instrumental Neutron Activation Analysis and hot acid digestion techniques. The main benefits of this digestion technique are (1) complete and consistent digestion of all sample material, (2) digestion time is approximately 30 min, and (3) analytical blanks are consistently low. This chapter has been published in *Biogeochemistry* (Rea and Keeler, 1998).

Chapter 3, "The deposition of mercury in throughfall and litterfall in the Lake Champlain Watershed: a short-term study," reports on the pilot study for this project. This study found that the Hg concentration of litterfall was 60% higher than the Hg concentration of live foliage collected in August. The mean Hg concentrations in throughfall were significantly greater than the mean Hg concentrations in precipitation during the study period. Based on the limited data set, it appeared that atmospheric deposition was a significant input of Hg to this forest. This pilot study pointed to the need for a more detailed investigation on the origin of Hg in litterfall and throughfall. This chapter has been published in *Atmospheric Environment* (Rea *et al.,* 1996).

Chapter 4, "Accumulation of atmospheric mercury in foliage in the Lake Champlain and Lake Huron Watersheds," examines the increase in the Hg concentrations between foliage and litterfall. Live foliage was collected throughout the growing season and litterfall was collected in autumn at the Vermont site in 1995 and at the Michigan site in 1996. Foliar Hg concentrations uniformly increased ten-fold throughout the growing season across all species sampled at both sites; a trend which was not observed for any other element measured. Differences in foliar concentrations of the other elements appeared to be due to differing atmospheric or soil inputs at the two sites, or to metabolic differences between tree species. Various sources of Hg in foliage were examined including soil, soil water, and the atmosphere. Based on elemental ratios in foliage, soil uptake of Hg was not significant. Estimates of Hg uptake from soil water accounted for 3-14% of the Hg in litterfall. Based on foliar Hg measurements, leaves needed to accumulate, on average, 25% (16-34%) of the available Hg^0 in the atmosphere. This accumulation rate could account for all the Hg measured in foliage throughout the growing season. The remaining dry deposited Hg^0 may be transformed on the leaf surface to a water soluble Hg compound that will wash-off in throughfall or may be re-emitted from the canopy.

Chapter 5, “Development of a washing technique for measuring dry deposition of mercury and selected trace elements to foliage and surrogate surfaces,” describes leaf washing experiments that were conducted to determine the influence of dry deposition and foliar leaching of Hg from forest foliage. Various experiments were conducted to wash dry deposition off the leaf surface and leach material out of the leaf. Dry deposition fluxes were also measured using live foliage and surrogate Teflon surfaces. These experiments found that that removal of dry deposited Hg, not internal plant Hg, was the origin of Hg in the leaf wash.

Chapter 6, "Dry deposition and foliar leaching of mercury and selected trace elements in a northern mixed-hardwood forest," examines the origin of Hg in throughfall collected at the Michigan site. One of the inherent problems with analyzing throughfall data is decoupling the dry deposition and foliar leaching components. These components were separated using several approaches, including elemental ratios, enrichment factors, and multiple linear regression. These approaches indicated that dry deposition had the most important influence on Hg in throughfall. To determine if atmospheric Hg could account for all the Hg measured in net throughfall, gaseous and aerosol Hg measurements were integrated with modeled deposition velocities. Modeling the dry deposition of Hg^0, Hg^{2+}, and fine fraction particulate Hg indicated that there was enough dry deposited Hg to account for all of the Hg deposited in net throughfall and litterfall. To complete the forest mass balance, a re-emission estimate for Hg^0 was also made.

Chapter 7, "Conclusions and Synthesis," summarizes this research and compares the methods used in each chapter to measure dry deposition. In addition, suggestions for future research are discussed.

CHAPTER II[i]

MICROWAVE DIGESTION AND ANALYSIS OF FOLIAGE FOR TOTAL MERCURY BY COLD VAPOR ATOMIC FLUORESCENCE SPECTROSCOPY

Abstract. A microwave technique for digesting foliage samples was developed and evaluated for quantifying low levels of Hg by cold vapor atomic fluorescence spectroscopy, CVAFS. The method meets three criteria: (1) to digest all sample material completely and consistently, (2) to reduce sample digestion time to less than one hour, and (3) to maintain a low analytical blank. Mean recovery of NIST standards was 90 ± 6%. Samples that were analyzed by this technique and by Instrumental Neutron Activation Analysis compared within 15%. This method also compared within 15% of hot acid digestion methods on samples prepared and analyzed by CVAFS at different laboratories in the First International Mercury in Foliage Intercomparison of Methods (FIM)[2]. The largest source of variability in all of the interlaboratory comparisons was sample inhomogeneity rather than analytical error.

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INTRODUCTION

Throughout the world, vegetation, fungi, and mosses grown near areas of elevated levels of mercury (Hg) (i.e. volcanoes, mines, chlor-alkali plants, and incinerators) have extremely high levels of Hg in their tissues (Lindberg *et al.* 1979; Siegel *et al.* 1984; Shaw and Panigrahi, 1986; Barghigiani and Bauleo, 1992; Carpi *et al.*, 1994; Fischer *et al.*, 1995). As a result, plants have been used as Hg biomonitors for decades. At these high levels (less than 1 to over 10,000 µg/g) sample preparation for samples of vegetation, fungi, mosses, and lichen by hot acid digestion and analysis by cold vapor atomic absorption spectrometry (CVAAS) or cold vapor atomic fluorescence spectroscopy (CVAFS) has proved sufficient (Stokes *et al.*, 1983; Shaw and Panigrahi, 1986; Kojo and Lodenius, 1989; Barghigiani *et al.*, 1990; Bargagli *et al.*, 1991; Carpi *et al.*, 1994; Moore *et al.*, 1995). Using extreme care to avoid contamination and analytical error, hot acid digestion and analysis by CVAAS or CVAFS has been successfully carried out on vegetation samples with much lower total Hg concentrations (Rasmussen *et al.*, 1991; Iverfeldt, 1991a; Munthe *et al.*, 1995; Lindberg, 1996).

Studies have shown that there are many sources of variability in the analysis of plant tissues for total Hg. Sources of variation include not only differences between plants of the same species (Rasmussen *et al.*, 1991) but also within different species at the same site (Kovalevskii, 1986; Barghigiani *et al.*, 1990). Additionally, tissue age, type, and calcium content have been found to influence the variability of Hg within plants (Rasmussen, 1994). Sources of analytical variability include incomplete digestion and inadequate mixing of the sample (Rasmussen, 1994). Also, the concentrated nitric (14M) and/or sulfuric acids (18M) frequently used to digest samples can cause elevated reagent blanks. Despite efforts to homogenize vegetation samples without causing contamination, variability within the sample matrix remains a problem, especially at low Hg levels. Generally, within sample replication can be kept to within 10% (Siegel *et al.*, 1984; Rasmussen *et al.*, 1991; Rasmussen, 1994; Carpi *et al.*, 1994).

Microwave digestion has been used successfully to extract organic samples for other types of analyses, such as atomic absorption, inductively coupled plasma mass spectroscopy, and chromatography. Microwave digestion and analysis of *Rosmarinus officinalis* L. (rosemary) for total Hg by CVAAS has been reported, but the method was not described (Barghigiani and Ristori, 1995). Our laboratory has successfully used microwave digestion of glass-fiber filters for trace level Hg (pg) analysis (Keeler *et al.*, 1995). A similar technique was investigated for digesting foliage samples that would (1) digest all of the sample material completely and consistently, (2) require little effort and rapid digestion (less than 1 h), and (3) require less concentrated acid thereby reducing reagent blanks.

METHODS

Foliage collection and processing

Foliage samples were collected from a site located at the Proctor Maple Research Center in Underhill Center, Vermont (44° 31'N, 72° 52' W, 400 m elevation) on 30 August 94. The species sampled were *Acer saccharum* Marsh. (sugar maple), *Betula alleghaniensis* Britt. (yellow birch), *Fagus grandifolia* Ehrh. (American beech), and

Ostrya virginiana (Mill.) K. Koch (hop-hornbeam). These samples were collected as part of a larger Hg in throughfall and litterfall study (Rea *et al.*, 1996). To determine if there were any significant differences between individual trees of the same species or between tree species, three samples were collected from three trees of each species. Foliage samples were collected using a pole pruner with four to six extensions to clip branches from trees at a height of 12 m. Branches were caught before hitting the ground and the leaves were carefully picked from the branches and placed into plastic bags. Approximately 20 leaves from each branch were collected into plastic bags for Hg analysis. These samples were triple bagged and frozen until dried at the University of Michigan Air Quality Laboratory (UMAQL). Particle-free gloves were worn at all times during sample collection and handling.

Clean techniques were incorporated into all phases of the drying and digestion procedures in order to minimize contamination or volatilization of Hg from the leaves. Oven-drying plant samples for Hg analysis has been shown to cause losses of Hg (Rasmussen *et al.*, 1991; Carpi *et al.*, 1994). Therefore, to minimize Hg losses due to volatilization, samples were kept triple bagged and frozen until dried in a Class 100 clean bench at room temperature. The foliage samples were dried inside acid-cleaned polyethylene buckets with HEPA filtered air (class 100) drawn through the buckets by vacuum pumps for three to four days. Particle-free gloves were worn during all stages of sample handling and were changed between samples to prevent cross-contamination. Petioles were removed to prevent dilution of the sample (Rasmussen *et al.*, 1991). Petioles were removed by breaking them from the leaf base. Each sample was placed in an acid-cleaned Teflon bottle and ground to approximately 0.5-1 mm in diameter using an acid-cleaned polyethylene spatula; a clean spatula was used for each sample. The bottles were sealed with Teflon-tape, triple bagged, and stored at room temperature until digested and analyzed for Hg.

Rasmussen *et al.* (1991) found that air dried samples retained approximately 5% of their moisture content. Therefore, a second set of 20 leaves from each branch was collected to determine differences in the dry weight of leaves dried at room temperature versus conventional drying techniques. The petioles were also removed from these leaves before they were oven-dried. The dry weight ratio of leaves dried in an oven to leaves dried at room temperature was 0.94-0.96. Therefore, it was determined that samples for Hg analysis were sufficiently dried at room temperature.

Microwave digestion and analytical procedures

Foliage samples to be analyzed for total Hg were handled while wearing particle-free gloves in the Class 100 clean bench and analyzed in a Class 100 clean room. The microwave sample preparation accessories described below are from CEM Corporation for use with the MDS-2000. Lined digestion vessels with vent stems were used to microwave the samples. After thorough mixing of the sample, a 0.25 g aliquot was weighed into the acid-cleaned Teflon microwave vessel using an acid-cleaned polyethylene spatula. Next, 20 mL of 1.6 M HNO_3 (Suprapur, EM Science) were added to the vessel. The Teflon vessels and lids were sealed inside vessel shells. The MDS-2000 has an internal pressure control system which passively monitors the pressure inside one vessel without contaminating the sample. The microwave oven was programmed in three stages. The pressure was first raised and held at 40 PSI for three minutes, then it was raised to 85 PSI and held for three minutes, and, finally, the pressure was raised to 150 PSI and held for five minutes (CEM 1991). A transparent, deep yellow solution, with no visible solid or particulate material, remained in the vessel after digestion. The microwave digestion procedure took approximately 35 minutes to complete.

After the vessels had cooled, the Hg forms in the extract were oxidized to Hg^{2+} with 0.2N BrCl to a 0.005N BrCl solution and allowed to react for at least 12 h before analysis. A 1 mL aliquot of the extract was taken for analysis, the excess BrCl was reduced with NH_2OH and the Hg^{2+} in solution was reduced to Hg^0 with $SnCl_2$. The solution was purged with high purity N_2 and the Hg^0 liberated was collected onto a gold-coated bead trap. The gold traps were thermally desorbed in a high purity He stream and analyzed by CVAFS using the dual amalgamation technique (Fitzgerald and Gill, 1979). Calibration curves were run on each day of analysis. Control standards were checked throughout the course of analysis. If a control standard was not within 10% of the expected value, the instrument was recalibrated. Reagent blanks were run on each day of analysis and contributed to less than 3% of the sample concentration. The detection limit, calculated using three times the mean of the reagent blank for a 1 mL aliquot, was 2.8 ng/g. All foliage samples were analyzed in duplicate and reported concentrations have been blank corrected.

RESULTS AND DISCUSSION

NIST recoveries

To test this digestion technique, 20 aliquots of National Institute of Standards & Technology (NIST) Standard Reference Material (SRM) #1515 (*Pyrus* spp.) were digested and analyzed in duplicate. Mean recovery of NIST SRM #1515 after microwave digestion was 90 ± 6% of the certified value. On each day of analysis, two aliquots of the NIST standard were digested and analyzed in duplicate; variation between analytical duplicates ranged from 0.01-9.0%. The NIST suggests that digestion in nitric acid alone is incomplete and hydrofluoric (HF) acid should also be used to provide full recovery. Since samples are purged in acid-cleaned glassware, our analytical system cannot tolerate HF and it was not used. Although recovery usually fell within the certified range, the lack of HF in the sample digestion could account for recovery being less than 100%.

Interlaboratory Comparisons

As a test of this microwave digestion procedure, two 0.1 g aliquots of dried sample from *Acer saccharum*, *Betula alleghaniensis*, and *Ostrya virginiana* were analyzed for Hg by Instrumental Neutron Activation Analysis (INAA) at the Nuclear Reactor Laboratory at the Massachusetts Institute of Technology (Olmez, 1995). Since the entire sample is analyzed, any problems associated with incomplete digestion are avoided with INAA. Two aliquots of these same samples were digested and analyzed for Hg by CVAFS at the UMAQL. The results of these analyses are presented in Table 2.1. Agreement between the two analytical methods was better than 15% except for one replicate of *Ostrya virginiana*. Both sample inhomogeneity and differences in analytical procedures probably account for the differences observed between laboratories. Despite our efforts to thoroughly grind and mix the samples, the largest source of variability appears to be inhomogeneity within the sample. The differences between INAA and CVAFS may be due to variability between the individual leaves in the sample or, more likely, to more vein tissue and less leaf tissue being present in one aliquot versus another. It was observed upon grinding the leaves, that the vein tissue was thicker and more difficult to break apart than rest of the leaf tissue. Rasmussen *et al.* (1991) observed that the addition of the petiole to foliar samples caused dilution of the sample for total Hg. The same influence may be seen in vein tissue if it was not thoroughly ground and mixed within the sample.

The microwave digestion procedure was also tested against other sample preparation procedures in the First International Mercury in Foliage Intercomparison of Methods $(FIM)^2$ (Lindberg, 1997). Foliage samples were dried at room temperature, ground, and homogenized at Oak Ridge National Laboratory (ORNL) and were prepared and analyzed by CVAFS at the different laboratories involved in the $(FIM)^2$. The laboratories involved were ORNL, Frontier GeoSciences (FGS), the Swedish Environmental Research Institute (IVL), and the UMAQL. ORNL digested samples using EPA Hg digestion method 245.5 CLP-M which heats samples at 95°C in a sulfuric/nitric

Table 2.1. Mean ± standard deviation of replicate foliage samples analyzed for total Hg by Instrumental Neutron Activation Analysis (INAA) and microwave digestion and analysis by cold vapor atomic fluorescence spectroscopy (CVAFS). (ng Hg/g dry weight)

Species	**Replicate**	**MIT[1]** **(INAA)**	**UMAQL[2]** **(mic. dig. & CVAFS)**
Acer saccharum	**1**	**39 ± 5**	**38.8 ± 3**
	2	**36 ± 5**	**35.3 ± 2**
Betula	**1**	**36 ± 4**	**32.0 ± 5**
alleghaniensis	**2**	**33 ± 3**	**33.1 ± 9**
Ostrya virginiana	**1**	**41 ± 6**	**38.0 ± 5**
	2	**24 ± 4**	**39.4 ± 2**

[1] MIT: Massachusetts Institute of Technology

[2] UMAQL: University of Michigan Air Quality Laboratory

acid mixture. FGS and IVL also digested the samples in a nitric/sulfuric acid mixture followed by reflux heating in a glass vessel. The UMAQL used the microwave digestion procedure described in this paper.

Results of two of the foliage samples analyzed by the laboratories are shown in Table 2.2. Data shown include effects of differences in sample digestion procedures. Agreement between the laboratories ranged from 4 to 14% on the *Quercus prinus* L. (chestnut oak) sample and between 4 and 15% on the litterfall sample. The similarity between the digestion procedures used by ORNL, FGS, and IVL most likely accounts for the closer agreement between those methods than the microwave digestion method used by the UMAQL. The lower recovery (6-14%) on the samples in the $(FIM)^2$ by the UMAQL may be due to the digestion procedure, as a similarly low recovery was found for the NIST reference material. The results obtained by each laboratory, however, fell within the error associated with each sample value. The differences between laboratories may also be attributed to inhomogeneity between the sample aliquots. This would account for the good internal laboratory precision and the larger variation between laboratory analyses of these samples.

Table 2.2. Mean ± coefficient of variation expressed in ng/g of a live foliage and a litterfall sample prepared and analyzed for total Hg by cold vapor atomic fluorescence spectroscopy in separate laboratories involved in the First International Mercury in Foliage Intercomparison of Methods (FIM)[2]. (ng Hg/g dry weight)

	ORNL[1]	**FGS[2]**	**IVL[3]**	**UMAQL[4]**
preparation method	**heated H_2SO_4/HNO_3**	**heated H_2SO_4/HNO_3**	**heated H_2SO_4/HNO_3**	**microwave digestion**
Quercus prinus	**52.5 ± 2.5**	**54.4 ± 2.2**	**n/a**	**47.5 ± 4.5**
Mixed-hardwood litterfall	**115 ± 4.9**	**110.4 ± 1.5**	**120**	**103.3 ± 7.1**

[1] ORNL: Oak Ridge National Laboratory
[2] FGS: Frontier GeoSciences
[3] IVL: Swedish Environmental Research Laboratory
[4] UMAQL: University of Michigan Air Quality Laboratory

Foliar analysis

The results of the foliar analysis for samples collected in the Lake Champlain Watershed are summarized in Table 2.3. All of the samples were analyzed in duplicate with less than 10% variation between duplicate analyses. Total Hg concentrations ranged from 21.5 to 49.1 ng Hg/g (dry weight) for the species sampled in this study. The source of the variation in these samples is not incomplete digestion, as there were no traces of leaf material in the sample digests. More likely, the source of the variation was the inhomogeneity of the ground foliar samples.

Due to the large variation between samples of the same species, no significant differences were found ($p < 0.05$) between trees of the same species or between the four species sampled at this site. Rasmussen *et al.* (1991) also observed similarity in total Hg concentrations between leaves/needles of *Acer saccharum*, *Abies balsamea* (L.) Mill (balsam fir), and *Picea glauca* (Moench) Voss (white spruce). The total Hg concentrations measured in this study fall within the ranges reported for other forest species: *Picea mariana* (Mill.) BSP. (black spruce), *Pinus banksiana* Lamb. (jack pine), *Betula papyrifera* Marsh. (American white birch), and *Larix laricina* (Du Roi) K. Koch (Tamarack) (Moore *et al.,* 1995) and *Acer saccharum* and *Abies balsamea* (Rasmussen, 1994).

Table 2.3. Mean ± standard deviation, minimum, and maximum total Hg concentrations (ng/g dry weight) of four species of foliage collected from Underhill Center, Vermont on 30 Aug 94.

	Acer saccharum	*Betula alleghaniensis*	*Fagus grandifolia*	*Ostrya virginiana*
mean ± std. dev.	**39.1 ± 6.0**	**30.4 ± 4.1**	**34.9 ± 5.2**	**36.7 ± 7.3**
minimum	**33.0**	**21.5**	**27.7**	**24.2**
maximum	**49.1**	**35.5**	**40.7**	**45.9**
n	**9**	**9**	**8**	**9**

CONCLUSIONS

We have developed a microwave digestion procedure for deciduous leaves that is suitable for low level Hg determination by CVAFS. This method has accomplished all of our objectives; it (1) completely digests all sample material with no solids remaining, (2) requires little effort while reducing sample digestion time to approximately 35 minutes, and (3) requires only 1.6 M nitric acid instead of concentrated acids, which reduces analytical blanks. Mean recovery of NIST standards was 90 ± 6% and agreement with INAA was generally less than 15%. The microwave digestion procedure compared within 15% of other digestion procedures in the (FIM)^2. The largest source of variability between laboratories appears to be sample inhomogeneity rather than analytical error.

The problem of sample inhomogeneity which was brought out in this study has led to the development and use of acid-cleaned ground glass mortars and pestles. Not only do foliar samples appear to be much more homogeneous (sample variability is typically less than 5%), but also vein tissue is more easily broken down and the process of grinding samples is much faster and easier.

CHAPTER III[ii]

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

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 ± 8.5 ng ℓ^{-1}) was higher than in precipitation (6.5 ± 2.8 ng ℓ^{-1}). In August and September, 1994, the total deposition of Hg in throughfall was estimated to be 3.1 μg m^{-2} (1.9 μg m^{-2} in precipitation) to the deciduous hardwood forests in the Lake Champlain basin. The mean Hg concentration in litterfall (53.2 ± 11.4 ng g^{-1}) was significantly greater than the mean concentration in green foliage (34.2 ± 7.2 ng g^{-1}), suggesting uptake of Hg from the atmosphere by foliage. Estimated annual litterfall deposition to the Lake Champlain basin was 13 μg 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.

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INTRODUCTION

In assessing ecosystem cycling of mercury (Hg) and regulatory concerns about Hg accumulation in forested ecosystems, 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, 1991b). 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, 1991a), 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 17-19 μg m^{-2} in 1989 (Iverfeldt, 1991a) and ranged from 15.4 to 16.5 μg m^{-2} during 1991-1994 (Munthe *et al.,* 1995). Annual throughfall deposition of Hg in the Walker Branch Watershed was approximately 20 μg m^{-2} in 1991 (Lindberg *et al.,* 1994) and averaged 14 μg m^{-2} from 1992-1994 (Lindberg, 1996).

METHODOLOGY

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 ($44^0 31'$ N, $72^0 52'$ 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 year 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.

Field sampling techniques

Ultra-clean 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-Liter 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 3.1. 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 September 11, 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 August 16-30, 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, N. C.). Vapor-phase Hg was collected on gold-coated bead traps (using glass-fiber pre-filters) at a nominal flow rate of 300 $cm^3 \ min^{-1}$ 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 $\ell \ min^{-1}$ for 24 h (Burke *et al.*, 1995).

Table 3.1 Summary of blanks and analytical precision of the Lake Champlain throughfall study.

Sample type	Blanks	Mean analytical precision	Duplicate analyses performed
Throughfall & precipitation Hg:	Avg. bottle blank: 20 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 & litterfall Hg:	Vessel blank: 0.23 ng vessel^{-1}	foliage 4% litterfall 5%	100%

Green foliage and litterfall samples were collected to quantify the amount of Hg in canopy foliage and litterfall deposited on the forest floor. On August 30, 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 (September 20-October 7, 1994) and late (October 8-21, 1994) season samples.

Sample processing

From August 15-31, 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 ultra-pure 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 August 31, samples were shipped to the UMAQL and processed in a Class 100 clean room. All samples were allowed to react for at least 24 hours 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, N. C.) at 160 °C for 20 minutes (Keeler *et al.*, 1995). The extract was oxidized with concentrated BrCl to a 2.5% solution and allowed to react for at least one hour before analysis.

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 ± 3 ng g^{-1}) based on the reported NIST value of 44 ± 4 ng g^{-1}. While the analytical precision for replicate foliage samples was greater than 95% (< 2.2 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).

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 the dual amalgamation technique (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 re-calibrated if the control standard was not within 10% of the expected value.

RESULTS AND DISCUSSION

Throughfall and precipitation

The mean volume-weighted throughfall and precipitation concentrations (± std. dev.) of Hg were 12.0 ± 8.5 ng ℓ^{-1} (range 4.5-35.8 ng ℓ^{-1}) and 6.5 ± 2.8 ng ℓ^{-1} (2.1-12.4 ng ℓ^{-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 hours on September 23, 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 (Figure 3.1a), due to evaporation of water in the canopy.

Comparing the Hg concentrations and subsequent depositions (Figure 3.1a and Figure 3.1b), 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.

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 (± std. dev.) was 70.5 ± 21 ng m^{-2} (range 46.8-109 ng m^{-2}) in the mixed hardwood stand and 89.9 ± 37 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 ± 25 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 August 21, 1994 which was characterized by heavy rain of over six cm in four hours. At this time the sample bottles were replaced and the storm continued as a light, steady drizzle lasting over nine hours. In this storm,

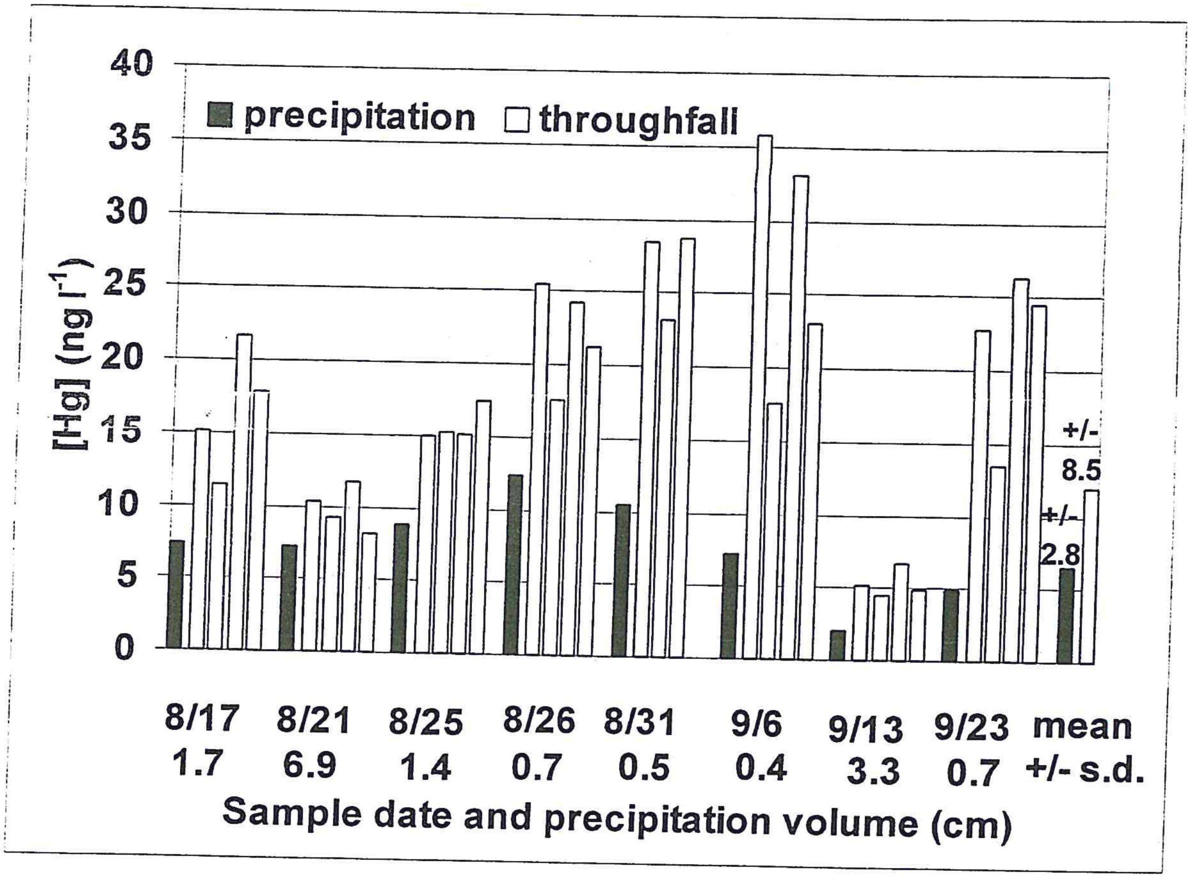


Figure 3.1a. Total Hg concentration (ng ℓ^{-1}) in precipitation and throughfall samples by collector and precipitation volume during each event for which throughfall was collected (last two bars indicate mean ± std. dev. of precipitation and throughfall concentrations, respectively)

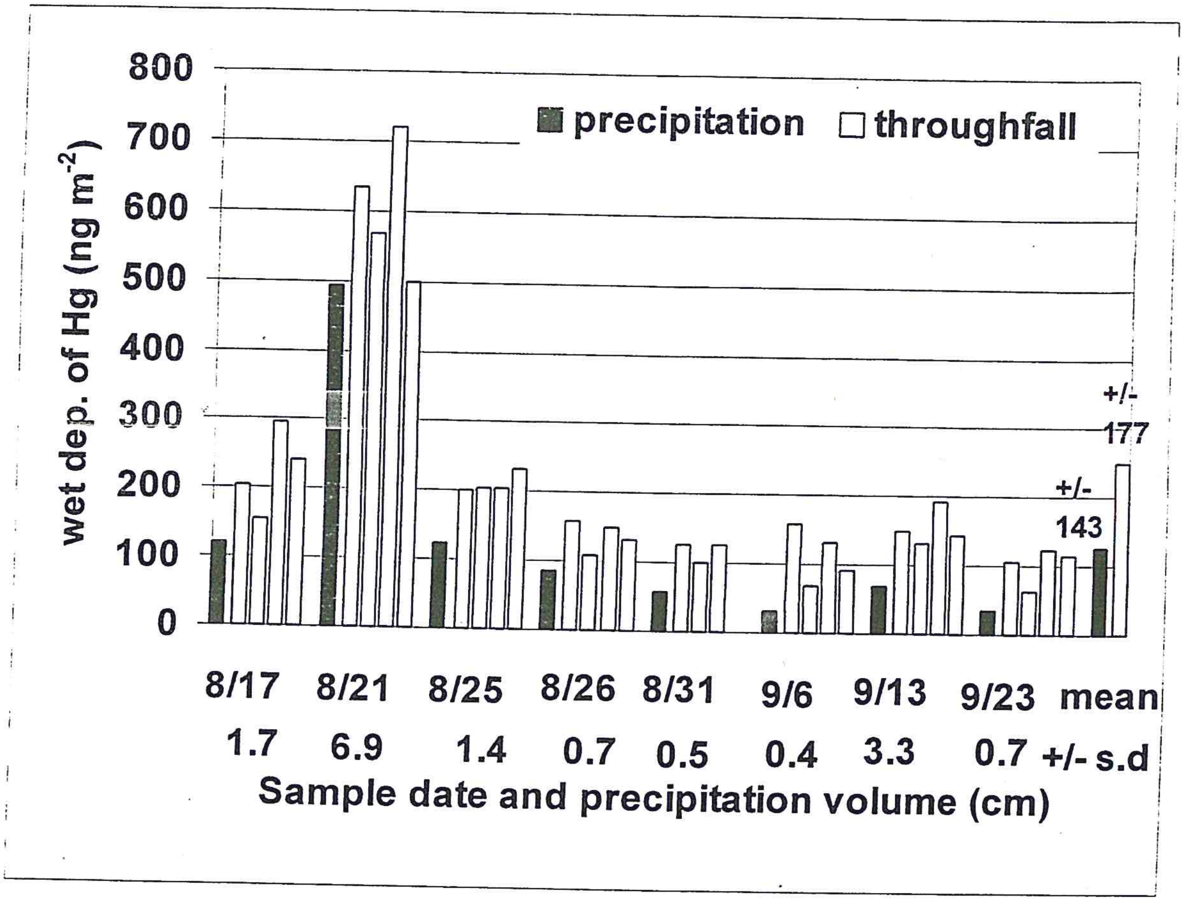


Figure 3.1b. Total precipitation and total throughfall Hg deposition (ng m^{-2}) by collector and precipitation volume during each event for which throughfall was collected (last two bars indicate mean ± std. dev. of precipitation and throughfall deposition, respectively)

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 ng m^{-2} 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 cm hr^{-1} and 0.096 cm hr^{-1} during the first and second part of the storm, respectively. The residence time of water on the leaf surface was estimated to be 24 seconds during the first part of the storm and estimated to be 6 minutes 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.

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 $\mu g\ m^{-2}$ or 41 kg (1.9 $\mu g\ m^{-2}$ 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 $\mu g\ m^{-2}$ during the months of August and September (Table 3.2). The deposition of Hg in throughfall (9.4 $\mu g\ m^{-2}$ 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.*, 1997), net throughfall Hg deposition adds an estimated 4 $\mu g\ m^{-2}\ yr^{-1}$ (53 kg yr^{-1}) to the estimated 7.9 $\mu g\ m^{-2}\ yr^{-1}$ (169 kg yr^{-1}) of Hg deposited by precipitation in 1994. Notably, this net throughfall deposition is similar to the 4.9 $\mu g\ m^{-2}\ yr^{-1}$ reported for Lake Gardsjon (Munthe *et al.*, 1995), and the 4-6 $\mu g\ m^{-2}\ yr^{-1}$ reported for the Walker Branch Watershed (Lindberg, 1996; Lindberg *et al.*, 1994). Thus, an estimated total of 10.4 $\mu g\ m^{-2}\ yr^{-1}$ 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.

Ambient mercury

During August 16-30, 1994, daily 24-hour 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.

Table 3.2. Summary of data from four studies on Hg in total throughfall deposition and precipitation deposition ($\mu g\ m^{-2}$) for the months of August and September.

Location	**Months and year**	**Forest type**	**Total throughfall deposition**	**Total precipitatio deposition**	**Ref.**
Lake Gardsjon, Sweden	**Aug-Sep, 1989**	**Spruce**	**5.0-6.0**	**2.4**	**a**
Walker Branch Watershed, TN	**Aug-Sep, 1991**	**Oak**	**2.7**	**1.4**	**b, c**
	Aug-Sep, 1994	**"**	**2.3**	**0.9**	**c**
Lake Champlain Underhill Cente VT	**Aug-Sep, 1994**	**Mixed hardwood**	**3.1**	**1.9**	**d**

(a) Iverfeldt, 1991a
(b) Lindberg *et al.*, 1994
(c) Lindberg, personal communication
(d) This study

There were no statistical differences or trends between vapor-phase Hg concentrations between the field and canopy sites. Vapor-phase Hg levels averaged (± std. dev.) 1.6 ± 0.3 ng m^{-3} (range 1.2-2.3 ng m^{-3}) in the field and 1.6 ± 0.5 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 days) 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 (± std. dev.) particulate Hg concentration was 7 ± 2 pg m^{-3} (range 3-11 pg m^{-3}) in the field and 9 ± 3 pg m^{-3} (3-15 pg m^{-3}) in the canopy. These measurements were used to estimate the dry deposition of Hg.

Dry deposition estimates

The multiple resistance model developed by Hicks *et al.* (1987) and modified by Lindberg *et al.* (1992) for estimating the dry deposition of Hg to forest canopies was used to determine the deposition velocity (V_d) for both vapor- and fine particle-phase Hg forms during dry periods prior to rain events (Table 3.3). The modeled V_d was calculated using hourly on-site meteorological measurements. The model estimates (Table 3.3) indicate that if we assume particulate Hg was only in the fine fraction it would represent less than 5% (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

Table 3.3. 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. (hrs)	Range of ambient Hg over dry period		Modeled mean V_d(cm s^{-1})		Dry dep. rates (using V_d) Hg(g) (ng m^{-2} hr^{-1})	Dry dep. rates (using V_d) Hg(p) (ng m^{-2} hr^{-1})	Estimated net throughfall dry dep.rates (ng m^{-2} hr^{-1})
		vapor (ng m^{-3})	particulate (ng m^{-3})	Hg(g)	Hg(p)			
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

throughfall. This suggests that some Hg in net throughfall may be coarse particulate Hg, oxidized vapor forms (Hg-II compounds), and/or an Hg^0 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):

Est. Mean Dry Dep. Rate (ng m^{-2} hr^{-1}) = Net Throughfall (ng m^{-2}) / Antecedent Dry Period (hr) (3.1)

where the Antecedent Dry Period is the time (hours) between rain events. The Hg dry deposition rates calculated using Equation 3.1 generally fall between the vapor and particulate Hg dry deposition rates calculated using the modeled V_d (Table 3.3). 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 hrs).

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 (± std. dev.) in litterfall was 53.2 ± 11.4 ng g^{-1} (range 37.8-76.9) and the mean concentration in green foliage was 34.2 ± 7.2 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 Hg^{o}, 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 μg m^{-2} in September, 1994 and 2.26 μg 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 was available for October (0.056 cm s^{-1} 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 hrs; 10/94, 655 hrs).

The estimated net throughfall deposition of Hg (throughfall deposition minus precipitation deposition) was 0.43 μg m^{-2} in September and 0.22 μg 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 μg m^{-2}; 10/94, 0.64 μg 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 μg m^{-2} of dry deposited Hg remaining in the canopy (9/94, 1.05 μg m^{-2}; 10/94, 2.04 μg 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.

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 μg m^{-2} (155 kg) in throughfall and 13 μg m^{-2} (172 kg) in litterfall for a total below-canopy Hg deposition of 24.7 μg m^{-2} (327 kg). The deposition of Hg in precipitation only accounts for 7.9 μg m^{-2} 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.

CHAPTER IV

ACCUMULATION OF ATMOSPHERIC MERCURY IN FOLIAGE IN THE LAKE CHAMPLAIN AND LAKE HURON WATERSHEDS

Abstract. The largest input of Hg in forested watersheds is the flux of Hg to the forest floor in litterfall. The flux of Hg in litterfall was 15.8 ± 1.9 $\mu g\ m^{-2}\ y^{-1}$ to the Lake Champlain Watershed in 1995 and was 11.4 ± 2.8 $\mu g\ m^{-2}\ y^{-1}$ to the Lake Huron Watershed in 1996. Comparing the behavior of Hg to other trace elements (Al, V, Cu, Zn, Rb, Sr, Ba, and Pb) in various media (foliage, litterfall, soil, and ambient air) may indicate the source of Hg in litterfall. Concentrations of Hg in foliage collected from both the Lake Champlain Watershed in 1995 and the Lake Huron Watershed in 1996 increased ten-fold from spring bud break (mean ± std. dev. from both sites: 3.5 ± 1.3 ng g^{-1}) to autumn litterfall (36 ± 8 ng g^{-1}). Foliar concentrations of other elements did not follow the same trends as Hg, suggesting that uptake of gaseous Hg^0 from the atmosphere may be the primary mechanism influencing foliar Hg concentrations, and, ultimately, the deposition of Hg in litterfall. Comparisons of the estimated Hg^0 accumulation rate based on the foliar data and the modeled dry deposition flux of Hg^0 to both canopies indicated that an average uptake of 25% of the available dry deposited Hg^0 was needed to explain all of the Hg measured in foliage throughout the growing season. Estimates of Hg uptake from soil water accounted for 3-14% of the Hg in litterfall. Based on elemental ratios in foliage, uptake of Hg from the mineral soil was not significant.

INTRODUCTION

Mercury in unimpacted deciduous forest foliage has been measured as 52.3 ± 25.9 ng g^{-1} (mean ± 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 10^2-10^3 μg 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, 1991a; Lindberg, 1996; Rea *et al.*, 1996).

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, (3) assimilation of Hg by roots from the soil, or (4) uptake of dissolved Hg in soil water through the transpiration stream. Atmospheric Hg^0 is readily taken up by plants through the stomata (Browne and Fang, 1979; Mosbaek *et al.*, 1988), but, being highly volatile, it may also be re-released (Siegel *et al.*, 1974; Iverfeldt, 1991a; 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, 1991a; Lindberg *et al.*, 1994; Rea *et al.*, 1996).

Mercury in foliage may be attributed to many sources. Although roots may contain high levels of Hg, little of this Hg is translocated to aboveground tissues and this does not appear to be a significant pathway for plant accumulation (Beauford *et al.*, 1977; 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 thought to account for less than 10% of the Hg in litterfall (Lindberg, 1996; Bishop *et al.*, 1998). The role of dissolved Hg^0 in soil water as a source of Hg in plant tissue is unknown.

Measured average Hg concentrations in tree leaves (i.e. broadleaf and coniferous) range from 7.4 to 66 ng g^{-1} (Barghigiani *et al.*, 1990; Iverfeldt, 1991a; 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 (Iverfeldt, 1991a; Rea *et al.*, 1996) collected weeks before litterfall. An increase in foliar Hg concentrations of 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 was reported by Lindberg (1996). The increase in foliar Hg was suggested to result from atmospheric sources.

Because litterfall comprises from 50-70% of the Hg budget in a forested watershed (Lindberg, 1996; Rea *et al.*, 1996), it is critical to identify its source as internal (from soil or "recycled" Hg) or external (from the atmosphere or a new Hg input). Our goal in this study was to determine the origin of Hg in litterfall (i.e. the atmosphere, soil, or soil water) by measuring a suite of trace elements (Al, V, Cu, Zn, Rb, Sr, Ba, Hg, and Pb) in various media (foliage, litterfall, soil, and air) and examining several possible uptake pathways. We reasoned that comparing the behavior of Hg to other trace elements may indicate the origin of Hg in foliage, and, ultimately, litterfall.

METHODS

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 years old and dominated by maple trees (*Acer* spp.). 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. 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. Foliage and litterfall collection are described in Rea *et al.* (1996) and Rea and Keeler (1998). Litterfall from the Lake Champlain site was composited into early- and late-season samples; litterfall from the Lake Huron site was sorted and analyzed by species and then composited into early- and late-season samples. Extraction recoveries were examined using National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) #1515 (apple leaves) and, for most elements, were within ± 5 % of expected values, ranging from 82% (for Mg) 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 these elements, but was incompatible with the analytical systems.

Soil and ambient air samples were also collected at both sites. Soil samples were collected using a soil corer at 3 depths (2, 30, and 50 cm). Particle-free gloves were worn during sample collection and used to scrape away soil that did not come into contact with the corer. Soil was collected directly into acid-cleaned Teflon or polypropylene vials, sealed with Teflon tape, triple bagged, and frozen until processed. 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}. Total suspended particles (TSP) were collected using pre-fired 47 mm glass-fiber filters (Hg) or 47 mm Teflon filters (trace elements) mounted 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). Ambient air samples were collected every six days throughout the growing season. 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). NIST SRM #1643c (trace elements in water) and Certified Reference Material SLRS-3 (riverine water) were run to determine elemental recoveries. Recoveries were generally ± 1 % of expected values, and ranged from 99% (for Pb and Mg) to 105% (for Sr) (n=15).

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). Mercury samples were analyzed by cold vapor atomic fluorescence spectroscopy using the dual amalgamation technique (Fitzgerald and Gill, 1979). 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 in all media (except trace element aerosol samples from the Lake Champlain site) 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 ($\alpha=0.0036$).

RESULTS AND DISCUSSION

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) 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 4.1). 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 4.1). This ten-fold increase in foliar Hg concentrations occurred uniformly in all species sampled in both watersheds. There were no significant differences in Hg concentrations between species within a month at either site. Following senescence, however, significant differences in Hg concentrations were found between species in litterfall samples collected at the Lake Huron site. The continued increase and the significant differences in litterfall Hg concentrations between species may be explained by processes other than atmospheric uptake. This includes the length of time the leaf sat in the litter basket before 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. At the Lake Champlain site, foliar Hg concentrations were significantly different between all months. At the Lake Huron site foliar Hg concentrations in May and June were not significantly different, but all the other months were significantly different. This was probably due to the short collection interval (16 days) between the May and June samplings. For the other sampling periods, the collection interval was at least 27 days (Table 4.2).

Mercury was the only metal to show this large and very uniform increase in foliar concentrations (Figure 4.1). In addition to Hg, foliar concentrations of Al, Sr (Figure 4.1), and V also increased over the growing season. Unlike Hg, however, this increase was not statistically significant. Similar trends in foliar concentrations of Al, Sr, and V were observed for beech, horse chestnut, and sycamore leaves collected in Scotland (Guha and Mitchell, 1966), however, the authors did not identify sources of elements in foliage.

Foliar concentrations of Al (Figure 4.1) and V 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 and V were similar at 30 cm, the approximate rooting depth, but varied at other depths (Table 4.1). Aerosol concentrations of Al were higher at the Lake Champlain site (Table 4.1) which may have influenced the higher foliar Al concentrations. Aerosol concentrations of V were similar at both sites (4.1), suggesting that biochemical or metabolic processes may have influenced foliar V concentrations which differed significantly. Both the site and species differences for Al and V, which were not observed for Hg, suggest another process may have been influencing the accumulation of Hg in foliage.

Mercury forms strong sulfhydryl bonds and can react with plant proteins. If Hg was replacing a nutrient and being taken up through the soil, there would be significant differences in foliar concentrations between species as were measured for the

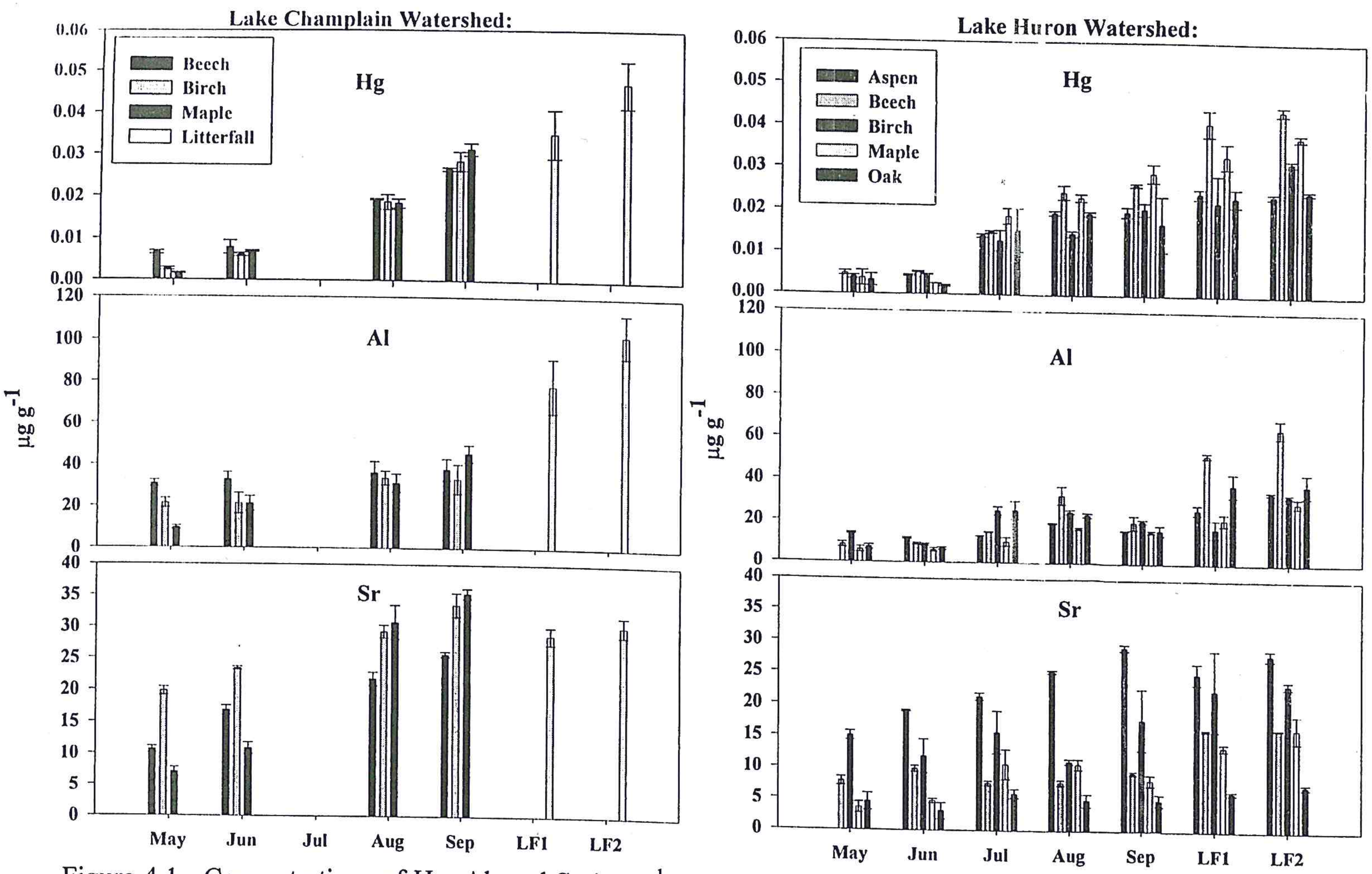


Figure 4.1. Concentrations of Hg, Al, and Sr (μg g^{-1} dry wt.; mean ± std. dev.) in foliage and litterfall measured in the Lake Champlain and Lake Huron Watersheds.

micronutrients Sr (Figure 4.1), Zn (Figure 4.2) , and Ba (not shown, but similar to Zn). In plants, Sr and Ba are taken up from soil and behave similarly to Ca which is also taken up from soil and is highly mobile in the xylem (Guha and Mitchell, 1966). Like Hg, foliar levels of Sr increase at the Lake Champlain site over the growing season, while, at the Lake Huron site, foliar Sr concentrations increased or fluctuated over time depending on the species sampled (Figure 4.1). The faster growing species, birch and aspen, had higher concentrations of Sr, probably due to metabolic or biochemical differences between species. Uptake of Zn (Figure 4.2) and Ba also were species-specific, with the highest concentrations measured in fast-growing birch and aspen trees. 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). Levels of Zn, Ba, and Mg were constant over the growing season.

As opposed to Hg, foliar concentrations of Rb decreased dramatically throughout the growing season (Figure 4.2). Rubidium behaves similarly to phloem mobile K, which is needed in young, growing leaves and cycles rapidly through plants (Guha and Mitchell, 1966). Similarly, foliar concentrations of Cu, another plant micronutrient, peaked early and then slowly declined over the rest of the growing season. This was also observed for foliar concentrations of K and Cu throughout the growing season by Guha and Mitchell (1966). If Hg was behaving similar to a nutrient and was being taken up from the mineral soil, then it might behave similarly to Sr, Zn, Ba, Rb, or Cu. Since Hg does not behave similarly to these elements, other sources of Hg in foliage need to be considered, such as

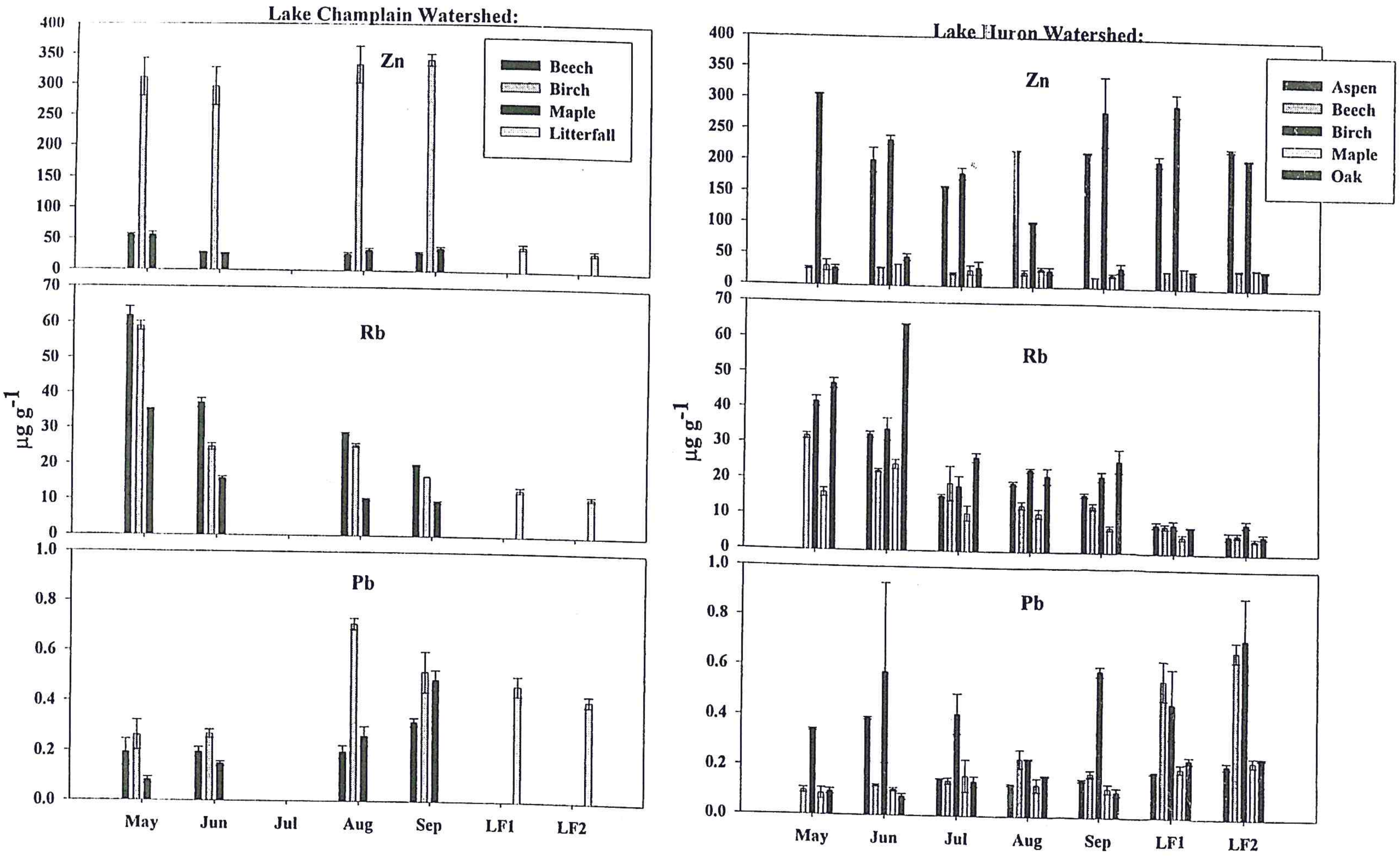


Figure 4.2. Concentrations of Zn, Rb, and Pb (μg g^{-1} dry wt.; mean ± std. dev.) in foliage and litterfall measured in the Lake Champlain and Lake Huron Watersheds.

accumulation of airborne gaseous Hg by foliage, particulate Hg deposition from the atmosphere, or uptake and accumulation of dissolved Hg in soil water.

One possible source of Hg to foliage is the adsorption of particles to foliar surfaces. This process is a function of both meteorology and leaf surface characteristics, such as leaf hairs, waxes, and roughness. Leaf surface roughness will enable some species to collect dry depositing particles more efficiently than others. Lead in foliage is primarily due to aerosol deposition to the leaf surface (Heinrichs and Mayer, 1980; Lindberg and Harriss, 1981; Lindberg, 1989), especially to pubescent leaf surfaces, such as birch, and Pb is not easily washed off leaf surfaces in throughfall (Lindberg, 1989). Both foliar and aerosol Pb concentrations were higher at the Lake Huron site than at the Lake Champlain site (Figure 4.2; Table 4.1). If foliar Hg concentrations were primarily due to aerosol adsorption, then species differences should be expected based on leaf surface characteristics. Surface soil Pb concentrations also were higher at the Lake Huron site, possibly due to atmospheric deposition, because soil Pb concentrations at 30 cm and 50 cm were similar at both sites (Table 4.1). This surface enrichment in Pb concentrations through the soil profile has been observed in other forests (Van Hook *et al.,* 1978; Parker *et al.,* 1978; Heinrichs and Mayer, 1980).

A second possible source of Hg in foliage is accumulation of atmospheric Hg. The steady increase in foliar Hg concentrations throughout the growing season suggests that the leaves are accumulating gaseous Hg 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^0 levels at both sites remain relatively constant throughout the

Table 4.1. 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
Mg	201 ± 45	432 ± 197	374 ± 84	171 ± 81	356 ± 81	572 ± 90	29 ± 19	36 ± 32
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

year, continuous uptake of gaseous Hg^0 and/or reactive gaseous Hg through the leaf stomata and surface absorption of both gaseous and particulate Hg might be able to account for the Hg in foliage. If aerosol adsorption was important, species differences as observed for Pb also may be expected. Aerosol absorption of Hg is likely to be minimal, since ambient total aerosol Hg concentrations were very low (mean ± std. dev. from both sites 0.007 ± 0.005 ng m^{-3}; n=64) compared to total gaseous Hg^0 (1.3 ± 0.3 ng m^{-3}; n=64).

A third possible source of Hg in foliage may be related to uptake of Hg from soil. 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 between species. Total Hg concentrations in soil are 5-18 times higher at the Lake Champlain site than at the Lake Huron site (Table 4.1). The enrichment of Hg in surface soils at the Lake Champlain site may be influenced by local sources of atmospheric Hg deposition, and both the humic and clay content of the soil which was greater at the Lake Champlain sited than 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).

Ratios of elements in foliage samples were used to examine the influence of soil uptake on Hg. Magnesium was chosen to represent soil uptake because it is a macronutrient which is known to be taken up by plants from soil (Epstein, 1972) and foliar Mg concentrations were relatively constant over the growing season. The ratio of the mean monthly foliar concentration of an element to the mean monthly Mg concentration was used to identify elemental behavior indicative of soil uptake. The foliar Hg:Mg ratio increased at both sites throughout the growing season and were similar between sites (Figure 4.3), which indicates that soil uptake of Hg was not important. The foliar ratios of the other elements which had increasing concentrations throughout the growing season, V, Al, and Sr, showed increasing or fluctuating ratios at the Lake Champlain site, and fluctuated or remained steady at the Lake Huron site (Figure 4.3). The ratios of these elements were not similar between sites as observed for the Hg:Mg ratios. This suggests that the source of V, Al, and Sr in foliage was not the same as the source of Hg. The ratios of other elements such as Zn and Ba were relatively stable, suggesting the same source as Mg (Figure 4.3). Ratios of the mobile elements, Rb and Cu, were similar between sites and decreased over the growing season, as these elements are needed primarily in growing leaves. These ratios show that Hg was not behaving similarly to other soil derived elements or mobile nutrients in foliage and, therefore, that soil uptake of Hg was not a significant source of Hg in foliage.

Estimates of foliar Hg uptake from soil water

The measured deposition of Hg to the forest floor in litterfall was 15.8 ± 1.9 µg m^{-2} y^{-1} in the Lake Champlain Watershed in 1995 (litter flux: 335 g m^{-2}; Leon, pers. comm.) and 11.4 ± 2.8 µg m^{-2} y^{-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 in

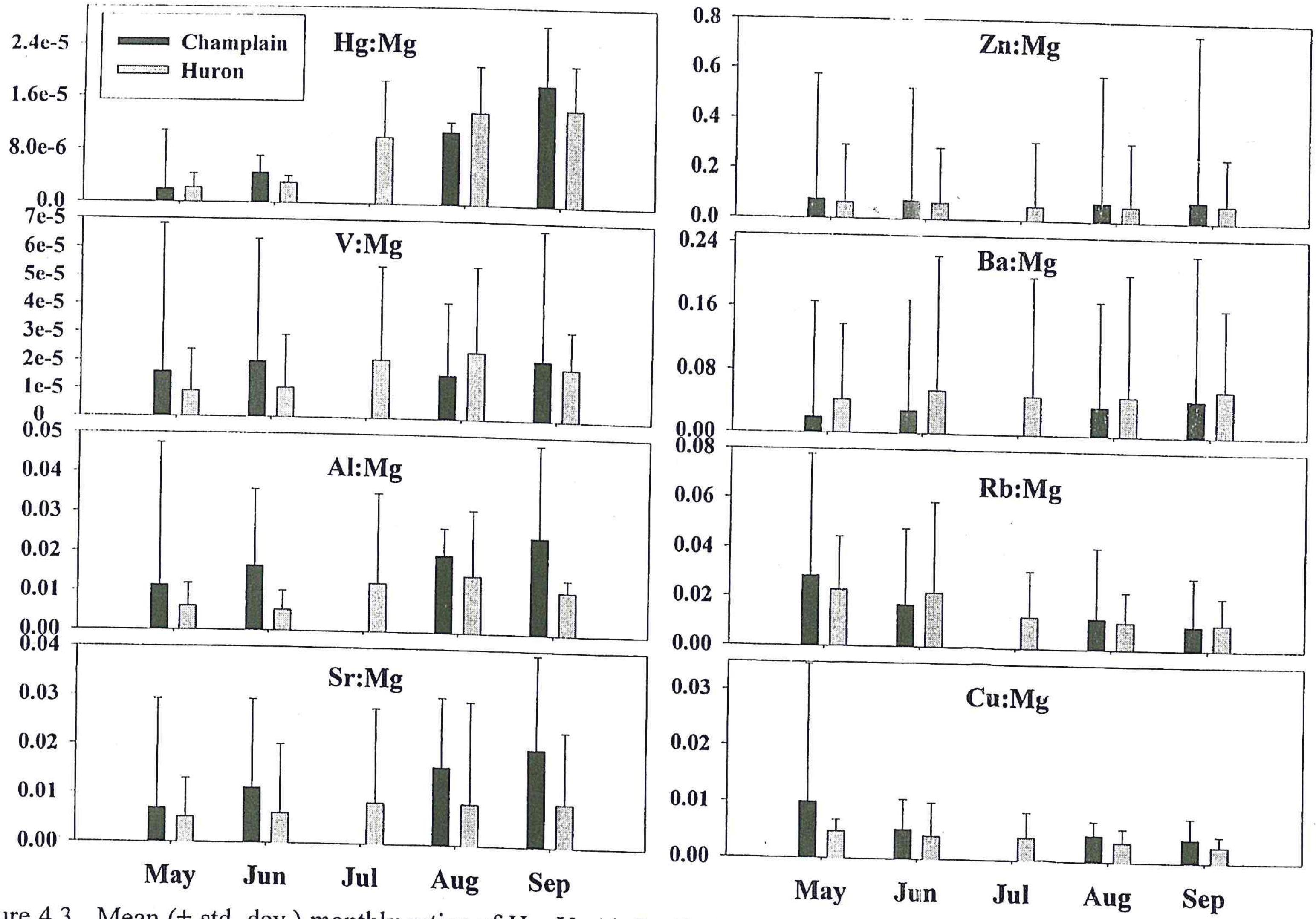


Figure 4.3. Mean (± std. dev.) monthly ratios of Hg, V, Al, Sr, Zn, Ba, Rb, and Cu to Mg in foliage throughout the growing season in the Lake Champlain and Lake Huron Watersheds.

1997 at several locations in Underhill Center, VT, approximately 4 km from our sampling sites (Donlon, pers. comm.). The volume-weighted mean (± 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 by evapotranspiration, then multiplying the volume-weighted soil water Hg concentration by 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. Also, this estimate does not account for any emission of Hg^0 from leaves, which has been reported elsewhere (Siegel *et al.,* 1974; Hanson *et al.,* 1995; Lindberg, 1996).

Based on measurements of xylem sap and soil water, Bishop *et al.* (1998) found that approximately 25% of the Hg in soil water was taken up into xylem sap and that this 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 these systems, 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 deposited in litterfall at the Walker Branch Watershed (Lindberg, 1996). Dissolved Hg in soil water may be in the form of Hg^0 or Hg^{2+}. Another endpoint for the uptake of dissolved Hg in soil water is emission of Hg^0 from the plant along with water vapor. Any dissolved Hg^{2+} taken up from soil water may be transformed to Hg^0 and similarly released. This may be one source of the measured Hg^0 emitted from plant canopies (Hanson *et al.*, 1995; Lindberg, 1996; Lindberg *et al.*, 1998).

Estimates of foliar Hg accumulation from the atmosphere

Foliar accumulation of Hg from the atmosphere 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 Hg^0 uptake rate from the atmosphere (ng m^{-2} d^{-1}) was calculated based on the Hg accumulated in foliage between collections multiplied by the number of days between collections (Table 4.2). 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 4.2). To determine if this accumulation rate could be accounted for by dry deposited Hg^0, it was compared 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) 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, individual canopy characteristics, and assumed particle aerodynamic diameter. 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

Table 4.2. 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})	days 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	May	11	3.6 ± 2.6					
Champlain	Jun	9	6.9 ± 0.9	28	8 ± 2	1.3 ± 0.1	0.056 ± 0.041	63 ± 46
Watershed	Aug	10	18.8 ± 0.5	51	15 ± 3	1.4 ± 0.3	0.060 ± 0.050	73 ± 62
1995	Sep	11	28.8 ± 2.4	50	13 ± 2	1.1 ± 0.2	0.041 ± 0.031	39 ± 30
Lake	May	12	3.3 ± 1.1					
Huron	Jun	9	4.9 ± 0.4	16	14 ± 5	1.2 ± 0.1	0.071 ± 0.024	74 ± 26
Watershed	Jul	12	14.4 ± 2.4	46	29 ± 10	1.2 ± 0.1	0.064 ± 0.025	66 ± 27
1996	Aug	7	21.0 ± 2.4	27	34 ± 11	1.5 ± 0.3	0.083 ± 0.024	108 ± 38
	Sep	11	23.1 ± 4.1	24	12 ± 4	1.1 ± 0.2	0.050 ± 0.014	56 ± 18

taken up into foliage. Reactive gaseous Hg is highly water soluble and will likely be transformed and wash-off the leaf surface in throughfall, or may chemically react and be re-emitted from the canopy. Particulate forms of Hg may be absorbed on the leaf surface but atmospheric concentrations are typically too low to account for the Hg measured in foliage. For estimating Hg accumulation in foliage, only Hg^0 was used as water soluble reactive gaseous Hg and particulate Hg compounds will most likely wash-off the leaf surface in throughfall.

The model also 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 no net deposition or emission of Hg occurs. 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. It should be noted that seedlings may not be indicators or mature tree behavior. The compensation point is dependent on the ambient, soil, and soil water Hg concentrations, which will vary by site and forest type.

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} a the Lake Huron site (Table 4.2). The differences in mean V_d's were due to differences in meteorology between years and site 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's for Hg^0 are similar to the 0.009-

0.094 cm s^{-1} reported by Lindberg *et al.* (1994) to the Walker Branch Watershed and the 0.020-0.081 cm s^{-1} reported by Rea *et al.* (1996) for the Lake Champlain Watershed.

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

$$F=V_d*X,$$

where F is the dry deposition flux of Hg^0, V_d is the mean modeled dry deposition velocity between foliage collections, and X is the mean measured total gaseous Hg concentration during the time interval (Table 4.2). The mean modeled dry deposition flux of Hg^0 ranged from 39-70 ng m^{-2} d^{-1} at the Lake Champlain site to 49-107 ng m^{-2} d^{-1} at the Lake Huron site. Differences in Hg dry deposition fluxes are probably due to differences in meteorology at the two sites during different years. At both sites, the modeled dry deposition flux of Hg^0 is much greater than the estimated foliar Hg accumulation rate (Table 4.2). This indicates that Hg^0 dry deposition to the canopy is more than sufficient to account for the total Hg measured in foliage (Table 4.2). 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 which may be washed off the leaf surface in throughfall (Lindberg *et al.*, 1994; Rea *et al.*, 1996). Some of this Hg^0 may also be a source of the measured Hg^0 emission from plant canopies (Hanson *et al.*, 1995; Lindberg, 1996; Lindberg *et al.*, 1998). Although this analysis attributes the Hg in foliage as uptake of Hg^0 from the atmosphere, uptake of Hg^{2+} may also occur.

Summary

All of the approaches used to examine the origin of Hg in foliage and litterfall indicate that the Hg could have originated from the atmosphere and that it could not be derived from soil or soil water uptake. Foliar Hg concentrations uniformly increased by an order of magnitude throughout the growing season across all species sampled in two watersheds during different years; a trend which was not observed for any of the elements we measured which are known to be soil derived. Differences in foliar concentrations of these other elements appeared to be due to differing atmospheric or soil inputs at the two sites, or to metabolic differences between tree species. Based on elemental ratios in foliage, soil uptake of Hg was not important. These data suggested that another process was controlling the uptake of Hg, such as uptake of Hg from soil water or the atmosphere. Estimates of Hg uptake from soil water accounted for 3-14% of the Hg in litterfall. Comparisons of the estimated actual Hg^0 accumulation rate and the modeled dry deposition flux of Hg^0 to both canopies indicated that foliar accumulation of dry deposited atmospheric Hg could account for all of the Hg measured in foliage throughout the growing season.

CHAPTER V

DEVELOPMENT OF A WASHING TECHNIQUE FOR MEASURING DRY DEPOSITION OF MERCURY AND SELECTED TRACE ELEMENTS TO FOLIAGE AND SURROGATE SURFACES

Abstract. Leaf washing experiments were conducted to examine the influence of dry deposition and foliar leaching on the cycling of Hg and other trace elements in forested ecosystems. Fluxes of Hg, Mn, Rb, Ba, Sr, Cd, La, Ce, and Pb were measured in leachates of foliage that was washed with a dilute nitric acid solution (1×10^{-4} M). Examination of first-order kinetics of removal indicated that wash-off of dry deposition occurred within 30 min for all elements (mean removal constant ± std. dev. $k = 2.2 \times 10^{-2} \pm 1 \times 10^{-3}$ min^{-1}, $R^2 = 0.92$). After 1440 min, removal of Cd, La, Ce, Hg, and Pb was much lower ($k = 1.5 \times 10^{-4} \pm 1.0 \times 10^{-4}$ min^{-1}, $R^2 = 0.88$), and removal of Mn, Rb, Ba, and Sr was also lower ($k = 4.2 \times 10^{-4} \pm 2.9 \times 10^{-4}$ min^{-1}, $R^2 = 0.93$). These experiments suggested that fluxes of Hg, Cd, La, Ce, and Pb from washed leaves were due to the wash-off of dry deposition. After the initial removal of surface deposits of Mn, Rb, Ba, and Sr, additional fluxes of these elements were due to foliar leaching. Apparent dry deposition fluxes were also measured using live foliage and surrogate Teflon surfaces. Apparent dry deposition velocities computed from both surfaces were similar for Hg and Cd, within a factor of 2-3 for Sr, La, Ce, and Pb, whereas dry deposition velocities for Mn, Rb, and Ba were ~5-10

times higher from the foliar surfaces. These data suggest that wash-off of dry deposition influenced the fluxes of Hg, Cd, La, Ce, and Pb while foliar leaching influenced the fluxes of Mn, Rb, Ba, and Sr.

INTRODUCTION

Deposition of mercury (Hg) to forest canopies based on throughfall measurements is 59-88% higher than the deposition from precipitation alone (Iverfeldt, 1991a; Lindberg *et al.*, 1994; Munthe *et al.*, 1995; Rea *et al.*, 1996). The origin of the Hg in throughfall in these studies has often been attributed to wash-off of dry deposition from the atmosphere. Mercury in the atmosphere is predominately in the elemental gaseous form (Hg^0) but is also present as reactive gaseous Hg (e.g. $HgCl_2$) and as particulate Hg compounds. Studies have shown that foliage can both take up and emit Hg^0 (Browne and Fang, 1979; Siegel *et al.*, 1984; Hanson *et al.*, 1995; Lindberg, 1996), and that Hg^0 may be oxidized to form other Hg compounds which may adsorb to or wash off the leaf surface (Lindberg and Stratton, 1998). Most other elements in air are predominately in the aerosol phase.

Trace elements in plants may be absorbed by leaves from the atmosphere, taken up from the air via stomata, or taken up through the roots in various forms (e.g. gaseous or ionic) and transported to leaves. Factors influencing dry deposition processes include: forest canopy type, wind speed, particle size, gas solubility, temperature, cloud cover, as well as leaf pubescence, size, and moisture. Previous studies have used leaf washing techniques to evaluate the significance of dry deposition and foliar leaching processes (Evans *et al.*, 1981; Godt *et al.*, 1986; Scherbatskoy and Tyree, 1990). Other studies have used comparisons of extraction kinetics between leaves and surrogate surfaces to isolate dry deposition and foliar leaching (Lindberg *et al.*, 1982; Lindberg and Lovett, 1985; Hofschreuder *et al.*, 1997).

Leaching occurs when an aqueous solution (rain, dew, etc.) removes substances from a plant by diffusion (Tukey, 1970). The mobility of Ca, Mg, K, Mn, and Rb in plants is well known and leaching of these elements in throughfall or during laboratory experiments has been observed (Rolfe *et al.*, 1978; Tukey, 1970; Mecklenberg *et al.*, 1966; Rains *et al.*, 1964; Evans *et al.*, 1981; Scherbatskoy and Klein, 1983; Lovett *et al.*, 1985). In plants, the trace elements Rb and Sr behave similarly to the macronutrients K and Ca, respectively (Rains *et al.*, 1964; Guha and Mitchell, 1966). In a series of wash-off experiments, Godt *et al.* (1986) found that Ca, Mg, and Mn were influenced by foliar leaching, while the origin of Pb, Cu, and Cr was wash-off of dry deposition.

The main objective of this study was to determine if Hg in forest foliage was affected by dry deposition, foliar leaching, or both processes. Leaf washing experiments were designed to evaluate the influence of dry deposition and foliar leaching of Hg and other trace elements from forest foliage under short time intervals and controlled conditions. The behavior of Hg was compared to other elements (Mn, Rb, Ba, Sr, Cd, La, Ce, and Pb) that have been studied previously. First-order removal kinetics of trace elements were examined to determine influences from dry deposition and foliar leaching. The influence of dry deposition of trace elements was identified from washing both live foliage and surrogate Teflon surfaces.

METHODS

Study Sites

Samples were collected from the University of Michigan Biological Station, at the northern tip of the Lower Peninsula in Pellston, Michigan during August and September, 1996 (45.57 N; 84.80 W). Leaves were collected from trees growing in sandy, well-drained soils in a northern mixed-hardwood forest. The species sampled were *Acer rubrum* L. (red maple), *Quercus rubra* L. (red oak), *Fagus grandifolia* Ehrh. (American beech), *Betula papyrifera* Marsh. (white birch), and *Populus grandidentata* Michx. (bigtooth aspen). Experiments to determine appropriate washing procedures used leaves collected in Ann Arbor, MI (42.22 N; 83.75 W) between May and August, 1996.

Foliage and aerosol collection

Live foliage was collected at mid-canopy (7-12 m) using a hand held pole pruner. Branches were caught in mid-air and 10 leaves were carefully removed by the petiole and placed directly into acid-cleaned 500 ml wide-mouth Teflon bottles. Particle free gloves were worn during all phases of sampling, handling, and analysis. Three sets of 10 leaves were collected from each tree species for each experiment. Bottles were sealed with Teflon tape, triple bagged and taken directly to the laboratory. An additional set of 20 leaves was collected from each sampled branch for determination of leaf area and dry weight. All reported concentrations have been normalized to one-sided leaf area.

Trace elements were collected in ambient air samples every six days throughout the growing season. Aerosol samples were collected onto 47 mm pre-fired glass-fiber filters for Hg analysis and onto Teflon filters for trace elements analysis. Total suspended particulate (TSP) aerosols were collected at ~3 m above the ground using 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). Fine fraction (< 2.5 μm) aerosols were collected using Teflon coated aluminum cyclones for 24 hr at a nominal flow rate of 16.7 L min^{-1}. Ambient blanks were collected as described in Keeler *et al.* (1995) and contributed less than 2% (range 0.4-4%; n=20) of the mean sample mass for all elements. All ambient sample concentrations have been corrected using air volumes expressed at standard temperature and pressure (0°C; 1 atm). Glass-fiber filters were microwave digested for Hg analysis (Keeler *et al.*, 1995). Teflon filters were microwave digested as described in Rea and Keeler (1998) and analyzed for a suite of trace elements including Mn, Rb, Ba, Sr, Cd, La, Ce, and Pb.

Experimental design and leaf washing procedure

Within 1 hr of collection, 300 ml of wash solution was added to each set of 10 leaves. Washing solutions were freshly prepared before each experiment and consisted of either deionized water (18.2 MΩ cm) or a dilute nitric acid solution (1x10^{-4} M)

(Suprapur, EM Science). The bottles were sealed with Teflon tape, double bagged, and gently shaken on a modified titer plate shaker (Lab-line Instruments, Inc). To obtain sequential washing samples, the wash solution in each bottle was replaced by decanting the solution into an acid-cleaned narrow-mouth Teflon bottle and refilling the original wide-mouth Teflon bottle (leaves still inside) with 300 ml of fresh solution. All experiments were conducted in triplicate. At the end of each experiment the leaves were removed and the bottle was filled with 300 *ml of wash solution* and processed as a sample to quantify the mass of trace elements remaining in the bottle.

Surrogate surfaces (round Teflon surfaces; 64.2 ± 0.6 cm^2), were deployed in the forest canopy for a 5 day dry period after a rain event. The Teflon surfaces were secured to Teflon-taped, vinyl coated wire branches with a piece of Teflon tubing. The branches were attached to a wooden pole with a hook at its base. This “Teflon tree” was raised into the canopy with pole pruner extensions and hooked over a dead limb. The Teflon surfaces were suspended about 1.5 m above the dead tree, and approximately 7 m above the ground, the average height at which adjacent live foliage was collected. Foliage from nearby trees was also collected and washed for comparison with the Teflon surfaces.

Analytical procedures

All leaf washing samples were processed in a portable Class 100 clean bench at either the University of Michigan Air Quality Laboratory (UMAQL) (initial experiments) or the University of Michigan Biological Station (all other experiments). Fifty ml of leaf wash solution was poured out of the Teflon bottles into acid-cleaned polyethylene bottles and acidified with 15 M nitric acid to a 0.03 M solution for trace element analysis. The remaining solution in the Teflon bottles was preserved with 0.2 M bromine monochloride to a 2.5×10^{-3} M solution for Hg analysis.

Trace elements were analyzed using a Perkin Elmer 5000A Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) equipped with a thin film electron multiplier. Mercury samples were analyzed by cold vapor atomic fluorescence spectroscopy using the dual amalgamation technique (Fitzgerald and Gill, 1979). Fifty percent of the Hg samples and ten percent of the trace element samples were analyzed in duplicate. Blanks were collected during each experiment by adding 300 ml of wash solution to a Teflon bottle and processing it as a sample. Elemental concentrations in blanks were less than 10% of the mean sample mass, and all reported sample values have been blank corrected. Precision on replicate samples was less than 10% for Hg and from 0.05% (Sr) to 7% (Cd) for the other trace elements. National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) #1643c (water) and Certified Reference Material SLRS-3 (riverine water) were run to determine elemental recoveries. Recoveries were generally ± 3% of expected values, and ranged from 99% (for Pb) to 110% (for Cd) (n=15). Details on UMAQL analytical procedures can be found elsewhere (Keeler *et al.*, 1995; Landis and Keeler, 1997; Rea and Keeler, 1998).

Mean values from the three sets of 10 leaves were used to test for significant differences at each time interval using a paired two-sample *t*-test ($p < 0.05$). Differences between removal constants, and differences between the surrogate surfaces and live foliage were also tested using a paired two-sample *t*-test ($p < 0.05$).

RESULTS AND DISCUSSION

Initial experiments: wash-off of dry deposition and foliar leaching

The influence of solution pH on trace element stability was tested prior to evaluation of removal kinetics. Initial leaf washing experiments were conducted to determine if there was a significant difference between washing leaves with deionized water (pH=7.0) or a dilute nitric acid solution (pH=4.0). Mature leaves were collected and washed with one of the following: (1) deionized water, (2) deionized water followed by dilute acid solution, or (3) dilute acid solution. Results of each experiment were compared to determine removal efficiency, and removal of elements from leaves was clearly optimal using the dilute nitric acid solution (n=12) (concentrations exceeded the other wash solutions by a factor of 4 for Hg and by a factor of 2 for the other trace elements). The dilute nitric acid solution also prevented absorption of elements to the bottle walls and, therefore, was used in the remaining experiments. Although HCl would normally be preferred in order to stabilize Hg in solution, it could not be used due to interference with the analytical system (ICP-MS).

Further experiments were conducted to determine maximum removal of dry deposition and minimal foliar leaching. For these experiments, maple and oak leaves were collected in Ann Arbor, MI and birch and beech leaves were collected in Pellston, MI. Leaves were washed with the dilute nitric acid solution at intervals ranging from 5 to 480 min (n=12 sets of 10 leaves) for a total of 1440 min (beech leaves were washed for a total of 120 min).

The kinetics of removal for Hg, Pb, Rb, and Ba are shown in Figure 5.1. Most of the Hg, Pb, Cd, La, and Ce were removed rapidly, generally within 30 min. Wash-off of dry deposition was probably minimal after 30 min and additional increases in fluxes were due to the slow wash-off of less readily soluble material or foliar leaching (Lindberg *et al.*, 1982; Lindberg and Lovett, 1985). In contrast, fluxes of Rb, Ba (Figure 5.1), Mn, and Sr steadily increased throughout the entire 1440 min. This behavior was probably due to continual leaching of these elements during successive washes.

Removal rate constants, k, were calculated from the leaf wash data assuming that the kinetics of removal was a first-order process based on the natural log vs. time plot of the data. The data were divided into separate time intervals (5-30 min; 60-240 min; 240-1440 min) and k values were calculated for each interval. Removal constants were similar for all trace elements during each time interval indicating that similar processes were occurring for leaves collected in either urban or rural areas. Removal constants for all elements during each time interval ranged over three orders of magnitude, suggesting different processes were driving the fluxes over time. The highest removal constant was calculated for the first time interval, and was similar for all species and elements (mean ± std. dev.; $k=2.2\text{x}10^{-2} \pm 1\text{x}10^{-3}$ min^{-1}, $R^2=0.92$). The process being described in these initial time periods is most likely the removal of readily avilable dry deposited material, a physically similar process for all elements.

The removal constants for the second (60-240 min) and third (240-1440 min) time intervals were much lower than those for the first time interval. Unlike the first time interval, differences between elements were observed during the second and third time

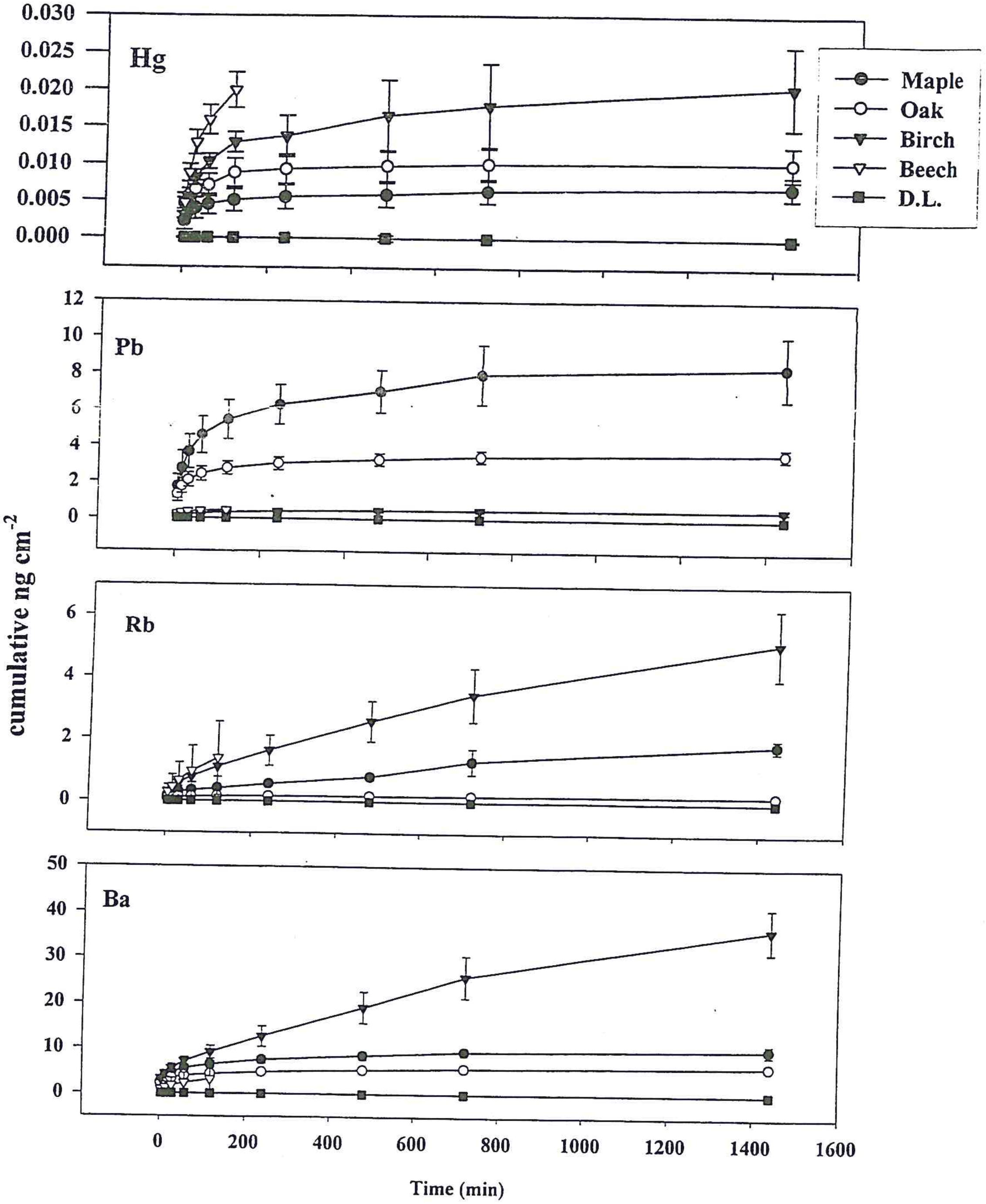


Figure 5.1. Cumulative ng cm^{-2} (± std. dev.) Hg, Pb, Rb, and Ba washed from live foliage (n=12 sets of 10 leaves) and detection limits (D.L.) for each element. Maple and oak leaves were collected in Ann Arbor, MI, on 17 July 96 and 4 August 96, respectively. Birch and beech leaves were collected in Pellston, MI, on 22 August 96 and 19 September 96, respectively. Note plots are not on the same scale.

intervals. The removal constants for the second time interval were nearly two times higher for Mn, Rb, Ba, and Sr (k=3.4x10^{-3} ± 2.4x10^{-3} min^{-1}, R^{2}=0.97) than for Hg, Cd, La, Ce, and Pb (k=1.9x10^{-3} ± 1.3x10^{-3} min^{-1}, R^{2}=0.93). During the second time interval, elements were probably influenced by both dry deposition and foliar leaching. The higher removal constant for Mn, Rb, Sr, and Ba may indicate that, for these elements, wash-off of dry deposition slowed considerably and foliar leaching was important. The contrasting behavior of Hg, Cd, La, Ce, and Pb may be explained by the slow removal of surface soluble material. The removal constant for the last time interval was nearly three times higher for Mn, Rb, Ba, and Sr (k = 4.2x10^{-4} ± 2.9x10^{-4} min^{-1}, R^{2}=0.93) than for Hg, Cd, La, Ce, and Pb (k=1.5x10^{-4} ± 1.0x10^{-4} min^{-1}, R^{2}=0.88). Significant removal of Mn, Rb, Ba, and Sr continued during this time interval indicating that foliar leaching was still occurring.

To better examine the removal of dry deposition in the initial washes, new sets of leaves were washed repeatedly at either five or two minute intervals. Species with different structural characteristics were selected for these experiments and were collected from the forest in Pellston, MI. Birch and beech leaves have thin cuticles, rough-surfaces, and are noticeably pubescent, while maple and oak leaves have thicker cuticles and smooth or glabrous surfaces. Because of surface morphologies, birch and maple leaves (n=6 sets of 10 leaves) were washed for three 5 min intervals while beech and oak leaves (n=6 sets of 10 leaves) were washed for four 2 min intervals.

Results from these more intensive leaf washing experiments were similar to the previous experiments, strongly supporting the idea that removal of dry deposition was occurring for all elements during the short interval washes. Removal constants were similar for both sets of elements discussed above during both the 5 (k=6.7x10^{-2} ± 1x10^{-2} min^{-1}, R^2=0.99) and 2 min washes (k=1.1x10^{-1} ± 1x10^{-2} min^{-1}, R^2=0.97). By examining the data from these experiments, it appeared that wash-off of most surface soluble particles occurred within the first 5 min (Figure 5.2). A similar conclusion was reported for oak and hickory leaves collected in Tennessee (Lindberg *et al.*, 1982; Lindberg and Lovett, 1985). Fluxes of all elements from birch and maple leaves (column 1 of Figure 5.2) appeared to be due to wash-off of dry deposition at the 5 and 10 min intervals. Fluxes of Mn, Rb (Figure 5.2), Ba, and Sr in the final wash (15 min) remained constant from the birch leaves, probably due to foliar leaching, while fluxes of Hg, Cd, and Pb in the final wash were close to or below the detection limit. The shorter time resolution obtained from the 2 min washes (column 2 of Figure 5.2) confirmed this behavior. Fluxes of Mn, Rb (Figure 5.2), Ba, and Sr remained constant after the 4 min wash, while fluxes of Pb, Hg (Figure 5.2), Cd, La, and Ce continued to decline or were near the detection limit.

Although the removal constants were similar, the fluxes of Mn, Rb, Ba, and Sr were significantly greater from the birch leaves than the maple leaves (Figure 5.2). These differences were not observed between the oak and beech leaves (Figure 5.2). To examine this difference between birch and maple leaves and to determine if these differences were due to foliar leaching, leaves were either washed for 5 min or simply flushed with solution, i.e. the wash solution was poured into the bottle and then immediately poured out without agitation (n=12 sets of 10 leaves). The fluxes from the 5 min birch leaf wash were significantly higher ($p<0.05$) than the birch flush for all elements. In contrast, the fluxes from the 5 min maple leaf wash were significantly

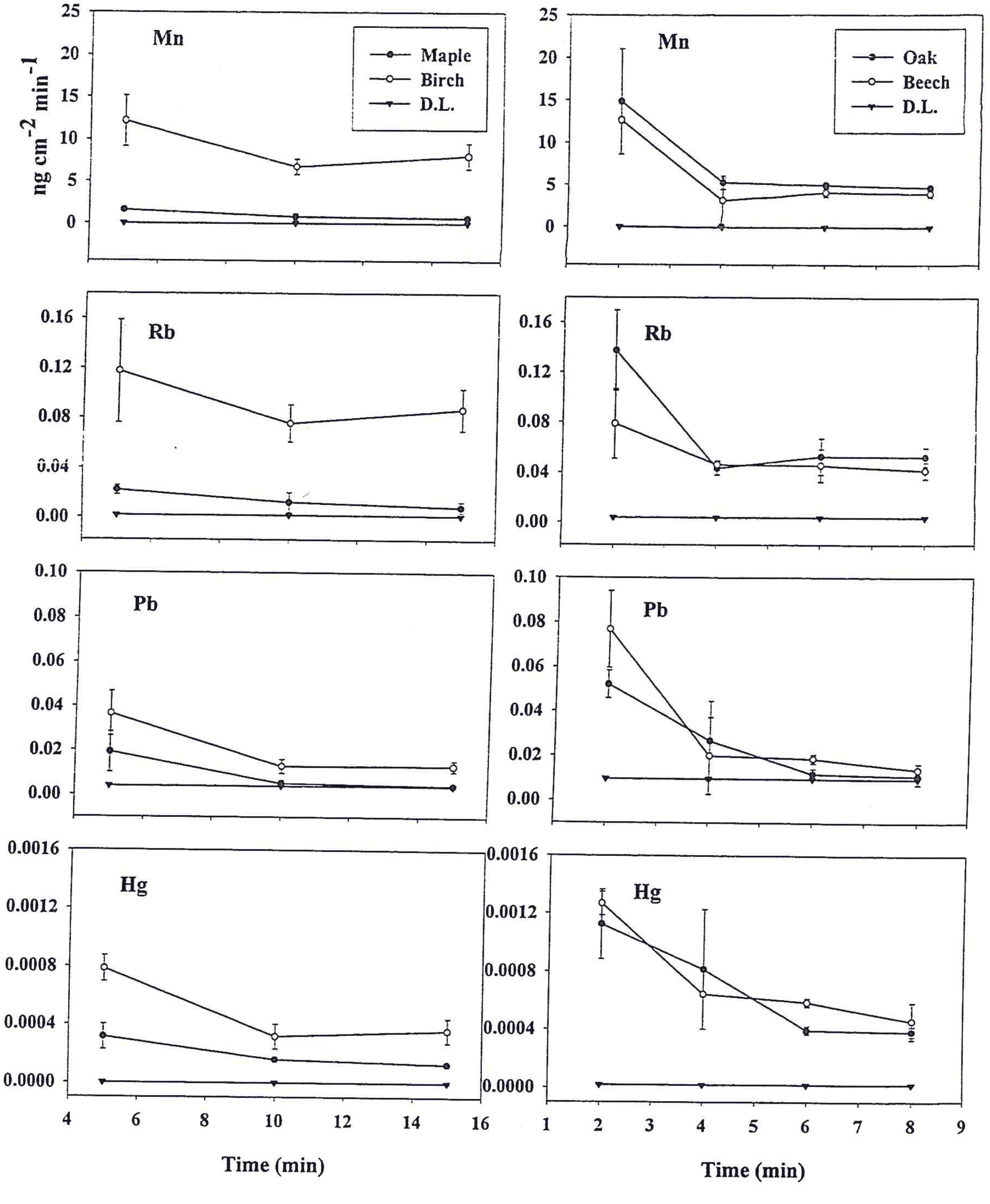


Figure 5.2. Fluxes of Mn, Rb, Pb, and Hg (ng cm^{-2} min^{-1}; mean ± std. dev.) from washed birch, maple, oak, and beech foliage collected and washed in Pellston, MI on 20 September 96 (n=12 sets of 10 leaves) and detection limits (D.L.) for each element. Note plots are not on the same scale.

higher than the maple flush only for Mn, Rb, Sr, and Ba ($p<0.05$). Differences in trace element fluxes between species may be due to physiological or metabolic differences. The leaf hairs on the birch leaves may be more efficient collectors of dry deposition (Hg, Cd, La, Ce, and Pb) than the smooth-surfaced maple leaves, resulting in larger fluxes due to wash-off of dry deposition. The significant increase in fluxes of Mn, Rb, Ba, and Sr from both species strongly suggests that foliar leaching was occurring.

Teflon surfaces

In an effort to collect dry deposition without the complication of foliar leaching, washed Teflon surfaces were compared to live foliage. The "Teflon tree" was suspended in the canopy for 98 hr from 16-20 September 96. The Teflon surfaces (n=3 sets of 10 Teflon surfaces) and leaves (n=15 sets of 10 leaves) from adjacent aspen, beech, birch, maple, and oak trees were collected and washed for 5 min to remove surface material. It was assumed that the previous rainfall (3.7 cm in an event on 15 September 96 lasting over 19 hr) had thoroughly washed any dry deposition from the foliage, and that both the Teflon and foliar surfaces were exposed to the same amount of dry deposition prior to collection.

While these data are limited, and more work is necessary to determine the accuracy of this procedure for collecting dry deposition, the results may be used to determine the most important process (dry deposition or foliar leaching) influencing these elements. Differences in mean particle size and surface characteristics may account for the differences in fluxes between the Teflon and foliar surfaces. Particle deposition is a function of aerodynamic diameter, and the fraction of the particle distribution present as coarse particles (greater than 2 µm) has a strong influence on the deposition velocity (V_d) (Milford and Davidson, 1985). Our measurements of total and fine fraction (< 2.5 µm) aerosol samples at the Michigan site indicated that Mn, Rb, Ba, Sr, La, and Ce were predominately in coarse aerosols and Hg, Cd, and Pb were mostly in fine aerosols (Table 5.1). These data are in agreement with data reported by Milford and Davidson (1985) based on the measured mass median diameter for aerosols collected throughout the world. Leaf surface characteristics also may influence dry deposition collection efficiency, leading to differences between species. Leaf hairs, for example, may be more likely to trap particles, causing adsorption of particles to the leaf surface, than smooth leaves or Teflon surfaces.

Significant differences were found between the fluxes from the Teflon leaves and the mean 5 min wash-off from all 5 species ($p<0.02$) for Mn, Rb, Ba, and Pb. The fluxes of Mn, Rb, and Ba were higher from the foliar surfaces while the flux of Pb was higher from the Teflon surfaces. Dry deposition rates of elements mainly associated with fine fraction aerosols (Hg, Cd, and Pb) were within a factor of two between the Teflon and foliar surfaces (Table 5.1). The largest difference was for Pb, which, unlike Hg and Cd, had a higher flux from the Teflon surfaces than the foliar surfaces. This is probably due to the irreversible adsorption of Pb to the leaf surface. Adsorption of Pb to foliar surfaces has been observed from laboratory experiments (Scherbatskoy and Tyree, 1990), from comparisons of leaves with inert surfaces (Lindberg *et al.,* 1982), and from measurements of throughfall (Lindberg, 1989).

Table 5.1. Mean (± std. dev.) total aerosol concentrations during the dry period (n=5) and % of the total aerosol present in the fine fraction (<2.5 μm). Dry deposition rates (mean ± std. dev.; pg cm^{-2} hr^{-1}) were calculated from washed foliar (n=15 sets of 10 leaves) or Teflon surfaces (n=3 sets of 10 Teflon surfaces) based on a 98 hr dry period and mean 24 hr total aerosol concentrations. Deposition velocities (V_d foliage and V_d Teflon; mean ± std. dev.) were calculated based on the dry deposition rate and total aerosol concentrations. The large discrepancies between the V_d to the Teflon and foliar surfaces for Mn, Rb, Ba, and Sr are probably due to bounce off of large particles from the Teflon surfaces in additiion to some contribution from foliar leaching.

Element	total aero. ng/m^3	% <2.5 μm aerosol	dry dep. Foliage pg cm^{-2} hr^{-1}	dry dep. Teflon pg cm^{-2} hr^{-1}	V_d foliage cm s^{-1}	V_d Teflon cm s^{-1}
Mn	2.1 ± 1.2	31%	183 ± 137	14 ± 2	25 ± 18	1.8 ± 0.2
Rb	0.17 ± 0.09	33%	1.5 ± 0.8	0.27 ± 0.02	2.5 ± 1.3	0.44 ± 0.03
Ba	0.67 ± 0.54	22%	12 ± 8	1.6 ± 0.4	5.0 ± 3.2	0.66 ± 0.18
Sr	0.43 ± 0.41	25%	1.2 ± 0.8	0.49 ± 0.03	0.77 ± 0.48	0.31 ± 0.02
Hg	0.0055 ± 0.0034	60%	0.023 ± 0.025	0.019 ± 0.025	1.2 ± 1.3	0.98 ± 1.3
Cd	0.058 ± 0.044	87%	0.14 ± 0.12	0.16 ± 0.20	0.67 ± 0.57	0.79 ± 1.0
La	0.032 ± 0.028	17%	0.032 ± 0.014	0.022 ± 0.003	0.28 ± 0.13	0.19 ± 0.03
Ce	0.069 ± 0.060	20%	0.060 ± 0.030	0.029 ± 0.005	0.24 ± 0.12	0.12 ± 0.02
Pb	2.9 ± 2.1	90%	1.2 ± 0.4	2.1 ± 0.4	0.12 ± 0.04	0.20 ± 0.04

The apparent dry deposition rates of elements associated with coarse aerosols (Mn, Ba, Sr, and Ce) were larger to the foliar than to the Teflon surfaces as might be expected. While dry deposition rates of Sr, La, and Ce were similar, the apparent dry deposition rates for Mn, Rb, and Ba were 5-13 times higher to the foliar than to the Teflon surfaces (Table 5.1). This may be partially due to bounce-off of large particles from the smooth, ungreased Teflon surfaces. Dry deposition rates are larger for coarse particles and coarse particles may be more likely to bounce off the Teflon surface. The Teflon surface may be an inefficient collector for particles, and is less likely to collect fine particles (an attempt to use greased surfaces was unsuccessful due to analytical problems, large uncertainties, and high blanks). In addition, the influence of rapid foliar leaching on elemental behavior will result in increased fluxes of Mn, Rb, and Ba from the foliar surfaces.

Dry deposition rates and deposition velocities

To determine if the elemental flux from the washed surfaces could be accounted for by particle dry deposition, V_d were calculated based on the measured dry deposition rates and mean aerosol concentrations (Table 5.1). The V_d were calculated from the equation:

$$V_d=F/X,$$

where V_d (cm s^{-1}) is the deposition velocity, F is the flux to the surface (pg cm^{-2} hr^{-1}) based on the wash measurements, and X is the mean trace element concentration in aerosol samples (ng m^{-3}) collected daily during the dry period. For Hg, this assumes that all of the material washed off these surfaces originates from aerosol Hg and not gaseous Hg sources. If gaseous Hg also contributes, the V_d will be reduced.

The computed V_d for different trace elements ranged from 0.12 ± 0.02 to 1.8 ± 0.2 cm s^{-1} to the Teflon surfaces and from 0.12 ± 0.04 to 25 ± 18 cm s^{-1} to the foliar surfaces (Table 5.1). Dry deposition velocities between the Teflon and foliar surfaces were similar for Hg and Cd, within a factor of 2-3 for Sr, La, Ce and Pb, but differed by a factor of ~5-10 for Mn, Rb, and Ba (Table 5.1). The elements associated with fine aerosols (Hg, Cd, and Pb) and La had the best agreement between the Teflon and foliar surfaces. This agreement strongly suggests that dry deposition was the source of these elements in the leaf wash. The elements with larger discrepancies between the V_d to the Teflon and foliar surfaces (Mn, Rb, Ba, and Sr) were associated with coarse aerosols, and also showed signs of leaching in the leaf wash experiments. The differences in the measured V_d of Mn, Rb, Ba, and Sr from the Teflon and foliar surfaces may be due to a combination of bounce-off of large particles from the ungreased Teflon surfaces and leaching of nutrients from the foliar surfaces. The relatively good agreement for La may be due to its low potential for foliar leaching.

Summary and comparisons with published data

The similarities between the V_d calculated for both the Teflon and foliar surfaces indicate that wash-off dry deposition was occurring for Hg, Cd, La, Ce, and Pb. The large discrepancies between the Teflon and foliar surfaces for Mn, Rb, Ba, and Sr may be due to a combination of large particle bounce-off and foliar leaching. The leaf washing experiments also support these findings, indicating that fluxes of Mn, Rb, Ba, and Sr were influenced primarily by foliar leaching while fluxes of Hg, Cd, La, Ce, and Pb from washed foliage were primarily due to the wash-off of dry deposition from the atmosphere. The estimated V_d to the Teflon surfaces for Mn and Cd are similar to those reported by Milford and Davidson (Mn 1.3 ± 0.9 cm s^{-1}; Cd 1.0 ± 0.9 cm s^{-1}) but differ from the V_d reported for Ba, Sr, and Pb (Ba 1.7 ± 0.9 cm s^{-1}; Sr 4.4 ± 1.3 cm s^{-1}; Pb 0.57 ± 0.46 cm s^{-1}) (1985). These differences may be due to the particle size distribution and influence of local sources at the urban sites discussed in Milford and Davidson (1985).

Our estimates for dry deposition for Hg may be compared with dry deposition estimates at other sties using different methods. The V_d for particulate Hg estimated by washing both foliar and Teflon surfaces (0.98 ± 1.3 cm s^{-1}) was within a factor of 2 of the V_d reported for particulate Hg (0.64 ± 0.56 cm s^{-1}) by Milford and Davidson (1985). Based on throughfall measurements, Lindberg *et al.* (1994) and Rea *et al.* (1996) report V_d for fine aerosol Hg that ranged from 0.029 to 0.176 cm s^{-1} and dry deposition rates for fine particulate Hg (0.013-0.12 ng m^{-2} hr^{-1}) which were lower than those reported here (V_d 0.98–1.2 cm s^{-1}; dry dep. rate 0.19-0.23 ng m^{-2} hr^{-1}). These differences may be due to the influence of coarse aerosol Hg which was not considered in the throughfall estimates, the differences in measurement techniques (throughfall vs. washed foliar and surrogate surfaces), and the influence of dry deposition of gaseous Hg compounds to the washed surfaces. Our aerosol Hg measurements indicate that coarse aerosol Hg deposition to this canopy was important because 40% of the aerosol Hg was associated with coarse aerosols. Dry deposition of gaseous Hg compounds was not considered in this study because it was assumed that washing leaves would remove surface soluble particulate Hg compounds and that gaseous Hg would either be re-emitted from the foliar or Teflon surfaces or deposit to foliage through stomata, and, therefore, was not likely to enter into the wash solution.

CHAPTER VI

DRY DEPOSITION AND FOLIAR LEACHING OF MERCURY AND SELECTED TRACE ELEMENTS IN A NORTHERN MIXED-HARDWOOD FOREST BASED ON THROUGHFALL ANALYSIS

Abstract. Concentrations of Hg in throughfall are generally higher than those in precipitation. The source of the additional Hg in throughfall is often attributed to wash-off of dry deposition, but foliar leaching of Hg also may be important. To determine the influence of both dry deposition and foliar leaching of Hg and selected trace elements in throughfall, a suite of trace elements (Hg, Al, Mg, V, Mn, Cu, Zn, As, Rb, Sr, Cd, Ba, La, Ce, and Pb) were measured in throughfall and precipitation events, ambient air, and soil samples from a northern mixed-hardwood forest. Various approaches were used to identify the source of Hg and other trace elements in throughfall including elemental ratios, multiple linear regression, and modeling techniques. Overall, dry deposition had the most important influence on Hg, Al, V, As, Cu, Zn, Cd, La, Ce, and Pb while foliar leaching strongly influenced Mg, Mn, Rb, Sr, and Ba in throughfall. To determine if atmospheric Hg could account for all the Hg measured in net throughfall, gaseous and aerosol Hg measurements were integrated with modeled deposition velocities. The modeling results indicated that atmospheric deposition of Hg could not only account for all the Hg deposited in net throughfall, but also for all the Hg deposited in litterfall, in addition to emission of Hg from the canopy. These findings show that the biogeochemical cycling of Hg in this forested ecosystem is driven by atmospheric inputs.

INTRODUCTION

Concentrations of most elements in throughfall (i.e. precipitation that passes through a forest canopy) are usually higher than concentrations in precipitation alone (Rolfe *et al.,* 1978; Heinrichs and Mayer, 1980; Lovett and Lindberg, 1984; Lindberg, 1989; Lovett *et al.,* 1996). Net throughfall concentrations (total throughfall concentration minus precipitation concentration) represent the contribution of an element from the canopy, due to wash-off of dry deposition and/or foliar leaching. In northern mixed-hardwood forests the canopy leaf area can be 5-8 times larger than the ground area it covers (as measured by the Leaf Area Index). The canopy area may be viewed as a large surface to collect dry deposition, made even larger by the many leaf hairs, crevices, and high relief of the cuticle surface on leaves. The canopy also enables essential nutrients to cycle rapidly within the ecosystem via foliar leaching. Foliar leaching occurs actively by metabolic processes which transport substances across the cell wall (symplastic transport), or passively by diffusion or ion exchange processes which transport water soluble ions in the free spaces between cells (apoplastic transport).

Mercury may be deposited to the forest canopy in both gaseous and aerosol forms. Gaseous Hg forms include elemental gaseous Hg (Hg^0) and reactive gaseous Hg (e.g. $HgCl_2$). Once deposited, Hg may react with other compounds on the leaf surface and be washed off in throughfall. Dry deposited Hg^0 also may be taken up by foliage through stomata (Browne and Fang, 1979; Lindberg *et al.,* 1979; Mosbaek *et al.,* 1988). Previous studies have shown that concentrations of Hg in throughfall are elevated over the associated concentrations in precipitation and have attributed the additional Hg to dry deposition (Iverfeldt 1991a; Lindberg *et* al., 1994; Munthe *et al.,* 1995; Rea *et al.,* 1996).

Foliar leaching of Hg in throughfall has been considered negligible because Hg in soil tends to stay tightly bound to roots, and root uptake and translocation from soil are minimal (Beauford *et al.*, 1977; Lindberg *et al.*, 1979; Godbold and Huttermann, 1988). None of these previous studies, however, have examined the foliar leaching pathway in detail.

The main objective of this study was to determine the contribution of Hg in net throughfall that originated from the wash-off of dry deposition and from foliar leaching. Separating the dry deposition and foliar leaching components of net throughfall is difficult especially for Hg, because Hg is present in many forms in the atmosphere. A multi-element approach was used to examine both dry deposition and foliar leaching as sources of Hg in net throughfall by comparing the behavior of Hg to 14 other elements (Al, Mg, V, Mn, Cu, Zn, As, Rb, Sr, Cd, Ba, La, Ce, and Pb) in various media (throughfall, precipitation, and aerosol samples). Several approaches were used to identify the origin of the Hg deposited in throughfall including elemental ratios, multiple linear regression, and modeling techniques.

METHODS

Study site and sample collection

Throughfall samples were collected from an 80 to 90 yr old second-growth northern-mixed hardwood forest at the University of Michigan Biological Station in Pellston, Michigan (45.57 N; 84.80 W). The stand was dominated by maple (*Acer* spp.), beech (*Fagus* spp.), and birch (*Betula* spp.), in addition to oak (*Quercus* spp.) and aspen (*Populus* spp.) trees. The soil was sandy, well-drained Haplorthod. Precipitation and ambient air samples were collected in a 6-acre clear-cut approximately 200 m from the throughfall collectors. Three modified automated precipitation collectors (Landis and Keeler, 1997) were placed in the forest to collect throughfall and one was placed in the clear-cut to collect precipitation. Throughfall and precipitation samples were collected on an event basis throughout the 1996 growing season from 21 June to 7 November (n=27) using methods described in Landis and Keeler (1997). An event was defined as a discrete period of precipitation followed by at least a 6 hr dry period. Elemental concentrations in funnel rinses (i.e. the funnels were rinsed with deionized water) indicated that the funnels contributed less than 1% of the mean sample mass (range 0.2-4%; n=10) for all elements. Precipitation event characteristics were measured using a Belfort rain gauge.

Trace elements in total suspended particulate (TSP) aerosols, fine fraction (<2.5 μm) aerosols, and total gaseous Hg were collected every six days throughout the growing season (n=35). Ambient air collection is described in chapter 5.

Sample processing and analysis

Throughfall and precipitation samples were preserved with 0.2 M bromine monochloride to a $5x10^{-3}$ M solution for Hg analysis and with 15 M nitric acid to a 0.03 M solution for trace element analysis. Aerosol samples were microwave digested as described in Keeler *et al.* (1995) for Hg and as described in Rea and Keeler (1998) for trace elements. Samples were analyzed for Hg by cold vapor atomic fluorescence spectroscopy using the dual amalgamation technique (Fitzgerald and Gill, 1979), and for trace elements by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). 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. Recoveries were generally ± 2% of expected values, and ranged from 99% (for Pb) to 110% (for Cd) (n=19). Precision on replicate analyses was within 10% for all trace elements. Details on the analytical procedures have been reported elsewhere (Keeler *et al.*, 1995; Rea *et al.*, 1996; Landis and Keeler, 1997; Rea and Keeler, 1998). Event throughfall concentrations are reported as the mean of the three collectors. Multiple linear regression was performed using the general linear models procedure (SAS Institute, Inc. 1996).

RESULTS AND DISCUSSION

Precipitation and throughfall concentrations

Total throughfall refers to the concentration of an element measured beneath the canopy due to inputs from precipitation, wash-off of dry deposition, and foliar leaching. The net throughfall concentration is defined as the total throughfall concentration minus the precipitation concentration, and represents the canopy contribution to throughfall concentrations. Total throughfall concentrations of all elements were significantly greater than precipitation concentrations with the level of significance ranging from

$p<0.0001$ for Mg, Mn, Cu, Rb, Sr, Cd, and Ba; to $p<0.01$ for Hg, V, Zn, As, and Pb; to $p<0.07$ for La, Ce, and Al (Kruskal-Wallis test).

One group of elements are either essential nutrients (Mg, Mn, Cu) or behave similarly to nutrients in plants (Rb, Sr, Ba). Although there is no known nutritional requirement for Cd, it was also placed in this group. All of these elements have been attributed to foliar leaching in other studies (Tukey, 1970; Rolfe *et al.,* 1978; Heinrichs and Mayer, 1980; Rains *et al.*, 1964; Evans *et al.,* 1981; Lindberg, 1989). In plants, Ba and Sr behave similarly to Ca, and Rb behaves similarly to K; both Ca and K are highly mobile macronutrients (Epstein and Leggett, 1954; Epstein, 1961; Rains *et al.,* 1964; Guha and Mitchell, 1966). Uptake of Cd and translocation of Cd from soil solutions has been shown (Arduini *et al.,* 1996; Gussarsson *et al.,* 1996). Leaching of Cd in throughfall has been observed (Lindberg, 1989). All of these elements were significantly higher in total throughfall than precipitation at $p<0.0001$.

Another group of elements (Hg, V, Zn, As, and Pb) have known atmospheric sources resulting from combustion processes, mines, smelters, etc. (Milford and Davidson, 1985). Mercury and Pb in throughfall have been attributed to wash-off of dry deposition in other studies (Iverfeldt, 1991a; Lindberg *et al.,* 1994; Munthe *et al.,* 1995; Rea *et al.,* 1996; Lindberg, 1989). Except for Zn, these elements have no known physiological importance to plants. These elements were significantly higher in total throughfall than precipitation at $p<0.01$. The soil elements which have no nutritional value in plants showed the least significant difference ($p<0.07$) between total throughfall and precipitation concentrations (La, Ce, and Al).

Mean total throughfall and precipitation concentrations of representative elements from each group are shown in Figure 6.1. A few events between June and September had total throughfall concentrations that were ~2 (Hg, V, As, and Pb) to 55 (Rb) times higher than precipitation for most elements (Figure 6.1). These events corresponded to low volume precipitation (less than 0.3 cm) with antecedent dry periods ranging from 90-166 hr. Several high volume events (1.6-5.1 cm) in late July had total throughfall concentrations that were less than 2 times higher than precipitation concentrations for Hg, Al, V, Cu, Zn, As, La, Ce, and Pb. This behavior, where small precipitation events deliver high concentrations and large precipitation events deliver low concentrations, is known as a dilution effect and has been observed to affect trace element concentrations in throughfall (Lindberg, 1989).

During October, total throughfall concentrations of Mg, Mn, Cd (Figure 6.1), Zn, Rb, Sr, and Ba ranged from 3 (Cd) to 218 (Mn) times higher than precipitation concentrations during two high volume events (2.7 and 3.6 cm, respectively). Most likely, the elevated concentrations of these elements in total throughfall were due to foliar leaching from leaves which were in late senescence. In contrast, total throughfall concentrations of Hg, Pb (Figure 6.1), V, and As (which are generally attributed to atmospheric sources) and La (Figure 6.1), Ce, and Al (which are generally attributed to soil sources) were not significantly different ($p<0.1$) than precipitation concentrations during the last 8 events (October and November).

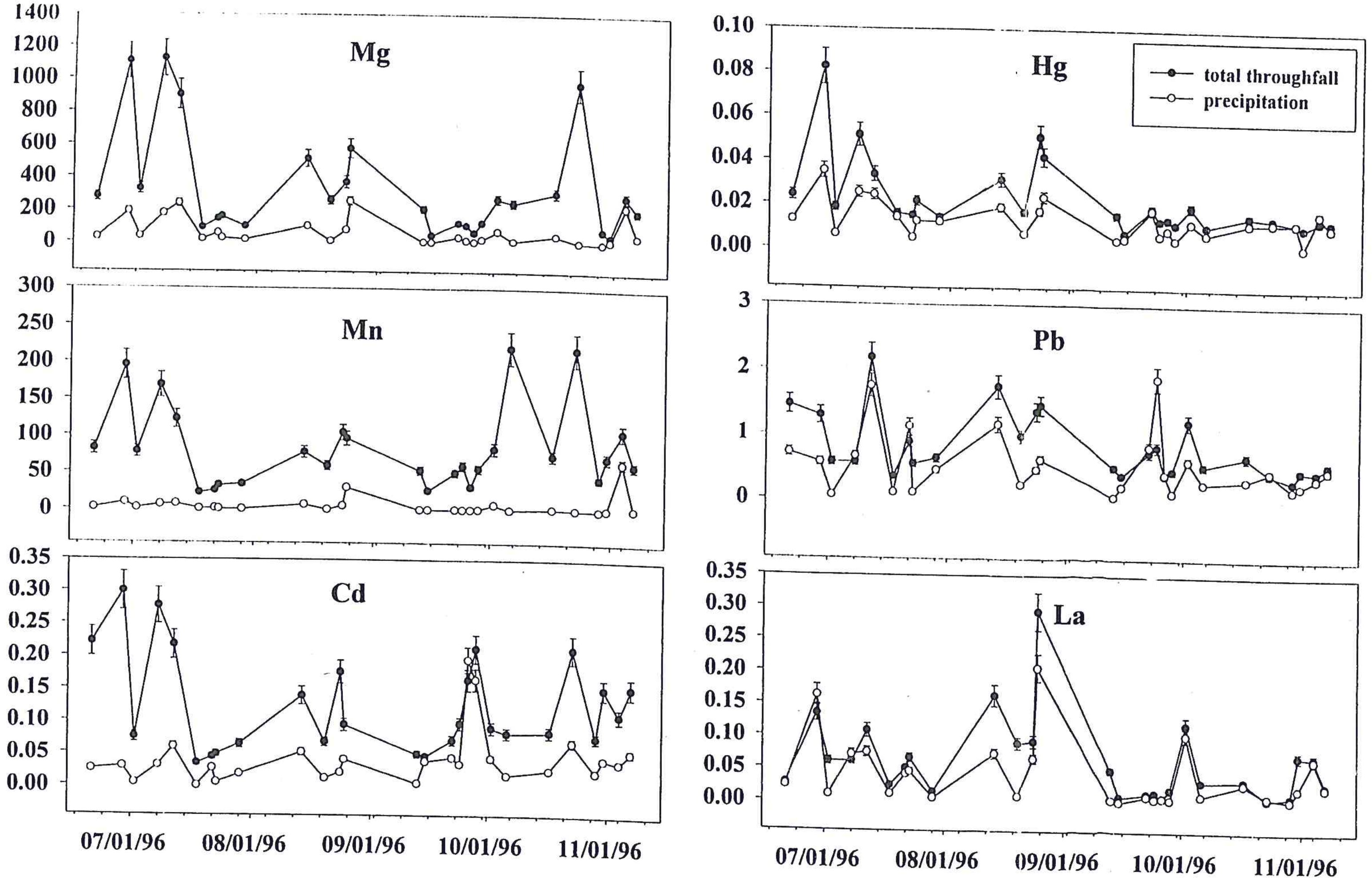


Figure 6.1. Concentrations (± std. dev.) of Mg, Mn, Cd, Hg, Pb, and La ($\mu g\ L^{-1}$) in event precipitation and total throughfall samples collected in Pellston, MI from June 21- November 7, 1996

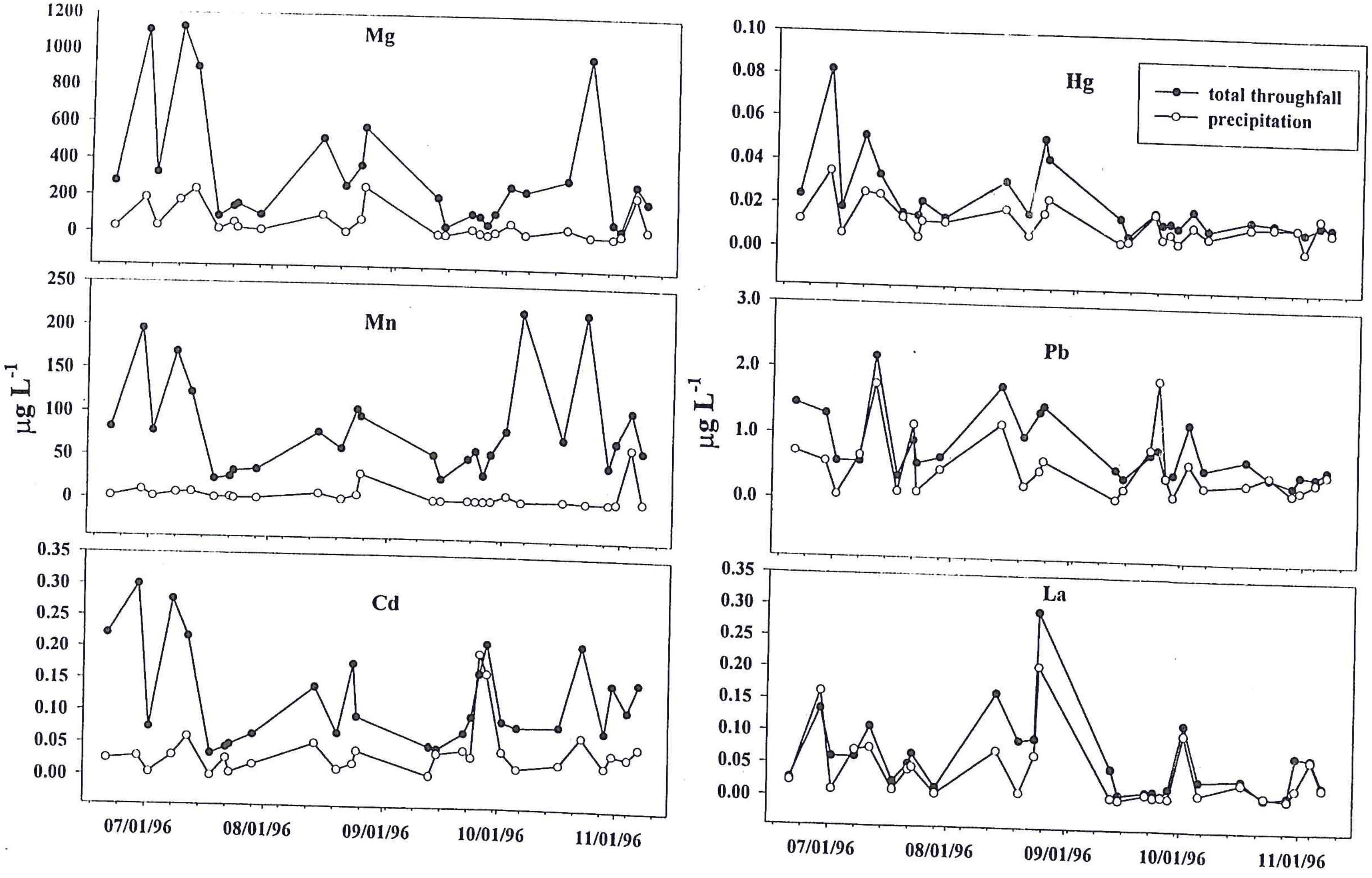


Figure 6.1. Concentrations (± std. dev.) of Mg, Mn, Cd, Hg, Pb, and La (μg L^{-1}) in event precipitation and total throughfall samples collected in Pellston, MI from June 21- November 7, 1996

Concentrations of La (Figure 6.1), Ce, and Al in total throughfall were generally less than two times higher than precipitation concentrations during the majority of the study period suggesting that they were not leached from within-leaf sources. The two events in which total throughfall concentrations were up to 15 (Ce) times higher than precipitation concentration were associated with antecedent dry periods of 364 (maximum for study period) and 131 hr, respectively. The behavior shown by La, Ce, and Al may be expected for soil elements that do not leach from foliage in throughfall. Increases in total throughfall concentrations of La, Ce, and Al over associated precipitation concentrations were probably due to wash-off of wind blown soil dust on the leaf surface.

The soil elements may be useful for examining the processes (dry deposition or foliar leaching) affecting the other elements in throughfall. Because foliar leaching does not appear to be occurring for La, Ce, or Al they may be used as a marker for atmospheric deposition. By taking the ratio of an element in precipitation and total throughfall to La, Ce, or Al, the influence of dry deposition and foliar leaching becomes apparent. Figure 6.2 shows the ratio of Hg, Cd, As, Zn, Rb, and Sr to La in precipitation and total throughfall (ratios to Ce and Al were similar). Ratios of Hg, Cd, As (Figure 6.2), V, Cu, Pb, Al, and Ce to La in precipitation and total throughfall were generally similar to each other throughout the growing season. In contrast, ratios of Rb, Sr (Figure 6.2), Mg, Mn and Ba to La in total throughfall were frequently higher than the ratios in precipitation. The similarities in the Hg, Cd, As, V, Cu, and Pb to La ratios in precipitation and total throughfall suggests that elements in both precipitation and

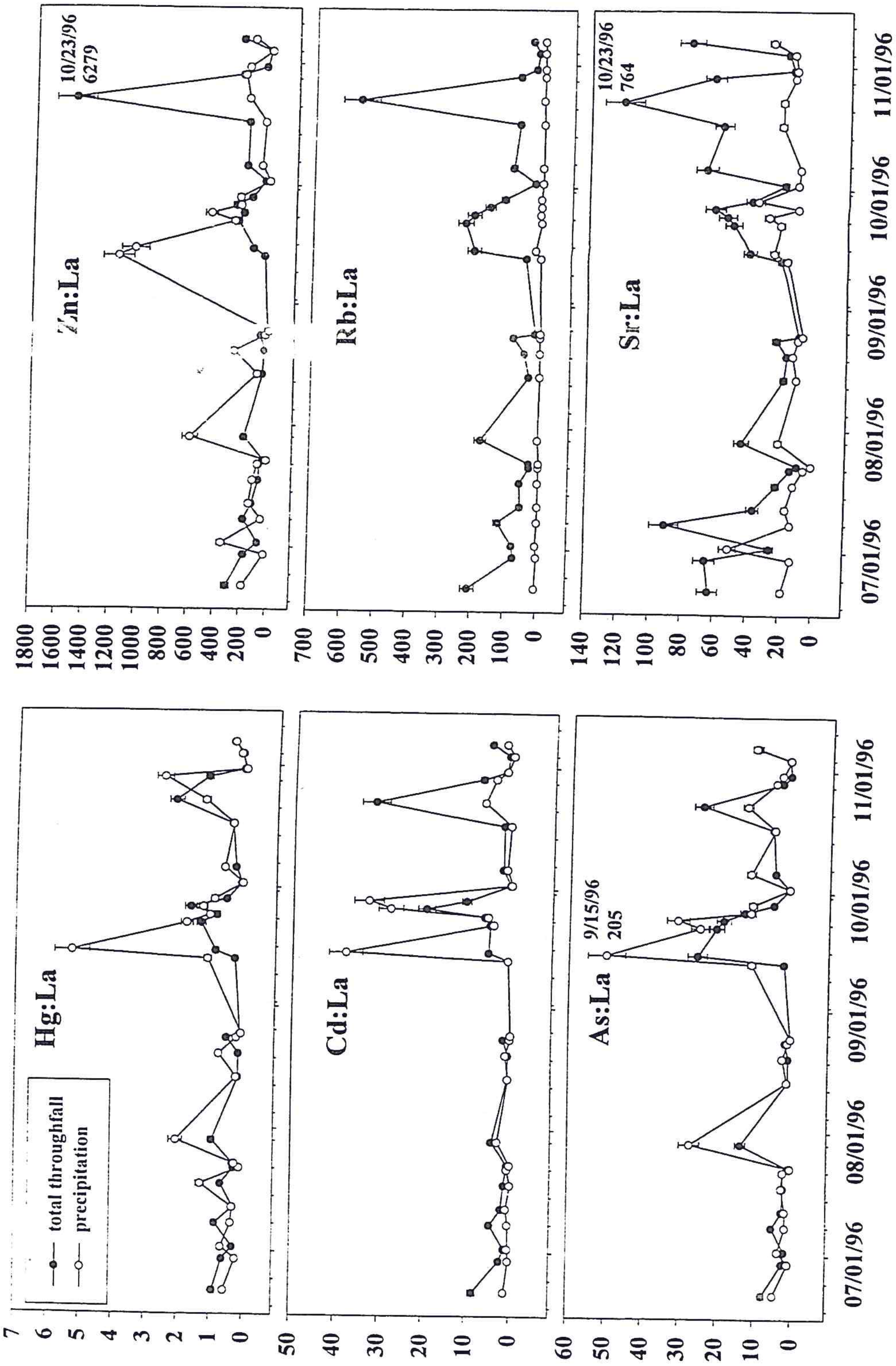


Figure 6.2. Ratios of concentrations (± std. dev.) of Hg, Cd, As, Zn, Rb, and Sr to La in precipitation and total throughfall.

throughfall were derived from similar external sources. The likely source of these elements in throughfall was wash-off of dry deposition. The large differences in the ratios of Rb, Sr, Mg, Mn, and Ba to La in precipitation and total throughfall suggests the source of these elements in total throughfall is different than the source in precipitation. Most likely, the source of these elements in throughfall was foliar leaching.

The elevated ratios of Hg, Cd, As, Zn (Figure 6.2), V, Cu, and Pb to La in precipitation correspond to large events (3.5 and 3.9 cm, respectively) that occurred on July 29 and September 15 when the La concentration in precipitation was minimal. Elevated ratios only occurred for the elements that were influenced by dry deposition, not elements largely influenced by foliar leaching. The La ratios in total throughfall were elevated throughout the growing season for Rb, Sr (Figure 6.2), Mg, Mn, and Ba, and reached a maximum on October 23. This was a large volume event (3.4 cm) which lasted over 26 hr, and the throughfall samples were visibly discolored (orange) due to leaching of pigments from senesced foliage. The total throughfall concentration of La was also at a minimum during this event. This strongly suggests that foliar leaching was occurring for Rb, Sr, Mg, Mn, and Ba. A few elements (Cd, As, Zn (Figure 6.2), and Cu) that did not have elevated La ratios in total throughfall during the rest of the growing season had elevated ratios for this event, suggesting that foliar leaching had occurred. Although Cu and Zn are essential micronutrients, they are toxic in large amounts. Leaching of Cu, Zn, Cd, and As at the end of the growing season before leaf abscission may be a tolerance mechanism to avoid toxic accumulation of these elements in trees, as has been suggested for Cd (Lindberg, 1989).

Throughfall deposition

The deposition flux (μg m^{-2}) of an element in throughfall indicates the amount of an element reaching the forest floor due to inputs from precipitation, wash-off of dry deposition, and foliar leaching. The total deposition of the elements measured in precipitation, total throughfall, and net throughfall (total throughfall deposition minus precipitation deposition) during the study period are listed in Table 6.1. The ratio of the deposition of each element in precipitation to total throughfall illustrates the importance of precipitation for many elements (Table 6.1). A large portion of the Hg, Al, V, Cu, As, Cd, La, Ce, and Pb deposited in total throughfall was due to precipitation while most of the Mg, Mn, Rb, Sr, and Ba deposited in total throughfall was due to canopy processes. Most likely, this increased deposition was due to foliar leaching. The large canopy influence on the deposition of Zn may be attributed to one event (23 October) in which the deposition of Zn in net throughfall was 21 times higher than the mean net throughfall deposition of Zn during the other events. The net throughfall deposition of Mg, Mn, Rb, Sr, Cd, and Ba also was elevated, ranging from 3 (Rb) to 11 (Mg) times higher than the mean net throughfall deposition for these elements. In contrast, the net throughfall deposition of Hg, Al, V, Cu, As, La, Ce, and Pb was less than two times higher than the mean net throughfall deposition. This behavior suggests that Zn, Mg, Mn, Rb, Sr, Cd, and Ba were strongly influenced by foliar leaching during this event.

Table 6.1. The measured deposition ($\mu g\ m^{-2}$) of trace elements in precipitation (PCP), total throughfall (TTF), and net throughfall (NTF) from 21 June to 7 Nov 96 from a northern mixed-hardwood forest in Pellston, Michigan. Ratios of precipitation to total throughfall deposition (PCP:TTF) are also listed.

Element	**PCP deposition ($\mu g\ m^{-2}$)**	**TTF deposition ($\mu g\ m^{-2}$)**	**NTF deposition ($\mu g\ m^{-2}$)**	**PCP:TTF**
Hg	**4.9 ± 0.2**	**6.7 ± 0.2**	**1.8 ± 0.1**	**0.73**
Al	**3826 ± 127**	**6963 ± 223**	**3137 ± 142**	**0.55**
V	**55 ± 2**	**68 ± 2**	**13 ± 0.7**	**0.81**
Cu	**139 ± 4**	**265 ± 8**	**126 ± 6**	**0.52**
As	**50 ± 2**	**63 ± 2**	**13 ± 1**	**0.79**
Cd	**19 ± 1**	**37 ± 2**	**18 ± 1**	**0.51**
La	**6.7 ± 0.2**	**12.5 ± 0.5**	**5.8 ± 0.3**	**0.54**
Ce	**13.3 ± 0.5**	**24.2 ± 0.9**	**10.9 ± 0.6**	**0.58**
Pb	**192 ± 7**	**236 ± 7**	**44 ± 5**	**0.81**
Mg	**12829 ± 450**	**91096 ± 5883**	**78267 ± 5856**	**0.14**
Mn	**1033 ± 104**	**26831 ± 1418**	**25798 ± 1421**	**0.04**
Zn	**1102 ± 36**	**2623 ± 253**	**1521 ± 247**	**0.42**
Rb	**16 ± 1**	**986 ± 32**	**970 ± 32**	**0.02**
Sr	**115 ± 3**	**549 ± 31**	**434 ± 30**	**0.21**
Ba	**203 ± 5**	**1415 ± 79**	**1212 ± 77**	**0.14**

The net throughfall deposition of an element includes inputs from both wash-off of dry deposition and foliar leaching. These inputs have been isolated for major ions by multiple linear regression analysis (Lovett and Lindberg, 1984; Potter *et al.*, 1991; Lovett *et al.*, 1996). The regression is based on the equation:

$$\mathrm{NTF_{dep}} = \mathrm{DD} + \mathrm{FL}$$

where $\mathrm{NTF_{dep}}$ is the net throughfall deposition flux, DD is the dry deposition component, and FL is the foliar leaching or canopy exchange component. This approach assumes that: (1) the dry deposition component of net throughfall is correlated to the antecedent dry period, (2) the foliar leaching component is correlated to the depth of rain, (3) these relationships are linear, and (4) dry deposition is quickly and completely removed from the canopy (Lovett and Lindberg, 1984).

Previous studies have used linear regression of various event characteristics (including antecedent dry period, depth of rain, precipitation concentrations of the solute, pH, duration, and date) to account for the net throughfall deposition of major ions such as Ca^{2+}, K^+, Mg^{2+}, Na^+, H^+, SO_4^{2-}, NO_3^-, and NH_4^+ (Lovett and Lindberg, 1984; Potter *et al.*, 1991; Lovett *et al.*, 1996). In this study, a general linear regression model was used to test the rainfall characteristics listed above (independent variables) against the net throughfall deposition (dependent variable). The regression found that antecedent dry period, depth of rain, and precipitation concentration of the solute significantly influenced the net throughfall deposition ($p<0.05$). Therefore, the regression equation used was:

$$\mathrm{NTF_{depX}} = b + m_1\mathrm{ADP} + m_2\mathrm{depth} + m_3\mathrm{PCP_{concX}}$$

where NTF_{depX} is the deposition of solute X in net throughfall ($\mu g\ m^{-2}$); b is the intercept; m_{1-3} are the associated regression coefficients; ADP is the antecedent dry period before an event (hr); depth is the depth of rain per event (cm); and PCP_{concX} is the concentration of solute X in precipitation ($\mu g\ L^{-1}$). The regression coefficients represent the net dry deposition rate (m_1; $\mu g\ m^{-2}\ hr^{-1}$), the mean canopy exchange rate (m_2; $\mu g\ m^{-2}\ cm^{-1}$), and the influence of retention of ions from incoming precipitation (m_3; $\mu g\ m^{-2}$ per $\mu g\ L^{-1}$). The intercept term (b) was not significant for all elements, but was retained in the equations.

Multiple linear regression explained most of the variability in the net throughfall deposition of all elements except Hg (Table 6.2). The significant correlation with antecedent dry period (and precipitation concentration for V and Pb) indicate that Hg, Al, V, and Pb in net throughfall were influenced by dry deposition (Table 6.2). The correlation to precipitation concentration for V and Pb illustrates the importance of retention of these elements by the canopy. The net throughfall deposition of V and Pb was frequently negative throughout the growing season. The net throughfall deposition of Pb also was observed to be negative by Lindberg (1989). Zinc, Cu, As, Mg, Cd, and Sr were influenced by both dry deposition and foliar leaching as shown by the correlation with antecedent dry period and depth of rain (Table 6.2). Manganese, Ba, and Rb only showed a significant correlation with depth of rain indicating that these elements were strongly influenced by foliar leaching (Table 6.2).

Using multiple linear regression analysis, previous studies have found that Mg and Ca have both dry deposition and foliar leaching components, while K has been found to be influenced either solely by foliar leaching or both wash-off of dry deposition and

Table 6.2. Coefficient of determination (R^2) and regression coefficients (± std. error) based on multiple linear regression analysis of the net throughfall deposition (dependent variable; n=27) versus various event characteristics (independent variables). Regression coefficients are: b, intercept; m_{ADP}, slope of the antecedent dry period ($\mu g\ m^{-2}\ hr^{-1}$); m_{depth}, slope of the depth of rain ($\mu g\ m^{-2}\ cm^{-1}$); and $m_{PCPconcX}$, slope of the concentration of solute X in precipitation ($\mu g\ m^{-2}$ per $\mu g\ L^{-1}$). * significant at $p<0.05$; ** significant at $p<0.01$; ns, not significant.

	NTFdep Hg	**NTFdep Al**	**NTFdep V**	**NTFdep Pb**	**NTF dep Zn**	**NTFdep Cu**	**NTFdep As**
R^2	**0.38**	**0.48**	**0.51**	**0.54**	**0.47**	**0.67**	**0.64**
b SE	**ns**	**-310 ± 123 ***	**ns**	**-11 ± 3.7 ****	**ns**	**-15 ± 4 ****	**-3.5 ± 0.7 ****
m_{ADP} SE	**0.04 ± 0.01 ***	**86 ± 28 ****	**0.47 ± 0.14 ****	**2.1 ± 0.8 ****	**1.0 ± 0.3 ****	**4.5 ± 0.9 ****	**0.44 ± 0.15 ****
m_{depth} SE	**ns**	**ns**	**ns**	**ns**	**0.35 ± 0.17 ***	**1.2 ± 0.6 ***	**0.42 ± 0.08 ****
m_{PCP} conc X SE	**ns**	**ns**	**-3.4 ± 1.3 ***	**-2.8 ± 0.8 ****	**ns**	**ns**	**ns**

	NTFdep Mg	**NTFdep Cd**	**NTFdep Sr**	**NTFdep Mn**	**NTFdep Rb**	**NTFdep Ba**
R^2	**0.68**	**0.61**	**0.67**	**0.64**	**0.73**	**0.68**
b SE	**3.4 ± 0.9 ****	**-2.9 ± 0.8 ****	**ns**	**3.9 ± 0.8 ****	**1.6 ± 0.7 ***	**ns**
m_{ADP} SE	**0.64 ± 0.18 ****	**0.45 ± 0.16 ****	**0.45 ± 0.17 ***	**ns**	**ns**	**ns**
m_{depth} SE	**0.52 ± 0.13 ****	**0.45 ± 0.10 ****	**0.55 ± 0.13 ****	**0.52 ± 0.12 ****	**0.63 ± 0.10 ****	**0.58 ± 0.13 ****
m_{PCP} conc X SE	**ns**	**ns**	**ns**	**ns**	**ns**	**ns**

foliar leaching (Lovett and Lindberg, 1984; Potter *et al.*, 1991; Lovett *et al.*, 1996). In plants, Sr and Ba behave similarly to Ca and Rb behaves similarly to K (Guha and Mitchell, 1966). This analysis has provided similar results, indicating that Ba and Rb were influenced by foliar leaching processes and Mg and Sr were influenced by both wash-off of dry deposition and foliar leaching. Although many studies have used multiple linear regression, to our knowledge there are no similar data to compare with the other elements reported here. Lindberg (1989) attempted to use multiple linear regression on the trace elements Mn, Cd, and Pb, but found it unsuccessful due to a small sample size (n=15).

Multiple linear regression applied to this data set explained 38% of the variance in the net throughfall deposition of Hg. The only significant correlation for Hg was to antecedent dry period indicating that dry deposition was important. Multiple linear regression analysis works best for particulate species and the correlation coefficient for Hg may indicate the importance of wash-off of particulate Hg forms in throughfall. Mercury in throughfall may also be present in water soluble gaseous (Hg^{2+}) forms, but only total Hg was measured in this study. Multiple linear regression analysis has been useful for explaining various forms of N deposited in net throughfall, such as NO_3^- and NH_4^+, but has been less successful for S compounds which also are present in both particle and gaseous forms. Until reliable and precise analytical techniques are developed for the speciation of Hg in aqueous samples, regression analysis may not be adequate for fully explaining the influence of dry deposition and foliar leaching on Hg in net throughfall.

The mean dry deposition rate for Hg (40 ± 10 ng m^{-2} hr^{-1}) determined by the multiple linear regression analysis is much higher than the dry deposition rate estimated for particulate Hg based on washed foliar and Teflon surfaces (0.19-0.23 ng m^{-2} hr^{-1}) (Chapter 5). These differences are probably due to the influence of dry deposition of gaseous Hg compounds and the wash-off of reactive gaseous Hg species which were *not* considered for the washed foliar and Teflon surfaces. The dry deposition rate for Hg reported here is also higher than those based on throughfall measurements (1.4-17 ng m^{-2} hr^{-1}) reported by Lindberg *et al.* (1994) and Rea *et al.* (1996). These differences may be due to site differences and methods of determining dry deposition rates. Measurements of Hg gradients over forest canopies (Lindberg *et al.*, 1998) indicate that deposition fluxes can range from 8-230 ng m^{-2} hr^{-1}, confirming that the mean dry deposition rate reported here may be reasonable. The estimated dry deposition flux based on multiple linear regression may be higher than other estimates due to complications from wash-off of gaseous Hg compounds and incomplete wash-off of dry deposition during rain events.

Modeling Hg deposition to the forest

All of the approaches used to examine the source of Hg in throughfall have indicated that wash-off of dry deposited Hg was important. To determine if atmospheric Hg could account for the Hg present in throughfall, gaseous and aerosol Hg measurements were integrated with modeled deposition velocities. During the study period, the mean (± std. dev.) total gaseous Hg concentration was 1.3 ± 0.3 ng m^{-3} (n=34). Aerosol Hg concentrations were much lower than gaseous Hg concentrations, mean aerosol Hg concentraitons were 0.007 ± 0.005 ng m^{-3} (n=35) in TSP samples and 0.004 ± 0.003 ng m^{-3} (n=35) in fine fraction (<2.5 μm) aerosols. Although the majority of the aerosol Hg measured at this site was in the fine fraction (60%), the influence of coarse particle Hg may be important. Particle deposition is a function of aerodynamic diameter, and coarse particles have higher deposition velocities than fine particles (Milford and Davidson, 1985). This influence causes coarse particles to have a greater impact on dry deposition than fine particles.

Estimates of Hg dry deposition to the forest canopy was calculated using both measurements and modeled parameters. A multiple resistance model developed by Hicks *et al.* (1987) and modified by Lindberg *et al.* (1992) was used to determine deposition velocities (V_d) to the forest canopy. The model calculates the V_d for elemental gaseous Hg^0, reactive gaseous Hg^{2+}, and fine aerosol Hg based on hourly meteorological data, site characteristics, and cuticular, stomatal, and mesophyll resistances. The stomatal and mesophyll resistances are important for Hg^0 deposition to the leaf interior (i.e. through the stomata). The model treats reactive gaseous Hg (Hg^{2+}) as nitric acid vapor (HNO_3). Both Hg^{2+} and HNO_3 are highly water soluble gases and are assumed to have similar deposition characteristics. The model assumes that aerosol Hg is in the fine fraction and the deposition velocity is calculated by eddy diffusion.

Measurements of Hg^{2+} in the atmosphere indicate that concentrations are approximately 3% (1.7-3.1%) of total gaseous mercury (Hg^0 and Hg^{2+}) (Lindberg and Stratton, 1998). Therefore, to estimate the potential dry deposition flux of Hg^{2+} to the canopy, the ambient Hg^{2+} concentration was estimated from 1-5% of the measured ambient Hg^0 concentration. Based on the fine and coarse aerosol measurements, approximately 60% of the aerosol Hg is in the fine fraction. Since the model calculates V_d for fine particles only, the aerosol deposition flux is likely to be underestimated at this site, by as much as 4-8 times.

Based on the modeled V_d and ambient air concentrations, the dry deposition rate of Hg^0, Hg^{2+} and fine fraction aerosol Hg can be calculated. The modeled V_d and calculated dry deposition rates are listed in Table 6.3. These V_d and dry deposition rates are similar to those reported by Lindberg *et al.* (1994) and Rea *et al.* (1996) using similar methods for Hg^0 and aerosol Hg. These studies reported V_d for Hg^0 ranging from 0.020-0.094 cm s^{-1} and for fine fraction aerosol Hg ranging from 0.029-0.176 cm s^{-1}. The associated dry deposition rates for Hg^0 and fine fraction aerosol Hg were 1.4-17 ng m^{-2} hr^{-1} and 0.013-0.12 ng m^{-2} hr^{-1}, respectively (Lindberg *et al.*, 1994; Rea *et al.,* 1996).

The net throughfall measurements also can be used to estimate the dry deposition rate. The dry deposition rate is calculated on an event basis by dividing the net throughfall deposition (ng m^{-2}) by the antecedent dry period (hr) (Lindberg *et al.,* 1994). The mean (± std. dev.) dry deposition rate for the study period was 1.00 ± 1.41 ng m^{-2} hr^{-1}. This estimate compares well with the reported dry deposition rates (0.02 - 8.57 ng m^{-2} hr^{-1}) calculated similarly for other forests (Lindberg *et al.,* 1994; Rea *et al.,* 1996). In comparison, the mean (± std. error) dry deposition rate estimated using multiple linear regression, 40 ± 10 ng m^{-2} hr^{-1}, was much higher than any of these estimates which suggests that multiple linear regression may not be as useful for identifying sources of Hg in net throughfall as it is for major ions.

Another way to calculate Hg dry deposition is based on the modeled V_d and measured ambient Hg concentrations. The dry deposition flux between rain events was

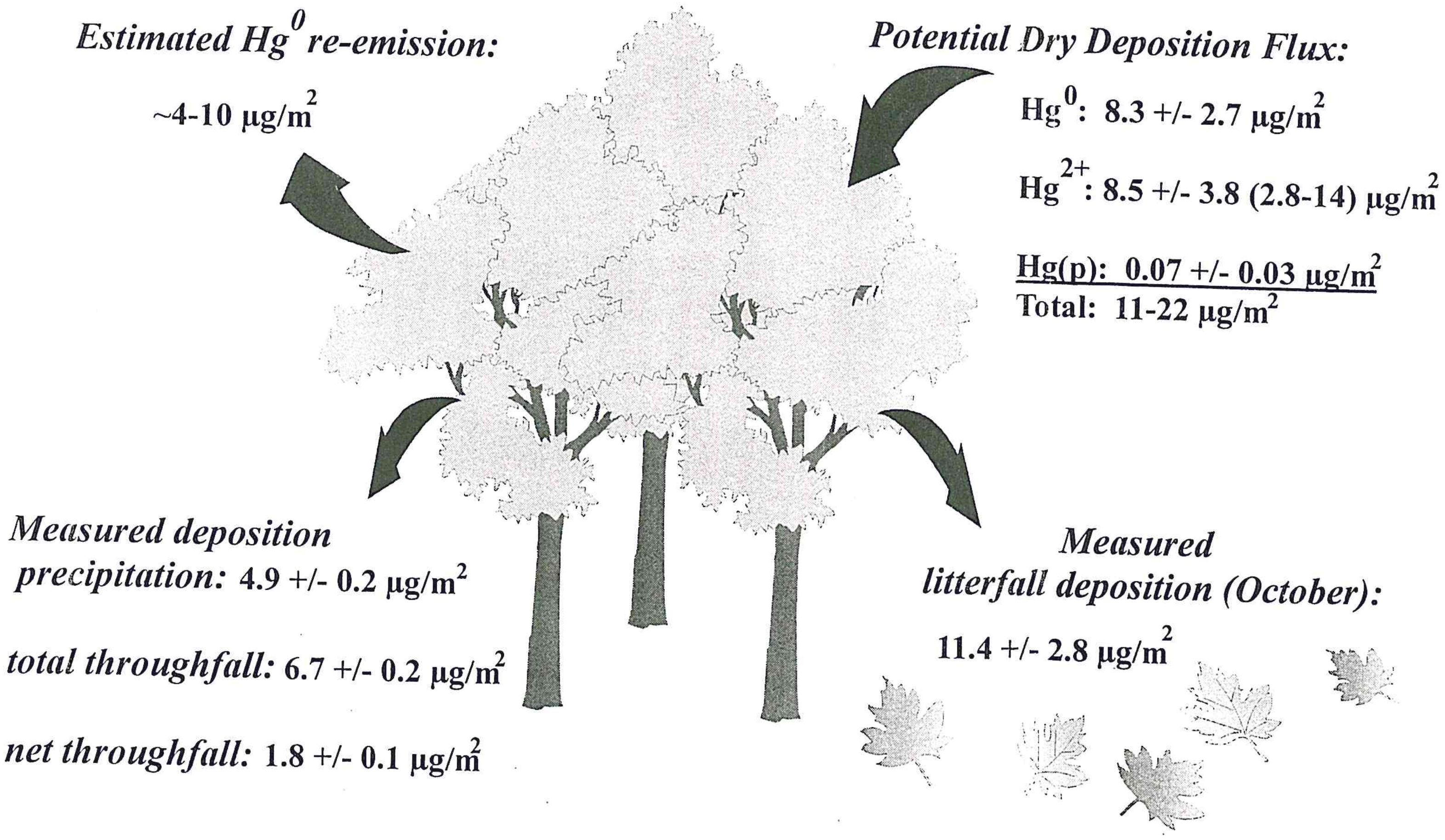
Table 6.3. Mean (± std. dev.) Hg dry deposition velocities and dry deposition rates to the forest canopy during June-November, 1996.

Hg Species	Deposition velocity (cm s^{-1})	Dry deposition rate (ng m^{-2} hr^{-1})
Hg^0	0.054 ± 0.020	2.48 ± 1.01
Hg^{2+}	1.9 ± 0.3	2.6 ± 0.5
Hg (p)	0.092 ± 0.028	0.023 ± 0.017

calculated for gaseous Hg^0, gaseous Hg^{2+}, and aerosol Hg by multiplying the mean V_d by the associated mean ambient Hg concentration and the antecedent dry period. These fluxes were summed to obtain the total dry deposition flux for Hg during the study period (17-22 μg m^{-2}; Figure 6.3). Comparing the dry deposition flux of Hg to the measured net throughfall Hg flux on an event basis indicated that more Hg was depositing to the canopy than washing off the leaves in throughfall. The dry deposition flux of Hg was more than ten times higher than the measured net throughfall flux of Hg (Figure 6.3). The majority of the dry deposition flux is in a gaseous form (Figure 6.3), which may undergo many reactions and transformations on the leaf surface. Any resulting water soluble Hg compounds may wash-off the leaf surface in throughfall. Gaseous Hg^0 may also be taken up through the leaf stomata (Mosbaek *et al.*, 1988; Browne and Fang, 1979). Gaseous Hg^{2+} may react on the leaf surface and be re-emitted as Hg^0 which may account for some of the emission of Hg^0 from forest canopies (Siegel *et al.*, 1974; Iverfeldt, 1991a; Hanson *et al.*, 1995; Lindberg, 1996; Lindberg *et al.*, 1998).

After subtracting the measured net throughfall flux of Hg (1.8 μg m^{-2}) from the dry deposition flux of Hg (17-22 μg m^{-2}), approximately 15-21 μg m^{-2} is left behind in the canopy which is equivalent to a total leaf Hg concentration of 101-140 ng g^{-1} (using 149 ± 46 g m^{-2} foliar density, measured from foliar data). Only 20-30% of this remaining Hg needs to be in a form suitable for uptake through the leaf stomata to account for all of the Hg measured in litterfall (32.5 ± 8.1 ng Hg g^{-1}; Chapter 4) at this site. All of the Hg in litterfall may not be due to uptake from the atmosphere, because there may be some (<10%) contribution from Hg^0 taken up from soil water via the transpiration stream

Figure 6.3. Measured and modeled fluxes (mean +/- std. dev.) of mercury in a northern mixed-hardwood forest (June-November, 1996)



(Bishop *et al.*, 1998). After subtracting the Hg deposited in litterfall from the remaining potential dry deposition flux, ~4-10 μg m^{-2} remains. This remaining Hg may be due to the uncertainty associated with the modeled estimates or it may have been re-emitted from the canopy throughout the growing season. While measuring the emission of Hg from the canopy was not in the scope of this work, canopy emission of Hg has been observed (Hanson *et al.*, 1995; Lindberg, 1996; Lindberg *et al.*, 1998) and cannot be overlooked in the biogeochemical Hg cycle. Although the source of the Hg that is emitted from the canopy has not been determined, it has been hypothesized that this Hg is emission of dissolved gaseous Hg from soil water transpiration (Hanson *et al.*, 1995; Lindberg, 1996; Lindberg *et al.*, 1998)

Data from one forest may not necessarily be applicable to forests elsewhere. The Hg^0 re-emission estimated for this forest in the Lake Huron Watershed is much lower than the scaled mean annual Hg^0 emission flux (70 μg m^{-2}) reported for the Walker Branch Watershed in Tennessee based on 1-3 hr gradient measurements (n=23) measured during 2 months of the growing season (Lindberg *et al.*, 1998). The Hg^0 emission flux from the Walker Branch canopy is likely to be much higher than the Hg^0 emission flux from the forest in Pellston, MI due to local source influences near the Walker Branch site (2 coal-fired power plants) and the Walker Branch site history (near a former weapons plant which released ~20 tons of Hg in the 1950's and passively emits Hg to date) (Lindberg, 1996). The estimated Hg^0 emission flux in this study only accounts for the re-emission of dry deposited Hg from the atmosphere, and not Hg^0 possibly emitted from other sources, such as soil water transpiration.

SUMMARY

These findings demonstrate that the biogeochemical cycling of Hg in this forested ecosystem is driven by atmospheric inputs. Comparing the behavior of Hg to other trace elements in throughfall indicated that wash-off of dry deposition was the source of the Hg in throughfall. These findings are in agreement with those reported elsewhere (Iverfeldt, 1991a; Lindberg *et al.*, 1994; Munthe *et al.*, 1995; Rea *et al.*, 1996). Multiple linear regression analysis also suggested that dry deposition of Hg was significant. Modeled V_d and calculated dry deposition rates were similar to those reported elsewhere (Lindberg *et al.*, 1994; Rea *et al.*, 1996). Calculating the dry deposition flux (11-22 μg m^{-2}) of Hg to the canopy indicated that atmospheric deposition of Hg could account for all of the Hg deposited in net throughfall (1.8 ± 0.1 μg m^{-2}). In addition, the modeling estimates show that atmospheric Hg can account for all of the Hg deposited in litterfall (11.4 ± 2.8 μg m^{-2}) while also accounting for some emission of Hg from the canopy (4-10 μg m^{-2}). Further research is needed to determine if the Hg entering the forested ecosystem is being incorporated into terrestrial ecosystems or entering surrounding aquatic ecosystems in soil water run-off.

CHAPTER VII

CONCLUSIONS AND SYNTHESIS

Summary and conclusions

It is well known that the atmosphere plays an important role in the global biogeochemical Hg cycle. Previous research has shown that the largest deposition pathways for Hg in forested ecosystems are litterfall and throughfall (Iverfeldt, 1991a; Munthe *et al.,* 1995; Lindberg *et al.,* 1994; Lindberg, 1996). For example, the measured total Hg deposition to the forest floor in litterfall (11.4 ± 2.8 μg m^{-2}) and throughfall (6.7 ± 0.2 ug m^{-2}) in the Lake Huron Watershed was 18.1 ± 3.0 μg m^{-2} during June through November, 1996. Of this total, 63% was deposited to the forest floor in litterfall and the remaining 37% was deposited in throughfall (10% in net throughfall, 27% in precipitation) during June–November, 1996 (Figure 6.3). Identifying the source of the Hg deposited to the forest floor in litterfall and throughfall is critical in assessing the impact of atmospheric sources of Hg in forested ecosystems. The research hypotheses identified in this thesis were:

1) Total Hg in litterfall is controlled by atmospheric processes: the uptake of Hg by foliage and the accumulation of Hg on foliage, and

2) Total Hg in throughfall is due to the wash-off of dry deposited atmospheric Hg.

To identify the source(s) of Hg in litterfall and throughfall, a comprehensive study was undertaken which measured Hg in various ecosystem components (foliage, litterfall, precipitation, throughfall, ambient air, and soil). These data were compared with data collected in pilot studies from a northern mixed-hardwood forest in the Lake Champlain Watershed. This was the first study to use a multi-element approach to identify the source(s) of Hg in litterfall and throughfall. The behavior of Hg was compared to other elements that were known macro- or micronutrients (Mg, Mn, Cu, Zn), behaved similarly to nutrients (Rb, Ba, Sr), or had no nutritional value in plants with soil (Al, La, Ce) or atmospheric (As, Cd, Pb) sources.

Various approaches were taken to identify the source of Hg in litterfall and throughfall. To identify the source of Hg in litterfall, live foliage was collected throughout the 1995 growing season in the Lake Champlain Watershed and the 1996 growing season in the Lake Huron Watershed; litterfall was collected during the autumn months. At both sites, foliar Hg concentrations increased ten fold from 3.5 ± 1.3 ng g^{-1} at spring bud break to 36 ± 8 ng g^{-1} in litterfall (mean ± std. dev. from both sites). This strongly uniform increase was not observed for any of the other elements measured. In addition, there were no significant foliar Hg concentration differences in all species sampled within a month, however, significant differences between species were observed for the other elements measured. These findings suggested stomatal uptake of gaseous Hg in the atmosphere may be the source of the Hg in foliage because the other elements measured did not have significant gaseous contributions. Various sources for the Hg measured in foliage were examined, including root absorption from the mineral soil, uptake of dissolved gaseous Hg in soil water, and uptake of dry deposited Hg^0 from the atmosphere. Although soil water Hg concentrations were not measured in this study, uptake of Hg from soil water was estimated based on measurements in the Lake Champlain Watershed. These estimates indicated that uptake of Hg from soil water could account for, at most, 3-14% of the Hg in litterfall. Atmospheric uptake of gaseous Hg was estimated two ways: from the foliar Hg measurements and from dry deposition of Hg^0 based on the measured ambient Hg^0 concentrations and modeled V_d. These estimates indicate that atmospheric Hg^0 could account for all of the Hg measured in foliage. On average, only 25% (16-34%) of the available Hg^0 needed to be accumulated by leaves to account for all the Hg measured in foliage at both sites. The remaining Hg^0 may have been re-emitted from the canopy or transformed to a more water soluble Hg compound and washed-off the leaf surface in throughfall.

Since the Hg concentration in leaves is constantly increasing throughout the growing season, leaf washing experiments were designed to evaluate the influence of dry deposition and foliar leaching of Hg in foliage. These experiments were conducted under short time intervals (compared to the length of a rain event) and under controlled conditions. Foliage was collected at an urban site and from the forested site in the Lake Huron Watershed. Fluxes of elements washed from foliage indicated that removal of elements followed first order kinetics. Removal constants were similar for all trace elements during set washing time intervals, indicating that similar processes were occurring for leaves collected in either urban or rural areas. Wash-off of dry deposition occurred for Hg, Cd, La, Ce, and Pb, and foliar leaching occurred for Mn, Rb, Ba, and Sr. More intensive washing confirmed these results, indicating that Hg was subject to wash-off of dry deposition, not foliar leaching. Another experiment was conducted in which both foliage and surrogate Teflon surfaces were collected and washed after a 5 day dry period. Dry deposition velocities and dry deposition rates for Hg calculated for both the foliar and Teflon surfaces were similar, indicating that wash-off of dry deposition was the source of the Hg removed from foliage.

Event throughfall and precipitation samples were collected from June through November, 1996 and these data were used to examine the source of Hg in throughfall. Comparison of the temporal trends in total throughfall and precipitation concentrations indicated that Hg was not behaving similarly to the elements which showed strong leaching behavior (Mn, Rb, Ba, Sr). A multiple linear regression approach was used to separate the dry deposition and foliar leaching components of trace elements in net throughfall. This analysis indicated that some elements deposited in net throughfall were due to foliar leaching (Mn, Rb, Ba) while other elements (Hg, Al, V, and Pb) in net throughfall were due to wash-off of dry deposition. Multiple linear regression was not as successful for Hg as it was for the other trace elements, because of the influence of both gaseous and aerosol Hg compounds in net throughfall and total Hg, not the various Hg species present, was measured. Various approaches indicated that a large portion of the Hg deposited in total throughfall was due to precipitation and the remainder was due to wash-off of dry deposited Hg compounds in the canopy. Estimates of V_d and dry deposition rates for Hg using both measured and modeled data were similar to those reported elsewhere. The dry deposition flux of Hg to the canopy was calculated and indicated that dry deposition of atmospheric Hg could account for all of the Hg deposited to the forest floor in both litterfall and throughfall.

Synthesis

All of the approaches used to identify the source of Hg in litterfall and throughfall in this study used different techniques to measure the dry deposition of Hg. The methods used for measuring the dry deposition of Hg included throughfall, precipitation, foliage, litterfall, and ambient air measurements; modeling estimates; foliar accumulation estimates; and leaf wash fluxes. The V_d (cm s^{-1}) and dry deposition rates (ng m^{-2} hr^{-1}) calculated using each method and reported in Chapters 3-6 are summarized in Table 7.1. Although the estimates apply to different years and time intervals, the data from northern mixed-hardwood forests in the Lake Champlain and Lake Huron Watersheds are comparable. These two forests are similar to each other in terms of species composition; stand age; Hg concentrations in foliage, litterfall, precipitaiton, throughfall, and air; meteorology; and latitude. Similarities between V_d and dry deposition rates computed for other forests may be due to the characteristics listed above or to the relative importance placed on one fraction vs another (for example, Hg^{2+} vs aerosol Hg).

The throughfall studies (Chapters 3 and 6) yielded similar V_d and dry deposition rates for Hg as might be expected because a similar modeling technique was used. The mean (± std. dev.) V_d for Hg^0 reported for the 1996 growing season in the Lake Huron Watershed falls within the range reported for August and September, 1994 in the Lake Champlain Watershed. These V_d are similar to those reported in Chapter 4 for foliage collected in both watersheds during either the 1995 or 1996 growing season. Although calculated similarly, the V_d for Hg^0 reported in Chapter 4 are slightly different that those reported in Chapter 6 because they are based on different time intervals (foliage collection intervals in Chapter 4 and event throughfall collection intervals in Chapter 6).

Table 7.1. Summary of deposition velocities (V_d; cm s^{-1}) and dry deposition rates (ng m^{-2} hr^{-1}) for Hg species using various techniques. Results are presented as mean ± std. dev. or range; MLR is presented as mean ± std. error. NTF indicates net throughfall; MLR indicates multiple linear regression; * indicates modeled dry deposition rate to foliage; ** indicates the estimated Hg^0 accumulation rate based on foliar Hg measurements.

	Lake Champlain Throughfall	Deposition to foliage		Leaf Wash Huron		Lake Huron Throughfall
		Champlain	Huron	Foliage	Teflon	
V_d (cm s^{-1})						
Hg^0	0.020 - 0.081	0.052 ± 0.041	0.067 ± 0.022			0.054 ± 0.020
Hg^{2+}						1.9 ± 0.3
Hg (p)	0.029 - 0.176			1.2 ± 1.3	1.0 ± 1.3	0.092 ± 0.028
Dry deposition rate (ng $m^{-2}hr^{-1}$)						
Hg^0	1.4 - 9.04	*2.4 ± 1.9 **0.5 ± 0.1	*3.2 ± 1.1 **1.0 ± 0.3			2.48 ± 1.01
Hg^{2+}						2.6 ± 0.5
Hg (p)	0.013 - 0.063			0.23 ± 0.25	0.19 ± 0.25	0.023 ± 0.017
Total Hg NTF	0.70 - 8.57					1.00 ± 1.41
Total Hg MLR						40 ± 10
Time interval	Aug-Sep, 94	May-Sep 95	May-Sep 96	Sep. 16-20, 96		Jun-Nov, 96
Chapter	3	4		5		6

The Hg^0 V_d reported here are similar to the 0.076-0.094 cm s^{-1} reported by Lindberg *et al.* (1994) using a similar method. The Hg^{2+} V_d reported here, 2.6 ± 0.5 cm s^{-1}, are much lower than the 5.1-5.9 cm s^{-1} reported for forest canopies based on measured Hg^{2+} gradients (Lindberg and Stratton, 1998). The differences in V_d may be due to the uncertainties associated with the measurement techniques.

The V_d for aerosol Hg in the throughfall studies also are similar to each other and to the 0.11 cm s^{-1} reported by Lindberg *et al.* (1994). All of these studies used a similar model for calculating the aerosol Hg V_d. Deposition velocities for aerosol Hg were not reported for the foliar data because it was assumed that the Hg measured in leaves was due to uptake of Hg^0 through the leaf stomata. Deposition of aerosol Hg to foliage was considered negligible because aerosol Hg would mostly likely be washed off the leaf surface in throughfall. However, the leaf washing experiments reported in Chapter 5 examined aerosol Hg deposition to foliage. Although the V_d calculated from the measured fluxes from washed foliar and Teflon surfaces compared well with each other, they are much higher than the modeled V_d for fine fraction (< 2.5 μm) aerosol Hg reported in the throughfall studies. The modeled V_d are for fine fraction aerosol Hg only and are likely underestimates of the total aerosol Hg V_d. Based on total and fine fraction aerosol Hg measurements at the Lake Huron site, ~40% of the Hg in aerosols was in the coarse fraction, suggesting that coarse particle Hg deposition was significant. This influence may cause the aerosol Hg dry deposition estimates to be increased from 4 to 8 times. It was assumed that the V_d calculated based on the washed foliar and Teflon surfaces were due to wash-off of aerosol Hg only and not gaseous Hg forms. If wash-off of gaseous Hg compounds occurred during washing, then the reported V_d are overestimated. The aerosol Hg V_d calculated from the washed foliar and Teflon surfaces compare well with the 0.64 ± 0.56 cm s^{-1} reported for aerosol Hg by Milford and Davidson (1985).

Estimates of Hg dry deposition rates based on the data reported in Chapters 3-6 are also listed in Table 7.1. The dry deposition rates for Hg^0, Hg^{2+}, and aerosol Hg were calculated based on the V_d listed above and the measured ambient Hg^0 and aerosol Hg concentrations. The ambient Hg^{2+} concentration was estimated as 3% of the total gaseous Hg (Hg^0) concentration. As expected, the dry deposition rates reported for Hg^0 and aerosol Hg in the throughfall studies and in the foliage study are similar because they used similar approaches. The Hg^0 accumulation rate in foliage was calculated from the measured foliar Hg concentrations and is much lower than the Hg^0 dry deposition rate. This is to be expected because it is unlikely that all of the Hg^0 in the atmosphere will be taken up by leaves. As discussed in Chapter 4, an average of 25% (16-34%) of the available Hg^0 was taken up into foliage. The remaining Hg^0 was probably re-emitted from the canopy or transformed on the leaf surface to a more water soluble Hg compound (e.g. Hg^{2+}) and washed off the canopy in throughfall. Although the V_d are similar, the Hg^0 dry deposition rates reported here are much lower than the 8-17 ng m^{-2} hr^{-1} reported for the Walker Branch Watershed (Lindberg *et al.*, 1994). These differences are due to the lower ambient Hg^0 concentrations at the Lake Champlain and Lake Huron sites than at the Walker Branch site.

The dry deposition rates for Hg^{2+} reported here are much lower than the 21-58 ng m^{-2} hr^{-1} reported for the Walker Branch Watershed (Lindberg and Stratton, 1998). The differences between these estimates are due uncertainties in measurement techniques. The influence of Hg^{2+} is sensitive to the fraction of total gaseous Hg that is in a Hg^{2+} form. If only 1% of the total gaseous Hg is Hg^{2+}, then the deposition flux of Hg^{2+} may be as low as 2.8 $\mu g\ m^{-2}$. The aerosol Hg dry deposition rates calculated in the throughfall studies also are similar to the 0.08-0.12 ng $m^{-2}\ hr^{-1}$ reported by Lindberg *et al.* (1994). The aerosol Hg dry deposition rates calculated based on the washed foliar and Teflon surfaces are higher than those calculated in the throughfall studies due to the higher V_d. The V_d and dry deposition rates reported here are particular to this forest and should not be applied to forests elsewhere. The forests int his study were in rural locations removed from local urban sources. The influence of local Hg sources need to be considered because it may cause the aerosol Hg contribution to be much larger, and the influence of Hg^{2+} also may be different. For example, if we assume that Hg^{2+} is 1% of total gaseous Hg, and that aerosol Hg deposition is ten times larger (due to a larger fraction of Hg associated with coarse aerosols), then the dry deposition flux of Hg^{2+} will be 2.8 $\mu g\ m^{-2}$ and the aerosol Hg flux will be closer to 1.0 $\mu g\ m^{-2}$. It becomes apparent that the importance of these fluxes will be a function of the forested ecosytem under study.

Based on the measurements of total Hg in net throughfall, dry deposition rates were calculated by dividing the net throughfall deposition (ng m^{-2}) by the antecedent dry period (hr) for each event. This is the NTF dry deposition rate listed in Table 7.1. These estimates at the Lake Champlain and Lake Huron Watersheds are comparable and are similar to the 0.02-2.86 ng $m^{-2}\ hr^{-1}$ calculated similarly for the Walker Branch Watershed (Lindberg *et al.*, 1994). The large dry deposition rate reported for the Lake Champlain Watershed (8.57 ng $m^{-2}\ hr^{-1}$) is due to one sample as discussed in Chapter 3. In the Lake

Huron throughfall study (Chapter 6), multiple linear regression also was used to identify the source of Hg in throughfall. The mean (± std. error) Hg dry deposition rate calculated using this method is also listed in Table 7.1 ("MLR"). This Hg dry deposition rate is much higher than those calculated using the other techniques, however, it falls within the 8-230 ng m^{-2} hr^{-1} reported by Lindberg *et al.* (1998) based on measured Hg gradients over forest canopies.

This thesis has identified dry deposition of atmospheric Hg as the source of Hg in litterfall and throughfall. Over 70% (13.2 ± 2.9 μg m^{-2}) of the Hg entering this forested ecosystem was due to dry deposition of atmospheric Hg to the canopy. Based on this work, future research should be directed towards understanding the role of various Hg species, such as Hg^{2+} and methylHg, in forested ecosystems. Some of the Hg deposited to the forest floor in litterfall and throughfall may enter surrounding aquatic ecosystems through soil water run off. If a large portion of this Hg is being transported to aquatic ecosystems, it may be a significant and frequently overlooked source of Hg in fish tissue.

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