Mercury dynamics of a northern hardwood canopy

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A B S T R A C T

Atmospheric emissions have led to widespread concern over mercury (Hg) contamination in aquatic and terrestrial ecosystems. Plant litter is an important pathway of Hg inputs to forest ecosystems. We investigated the role of the canopy in Hg accumulation, transport and deposition in an upland forest ecosystem. The total Hg content of leaf tissue increased approximately 10-fold over the growing season across all species, from 4.4 ± 2.7 to $37.3 \pm 12.4 \, \text{ng g}^{-1}$, with estimated average linear Hg accumulation rates of 0.22, 0.23, and $0.35 \, \text{ng g}^{-1} \, \text{day}^{-1}$ for yellow birch (*Betula alleghaniensis*), sugar maple (*Acer saccharum*), and American beech (*Fagus grandifolia*), respectively. This linear concentration relationship suggests that the accumulation is regulated by mass transfer processes between the atmosphere and leaf tissue. Conversely, the methyl Hg content ($0.17 \pm 0.18 \, \text{ng g}^{-1}$) and accumulations were low. Concentrations of total Hg were also 42% higher in understory ($\sim 1 \, \text{m}$), compared to overstory ($\sim 10 \, \text{m}$), beech. Such disparities in leaf Hg content may result from within-canopy variation in environmental variables, a canopy $\text{Hg}^0_{(g)}$ concentration gradient, or species-specific growth strategies. Annual Hg litterfall was 17.9 and $16.4 \, \text{mg m}^{-2} \, \text{yr}^{-1}$ for 2004 and 2005, respectively, representing the largest input of Hg to this forest ecosystem. Methyl Hg litter input was $<0.12 \, \text{mg m}^{-2} \, \text{yr}^{-1}$ for 2005. Modeling estimates of transpiration uptake and $\text{Hg}^0_{(g)}$ deposition suggest that Hg in leaf tissue is largely derived from atmospheric sources. Thus, litter Hg represents largely a new, rather than recycled, input to the forest ecosystem.

1. Introduction

Due to atmospheric transport and deposition, mercury (Hg) contamination is widespread in remote ecosystems of the northeastern United States (Fitzgerald et al., 1998; Miller et al., 2005), although there are variations in watershed sensitivity (Bishop and Lee, 1997; Driscoll et al., 2007; Evers et al., 2007). The exchange of Hg between plants and the atmosphere is an important process of the biogeochemical cycle of Hg (e.g. Lindberg, 1996), particularly as canopy processes enhance atmospheric deposition to remote forest ecosystems (Grigal, 2003; Driscoll et al., 2007). At many sites, litterfall is an important pathway of Hg to the forest floor (e.g., Rea et al., 2002; Sheehan et al., 2006; St. Louis et al., 2001; Demers et al., 2007), ranging from 52 to 60% of the total inputs.

Field (Lindberg, 1996; Rea et al., 2002; St. Louis et al., 2001) and laboratory studies (e.g. Millhollen et al., 2006a,b; Ericksen et al., 2003; Frescholtz et al., 2003) have shown atmospheric Hg as the major source of the Hg in leaf tissue. Model estimates comparing transpiration uptake with atmospheric exchange (Lindberg et al., 1992; Rea et al., 2002) and field measurements of low levels of Hg in xylem sap (Bishop et al., 1998) suggest limited uptake of Hg by roots. Field results (Rea et al., 2002; St. Louis et al., 2001) and laboratory studies (Millhollen et al.,

2006b; Frescholtz et al., 2003) indicate that canopy accumulation is "new" Hg, rather than Hg recycled within the forest ecosystem. However, studies have demonstrated the importance of soil evasion (Grigal, 2002; Gustin et al., 2002) potentially contributing to within-canopy recycling of Hg between the forest floor and vegetation (Lindberg et al., 1992).

Laboratory investigations have shown Hg concentrations in foliage increase over the growing season for a variety of plant species (e.g. Millhollen et al., 2006b; Ericksen et al., 2003; Frescholtz et al., 2003). Corroboration of this phenomenon by field data, however, is limited (Lindberg, 1996; Rasmussen, 1995; Rea et al., 2002; Wyttenbach and Tobler, 1988), particularly with regard to inter-species variability, environmental factors influencing accumulation, and associated methyl Hg (MeHg) accumulation. Rea et al. (2002) reported a 10-fold increase in average leaf content from 3.5 ± 1.3 to 36.8 ± 8 ng g^{-1}, without significant species differences, among five hardwood species including *Fagus grandifolia* (American beech), *Betula papyrifera* Marsh. (white birch), and *Acer rubrum* L. (red maple) in Vermont and Michigan. Uptake rates for Hg during the growing season ranged from 8 to 34 ng m^{-2} day^{-1} without significant within-canopy variability. Lindberg (1996) measured higher leaf Hg concentrations, up to 105 ng g^{-1}, in leaf tissue of *Quercus rubra* L. (red oak) in Tennessee, although the site is likely influenced by nearby atmospheric Hg sources (coal-fired power plants, incinerators, contaminated soil; Lindberg et al., 1992). Conifer needles also have shown increased Hg content from 5 to 125 ng g^{-1}, with average uptake rates of $\sim$15 ng g^{-1} yr^{-1} (Rasmussen, 1995) and $\sim$40 ng g^{-1} over three growing seasons (Wyttenbach and Tobler, 1988). However, only Rea et al. (2002) and Wyttenbach and Tobler (1988) included a measure of uncertainty. The MeHg content of plant tissue is thought to be low (1–2% of THg; Grigal, 2003; Ericksen et al., 2003). Laboratory experiments, with the associated control of environmental conditions, have provided valuable insight on Hg–plant tissue interactions. However, it is difficult to extrapolate results of laboratory experiments to field conditions, necessitating corroboration with field data.

Hg exchange across the leaf tissue boundary has been shown to be dependent upon the relative concentrations within air and the leaf (e.g. Ericksen and Gustin, 2004; Hanson et al., 1995), and is thought to occur via Hg$^0_{(g)}$ exchange with the atmosphere (Du and Feng, 1982; Ericksen et al., 2003; Millhollen et al., 2006a). As such, uptake into plant tissue is complicated by environmental conditions that affect canopy processes, including temperature, humidity, CO$_{2(g)}$ concentration, and solar radiation (Millhollen et al., 2006a; Graydon et al., 2004; Lindberg et al., 1992). Controlled laboratory (Ericksen and Gustin, 2004) and field (Lindberg et al., 1998) measurements have documented both deposition to and evasion of Hg from leaves. Evasion, the reduction and volatilization of elemental mercury (Hg$^0_{(g)}$), has been demonstrated for soils (Grigal, 2002; Gustin et al., 2002) and may influence the leaf Hg content as a function of exposure to solar radiation (Graydon et al., 2004). Finally, wash-off of dry deposition, predominantly ionic mercury (Hg^{2+}), from leaf surfaces during precipitation events may affect leaf tissue Hg content (Rea et al., 2000).

In this field study, we investigated the accumulation of Hg species in foliage and assessed the potential impact of litter in Hg inputs to a northern forest ecosystem. Plant leaf samples were collected monthly during two growing seasons from an upland forest within the Adirondack region of New York. Additionally, leaf litter was collected during the autumn season (September–December) during both sampling years. Our specific objectives were to: (1) examine field Hg accumulation rates in the foliage of northern hardwood species; (2) assess the canopy Hg pool; and (3) determine litter inputs of total Hg and MeHg to the ecosystem.

2. Methods

2.1. Study site

Plant tissue samples were collected at the Huntington Wildlife Forest (HFNY; www.esf.edu/aec) of the central Adirondack Mountains of New York State, USA (43°59′N, 74°14′W), from a section of forest $\sim$200 m southeast of the Arbutus Lake complex (Fig. 1). The area of upland forest studied was previously investigated as part of the Integrated Forest Study (Johnson and Lindberg, 1992), an investigation of atmospheric deposition and forest nutrient cycling across a variety of forest ecosystems. The climate is cool, moist, and continental, with an average annual temperature of 4.4 °C and average annual precipitation of 1010 mm for the period 1951–1980 (Shepard et al., 1989). Site elevation was 530 m and characterized by coarse, loamy, mixed frigid Typic Haplorthods soils typically <1 m thick underlain by a thin layer of bouldery glacial till derived from local bedrock (Johnson and Lindberg, 1992). The HFNY is a northern hardwood forest with a stand age of $\sim$100 yrs and dominated by *A. saccharum* Marsh (sugar maple), *F. grandifolia* Ehrh (American beech), and *Betula alleghaniensis* (yellow birch) with some *A. rubrum* (red maple), *Prunus serotina* Ehrh. (black cherry), and *Picea rubens* Sarg. (red spruce).

2.2. Sample collection

Leaf tissue was collected from sugar maple, American beech, and yellow birch. Fresh leaf samples from individual trees interspersed within the forest plot area were collected approximately monthly from leaf-out through litterfall beginning in July 2004 through October 2005. Five individuals of sugar maple and American beech, and three yellow birch trees, were selected and marked for sampling, so as to ensure collection of overstory leaf tissue from the same individuals over the study. Fresh leaf samples were obtained by shooting down branches using a 12-gauge, single barreled, single-shot, break-open type shotgun with $2^3/_4$ ″ #4 steel shot shells carrying a $1^1/_2$ ounce load. Spent casings and shell waddings were collected after each sampling to minimize the potential for contamination within the forest stand. Branches were shot from as high in the canopy as possibly, generally a height of $\sim$10 m. A separate set of American beech samples was hand-collected within the understory for comparison of Hg content with canopy
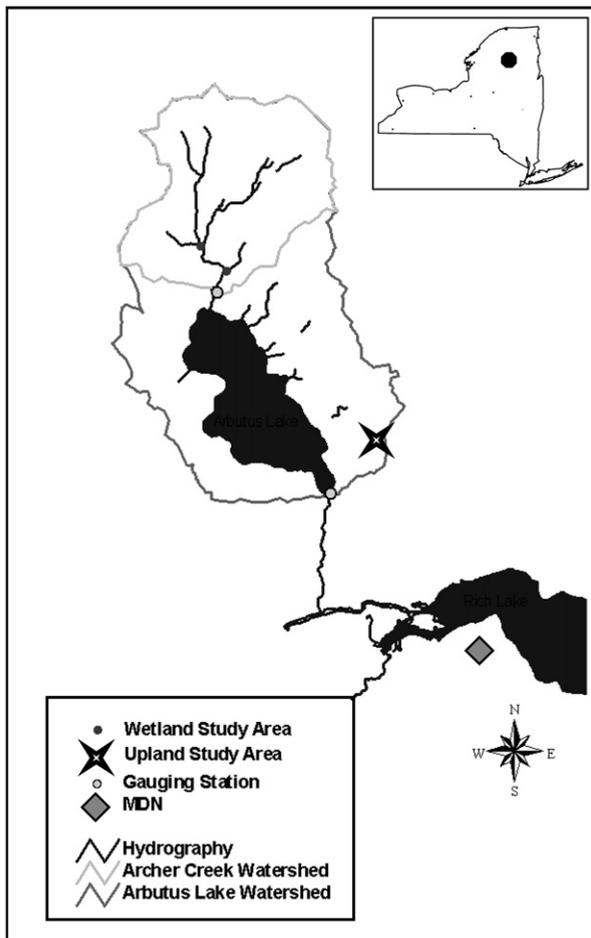
Fig. 1. A map of the intensive study area for Hg cycling at Huntington Wildlife Forest, NY (●). Plant leaf tissue and litter were collected at the upland study area within the Arbutus Lake watershed. The location of the Mercury Deposition Network site is shown for reference.

Litter was collected via two methods in the autumn to estimate the canopy Hg pool and to assess the total mass input of Hg to the upland forest ecosystem. The primary method of collection involved litter traps. Ten square collectors ($^1/_2$ m × $^1/_2$ m) made from treated lumber and wire mesh were placed strategically on the forest floor. While physically cleaned between sample collections, the litter traps were not acid-washed. Litterfall was collected monthly from the traps during the 2004 growing season with the final collection on November 24. As litterfall mass was dominated by the autumn period, the traps were collected only twice during 2005, October 22 and December 1. Litter trap samples were stored in brown paper bags to allow samples to dry and to prevent mold growth. Separate fresh leaf litter samples were also collected on October 19 (2004 and 2005) to assess the potential for changes in chemistry while in the litter traps prior to collection and to assess potential contamination resulting from the collection protocol. Fresh litterfall was sampled by deploying acid-cleaned (3% HCl, v/v) plastic tarps (∼9 m^2) during dry autumn days for several hours, collecting leaves falling naturally within the upland canopy. Fresh litter was collected as per clean-hands protocol (EPA, 1996), transported to the laboratory, and stored as per fresh leaf tissue.

2.3. Sample preparation

Leaf tissue samples were freeze-dried prior to analysis to obtain Hg content on a dry weight basis. All glassware used for freeze-drying was first soaked in 3% HCl (v/v) for 24 h, rinsed with deionized water, and air-dried prior to use. The polyethylene bags containing the leaves were placed inside the acid-cleaned flasks, stoppered, and freeze-dried (Labconco Corporation, Kansas City, MO) for 24 h at a vacuum pressure of 1.0 Pa and temperature of −87 °C. After lyophilization, the samples were hand-ground in the polyethylene bags and transferred to acid-cleaned (3% HCl) polypropylene containers for storage. Control polypropylene containers were found not to contain any detectable Hg, potentially contributing <0.4 ng g^{-1} to tissue samples. Thus, contamination of the leaf samples during storage was minimal.

Fresh leaf litter collected using tarps was treated as fresh leaf tissue, collected using clean techniques and stored at 4 °C in polyethylene bags. In the laboratory, the majority of the litter, that from traps, was covered with breathable material to prevent particulate deposition and allowed to air-dry. Once dried, leaves were segregated according to species, weighed, placed in polyethylene bags, and hand-ground. The ground leaves were stored in acid-cleaned (3% HCl, v/v) polypropylene containers until analysis. Litter trap samples for 2005 were freeze-dried after air-drying and separation to check the moisture content remaining in air-dried samples (8.2 ± 1.8% w/w) and the subsequent effect upon Hg (THg) analysis.

2.4. Hg analysis

All leaf tissue and litter samples were analyzed for THg using a DMA-80 Direct Mercury Analyzer (Milestone,

height. So as not to stress the relatively small understory trees, individuals sampled varied between collections. Foliage was collected from branches using powderless nitrile gloves, stored in double polyethylene bags, transported to the laboratory at 4 °C, and frozen until processed. Leaf samples were handled by the non-shooter to prevent potential contamination from shot handling using a fresh pair of gloves for each individual. Clean-hands, dirty-hands protocol were followed for all fresh leaf sample collection (EPA, 1996).

To investigate the effect of precipitation events on plant tissue Hg content, particularly due to dry deposition and wash-off of leaf surfaces, plant tissue samples were collected immediately before and following summer rainfall events. The first set of samples on June 28 and 30, 2005, were interceded by a moderate period of thunderstorms (total precipitation = 12.7 mm). In contrast, samples collected between September 8 and 10, 2005, bracketed a relatively minor event (total precipitation = 1.52 mm). Both samplings followed periods of at least three days without precipitation.

Microwave Laboratory Systems, Shelton, CT) utilizing thermal decomposition, catalytic reduction, amalgamation, desorption, and atomic absorption spectroscopy. Leaf and litter samples ($\sim$30 mg) were dried at 300 °C for 60 s and oxidized at 900 °C for 210 s, with liberated $Hg^0_{(g)}$ collected on a gold-trap amalgamator. The amalgamator was subsequently heated at 900 °C for 12 s to release the $Hg^0_{(g)}$ in a concentrated peak to the spectrophotometer, where absorbance (peak height or peak area) at 253.65 nm was measured as a function of THg mass. Apple leaf (NIST-SRM 1515; National Institute of Standards, Gaithersburg, MD, 44.0 ng g^{-1} THg) certified Hg standard reference material (SRM) was used as the standard for calibration and quality control checks every 10 analyses (average recovery $= 93.1\%$; $s = 7.3\%$; $n = 156$). Hg analyses were performed in duplicate for all samples with blanks analyzed between samples to clean the system and check for carryover.

For MeHg analysis, approximately 20 mg of plant tissue sample was added to 3 mL of 25% KOH in methanol (w/w) in Teflon vials and digested for 24 h. A temperature of 55 °C was selected to maximize recovery by preventing decomposition during digestion (Hintelmann and Nguyen, 2005). Following digestion, 300 mL of the digest was diluted in 50 mL of Milli-Q water, buffered with 850 mL of 3 M acetate buffer, reacted with 300 mL of Sodium tetraethylborate solution (1% NaBEt$_4$ in 2% KOH; w/w) for 17 min, and purged with nitrogen gas (100–125 mL min^{-1}) for 17 min. The volatile Hg species were adsorbed from the gas onto a 10 cm trap consisting of 0.15 g of 60/80 mesh Tenax-TA adsorbent (Supelco, Bellefonte, PA) packed within Pyrex tubing (6.5 mm OD × 4 mm ID). The trap was dried for 7 min before auto-desorption (350 ATD; Perkin-Elmer, Waltham, MA), Hg species separation via gas chromatography (Clarus 500, Perkin-Elmer), pyrolytic reduction to $Hg^0_{(g)}$, and detection via CVAFS (Tekran 2500; Tekran Instruments Corporation, Toronto, ON). The method detection limit calculated from a series of spiked blanks was 0.64 ng g^{-1} with spike recovery during MeHg analysis of 100–129% with a MeHg analytical detection limit of 0.0014 ng. Certified recoveries were 100–118% for muscle tissue (SRM-2976, National Institute of Standards, Gaithersburg, MD, 0.0278 ng g^{-1}) and 85–115% for lobster hepatopancreatic tissue (NRC-TORT, National Research Council, Ottawa, CAN; 0.152 ng g^{-1}).

2.5. Statistical analysis

Monthly leaf THg content was calculated as the average of the value for the five individual trees sampled for each species (three for yellow birch). Trends in foliar Hg were assessed for each individual tree relative to the average for a species over the growing season to assess variability within a species. The accumulation rate for each species over the growing season was obtained via linear regression. Inter-species differences in THg accumulation were assessed by comparison of the slopes obtained by linear regression during both growing seasons. We had insufficient data for a thorough evaluation of inter-annual variability in THg accumulation as samples were collected for only three dates in 2004. Statistical analyses were performed using JMP™ (SAS Institute Inc., Cary, North Carolina).

Average litter Hg concentration for each species was estimated for each time period sampled. Using the litter mass collected within the litter traps, the Hg influx was estimated for each species, normalized by the litter trap cross-sectional area (2.5 m^2). The annual litter flux was compared with an estimate of the THg canopy pool calculated using the leaf tissue THg data and canopy biomass estimates from the Integrated Forest Study (Johnson and Lindberg, 1992).

3. Results and discussion

3.1. Plant tissue

The THg content of leaf tissue increased over the 2004 and 2005 growing seasons for all three species. Between leaf-out (May 31) and senescence (October 2) in 2005, average THg concentrations ($\pm$standard deviation) increased from 4.4 ± 3.3 to 29.1 ± 4.6 ng g^{-1} for birch (Fig. 2a), 3.2 ± 0.4 to 32.3 ± 9.4 ng g^{-1} for maple (Fig. 2b), and 5.6 ± 3.6 to 47.3 ± 12.4 ng g^{-1} for beech (Fig. 2c). Conversely, the MeHg content (0.17 ± 0.18 ng g^{-1}) did not increase, remaining below the method detection limit (0.64 ng g^{-1}) over the growing season regardless of species and canopy position (data not shown). Trends for THg leaf content of individual trees within each species group did not significantly differ ($a = 0.05$) from mean values, except of one sugar maple that was in a small clearing. Analysis without this individual maple tree did not affect the significance of the inter-species relationships. Elevated solar radiation within the clearing (see Section 3.2) may have contributed to the lower concentrations observed for this sugar maple as solar radiation has been demonstrated to increase Hg flux from leaf tissue (Graydon et al., 2004). Leaf tissue THg accumulation rates obtained from linear regression of the 2005 data (Table 1) were 0.22 ± 0.02, 0.23 ± 0.02, and 0.35 ± 0.03 ng g^{-1} day^{-1} for birch, maple, and beech, respectively, with values increasing approximately 10-fold over the growing season. The less complete data for 2004 also demonstrate seasonal increases (Fig. 2) in concentrations and accumulation rates for each species similar ($a = 0.05$) to 2005 data. These data suggest that Hg accumulation within plant tissue did not vary significantly between sample years, neither of which varied significantly from typical site climatic conditions. Note, our data are not sufficient for a thorough inter-annual comparison.

Although sufficient data do not exist to conclusively assess the effect of precipitation events on leaf Hg content, samples collected before and following summer rainfall events demonstrate the potential variability associated with wash-off effects (Figs 2 and 3). Generally, concentrations across all plant species decreased following a moderate period of thunderstorms (June 28 and 30, 2005; total precipitation $= 12.7$ mm) but increased following a relatively minor event (September 8–10, 2005; total precipitation $= 1.52$ mm). Such variability in response between events demonstrates the potential impact of rainfall intensity and climatic conditions on leaf Hg exchange during events.
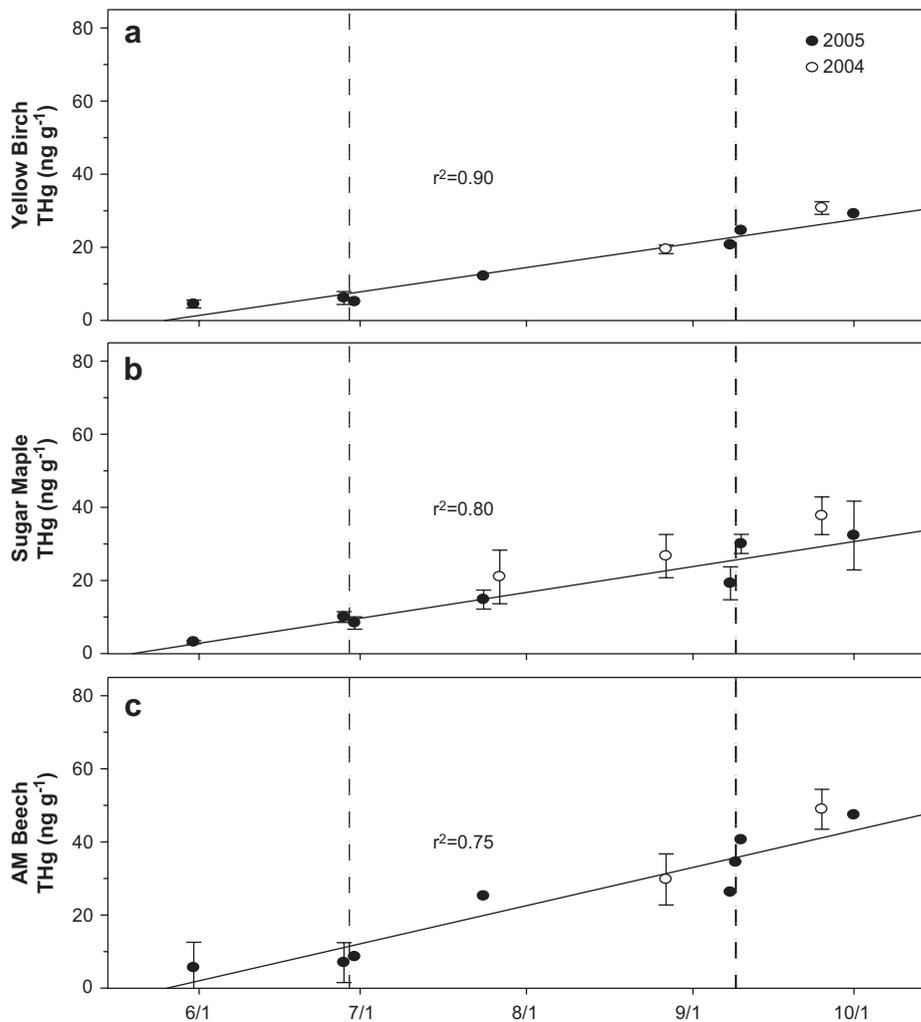
Fig. 2. THg concentration (±standard deviation) trends for yellow birch (a), sugar maple (b), and American beech (c) over the 2004 and 2005 growing seasons. Concentration data are averages of five individual trees (three for birch). Trend lines represent regression for 2005 data (r^2 represents fit). Accumulation rate estimated via regression is in Table 1. The regression is not shown for 2004 due to limited data. Vertical lines represent event sample collection pre- and post-rainfall.

Foliage Hg concentrations were consistent with previous field studies for hardwood species in Vermont, Michigan, and Tennessee (Lindberg, 1996; Rea et al., 2002). Rea et al. (2002) reported an average increase from 3.5 ± 1.3

Table 1

Leaf tissue Hg accumulation rates for the 2005 growing season (±standard deviation)

	Yellow birch	Sugar maple	American beech
Accumulation rate (ng g^{-1} day^{-1})	0.22 (0.02)	0.23 (0.02)	0.35 (0.03)/ 0.47 (0.03)
Leaf mass per area (g m^{-2})	66.3	62.6	61.1
Stomatal conductance (mm s^{-1})	5.7	2.6	4.4

The two values for American beech represent the overstory and understory accumulation rates, respectively. Also shown are species physiological parameters that may affect Hg accumulation. Leaf mass per area measured using optical techniques (Smith and Martin, 2001). Stomatal conductance reflects yearly-averaged data from overstory (15–20 m) canopy measurements for water (Hong et al., 2006).

to 36.8 ± 8 ng g^{-1}, including American beech, white birch, and sugar maple. Lindberg (1996) measured higher concentrations in red oak leaves, potentially influenced by nearby atmospheric Hg sources. Both of these studies demonstrated, under field conditions, a steady increase in Hg leaf tissue content of hardwoods over the growing season. However, unlike field studies (Rea et al., 2002), yet consistent with laboratory growth chamber studies (e.g. Millhollen et al., 2006a; Ericksen et al., 2003), we observed significant differences in Hg accumulation rates among plant species (Table 1). Our ability to differentiate foliar Hg concentrations among species may have been due to the sampling of individual trees. Accumulation rate and tissue concentrations increased from yellow birch to sugar maple to American beech. Significantly higher values were determined for American beech ($a = 0.05$). Plant tissue values have not been adjusted to a per area basis to reflect potential surface-accumulation processes. Differences in leaf mass per area (LMA; Table 1, Smith and Martin, 2001) do not appear to affect the relative differences in the THg
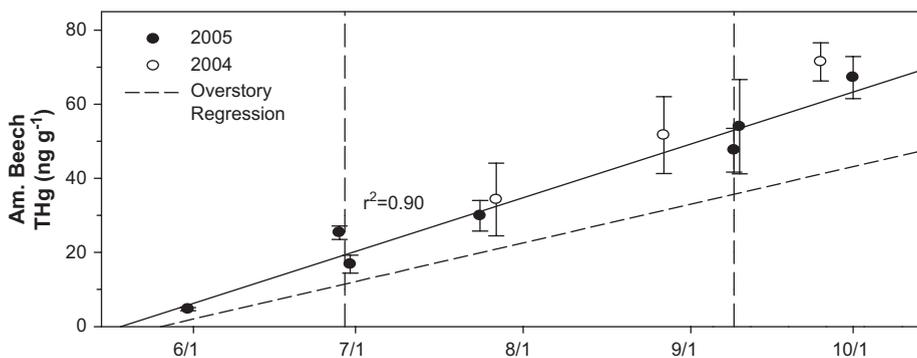
Fig. 3. THg concentration (±standard deviation) trends for understory American beech over the 2004 and 2005 growing seasons. Concentration data are averages of five individual trees. Solid trend line represents regression for 2005 understory data (r^2 represents fit). Dashed trend line represents regression for 2005 overstory American beech from Fig. 2c. Accumulation rate estimated via regression is in Table 1. The regression is not shown for 2004 due to limited data. Vertical lines represent event sample collection pre- and post-rainfall.

content expressed on an area basis. However, LMA differences are site specific and variable (Meyer et al., 2006). Differences among species suggest that forest composition may influence inputs to the forest floor, as well as subsequent accumulation and losses, within northern hardwood forests. Changes in species composition may occur in response to elevation, soil, aspect and disturbance, including acidic deposition (Bormann and Likens, 1979; Lovett and Mitchell, 2004). Our results suggest that a shift towards higher biomass of beech would increase Hg accumulation while an increase in sugar maple contributions would decrease Hg inputs.

The reason for elevated Hg content in American beech foliage relative to values observed in sugar maple or yellow birch is unclear. The stomatal conductance of American beech foliage (4.4 mm s^{-1}) is intermediate to that of yellow birch (5.7 mm s^{-1}) and sugar maple (2.6 mm s^{-1}; Hong et al., 2006), so it is unlikely that the higher Hg concentrations are due to greater Hg^0 exchange with the leaves. Alternatively, the higher Hg concentrations could be due to greater surface roughness of beech leaves associated with foliar pubescence (Hardin and Johnson, 1985) or greater shading of beech leaves compared to yellow birch or sugar maple. Increased shading may decrease the reduction and loss of Hg^0 from the leaf surface. Note that the elevated concentrations of Hg in American beech understory compared to values in the overstory foliage may also reflect the attenuation of light and decreases in photoreduction and Hg$^0_{(g)}$ emissions from leaves (Fig. 3). As discussed in Section 3.2, diminishing radiation with decreasing canopy height could lead to increasing Hg content. However, understory vegetation is characterized by thinner leaves with decreased LMA (Meyer et al., 2006), potentially reflecting a physiological effect upon surface processes.

3.2. Position within canopy

Significant differences ($a = 0.05$) existed between beech overstory (~10 m) and understory (~1 m) samples. Although understory foliage is a minor contribution of total litterfall (Johnson and Lindberg, 1992; Lindberg et al., 1992), such comparisons may be important in elucidating uptake

mechanism(s) and the potential for species differences. Leaf tissue within the understory (Fig. 3) contained significantly higher THg ($a = 0.05$), with concentrations averaging 68% greater than that in overstory foliage regardless of similar initial leaf-out concentrations (Figs 2c and 3). The THg accumulation rate of understory beech foliage (0.47 ± 0.03 ng g^{-1} day^{-1}) was significantly ($a = 0.05$) higher than overstory foliage (Table 1). Such differences possibly could result from variations in leaf Hg^0 evasive flux within the canopy (Graydon et al., 2004), a within-canopy Hg^0 air concentration gradient (Lindberg et al., 1992), the proximity of understory foliage to soil emissions of Hg^0, or physiological differences (see Section 3.1).

Light, more specifically UV radiation, is a critical controller of soil Hg^0 evasion (Grigal, 2002), which in turn is supplied to the forest canopy. While such "recycling" has not been assessed herein, a similar effect of solar radiation has been documented for foliar exchange. This phenomenon has been attributed to decreases in stomatal resistance (Ericksen and Gustin, 2004), with the flux increase likely due to transpiration, a mechanism supported by Graydon et al. (2004) using isotopic Hg^{2+} spikes. However, these studies have not directly assessed re-emission of Hg$^0_{(g)}$ from leaf tissue, a process shown to affect emissions from solid surfaces (Johnson and Lindberg, 1995). Secondly, the presence of a concentration gradient within the canopy decreasing upward from the forest floor could potentially increase uptake within the understory. A gradient of 0.3 ng m^{-3} as reported by Lindberg et al. (1992), using a deposition velocity of 0.1 cm s^{-1}, full leaf canopy of 350 g m^{-2}, and growing period of 135 days, results in an estimated difference in Hg$^0_{(g)}$ deposition to leaf surfaces of 15 ng g^{-1} between 20 and 43 m, similar to the difference we observed. Conversely, a third consideration, wash-off from leaf surfaces, is likely not the source of the differences in accumulation with canopy height. Particulate-deposited Hg does not appear to affect overall accumulation rate (see Section 3.1) and particulates readily wash-off leaf surfaces (Rea et al., 2000). In general, knowledge of Hg–plant–atmosphere interactions would benefit from additional research as within-canopy processes and their effects upon Hg deposition and cycling are not well understood.

3.3. Litter

THg concentrations in leaf litter varied with the time of sample collection (Table 2). Samples collected from the litter traps on November 24, 2004 contained 48.2 and 92.4 ng g^{-1} Hg for maple and beech, respectively, an increase relative to values collected on October 29 with 35.8, 35.8, and 58.3 ng g^{-1} for birch, maple, and beech, respectively. In 2005, leaf litter Hg content was 41.1 and 51.9 ng g^{-1} for maple and beech on October 22, while concentrations increased to 45.5, 50.9, and 69.3 ng g^{-1} for birch, maple, and beech, respectively, by December 1 (Table 2). Although not significantly different, fresh litter concentrations collected on October 19 of both years using acid-cleaned tarps were higher than those collected from the litter traps, suggesting a slight under-estimation of litter THg flux. The THg content fresh litter for maple and beech measured 46.9 ± 5.6 and 61.6 ± 5.9 ng g^{-1}, respectively, for 2004 and 51.8 ± 1.0 and 57.9 ± 0.2 ng g^{-1} for 2005. Note that the differences between litter Hg concentrations in maple and beech are consistent with the differences we observed for these species in foliage. These litter THg values are generally in agreement with those previously reported for upland hardwood forests, including Vermont (36 ± 8 ng g^{-1}, Rea et al., 2002) and Maine (31.6 ± 2.6 ng g^{-1}, Sheehan et al., 2006), as well as an upland conifer forest in Ontario, Canada (42 ± 19 ng g^{-1}, St. Louis et al., 2001). Similar to leaf tissue, the MeHg content of litter was low (0.3–0.6 ng g^{-1}), consistent with previous studies (Grigal, 2003) and with the MeHg content within the site soil collected within soil pits (0.1–1.4 ng g^{-1}).

Litter concentrations were comparable for 2004 and 2005 with litter content significantly higher ($a = 0.05$) relative to final leaf tissue content. The continued Hg increase through leaf senescence (Table 2) could reflect a continued accumulation from the air or mass-loss decrease due to senescence processes, increasing THg content. In general, litter values reflect THg concentrations in canopy leaves at the time of collection ($a = 0.05$), including measured and regressed data (e.g. July leaf ~ July litter; Fig. 4). However, actual measured leaf tissue THg content was higher than the corresponding litter THg for July–September 2004 (Fig. 4), potentially reflecting the continued accumulation of THg within plant leaf tissue over the period between litter accumulation within the traps and leaf tissue collection. Conversely, autumn leaf tissue THg content predicted for the corresponding litter collection dates using the leaf tissue regression (Fig. 4) was less than that measured in litter, suggesting that senescence processes may affect Hg leaf tissue content as intimated previously (Rea et al., 2002). However, the increase in THg litter content relative to that predicted from leaf tissue regression also could reflect the effect of canopy coverage on throughfall contributions to litter trap samples, inter-annual variability as data for direct comparison reflected only 2004 samples, or the accumulation of THg in litter post-litterfall within the litter traps (Demers et al., 2007).

The majority of the litter mass was collected during September through November, with the majority of litterfall occurring in October. Litter THg flux for the remainder of the year was negligible (<0.8%). Litter mass was dominated by beech and sugar maple with a minor contribution from birch (Table 2). The total litter mass of 387 g m^{-2} yr^{-1} for 2004 and 329 g m^{-2} yr^{-1} for 2005 are in agreement with the total canopy estimate of 365 g m^{-2} for August determined for the Integrated Forest Study (Johnson and Lindberg, 1992). Multiplying the litter mass by the corresponding litter Hg content during the collection period, THg flux estimations due to litterfall of 17.9 and 16.4 mg m^{-2} yr^{-1} for 2004 and 2005, respectively, were obtained with approximately equal contributions from maple and beech (Table 2). Both values are similar to previous estimates of litterfall THg mass flux within upland forests in North America of 10–16 mg m^{-2} yr^{-1} (Rea et al., 2002; St. Louis et al., 2001; Sheehan et al., 2006; Demers

Table 2
Litter trap total Hg content ($\pm$standard deviation; $n \geq 4$) and flux for 2004 and 2005 growing seasons

			Yellow birch	Sugar maple	American beech	Total
2004	October 29	THg (ng g^{-1})	35.8 (1.9)	36.4 (1.5)	58.3 (3.2)	NA
		Litter Mass (g m^{-2})	6.7	213	108	327
		Litter THg Flux (μg m^{-2})	0.24	7.76	6.27	14.3
	November 24	THg (ng g^{-1})	NA	48.2 (1.0)	92.4 (13.8)	NA
		Litter Mass (g m^{-2})	NA	1.9	32	34
		Litter THg Flux (μg m^{-2})	NA	0.91	2.93	3.0
	Total[a]	Litter Mass (g m^{-2})	7.2	232	148	387
		Litter THg Flux (μg m^{-2} yr^{-1})	0.3	8.21	9.44	17.9
2005	October 22	THg (ng g^{-1})	NA	41.1 (1.1)	51.9 (5.5)	NA
		Litter Mass (g m^{-2})	NA	177	71	248
		Litter THg Flux (μg m^{-2})	NA	7.28	3.68	11.0
	December 2	THg (ng g^{-1})	45.5 (NA)	50.9 (NA)	69.3 (6.8)	NA
		Litter Mass (g m^{-2})	0.3	8.8	72	81
		Litter THg Flux (μg m^{-2})	0.02	0.45	4.99	5.5
	Total	Litter Mass (g m^{-2})	0.3	186	143	329
		Litter THg Flux (μg m^{-2} yr^{-1})	0.02	7.73	8.67	16.4

Litter mass input estimated from air-dried (2004) or freeze-dried (2005) sample mass collected from 10 traps (2.5 m^2). Flux equals concentration times mass. Na – not applicable.
[a] Total values for 2004 reflect minor contributions from July through September litter trap samples.
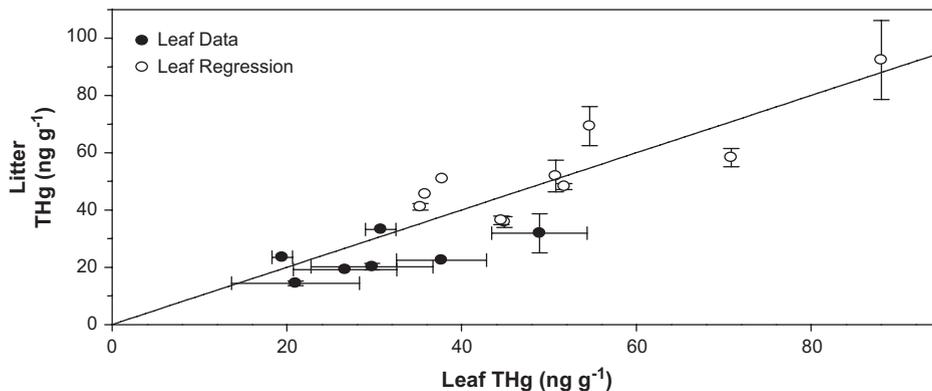
Fig. 4. THg concentrations (±standard deviation) in litter and leaf tissue for the 2004 and 2005 growing seasons. Leaf tissue represents measured data (●), collected during the summer of 2004, or values estimated from the regression (○) of actual leaf tissue concentration data (Fig. 2) to the autumn litter collection dates. Solid line represents equivalent tissue Hg content (1:1).

et al., 2007) and within the range of total deposition of 3–30 mg m^{-2} yr^{-1} estimated by Miller et al. (2005), but less than that of 31 mg m^{-2} yr^{-1} estimated for a forested catchment in Germany (Grigal, 2003). As with these previous investigations, litterfall was the largest influx of THg within the upland hardwood ecosystem, and was greater than the average annual wet THg deposition of 5.8 mg m^{-2} yr^{-1} (MDN, 2007) and throughfall Hg (Choi et al., 2007). Although MeHg content was less than the method detection limit, a maximum MeHg litter flux of 0.12 mg m^{-2} yr^{-1} was estimated for 2005 from the litter concentration data, consistent with previous estimates (St. Louis et al., 2001; Bishop et al., 1998).

3.4. Source of Hg to leaf tissue

Due to the significance of litterfall within the upland forest THg mass balance, it is important to characterize whether leaf tissue represents a "new" or "recycled" source (St. Louis et al., 2001). Previous estimates have shown that transpiration contributions to leaf tissue Hg are minor (Bishop et al., 1998; Rea et al., 2002), with deposition sufficient to account for the accumulation within leaf tissue during the growing season (Rea et al., 2002). Potential transpiration and deposition were estimated as per Rea et al. (2002) to assess the potential for the recycling of soil Hg. Transpiration was estimated for the 2005 growing season using BROOK90, an upland hydrologic model (Federer et al., 2003), with soil water THg measured in upland lysimeters at HFNY and soil parameters previously determined by Mitchell et al. (2001). Teflon zero-tension lysimeters were installed beneath the Oa ($n = 3$), Bh ($n = 4$), and Bs$_2$ ($n = 2$) horizons in June 2004 and sampled monthly between September 2004 and January 2006. Average THg soil water concentrations during the 2005 growing season (May–October) for the site were 10.2 ± 7.2, 3.4 ± 2.7, and 1.4 ± 0.1 ng L^{-1} for the Oa, Bh, and Bs$_2$ layers, respectively. Assuming 100% uptake at the roots (an unlikely scenario; Bishop et al., 1998), the THg transpiration flux of 2 mg m^{-2} yr^{-1} would account for only 12% of the leaf tissue Hg, a percentage (<14%) consistent with previous estimates (Bishop et al., 1998; Rea et al., 2002). Potential deposition to

the leaf surface was estimated as per Lindberg et al. (1992) assuming a unidirectional flux. Deposition velocity was estimated as a function of temperature and time of day from relationships determined by Lindberg et al. (1992) for a hardwood forest in eastern Tennessee. Total deposition was determined by multiplying the average deposition velocity by the average air Hg^0$_{(g)}$ content of 1.4 ± 0.3 ng m^{-3} measured at HFNY from 2005 through 2007 (Choi, 2007). Results indicate that the estimated atmospheric deposition flux of 6.4 mg m^{-2} yr^{-1} would account for 38% of Hg accumulation in leaf tissue. While these results suggest that the majority of leaf Hg represents a "new" input within the upland ecosystem, additional surface accumulation processes may be important. The uptake of soil-evaded Hg "recycling" within canopy leaf tissue has not been examined, but may be an important pathway suggested by elevated uptake within understory vegetation.

4. Conclusions

We conducted a field research study at HFNY to investigate the role of the forest canopy in the transport and deposition of Hg species. Average THg content increased approximately 10-fold over the growing season from 4.4 ± 2.7 to 37.3 ± 12.4 ng g^{-1} across three plant species with estimated average linear Hg accumulation rates of 0.22, 0.23, and 0.35 ng g^{-1} day^{-1} for yellow birch (*B. alleghaniensis*), sugar maple (*A. saccharum*), and American beech (*F. grandifolia*), respectively. In contrast, the MeHg content and accumulation were not large. American beech demonstrated the highest THg accumulation, particularly within the understory vegetation, followed by sugar maple and yellow birch. The variation of THg accumulation by plant species suggests that plant species physiology may affect the accumulation, and subsequent input of Hg to the forest ecosystem. Variations in plant species distribution within a forest potentially could alter the deposition, accumulation and subsequent transport of Hg in the ecosystem.

While, event sampling demonstrated the effects of precipitation intensity on leaf Hg content, surficial

deposition and wash-off likely were not important processes. The linear concentration relationships for foliar THg over time suggest that the accumulation is regulated by mass transfer processes between the atmosphere and leaves. Variation in environmental conditions within the canopy, or a $Hg^0_{(g)}$ concentration gradient developed from soil evasion, also may have been responsible for spatial patterns in the foliar Hg content within the canopy.

Annual litterfall deposition fluxes of THg within forest were similar for the two years of study, with estimates of 14.9 and 16.4 mg m^{-2} for 2004 and 2005, respectively. Litterfall represented the largest ecosystem input of THg, significantly higher than that measured in wet deposition at the nearby MDN site and throughfall. Hydrologic modeling estimated a minor potential contribution of transpiration to leaf tissue Hg content. Conversely, $Hg^0_{(g)}$ deposition estimates suggest atmospheric sources of the Hg accumulated within leaf tissue. Thus, litter Hg represents largely a new, rather than recycled, input to the forest ecosystem.

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