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Accumulation of atmospheric mercury in forest foliage

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Abstract

We used unique mesocosms to examine the role that plants play in accumulating and transforming atmospheric Hg. Several stands of quaking aspen were grown in large gas-exchange chambers in Hg-enriched soil ($12.3 \pm 1.3\,\mu g\,g^{-1}$), and the Hg content in the vegetation was determined over time. Foliar Hg concentrations increased as a function of leaf age and leveled off after 2–3 months in the oldest tissue with a mean tissue concentration of $150\,ng\,g^{-1}$. Approximately 80% of the total Hg accumulated in the aboveground biomass was found in the leaves, and roughly 1% of that Hg was methylated. Leaves of additional aspen grown within the mesocosms in containers of low Hg soil ($0.03 \pm 0.01\,\mu g\,g^{-1}$) exhibited foliar Hg concentrations similar to those of trees grown in the Hg-enriched soil. Leaf rinses and surrogate Teflon surfaces were analyzed to characterize surface deposition processes. Small gas-exchange systems were used to measure stomatal uptake of Hg vapor, and the mean Hg flux was $-3.3\,ng\,m^{-2}\,h^{-1}$. These experiments showed that almost all of the Hg in foliar tissue originated from the atmosphere. Thus, in the fall when deciduous trees enter dormancy and leaves senesce, litterfall would represent a new Hg input to terrestrial ecosystems.
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1. Introduction

Mercury (Hg) is emitted from anthropogenic and natural sources to the atmosphere, principally in the gaseous form, and can be transported to remote and pristine locations. Elemental Hg (Hg^0), the dominant form of Hg in the atmosphere (>95%), has a long atmospheric residence time and is considered a global pollutant (Schroeder and Munthe, 1998). Current research has identified previously undetected sources of atmospheric Hg (Lindberg and Price, 1999; Carpi and Lindberg, 1998; Friedli et al., 2001) and demonstrated that known sources of Hg are greater than realized (Engle et al., 2001; Gustin et al., 2000; Pirroni et al., 2001). With the addition of new and greater sources of atmospheric Hg, researchers have begun to investigate unrecognized sinks (Lindberg et al., 2002).

Little has been published in open literature on the fate of mercury in the soil–plant–air continuum (e.g. Hanson et al., 1995; Lindberg, 1996; Leonard et al., 1998; Lindberg et al., 1998), and understanding the relative importance of forested systems within regional or global cycles is critical to developing a global Hg budget (Leonard et al., 1998). For instance, the magnitude of the global Hg pool presently residing in plant biomass has not been estimated. Although litterfall has been demonstrated to be an important source of Hg to the forest floor (Lindberg, 1996; Iverfeldt, 1991; Rea et al., 1996, 2002; St. Louis et al., 2001), where it can leach or erode into aquatic systems, the ultimate source of inorganic or organic Hg in litterfall has not been determined. A central question in the global cycling of

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Hg is whether the large amount of Hg and methylmercury (MeHg) stored in forest vegetation originates from the soil or from the atmosphere. In other words, do plants simply recycle Hg by uptake via soil and then return it by way of litterfall, or do leaves directly capture atmospheric Hg and deliver it to the soil as a new source?

Small-scale experiments indicate that plants can act as both a source and sink of atmospheric Hg (Hanson et al., 1995; Lindberg, 1996; Leonard et al., 1998; Lindberg et al., 1998; Iverfeldt, 1991; Hultberg et al., 1994; Munthe et al., 1995; Lee et al., 1998; Fleck et al., 1999; Schwesig and Matzner, 2000), as well as transport some Hg from soil to foliage (Bishop et al., 1998); however, the relative importance of these roles within forested systems is not well known. Several researchers have suggested that the largest "airborne" flux of Hg to forested systems occurs in the transfer of Hg to the forest floors in litterfall (Lindberg, 1996; Iverfeldt, 1991; Rea et al., 1996).

In order to characterize the mobility of Hg across air-soil-plant interfaces, several aspen stands were grown in controlled mesocosm-scale gas-exchange systems, allowing for a full canopy of leaves to develop. The objectives of this study were to assess uptake of Hg in plants via root and atmospheric pathways and characterize foliar Hg fluxes using large mesocosm chambers with high resolution.

This project was part of a larger study to assess the biogeochemical role of plants and soils in controlling the fate of Hg in the environment at the ecosystem level. The effect of vegetation on air/soil exchange and atmospheric soil Hg processes is described elsewhere (Gustin et al., 2003; Johnson et al., 2003). Ancillary experiments, performed in smaller scale chambers with aspen, further characterized the exchange of Hg between vegetation and the atmosphere (Frescholtz et al., 2003; Benesch, 2002). Here we describe the relative importance of plants as receptors for Hg in a contaminated system and demonstrate that foliage can be a major sink for airborne Hg, which then enters the soil ecosystem after litterfall.

2. Materials and methods

2.1. Location and description of site

Two Ecologically Controlled Enclosed Lysimeter Laboratories or EcoCELLs (Griffin et al., 1996), located at Desert Research Institute (Reno, NV), were used to investigate the role of plants in the biogeochemical cycle of Hg. The dimensions of each EcoCELL were $7.3 \times 5.5 \times 4.5\,m$ ($l \times w \times d$) with a total volume of $183.5\,m^3$. Each cell contained three lysimeter/rhizotron weighing containers $2.88 \times 1.37 \times 1.8\,m$ ($l \times w \times d$) with a total volume $20.1\,m^3$ and a soil surface of $11.8\,m^2$. Daily watering was done to maintain a moisture content of approximately 15% for 5–20 cm depth and 20% for 30–50 cm depth. Soil moisture was verified using Time Domain Reflectometry (TDR) probes (model 6005L2) and a Tektronix 1502C cable tester. Air temperatures were maintained at 18°C at night and 26°C during daylight hours. Relative humidity and CO_2 and H_2O flux (Li-COR model LI-6262), infrared (Everest Interscience series 3000.4) and *PAR* photon flux (LI-190SA), and soil temperature (type T thermocouples) at different depths (1, 5, 10, and 40 cm) were monitored continuously using Campbell Scientific dataloggers model CR10T. The ambient CO_2 range was 380–480 ppmv.

Each CELL contained three soil containers filled with approximately 5 tonnes of gravel covered with a liner and overlain by approximately 4.5 tonnes of sandy loam topsoil (60 cm depth). The soil had $1.2 \pm 0.1\%$ organic matter with $200 \pm 70\,\mu g\,g^{-1}$ Cl, $100 \pm 20\,\mu g\,g^{-1}$ SO_4–S (A&L Labs, Modesto CA), and a bulk density of $1.37 \pm 0.07\,g\,cm^{-3}$. Prior to addition, the soil was uniformly amended with mine tailings (Carson River Superfund Site, NV) to enrich the soil in Hg to $12.3 \pm 1.3\,\mu g\,g^{-1}$. Soils were analyzed for total Hg with a Varian Spectra™ AA 220 after aqua regia digestion using cold vapor atomic absorption spectrophotometry (CVAAS). Certified reference soil (San Joaquin, NIST ♯2709) was analyzed for quality assurance, and error was $<10\%$.

As a result of Hg evasion from the soils in the EcoCELLs, air Hg concentrations were elevated above typical ambient concentrations of $1–3\,ng\,m^{-3}$. Atmospheric Hg concentrations were monitored using a Tekran™ 2537A Mercury analyzer with a solenoid switching unit, which measured Hg vapor concentrations in incoming air and within each CELL for consecutive ten minutes every hour. A known volume of air was pulled through the Tekran and gaseous Hg was collected on gold-coated quartz traps from which Hg was thermally desorbed and analyzed by cold vapor atomic fluorescence spectrophotometry (CVAFS) (Dumarey et al., 1985; Bloom and Fitzgerald, 1988). A daily diel pattern of Hg emissions from soils in response to increase in irradiance and temperature was observed with maximum air Hg concentrations at midday and minimum concentrations at 2 AM.

Approximately 100 one-year-old, bare rooted, dormant whips of *Populus tremuloides* (Rail City Nursery, NV), commonly known as quaking aspen, were grown in each CELL to create a full canopy. Aspen were 15 ± 5 cm in height and spaced 30–35 cm apart. Prior to planting, aspen were dipped in Captan™ solution (N-trichloromethyl mercapto-4-cyclohexane-1,2-dicarboximide, Lilly Miller, $<0.1\,ng\,l^{-1}$ Hg) to protect plants from fungus and improve root quality. Two EcoCELLs were used in a two-year study (2000–2001). In 2000

(07/05/00 to 12/7/00) aspen were grown in both CELL 1 and CELL 2; and in 2001 (04/25/01 to 09/26/01) trees were grown only in CELL 2 (a temporal replicate). The total leaf area was estimated weekly by hand measuring total leaf area of six randomly selected aspen from each CELL and using these to estimate the total leaf area. The leaf area index (LAI) was determined weekly by dividing the leaf area in the cell by the soil surface area. The photosynthetic and conductance rates of new, intermediate, and old leaves were measured using a small leaf cuvette (LI-6400).

2.2. Hg concentrations in leaves as a function of time

During the experiment, subsets of aspen leaves were tagged and divided into new (<21 d), intermediate (22–35 d), and old (>35 d) categories in order to estimate the age of all leaves each week. Several leaves of each category were randomly sampled from 9 aspen (3 per container) at 0.5, 1, 2, 3, and 4 months after planting. The petioles were removed and leaves were rinsed twice with 100 ml of ultra pure deionized water. The analyses of total Hg in rinses were performed within 2 d of sample collection. Following BrCl oxidation and $SnCl_2$ reduction, Hg^0 was purged onto gold-coated silica sand traps and analyzed using dual amalgamation and CVAFS (Bloom and Fitzgerald, 1988; Fitzgerald and Gill, 1979). The detection limit for total Hg in solution was $0.3\,ng\,l^{-1}$.

Leaf material was frozen with liquid nitrogen, homogenized by mortar and pestle, and freeze-dried for 48 h using a Virtis Benchtop 3L (Sentry™). Total Hg in plant samples was determined by thermal decomposition, amalgamation, and atomic absorption spectrometry using a Milestone™ Mercury analyzer (EPA method 7473). National Institute of Standards and Technology (NIST) reference materials (San Joaquin soil #2709, Peach #1547, and Apple leaves #1515) were used for quality assurance, and error was <5%. In order to verify that no Hg loss occurred during lyophilization, reference material ($n = 10$) was freeze-dried, and leaves ($n = 10$) from the EcoCELLs were divided in two halves, one lyophilized with liquid nitrogen and the other air-dried. Analysis showed that Hg concentrations were not statistically different ($p > 0.05$).

Limited subsets of leaves were analyzed for MeHg. Following digestion, MeHg concentrations in leaves were determined by distillation extraction, aqueous-phase ethylation, and CVAFS detection (Liang et al., 1994). MeHg concentrations in leaf rinses were similarly determined after distillation of rinse solution, aqueous-phase ethylation, and CVAFS detection. The detection limit for MeHg was $5\,pg\,g^{-1}$ leaf sample and $100\,pg\,l^{-1}$ for leaf rinse samples. Certified reference material from the National Research Council Canada (DORM-2) dissolved in 0.5% KOH methanol solution was used for quality assurance, and error was <15%. Matrix spikes of MeHg had 82 and 95% recovery.

2.3. Assessment of direct atmospheric uptake of Hg in foliage

Additional aspen grown in individual pots containing sandy loam topsoil of low Hg concentration ($0.03 \pm 0.01\,\mu g\,g^{-1}$ Hg) were placed in each EcoCELL. The soil and below ground portion of the plant was covered with plastic, and the containers were placed along the north and south walls of each EcoCELL. Throughout the experiment, leaves (1 to 2 months in age) were sampled from three or four of these aspen in each CELL. The leaf area was recorded, and the leaves were similarly rinsed and freeze-dried. Rinses and foliar material were analyzed for total Hg, and a subset was analyzed for MeHg.

2.4. Hg concentrations in non-foliar tissue and determination of biomass

At the end of each experiment, samples of stems (top, middle, and bottom by height), branches, petioles, and roots were similarly collected from 9 trees in each CELL. The remaining above ground plant material was collected, oven-dried at 60°C for 7 d, and weighed to determine total biomass in each CELL. Nine randomly located soil cores ($1.9\,m^3$) were taken from each CELL and sieved to collect roots, which were then washed and oven-dried to assess root biomass. Coarse roots (>1 mm diameter) were rinsed with copious amounts of water until free of soil (verified by microscope) and freeze-dried for analysis of Hg.

2.5. Assessment of dry deposition to surrogate surfaces

Teflon membranes (PTFE membranes, 45 mm diameter, Cole Palmer #2916-54; e.g. Rea et al., 2002), taped to individual, level watch-glasses (65 mm diameter) attached to wooden dowels 75 cm above the soil, were placed two per pot in each CELL. Membranes were collected, replaced, and analyzed monthly for total Hg while aspen were in the CELLs. The Teflon membranes were digested in a solution 20 ml of 0.5 M BrCl for 24 h and analyzed as described above.

2.6. Assessment of foliar Hg flux

A portable single-pass gas-exchange system was used to characterize the flux of Hg from the foliage in the EcoCELLs. The system consisted of a 25 litre polycarbonate chamber within which 20–30 leaves were isolated. Chamber seams were sealed with plastic food-wrap (Stretch-tite®, Provinyl Films, Inc., Sutton, MA),

and a small pump was used to force ambient air through a mass flow controller (Sierra Instruments, Monterey, CA) into the chamber at 7.5 l min^{-1} so that a slight positive pressure was maintained. A small fan continuously mixed the air reservoir to maintain light leaf flutter. Inlet and outlet airstreams were sampled using a Tekran™ 2537A Mercury analyzer with a solenoid switching unit. The flux rate of gaseous Hg (J_{Hg}) to or from the plant was calculated as follows:

$$J_{Hg} = \Delta_{Hg} F/A,$$

where Δ_{Hg} equals the change in Hg gas concentration between the chamber's inlet and outlet (ng m^{-3}); F equals the flow rate of air through the chamber (m^3 h^{-1}), and A equals the leaf area (m^2). After a tree had been in the chamber 10 min, the Hg flux was measured for 1 h. Trees grown in the low Hg soil ($n = 3$) and trees grown in the Hg-enriched soil ($n = 5$) were sampled in July and August of 2001, and all gas-exchange measurements were made during daylight hours.

2.7. Statistical analysis

Randomized sampling techniques were used and results were analyzed using ANOVA in StatMost (SAS Institute Inc, Cary, NC).

3. Results and discussion

Foliar Hg concentrations increased as a function of age in both experiments with significantly different ($p < 0.0001$) Hg concentrations in new, intermediate, and old leaves (Table 1). Concentrations from the duplicate experiment in 2001 were approximately 60% of those observed in 2000. The lower Hg content is attributed to the lower mean Hg air concentrations in the CELLs as a result of reduced soil emissions during year 2001. Due to Hg-enriched soils, net Hg flux in the EcoCELLs was positive. Atmospheric Hg concentrations ranged from 20 to 50 ng m^{-3} in 2000 and 10 to 30 ng m^{-3} in 2001, based on means of monthly maximum and minimum concentrations while plants were grown within the CELLs.

Table 1
Total Hg concentration in leaves as a function of leaf age and soil Hg concentration

Year	Soil HG	Leaf age	Hg conc. (μg g^{-1})	n
2000	High	New	0.06 ± 0.02	126
2000	High	Inter	0.10 ± 0.03	105
2000	High	Old	0.16 ± 0.03	74
2000	Low	Inter	0.11 ± 0.03	70
2001	High	New	0.03 ± 0.02	45
2001	High	Inter	0.07 ± 0.03	36
2001	High	Old	0.13 ± 0.02	27
2001	Low	Inter	0.09 ± 0.01	7
2001	Low	Old	0.13 ± 0.04	24

New, intermediate, and old leaves (ages <21, 22–35, and >35 days, respectively) were collected from aspen grown in high (12 μg g^{-1}) and low (0.03 μg g^{-1}) Hg soils.

Leaves sampled from aspen grown in low Hg soil had Hg concentrations comparable to concentrations of leaves similar in age from aspen grown in Hg-enriched soil (Table 1, Fig. 1). If translocation of Hg from the soil to leaves was a significant pathway, then foliar Hg concentrations would logically reflect differences in soil Hg concentrations. The fact that foliar Hg concentrations were not significantly different ($p > 0.06$), regardless of soil Hg content, is strong evidence that uptake of gaseous Hg^0 (probably by a stomatal pathway, Hanson et al., 1995) was the predominant pathway by which Hg accumulated in the foliage.

In a project that used multiple plant exposure closed system growth chambers and aspen planted in three soil Hg concentrations and three air Hg concentrations, Frescholtz et al., 2003 demonstrated that accumulation of Hg in foliage occurred as a function of time and air concentration. With increasing air concentrations more Hg was sequestered into the leaves. They also found that soil Hg concentration did influence leaf Hg concentration.

Mercury concentrations in other plant compartments (besides leaves) were higher in the aspen grown in Hg-enriched soil than in the low Hg soil (Fig. 1), indicating that a fraction of the overall Hg in the trees was entering via the roots. However, based on the foliar concentrations of aspen grown in low and high Hg soils, almost all of the Hg in the foliage originated from atmospheric uptake. Other studies have suggested that at most ~10% of Hg in foliage originates from soil uptake (Lindberg, 1996; Rea et al., 2002; Bishop et al., 1998). For aspen grown in Hg-enriched soil, mean concentrations in woody tissues (0.02–0.04 μg g^{-1} Hg) and roots (0.06–0.07 μg g^{-1} Hg) for 2000 and 2001 were significantly ($p < 0.0001$) lower than mean concentrations in leaves (0.09–0.13 μg g^{-1} Hg). For aspen grown in low Hg soil, mean concentrations in woody tissues and roots (0.03–0.07 μg g^{-1} Hg) were significantly ($p < 0.0001$) lower than mean concentrations in leaves (0.11–0.12 μg g^{-1} Hg). The Hg content in woody tissue and roots from aspen grown in low Hg soil were also significantly ($p < 0.05$) lower than that of plants grown in Hg-enriched soil (Fig. 1). Stems sampled from the bottom third of the trees grown in high Hg soil were significantly higher ($p < 0.05$) in Hg concentration than stems sampled from the top portion. Frescholtz et al., 2003 have shown that the stems accumulated Hg principally as a function of air Hg concentrations rather than soil Hg concentrations. The differences in Hg

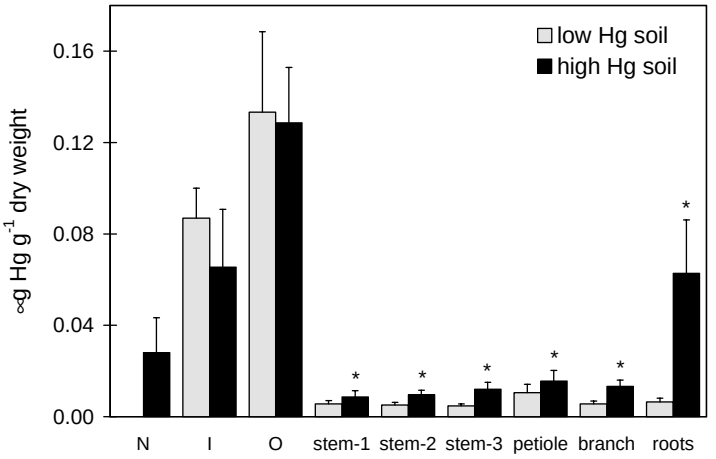

Fig. 1. Foliar and non-foliar Hg concentrations in aspen grown in low Hg soil ($0.03\,\mu g\,g^{-1}$) and high Hg soil ($12\,\mu g\,g^{-1}$) in 2001. Foliar Hg concentrations are reported for new (N, <21 d old), intermediate (I, 22 to 35 d old), and old (O, >35 d old) leaves. New leaves were not collected from aspen in low Hg soil. Stems were sampled from the top 1/3 (stem-1), middle 1/3 (stem-2) and bottom 1/3 (stem-3) of the tree. The symbol * indicates Hg content is statistically different ($p<0.05$) between samples from low and high Hg soil.

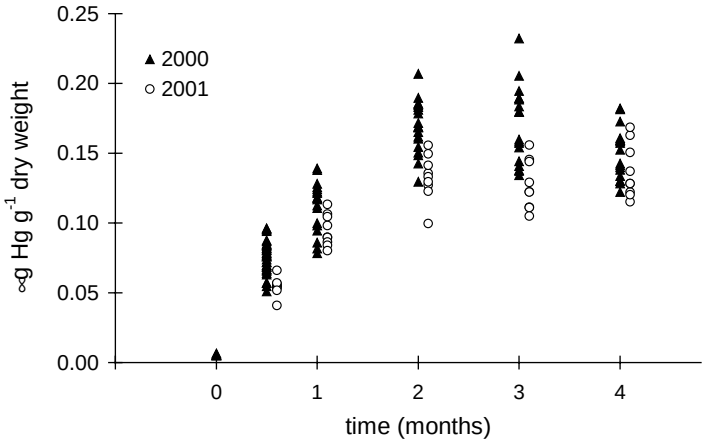

Fig. 2. Hg in foliage as a function of time; leaves were harvested at 0, 0.5, 1, 2, 3, and 4 months after planting during years 2000 and 2001 of separate experiments. Time 0 represents leaves removed from whips before planting, and all plants had leaves after approximately 7 d.

content as a function of stem height could have been influenced by three factors: (1) differences in atmospheric Hg concentrations within the CELLs, which were 20% higher at 3 cm and declined exponentially with height above the soil surface; (2) differences in age of stem (the top 1/3 of the stem was the newest) and therefore had less time to accumulate Hg vapor; and/or (3) the differences were related to soil Hg concentrations, and translocation of Hg to the newest, top most portion of the stem was less. The concentration of Hg in the aspen tissue grown in high Hg soil increased in the order of stems < branches < petioles < roots < leaves. Lindberg et al. (1979) suggested that a dual mechanism controlled Hg uptake in plants with some uptake from the soil by the roots and the majority of uptake from atmospheric sources by the leaves. Our finding that roots accumulated Hg proportional to soil concentrations and that foliage accumulated Hg in relation to atmospheric concentrations supports this.

Fig. 2 shows the concentrations in the oldest obtainable foliage as a function of time after planting. Around 2–3 months the Hg concentrations in the foliage leveled off at approximately $0.15\,\mu g\,g^{-1}$. The same trend was observed in a field study at background soil and air Hg concentrations where Hg concentrations in aspen foliage (budbreak to litterfall) leveled at $0.025\,\mu g\,g^{-1}$ (Rea et al., 2002). Mean photosynthetic rates (14.8 ± 1.9, 12.2 ± 2.1, and $8.2\pm2.7\,\mu mol\ CO_2\,mol^{-1}$ air) and mean

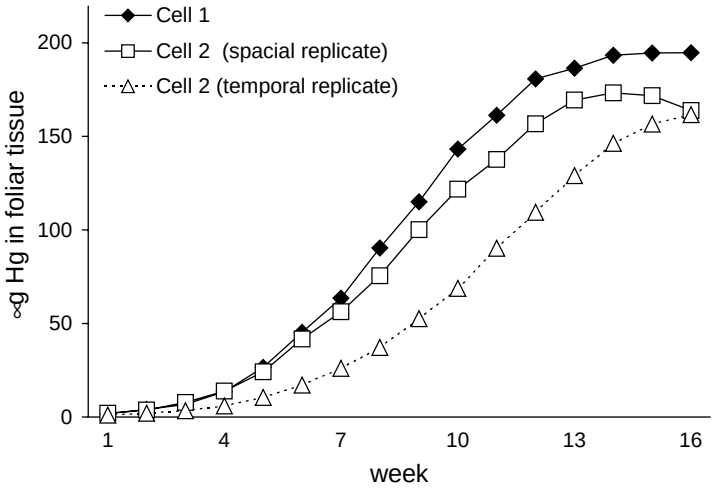

Fig. 3. Total Hg in foliage of aspen stand (grown in Hg-enriched soil). Leaf area was estimated weekly with hand measurements of six randomly selected aspen in each CELL and calculated based on an established allometric relationship of a subset of leaves ($n = 53$; $r^2 = 0.99$).

conductance rates (0.22 ± 0.05, 0.18 ± 0.09, and 0.12 ± 0.04 mol H_2O mol^{-1} air) for new, intermediate, and old leaves ($n = 12$), respectively, significantly ($p < 0.05$) decreased as a function of leaf age. It appears that the plants assimilated less gaseous Hg through their stomata as the leaves stopped growing and as photosynthetic rates decreased.

Total Hg in the foliar canopy of aspen grown in Hg-enriched soil was estimated each week, based on total leaf area and foliar Hg concentrations (Fig. 3). Leaf area increased as a function of time for both experiments, and leaf area index values are reported in Table 2. The foliar mass percentage of new, intermediate, and old-leaves was determined from tagged subsets of leaves, leaf area measurements, and leaf weight-to-area ratios. Because aspen are deciduous, at the end of the season all the Hg in the leaves after senescence would be deposited to the forest floor in the form of litterfall. Based on the soil surface area within the EcoCELLs and assuming that live leaf concentrations closely approach those of the ensuing litterfall (Lindberg, 1996), the Hg flux in litterfall would range from 15 to 16 $\mu g\,m^{-2}\,yr^{-1}$ (CELLs 1 and 2) in 2000 and 15 $\mu g\,m^{-2}\,yr^{-1}$ (CELL 2) in 2001. These values are similar to values reported by others at sites with background air and soil Hg concentrations (Rea et al., 2002), but below those for sites near Hg^0 sources (25–35 $\mu g\,m^{-2}\,yr^{-1}$) (Lindberg, 1996). The estimated mean daily Hg^0 uptake rate from the atmosphere exhibited temporal trends and ranged from 160 to 220 $ng\,m^{-2}\,d^{-1}$ in 2000 (CELL 1 and 2) and 125 $ng\,m^{-2}\,d^{-1}$ in 2001 (CELL 2) for the first month and gradually decreased to 57–61 $ng\,m^{-2}\,d^{-1}$ and 44 $ng\,m^{-2}\,d^{-1}$, respectively, by the fourth month when plant growth had slowed.

Table 2
Leaf area index (LAI) as a function of time for EcoCELLs in 2000 and 2001

Week	2000 CELL 1	2000 CELL 2	2001 CELL 2
1	0.04	0.05	0.05
4	0.37	0.38	0.25
8	1.70	1.48	1.04
12	2.58	2.29	2.33
16	2.43	1.96	2.95

Because deciduous trees annually deposit their foliage to the forest floor, it is important to determine the Hg speciation within leaves in order to assess environmental impacts. At the end of the experiment, approximately 80% of the Hg in the above-ground biomass was found in the leaves, and approximately 0.8% of that was MeHg (based on composition of 15% new, 45% intermediate, and 40% old leaves; see Table 3). The percentage of MeHg in foliage decreased as a function of leaf age, and new leaves had the highest percentage of MeHg ($2.8 \pm 1.8\%$) compared to other leaves (Table 3).

The source of MeHg in litterfall has not been determined (Munthe et al., 1995; St. Louis et al., 2001). The MeHg concentrations of leaves (taken from the same leaf category) from aspen grown in low Hg soil did not significantly differ from aspen grown in Hg-enriched soil indicating that the accumulation of MeHg in foliage did not reflect soil Hg concentrations. Based on this, the MeHg in leaves most likely was derived from Hg in the atmosphere. Because atmospheric MeHg concentrations were not measured, it is not known

Table 3
Methylmercury in foliage

Soil Hg	Leaf age	MeHg conc. ($ng\,g^{-1}$)	Total Hg conc. ($ng\,g^{-1}$)	% MeHg	n
High	New	0.54 ± 0.27	22 ± 10	2.8 ± 1.8	6
High	Inter	0.37 ± 0.19	71 ± 19	0.6 ± 0.5	11
High	Old	0.38 ± 0.14	138 ± 16	0.3 ± 0.1	6
Low	Inter	0.24 ± 0.09	111 ± 20	0.2 ± 0.1	4

whether inorganic gaseous Hg was methylated within the foliage or dry deposition of gaseous MeHg occurred. In addition, although MeHg was not detected in leaf rinses ($n=9$), this may have been due to analytical methods and instrument sensitivity (5 pg per 50 mL). These preliminary data show that MeHg concentrations were less in old compared to new leaves, indicating that perhaps dilution of MeHg with leaf growth or demethylation within the leaves occurred. The suggestion that Hg is methylated or demethylated in the phyllosphere is interesting, but requires further study. The presence of MeHg in vegetation has been documented by others who have suggested that there is sufficient atmospheric deposition and leaching of MeHg from forested systems to account for all of the MeHg accumulating in fish in Swedish lakes (Hultberg et al., 1994; Bishop et al., 1998; Mierle and Ingram, 1991). Concentrations of Hg and MeHg were within the ranges reported by other scientists (Lindberg, 1996; St. Louis et al., 2001; Munthe et al., 1995).

Surface deposition rates determined by measuring Hg in leaf rinses were similar for aspen grown in low and high Hg soil. Based on the mean rates of deposition of surface soluble Hg to leaves (0.05 ± 0.03 and $0.08\pm0.05\,ng\,m^{-2}\,h^{-1}$ in 2000 and 2001, respectively), approximately 1.5–3% of the total Hg present in leaves was water soluble and could be rinsed from the surface of leaves. Rinses of old leaves had at least 2–5 times more Hg per leaf area than rinses of new leaves from the same tree ($p<0.05$, $n=12$), presumably because new leaves had been exposed to atmospheric Hg deposition for a much shorter amount of time. Analysis of second 100 mL rinse solutions showed that more than 90% of Hg was removed with the first 100 mL rinse of water. Assuming that aspen are foliated for approximately 6 months of the year and field conditions were similar to the conditions in the EcoCELLs, then the rate of dry deposition of Hg that could be removed with precipitation and reach the forest floor would range from 0.4 to $1.0\,\mu g\,m^{-2}\,yr^{-1}$. These values are lower than annual estimates of dry deposition ($6\,\mu g\,m^{-2}\,yr^{-1}$) in a short-term throughfall study at Walker Branch Watershed (Lindberg et al., 1994), most likely due to the fact that by the end of our experiments the LAI ranged from 2 to 3 and at the Walker Branch Watershed the LAI was roughly 5 (Table 1). In natural settings precipitation could be concentrated in Hg such that significant wet deposition of Hg to foliar surfaces occurred (Lindberg et al., 1994; Rea et al., 2002). Other experiments indicated that wash-off of dry Hg deposition and foliar leaching of internal sources of Hg occurs during precipitation events (Rea et al., 2000).

In 2000 the mean dry deposition rate to the Teflon surrogate surfaces was $0.40\pm0.23\,ng\,m^{-2}\,h^{-1}$ and the mean local deposition velocity was $4.7\pm2.2\times10^{-4}\,cm\,s^{-1}$ ($n=36$); in 2001 the mean deposition rate and velocity were $0.25\pm0.15\,ng\,m^{-2}\,h^{-1}$ and $5.6\pm3.3\times10^{-4}\,cm\,s^{-1}$ ($n=24$), respectively. Deposition velocities were calculated by dividing the deposition rate by the mean total Hg air concentration. There were several problems with assessing dry deposition of Hg through the use of Teflon surrogate surfaces. The membranes were mounted on watch glasses that were horizontal to the ground, whereas the leaves were constantly agitated by the ventilation system and fluttered at roughly a 45° angle to the soil floor. The Teflon membranes have relatively inert surfaces, whereas leaves have active surfaces with waxy cuticles and gaseous exchange via transpiration through the stomata. Additionally, vegetation would be subject to various natural pathogens, such as insects or fungus, which might also breach the leaf exterior. For these reasons, the gas-exchange system was deemed a more suitable method for measuring foliar Hg exchange.

The foliar Hg flux measured by the portable gas-exchange system was negative on average indicating deposition of Hg to leaves, with the exception of one tree in August that showed a positive Hg flux (Fig. 4). It appears that the aspen in the low Hg soil exhibited greater deposition compared to the aspen in the high Hg soil based on the limited data in Fig. 4. Hanson et al. (1995) showed that Hg flux from foliage was bi-directional for plants grown in background soil Hg concentrations. The direction and magnitude of Hg flux from leaves was dependent on air Hg concentrations (ranging from 0.5 to $70\,ng\,m^{-3}$), and the air concentration that produced no net flux was termed the compensation point. Our gas-exchange data confirm the suggestion by Hanson et al. (1995) that the Hg supply to foliage from roots will also influence

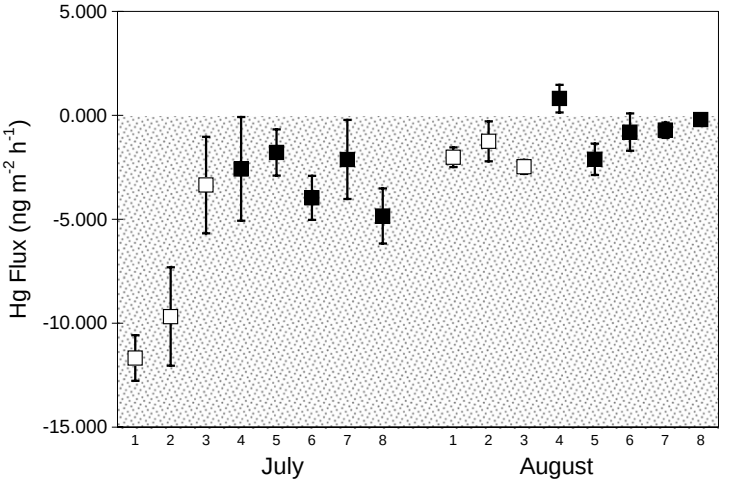

Fig. 4. Foliar exchange of Hg vapor (flux) measured from individual aspen trees grown in low (□) and high (■) Hg soil in the EcoCELL during July and August of 2001. Shaded region indicates deposition (or foliar uptake) of Hg vapor.

compensation points (Benesch, 2002). Based on measurements with the portable gas-exchange system, the net Hg flux to foliage in the EcoCELLs during July and August 2001 ranged from -0.2 to $-12\,ng\,m^{-2}\,h^{-1}$ and deposition velocities to foliage ranged from 0.0003 to $0.2\,cm\,s^{-1}$. Rates of Hg^0 uptake determined from total Hg in the foliar canopy were within the same range as those measured by the gas-exchange system. Additionally, our local deposition velocities overlap those modeled by Lindberg et al. (1992) for deciduous foliage ($0.006–0.12\,cm\,s^{-1}$) using a stomatal gas-exchange model. Furthermore, deposition of Hg measured using surrogate Teflon filters underestimated the actual deposition of Hg to foliage.

4. Conclusions

Using large mesocosms, Hg exchange between air and vegetative surfaces of several aspen stands was monitored in a controlled system. Air concentrations were naturally elevated due to Hg evasion from contaminated soils, and plants had ample rooting volume, natural lighting, and a season to grow. In this system the net Hg flux associated with all foliar surfaces, including vegetation grown in low and high Hg soils, was deposition. The Hg content in foliage from trees grown within the EcoCELLs in background soil Hg concentration ($0.03\,\mu g\,g^{-1}$) was similar to that of foliage from trees in Hg-enriched soil ($12\,\mu g\,g^{-1}$). These findings demonstrate that nearly all of the Hg in foliage was clearly derived from the atmosphere. Even though MeHg constituted a small portion ($\sim 1\%$) of the total Hg found in leaves, the methylated form poses the greatest environmental threat.

Considering that gaseous Hg concentrations are generally homogenous due to turbulent mixing and that tree foliage is exposed primarily to air from aloft, foliage could act as a significant sink for atmospheric Hg, and the Hg content in litterfall would mainly represent a new Hg input to terrestrial ecosystems. Here we show that Hg in foliage originated from the atmosphere and that $<3\%$ of that Hg would have been removed with precipitation. The implication of these findings is that litterfall measurements may be a simple and effective way to estimate Hg deposition rates in deciduous forests.

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