



New Approaches to Understand Mercury in Trees: Radial and Longitudinal Patterns of Mercury in Tree Rings and Genetic Control of Mercury in Maple Sap

Ruth D. Yanai · Yang Yang · Adam D. Wild · Kevin T. Smith · Charles T. Driscoll

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Abstract Mercury (Hg) in the environment has been receiving considerable attention in recent years, but little is known about Hg accumulation in trees. We analyzed Hg in tree rings from four tree species at the Hubbard Brook Experimental Forest in New Hampshire to determine whether Hg concentrations are more influenced by soil Hg concentrations, which have been stable or increasing due to the cumulative retention of historical atmospheric Hg deposition, or by atmospheric Hg deposition, which has declined in recent decades. Declining concentrations from the top to the bottom of the bole ($p < 0.001$) and from older to newer tree rings ($p = 0.001$) suggest that foliar uptake of Hg is more impor-

tant than root uptake. Ten sugar maple clones planted in six blocks at the Heiberg Forest in New York State showed significant genetic control of sap Hg concentration ($p = 0.02$), which was not related to soil Hg concentration differences across blocks. Clones could differ in stomatal uptake, root uptake, or translocation of Hg. Better understanding of the source of Hg in wood is needed to forecast future changes in Hg cycling in forested ecosystems.

Keywords *Acer saccharum* Marsh. · Maple sap · Mercury cycling · Mercury pollution

R. D. Yanai (✉)
Department of Sustainable Resources Management, State
University of New York College of Environmental Science and
Forestry, 1 Forestry Dr. 106 Marshall Hall, Syracuse, NY 13210,
USA
e-mail: rdyanai@syr.edu

Y. Yang
Sierra Nevada Research Institute, University of California,
Merced, Merced, CA 95340, USA

A. D. Wild
Department of Natural Resources, Cornell University, Ithaca, NY
14853, USA

K. T. Smith
USDA Forest Service, Northern Research Station, 271 Mast Road,
Durham, NH 08324, USA

C. T. Driscoll
Department of Civil and Engineering, Syracuse University,
Syracuse, NY 13244, USA

1 Introduction

Terrestrial ecosystems receive significant inputs of broadly toxic mercury (Hg) from atmospheric deposition of direct natural and human emissions as well as re-emissions (Grigal 2003; Driscoll et al. 2013). Trees are important to Hg cycling in forests, although their tissue concentrations are low (Obriest et al. 2011, 2012), because they are so massive that they contain significant amounts of Hg (Blackwell et al. 2014; Yang et al. 2018). Although information on tree Hg contents is increasing, the pathways of Hg uptake and translocation are uncertain and difficult to study, especially in field settings.

Part of the difficulty in interpretation of foliage and bark chemistry is that analysis includes compounds adsorbed onto exposed surfaces as well as compounds actually taken up into the plant. Foliage takes up elemental mercury (Hg^0) through stomata (Lindberg et al.

1992; Hanson et al. 1995; Lindberg 1996; Laacouri et al. 2013) and through the leaf cuticle (Stamenkovic and Gustin 2009; Laacouri et al. 2013; Arnold et al. 2018). Upon uptake, Hg^0 is oxidized and bound to leaf cell walls or to phytochelatin (Du and Fang 1982, Frescholtz et al. 2003, Dennis 2019). Root uptake of the divalent cation Hg^{2+} has been demonstrated in growth chambers for quaking aspen (Frescholtz et al. 2003) and olive and grape (Naharro et al. 2019), but Hg^{2+} tends to bind to cell walls, reducing the translocation of Hg from roots into the bole (Greger et al. 2005; Wang et al. 2011; Wang et al. 2012). Measuring uptake at the root surface using intact roots in the field is feasible for some nutrient elements (Yanai et al. 2009) but not for Hg, because disappearance from solution could be due to sorption to the root surface (Wang et al. 2011), and thus might not indicate uptake and translocation. Mercury has been measured in xylem sap of mature Scots pine (*Pinus sylvestris* L.), Norway spruce (*Picea abies* L.) (Bishop et al. 1998), and Masson pine (*Pinus massoniana* L.; Luo et al. 2016), which suggests that Hg is transported from soil into wood with the transpiration stream. Notably, these studies all involved conifers; we are not aware of any similar measurements in hardwoods.

The pattern of Hg concentration across dated tree rings could help distinguish the importance of atmospheric vs. soil sources of Hg to wood. Atmospheric Hg concentrations have declined in recent decades in the northeastern USA (Drevnick et al. 2012; Zhou et al. 2017) and worldwide (Slemr et al. 2011). If atmospheric deposition to foliage is the source of Hg in tree tissues, radial trends of Hg in the bole would be lower in more recently formed tree rings. Alternatively, if soil is the source of Hg to wood tissues, concentrations should be relatively stable or even increasing over time, due to the continued, albeit lessened, rate of Hg accretion in soils from throughfall and litterfall. The residence time of Hg in soil is very long, so we anticipate limited loss of Hg from soil pools (Yu et al. 2014).

Additional insight concerning Hg uptake by trees might be gained through study of clonal material planted in a field trial. Differences among clones under uniform Hg exposure would indicate genetic control of stomatal or root uptake. Comparisons of foliage and soil concentration could also identify the relative importance of atmospheric vs. soil sources of Hg.

This paper reports on novel approaches to address two questions concerning the uptake and movement of

Hg in trees. First, are there vertical or radial patterns of Hg concentrations in bole wood that could provide insight on the source of Hg to trees? To address this question, we analyzed Hg concentrations in the wood of four trees of different species as a function of height along the bole and date of wood formation. Second, does sap Hg concentration reflect soil or foliar sources? For this question, we compared replicate clones of 10 genetic individuals in a mature plantation of clonal sugar maple and related these to differences in foliar and soil Hg. Both studies are modest in scope but shed light on factors that control Hg accumulation in trees at two different locations, the Hubbard Brook Experimental Forest in New Hampshire and the Heiberg Memorial Forest in New York State.

2 Methods

2.1 Site Descriptions

The Hubbard Brook Experimental Forest is located in the White Mountain National Forest in the central New Hampshire (43°56'13" N, 71°74'20" W). Average temperature at the site is $-9\text{ }^{\circ}\text{C}$ in January and $18\text{ }^{\circ}\text{C}$ in July with an annual average precipitation of 140 cm (Bailey et al. 2003). Soils are well-drained Spodosols developed from granitic glacial drift (Bailey et al. 2003).

The Sven O. Heiberg Memorial Forest is located in the Alleghany plateau in Tully, New York (42°45'53" N, 76°04'46" W). The average temperature is $-7\text{ }^{\circ}\text{C}$ in January and $19\text{ }^{\circ}\text{C}$ in July, and annual average precipitation is 115 cm (<http://climate.ncsu.edu/cronos/?station=308627>). Soils are classified in the Mongaup-Hawksnest Complex, formed from till of sandstone and siltstone.

Total atmospheric Hg deposition is $\sim 20\text{ }\mu\text{g m}^{-2}\text{ yr}^{-1}$ at the Heiberg Forest and $\sim 22\text{ }\mu\text{g m}^{-2}\text{ yr}^{-1}$ at the Hubbard Brook, based on wet Hg deposition data from the National Atmospheric Deposition Program Mercury Deposition Network and model estimates of dry Hg deposition (Yu et al. 2014).

2.2 Wood Collection and Processing

Wood samples were collected from the American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.), yellow birch (*Betula alleghaniensis* Britt.), and red spruce (*Picea rubens* Sarg.) near Rain

Gage #23 at the Hubbard Brook Experimental Forest on July 7, 2015. One tree at least 20 cm in diameter at breast height of each of the four species was felled, and single transverse discs (~5 cm in thickness) were cut from the bottom, middle, and top of the bole. Samples were placed on ice in the field and stored in a laboratory freezer until further analysis.

The sawn surfaces were shaved with a plane that was rinsed with methanol between discs. The bottom discs were dated through a dissecting scope, beginning from the most recent growth ring next to the bark, using the skeleton plot technique (Swetnam et al. 1985). Dates were confirmed by comparing years with wide and narrow rings among our discs and with reported ring widths for red spruce (Engel et al. 2016) and sugar maple and the American beech (Kim 1988; Halman et al. 2014) at the Hubbard Brook Experimental Forest. From the transverse surface of each bottom disk, wood shavings of each 5-year growth increment were extracted with a stainless steel drill bit along a radius from the most recently formed annual ring to the pith. Drill bits of different diameters were used to match the width of the 5-year growth increments. For discs obtained from the middle and top of the bole, wood shavings from only the most recent 5-year growth increment were collected. In all cases, multiple samples (~10) from each disk were pooled to provide enough material for Hg analysis. To prevent cross contamination, the drill bit was rinsed with methanol between samples. This work was done in a clean room previously shown to be free of Hg contamination (Yang et al. 2017).

2.3 Sap, Foliage, and Soil Collection from Clonal Sugar Maple

Clones were derived in the 1970s from ten parent sugar maple trees from the Heiberg Forest (3 trees); Oakwood Cemetery, Syracuse, New York (3 trees); and locations in Vermont (4 trees). Clones were propagated by selecting current year shoots in the spring of 1971, 1972, and 1973 just after elongation. Cuttings were placed in media under a mist system to establish roots. Following root establishment, young cuttings were potted and overwintered in a cold frame. Clonal trees were planted at the Heiberg Forest in 1973 and 1974 at a spacing of 3–4 m, interspersed with wild type sugar maples grown from seed. Clonal trees were distributed among six adjoining replicate blocks in a randomized complete block design.

Xylem sap of sugar maple was collected using a mini-tap procedure (Gabriel 1982; Wild and Yanai 2015) based on traditional tapping for maple syrup production. Late in the dormant season, subfreezing nighttime temperatures followed by a daytime thaw results in positive sap pressure within the sapwood (Tyree 1983). In March 2014, all clonal trees and a selection of wild type trees were tapped, and sap was collected on April 9, 2014, during a warm period following a freeze. The sap passed through a metal spile and was collected in a plastic tube. Sap samples were frozen until they could be processed. Fifty-four sap samples with adequate volume (> 15 mL) were selected for analysis based on distribution across clones and blocks. Samples collected from Clone 3 and Clone 5 were not included in this study because of limited sample volume (< 15 mL).

Foliage and soil samples were collected in late July of 2016. We used pole pruners to collect sun-lit leaves from three replicate trees of each of Clones 1, 4, 2, and 9, which had the highest and lowest Hg concentrations in the sap. The 12 trees were selected to include two trees (of two different clones) in each of the six blocks. To collect soils, we divided each block into a 3 × 3 grid (forming 9 subplots) and sampled 5 locations with soil corers at the center of each of the middle and four corner subplots. Samples of the organic horizon (O_{ea}) and mineral soil (0–10 cm) were collected from these 5 locations in each of the six blocks and composited for analysis.

2.4 Mercury Analysis

Samples were freeze-dried at –80 °C and 7 Pa, using FreeZone Plus 6 (Labconco, Kansas City, MO). The sample sizes needed to obtain detectable amounts of Hg differed by type ~50 mg for soils and foliage, ~100 mg for wood, and 400–800 mg for sap. Samples were weighed into nickel boats, and aluminum oxide (Al₂O₃; basic) was added to improve combustion. Total Hg concentration was determined by thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry (Method 7473, USEPA 1998), using a Milestone DMA 80 direct Hg analyzer (Shelton, CT). Samples of soil, foliage, and wood were dried at 300 °C for 60 s, combusted at 925 °C for 270 s, cooled for 70 s, and amalgamated for 18 s (Yang et al. 2017). We found that a longer processing time was needed for the dried sap to be fully combusted. For sap, samples were

dried at 250 °C for 135 s, combusted at 750 °C for 330 s, cooled for 150 s, and amalgamated for 20 s.

Quality control included analysis of two blanks, two primers (NIST DORM-2, dogfish muscle, ~ 50 mg, 410 ± 41 ng g⁻¹), two continuing calibration verification samples (NIST 2976 mussel tissue, ~ 15 mg, 61 ± 6 ng g⁻¹, Gaithersburg, MD, USA), two quality control samples (NIST 1515 apple leaves, ~ 5 mg, 44 ± 4 ng g⁻¹), and one method blank sample (with aluminum oxide) at the beginning of each run. After every 10 samples, we analyzed continuing calibration verifications (NIST 2976) and continuing calibration blanks. The blanks had a Hg concentration of 0.01 ± 0.02 pg g⁻¹. Recoveries averaged 98–100% of the certified values with relative standard deviations of 3–8%, which fell within the acceptable range.

The method detection limit (MDL) was calculated using the US Environmental Protection Agency Method Detection Limit procedure (USEPA 1984). To determine the MDL, the critical Student's t value was multiplied by the standard deviation of the mean concentration of seven replicate 0.5 g samples of NIST 1515 (apple leaves). The calculation yielded the MDL of 0.03 ng in units of mass (corresponding to a concentration of 1.27 ng g⁻¹). This value was lower than our measured Hg concentrations, which ranged from 0.05 to 0.45 ng for sap, 0.10 to 0.43 ng for wood, and > 0.7 ng for foliage and soils.

2.5 Data Analysis

Because the patterns in wood Hg concentrations were non-linear, we used piecewise regression to describe change over time for the two oldest trees, with ring ages dating from 1930 to 2015. For each tree, the value of the breakpoint of two models with different slopes was estimated using the NLIN function in SAS. All four trees provided data from 1955 to 2015; we used a linear regression blocked by tree using PROC MIXED in SAS.

For vertical pattern, the effect of height was tested with a general linear model of wood Hg concentration blocked by tree. Wood concentration data were log-transformed to meet the assumption of normality of the residuals.

Mercury concentrations of maple sap were calculated from the measured Hg content and the volume of the liquid sap sample. An aligned rank test was used to examine the effects of block and clone on Hg

concentration in sap, due to the small number of samples (54 in total). The Nemenyi *post-hoc* test was used to compare means where the null hypothesis of no effect was rejected ($\alpha = 0.10$). Pearson correlation was used to compare foliar Hg to sap Hg concentrations based on the 12 trees. Pearson correlation was also used to compare foliar and sap Hg concentrations to organic and mineral soil Hg concentrations for each of the six blocks.

Statistical tests were performed using SAS 9.4 (SAS Institute Inc. 2013).

3 Results

3.1 Mercury Concentrations in Wood

The concentration of Hg for all wood samples ranged from 1.2–3.7 ng g⁻¹ for American beech, 1.4–4.0 ng g⁻¹ for sugar maple, 2.6–4.1 ng g⁻¹ for red spruce, and 1.5–7.5 ng g⁻¹ for yellow birch. Radial trends of Hg concentration were described in sugar maple and yellow birch for wood formed from the 1930s to 2015 and for American beech and red spruce for wood formed from 1960 to 2015 (Fig. 1). The longer series from sugar maple and yellow birch showed increasing Hg concentrations from the 1930s to a significant breakpoint in 1960 ($p = 0.03$ and 0.02 , respectively). Treating the four trees as replicates, Hg concentrations declined in wood formed after 1960 ($p < 0.001$, Fig. 1).

Longitudinal trends in individual trees showed peak concentration of Hg at the top of the bole, decreasing with decreased stem height for all four trees tested ($p = 0.001$; Fig. 2) with an average difference of 0.59 ± 0.04 ng g⁻¹ from top to bottom of the bole.

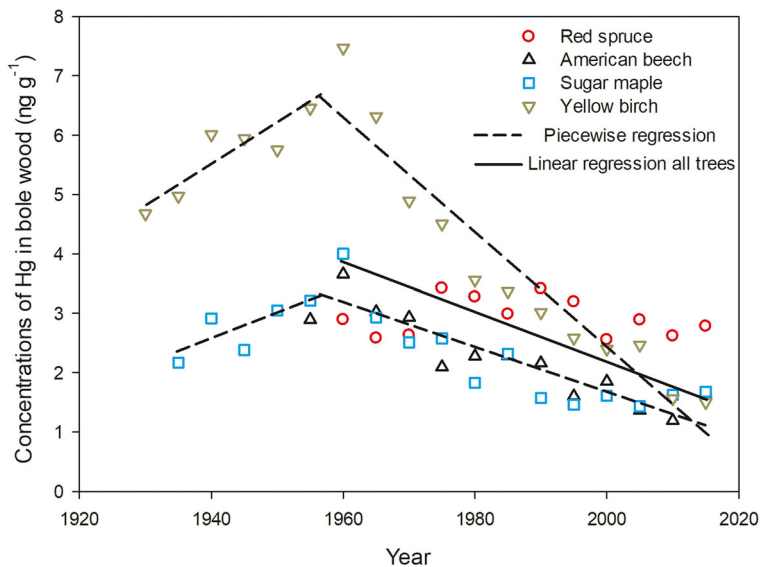
3.2 Mercury Concentrations in Maple Sap

The concentration of Hg in sugar maple sap ranged from 1.6 to 10.4 ng L⁻¹ with an average of 4.8 ± 0.3 ng L⁻¹. Sap concentration varied by maple clone ($p = 0.02$, Fig. 3a). Clones 1 and 4 had the highest concentrations (6.8 and 6.4 ng L⁻¹), while Clones 2 and 9 had the lowest (3.2 ng L⁻¹ for both).

3.3 Soil and Foliar Hg Concentration Compared with Hg in Sap

Soil Hg concentrations ranged from 102 to 127 ng g⁻¹ in the organic horizon and from 74 to 100 ng g⁻¹ in the

Fig. 1 Radial patterns of Hg concentrations in bole wood of four trees sampled at the Hubbard Brook Experimental Forest in New Hampshire. Samples were taken in 5-year increments of growth rings



mineral soil, across the six blocks. Sap Hg concentrations were not correlated with Hg concentrations in the organic horizon ($p = 0.20$) nor with Hg concentration in the mineral horizon ($p = 0.28$). Organic and mineral Hg concentrations were positively correlated ($r = 0.97, p < 0.01$).

The two clones with the highest and the two clones with the lowest Hg concentrations in sap were analyzed for foliar Hg concentration. Foliar Hg concentration was not related to concentration in the sap ($p = 0.29$). Foliar Hg was similar among the four clones sampled ($p = 0.32$), with an average of $17.8 \pm 0.6 \text{ ng g}^{-1}$ (data not shown). Variation in foliar Hg concentrations was also

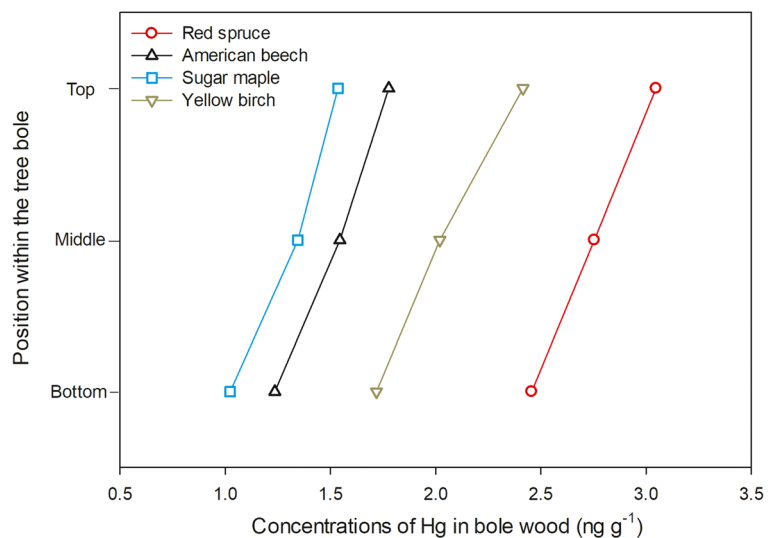
not attributable to planting block ($p = 0.44$) or the interaction of clone and block ($p = 0.19$).

4 Discussion

4.1 Evidence for Foliar Uptake as a Source of Wood Hg

Despite the absence of local point sources, trees at the Hubbard Brook Experimental Forest contained measurable amounts of Hg, and we sought to determine whether this Hg came primarily from the soil or the atmosphere. Foliar uptake of gaseous Hg⁰ involves oxidation

Fig. 2 Concentrations of Hg in wood from different heights along the bole of four northern hardwood trees. Samples were taken from the most recent 5 growth rings (2011–2015)



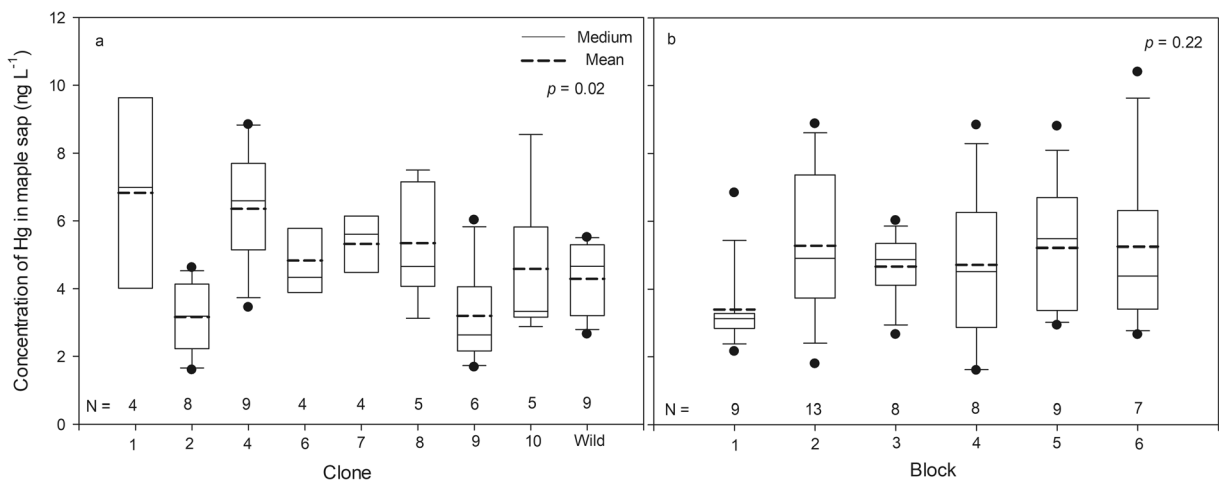


Fig. 3 Concentrations of Hg in maple sap by **a** clone and **b** block. Aligned rank testing found significant effects of clone ($p = 0.02$) but not block ($p = 0.22$)

to Hg(II), which is complexed with sulfur as particles (Du and Fang 1982; Frescholtz et al. 2003) or with sulfur-rich oligo- or polypeptides in leaf tissues (metallothioneins and phytochelatins) (Dennis et al. 2019; Manceau et al. 2018). Complexation may also involve microbial transformation of Hg at the leaf surface (Grégoire and Poulain 2018). Translocation of Hg from foliage to wood likely requires additional transformation during phloem transport (O'Connor et al. 2019). Uptake via stomata and subsequent translocation through the phloem has been described in a greenhouse manipulation experiment in which wood Hg concentrations reflected the daytime total Hg⁰ concentrations in air supplied to 4-year-old Austrian pine (*Pinus nigra* J.F.Arnold) (Arnold et al. 2018). Higher concentrations in wood near the top of the trees we studied (Fig. 2) are consistent with foliar uptake of atmospheric Hg, as phloem could be presumed to lose Hg to adsorption and unloading in the wood as it descends.

4.2 Declining Atmospheric Sources of Hg to Wood at the Hubbard Brook

The radial pattern of Hg in tree rings also supports the hypothesis of an atmospheric source. A soil source would be expected to result in consistent or increasing concentrations over time, due to the continued, albeit declining, deposition of Hg to soil via throughfall and litter (Risch et al. 2012, 2017; Wang et al. 2016), whereas we observed lower concentrations in more recently formed tree rings (Fig. 1). This pattern was significant overall for the four

trees treated as replicates; the fact that the one conifer we studied showed little change over time may be noteworthy. Observations of additional replicate trees would be required to assess species differences with confidence.

In a study of hardwood and conifer forests across four sites in the northeastern USA, yellow birch was significantly higher in wood Hg concentration than the other five species studied (Yang et al. 2018). Yellow birch was also the species most sensitive to experimental soil warming, with greater Hg accumulation in foliage (Yang et al. 2019). The fact that yellow birch experienced the greatest decrease over time in wood Hg in our study (Fig. 1) is consistent with these other observations of yellow birch having a high capacity for Hg accumulation. Thus, accumulation of Hg by yellow birch may be more sensitive to changes in the environment than other species.

Decreasing Hg concentrations in tree rings formed from 1960 to 2015 likely reflects declines in atmospheric Hg concentrations. Measurements of atmospheric Hg concentrations at the nearest monitoring station, in Underhill, Vermont, were not initiated until 1992, but they declined from 1992 to 2015 (Zhou et al. 2017). Lake sediment cores give a longer history of environmental Hg, and these show declines from 1960 to 1998 in New Hampshire and Vermont (Kamman and Engstrom 2002), from 1960 to 1993 in Minnesota (Engstrom and Swain 1997), and from the mid-1980s to the present for a large number of sites across the upper Midwest and northeast (Drevnick et al. 2012). Concentrations of Hg in fish declined in the region between 1969 and 2005, as in most of the USA (Chalmers et al.

2011), and were associated with reductions in industrial use of Hg during the 1960s and 1970s.

Interpretation of dendrochemistry is hampered by uncertainty in both the uptake and translocation pathways within trees as well as uncertainty in the speciation and binding complexes of Hg in the apoplast and symplast (Smith and Shortle 1996). In Ontario, Canada, radial patterns of Hg concentrations in rings from willow (*Salix*), sugar maple, red oak (*Quercus rubra* L.), and poplar (*Populus*) were not related to known trends in atmospheric Hg deposition (Temme et al. 2007). However, in places with severe local contamination, the radial patterns of Hg concentrations in rings has reflected trends in Hg contamination and industrial activity for European beech (*Fagus sylvatica* L.), Norway spruce (Hojdová et al. 2011), Scots pine (Navrátil et al. 2017), and European larch (*Larix decidua*) (Navrátil et al. 2018) in the central Czech Republic, Japanese cedar (*Cryptomeria japonica*) in southern Korea (Jung and Ahn 2017), and pine in Nevada and California (Wright et al. 2014). There have been few reports of Hg concentrations in tree rings that show the effect of improvements in atmospheric Hg exposure (Scanlon et al. 2020).

4.3 Unknown Mechanism for Genetic Control of Hg in Tree Sap at the Heiberg Forest

Patterns of Hg concentrations in the clonal plantation of sugar maple that we studied did not support the importance of soil sources to Hg in trees: neither sap nor foliar Hg reflected the variation in soil Hg across six blocks. Similarly, adding Hg to soils in a mesocosm experiment did not increase foliar Hg of aspen relative to controls (Ericksen et al. 2003). However, sap Hg concentrations were also not correlated with foliar Hg concentrations; we would expect a positive correlation if the differences in clones were due to differences in stomatal uptake of Hg.

This study is the first to report genetic control of Hg concentrations in trees. The traits responsible for this difference might affect Hg uptake through roots or through foliage, or both. Although it has been asserted that root uptake is not commonly an important source of Hg to trees (Grigal 2002), wood Hg concentrations were attributed to root uptake in a study of black poplar near a chlor alkali plant in Portugal, because the radial pattern of Hg concentrations in wood was related to Hg concentrations in

industrial effluent (Abreu et al. 2008). Other studies have shown that Hg uptake via roots does occur (Wang et al. 2011; Naharro et al. 2019), but they did not examine wood Hg.

Genetic control of uptake of other heavy metals from soil solution has been reported. Poplar (Laureysens et al. 2004; Zacchini et al. 2009), willow (Dickinson et al. 1994; Wang and Greger 2004), and birch (*Betula*) (Keinänen et al. 2007) have been genetically selected for uptake of trace metals and clonally propagated to decontaminate polluted soils. Thus, it seems likely that trees vary in the degree to which they take up Hg from soil. Analysis of Hg isotopes might shed more light on the sources of Hg to xylem sap and to wood (Scanlon et al. 2020).

4.4 Differences Across Sites

The two sites we studied are similar in estimated atmospheric Hg deposition (20 vs 22 $\mu\text{g m}^{-2} \text{yr}^{-1}$, Yu et al. 2014), but quite different in soil Hg. Mercury concentrations in organic and mineral horizons at the Hubbard Brook averaged $255 \pm 13 \text{ ng g}^{-1}$ and $195 \pm 30 \text{ ng g}^{-1}$ (Yang et al. 2019), over twice that at the Heiberg Forest (mean of $116 \pm 5 \text{ ng g}^{-1}$ and $87 \pm 6 \text{ ng g}^{-1}$). Mercury in sugar maple foliage at the Heiberg site ($17.8 \pm 0.6 \text{ ng g}^{-1}$) was similar to that at the Hubbard Brook ($18.0 \pm 1.5 \text{ ng g}^{-1}$; Yang et al. 2018), consistent with the similarity of atmospheric deposition rates. If soils were an important source of Hg to trees, we would expect to find higher foliar Hg at the Hubbard Brook.

Our findings of Hg in the spring flush of xylem sap are consistent with transport in the apoplast, the system of open conducting elements and cell walls in xylem. There are few reports of Hg in tree sap from other sites, and no reports of Hg in the spring flush of sap prior to and during foliar budbreak. Xylem sap of Norway spruce and Scots pine in northern Sweden had higher concentrations ($10\text{--}15 \text{ ng L}^{-1}$; Bishop et al. 1998) than we observed for sugar maple ($4.8 \pm 0.3 \text{ ng L}^{-1}$). This pattern could be related to the higher Hg concentrations of conifer tissues in general (Obrist et al. 2012; Yang et al. 2018). Mercury in soils was not reported by Bishop et al. (1998), but other sites in northern Sweden had higher Hg in organic horizons ($170\text{--}250 \text{ ng g}^{-1}$, Kronberg et al. 2016) than in our study ($116 \pm 5 \text{ ng g}^{-1}$); mineral soil Hg was not reported in that study.

4.5 Implications for Human Health and Forest Management

Finding Hg in maple sap could be alarming as maple sap is concentrated to produce maple syrup and sugar. However, even after concentrating maple sap (with a sugar concentration of 2.5%) into maple syrup (with a sugar concentration of 67%), the Hg concentration would be only 0.1 ng g^{-1} , which is orders of magnitude lower than the safe level in food of 500 ng g^{-1} (Choi 2011). Plant materials generally are unlikely to contain enough Hg to pose a threat to human health, with the notable exception of rice (Meng et al. 2014; Brombach et al. 2017); predators high on the food chain are at greatest risk of Hg poisoning due to bioaccumulation (Driscoll et al. 2007, 2013).

The dendrochemistry of Hg could open a new avenue to investigate past impacts of Hg on terrestrial ecosystems and to predict future changes in Hg cycling in forests. If concentrations in wood were highest in the most recent rings, due to uptake from soil, we would expect Hg contamination of wood to persist beyond the current crop of trees. However, our modest results (four trees at the Hubbard Brook) suggest that Hg concentrations in recent tree rings are lower than in the older ones, reflecting improved air quality. If this pattern is widespread (Scanlon et al. 2020), we would predict that tree tissues will become increasingly free of Hg in the future. Predictions of the future trajectory of Hg concentrations in forest biomass are relevant to forest management, particularly regarding the fate of harvested materials, but also to Hg cycling, as coarse woody debris is a major flux of elements in unmanaged ecosystems.

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References

- Abreu, S. N., Soares, A. M. V. M., Nogueira, A. J. A., & Morgado, F. (2008). Tree rings, *Populus nigra* L., as mercury data logger in aquatic environments: case study of a historically contaminated environment. *Bulletin of Environmental Contamination and Toxicology*, 80(3), 294–299.
- Arnold, J., Gustin, M. S., & Weisberg, P. J. (2018). Evidence for nonstomatal uptake of Hg by aspen and translocation of Hg from foliage to tree rings in Austrian pine. *Environmental Science & Technology*, 52(3), 1174–1182.
- Bailey, S. W., Buso, D. C., & Likens, G. E. (2003). Implications of sodium mass balance for interpreting the calcium cycle of a forested ecosystem. *Ecology*, 84(2), 471–484.
- Bishop, K. H., Lee, Y. H., Munthe, J., & Dambrine, E. (1998). Xylem sap as a pathway for total mercury and methylmercury transport from soils to tree canopy in the boreal forest. *Biogeochemistry*, 40(2–3), 101–113.
- Blackwell, B. D., Driscoll, C. T., Maxwell, J. A., & Holsen, T. M. (2014). Changing climate alters inputs and pathways of mercury deposition to forested ecosystems. *Biogeochemistry*, 119(1–3), 215–228.
- Brombach, C. C., Manurut, P., Kolambage-Dona, P. P. P., Ezzeldin, M. F., Chen, B., Corns, W. T., et al. (2017). Methylmercury varies more than one order of magnitude in commercial European rice. *Food Chemistry*, 214, 360365. <https://doi.org/10.1016/j.foodchem.2016.07.064>.
- Chalmers, A. T., Argue, D. M., Gay, D. A., Brigham, M. E., Schmitt, C. J., & Lorenz, D. L. (2011). Mercury trends in fish from rivers and lakes in the United States, 1969–2005. *Environmental Monitoring Assessment*, 175(1–4), 175–191.
- Choi, Y. Y. (2011). International/national standards for heavy metals in food. *Government Laboratory (Australia)*, 1–13.
- Dennis, K. K., Uppal, K., Liu, K. H., Ma, C., Liang, B., Go, Y. M., & Jones, D. P. (2019). Phytochelatin database: a resource for phytochelatin complexes of nutritional and environmental metals. *Database*, volume 2019, baz083, <https://doi.org/10.1093/database/baz083>.
- Dickinson, N. M., Punshon, T., Hodkinson, R. B., & Lepp, N. W. (1994). Metal tolerance and accumulation in willows. Willow Vegetation Filters for Municipal Wastewater and Sludges, Swedish University of Agricultural Sciences, Uppsala, 121–127.
- Drevnick, P. E., Engstrom, D. R., Driscoll, C. T., Balogh, S. J., Kamman, N. C., Long, D. T., Muir, D. G. C., Parsons, M. J., Rolffhus, K. R., Rossmann, R., & Swain, E. B. (2012). Spatial and temporal patterns of mercury accumulation in lacustrine sediments across the Laurentian Great Lakes region. *Environmental Pollution*, 161, 252–260. <https://doi.org/10.1016/j.envpol.2011.05.025>.
- Driscoll, C. T., Han, Y. J., Chen, C. Y., Evers, D. C., Lambert, K. F., Holsen, T. M., et al. (2007). Mercury contamination in forest and freshwater ecosystems in the northeastern United States. *BioScience*, 57(1), 17–28.
- Driscoll, C. T., Mason, R. P., Chan, H. M., Jacob, D. J., & Pirrone, N. (2013). Mercury as a global pollutant: sources, pathways, and effects. *Environmental Science & Technology*, 47(10), 4967–4983. <https://doi.org/10.1021/es305071v>.

- Du, S. H., & Fang, S. C. (1982). Uptake of elemental mercury vapor by C3 and C4 species. *Environmental and Experimental Botany*, 22(4), 437–443.
- Ericksen, J. A., Gustin, M. S., Schorran, D. E., Johnson, D. W., Lindberg, S. E., & Coleman, J. S. (2003). Accumulation of atmospheric mercury in forest foliage. *Atmospheric Environment*, 37(12), 1613–1622.
- Engel, B. J., Schaberg, P. G., Hawley, G. J., Rayback, S. A., Pontius, J., Kosiba, A. M., & Miller, E. K. (2016). Assessing relationships between red spruce radial growth and pollution critical load exceedance values. *Forest Ecology and Management*, 359, 83–91.
- Engstrom, D. R., & Swain, E. B. (1997). Recent declines in atmospheric mercury deposition in the upper Midwest. *Environmental Science & Technology*, 31(4), 960–967.
- Frescholtz, T. F., Gustin, M. S., Schorran, D. E., & Fernandez, G. C. (2003). Assessing the source of mercury in foliar tissue of quaking aspen. *Environmental Toxicology and Chemistry: An International Journal*, 22(9), 2114–2119.
- Gabriel, W. J. (1982). Mini-tapping sugar maples for sap-sugar testing. Research Note NE-305. Broomall, PA: US Department of Agriculture, Forest Service, Northeastern Forest Experiment Station. NE-305. https://www.nrs.fs.fed.us/pubs/m/rm_ne305.pdf
- Greger, M., Wang, Y., & Neuschütz, C. (2005). Absence of Hg transpiration by shoot after Hg uptake by roots of six terrestrial plant species. *Environmental Pollution*, 134(2), 201–208.
- Grégoire, D. S., & Poulain, A. J. (2018). Shining light on recent advances in microbial mercury cycling. *FACETS*, 3(1), 858–879.
- Grigal, D. F. (2002). Inputs and outputs of mercury from terrestrial watersheds: a review. *Environmental Reviews*, 10(1), 1–39.
- Grigal, D. F. (2003). Mercury sequestration in forests and peatlands. *Journal of Environmental Quality*, 32(2), 393–405.
- Hanson, P. J., Lindberg, S. E., Tabberer, T. A., Owens, J. A., & Kim, K. H. (1995). Foliar exchange of mercury vapor: evidence for a compensation point. *Water, Air, and Soil Pollution*, 80(1–4), 373–382.
- Halman, J. M., Schaberg, P. G., Hawley, G. J., Hansen, C. F., & Fahey, T. J. (2014). Differential impacts of calcium and aluminum treatments on sugar maple and American beech growth dynamics. *Canadian Journal of Forest Research*, 45(1), 52–59.
- Hojdová, M., Navrátil, T., Rohovec, J., Žák, K., Vaněk, A., Chrástný, V., et al. (2011). Changes in mercury deposition in a mining and smelting region as recorded in tree rings. *Water, Air, & Soil Pollution*, 216(1–4), 73–82.
- Jung, R., & Ahn, Y. S. (2017). Distribution of mercury concentrations in tree rings and surface soils adjacent to a phosphate fertilizer plant in southern Korea. *Bulletin of Environmental Contamination and Toxicology*, 99(2), 253–257.
- Kamman, N. C., & Engstrom, D. R. (2002). Historical and present fluxes of mercury to Vermont and New Hampshire lakes inferred from ²¹⁰Pb dated sediment cores. *Atmospheric Environment*, 36(10), 1599–1609.
- Keinänen, S. I., Hassinen, V. H., Kärenlampi, S. O., & Tervahauta, A. I. (2007). Isolation of genes up-regulated by copper in a copper-tolerant birch (*Betula pendula*) clone. *Tree Physiology*, 27(9), 1243–1252.
- Kim, E. (1988). Radial growth patterns of tree species in relation to environmental factors. Ph. D. Dissertation. Graduate School, Yale University.
- Kronberg, R. M., Jiskra, M., Wiederhold, J. G., Björn, E., & Skyllberg, U. (2016). Methyl mercury formation in hillslope soils of boreal forests: the role of forest harvest and anaerobic microbes. *Environmental Science & Technology*, 50(17), 9177–9186.
- Laacouri, A., Nater, E. A., & Kolka, R. K. (2013). Distribution and uptake dynamics of mercury in leaves of common deciduous tree species in Minnesota, USA. *Environmental Science & Technology*, 47(18), 10462–10470.
- Laureysens, I., Blust, R., De Temmerman, L., Lemmens, C., & Ceulemans, R. (2004). Clonal variation in heavy metal accumulation and biomass production in a poplar coppice culture: I. Seasonal variation in leaf, wood and bark concentrations. *Environmental Pollution*, 131(3), 485–494.
- Lindberg, S. E., Meyers, T. P., Taylor Jr., G. E., Turner, R. R., & Schroeder, W. H. (1992). Atmosphere-surface exchange of mercury in a forest: Results of modeling and gradient approaches. *Journal of Geophysical Research: Atmospheres*, 97(D2), 2519–2528.
- Lindberg, S. E. (1996). Forests and the global biogeochemical cycle of mercury: the importance of understanding air/vegetation exchange processes. In *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances* (pp. 359–380). Springer, Dordrecht.
- Luo, Y., Duan, L., Driscoll, C. T., Xu, G., Shao, M., Taylor, M., Wang, S., & Hao, J. (2016). Foliage/atmosphere exchange of mercury in a subtropical coniferous forest in south China. *Journal of Geophysical Research: Biogeosciences*, 121(7), 2006–2016. <https://doi.org/10.1002/2016JG003388>.
- Manceau, A., Wang, J., Rovezzi, M., Glatzel, P., & Feng, X. (2018). Biogenesis of mercury–sulfur nanoparticles in plant leaves from atmospheric gaseous mercury. *Environmental Science & Technology*, 52(7), 3935–3948.
- Meng, B., Feng, X., Qiu, G., Anderson, C. W., Wang, J., & Zhao, L. (2014). Localization and speciation of mercury in brown rice with implications for pan-Asian public health. *Environmental Science & Technology*, 48(14), 7974–7981. <https://doi.org/10.1021/es502000d>.
- Naharro, R., Esbrí, J. M., Amorós, J. Á., García-Navarro, F. J., & Higuera, P. (2019). Assessment of mercury uptake routes at the soil-plant-atmosphere interface. *Geochemistry: Exploration, Environment, Analysis*, 19(2), 146–154.
- Navrátil, T., Nováková, T., Shanley, J. B., Rohovec, J., Matoušková, S., Vaňková, M., & Norton, S. A. (2018). Larch tree rings as a tool for reconstructing 20th century Central European atmospheric mercury trends. *Environmental Science & Technology*, 52(19), 11060–11068.
- Navrátil, T., Šimeček, M., Shanley, J. B., Rohovec, J., Hojdová, M., & Houška, J. (2017). The history of mercury pollution near the Spolana chlor-alkali plant (Neratovice, Czech Republic) as recorded by Scots pine tree rings and other bioindicators. *Science of the Total Environment*, 586, 1182–1192.
- Obrist, D., Johnson, D. W., Lindberg, S. E., Luo, Y., Hararuk, O., Bracho, et al. (2011). Mercury distribution across 14 US forests. Part I: Spatial patterns of concentrations in biomass,

- litter, and soils. *Environmental Science & Technology*, 45(9), 3974–3981.
- Obrist, D., Johnson, D. W., & Edmonds, R. L. (2012). Effects of vegetation type on mercury concentrations and pools in two adjacent coniferous and deciduous forests. *Journal of Plant Nutrition and Soil Science*, 175(1), 68–77.
- O'Connor, D., Hou, D., Ok, Y. S., Mulder, J., Duan, L., Wu, Q., et al. (2019). Mercury speciation, transformation, and transportation in soils, atmospheric flux, and implications for risk management: a critical review. *Environment International*, 126, 747–761.
- Risch, M. R., DeWild, J. F., Krabbenhoft, D. P., Kolka, R. K., & Zhang, L. (2012). Litterfall mercury dry deposition in the eastern USA. *Environmental Pollution*, 161, 284–290.
- Risch, M. R., DeWild, J. F., Gay, D. A., Zhang, L., Boyer, E. W., & Krabbenhoft, D. P. (2017). Atmospheric mercury deposition to forests in the eastern USA. *Environmental Pollution*, 228, 8–18.
- Scanlon, T. M., Riscassi, A. L., Demers, J.D., Camper, T. D., Lee, T. R., and Druckenbrod, D. L. (2020). Mercury accumulation in tree rings: observed trends in quantity and isotopic composition in Shenandoah National Park, Virginia. *Journal of Geophysical Research: Biogeosciences* 125, e2019JG005445.
- Slemr, F., Brunke, E. G., Ebinghaus, R., & Kuss, J. (2011). Worldwide trend of atmospheric mercury since 1995. *Atmospheric Chemistry and Physics*, 11(10), 4779–4787.
- Smith, K. T., & Shortle, W. C. (1996). Tree biology and dendrochemistry. In J. S. Dean, D. M. Meko, & T. W. Swetnam (Eds.), *Tree rings, environment, and humanity, Radiocarbon [press]* (pp. 629–635). Arizona: Tucson.
- Stamenkovic, J., & Gustin, M. S. (2009). Nonstomatal versus stomatal uptake of atmospheric mercury. *Environmental Science & Technology*, 43(5), 1367–1372.
- Swetnam, T. W., Thompson, M. A., & Sutherland, E. K. (1985). *Using dendrochronology to measure radial growth of defoliated trees*. US Department of Agriculture, Agriculture Handbook 639. 39 p.
- Temme, C., Blanchard, P., Steffen, A., Banic, C., Beauchamp, S., Poissant, L., Tordon, R., & Wiens, B. (2007). Trend, seasonal and multivariate analysis study of total gaseous mercury data from the Canadian atmospheric mercury measurement network (CAMNet). *Atmospheric Environment*, 41(26), 5423–5441.
- Tyree, M. T. (1983). Maple sap uptake, exudation, and pressure changes correlated with freezing exotherms and thawing endotherms. *Plant Physiology*, 73(2), 277–285.
- US Environmental Protection Agency. (1984). Definition and procedure for the determination of the method detection limit—Revision 1.11, 40 CFR Part 136, Appendix B.
- Wang, Y., & Greger, M. (2004). Clonal differences in mercury tolerance, accumulation, and distribution in willow. *Journal of Environmental Quality*, 33(5), 1779–1785.
- Wang, J. J., Guo, Y. Y., Guo, D. L., Yin, S. L., Kong, D. L., Liu, Y. S., & Zeng, H. (2011). Fine root mercury heterogeneity: metabolism of lower-order roots as an effective route for mercury removal. *Environmental Science & Technology*, 46(2), 769–777.
- Wang, J., Feng, X., Anderson, C. W., Wang, H., Zheng, L., & Hu, T. (2012). Implications of mercury speciation in thiosulfate treated plants. *Environmental Science & Technology*, 46(10), 5361–5368.
- Wang, X., Bao, Z., Lin, C. J., Yuan, W., & Feng, X. (2016). Assessment of global mercury deposition through litterfall. *Environmental Science & Technology*, 50(16), 8548–8557.
- Wild, A. D., & Yanai, R. D. (2015). Soil nutrients affect sweetness of sugar maple sap. *Forest Ecology and Management*, 341, 30–36.
- Wright, G., Woodward, C., Peri, L., Weisberg, P. J., & Gustin, M. S. (2014). Application of tree rings [dendrochemistry] for detecting historical trends in air Hg concentrations across multiple scales. *Biogeochemistry*, 120(1–3), 149–162.
- Yanai, R. D., McFarlane, K. J., Lucash, M. S., Kulpa, S. E., & Wood, D. M. (2009). Similarity of nutrient uptake and root dimensions of Engelmann spruce and subalpine fir at two contrasting sites in Colorado. *Forest Ecology and Management*, 258(10), 2233–2241.
- Yang, Y., Yanai, R. D., Montesdeoca, M., & Driscoll, C. T. (2017). Measuring mercury in wood: challenging but important. *International Journal of Environmental Analytical Chemistry*, 97(5), 456–467.
- Yang, Y., Yanai, R. D., Driscoll, C. T., Montesdeoca, M., & Smith, K. T. (2018). Concentrations and content of mercury in bark, wood, and leaves in hardwoods and conifers in four forested sites in the northeastern USA. *PLoS One*, 13(4), e0196293.
- Yang, Y., Meng, L., Yanai, R. D., Driscoll, C. T., Montesdeoca, M., Templer, P., et al. (2019). Climate change may alter mercury fluxes in northern hardwood forests. *Biogeochemistry*. <https://doi.org/10.1007/s10533-019-00605-1>.
- Yu, X., Driscoll, C. T., Warby, R. A., Montesdeoca, M., & Johnson, C. E. (2014). Soil mercury and its response to atmospheric mercury deposition across the northeastern United States. *Ecological Applications*, 24(4), 812–822.
- Zacchini, M., Pietrini, F., Mugnozza, G. S., Iori, V., Pietrosanti, L., & Massacci, A. (2009). Metal tolerance, accumulation and translocation in poplar and willow clones treated with cadmium in hydroponics. *Water, Air, and Soil Pollution*, 197(1–4), 23–34.
- Zhou, H., Zhou, C., Lynam, M. M., Dvonch, J. T., Barres, J. A., Hopke, P. K., Cohen, M., & Holsen, T. M. (2017). Atmospheric mercury temporal trends in the northeastern United States from 1992 to 2014: are measured concentrations responding to decreasing regional emissions? *Environmental Science & Technology Letters*, 4(3), 91–97.

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