Concentration, Content and Dendrochronology of Mercury in Northeastern Forests in USA

by

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Abstract

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Mercury (Hg) deposition affects remote areas such as forests, but the amount of Hg in trees is not well known, in part because Hg concentrations in wood are below detection limits of some methods. Solid samples can be directly analyzed by thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry through a Total Mercury Analyzer, but questions remain about sample preparation and instrumental parameters. I examined the effects of drying temperature during sample preparation using wood samples at the Hubbard Brook Experimental Forest in New Hampshire. Samples that were freeze-dried or oven-dried at 65 ˚C were suitable for Hg analysis, whereas oven-drying at 103 ˚C resulted in Hg losses, and air-drying resulted in Hg gains.

Having established suitable methods, I analyzed Hg in wood, bark, and foliage of eight tree species across four sites in the northeastern USA. Foliar concentrations of Hg averaged 16.3 ng g^{-1} among the hardwood species, which was significantly lower than values in conifers (mean of 28.6 ng g^{-1}) ($p < 0.001$). Similarly, bark concentrations of Hg were lower ($p < 0.001$) in hardwoods (7.7 ng g^{-1}) than conifers (22.5 ng g^{-1}). For wood, concentrations of Hg were higher in yellow birch (2.5 ng g^{-1}) and white pine (2.5 ng ng g^{-1}) than in the other species (mean of 1.4 ng g^{-1}) ($p < 0.0001$). Sites differed significantly in Hg concentrations of foliage and bark ($p = 0.02$) but not wood ($p = 0.60$); the concentration of Hg in wood depended more on species than site. The estimated Hg contents of tree tissues in hardwood stands were higher in bark (mean of 0.10 g ha^{-1}) and wood (0.16 g ha^{-1}) than in foliage (0.06 g ha^{-1}). In conifer stands, woody did not always contain more Hg than needles. I also determined the radial pattern of Hg concentrations in bole wood collected from New Hampshire. Concentrations of Hg in bole wood for American beech, sugar maple and yellow birch tended to increase first and then decreased from 1960 to 2015. This pattern is consistent with the temporal trends in Hg in watershed sediments in New Hampshire.

Keywords: wood mercury, sample preparation, mercury budget, mercury pool, temperate hardwood forests, temperature coniferous forests, dendrochemistry.

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Chapter 1: Introduction

1. Background

Mercury (Hg) is considered as a neurotoxic element because once it is oxidized and methylated, the methylmercury (MeHg) can be bioconcentrated and biomagnified into the upper levels of aquatic and terrestrial food chains. Negative health effects and risks will then be introduced to wildlife and humans (Chan et al., 2003; Mergler et al., 2007; Chen et al., 2008).

Forested ecosystems generally accumulate Hg but also release Hg back to the atmosphere or aquatic systems. Understanding Hg cycling in forests would help better understand Hg cycling in terrestrial ecosystems and thus the global Hg cycle.

2. Source of mercury in forests and mercury deposition

Anthropogenic emissions of Hg have doubled Hg emissions in terrestrial ecosystems globally (Mason and Sheu 2002). Anthropogenic Hg emission is usually from point sources which may come from coal-fired electric utilities, municipal incinerators, industrial manufacturing, wastewater treatment plants; and non-point sources such as improper disposal of consumer products (e.g. batteries, Hg switches) and automobile gas emissions. Mercury emitted into the atmosphere has three forms: elemental Hg (Hg^0) with a residence time of 0.5-2 yrs, reactive gaseous Hg (e.g. $HgCl_2$) with a residence time of 0.5-2 days, and particulate Hg (Hg^P) with a residence time of 0.5-3 days (Bergan et al., 1999; Seigneur et al., 2004; Selin et al., 2007). Elemental Hg is the dominant form of Hg in the atmosphere and can travel long distances to remote areas because of its long residence time (Schroeder and Munthe 1998).

Atmospheric Hg deposition in forests includes two pathways, dry and wet deposition. Dry deposition consists of gaseous elemental Hg and particle-bound Hg. Wet deposition refers to Hg^{2+} in rain and snow. In northeast America, dry Hg deposition is greater than wet Hg deposition

in 92% of the area because of the high uptake rate of Hg^0 by the forest canopy (Rea et al., 2002). Dry deposition of gaseous elemental Hg has reached 11 μg m^{-2} yr^{-1} annually in the northeastern US (Rea et al., 2002) and 7.2 μg m^{-2} yr^{-1} in New Brunswick, Canada (Miller et al. 2005). Dry deposition of total Hg can reach 10.5-20.1 μg m^{-2} yr^{-1} in forests in northwest Ontario (Graydon et al. 2008). Wet Hg deposition has been estimated to be from 3.8 to 12.6 μg m^{-2} yr^{-1} in the northeastern US (Rea et al., 2002; Driscoll et al., 2007b; Choi et al., 2008).

Environmental controls have decreased the amount of Hg emitted into the atmosphere and thus decreased the deposition rate. Throughout the United States, anthropogenic Hg emissions declined by 77% from 1990-2014 (Zhang et al. 2016). A decline in wet Hg deposition and Hg air concentrations was reported in 19 sites across North America using data from 1997 to 2013 (Weiss-Penzias et al. 2016). Dry Hg deposition rates at Underhill, VT, and Huntington Forest, NY, in the Northeastern US decreased from 1992 to 2014 associated with declines in regional emissions (Zhou et al. 2017a). Wet Hg deposition in the Adirondack region of NY was also reported to decrease from 2000 to 2015 (Gerson and Driscoll 2016; Mao et al., 2017).

3. Importance of forests to Hg cycling in the environment

3.1 Hg fluxes from atmosphere to forests

Plants can absorb atmospheric Hg^0 via stomata on both sides of the leaf (Lindberg et al., 1992; Hanson et al., 1995; Lindberg 1996; Laacouri et al., 2013). Stomatal conductance, which is correlated with transpiration, photosynthesis, and growth rates, has been considered as an important predictor of Hg^0 uptake by foliage. Larger leaf area or higher stomatal conductance in hardwood species has been found to facilitate foliar uptake of atmospheric Hg^0 in a greenhouse experiment (Millhollen et al. 2006). Once Hg^0 is absorbed by a leaf, it can be oxidized and bound tightly to the leaf tissue for C_3 and C_4 plants (Du and Fang 1982), and for quaking aspen

(*Populus tremuloides* Michx.) in Minnesota (Frescholtz et al., 2003). However, whether Hg is methylated or demethylated within tree tissues has been less studied. Methyl-Hg has been reported to constitute ~1% of the total Hg in foliage and the concentration of MeHg is diluted over time due to foliar growth or demethylation within foliage for quaking aspen in Minnesota (Ericksen et al. 2003). Foliage can accumulate Hg over the growing season for hardwood species (Rea et al., 2002; Ericksen et al., 2003; Bushey et al., 2008) and over years for conifers (Rasmussen et al., 1991; Rasmussen 1995). Foliage within the understory had larger Hg concentration than foliage within the overstory in Adirondack regions in New York (Bushey et al. 2008). Nonstomatal uptake of atmospheric Hg can also occur because gaseous Hg and particular-Hg can be absorbed at the foliar surface and then transferred into cuticles (Stamenkovic and Gustin 2009).

Soils receive both dry and wet deposition of atmospheric Hg. Soil Hg can be divided into mineral Hg, Hg loosely absorbed to the surface of soil particles (Hg^0 and Hg^{2+}), and Hg bound to organic carbon complexes (O-Hg) (Smith-Downey et al. 2010). Accumulation of Hg in soils depends on geographic factors such as latitude, longitude, soil temperature, annual precipitation. Colder soils had a slower decomposition rate of organic matter, and thus accumulated more Hg in a study of 14 sites across USA (Obrist et al. 2011). Warmer soils accumulate less Hg in party because of higher Hg^0 volatilization (Schlüter 2000). Soils receiving more precipitation accumulate more Hg because wet deposition is a major pathway of Hg entering from atmosphere to soils (Demers et al., 2007; Obrist et al., 2011; Juillerat et al., 2012; Stankwitz et al., 2012). Accumulation of Hg in soil also depends on soil properties such as soil organic matter, pH, iron, clay and metal oxides. Soils with more organic matter accumulate more Hg because of the higher sorption capacity of Hg in both organic and mineral horizons (Gabriel and Williamson 2004).

Organic soils with higher Hg concentrations were correlated with lower soil pH in northeastern USA (Richardson et al. 2013) but also with higher soil pH in terrestrial watersheds in a review article (Gabriel and Williamson 2004). Mineral soils with larger iron oxides accumulate more Hg because of the increased surface binding area (Schuster, 1991; Yin et al., 1996; Han et al., 2003; Gabriel and Williamson, 2004; Liao et al., 2009; Obrist et al., 2011).

Plants also capture and retain atmospheric Hg in their bark (Obrist et al., 2009; Rykowska and Wasiak 2011; Guéguen et al., 2012). A recent study of Hg speciation in bark from Australia pine (*Pinus nigra* J.F.Arnold) found that tree bark first captured particulate Hg or gaseous Hg on the surface, then Hg was partly bound to thiol-containing molecules or tannins (Chiarantini et al., 2016; 2017). The Hg formed in the bark included inorganic species (e.g. HgS), and the organic-bound fraction increased from outer bark layer to inner (Chiarantini et al. 2017).

Moss and lichens on trees can capture trace metals via ion-exchange and chelation from rain and atmospheric particles (Rühling and Tyler 1984). Thus, they have been proposed as biomonitors for Hg contaminations (Thompson et al., 1987; Mitchell et al., 2000; Blagnytė and Paliulis 2010; Samecka-Cymerman et al., 2013).

3.2 Hg fluxes from forests to atmosphere

Plants can reemit Hg^0 back to the atmosphere via foliage because 1) the exchange of Hg^0 between foliage and the atmosphere is bidirectional, 2) deposited of Hg on the leaf can be photoreduced to Hg^0 (Graydon et al., 2006; 2012), and 3) Hg^0 is transported from soil to foliage by transpiration and then to be emitted to the atmosphere (Bishop et al., 1998; Luo et al., 2016).

Soils can emit Hg^0 from the soil surface which is called soil Hg evasion. The evasion process usually includes three steps (Zhang and Lindberg 1999): 1) production of Hg^0, 2) diffusion or mass transport of Hg^0 from deeper soil to the soil surface, and 3) transport of Hg^0

across the soil-air boundary layer into atmosphere. Factors influencing soil Hg evasion include soil physicochemical characteristics and meteorological variables. Forest soils with background Hg concentration < 100 ng g^{-1} have low Hg evasion (Carpi and Lindberg, 1998; Kuiken et al., 2008a, 2008b; Choi and Holsen, 2009a; 2009b). Soils with larger content of metal oxides (e.g. Fe, Al) (Zhang and Lindberg 1999) or larger content of organic matter or lower pH (Yang et al. 2007) have lower soil Hg evasion due to the high affinity of Hg binding to organic matter. Higher soil temperature increased Hg evasion (Gabriel et al., 2006; Park et al., 2013). Soils with higher moisture content produce more Hg evasion because water molecules can displace Hg^0 from mineral soil surfaces (Zhang and Lindberg 1999). Higher solar radiation increases Hg evasion by converting Hg^{2+} to Hg^0 and releasing of soil bound Hg to the air (Carpi and Lindberg 1997; Zhang and Lindberg 1999; Gustin et al., 2002; Xin and Gustin 2007; Park et al., 2013).

Tree bark has been found to emit Hg^0 with a rate of 1.9 -10.8 ng m^{-2} h^{-1} for red maple (*Acer rubrum* L.), yellow-poplar (*Liriodendron tulipifera* L.), chestnut oak (*Quercus prinus* L.) and white oak (*Quercus alba* L.) (Hanson et al. 1997). Emission of Hg^0 from bark has been estimated to be less than 10% of all Hg^0 emission from the forests (> 90% is from foliage and soils) (Hanson et al. 1997).

3.3 Hg fluxes from forests to aquatic systems

Soils can release soluble inorganic Hg(II) to surface water. The Hg^{2+} transported from soil water to streams and lakes can then be methylated and accumulated in the aquatic food chain. Soils with more dissolved organic carbon had higher Hg concentrations in soil water because of Hg binding with dissolved organic matter (Driscoll et al., 1995; Scherbatskoy et al., 1998; Brigham et al., 2009). Other soil characteristics such temperature, moisture, pH,

competitive cations, metal oxides, sulfur content, selenium and bromine have also been reported to influence Hg mobility in soils (Figure 1).

3.4 Mercury emission and runoff due to disturbance

Natural and human disturbances can affect Hg emission from forests to the atmosphere and runoff to the downstream. Wildfire in forested areas reemits large amounts of Hg^0 from burned vegetations, soils and litter across the world (Harden et al., 2004; Brunke et al., 2001; Friedli et al., 2001; Friedli et al., 2003a; Friedli et al., 2003b; Sigler et al., 2003; Mailman and Bodaly 2005; Engle et al., 2006; Biswas et al., 2007; Dicosty et al., 2006; Burke et al., 2010; Carpi et al., 2014). Wildfire also elevates both total Hg and MeHg concentrations in downstream water (Caldwell et al., 2000; Amirbahman et al., 2004; Kelly et al., 2006) because of the large loss of carbon and Hg from soils and vegetation (Biswas et al., 2008; Navrátil et al., 2009; Mitchell et al., 2012; Homann et al., 2015). Forest harvesting can also increase soil Hg evasion (Mazur et al. 2014) by altering soil temperature, moisture and solar radiation. Harvesting activities such as thinning and clear-cutting can also decrease Hg concentrations in both organic and mineral soils (Homann et al. 2015). Other disturbances such as ice storm events also destroy aboveground vegetations and disturb soils, which could introduce large amounts of Hg to the environment.

4. Roles of trees in Hg cycling inside forests

4.1 Hg fluxes from soils to trees

Roots have been observed to absorb Hg^{2+} from soils and store Hg in cell walls and membranes in experiments with radiotracer techniques (Murray and Kidby 1975) and solution culture (Beauford et al., 1977). Mercury has been detected in xylem sap of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* L.) (Bishop et al. 1998). Mercury usually binds

with sulphur and nitrogen ligands, and then enters the cell through ionic channels (Blazka and Shaikh, 1992). Different orders of roots have different roles in Hg absorption and translocation. Lower-order roots have higher Hg concentration than high-order roots (Wang et al. 2012) due to their larger root area and higher absorptive potential (Rewald et al. 2011) whereas high-order roots are responsible for translocating Hg^{2+} up to the shoots.

Soil characteristics influence the uptake Hg by roots. Roots can accumulate more Hg in soils containing higher Hg concentrations (Millhollen et al. 2006), higher sulfur concentration, lower carbon concentration (Wang et al. 2012) and lower selenium concentration in a greenhouse experiment (Zhang et al. 2012). Two types of bacteria, mercuric reductase (merA) and organomercurial lyase (merB), were observed to transform the Hg^{2+} into gas Hg to create a mercury resistant root system (Bizily et al., 2000; Barkey et al., 2010).

4.2 Hg translocation within trees

Translocation of Hg from foliage to bole wood has been reported for red pine (*Pinus resinosa* Ait.) (Fleck et al. 1999), Austrian pine (*Pinus nigra* L.) (Arnold et al. 2017) and in a review (Grigal 2003). On the other hand, translocation of Hg from roots to aboveground tissues has been found to be limited in quaking aspen (Ericksen et al. 2003) and sawgrass (*Cladium jamaicense*) (Mao et al. 2013).

Uptake of Hg from soil solutions via tree roots to bole wood have been reported for Scots pine (*Pinus sylvestris* L.), Norway spruce (*Picea abies* L.) (Bishop et al. 1998).

4.3 Hg fluxes from trees to soils

Litterfall Hg flux depends on both foliar Hg concentration and the litterfall mass. The decomposition of leaf litter has been observed to stimulate MeHg production in soils (Hall et al. 2004). Throughfall is the wash-off of Hg deposited previously on the leaf surface, which is

another important input of Hg to forest floor. Input of Hg via throughfall depends on the amount of rain or snow, dry Hg deposition rate, leaf surface area and adsorption of Hg to foliage. Increased throughfall Hg has been reported during the growing season compared to other months (Iverfeldt 1991). Conifer stands exhibit greater throughfall Hg fluxes than hardwood stands (Blackwell et al. 2015).

Litterfall and throughfall dominate the input of total Hg and MeHg to forest soils in the Adirondacks of New York (Demers et al., 2007; Bushey et al., 2008), Acadia National Park in Maine (Sheehan et al. 2006), western Ontario (St. Louis et al. 2001), northern Minnesota (Grigal et al. 2000) and Vermont (Rea et al. 1996). The ratio of mean annual Hg flux in precipitation to throughfall to litter Hg flux is 1:1.5:1.5 (Sheehan et al., 2006) and 1:1.8:2.2 in mixed forest stands (Grigal 2002); and 1:1.5:3 in conifer forests (Munthe et al., 1995). Mercury inputs to the forest floor in deciduous forests are split evenly between litterfall (~60%) and throughfall (~40%) (Lindberg, 1996; Rea et al., 1996; Grigal et al., 2000; St. Louis et al., 2001; Demers et al., 2007).

Ionic Hg can export via dead or decomposed roots caused by root mortality. The rate of Hg export due to root mortality or turnover has been less reported. The Hg flux from fine root was estimated to be 12.0−53.5 mg ha^{-1} yr^{-1}, much larger than the leaf litter return flux (7−27.1 mg ha^{-1} yr^{-1}) in China (Wang et al. 2012).

5 Comparison of major Hg pools and fluxes in the forested ecosystems

Concentrations of Hg in hardwood foliage have been reported to increase from spring bud break to autumn before leaf fall in Vermont and Michigan (2 to 44 ng g^{-1}, Rea et al. 2002) and in Adirondack Mountains of New York State (2 to 50 ng g^{-1}, Bushey et al., 2008; Blackwell et al., 2014). Concentrations of Hg in conifer needles have been reported to increase ~ 5-fold

during growing season (Blackwell et al. 2014) and again increase ~ 2-fold annually as needles are retained on trees (Hutnik et al., 2014; Nasr and Arp 2015).

Concentrations in tree tissues varies by tissue type, with litter or late-season leaf > bark > branches > wood > roots. Concentrations of Hg have been reported to be 21 – 59 ng g^{-1} in litter in a study of 23 sites across the eastern USA (Risch et al., 2012), 1.2 - 60 ng g^{-1} in bark in a review (Grigal 2003), 1- 57 ng g^{-1} in branches in a study of 14 sites across USA (Obrist et al. 2011), 0.6 – 20 ng g^{-1} in wood in a review (Grigal 2003), and 0.12 – 0.87 ng g^{-1} in roots in China (Wang et al. 2012).

Concentrations of Hg range from 68 to 250 ng g^{-1} in organic soils and from 9 to 147 ng g^{-1} in mineral soils (Grigal 2003; Obrist et al., 2011; Blackwell et al., 2014; Yu et al., 2014).

The magnitude of annual Hg fluxes in the forests varies by pathways with litterfall (4 – 88 μg m^{-2}, Lindberg 1996; Rea et al., 1996; Grigal et al., 2000; Rea et al., 2002; Risch et al., 2012) > atmospheric dry deposition (37 μg m^{-2}, Xu et al. 2000) > atmospheric wet deposition (4.4 – 19.7 μg m^{-2}, Risch et al., 2012) > throughfall (6.9 and 18.2 μg m^{-2}, Blackwell et al. 2014) > Hg emission leaf transpiration (1.7 and 9.2 μg m^{-2}, Luo et al. 2016) > root turnover (1 – 5 μg m^{-2}, Wang et al. 2012) > soil Hg evasion (-0.1 and 7 μg m^{-2}, Choi and Holsen 2009a; Yu et al., 2018) > soil leaching (0.25 – 0.86 μg m^{-2}, Driscoll et al. 2014). Annual fluxes of MeHg have been reported to be only 0.8% of litterfall total Hg fluxes (Risch et al. 2012).

6. Dendrochemistry

Dendrochemistry has been studied to reconstruct historical air pollution with the assumption that each growth ring stores the pollutants that are available to the tree during that year. Most dendrochemical studies focused on trace metals such as copper, cadmium, lead and

zinc (Baes and McLaughlin 1984; Hagemeyer and Schäfer 1995; Watmough and Hutchinson 2002). Studies examining Hg in trees rings commenced in the early 2000s.

Radial patterns of Hg concentrations in tree rings of black spruce (*Picea mariana* Mill. B.S.P) in Quebec Canada (Zhang et al. 1995), pine (*Pinus* spp.) in Nevada and California USA (Wright et al. 2014) and Czech Republic (Navrátil et al. 2017), black poplar (*Populus nigra* L.) in Portugal (Abreu et al. 2008), Norway spruce (*Picea abies* L.) and European beech (*Fagus sylvatica* L.) in central Czech Republic (Hojdová et al. 2011) have been found to be consistent with historical patterns of atmospheric Hg pollution. On the other hand, radial pattern of Hg in tree rings of maple (*Acer* spp.), red oak (*Quercus rubra* L.), eastern cottonwood (*Populus deltoides*) and willow (*Salix* spp.) in Ontario Canada (Siwik et al. 2010) were found not to reflect any trends in atmospheric Hg concentrations which the authors attributed to radial translocation of Hg across growth rings. Thus, examining more tree species in other locations would help improve our understanding of using dendrochemistry to monitor historical Hg deposition trend.

7. Study objectives

The northeastern US is an important receptor of atmospheric Hg deposition mainly because of the large surface area of forest foliage that collects Hg. Soil and atmospheric Hg have been intensively studied but not Hg concentrations and pools in tree components.

This project started in 2014 with exploring an appropriate way to detect Hg concentration in tree wood which included sample preparation and analysis. In 2015, I conducted field work in four different forests: Huntington Wildlife Forest in New York, Sleepers River Research Watershed in Vermont, Hubbard Brook Experimental Forest in New Hampshire, and Bear Brook Watershed in Maine, to sample different tree components in both hardwood sand conifer stands

at those four sites. In 2015, tree disks were acquired to study the dendrochemistry of Hg for different tree species at the Hubbard Brook in New Hampshire.

This project had the following objectives: 1. Determine the preparation and analytical methods to accurately quantify Hg in bole wood. 2. Determine the Hg concentrations in three tissue types of eight tree species in four sites. 3. Compare Hg pools among tissue types and between conifer and hardwood stands. 4. Determine whether Hg concentration in tree rings can be used to monitor historical changes in atmospheric Hg pollution. This project fills a gap in knowledge of Hg in aboveground tree components in the northeastern USA to improve our understanding in the importance of trees in Hg cycling in forests.

Chapter 2: Measuring mercury in wood: challenging but important

Abstract

Mercury (Hg) in tree wood has been overlooked, in part because concentrations are so low as to be below detection limits of some analytical methods, but it is potentially important to forest ecosystem processes and budgets. I tested methods for the preparation and determination of Hg in tree wood by analyzing samples of four tree species at the Hubbard Brook Experimental Forest, New Hampshire, USA, using thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry (USEPA Method 7473). Samples that were freeze-dried or oven-dried at 65 ˚C were suitable for determination of Hg, whereas oven-drying at 103 ˚C resulted in Hg losses, and air-drying resulted in Hg gains, presumably due to sorption from indoor air. Mean (± SE) concentrations of Hg tree bolewood were 1.75 ± 0.14 ng g^{-1} for American beech, 1.48 ± 0.23 ng g^{-1} for sugar maple, 3.96 ± 0.19 ng g^{-1} for red spruce, and 4.59 ± 0.06 ng g^{-1} for balsam fir. Based on these concentrations and estimates of wood biomass by species based on stand inventory, I estimated the Hg content of wood in the reference watershed at Hubbard Brook to be 0.32 g ha^{-1}, twice the size of the foliar Hg pool (0.15 g ha^{-1}). Mercury in wood deserves more attention and is feasible to measure using appropriate techniques.

Keywords: *Fagus grandifolia* Ehrh., *Acer saccharum* Marsh., *Picea rubens* Sarg., *Abies balsamea* (L.) Mill., wood mercury, sample preparation

1 Introduction

Mercury (Hg), a neurotoxic pollutant, has increased greatly in the environment due to emissions from anthropogenic activities such as coal combustion and gold mining (Krabbenhoft and Sunderland 2013). A potentially important but poorly characterized source of Hg emissions

is biomass burning (Friedli et al. 2009). Mercury has been studied extensively in aquatic ecosystems, but is less well described in forests, although forests are important receptors and biological Hg hotspots largely occur in forested regions (Evers et al., 2007; 2011).

Studies have been conducted in forest ecosystems to determine Hg concentrations in tree foliage (Rea et al., 2002; Ericksen et al., 2003; Bushey et al., 2008; Siwik et al., 2009), leaf litter (Sheehan et al., 2006; Risch et al., 2012; Blackwell et al., 2014) and bark (Obrist et al., 2009; Guéguen et al., 2012). Mercury concentrations in wood were lower than values in the foliage or branches in a study of 14 forest sites across the United States (Obrist et al. 2011). Because wood is the largest component of forest biomass, it can represent a larger Hg pool than foliage. Thus, quantifying concentrations in wood is important to Hg budgets in forests. Current studies of concentrations of Hg in wood are often reported for conifer species (Zhang et al., 1995; Abreu et al., 2008; Wright et al., 2014), whereas the reported values in hardwood species are often below the analytical detection limits (Siwik et al., 2010; Obrist et al., 2011). As Hg concentrations in wood are low relative to other tree tissues, it is important to understand the consequences of choices of instrumental techniques, size of the sample, and sample preparation.

The method of cold vapor atomic fluorescence spectrometry (CV AFS) (US EPA 2002) used by Siwik et al (2010), like inductively coupled plasma-atomic emission spectrometry (US EPA 1996), requires a liquid sample, which might be 1% of the concentration of the tissue sample prior to digestion and dilution. Solid samples can be analyzed directly by thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry through a direct Hg analyzer, giving much lower detection limits (US EPA 2007). However, if too small a mass of sample is analyzed, values will still be below detection (Obrist et al. 2011). Also, if too large a mass of sample is analyzed, the sample itself can produce interference due to

high carbon content. Soot can form due to incomplete combustion of organic matter, decreasing the precision of the analysis and shortening the lifetime of the instrument.

Samples are commonly oven dried before analysis to allow the results to be reported on a dry-weight basis. One study of soil preparation found greater Hg losses upon oven drying (24%) than air drying (3-8%) (Hojdová et al. 2015), whereas peat samples lost more Hg upon oven drying (8-10%) than air drying, which increased Hg by 2% (Roos-Barraclough et al. 2002). Contamination of samples during air drying was attributed to sorption from the atmosphere.

The effects of sample preparation on bole wood have not previously been reported. Freeze-drying is a standard procedure of pretreatment for measuring Hg in tree tissues, but many wood samples that were previously air-dried or oven-dried could be appropriate for Hg determination if these approaches could be validated.

The purpose of this study was to determine the methods necessary to accurately quantify Hg in bole wood, using four North American tree species. I analyzed wood tissue samples by thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry, using a direct Hg analyzer. I determined the relationship between aliquot size and detection limits using dosing techniques. I evaluated the effect of air-drying and oven-drying samples on Hg recovery, compared to freeze-drying samples prior to analysis, which is the standard procedure. Because we observed Hg contamination in air-dried samples, air-drying was tested in multiple labs and locations to determine whether this procedure should generally be avoided.

2 Materials and methods

2.1 Sample source

Tissue samples were collected from the dominant species, American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marshall.), red spruce (*Picea rubens* Sarg.) and balsam fir (*Abies balsamea* (L.) Mill), at the Hubbard Brook Experimental Forest in the White Mountain National Forest in central New Hampshire. Soils are well drained Spodosols developed in glacial drift. Average temperature is -9˚C in January and 18˚C in July; annual average precipitation is 1400 mm (Bailey et al. 2003).

2.2 Sample collection and preparation

Samples for method comparison: One tree > 10 cm in diameter at breast height (1.3 m) of each species (beech, maple, spruce, and fir) was felled, and cross-sectional disks about 5 cm in thickness were cut near breast height in July 2014. Samples were stored in Ziploc bags and transported on ice in a cooler to the laboratory. The sawn surfaces were shaved with a plane and rinsed with methanol. Samples were stored frozen before further processing. From each disk, dedicated stainless-steel drill bits were used to obtain a homogenized sub-sample of wood particles. I did not sample the dead heartwood or dark wood at the center of the disk, which might differ in Hg concentration (Siwik et al., 2010; Wright et al., 2014). To prevent cross contamination, drill bits were rinsed with methanol before processing each disk.

From each of the four sampled trees, five replicates of ~0.8 g were prepared for each of five different processing methods: fresh, air drying, freeze drying, and oven drying at 65˚C and 103˚C. Fresh samples were analyzed immediately. Freeze-dried samples were dried at -80˚C and 7 Pa for five days, using FreeZone Plus 6 Freeze Dry System (Labconco, Kansas City, MO). Air-dry samples were dried in covered foil trays in a lab drawer for a week. Oven dry samples were

dried at 65˚C or 103˚C in an oven for two days. Samples were weighed before drying and after drying.

Samples for air-dry contamination test: To test for Hg contaminations during air drying, we used an additional disk cut near breast height from one sugar maple tree in August 2015. Saw-dust size samples of ~0.8 g were prepared by the same methods described above. Triplicate samples were dried in each of seven locations: a clean room at Syracuse University in New York; a drying room at the State University of New York College of Environmental Science and Forestry; a soil room at the Coweeta Hydrological Laboratory in North Carolina; a garage containing sample drying racks at the Bartlett Experimental Forest in New Hampshire; and the barn, the archive building, and soil sample processing room at the Hubbard Brook Experimental Forest in New Hampshire. All the locations were heated (~20˚C) except the garage at Bartlett and barn at Hubbard Brook, which were unheated (~5˚C). Samples were stored in folded foil trays to protect them from dust deposition during the drying period. Two sets of triplicate samples were used as controls. For minimal contamination, one set was kept frozen. For extreme contamination, one set was dried in a closed chamber with air exposed to liquid Hg. The concentration of mercury in the atmosphere of the closed chamber was measured every week (four times in total) on a 10 μL air sample using a Mercury Vapor Analyzer (Tekran 2537A, Canada). The average concentration was 6480 ng m^{-3}.

After air drying for 30 days (33 days for samples at Hubbard Brook), all the samples were freeze dried before analysis to eliminate differences in moisture content.

2.3 Hg determination and detection limits

I conducted the analyses by thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry (US EPA 2007), using a Milestone DMA 80 direct Hg

analyzer (Shelton, CT). This method requires a smaller sample size and less preparation than other methods (Table 1). Parameter settings were: drying temperature at 300 ˚C, drying time at 60s, decomposition temperature at 925˚C, decomposition time at 270s, waiting time at 70s, and amalgam time at 18s. For each sample, two replicate samples of ~ 100 mg of tissue were weighed into tared nickel boats and auto-loaded into the instrument. About 5 -10 mg of aluminum oxide (Al_2O_3) was added to each tissue sample to ensure that the samples were fully combusted. The usage of aluminum oxide is recommended by the manufacturer to slow the combustion process, which facilitates complete burning of samples high in organic matter and increases the lifetime of the analytical tube of the instrument. The Hg concentration reported is the average of the two replicate samples. A standard reference material (NIST 1515 apple leaves) was used to test the dosing technique. Five aliquots were accumulated as one burn, to be compared with the burn with one aliquot.

2.4 Quality control

The certified reference material I used for quality control was NIST 1515, apple leaves. This CRM was validated for Hg analysis by CVAAS (cold-vapor atomic absorption spetrometry) and RNAA (radiochemical neutron activation analysis). Before running tissue samples, I analyzed 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, ~5 mg, 44 ± 4 ng g^{-1}) and one method blank sample (with Al_2O_3), to verify the calibration curve; I did not proceed with sample analysis unless the difference between measured and certified values of our quality control samples was < 10%. After every 10 wood samples, I ran continuing calibration verifications (NIST 2976) and continuing calibration blanks. A sample batch consisted of a

method blank, a quality control sample (NIST 1515), a duplicate, a matrix spike and a matrix spike duplicate. The matrix spike was a wood sample matrix spiked with a standard reference material (NIST 2976). The average recovery for Hg was 99 % (n =32, rsd = 8%) of NIST 2976, 100 % (n = 16, rsd = 5%) of DORM-2, 100 % (n =8, rsd = 5.7%) of NIST 1515 and 107 % (n =8, rsd = 14%) of the matrix spike, which were all within the accepted range of values. This information indicated there was no interference during the analysis. The blanks and the method blank had a Hg concentration of 0.01± 0.02 pg g^{-1}. Thus, I did not perform standard additions.

2.5 Data analysis

The moisture content of wood samples was calculated as the weight loss on drying divided by the fresh weight. The moisture content of the five replicates determined under each drying condition were compared with values determined by freeze-drying samples, which is the method that removes the most moisture (Table 2). To calculate Hg concentrations on a freeze-dried mass basis, we corrected the measured concentrations using the remaining moisture content under other drying conditions.

To test the effect of the five drying treatments on moisture loss of wood samples, I used one-way ANOVA separately for each species, using the five replicates for each treatment. I used the same model to examine the effect of drying treatment on wood Hg concentrations. I tested the normality of the residuals in this and other analyses using the Shapiro-Wilk test.

To test for differences in Hg concentration in sugar maple wood samples dried in different locations, I used one-way ANOVA, using three replicates dried at each location. Tukey's honestly significant difference was used to compare means.

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

3 Results

3.1 Detection limits and dosing technique

The instrument detection limit (IDL) is the smallest quantity of Hg that can be detected by the analytical instrument. The IDL for Method 7473 (US EPA 2007) was calculated using the U.S. Environmental Protection Agency Method Detection Limit procedure found in Title 40 Code of Federal Regulations Part 136 (US EPA 2011), where the Student's t value was multiplied by the standard deviation of concentrations of seven replicate samples. I analyzed seven blanks, which had a mean Hg content of 0.009 ng and a standard deviation of 0.002 ng. Thus, the IDL was 0.01 ng.

The Method Detection Limit (MDL) is the smallest quantity of Hg that can be quantified with the method. To calculate the MDL, I analyzed seven replicates of 5 mg of a standard reference material (NIST1515-apple leaves) with a multiplication factor of 3.14 derived from a T table. The mean Hg content was 0.22 ng (44 ng g^{-1} in units of concentration) with a standard deviation of 0.01 ng (0.41 ng g^{-1}). Thus, the MDL was 0.05 ng in units of mass (1.27 ng g^{-1}). The IDL and MDL should be reported in units of mass because the calibration curve is based on mass. The MDL can be calculated in units of concentration but the result is specific to the concentration of the material analyzed.

Dosing is a technique that accumulates multiple aliquots as one burn to increase the absorbance for detection in the direct Hg analyzer. Five aliquots were dosed as one burn, which increased of absorbance by a factor of 5 (Table 3). This approach shows that wood samples with Hg concentrations that are below the detection limits we report using one aliquot could be analyzed successfully by increasing the effective mass of the sample.

3.2 Sample preparation and Hg concentrations

Freeze-drying resulted in greater moisture loss than air-drying or oven-drying ($p < 0.001$) (Table 2). The freeze-dried samples lost 11 - 28% of their fresh weight, depending on the species, averaged over the five replicates of each species. Oven-drying removed almost as much moisture as freeze-drying, with moisture losses of 9 - 26% for both drying temperatures. Drying at 103 ˚C removed only 0.7% more of the fresh weight, on average, than drying at 65 ˚C. Air-drying resulted in moisture losses of only 3-15% of the fresh weight. I used the mass loss from the freeze-dried samples as the total moisture content, and corrected the measured Hg concentration of the samples prepared by other drying treatments using the difference in average moisture contents of the five replicate samples in that drying treatment compared to the freeze-drying treatment.

Concentrations of Hg in samples that were analyzed fresh, freeze-dried, or oven-dried at 65 ˚C were in close agreement after correcting for moisture content for all four species (Figure 2). Thus it appears that samples could be analyzed fresh, freeze-dried, or oven-dried at low temperature without altering Hg concentrations by more than 4%. The difference in Hg concentrations for the different preparation treatments was significant for American beech ($p < 0.001$) and balsam fir ($p = 0.01$), but not for sugar maple ($p = 0.10$) or red spruce ($p = 0.20$). For American beech and sugar maple, concentrations of Hg were overestimated by 34 to 45% in the air-dry samples and were underestimated by 44 to 66% in the samples oven-dried at 103 ˚C, compared to Hg concentrations in the freeze-dried samples. For red spruce and balsam fir, concentrations of Hg were higher in the air-dry samples, but by only 6.1 to 6.5%, and they were only 9.9 to 12% low in the samples oven-dried at 103 ˚C.

Although Hg losses due to oven-drying at 103 ˚C were greater in the two hardwood trees than the two conifers when reported as a percentage of the concentration, they were more similar across samples when reported in units of concentration: 1.1 ng g^{-1} for American beech and 0.4 to 0.5 ng g^{-1} for the other three trees. Similarly, gains in Hg due to air-drying ranged from 0.3 ng g^{-1} for the conifers to 0.6 - 0.7 ng g^{-1} for the hardwoods, which was a much smaller percentage of the total Hg concentration in the conifers than the hardwoods (Figure 2).

3.3 Contamination of air-dried samples

Mercury concentration of air-dried samples differed by location ($p < 0.001$, Figure 3). Samples dried in the clean room at Syracuse University, the barn at Hubbard Brook, and the soil sample processing room at Hubbard Brook all had Hg concentrations indistinguishable from the standard (freeze dried samples), based on Tukey' honestly significant difference. Not surprisingly, samples in air exposed to liquid Hg had the highest Hg concentration (2133 ± 111 ng g^{-1}). Samples dried in the drying room at ESF and the garage at Bartlett had quite elevated concentrations, 196-258% higher than the freeze-dried samples. Samples dried in the soil room at Coweeta and the archive building at Hubbard Brook had 63% and 57% higher concentrations compared to the freeze-dried samples.

4 Discussion

4.1 Techniques for measuring Hg in wood

I demonstrated that thermal decomposition, amalgamation, and atomic absorption spectrophotometry can be used to measure concentrations of Hg in wood with a MDL of 0.05 ng (1.27 in unit of ng g^{-1}). Method detection limits should be reported in units of ng per sample because the calibration curve in used for this method is based on a mass of Hg, not a concentration.

Concentration of Hg in wood samples have been measured using other techniques, such as CV AFS (Zhang et al., 1995; Siwik et al., 2010) and manual cold vapor atomic absorption spectrometry (CV AAS) (Abreu et al. 2008). These methods provide a lower detection limit than the method used in this paper (Table 1). However, both require sample preparation that involves a digestion process, whereas the Milestone DMA 80 direct Hg analyzer allows the processing of solid samples. The digestion process is especially complex and challenging for CV AFS, for which all the organic Hg must be converted into inorganic Hg to ensure the transformation of inorganic Hg to elemental Hg using $SnCl_2$ (Liang et al. 2013).

Our method could be modified to further improve the detection of Hg at low concentration. I analyzed samples of 100 mg; analyzing a larger sample would increase the amount of Hg in the sample and thus reduce the detection limit in units of concentration. However, there is a limit to the mass of sample that can be placed into a tared nickel boat, which depends on the sample density and the boat volume. Ten times more sample can be analyzed by using the instrument dosing feature, which allows multiple aliquots to be burned before desorption. I demonstrated this approach using five aliquots (Table 3). Using ten aliquots would bring the detection limit down by an order of magnitude compared to only one aliquot.

4.2 Sample preparation

The loss of Hg from wood samples by oven-drying at 103 ˚C was presumably due to volatilization at this high drying temperature. The loss of Hg by oven-drying at 65 ˚C was negligible, compared to freeze-drying, and the moisture content was similar between samples dried at 65 ˚C and 103 ˚C. Thus there is little advantage to drying at temperatures above 65 ˚C.

Air-drying in some locations resulted in significantly elevated Hg concentrations. Indoor air is generally elevated in Hg (Carpi and Chen 2001) and varies by location due to history of Hg

exposure. A dentist's office was reported to have high indoor airborne Hg due to the use of dental amalgam containing Hg (Foot 1972; Khwaja and Abbasi 2014). Broken Hg thermometers or Hg manometers (Smart 1986), gas pressure regulators containing Hg (Hryhorczuk et al. 2006), and Hg in paint (Mielke et al. 2008) are possible sources of elevated concentrations of Hg in indoor air. The highest Hg contamination we observed was in a garage at the Bartlett Experimental Forest, which houses snowmobiles. Vehicle exhaust and brake wear are both likely sources of Hg contamination (Hoyer 2004).

I dried wood samples in air exposed to liquid Hg, which showed that wood absorbs Hg in gaseous form (Figure 3). The samples that were air dried in various laboratories were covered to prevent contamination by dust particles, which showed that the contamination we observed was due to gaseous Hg. Studies that reported Hg losses during air-drying of soils (Gustin et al., 1999; Hojdová et al., 2015) attributed these losses to microbiological process that would reduce Hg^{2+} to gaseous Hg. Wood samples have very little Hg to begin with and less microbial activity than soils, so it is not surprising that we did not observe Hg losses with air drying.

I recommend that samples be freeze-dried or oven-dried at low temperatures for determination of Hg. Oven-drying is easier than freeze-drying, and the difference in water content was small as a fraction of sample fresh mass (5% for spruce, 3% for fir, 2% for sugar maple and 3% for beech; Table 2). Thus although oven-dried tissues contain slightly more moisture than freeze-dried tissues, most tissue concentrations are reported on an oven-dry basis, and this should be acceptable for Hg concentrations.

Archived samples that have been oven-dried at high temperatures or stored exposed to the air may not be suitable for measurement of Hg. It is possible that large wood samples, such as logs or solid wood products, would contain interior tissue that is not contaminated.

Researchers interested in using such materials, for example using Hg in tree rings to evaluate historical changes in Hg exposure, would need to characterize the rate of Hg loss through the wood in the case of oven drying or the rate of transport of air-derived Hg through wood in the case of atmospheric exposure.

4.3 Importance of wood to Hg budgets

To evaluate the possible importance of Hg in wood to ecosystem budgets, I compared the pool size of Hg in wood to that in leaves at the Hubbard Brook Experimental Forest, New Hampshire. The four tree species I studied account for 76% of the wood biomass and 78% of the leaf biomass at Hubbard Brook (Whittaker et al. 1974). Using my data for these four species and the average of my values for the remaining softwood and hardwood species, I estimated the Hg content of bole wood at the ecosystem scale to be 0.32 g ha^{-1}. I sampled leaves from the same four species in 2015 (unpublished data), and found Hg concentrations of 22.7 ± 1.6 ng g^{-1} for American beech, 18.0 ± 1.5 ng g^{-1} for sugar maple, 19.5 ± 2.2 ng g^{-1} for red spruce, and 33.2 ± 3.5 ng g^{-1} for balsam fir. Although these concentrations are eight times those of wood, the mass of wood is 30 times the mass of leaves. Thus the Hg content of foliage was calculated to be 0.15 g ha^{-1}, only half of the Hg content of wood. Similarly, in a Douglas-fir stand in Washington State, the wood contained more Hg (0.5 g ha^{-1}) than the foliage (0.3 g ha^{-1}), because of its greater biomass (Obrist et al. 2012).

Including wood in estimates of Hg contained in forest vegetation is important, in spite of the low concentrations, because of the large mass of wood in forests. The magnitude of this pool suggests that biomass burning is potentially an important source of Hg to the atmosphere (Friedli et al. 2009). My study shows that it is feasible to detect and report concentrations of Hg in wood if the right methods are selected.

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Chapter 3: Concentrations and content of mercury in bark, wood, and leaves in hardwoods and conifers in four forested sites in the northeastern USA

Abstract

Mercury (Hg) is deposited from the atmosphere to remote areas such as forests, but the amount of Hg in trees is not well known. To determine the importance of Hg in trees, I analyzed foliage, bark and bole wood of eight tree species at four sites in the northeastern USA (Huntington Forest, NY; Sleepers River, VT; Hubbard Brook, NH; Bear Brook, ME). Foliar concentrations of Hg averaged 16.3 ng g^{-1} among the hardwood species, which was significantly lower than values in conifers, which averaged 28.6 ng g^{-1} ($p < 0.001$). Similarly, bark concentrations of Hg were lower ($p < 0.001$) in hardwoods (7.7 ng g^{-1}) than conifers (22.5 ng g^{-1}). For wood, concentrations of Hg were higher in yellow birch (2.1 – 2.8 ng g^{-1}) and white pine (2.3 ng ng g^{-1}) than in the other species, which averaged 1.4 ng g^{-1} ($p < 0.0001$). Sites differed significantly in Hg concentrations of foliage and bark ($p = 0.02$) but not wood ($p = 0.60$); the concentration of Hg in wood depended more on species than site. The Hg contents of tree tissues in hardwood stands, estimated from modeled biomass and measured concentrations at each site, were higher in bark (mean of 0.10 g ha^{-1}) and wood (0.16 g ha^{-1}) than in foliage (0.06 g ha^{-1}). In conifer stands, because foliar concentrations were higher, the foliar pool tended to be more important. Quantifying Hg in tree tissues is essential understanding the pools and transformations of Hg in forest ecosystems.

Keywords: mercury budget, mercury cycling, mercury pool, temperate hardwood forests, temperature coniferous forests.

1 Introduction

Forests are important receptors of atmospheric mercury (Hg) deposition mainly because of the large surface area of foliage that collects Hg (Driscoll et al. 2007b). Trees are secondary only to soils as the dominant Hg pool in forest ecosystems. Trees contribute Hg to the forest floor via litterfall (Zhang and Lindberg 1995; Rea et al., 2002) and throughfall (Rea et al., 1996; Graydon et al., 2008). Trees not only absorb Hg through phloem via foliar stomata, but take up Hg through xylem sap via roots (Bishop et al., 1998; Wang et al., 2012). Tree foliage can also re-emit Hg back to the atmosphere via transpiration (Luo et al. 2016). Thus, trees serve to transport Hg in both directions between the atmosphere and soils. The study of Hg in foliage would improve understanding of Hg bioaccumulation in terrestrial foodchains (Gnamuš et al., 2000; Rimmer et al., 2010). Understanding the content of Hg in tree tissues would also help predict the re-emission of Hg due to any loss of aboveground carbon pools (Obrist 2007); biomass burning is a potentially important but poorly characterized source of Hg emissions (Friedli et al. 2009).

Studies have been conducted to determine Hg concentration in tree foliage (Rea et al., 2002; Ericksen et al., 2003; Bushey et al., 2008; Siwik et al., 2009), leaf litter (Sheehan et al., 2006; Risch et al., 2012; Blackwell et al., 2014), bark (Obrist et al., 2009; Guéguen et al., 2012) and roots (Wang et al. 2011). Studies of wood Hg have examined historical Hg deposition via the accumulation of Hg in tree rings using conifer species (Zhang et al., 1995; Abreu et al., 2008; Siwik et al., 2010; Wright et al., 2014). Mercury in wood of hardwood species has also been reported, but is often below detection limits (Obrist et al. 2011) especially for maples (*Acer* spp.) (Becnel et al., 2004; Siwik et al., 2010). Concentrations of Hg in wood are much lower than in other tissues. However, because wood is the largest component of forest biomass, it can

represent a larger Hg pool than foliage (Obrist et al. 2012), and thus wood can be as important as foliage and bark to Hg budgets in forests in spite of its low concentration.

Differences in tree Hg concentrations with geographic location have been explained by variation in atmospheric Hg deposition. For example, Hg concentrations in foliage varied across sites within the Adirondack Park in New York due to differences in atmospheric Hg deposition (Blackwell and Driscoll 2015); across the continental United States, concentrations varied with annual precipitation, presumably also due to variation in Hg deposition (Obrist et al. 2011). Tree species within a site can differ in Hg concentration (Blackwell et al., 2014; Obrist et al., 2012), presumably due to different rates of absorption through stomata or uptake via roots. Lack of information on Hg concentrations from multiple species and tissue types across a geographic gradient makes it difficult to evaluate the relative importance of species differences in Hg accumulation rates and differential exposure to atmospheric deposition. For example, the previous study that compared 14 sites across North America rarely observed the same species at multiple sites (Obrist et al. 2011).

The first objective of this study was to determine the concentrations of Hg in foliage, bark, and wood across four study sites for eight tree species, five of which occur at more than two sites. I compared the importance of site and species in controlling tree Hg concentrations to indicate the relative importance of Hg exposure and the properties of tree species. I expected Hg concentrations in foliage and bark to show more influence of location as they are more exposed to the atmosphere to than is wood. Concentrations of Hg in wood were expected to be more consistent across sites because of the limited translocation of Hg to wood. My second objective was to compare Hg pools among tissue types and between conifer and hardwood stands. I

expected woody tissues such as bark and wood to contain more Hg than foliage on a landscape area basis because of their greater mass.

2 Materials and methods

2.1 Site description

Four forested sites in the northeastern USA, each with both hardwood and conifer stands, were selected for sample collection (Table 4), based on the availability of tree inventory data and previous Hg studies of throughfall, litter, soil and streams (Dittman et al., 2010; Blackwell et al., 2014). At the Huntington Wildlife Forest in New York (Somers 1986), the Hubbard Brook Experimental Forest in New Hampshire (Huntington et al. 1988), and Bear Brook Watershed in Maine (Norton et al. 1992), soils are dominantly well-drained Haplorthods developed in glacial drift. At Sleepers River Research Watershed VT, the conifer stand is on similar Spodosols, but the hardwood stand is on richer Inceptisols with a carbonate influence (Park et al. 2008). Pools of Hg in soil organic horizon averaged 4.6 mg m^{-2} in the Adirondacks, 3.5 mg mg^{-2} in central New England, and 2.7 mg m^{-2} in Maine (Yu et al. 2014). Mineral soil Hg pools averaged 18, 18, and 19 mg m^{-2} in these three regions, such that all three regions had a total soil Hg pool of 22 mg m^{-2} (Yu et al. 2014). Total atmospheric Hg deposition has been estimated at 32 µg m^{-2} yr^{-1} at Huntington Forest, 29 µg m^{-2} yr^{-1} at Sleepers River and Hubbard Brook, and 27 µg m^{-2} yr^{-1} at Bear Brook (Figure 4), using data from Yu et al. (2014). My four study sites were affected by anthropogenic Hg emission (Driscoll et al. 2007a) from powerplants in the Midwest and urban centers of the Northeast (Choi et al., 2008; Schmeltz et al., 2011).

2.2 Field sampling

Dominant hardwood and conifer species were sampled in each stand. They were American beech (*Fagus grandifolia* Ehrh.), white ash (*Fraxinus americana* L.), yellow birch

(*Betula alleghaniensis* Britt.), sugar maple (*Acer saccharum* Marshall.), red maple (*Acer rubrum* L.), red spruce (*Picea rubens* Sarg.), balsam fir (*Abies balsamea* (L.) Mill.) and white pine (*Pinus strobus* L.). Five of these species were sampled from at least three sites (Table 4). Nine individual trees of each species in dominant canopy positions were sampled from August 7th to 13th 2015. For American beech, I preferentially selected trees not severely affected by beech bark disease.

For each tree, bark without visible lichen was collected from the stem 1.3 m above the ground with a chisel and hammer. Two tree cores were taken from the outer wood to the pith from each tree at 1 m above the ground using a Pressler's increment borer 5 mm in diameter.

Sun-exposed leaves or needles without evidence of herbivory or pathogens were collected from the upper canopy position using a shotgun at Sleepers River and Hubbard Brook. At Huntington Forest and Bear Brook, foliage samples were collected using ladders and pole pruners. For conifers, needles from all age classes on a branch were collected. To avoid contamination, samples were collected wearing nitrile gloves and tools were rinsed with methanol between samples. Samples were stored in doubled Ziploc bags on ice in the field and kept frozen in the laboratory until further analysis.

2.3 Laboratory analysis

Samples were cleaned using DI water and freeze-dried to constant mass at -80˚C and 7 Pa, using FreeZone Plus 6 (Labconco, Kansas City, MO). Dried samples were ground into homogenized particles using a Freeze Mill (Metuchen, NJ). For each type of tissue and species, samples were composited in groups of three trees to prior to Hg analysis. This approach gives a more accurate estimate of the population mean than a sample of three trees, for the same analytical effort.

Composited samples were analyzed for Hg concentration using thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry (US EPA, 2007), using a Milestone DMA 80 direct Hg analyzer (Shelton, CT). For each sample, two replicate samples of ~ 100 mg of tissue were weighed into nickel boats and auto-loaded into the instrument. Aluminum oxide was added to each tissue sample to ensure that the samples were fully burned. The reported Hg concentration is the average of the two replicate samples.

2.4 Quality control

Before running tissue samples, I analyzed a batch of blanks, primers (NIST DORM-2, dogfish muscle, ~50 mg, 410 ± 41 ng g^{-1}), calibration verification samples (NIST 2976 mussel tissue, ~15 mg, 61 ± 6 ng g^{-1}), two quality control samples (NIST 1515 apple leaves, ~5 mg, 44 ± 4 ng g^{-1}) and one method blank with aluminum oxide. I did not proceed with sample analysis unless the Hg recovery values of NIST reference materials were within 10% of the certified values. After every 10 samples, I ran a calibration verification (NIST 2976), and a calibration blank and a matrix spike. The matrix spike was one actual tissue sample spiked with the standard reference material (NIST 2976). The average Hg recovery was 99 % (n =32, rsd = 8%) of NIST 2976, 100 % (n = 16, rsd = 5%) of DORM-2, 100 % (n =8, rsd = 5.7%) of NIST 1515 and 107 % (n =8, rsd = 14%) of the matrix spike, which were all within the acceptable range of values.

The measured Hg concentrations in samples ranged from 0.04 to 5.6 ng in units of mass, which were almost all higher than the method detection limit (MDL) of 0.04 ng in units of mass (1.27 ng g^{-1}). Two wood samples from sugar maple had measured values equal to the MDL

2.5 Statistical analysis

I treated the concentration of Hg measured for one composite sample of three trees as one individual observation in the following analyses. I log-transformed the data for all the analyses to meet the assumption of normality of the residuals.

To test the effects of tissue type on Hg concentrations, I applied a general linear model with tissue type as the main effect for each species in different sites. Because Hg concentration differed mainly by tissue type, I tested the effects of species and sites on Hg concentrations using a two-way ANOVA for each tissue type individually.

To describe the content of Hg, I used the average concentration of Hg multiplied by the biomass in bark, foliage and wood for each species in hardwood and conifer stands at the four sites. Aboveground biomass in foliage, bark and wood was estimated using stand inventory specific to Huntington Forest (Johnson and Lindberg 1992), Sleepers River (Park et al. 2008), Hubbard Brook (Battles et al. 2013) and Bear Brook (Elvir et al. 2010) and allometric models developed for these species at Hubbard Brook (Whittaker et al. 1974). To calculate the ratio of branch bark to wood, I used a weighted average of wood and bark based on the species and elements reported by Whittaker et al (1979). I estimated Hg content in branches using Hg concentrations of bark and wood times the estimated biomass in branch bark and wood. To estimate Hg concentrations of minor species that were not collected in this study, I used the average Hg concentration of dominant species. I summed across all the trees to obtain the total content of Hg in both hardwoods and conifer stands for each tissue type and site.

Statistical analyses were conducted with SAS 9.4 (SAS Institute Inc. 2013).

3 Results

3.1 Concentrations of Hg

Foliage had the highest Hg concentrations, with means by species and site ranging from 11 to 48 ng g^{-1}. Bole wood had the lowest concentrations (0.4-2.8 ng g^{-1}), and bark was intermediate (4-26 ng g^{-1}). This pattern was consistent across all the species and sites ($p < 0.001$).

Species also differed in Hg concentrations. For foliage, concentrations of Hg were higher in balsam fir (30 - 48 ng g^{-1}, depending on the site) and red spruce (20-37 ng g^{-1}); the other species ranged from 10-23 ng g^{-1} (average for each species within site) ($p < 0.001$; Figure 5). For bark, likewise, concentrations of Hg in balsam fir (22-26 ng g^{-1}) and red spruce (21-25 ng g^{-1}) were higher than in the other species (4-20 ng g^{-1}) ($p < 0.001$; Figure 6). For bole wood, concentrations of Hg were higher in yellow birch (2.1–2.8 ng g^{-1}) and white pine (2.3 ng g^{-1}) than the remainder of the species (0.4–2.2 ng g^{-1}) ($p < 0.001$; Figure 7).

Sites differed in concentrations of Hg for foliage ($p < 0.001$) and bark ($p < 0.001$) but not for bole wood ($p = 0.24$). For foliage, Hg concentrations were lower at Sleepers River (13-30 ng g^{-1} depending on the species) than Huntington Forest (15-48 ng g^{-1}), Hubbard Brook (17-31 ng g^{-1}), and Bear Brook (11-38 ng g^{-1}). For bark, the concentration of Hg was lower at Bear Brook (4-21 ng g^{-1}) than at Huntington Forest (6-26 ng g^{-1}), Sleepers River (6-25 ng g^{-1}) and Hubbard Brook (6-26 ng g^{-1}). Concentrations of Hg in bole wood was similar among the four sites (Figure 7).

3.2 Mercury pools

On an area of basis, non-leaf tissues contained more Hg than did foliage in hardwood stands, because of their larger mass, in spite of lower Hg concentrations. The average biomass by tissue type in the hardwood stands was 111 Mg ha^{-1} for bole wood, 11 Mg ha^{-1} for bark and 3 Mg

ha^{-1} for foliage. Across all four hardwood stands, bole wood averaged 0.16 g ha^{-1} and bark averaged 0.10 g ha^{-1}, while foliage averaged 0.06 g ha^{-1} (Table 5). For conifer stands, this pattern was true only at Hubbard Brook. At Huntington Forest, Sleepers River and Bear Brook, contents of Hg in foliage (averaging 0.05 g ha^{-1} across three sites) were comparable to or larger than those in bole wood (0.03 g ha^{-1}) and bark (0.04 g ha^{-1}), because of the high Hg concentration of conifer foliage.

For the sum of foliage, bark, wood, and branches (the latter estimated as intermediate between bark and wood), the hardwood stands contained more Hg than the conifer stands at Hubbard Brook (1.14 and 0.39 g ha^{-1}), Sleepers River (0.22 and 0.04 g ha^{-1}) and Huntington Forest (0.47 and 0.25 g ha^{-1}), because of the greater biomass in hardwood stands. The estimated total aboveground biomass was 304 Mg ha^{-1} in the hardwood stand but only 88 Mg ha^{-1} in the conifer stand at Hubbard Brook, 80 compared to 10 Mg ha^{-1} at Sleepers River and 165 compared to 34 Mg ha^{-1} at Huntington Forest. At Bear Brook, where the conifer stand (28 Mg ha^{-1}) was only modestly less massive than the hardwood stand (104 Mg ha^{-1}), the conifer stand had a larger content of Hg (0.32 g ha^{-1}) than the hardwood stand (0.26 g ha^{-1}), due to the high concentration of Hg in conifer needles.

4 Discussion

4.1 Concentrations of Hg in foliage, bark and wood

My finding of larger Hg concentrations in foliage (mean of 21 ng g^{-1} across species and site) and bark (mean of 13 ng g^{-1}) than in bole wood (mean of 2 ng g^{-1}) was consistent with studies in Norway (Reimann et al. 2007), Ontario Canada (Siwik et al., 2009; Siwik et al., 2010), Washington USA (Obrist et al. 2012), and Vermont and New Hampshire USA (Richardson and Friedland 2015). This pattern was also documented in a review paper of Hg concentrations in

forests (Grigal 2003) and a study of tree Hg concentrations across 14 sites in the USA (Obrist et al. 2011). Foliage has high Hg concentration because foliage absorbs Hg^0 from the atmosphere through stomata (Fleck et al. 1999). Mercury is accumulated over months for hardwood species (Rea et al. 2002; Ericksen et al. 2003) and over years for conifers (Bargagli et al., 1986; Rasmussen et al., 1991; Rasmussen 1995). Thus, it is not surprising that deciduous foliage collected late in the growing season and conifer needles including those older than one year had higher Hg concentrations than bark and wood. Foliage collected from hardwood species in early spring might have lower Hg concentrations than bark; at Huntington Forest, foliage collected on June 1st from American beech, sugar maple and yellow birch had Hg concentrations of only 4 to 7 ng g-1, whereas foliage collected on August 1st had concentrations four times higher (Bushey et al. 2008).

Bark and wood have less exposure to atmospheric Hg than the foliage. Bark can capture and retain atmospheric Hg through surface sorption. A recent study of Hg speciation in bark from Australia pine (*Pinus nigra* J.F.Arnold) found tree bark first captured particulate Hg on the surface or through physical absorption. Then, Hg was bound to thiol-containing molecules or tannins (Chiarantini et al., 2016; 2017). Mercury deposited on the surface of leaves and bark is not included in our analysis, as we removed dust and other foreign material from the tissue surfaces before analysis. The fact that Hg concentrations in wood are so low suggested that little Hg moves from the foliage through the phloem (Grigal 2003), from bark to the wood (Zhang et al., 1995; Sanjo et al., 2004), or from roots to aboveground tissues in xylem sap (Bishop et al. 1998).

4.2 Impact of species and site on Hg concentrations

The observation that different tree species are characterized by different Hg concentrations in foliage is not surprising, because the main pathway of Hg from the atmosphere to foliage is through gas exchange via stomata. Species differ in rates of leaf gas exchange (Körner 1994; Larcher 2003), which might account for the variation of Hg concentration in foliage.

Studies differ in reporting concentration differences among tree species. In this study, concentrations of Hg in balsam fir and red spruce foliage were twice those in the other species. This pattern of higher foliar Hg concentration in conifers than hardwood species agrees with studies in Ontario Canada (Rasmussen et al., 1991), Washington USA (Obrist et al., 2012), and Vermont and New Hampshire USA (Richardson and Friedland 2015). Higher foliar Hg concentration in American beech than red spruce has been reported in New York (Blackwell and Driscoll 2015) and Vermont and New Hampshire (Richardson and Friedland 2015), probably because only needles up to 2 years old were sampled. I observed higher Hg concentrations in conifer needles, collecting needles of all age classes. Conifers needles in 1-year age class had higher Hg concentrations than did hardwood leaves, but the current-year needles had lower Hg concentrations than hardwoods in a survey of 45 sites in the Adirondacks (Blackwell and Driscoll 2015). Black pine (*Pinus nigra* J.F.Arnold) continues to accumulate atmospheric Hg in needles for 3 years until they are deposited to the forest floor (Hutnik et al. 2014).

Mercury concentrations in bark and bole wood have less often been reported. My observation that balsam fir and red spruce had higher Hg concentration in bark than other species might suggest that conifers have a higher rate of Hg sorption from the bark surface than

hardwood species. The high Hg concentrations I observed in bole wood in yellow birch and white pine might be due to greater rates of Hg transport from either roots or foliage.

I found that sites differed in Hg concentrations in bark and foliage, but not in bole wood. Because foliage and bark are exposed to the atmosphere, Hg concentrations in these tissues may be more influenced by atmospheric Hg. The lower Hg concentration in bark at Bear Brook than in other three sites might be due to low Hg deposition in this site (Yu et al. 2014) due to its distance from Hg emission sources in the Midwest and urban centers of the northeastern U.S. (Choi et al., 2008; Schmeltz et al., 2011). Lack of an effect of site on Hg concentrations in bole wood could be due to the limited transport of Hg to wood from the environment, as discussed above.

4.3 Pools of Hg

The relative contribution of tree tissues to Hg pools at the study locations depends on both tissue concentrations and the biomass of those tissues, both of which vary across stands and sites (Table 2). The larger content of Hg in bole wood than in foliage in our hardwood stands was not surprising, because of the much larger biomass of bole wood than foliage. In this study, the bole wood biomass was 34 - 47 times foliar biomass, whereas the foliar Hg concentration was only 11 - 21 times bole wood Hg concentration across our four hardwood stands (Table 2). Similarly, wood contained more Hg than foliage for individual hardwood trees in Ontario, Canada (Siwik 2007) and for mixed hardwood forests in Beijing, China (Zhou et al. 2017b) and in New Brunswick, Canada (Nasr and Arp 2015). Thus, wood can be at least as important as foliage for Hg budgets of forests. Note that our hardwood foliage samples were collected in late summer. The Hg concentration in foliage collected in October might be 50 – 70% higher, based on observations of beech, sugar maple and yellow birch in the Adirondacks (Bushey et al. 2008).

The Hg pool in foliage would then be 0.09 g ha^{-1}, still less than the Hg pool in wood (0.16 g ha^{-1}).

In contrast, the content of Hg in bole wood in conifer stands was not always larger than the needles at my four sites. Though the bole wood biomass was 8 - 12 times the biomass of needles, the Hg concentration in needles was 16 - 17 times the wood Hg concentration, depending on the site. Previous studies of conifers have reported greater Hg content of bole wood than needles: a Douglas-fir stand in Washington State, the bole wood was reported to contain more Hg (0.5 g ha^{-1}) than the needles (0.3 g ha^{-1}), and in eight spruce-fir stands in New Hampshire and Vermont, the bole wood contained more Hg (0.3 g ha^{-1}) than the needles (0.2 g ha^{-1}) (Richardson et al. 2015). However, in both of these studies, only recent age classes of needles were collected (up to two years), which might underestimate Hg concentrations by a factor of 2, based on observations of balsam fir and red spruce in New Brunswick, Canada (Nasr and Arp 2015). Thus it is not uncommon for conifer forests to have a greater pool of Hg in needles than in the wood, due to the long exposure of evergreen foliage to the atmosphere, while for deciduous forests, foliage is a smaller Hg pool than bole wood.

4.4 Relating to previous Hg studies in the same stands

In a study of throughfall, litter inputs, and gaseous emissions of elemental mercury from the soil surface at the Huntington Forest, New York, Hg inputs were higher and losses were lower under conifers compared to hardwoods (Blackwell et al. 2014). My results appear consistent with this difference, as conifers seem to accumulate Hg to a greater degree than hardwoods. However, the amount of Hg contained in trees is too small to explain the budget discrepancy of 0.1 g ha^{-1} yr^{-1} (Blackwell et al. 2014). Soil Hg pools in northern forests (~300 g ha^{-1}) are orders of magnitude greater than those in trees (Blackwell et al., 2014; Yu et al., 2014),

so accumulation in soils is a more likely mechanism to explain the discrepancy in Hg budgets between stands at this site.

At Huntington Forest, the foliage of the same hardwood species I sampled in 2015 was sampled on a monthly basis throughout the growing season in 2009 and 2010 (Blackwell et al. 2014). Using their reported daily Hg accumulation rate (Blackwell et al. 2014), I estimated foliar Hg concentrations for the exact leaf age I sampled (early August) in 2009 and 2010. Foliar Hg concentrations appear to be decreasing over time, from 21.3 ± 0.8 ng g^{-1} in 2009 and 19.7 ± 0.3 ng g^{-1} in 2010, to 17.0 ± 0.4 ng g^{-1} in 2015. The rate of decrease is -0.7 ± 0.1% yr^{-1} (p = 0.002), using a simple linear regression with time as the independent variable and treating the three species as replicates. Similarly, fluxes of Hg in leaf litter Hg declined from 2004 to 2015 at Huntington Forest (Gerson and Driscoll 2016). Concentrations of atmospheric Hg^0 at Huntington Forest were reported to decline with a slope of -1.6 ± 2.0% yr^{-1} from 2005 to 2008 and a slope of -1.0 ± 2.0% yr^{-1} from 2009 to 2014 associated with declines in regional emissions (Zhou et al. 2017a). Thus, the decreases in foliar Hg likely reflect the decline in atmospheric Hg, the major source of Hg in tree foliage. Measurements of Hg concentration in foliage or litterfall would appear to be an effective approach to monitor future changes in atmospheric Hg deposition. Note a biomonitoring program involving conifer species would need to specify needle ages since Hg concentration in needles vary by age class (Hutnik et al. 2014).

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Chapter 4: Using tree rings to monitor historical mercury pollution: a case study in New Hampshire

Abstract

Dendrochemistry is the analysis and interpretation of chemical patterns of precisely dated tree rings. The dendrochemical radial trend may provide a historical record of environmental Hg pollution. To test the potential of dendrochemistry to provide insight into Hg pollution in the northeastern US, tree disc samples were collected from one tree of each of four species: American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marshall.), yellow birch (*Betula alleghaniensis* Britt.) and red spruce (*Picea rubens* Sarg.) at Hubbard Brook Experimental Forest in New Hampshire.

Concentrations of Hg in bole wood for American beech, sugar maple and yellow birch tended to increase first and then decreased from 1960 to 2015. This pattern is consistent with the temporal trends in Hg in watershed sediments in New Hampshire. Bole wood at higher tree height had larger Hg concentrations which might indicate that Hg in bole wood was derived from the foliage rather than root uptake. This suggested that the concentration of Hg was diluted while being translocated away from its source position.

Keywords: Dendrochemistry, *Fagus grandifolia* Ehrh., *Acer saccharum* Marshall., *Betula alleghaniensis* Britt., *Picea rubens* Sarg.

1 Introduction

Mercury (Hg) is a neurotoxic pollutant that threatens fish, wildlife and human health through methylation and bioaccumulation (Chan et al., 2003; Chen et al., 2008). Dendrochemistry has been used to reconstruct historical Hg pollution with the assumption that the growth ring of certain year stores Hg that is available to the tree during that year of its

growth. However, the feasibility of using Hg dendrochemistry by tree rings to monitor Hg deposition trends varies by species and location. Black spruce (*Picea mariana* Mill. B.S.P) in Quebec Canada (Zhang et al. 1995), pine (*Pinus* spp.) in Nevada and California (Wright et al. 2014) and Czech Republic (Navrátil et al. 2017), black poplar (*Populus nigra* L.) in Portugal (Abreu et al. 2008), Norway spruce (*Picea abies* L.) and European beech (*Fagus sylvatica* L.) in central Czech Republic (Hojdová et al. 2011) have been found to reflect the historical Hg pollution. On the other hand, maple (*Acer* spp.), red oak (*Quercus rubra* L.), eastern cottonwood (*Populus deltoides*) and willow (*Salix* spp.) in Ontario Canada (Siwik et al. 2010) were found not to reflect any environmental Hg trends which was explained by the radial translocation of Hg across growth rings (Siwik et al. 2010). Thus, examining more tree species would help improve our understanding of the applicability of using dendrochemistry to monitor Hg deposition trends. At Underhill, VT, and Huntington Forest, NY in the northeastern US, a decline of atmospheric Hg deposition from 1992 to 2014 have been reported associated with declines in regional emissions (Zhou et al. 2017a). If environmental regulations have been effective at reducing atmospheric Hg deposition, then recent tree rings should have lower Hg concentrations than the older rings given a stable dendrochemical record of Hg.

The mechanism of Hg uptake, translocation, and accumulation in bole wood is a matter of dispute. Foliar uptake of Hg and phloem translocation into the bole has been claimed for red pine (*Pinus resinosa* Ait.) (Fleck et al. 1999), Austrian pine (*Pinus nigra* L.) (Arnold et al. 2017) and in a review (Grigal 2003). Alternatively, root uptake of Hg from the soil solutions and xylem translocation has been reported for Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* L.) (Bishop et al. 1998).

My first objective was to determine the radial concentrations of Hg in dated tree rings and bole wood, to examine if the radial pattern of wood Hg was consistent with the historical atmospheric Hg pollution. Measuring the concentration of Hg by tree rings could also help determine the source of Hg in bole wood. Specifically, if the bole Hg concentrations was lower in more recent years, it might suggest that Hg in bole wood was more likely from atmosphere via foliar uptake and phloem transport because atmospheric Hg has been decreasing recently. If Hg concentrations stay constant for different years of rings, Hg in bole wood might come from root uptake because soil Hg concentration have stayed constantly over time.

My second objective was to determine the vertical pattern of Hg in bole wood within a tree. The foliar uptake concept would be supported if Hg concentrations in recent bole wood increased with height. Alternatively, the root uptake concept would be supported if Hg concentrations decreased with increased height.

2 Materials and methods

2.1 Site description

Wood samples were collected from the dominant species, American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marshall), yellow birch (*Betula alleghaniensis* Britt.) and red spruce (*Picea rubens* Sarg.), near Rain Gage #23 at the Hubbard Brook Experimental Forest in the White Mountain National Forest in central New Hampshire. Average temperature at the site is − 9°C in January and 18°C in July with an annual average precipitation of 1400 mm (Bailey et al. 2003). Soils are well drained Spodosols developed in glacial drift (Bailey et al. 2003).

2.2 Field sampling

One tree > 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 at bottom, middle and top of the bole. Samples were transported on ice in a cooler to the laboratory and stored in bags in a freezer until further analysis.

2.3 Laboratory processing and quality control

The sawn surfaces of each tree disc were shaved with a plane and rinsed with methanol. Tree bottom discs were dated beginning from the most recent growth ring next to the bark, using the skeleton plot technique (Swetnam et al. 1985) through a dissecting scope. I confirmed the years with narrow rings between discs and with existing ring information for red spruce (Engel et al. 2016), sugar maple and American beech (Kim 1988; Halman et al. 2015) at the Hubbard Brook Experimental Forest. For the bottom disks, a stainless steel drill bit was used to obtain a homogenized sub sample of wood particles every increment of 5 growth rings along a radial vector from the most recent formed ring through to the pith. For discs collected in the middle and top of the bole, wood particles from only the most recent 5 growth rings were collected. To prevent cross contamination, the drill bit was rinsed with methanol between samples.

Subsamples of wood particles were freeze-dried to constant mass at -80˚C and 7 Pa, using FreeZone Plus 6 (Labconco, Kansas City, MO). Samples (~100 mg) were weighed into nickel boats and auto-loaded for Hg concentration using thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry (EPA, U 1998), using a Milestone DMA 80 direct Hg analyzer (Shelton, CT). Aluminum oxide was added to each tissue sample to ensure that the samples were fully burned.

Quality control included analyzing 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 wood samples, I ran a sample set consisting of a method blank and two continuing calibration verification samples (NIST 2976). The average Hg recovery was 100 % (n =30, rsd = 8%) of NIST 2976, 99 % (n = 14, rsd = 5%) of DORM-2, and 99 % (n =10, rsd = 5.7%) of NIST 1515 which were all within the acceptable range of values. The measured Hg concentrations in samples ranged from 0.10 to 0.43 ng in units of mass, which were all higher than the method detection limit (MDL) of 0.04 ng in units of mass (1.27 ng g^{-1}).

2.5 Data analysis

Piecewise regression was used to detect radial patterns in Hg concentration of the four tree species. Piecewise regression allowed me to detect two different trends for the response of Hg concentration to years. The value of the breakpoint of two models with different slopes and was estimated using the NLIN function in SAS. For all the analyses, we log-transformed the data to meet the assumption of normality for residuals.

To determine the vertical pattern of Hg concentration in bole wood within a tree, I used a general linear model to test the effects of sample height on Hg concentrations, blocked by four trees.

Statistical analyses were conducted with SAS 9.4 (SAS Institute Inc. 2013).

3 Results

3.1 Concentration of Hg in bole wood

Concentrations of Hg across wood rings were 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 in this study.

3.2 Radial pattern of Hg concentrations in bole wood

Concentrations of Hg in bole wood did not change from 1925 to 1960 ($p = 0.83$) but they decreased from 1960 to 2015 ($p < 0.001$), using four tree species as replicates (Figure 8). For the red spruce tree, concentration of Hg in bole wood was similar across rings, and the variation of years was smaller than other three hardwood species (coefficient of variation = 15% for red spruce, 33% for American beech, 32% for sugar maple and 41% for yellow birch) (Figure 8).

3.3 Vertical pattern of wood Hg concentration within a bole

Bole wood had higher Hg concentrations at higher vertical tree position than lower position in trees using four trees as blocks ($p = 0.001$; Figure 9). The vertical variation of Hg concentration in bole wood was smaller in red spruce (coefficient of variation =11%) than American beech (18%), sugar maple (20%) and yellow birch (17%).

4 Discussion

4.1 Comparing Hg concentrations in bole wood

Concentrations of Hg in wood from American beech (2.2 ng g^{-1}, averaging across rings), yellow birch (4.4 ng g^{-1}) and red spruce (3.0 ng g^{-1}) at the Hubbard Brook were similar to the reported values for European beech in Central Czech Republic (2 – 9 ng g^{-1}; Hojdova et al. 2011), birch in Oslo Norway (1 – 5 ng g^{-1}; Reimann et al. 2007) and for spruce in Saskatchewan (Fleck et al. 1999) and Quebec Canada (Zhang et al. 1995).

Concentration of Hg in wood from sugar maple (2.3 ng g^{-1}, averaging rings) at the Hubbard Brook was higher than the reported values in Ontario Canada (0.04 – 0.8 ng g^{-1}; Siwik et al. 2010). This difference might be due to my sampling of an older tree. My wood samples had records of 80 years from 1935 to 2015, much longer than the 25-year record from 1981 – 2006 in Ontario.

4.2 Tree rings to monitor Hg pollution

Radial pattern of Hg in tree disks might reflect the historical changes in local atmospheric Hg deposition at the Hubbard Brook. The decrease of Hg concentration in wood after 1960s found in my study (Figure 8) was consistent with the temporal changes in stored Hg in the lake sediments from the atmosphere in New Hampshire and Vermont (Kamman and Engstrom 2002). Stored Hg concentrations in sediments decreased from 1960 to 1998. And the decrease was related to the declines in atmospheric Hg deposition (Kamman and Engstrom 2002). The closest monitoring station near my sampling site is in Underhill, Vermont. However, measurements of atmospheric Hg concentrations were not initiated until 1992, much later than my Hg data in tree rings. The decline in atmospheric Hg concentrations from 1992 to 2015 in Vermont (Zhou et al. 2017a) was similar to the decline in wood Hg concentrations from 1990 to 2015.

The correspondence of the radial pattern of Hg in tree rings to historical Hg contamination in the environment varies by species and location. In this study, decreases in Hg concentrations in rings from 1960 to 2015 were found in three hardwood species but not in red spruce (Figure 8), and this radial pattern was not explained by any local industrial activities in New Hampshire. In Ontario, Canada, radial patterns of Hg concentrations in rings from willows, sugar maple, red oaks and poplars was not related to known trends in atmospheric Hg deposition from CAMNet (Temme et al. 2007). However, in places with severe local contamination, the

radial patterns of Hg concentrations in rings has reflected the trend in Hg contamination and industrial activities successfully for European beech, Norway spruce (Hojdova et al. 2011) and Scots pine (Navrátil et al. 2017) in the central Czech Republic, Japanese cedar (*Crytomeria japonica*) in southern Korea (Jung and Ahn 2017), black poplar in Ria de Aveiro, Portugal (Abreu et al. 2008) and pine in Nevada and California (Wright et al. 2014) (Table 1). Thus, using tree rings to monitor temporal changes in Hg pollution might be more effective in contaminated sites. In less contaminated sites, small changes in exposure to Hg might be obscured by the annual variation in uptake rate of Hg by trees.

4.3 Source of Hg in bole wood

My findings of greater Hg concentrations higher up in the tree boles suggested that Hg in bole wood mainly comes from foliar uptake via stomata for the species I studied: American beech, sugar maple, yellow birch and red spruce. Accumulation of Hg in bole wood has also been attributed to uptake via stomata and subsequent translocation through phloem for Austrian pine (*Pinus nigra*) in a greenhouse manipulation experiment (Arnold et al. 2017). Thus, bole Hg can come from the uptake via foliar stomata. In a study of black popular near a chlor alkali plant in Portugal, the radial pattern of Hg concentrations in wood was related to Hg concentrations in industrial effluent (Abreu et al. 2008). Thus, Hg in bole wood was attributed to the uptake from root systems in their study (Abreu et al. 2008). For future research, more species at different habitats should be examined to determine their value in provided record of Hg pollution.

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Chapter 5: Conclusion

1. Conclusions on concentration, content and dendrochemistry of Hg in trees

The locations and methods used to dry tree tissue samples before Hg analysis should be chosen cautiously. A clean environment with minimal exposure to indoor atmospheric Hg is preferred especially for samples with low Hg concentrations and strong capability of Hg^0 absorption from the atmosphere. Achieved samples with low Hg concentrations such as tree wood might not be appropriate for Hg analysis. The method of thermal decomposition, amalgamation, and atomic absorption spectrophotometry with dosing technique was suitable to analyze wood samples with low Hg concentrations.

Concentrations of Hg varied by tree tissue type, with foliage > bark > bole wood in both hardwood and conifer stands. Concentrations of Hg in foliage and bark varied significantly with species and site, with species the more important explanatory variable. Concentrations of Hg in bole wood differed by species but not by site, suggesting that translocation of Hg from the environment is limited.

The Hg content of aboveground biomass varied by forest type and site. Bole wood contained more Hg than foliage and bark in hardwood stands because of the much larger biomass of bole wood; conifer stands had larger Hg concentrations in foliage than in wood because of the higher concentrations in conifer needles than deciduous leaves. Understanding the distribution of Hg in tree tissues could help inform management and policy decisions regarding the fate of harvested biomass.

Using dendrochemistry to monitor historical Hg pollution can be applied to some tree species at some locations. Use of conifers to document historical Hg pollution has been more successful than of hardwood species.

2. Suggestions for future research in forested ecosystems

The mechanism of Hg uptake and translocation within the tree is still mysterious. To better understand the amount of Hg uptake from roots vs foliage, future studies might apply Hg isotope addition to seedlings in a greenhouse. To understand the source of Hg in bole wood, stem samples from treated seedlings could be collected for Hg stable isotope analysis. This should be conducted for different species because of their differences in absorbing Hg from the environment. In my study, yellow birch accumulated more Hg than other hardwood and conifer species.

Fluxes of Hg are less often studied than Hg pools (e.g. tree tissues, soils) in forest ecosystems. Pathways of atmospheric Hg deposition, leaf litterfall Hg deposition, and throughfall Hg deposition are the main inputs of Hg to the forest floor and have been often reported. Pathways of soil Hg evasion and Hg runoff and leaching are rarely studied, although they are important as they export Hg to the surrounding atmosphere and streams.

The effects of climate change on Hg fluxes are also important for future study. Changes in temperature and precipitation would alter Hg fluxes in the forests. Climate change would also increase the intensity and frequent of natural disturbance (e.g., ice storm and wildfire) which would alter forest structure and possibly export more Hg to the environment. Altered Hg fluxes due to climate change would then influence the pools of Hg in forested ecosystems.

Tables and Figures

Table 1. Methods used for measuring mercury.

Method	Method detection limit (ng g^{-1})	Sample size (mg)	Preparation procedure	Method number	Reference
CV AFS (Cold vapor atomic fluorescence spectrometry)	0.0005	> 500	Digestion	1631	US EPA (2002) [19]
ICP-MS (Inductively coupled plasma mass spectrometry)	0.1	> 500	Acid digestion	6020A	US EPA (1998) [38]
Manual cold vapor atomic absorption spectrometry	0.2	500 - 600	Heating or digestion	7471B	US EPA (1998b) [39]
Thermal decomposition, amalgamation, and atomic absorption spectrophotometry	1.0	2 - 1000	None	7473	US EPA (2007) [21]
Microwave digestion	1.75	> 500	Acid digestion	3051A	US EPA (2007b) [40]
ICP-AES (Inductively coupled plasma atomic emission spectroscopy)	17	> 500	Acid digestion	6010B	US EPA (1996) [20]

Table 2. Moisture loss (Ave± SE) of five replicate samples prepared by different methods as a percentage of the fresh weight.

	Moisture loss (%)			
	American beech	Sugar maple	Red spruce	Balsam fir
Freeze-dry	13.8±0.1	11.2±0.1	27.5±0.04	28.8±0.09
Oven 65˚C	11.3±0.4	8.7±0.3	23.4±0.4	25.8±0.1
Oven 103˚C	11.6±0.5	9.1±0.3	25.0±0.2	26.1±0.1
Air-dry	3.2±0.4	6.3±0.1	14.2±0.5	15.1±0.4

Table 3. A standard reference material (NIST 1515 Apple leaves) was analyzed using a single sample and a dosing technique, which allows multiple aliquots to be burned before desorption. We used 5 mg of the standard reference material, consistent with the Hg content of the wood samples. In this test, we used 5 samples, which increases the absorbance by a factor of 5.

Procedure	Sample	Mass (g)	Signal (Absorbance)	Content (ng)	Concentration (ng g^{-1})	Recovery (%)	Relative standard deviation of each condition (%)
Single sample	1	0.0051	0.004	0.24	46.5	105.6	
	2	0.0049	0.0039	0.23	46.9	106.6	
	3	0.0050	0.004	0,24	46.6	105.9	0.48
Dosing technique	4	0.0051					
		0.0056					
		0.0053					
		0.0056					
		0.0050					
	Total	0.0266	0.0172	1.21	45.6	103.6	
	5	0.0047					
		0.0054					
		0.0056					
		0.0058					
		0.0046					
	Total	0.0261	0.017	1.20	46.1	104.7	
	6	0.0050					
		0.0055					
		0.0054					
		0.0056					
		0.0048					
	Total	0.0263	0.0171	1.20	45.9	104.3	0.53

Table 4. Four sites in the northeastern USA were used in this study.

Study location	Stands	Sampled species[a]	Annual mean temperature (˚C)	Annual mean precipitation (cm)	Latitude (N)	Longitude (W)	Elevation (m asl)
Huntington Forest, NY	Hardwood	BE, YB, SM	5.0	105	43˚59'2.3"	74˚14'1.1"	530
	Conifer	WP, BF			43˚58'25"	74˚13'26"	508
Sleepers River, VT	Hardwood	WA, YB, SM	6.0	110	44˚29'54"	72˚09'33"	540
	Conifer	RS, BF			44˚30'46"	72˚10'47"	670
Hubbard Brook, NH	Hardwood	BE, YB, SM	5.7	140	43˚56'13"	71˚74'20"	500
	Conifer	RS, BF			43˚56'24"	71˚44'24"	780
Bear Brook, ME	Hardwood	BE, YB, RM	5.2	132	44˚51'36"	68˚6'17"	430
	Conifer	RS			44˚51'42"	68˚6'12"	446

[a] tree species included American beech (BE), yellow birch (YB), red maple (RM), sugar maple (SM), red spruce (RS), white ash (WA), white pine (WP) and balsam fir (BF).

Table 5. Biomass and Hg content of foliage, bark and bole wood in hardwood and conifer stands in this study and three published studies.

Study location	Stand type[a]	Foliage		Bark		Bole wood		Branches		Reference
		Biomass (Mg ha^{-1})	Hg content (g ha^{-1})	Biomass (Mg ha^{-1})	Hg content (g ha^{-1})	Biomass (Mg ha^{-1})	Hg content (g ha^{-1})	Biomass (Mg ha^{-1})	Hg content (g ha^{-1})	
Huntington, NY, USA	Beech-maple	2.2	0.04	9.4	0.08	104.8	0.11	49.4	0.24	This study
	Fir-pine	1.7	0.05	2.5	0.05	20.7	0.04	8.6	0.11	
Sleepers River, VT, USA	Ash-maple	1.4	0.02	5.6	0.04	50.0	0.05	23.4	0.11	This study
	Spruce-fir	0.5	0.01	1.0	0.01	7.5	0.01	0.9	0.01	
Hubbard Brook, NH, USA	Beech-maple	7.6	0.15	21.4	0.26	221.7	0.36	53.0	0.37	This study
	Spruce-fir	4.7	0.11	8.7	0.12	73.3	0.14	1.1	0.02	
Bear Brook, ME, USA	Beech-maple	2.0	0.03	6.6	0.03	67.9	0.11	27.5	0.09	This study
	Spruce	2.3	0.09	2.9	0.06	21.9	0.05	0.9	0.12	
Dongling, Beijing, China	Chinese pine	13.5	0.43	5.8	0.02	51.7	0.14	24.5	0.48	*Zhou et al., 2017a*
	Oak	5.7	0.20	8.8	0.33	793.8	0.11	54.7	0.69	
	Larch	4.8	0.19	7.5	0.20	67.5	0.15	17.6	0.33	
	Birch-Carya	1.1	0.05	3.0	0.06	27.2	0.08	9.4	0.12	
New Hampshire and Vermont, USA	Beech-maple	5.7	0.18	N/A	N/A	24.5	0.15	N/A	N/A	*Richardson and Friedland, 2015*
	Spruce-fir	1.6	0.15	N/A	N/A	9.1	0.30	N/A	N/A	
Washington, USA	Red Alder	2	0.03	N/A	N/A	113	< d.l.	N/A	N/A	*Obrist et al., 2012*
	Douglas fir	3	0.32	N/A	N/A	136	0.54	N/A	N/A	

[a] Oak refers to Quercus liaotungensis Mayr. Chinese pine refers to Pinus tabulaeformis Carr. Larch refers to Larix principis-rupprechtii Mayr. Birch refers to Betula platyphylla Suk and Carya refers to Carya cathayensis Sarg.

Table 6. Studies matching radial pattern of wood Hg concentrations and historical Hg pollution successfully.

Study site	Local pollution	Species	Min – Max of Hg concentration (ng g^{-1})	Ring ages	References
Southern Korea	Phosphate fertilizer production	Japanese cedar (*Crytomeria japonica*)	2 – 14	1969 - 2014	Jung and Ahn 2017
Central Czech Republic	Chlor-alkali plant	Scots pine (*Pinus sylvestris* L.)	2 - 45	1916 - 2012	Navrátil et al. 2017
	Ore mining and Pb smelting	European beech (*Fagus sylvatica* L.)	2 - 9	~1760 - 2010	Hojdová et al. 2011
		Norway spruce (*Picea abies* L.)	3 - 15	1890 - 2005	
Nevada and California, USA	Gold Rush, global pollution from marine air	Pine (*Pinus*)	0.2 - 9	1600 - 2010	Wright et al. 2014
Ria de Aveiro, Portugal	Chlor-alkali discharge events	Black poplar (*Populus nigra* L.)	20 - 280	1950 - 2000	Abreu et al. 2008
Italy	Volcanic activity in Mount Etna	Corsican Pine (*Pinus nigra ssp. laricio*)	Qualitative data relative to ^{13}C	1904 - 2004	Watt et al. 2007

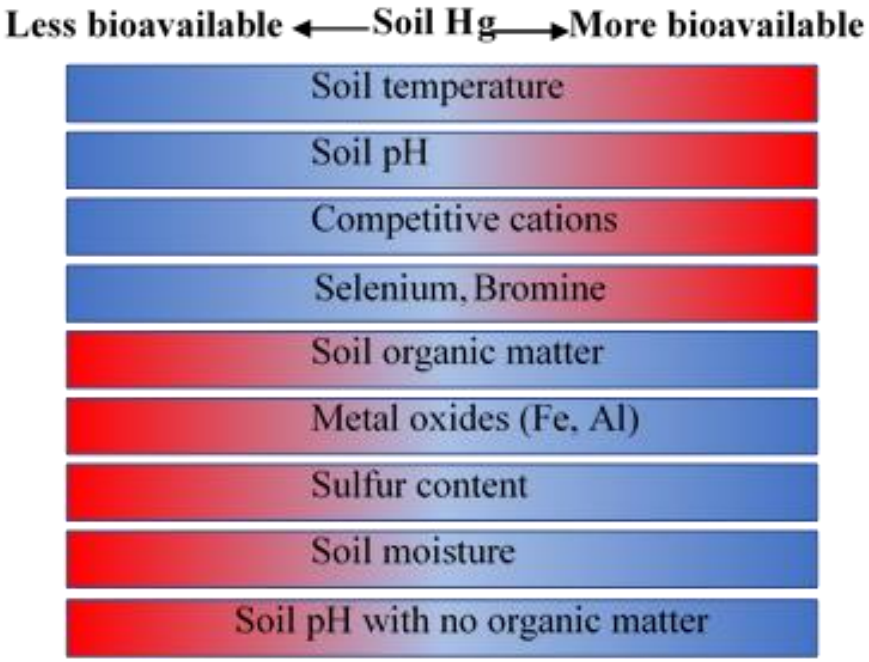


Figure 1. Influences of soil characteristics on Hg bioavailability in soils. Blue indicated lower level, and red indicated higher level of the soil.

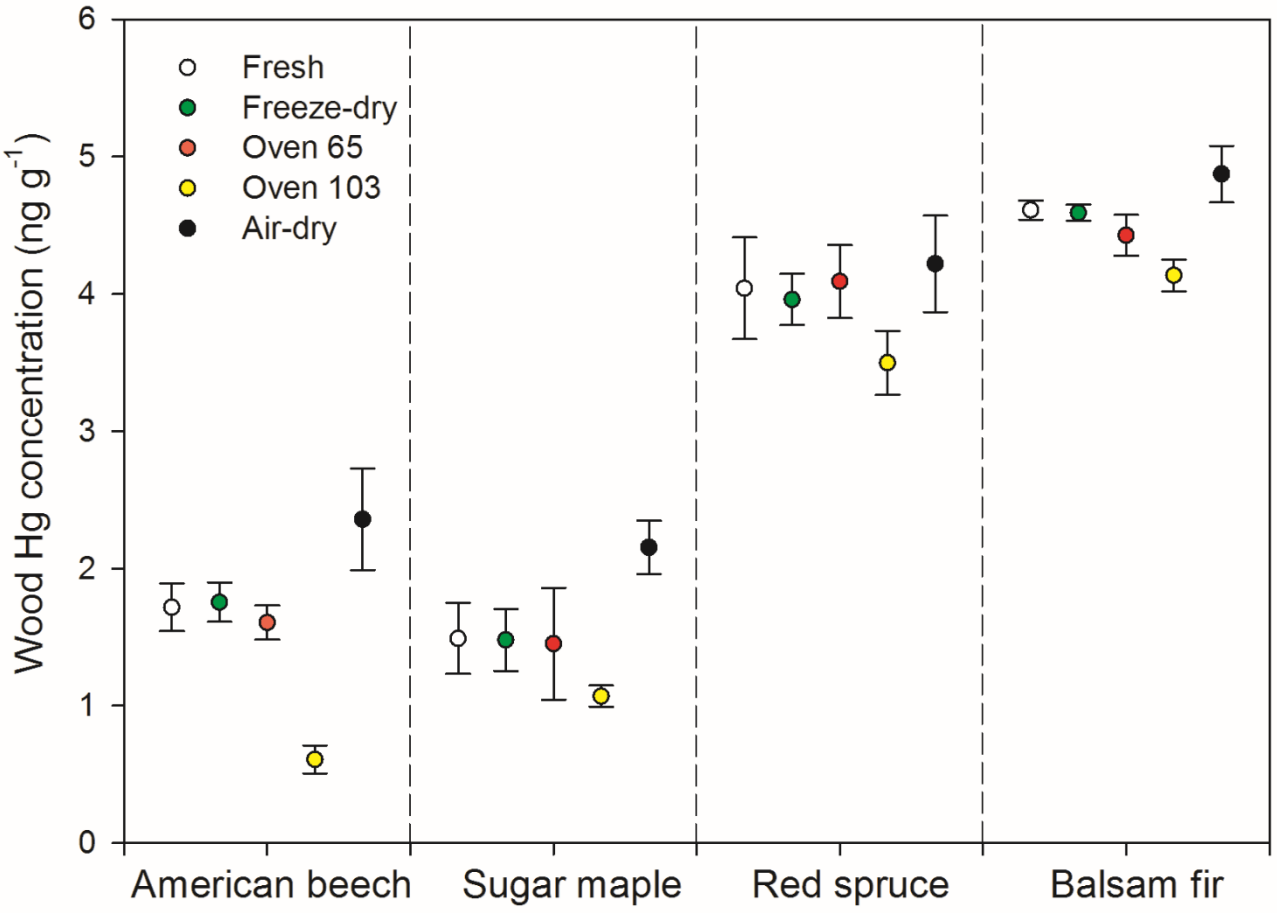


Figure 2. Corrected Hg concentrations measured in samples from four trees of different species prepared by five different methods. Oven-drying at 103 ˚C results in Hg loss, while air-drying results in Hg gain.

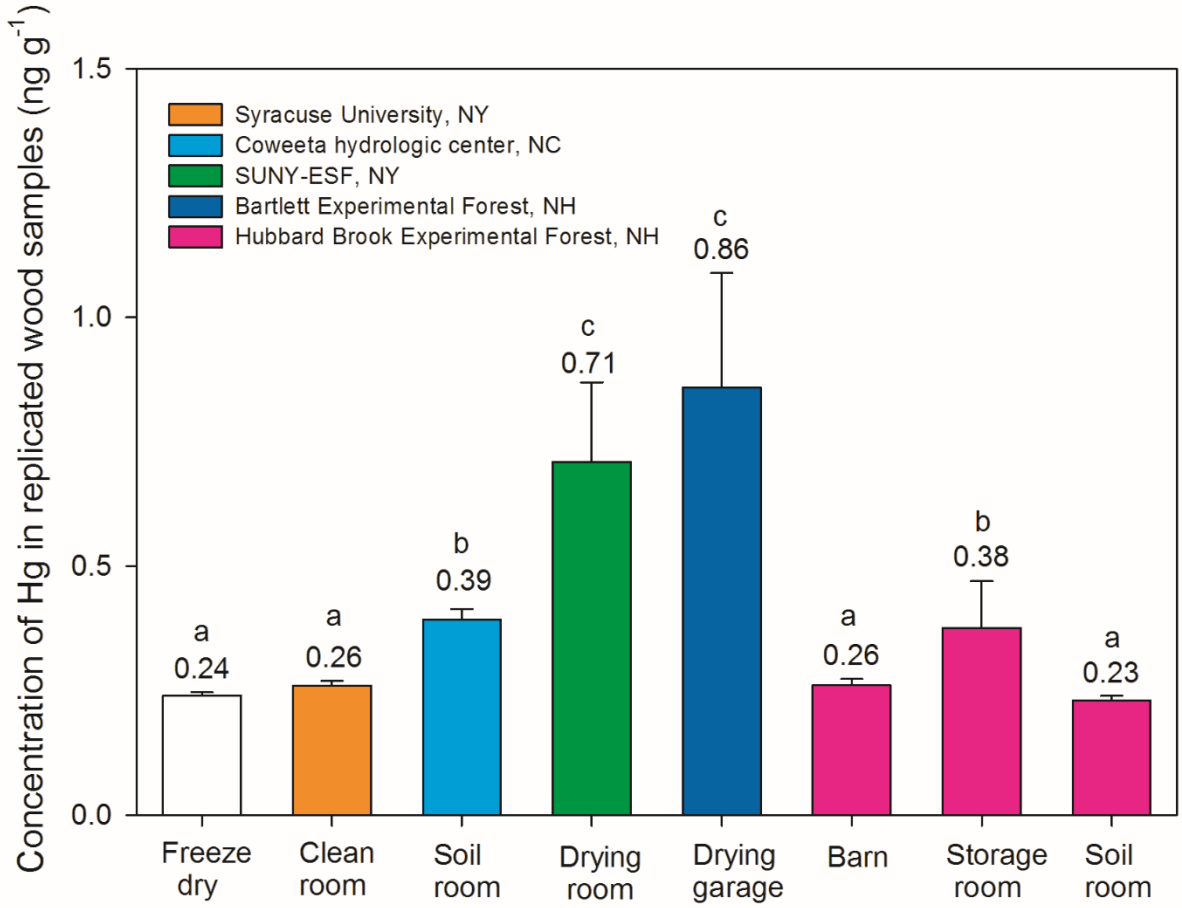
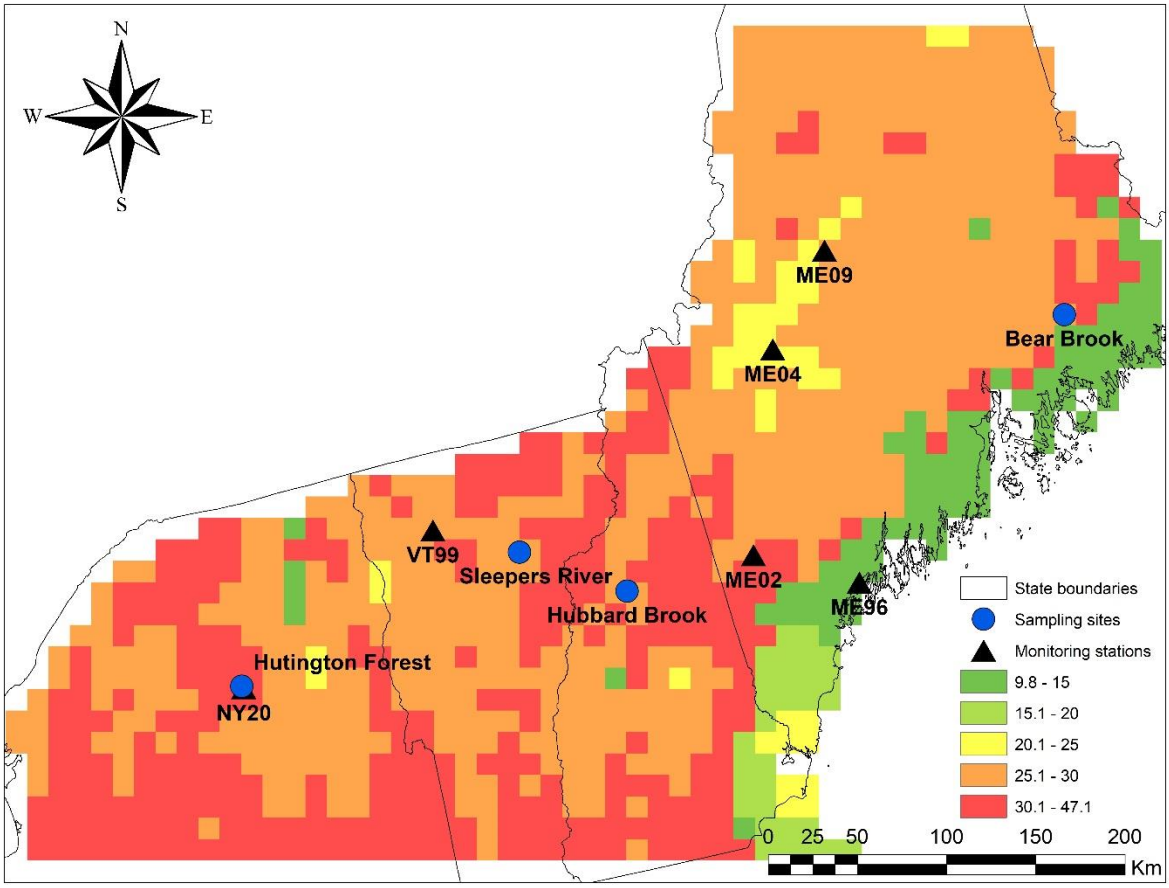


Figure 3. Mercury in sugar maple wood air-dried in different locations. For comparison, samples were prepared without any contamination (freeze-dried) and fully contaminated (in air exposed to liquid Hg). Different letters indicate significant differences (Tukey's honestly significant difference test).

Figure 4. Sampling location in this study (circles) and stations of monitoring atmospheric



Hg deposition (triangle) in northeastern USA. Estimated total Hg deposition was a sum of dry and wet Hg deposition from Yu et al. 2014.

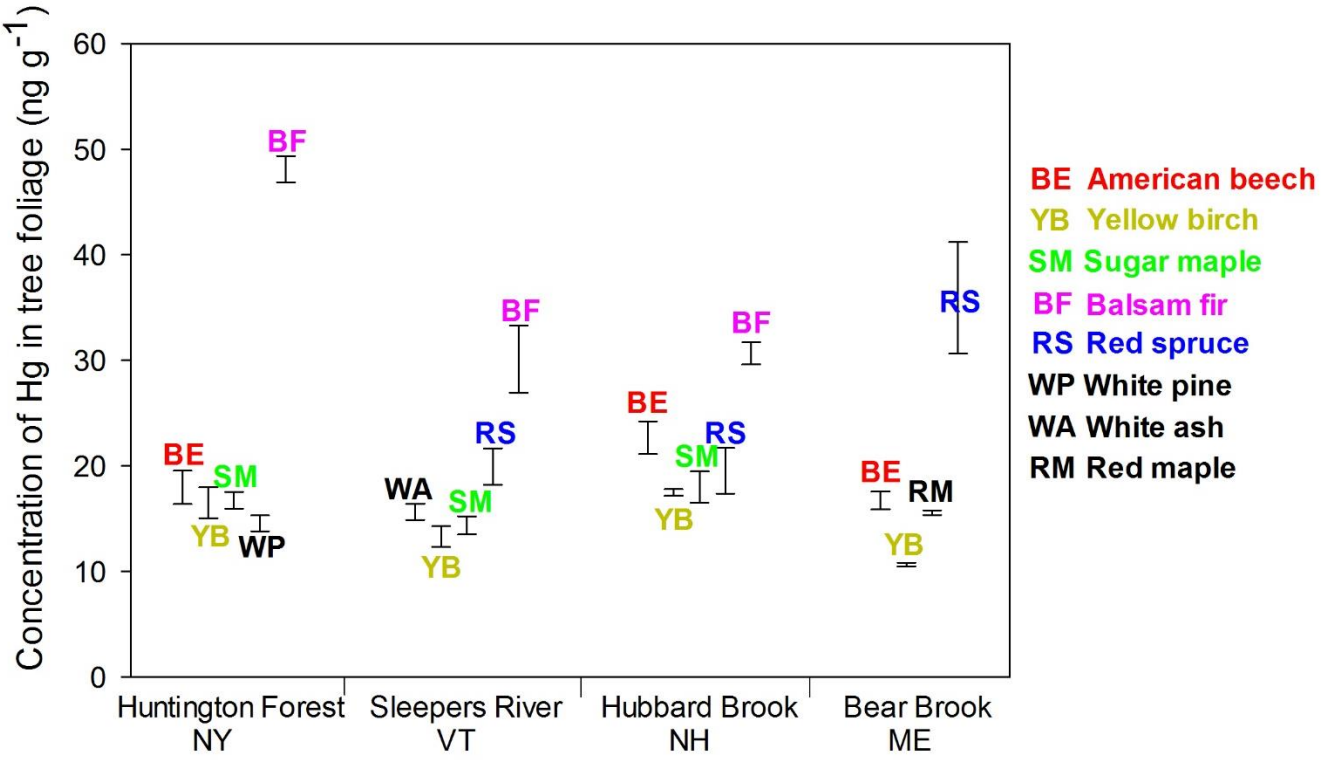


Figure 5. Concentrations of Hg in foliage of dominant species at four sites in the northeastern USA. Tree species included American beech (BE), yellow birch (YB), red maple (RM), sugar maple (SM), red spruce (RS), white ash (WA), white pine (WP) and balsam fir (BF). Error bar represents the SE of Hg concentrations measured from three composited samples.

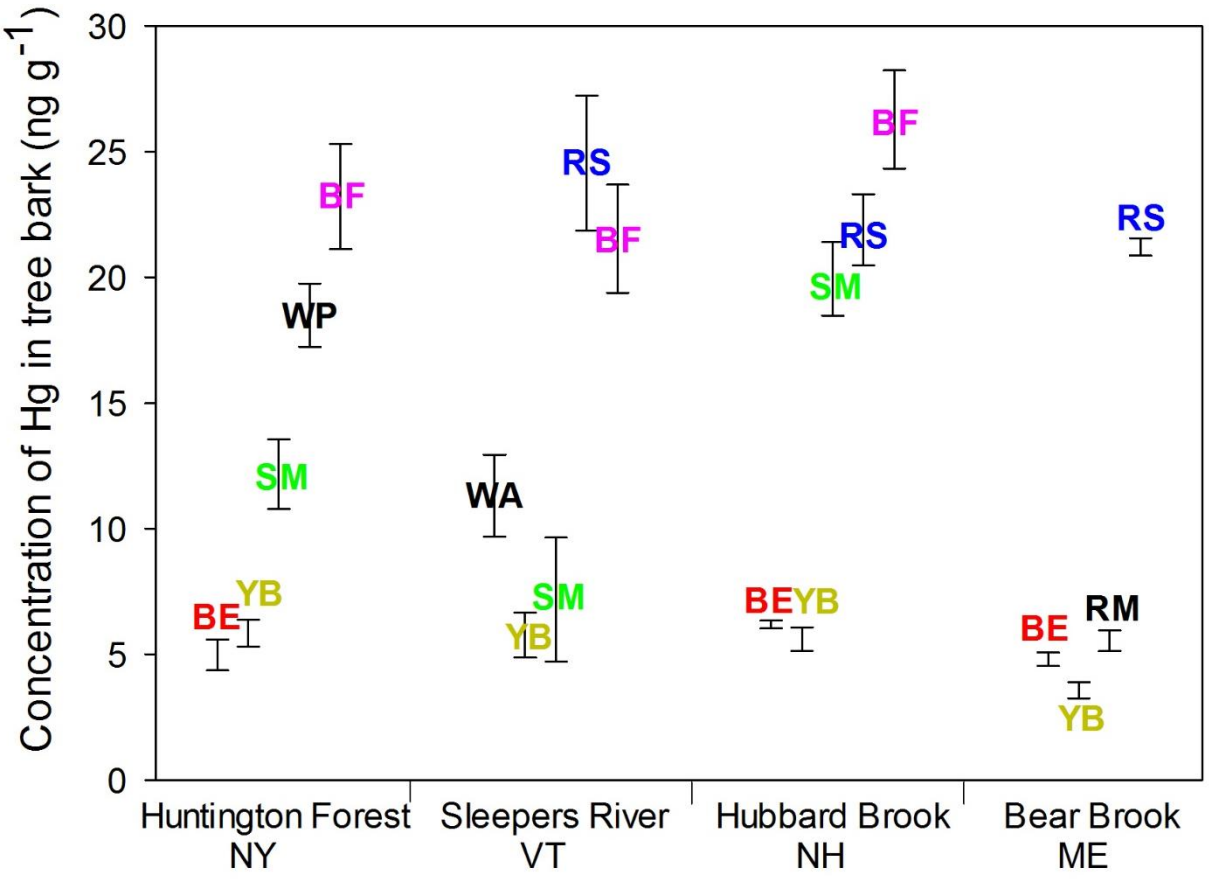


Figure 6. Concentrations of Hg in bark of dominant species at four sites in the northeastern USA. Tree species included American beech (BE), yellow birch (YB), red maple (RM), sugar maple (SM), red spruce (RS), white ash (WA), white pine (WP) and balsam fir (BF). Error bar represents the SE of Hg concentrations measured from three composited samples.

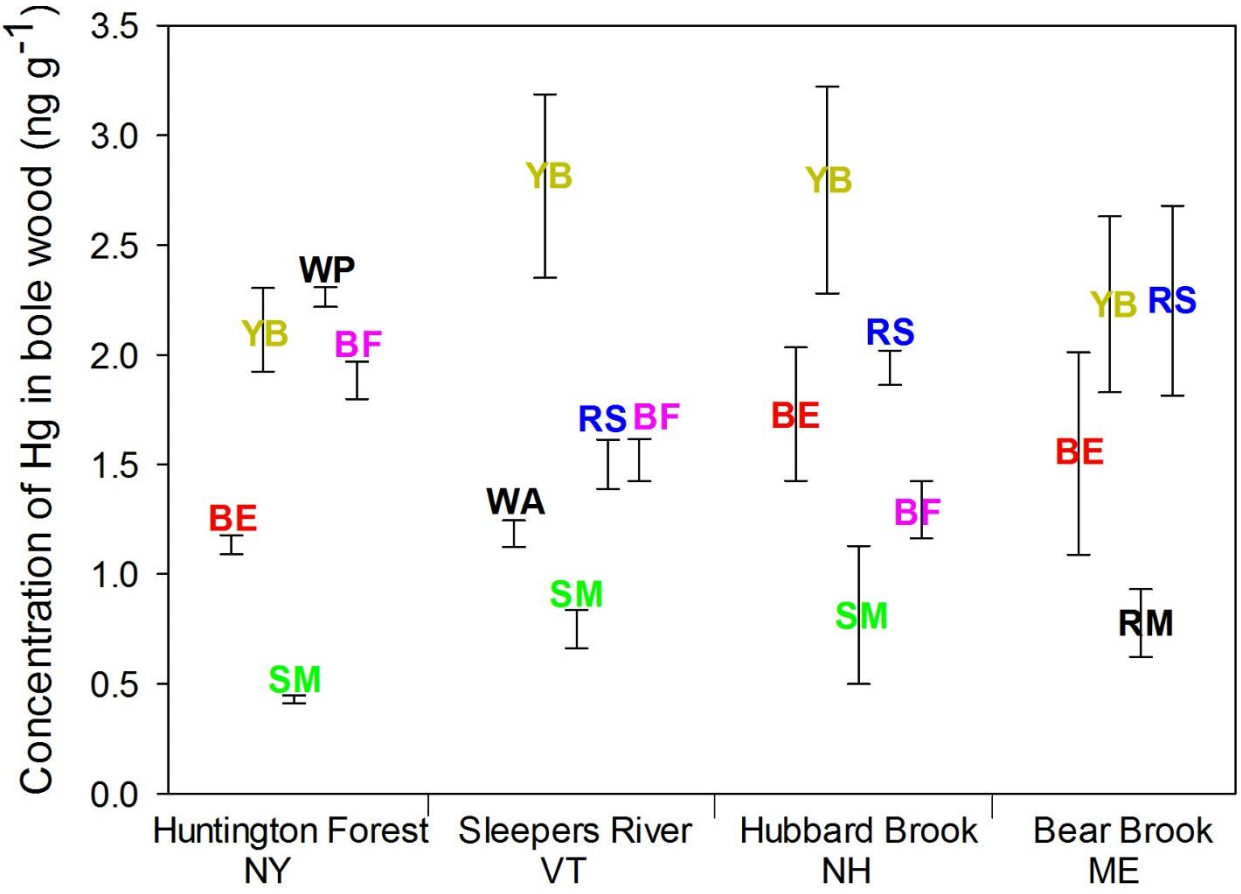


Figure 7. Concentrations of Hg in bole wood of dominant species at four sites in the northeastern USA. Tree species included American beech (BE), yellow birch (YB), red maple (RM), sugar maple (SM), red spruce (RS), white ash (WA), white pine (WP) and balsam fir (BF). Error bar represents the SE of Hg concentrations measured from three composited samples.

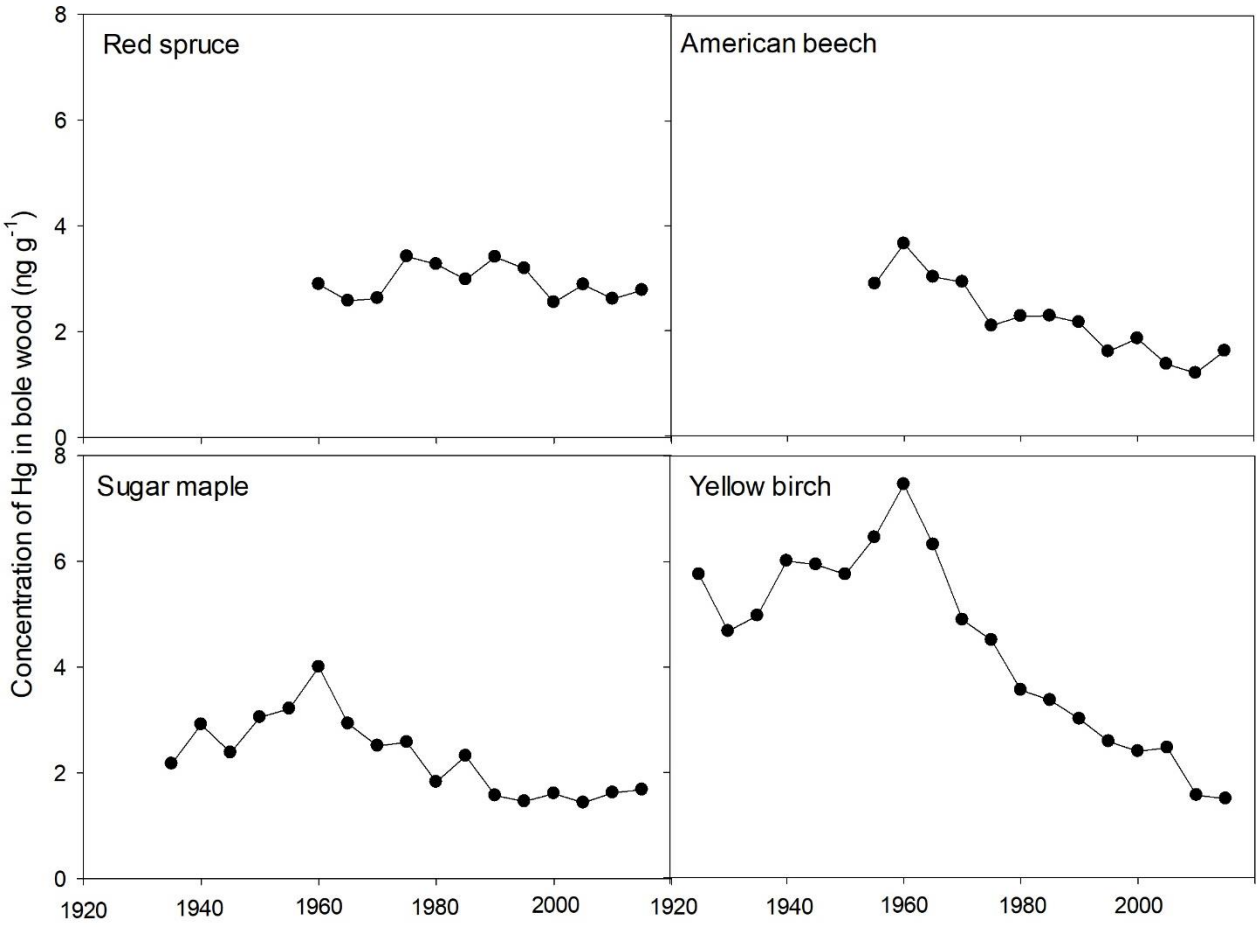


Figure 8. Radial pattern of Hg concentrations in bole wood of four tree species sampled at Hubbard Brook Experimental Forest in New Hampshire. Samples were taken in 5-year increments of growth rings.

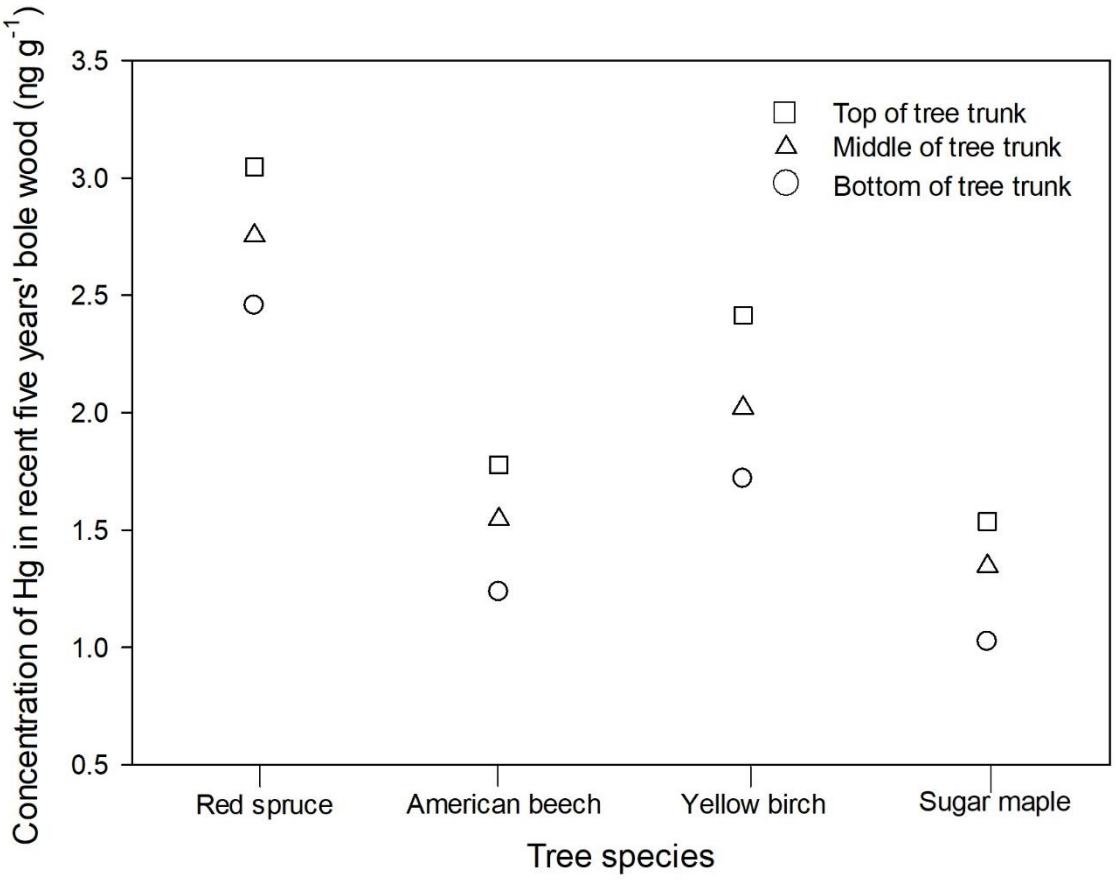


Figure 9. Concentrations of Hg in wood from different heights in the bole of four tree species. Samples were from the most recent 5 years of growth.

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Appendices

Concentrations of Hg in each Composited Tissue Sample in this Study. tree species included American beech (BE), yellow birch (YB), red maple (RM), sugar maple (SM), red spruce (RS), white ash (WA), white pine (WP) and balsam fir (BF).

Site	Stand type	Tree species	Tissue type	Composited replicates	Concentrations of Hg (ng g^{-1})
bear brook	hardwood	BE	bark	1	4.79
bear brook	hardwood	BE	bark	2	5.28
bear brook	hardwood	BE	bark	3	4.34
bear brook	hardwood	BE	leave	1	16.95
bear brook	hardwood	BE	leave	2	18.05
bear brook	hardwood	BE	leave	3	15.12
bear brook	hardwood	BE	wood	1	2.47
bear brook	hardwood	BE	wood	2	1.14
bear brook	hardwood	BE	wood	3	1.04
bear brook	hardwood	RM	bark	1	5.14
bear brook	hardwood	RM	bark	2	6.37
bear brook	hardwood	RM	bark	3	5.12
bear brook	hardwood	RM	leave	1	15.86
bear brook	hardwood	RM	leave	2	15.13
bear brook	hardwood	RM	leave	3	15.68
bear brook	hardwood	RM	wood	1	0.64
bear brook	hardwood	RM	wood	2	0.60
bear brook	hardwood	RM	wood	3	1.08
bear brook	conifer	RS	bark	1	21.21
bear brook	conifer	RS	bark	2	20.62
bear brook	conifer	RS	bark	3	21.82
bear brook	conifer	RS	leave	1	44.51
bear brook	conifer	RS	leave	2	31.32
bear brook	conifer	RS	leave	3	37.04
bear brook	conifer	RS	wood	1	3.07
bear brook	conifer	RS	wood	2	2.06
bear brook	conifer	RS	wood	3	1.61
bear brook	hardwood	YB	bark	1	4.20
bear brook	hardwood	YB	bark	2	3.24
bear brook	hardwood	YB	bark	3	3.28
bear brook	hardwood	YB	leave	1	10.89
bear brook	hardwood	YB	leave	2	10.72
bear brook	hardwood	YB	leave	3	10.30
bear brook	hardwood	YB	wood	1	2.42
bear brook	hardwood	YB	wood	2	2.81
bear brook	hardwood	YB	wood	3	1.46

hubbard brook	hardwood	BE	bark	1	6.30
hubbard brook	hardwood	BE	bark	2	5.88
hubbard brook	hardwood	BE	bark	3	6.37
hubbard brook	hardwood	BE	leave	1	25.72
hubbard brook	hardwood	BE	leave	2	20.66
hubbard brook	hardwood	BE	leave	3	21.62
hubbard brook	hardwood	BE	wood	1	1.22
hubbard brook	hardwood	BE	wood	2	2.27
hubbard brook	hardwood	BE	wood	3	1.70
hubbard brook	conifer	BF	bark	1	22.38
hubbard brook	conifer	BF	bark	2	28.39
hubbard brook	conifer	BF	bark	3	28.08
hubbard brook	conifer	BF	leave	1	28.75
hubbard brook	conifer	BF	leave	2	32.35
hubbard brook	conifer	BF	leave	3	30.89
hubbard brook	conifer	BF	wood	1	1.55
hubbard brook	conifer	BF	wood	2	1.14
hubbard brook	conifer	BF	wood	3	1.19
hubbard brook	conifer	RS	bark	1	24.68
hubbard brook	conifer	RS	bark	2	21.00
hubbard brook	conifer	RS	bark	3	20.02
hubbard brook	conifer	RS	leave	1	17.29
hubbard brook	conifer	RS	leave	2	17.44
hubbard brook	conifer	RS	leave	3	23.83
hubbard brook	conifer	RS	wood	1	2.07
hubbard brook	conifer	RS	wood	2	1.96
hubbard brook	conifer	RS	wood	3	1.80
hubbard brook	hardwood	SM	bark	1	21.23
hubbard brook	hardwood	SM	bark	2	17.03
hubbard brook	hardwood	SM	bark	3	21.58
hubbard brook	hardwood	SM	leave	1	16.51
hubbard brook	hardwood	SM	leave	2	16.48
hubbard brook	hardwood	SM	leave	3	20.94
hubbard brook	hardwood	SM	wood	1	1.43
hubbard brook	hardwood	SM	wood	2	0.41
hubbard brook	hardwood	SM	wood	3	0.60
hubbard brook	hardwood	YB	bark	1	6.04
hubbard brook	hardwood	YB	bark	2	6.11
hubbard brook	hardwood	YB	bark	3	4.67
hubbard brook	hardwood	YB	leave	1	17.54
hubbard brook	hardwood	YB	leave	2	16.92
hubbard brook	hardwood	YB	leave	3	17.95
hubbard brook	hardwood	YB	wood	1	1.89

hubbard brook	hardwood	YB	wood	2	2.84
hubbard brook	hardwood	YB	wood	3	3.52
huntington forest	hardwood	BE	bark	1	3.77
huntington forest	hardwood	BE	bark	2	5.76
huntington forest	hardwood	BE	bark	3	5.40
huntington forest	hardwood	BE	leave	1	19.26
huntington forest	hardwood	BE	leave	2	14.81
huntington forest	hardwood	BE	leave	3	19.78
huntington forest	hardwood	BE	wood	1	1.15
huntington forest	hardwood	BE	wood	2	1.05
huntington forest	hardwood	BE	wood	3	1.20
huntington forest	conifer	BF	bark	1	19.25
huntington forest	conifer	BF	bark	2	24.07
huntington forest	conifer	BF	bark	3	26.33
huntington forest	conifer	BF	leave	1	47.18
huntington forest	conifer	BF	leave	2	46.57
huntington forest	conifer	BF	leave	3	50.61
huntington forest	conifer	BF	wood	1	1.74
huntington forest	conifer	BF	wood	2	2.04
huntington forest	conifer	BF	wood	3	1.87
huntington forest	hardwood	SM	bark	1	14.94
huntington forest	hardwood	SM	bark	2	10.62
huntington forest	hardwood	SM	bark	3	10.97
huntington forest	hardwood	SM	leave	1	16.73
huntington forest	hardwood	SM	leave	2	18.07
huntington forest	hardwood	SM	leave	3	15.35
huntington forest	hardwood	SM	wood	1	0.41
huntington forest	hardwood	SM	wood	2	0.41
huntington forest	hardwood	SM	wood	3	0.47
huntington forest	conifer	WP	bark	1	16.10
huntington forest	conifer	WP	bark	2	20.36
huntington forest	conifer	WP	bark	3	19.04
huntington forest	conifer	WP	leave	1	13.09
huntington forest	conifer	WP	leave	2	15.45
huntington forest	conifer	WP	leave	3	15.10
huntington forest	conifer	WP	wood	1	2.23
huntington forest	conifer	WP	wood	2	2.21
huntington forest	conifer	WP	wood	3	2.35
huntington forest	hardwood	YB	bark	1	5.87
huntington forest	hardwood	YB	bark	2	6.75
huntington forest	hardwood	YB	bark	3	4.90
huntington forest	hardwood	YB	leave	1	16.22
huntington forest	hardwood	YB	leave	2	19.14

huntington forest	hardwood	YB	leave	3	14.07
huntington forest	hardwood	YB	wood	1	2.45
huntington forest	hardwood	YB	wood	2	2.09
huntington forest	hardwood	YB	wood	3	1.80
sleepers river	hardwood	WA	bark	1	8.97
sleepers river	hardwood	WA	bark	2	14.44
sleepers river	hardwood	WA	bark	3	10.54
sleepers river	hardwood	WA	leave	1	14.78
sleepers river	hardwood	WA	leave	2	14.93
sleepers river	hardwood	WA	leave	3	17.17
sleepers river	hardwood	WA	wood	1	1.25
sleepers river	hardwood	WA	wood	2	1.24
sleepers river	hardwood	WA	wood	3	1.06
sleepers river	conifer	BF	bark	1	19.30
sleepers river	conifer	BF	bark	2	19.47
sleepers river	conifer	BF	bark	3	25.83
sleepers river	conifer	BF	leave	1	28.71
sleepers river	conifer	BF	leave	2	25.44
sleepers river	conifer	BF	leave	3	36.21
sleepers river	conifer	BF	wood	1	1.51
sleepers river	conifer	BF	wood	2	1.69
sleepers river	conifer	BF	wood	3	1.36
sleepers river	conifer	RS	bark	1	19.63
sleepers river	conifer	RS	bark	2	25.17
sleepers river	conifer	RS	bark	3	28.86
sleepers river	conifer	RS	leave	1	18.26
sleepers river	conifer	RS	leave	2	23.39
sleepers river	conifer	RS	leave	3	18.12
sleepers river	conifer	RS	wood	1	1.43
sleepers river	conifer	RS	wood	2	1.35
sleepers river	conifer	RS	wood	3	1.72
sleepers river	hardwood	SM	bark	1	4.16
sleepers river	hardwood	SM	bark	2	5.31
sleepers river	hardwood	SM	bark	3	11.05
sleepers river	hardwood	SM	leave	1	15.71
sleepers river	hardwood	SM	leave	2	14.62
sleepers river	hardwood	SM	leave	3	12.73
sleepers river	hardwood	SM	wood	1	0.92
sleepers river	hardwood	SM	wood	2	0.66
sleepers river	hardwood	SM	wood	3	0.67
sleepers river	hardwood	YB	bark	1	7.55
sleepers river	hardwood	YB	bark	2	4.93
sleepers river	hardwood	YB	bark	3	4.81

sleepers river	hardwood	YB	leave	1	15.17
sleepers river	hardwood	YB	leave	2	11.88
sleepers river	hardwood	YB	leave	3	12.81
sleepers river	hardwood	YB	wood	1	3.22
sleepers river	hardwood	YB	wood	2	3.15
sleepers river	hardwood	YB	wood	3	1.93

Vita

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EDUCATIONAL BACKGROUND

Ph.D. (2015-2018) State University of New York, College of Environmental Science and Forestry, Syracuse, NY
- Dissertation title: "Concentration, content and dendrochronology of mercury in northeastern forests in USA"
- Advisor: Ruth D. Yanai

M.S. (2012-2015) State University of New York, College of Environmental Science and Forestry, Syracuse, NY
- Thesis title: "Detecting changes in tree tissue chemistry over time in northern hardwoods"
- Advisor: Ruth D. Yanai

B.A. (2008-2012) Minzu University of China, Beijing, China
- Area of focus: Environmental Chemistry
- Advisor: Jinchao Feng

PUBLICATIONS

10. Schoch, N., **Yang Y**., Yanai, R.D., Buxton, V.L., Evers, D.C., and Driscoll, C.T. Spatial patterns and temporal trends in mercury concentrations in common loons (Gavia immer) from 1998 to 2016 in New York's Adirondack Park: Has this top predator benefitted from mercury emission controls? Ecotoxicology. (under review)

9. **Yang, Y**., Meng, L., Yanai, R.D., Driscoll, C.T., Montesdeoca, M., Templer, P.H., Rustad, L.E., and Absbjornsen, H. Climate change may worsen mercury pollution in northern hardwood forests. Environmental Science and Technology. (under review)

8. Mobley, M.L., **Yang Y**., Yanai, R.D., Nelson, K.A., Bacon, A.R., and Richter, D.D. How to estimate statistically detectable trends in a time series: a case study of soil carbon and nutrient concentrations at the Calhoun Long-Term Soil-Ecosystem Experiment. Soil Science Society of America Journal. (under review)

7. **Yang, Y**., Yanai, R.D., Driscoll, C.T., Montesdeoca, M., and 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

6. **Yang, Y**., Yanai, R.D., Montesdeoca, M., and Driscoll, C.T. 2017. Measuring mercury in wood: Important but challenging. International Journal of Environmental Analytical Chemistry, 97: 456-467.

5. **Yang, Y**., Yanai, R.D, See, C.R., and Arthur, M.A. 2017. Sampling effort and uncertainty in leaf litterfall mass and nutrient flux in northern hardwood forests. Ecosphere, 8(11).

4. Yanai, R.D., Walsh, G.E., **Yang, Y**., Blodgett, C.A., Bae, K., and Park, B.B. 2017. Nutrient concentrations of roots vary with diameter, depth, and site in New Hampshire northern hardwoods. Canadian Journal of Forest Research, 48: 32-41.

3 Aulenbach, B.T., Burns, D.A., Shanley, J.B., Yanai, R.D., Bae, K., Wild, A., **Yang, Y**., and Yi, D. 2016. Approaches to stream solute load estimation for solutes with varying dynamics from five diverse small watersheds. Ecosphere. 7(6).

2. **Yang, Y**., Yanai, R.D., Fatemi, F.R., Levine, C.R., Lilly, P.J., and Briggs, R.D. 2015. Sources of variability in tissue chemistry in northern hardwood species. Canadian Journal of Forest Research. 46: 1-12.

1. Germain, R.H., Yanai, R.D., Mishler, A.K., **Yang, Y**., and Park, B.B. 2014. Landscape and individual tree predictors of dark heart size in sugar maple. Journal of Forestry.113: 20-29.

PROFESSIONAL EXPERIENCE

SUNY College of Environmental Science and Forestry Spring 2013-18

Research Project Assistant (Ruth Yanai's laboratory)

- Analyzed temporal trend in soil nutrient concentrations from 1962 to 2010 in the Calhoun Experimental Forest using nonparametric analysis in SAS
- Collected tree bark, foliage and wood ring samples for mercury analysis, mapped spatial pattern of atmospheric mercury deposition and tree mercury levels using GIS
- Modeled stream chemistry datasets using composite, regression and linear interpolation methods in SAS, calculated stream loads and evaluated bias for four solutes
- Helped measuring photosynthesis, sap flow rate and soil respiration, took minirhizotron images for root growth and conducted tree inventory at the Bartlett Experiment Forest, NH
- Provided sampling guidance to detect changes in litterfall fluxes and soil nutrients using power analysis and Monte Carlo sampling in R

Boston University Summer 2017

Research Intern under Sussman Foundation Fellowship (Pamela Templer's laboratory)

- Led a team to study effects of climate change on mercury cycling in temperate forests by measuring soil mercury evasion, throughfall mercury, litter mercury and soil mercury concentrations at three climate change manipulation sites: warming, drought and ice-storm treated plots at the Hubbard Brook Experimental Forest
- Coordinated with PIs for collaboration, led the research team and mentored undergraduate interns for laboratory work and a poster presentation

The New York State Energy Research and Development Authority Spring 2017

Environmental Analyst

- Analyzed temporal trend in mercury concentrations in Adirondack loons and fish in New York using parametric and nonparametric regression in SAS
- Mapped spatial pattern of fish and loon mercury levels in the Adirondack region using GIS, and performed risk assessment

- Provided sampling guidance for future detection of changes in loon and fish mercury concentrations using power analysis in R
- Delivered biweekly reports and helped to write a sampling methodology for monitoring fish mercury in New York State

SUNY College of Environmental Science and Forestry Fall 2012-17
Teaching Assistant, General Chemistry II and Survey of Chemical Principles
- Taught two laboratory sections, graded laboratory reports and exams, held weekly office hours

Syracuse City School District Spring 2015
Instructor, Science and Chemistry
- Developed syllabi, lectured, and designed experiments for fifth graders at Dr. King Elementary School and Van Duyn Elementary School
- Coordinated the production and distribution of print and web-based information materials
- Generated evaluations and reports for elementary mentoring program

United States Department of Agriculture Forest Service Summer 2013
Research Intern under Sussman Foundation Fellowship in the Northern Research Station
- Collected tree tissue samples by height and analyzed nutrient concentrations using CN analyzer and ICP-MS
- Assessed spatial and temporal variation in tree nutrient concentrations with sampling guidance provided for future monitoring program in SAS

Minzu University of China, Beijing, China 2012
Research Project Assistant (Jinchao Feng's laboratory)
- Performed nitrogen fertilization in urban grass and remote forests, collected soil samples, analyzed soil physical and chemical properties
- Measured plant respiration rate using IRGA along with soil moisture
- Performed data management and analysis, wrote and presented a report

Chinese Research Academy of Environmental Science (CRAES), Beijing, China Spring 2011
Research Intern in Environmental Ecological Research Institute
- Ground soil samples and analyzed soil nutrient concentrations using ICP-MS
- Assisted with data management, analysis and report writing

PRESENTATIONS

28. **Yang, Y**., Meng, L., Yanai, R.D., Driscoll, C.T., Montesdeoca, M., Templer, P.H., Rustad, L.E., and Absbjornsen, H. Climate change may worsen mercury pollution in northern hardwood forests. American Geophysical Union Fall Meeting, Washington, D.C. December 14, 2018.

27. **Yang, Y**., Yanai, R.D., Millard, D.G., Driscoll, C.T., Schoch, N., and Evers, D.C. Using uncertainty analysis to provide sampling guidance in monitoring fish and loons for mercury pollution. LTER All Scientists' Meeting Uncertainty Workshop, Pacific Grove, CA. October 3, 2018.

26. **Yang, Y**., Yanai, R.D., Phelps, K.E., Schoch, N., Lampman, G.G., and Evers, D.C. Monitoring mercury in Adirondack loons: how much is enough? LTER All Scientists' Meeting Poster Session. Pacific Grove, CA. October 2, 2018.

25. **Yang, Y**., Meng, L., Yanai, R.D., Driscoll, C.T., Montesdeoca, M., Templer, P.H., Rustad, L.E., and Absbjornsen, H. Climate change may worsen mercury pollution in northern hardwood forests. Ecological Society of America Annual Meeting, New Orleans, LA. August 10, 2018.

24. Mobley, M.L., **Yang Y**., Yanai, R.D., Nelson, K.A., and Richter, D.D. Detecting forest soil response to reforestation and ecological succession at the Calhoun Critical Zone Observatory, USA. Ecological Society of America Annual Meeting, New Orleans, LA. August 10, 2018.

23. **Yang, Y**., Schoch, N., Yanai, R.D., and Evers, D.C. Temporal and spatial pattern in mercury concentration in Adirondack loons with sampling guidance. New York State Fish Mercury Monitoring Meeting, Syracuse, NY. April 13, 2018

22. Montesdeoca, M., Driscoll, C.T., Millard, G.D., Yang, Y., Persson, M. Conversion equation: DEC fillet to plug Hg results. New York State Fish Mercury Monitoring Meeting, Syracuse, NY. April 13, 2018

21. L, Meng., **Yang, Y**., Yanai, R.D., Driscoll, C.T., and Montesdeoca, M. Climate change alters mercury transport and storage in northern hardwood forests. Environmental Group Seminar, Syracuse, NY. November 13, 2017

20. Driscoll, C.T., Gerson, J., Taylor, M., Millard, D.G., Shaw, A., **Yang, Y**., and Paul, E. Spatial patterns and temporal trends in atmospheric deposition, surface water and fish mercury in the Adirondack region of New York, USA. The 13th International Conference on Mercury as a Global Pollutant, Providence, Rhode Island. July 21, 2017

19. **Yang, Y**., Yanai, R.D., Driscoll, C.T., and Montesdeoca, M. The importance of mercury in leaves, bark and wood of eight tree species across four northeastern forests. The 13th International Conference on Mercury as a Global Pollutant, Providence, Rhode Island. July 17, 2017.

18. **Yang, Y**., Meng, L., Yanai, R.D., Montesdeoca, M., and Driscoll, C.T. Does climate change alter mercury fluxes in northern hardwood forests? The 54th Annual Hubbard Brook Cooperators' Meeting, Hubbard Brook Experimental Forest, NH. July 12, 2017.

17. **Yang, Y**. Mercury studies at Hubbard Brook. Hubbard Brook Committee of Scientists Meeting, Hubbard Brook Experimental Forest, NH. July 14, 2017.

16. Lasser, G. A., Hong, D.S., **Y. Yang.**, Phelps, K.E., Pu, G., and Yanai, R.D. Effect of nutrients on foliar characteristics of pin cherry, American beech, yellow birch and white birch. State University of New York Environmental Science and Forestry. ESF Spotlight on Student Research. Syracuse, NY. April 25, 2017

15. **Yang, Y**., Yanai, R.D., Fatemi, F.R., Levine, C.R., Lilly, P.J., and Briggs, R.D. Sources of variability in tissue chemistry in northern hardwood species. American Geophysical Union Fall Meeting, San Francisco, CA. December 12, 2016.

14. Yanai, R.D., **Yang, Y**., Montesdeoca, M., and Driscoll, C.T. The importance of mercury in leaves, bark and wood of eight tree Species across four northeastern forests. American Geophysical Union Fall Meeting, San Francisco, CA. December 14, 2016.

13. **Yang, Y**., Yanai, R.D., Montesdeoca, M., and Driscoll, C.T. Measuring mercury in wood: Important but challenging. Ecological Society of America Annual Meeting, Fort Lauderdale, FL, August 10, 2016.

12. **Yang, Y.,** Wild, A.D., Yanai, R.D., Montesdeoca, M., and Driscoll, C.T. Tapping clonal sugar maple provides an opportunity to test for genetic control of mercury uptake by trees. State University of New York College of Environmental Science and Forestry. ESF Spotlight on Student Research. April 19, 2016.

11. **Yang, Y**., Yanai, R.D., Montesdeoca, M., and Driscoll, C.T. Measuring mercury in wood: Important but challenging. SUNY/CUNY Graduate Research Poster Session. Albany, NY. February 11, 2015.

10. **Yang, Y**., Yanai, R.D., Montesdeoca, M., and Driscoll, C.T. Measuring mercury in wood: Important but challenging. New York Society of American Foresters Meeting, Syracuse, NY. January 22, 2015.

9. **Yang, Y**., Yanai, R.D., Montesdeoca, M., and Driscoll, C.T. Measuring mercury in wood: Important but challenging. American Geophysical Union Fall Meeting, San Francisco, CA. December 18, 2014.

8. **Yang, Y**., Yanai, R.D., and Briggs, R.D. Detecting differences of tissue chemistry in four northern hardwood tree species. Ecological Society of America Annual Meeting, Sacramento, CA. August 14, 2014

7. **Yang, Y**., See, C.R., and Yanai, R.D. Sampling intensity and uncertainty in litterfall mass and nutrient flux in northern hardwoods. Ecological Society of America Annual Meeting Later Poster Session, Sacramento, CA. August 15, 2014

6. **Yang, Y**., Yanai, R.D., and Briggs, R.D. Detecting differences of tissue chemistry in four northern hardwood tree species. State University of New York Environmental Science and Forestry. ESF Spotlight on Student Research. Syracuse, NY. April 18, 2014

5. **Yang, Y**. Source of variability in tissue chemistry in northern hardwood species. New York Society of American Foresters Meeting, Syracuse, NY. January 23, 2014

4. Aulenbach, B.T., Burns, D.A., Shanley, J.B., Yanai, R.D., Bae, K.K., Wild, A.D., **Yang, Y**., and Dong, Y. Uncertainty of stream water solute fluxes in five contrasting headwater catchments including model uncertainty and natural variability. American Geophysical Union Fall Meeting, San Francisco, CA. December 10, 2013

3. **Yang, Y**. Detecting change over time in tree tissue chemistry. Rochester Academy of Science Fall Paper Session, Rochester, NY. November 9, 2013

2. **Yang, Y.,** and Yanai, R.D. Detecting change over time in tree tissue chemistry Hubbard Brook 50th Cooperator's Meeting, Hubbard Brook Experimental Forest, NH. July 10, 2013

1. **Yang, Y.,** and Feng, J.C. Effects of simulated nitrogen deposition on soil microbial quantities in Fragrant Mountain in Beijing Undergraduate Research and Training Program Report Session, Minzu University of China, BJ, China. December 25, 2010

FELLOWSHIPS, GRANTS, AWARDS, AND CERTIFICATES

Alumni Association Grant SUNY-ESF (2018)
Sussman Foundation Fellowship Edna Bailey Sussman Foundation (2017)
Graduate Student Travel Award International Conference on Mercury as a Global Pollutant (2017)
Program Certificate of Advanced Study in Sustainable Enterprise Syracuse University (2017)
Graduate Student Travel Grant SUNY-ESF (fall 2014, fall 2016, spring 2016 and spring 2017)
C. Eugene Farnsworth Fellowship Dept Forest and Natural Resources Management SUNY-ESF (2015)
Sussman Foundation Fellowship Edna Bailey Sussman Foundation (2013)
Certificate of Level-1 Game of Logging Chainsaw Training Bill Lindloff's ProCUTS (2013)
Second-class Scholarship Minzu University of China, China (2012)
Second prize of 2nd Chemistry Experiment Competition Minzu University of China, China (2010)
Second prize of 1st Biology Experiment Competition Minzu University of China, China (2010)
Second-class Scholarship Minzu University of China, China (2010)
First-class Scholarship Minzu University of China, China (2009)
Undergraduate Research Training Grant Minzu University of China, China (2009)

PROFESSIONAL AFFILIATIONS

- **Reviewer** for Science of the Total Environment, Journal of Plant Nutrient and Soil Science, Biogeochemistry, Ecosystems
- **Member** of Ecological Society of America, American Geophysical Union