Environmental Pollution 228 (2017) 8–18

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Atmospheric mercury deposition to forests in the eastern USA☆

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ARTICLE INFO

Article history:
Received 5 January 2017
Received in revised form
28 April 2017
Accepted 2 May 2017

Keywords:
Mercury
Methylmercury
Litterfall
Atmospheric deposition
Forest

ABSTRACT

Atmospheric mercury (Hg) deposition to forests is important because half of the land cover in the eastern USA is forest. Mercury was measured in autumn litterfall and weekly precipitation samples at a total of 27 National Atmospheric Deposition Program (NADP) monitoring sites in deciduous and mixed deciduous-coniferous forests in 16 states in the eastern USA during 2007–2014. These simultaneous, uniform, repeated, annual measurements of forest Hg include the broadest area and longest time frame to date. The autumn litterfall-Hg concentrations and litterfall mass at the study sites each year were combined with annual precipitation-Hg data. Rates of litterfall-Hg deposition were higher than or equal to precipitation-Hg deposition rates in 70% of the annual data, which indicates a substantial contribution from litterfall to total atmospheric-Hg deposition. Annual litterfall-Hg deposition in this study had a median of 11.7 μg per square meter per year (μg/m^2/yr) and ranged from 2.2 to 23.4 μg/m^2/yr. It closely matched modeled dry-Hg deposition, based on land cover at selected NADP Hg-monitoring sites. Mean annual atmospheric-Hg deposition at forest study sites exhibited a spatial pattern partly explained by statistical differences among five forest-cover types and related to the mapped density of Hg emissions. Forest canopies apparently recorded changes in atmospheric-Hg concentrations over time because litterfall-Hg concentrations decreased year to year and litterfall-Hg concentrations were significantly higher in 2007–2009 than in 2012–2014. These findings reinforce reported decreases in Hg emissions and atmospheric elemental-Hg concentrations during this same time period. Methylmercury (MeHg) was detected in all litterfall samples at all sites, compared with MeHg detections in less than half the precipitation samples at selected sites during the study. These results indicate MeHg in litterfall is a pathway into the terrestrial food web where it can accumulate in the prey of songbirds, bats, and raptors.
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1. Introduction

Mercury (Hg) is a persistent environmental contaminant and can accumulate and concentrate in food webs as methylmercury (MeHg), presenting a health risk to humans and wildlife. A majority of the Hg in aquatic and terrestrial ecosystems comes from atmospheric deposition, and atmospheric Hg predominantly originates from human activities (Driscoll et al., 2013; Lindberg et al., 2007; National Research Council, 2000). The three operationally-defined species of atmospheric Hg are gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM), and particulate-bound Hg (PBM), as summarized by Driscoll et al. (2013); Lindberg et al. (2007); and Zhang et al. (2009). Transfers of GOM and PBM from the atmosphere to the biosphere occur episodically in precipitation (rain, snow, sleet, hail, and fog), which is sometimes called wet deposition and is called precipitation-Hg deposition hereafter. Other transfers of GEM, GOM, and PBM from the atmosphere to vegetation, soil, impervious surfaces, and water, called dry-Hg deposition hereafter, can be more continuous. The vertical dry-deposition velocity to a forest landscape can be 2 to 5 times larger than the velocity to other landscapes for all three Hg species because the

☆ This paper has been recommended for acceptance by Dr. Yong Sik Ok.
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http://dx.doi.org/10.1016/j.envpol.2017.05.004
0269-7491/Published by Elsevier Ltd.

greater leaf surface area and canopy roughness in a forest intercepts air flow and amplifies dry-Hg deposition to vegetation (Zhang et al., 2009).

Modeling studies indicate annual rates of dry-Hg deposition can exceed precipitation-Hg deposition in forest landscapes (Engle et al., 2010; Miller et al., 2005; Wang et al., 2016; Zhang et al., 2012, 2016). Litterfall Hg is thought to represent 75% of dry-Hg deposition to deciduous forests in North America and Europe (Wang et al., 2016) and was reported to be 60–80% of dry-Hg deposition at sites in the eastern USA (Demers et al., 2007; Grigal, 2002; Graydon et al., 2008; Johnson and Lindberg, 1995; Munthe et al., 2004; Risch et al., 2012a; St. Louis et al., 2001). The utility of litterfall-Hg data for understanding dry-Hg deposition has received increased attention (Wang et al., 2016; Wright et al., 2016; and Zhang et al., 2016). Earlier, Mason et al. (2005) and Lindberg et al. (2007) outlined broad agreement about the need for litterfall-Hg monitoring. Sams (2007) noted that managers of public lands and forests need information about MeHg inputs that impact water and wildlife. Studies by Blackwell and Driscoll (2015), Drenner et al. (2013), and Laacouri et al. (2013) promoted the value of a litterfall-Hg monitoring network to provide dry-Hg deposition information for forests related to Hg-emissions reductions and ecosystem-Hg accumulation.

A net accumulation of atmospheric Hg occurs in leaves and needles of forest canopies (Bash and Miller, 2009; Grigal, 2002; Graydon et al., 2008). The Hg mass measured in the leaves and needles is found to be largely atmospheric in origin (Ericksen et al., 2003; Fleck et al., 1999; Frescholtz et al., 2003) and includes mostly new Hg intercepted by the canopy and a minor amount of Hg in evasion from the forest (Bushey et al., 2008; Graydon et al., 2009; St. Louis et al., 2001; Rea et al., 2002). Studies by Blackwell et al. (2014), Bushey et al. (2008), and Rea et al. (2002) indicate that an annual accumulation of Hg in foliage of deciduous forests nears a maximum at autumn leaf senescence and leaf drop. Annual litterfall consists of leaves and needles, woody material such as twigs and bark, and reproductive bodies such as flowers, seeds, fruits, and nuts (Meier et al., 2006). In deciduous forests, at least 70 percent of autumn litterfall consists of leaves (Meier et al., 2006; Xiong and Nilsson, 1997).

The Hg in litterfall is likely to be mostly GEM, with minor and variable amounts of GOM and PBM (Driscoll et al., 2013; Wright et al., 2016; Zhang et al., 2012, 2016). It is believed that most of the Hg is irreversibly incorporated in the leaf tissue as GEM delivered by stomatal uptake (Ericksen et al., 2003; Millhollen et al., 2006; Rutter et al., 2011; Stamenkovic and Gustin, 2009). Non-stomatal Hg accumulation to foliage has been observed (Stamenkovic and Gustin, 2009), and GOM and PBM are known to attach to leaf surfaces, though not always permanently. Laacouri et al. (2013) reported more than 90% of Hg in deciduous tree species studied was in the leaf tissue rather than on the leaf surface. Laboratory (Millhollen et al., 2006) and field studies (Bishop et al., 1998) indicate uptake of soil Hg through tree roots to the canopy is substantially smaller than the transfer of Hg from the air to the foliage, as summarized by Bushey et al. (2008) and Gustin et al. (2008). Studies by Blackwell and Driscoll (2015), Demers et al. (2007), Graydon et al. (2006) and Rea et al. (1996, 2000, 2001) found that most of the Hg in deciduous and mixed deciduous-coniferous forest canopies was transported to the forest floor in litterfall. The rest of the Hg was in throughfall, when precipitation passing through the forest canopy generates a net increase in Hg transported to the forest floor, adding to the Hg from open-field precipitation.

This study of atmospheric-Hg deposition is important because forests comprise 50% of land cover in the eastern USA (Oswalt et al., 2014). Many forests are biological reserves particularly sensitive to the transfer of atmospheric Hg to terrestrial and aquatic ecosystems. Most headwater streams are in forests and their ecosystems receive carbon, nutrients, and trace elements from the leaves, needles, and other material that falls from the forest canopy to the water and soil (Allan and Castillo, 2007; Benfield, 1997; Weathers et al., 2012). Freshwater wetlands comprise 8% of the land cover in the 20 ecoregions of the eastern USA (Loveland and Acevedo, 2016) yet two-thirds of all wetlands in the USA are forest and shrub wetlands (Dahl, 2011). Wetlands are biochemical settings where anaerobic conditions promote iron- and sulfate-reducing microbes to convert inorganic Hg to biologically active MeHg (Brigham et al., 2009; Hurley et al., 1995; Morel et al., 1998; St. Louis et al., 2001).

2. Methods

2.1. Study sites

This study used uniform methods to make simultaneous, repeated measurements of Hg in autumn litterfall and annual precipitation in deciduous and mixed deciduous-coniferous forests in the eastern USA. Data were from 27 National Atmospheric Deposition Program (NADP) Mercury Deposition Network (MDN) sites in 16 states. New measurements from 2012 to 2014 and those from 2007 to 2009 (Risch et al., 2012a) provide an improved understanding of atmospheric-Hg deposition to a broad expanse of forests over a 6-year period. Study sites (Fig. 1, Table 1) were in rural locations generally distant from Hg-emissions sources and located on public lands administered by the National Park Service, the U.S. Fish and Wildlife Service, the U.S. Forest Service, state agencies and universities, and on tribal lands. The locations were east of the Plains region (National Oceanic and Atmospheric Administration, 2016a) and included the Great Lakes, Central and Southern Appalachians, Ohio Valley, Upper and Middle Mississippi Valleys, Northeast, Southeast, and mid-Atlantic regions.

Study sites were assigned to five forest-cover types in the eastern USA, based on groups from Oswalt et al. (2014). A 5-km buffer around each site was examined with a geographic information system to identify the dominant forest-cover type in the U.S. Geological Survey (2015) land cover dataset and classifications were made consistent with observations of tree species at each forest plot. A deciduous forest class was at 23 sites and included four forest-cover types: oak-hickory, maple-beech-birch, aspen-birch, and hardwood. A mixed deciduous-coniferous forest class, called the mixed forest-cover type hereafter, was at 4 sites (Table 1). Litterfall sites in the oak-hickory type were in Missouri, southern Wisconsin, Indiana, Ohio, Kentucky, Tennessee, and Virginia; sites in the maple-beech-birch type were in Vermont, New York, Pennsylvania, Maryland, and West Virginia; and sites in the aspen-birch type were in Minnesota and Wisconsin (Fig. 1). Sites in hardwood and mixed types were located throughout the eastern USA. The number of study sites in the forest-cover types generally corresponds with the area for some of these types in the forest inventory for the eastern USA. (Oswalt et al., 2014): 574,564 square kilometers (km^2) oak-hickory (9 of 23 sites), 219,777 km^2 maple-beech-birch (7 of 23 sites), and 66,785 km^2 aspen-birch (4 of 23 sites).

Annual precipitation-Hg data for the study sites were derived from weekly monitoring data in the NADP MDN data base. Annual precipitation-Hg deposition at an MDN site is the product of the total annual precipitation amount and the precipitation-weighted annual Hg concentration, based on a set of weekly sample data, and is measured in units of micrograms per square meter per year ($\mu g/m^2/yr$). Methods for sampling, analysis, and quality assurance of precipitation samples at MDN sites are documented by the NADP (National Atmospheric Deposition Program, 2016a).