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Dry deposition of gaseous elemental mercury to plants and soils using mercury stable isotopes in a controlled environment

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ABSTRACT

Uptake of gaseous elemental mercury ($Hg^0_{(g)}$) by three plant species and two soil types was measured using mercury vapor enriched in the 198 isotope ($^{198}Hg^0_{(g)}$). The plant species and soil types were: White Ash (*Fraxinus Americana*; WA); White Spruce (*Picea Glauca*; WS); Kentucky Bluegrass (*Poa Partensis*; KYBG); Plano Silt Loam (4% organic matter; PSL); and Plainfield Sand/Sparta Loamy Sand (1.25–1.5% organic matter: PS). The plants and soils were exposed to isotopically enriched $Hg^0_{(g)}$ in a 19 m^3 controlled environment room for 7 days under optimal plant growth conditions (20 °C, 140 Wm^{-2} between 300 nm and 700 nm; 70% RH) and atmospherically relevant $Hg^0_{(g)}$ concentrations. Mercury was recovered from the samples using acidic digestions and surface leaches, and then analyzed for enrichments in ^{198}Hg by ICPMS. The method was sensitivity enough that statistically significant enrichments in ^{198}Hg were measured in the plant foliage at the end of Day 1. Whole leaf digestions and surface-selective leaches revealed that accumulative uptake was predominantly to the interior of the leaf under the conditions studied.

Uptake fluxes for WA increased between the first and third days and remained constant thereafter (WA; Day 1 = $7 \pm 2 \times 10^{-5}$ ng m^{-2} s^{-1}; Days 3–7 = $1.3 \pm 0.1 \times 10^{-4}$ ng m^{-2} s^{-1}; where m^2 refers to one sided leaf area). KYBG demonstrated similar behavior although no Day 3 measurement was available (Day 1 = $7.5 \pm 0.5 \times 10^{-5}$ ng m^{-2} s^{-1}; Day 7 = $1.2 \pm 0.1 \times 10^{-4}$ ng m^{-2} s^{-1}). Fluxes to White Spruce were lower, with little difference between Days 1 and 3 followed by a decrease at Day 7 (WS; Days 1–3 = $5 \pm 2 \times 10^{-5}$ ng m^{-2} s^{-1}; Day 7 = $2.4 \pm 0.2 \times 10^{-5}$ ng m^{-2} s^{-1}). Uptake of Hg to soils was below the method detection limit for those media (PSL = 3×10^{-2} ng m^{-2} s^{-1}; PS = 3×10^{-3} ng m^{-2} s^{-1}) over the 7 day study period. Foliar resistances calculated for each species compared well to previous studies.

1. Introduction

Gaseous elemental mercury ($Hg^0_{(g)}$) is the predominant component of atmospheric mercury outside the influence of arctic depletion events and anthropogenic point sources. $Hg^0_{(g)}$ is emitted into the atmosphere by natural processes, and due to a variety of current and past human activities (Lin and Pehkonen, 1999; Pacyna et al., 2009; Rutter et al., 2008). The primary pathway for removal of $Hg^0_{(g)}$ from the atmosphere is currently thought to be oxidation to the Hg(II) species, followed by dry and wet deposition. However, direct dry deposition of $Hg^0_{(g)}$ to plants has also been observed (Ericksen et al., 2003; Millhollen et al., 2006; Stamenkovic et al., 2008), and uptake of only a small percentage of the atmospheric $Hg^0_{(g)}$ reservoir by plants could substantively impact the input of mercury to terrestrial ecosystems. In order to effectively model the residence time of $Hg^0_{(g)}$ in the atmosphere, its removal processes and kinetics from the atmosphere must be well understood. Furthermore, the relative magnitudes of $Hg^0_{(g)}$ and oxidized mercury deposition pathways, and their subsequent fates after deposition, must also be ascertained in order to predict the ecosystem impacts of these different input mechanisms.

Foliar accumulation of $Hg^0_{(g)}$ during the course of a growing season has been observed in a few publications in which trees and grasses were continually exposed to atmospherically relevant concentrations over several months (Ericksen et al., 2003; Millhollen et al., 2006). Accumulation of mercury in foliage progresses over the course of a growing season, even though foliage can

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both emit and take up mercury during different times of the day (Bash and Miller, 2009; Millhollen et al., 2006). Such behavior suggests that a fraction of $Hg^0_{(g)}$ taken into the leaf is fixed, with the remainder available for rapid exchange between the leaf and atmosphere in response to changing atmospheric concentrations (Du and Fang, 1982, 1983; Millhollen et al., 2006). These are complementary reservoirs of foliar mercury and are observed using different approaches. The fixed fraction of foliar mercury can be measured by the analysis of harvested foliage, whereas the exchangeable portion is best followed using a dynamic flux chamber method (Millhollen et al., 2006; Stamenkovic and Gustin, 2009). When leaves senesce (age) and fall off of the tree (litterfall) they constitute a new input of fixed atmospheric mercury into the ecosystem (Ericksen et al., 2003; St Louis et al., 2001). As leaf litter is decomposed, fixed total mercury can be redistributed into the soil if the initial leaf concentration is high enough (>30 ng g^{-1}) (Hall and St Louis, 2004). Hall and St Louis also observed that mercury in litterfall may be methylated even on dry soils suggesting that litterfall may be a source of methylmercury to ground and surface water.

Previous investigators have measured foliar accumulation from the atmosphere using either radioisotopic or non-isotopic, total mercury approaches (Browne and Fang, 1978; Ericksen et al., 2003; Millhollen et al., 2006). Although both methods were used successfully, they have limitations which can be overcome with the use of stable mercury isotopes: i) the radioisotope approach (^{203}Hg) uses a gamma-ray and x-ray emitting material (undesirable for laboratory work; unfeasible for field exposures) and high vapor concentrations (4000 ng m^{-3}); ii) foliar assimilation of mercury flux rates are low relative to the atmospheric and foliar backgrounds, meaning that non-isotopic, total mercury measurements require several weeks of exposure to achieve sufficient signal to noise ratios using atmospherically relevant $Hg^0_{(g)}$ concentrations. The limitations of these techniques can be overcome by quantifying perturbations in the natural isotopic ratios of mercury, a more sensitive way to measure uptake resistances.

The objective of this study was to use stable isotope enrichment techniques to directly measure the short term foliar uptake resistances of mercury in trees, grasses, and soils (Hintelmann et al., 2002; Hintelmann and Ogrinc, 2003). To our knowledge, the study presented here is the first published method for the use of gaseous elemental mercury enriched in stable isotopes to track uptake of mercury to foliage. In this study we exposed saplings of White Ash and White Spruce, Kentucky Blue Grass (also known as Common Meadow Grass), and two soils to $Hg^0_{(g)}$ enriched in the 198 mercury stable isotope ($^{198}Hg^0_{(g)}$). Exposures were conducted at environmentally relevant concentrations over 7 days in a large controlled environment room. Measurements of the enriched mercury retained by the foliage were performed by ICPMS on digests and leaches of the plant leaves.

2. Methods

2.1. Plants and soils

Plants and soils were exposed to gaseous elemental mercury enriched in stable isotope 198 (hereafter $^{198}Hg^0_{(g)}$), in a controlled environment room (UW-Biotron, Madison, WI). The plants and soils exposed were: White Ash (WA, *Fraxinus americana*); White Spruce (WS, *Picea glauca*); Kentucky Bluegrass (KYBG, *Poa partensis*; aka Common Meadow Grass); Plano Silt Loam; and, Plainfield Sand/Sparta Loamy Sand. The tree saplings were obtained from the Wisconsin Department of Natural Resources nursery: WA and WS were 1 year saplings transplanted from the ground to pots containing commercially available potting soil (Sphagnum Moss Peat) and placed in the UW-Biotron greenhouse on a timed watering system. KYBG was bought from a sod farm (Cambridge, WI), repotted in trays, and also kept in the greenhouse. The soils were collected from the University of Wisconsin Agricultural Research Stations at Arlington, WI and Hancock, WI, respectively. The upper 6–8 inches of soil were collected, placed into plastic buckets lined with plastic bags, sieved with a 0.5 inch wire mesh to remove roots and surface vegetation, and stored in air-tight containers at 4 °C. Quartz fiber filters were coated with gold sol by reducing a 2% solution gold chloride with acidified hydroxylamine. The coated QFFs were evaluated as a standard deposition surfaces to measure $Hg^0_{(g)}$ deposition, by measuring the uptake of Added $^{198}Hg^0_{(g)}$. The coupons did not perform with acceptable reliability during this study and will not be further discussed.

2.2. Controlled environment room

The controlled environment room (Fig. 1) was a windowless 19 m^3 chamber fitted with a closed loop air-conditioning system that allowed precise control over temperature (operational range = +10 °C to +30 °C; <2% precision at 99% CI) and relative humidity (operational range = 20%–80%; <3% precision at 99% CI), and replaced the air 3 times per minute, with particulate filtration between exit and re-entry. The lighting consisted of 60 fluorescent tubes (F96T12-CW-1500 General Electric Fluorescent tubes, 215 W). This article focuses on the performance of the stable isotope exposure method at 20 °C, a relative humidity of 70%, and an irradiance of 140 Wm^{-2} (300–700 nm), which have been identified as optimal growth conditions for temperate forests in the published literature (Jarvis, 1976; Jurik et al., 1988). The irradiance setting used was the maximum available from the fluorescent light bank and corresponded to the daily average irradiance (<700 nm) at Madison, WI in April (Figure S1). The 70% relative humidity was typical of monthly averages in Southern Wisconsin during all seasons except winter. Soil samples were placed on Teflon sheets (pre-washed in hot nitric acid baths overnight) positioned on the top shelves of stainless steel rolling trolleys at 1.5 m height, 0.3 m below the air-conditioning inlets.

2.3. Source of isotopically enriched gaseous elemental mercury

The $Hg^0_{(g)}$ enriched in the 198 stable isotope was introduced into the base of the room from a Teflon vessel containing a bead of liquid mercury enriched in the 198 isotope (ORNL, TN; 89.5% abundance, Table S3; natural abundance 10.04%). The use of a permeation tube was not feasible due to the large mass of isotopically enriched mercury needed to produce the required output. The target concentration in the room was defined as the minimum concentration of $^{198}Hg^0_{(g)}$ added to the natural $Hg^0_{(g)}$ background which led to a detectable uptake in the plants and soils. A minimum added $^{198}Hg^0_{(g)}$ concentration of 0.1 ng m^{-3} was found to be sufficient to achieve this. The required output from the source calculated to achieve this minimum concentration was approximately 1 pg min^{-1}, however the optimized output rate, which was not measured, was likely to have been higher than this due to wall losses in the chamber. A pump with a filtered outlet was used to blow air through the heated (30 °C) vessel at 5 LPM for the duration of each experiment. A box fan placed in front of the source dispersed the emitted mercury vapor into the room, and the air handling system returned the Hg-spiked air through vents below the Perspex ceiling (Fig. 1).

2.4. Measurements

Air concentrations of total $Hg^0_{(g)}$ (both the background $Hg^0_{(g)}$ and added $^{198}Hg^0_{(g)}$) in the room were determined using a Tekran