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Mosses and lichens enhance atmospheric elemental mercury deposition in a subtropical montane forest†

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Environmental context. Mosses and lichens are widely distributed in montane forests and their important role in global biogeochemical cycles has been increasingly recognised. This study of mercury accumulation and sources in mosses and lichens, using mercury isotopic data, provides evidence that they promote atmospheric mercury deposition in these forests, which is an important function that should be incorporated into current mercury mass balance budgets for forests.

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ABSTRACT

Rationale. Mosses and lichens, which are widely distributed in montane forests, are often used to monitor the atmospheric mercury (Hg) depositions. In this study we hypothesised that atmospheric Hg uptake by mosses and lichens could greatly promote Hg depositions in montane forests. **Methodology.** We comprehensively determined the Hg concentration and isotopic signatures of various species of mosses and lichens in a subtropical montane forest, to quantify the Hg accumulation, influencing factors and potential Hg depositions induced by mosses and lichens. **Results.** Our results show that the higher Hg concentrations in mosses than in lichens are mainly due to their species-specific, morphological and physiological differences. Hg isotopic mixing model results display that uptake of atmospheric elemental Hg (Hg^0) contributes 89.2 ± 22.8% of Hg in mosses and 88.4 ± 24.4% in lichens. The lichens growing on trees have a lower atmospheric Hg^0 source contribution than on the ground (61.3 ± 42.5% versus 93.6 ± 10.0%) because of the elevated rainfall Hg uptake on trees. The Hg storage in live moss and lichen is 28.0 ± 16.5 and 0.9 ± 1.0 μg m^{-2}, respectively. Given the 1–2-year lifespan of moss, the moss induced atmospheric Hg deposition is almost equivalent to litterfall Hg deposition which was previously used as a proxy for atmospheric Hg^0 deposition in forests. **Discussion.** Overall, we suggest mosses and lichens play an important role in atmospheric Hg depositions and recommend more research in montane forests.

Keywords: lichen, mercury deposition, mercury isotopes, mercury pool, mercury sources, mercury concentration, moss, subtropical forest.

Introduction

Mosses and lichens are globally abundant, growing on soils, rocks and epiphytically on trees. Specifically, they form extensive covers on the forest floor and canopy in subtropical montane forests. Mosses and lichens both lack root systems and thick waxy cuticles, have a high surface area-to-volume ratio and are largely dependent on atmospheric deposition for water and nutrients supply (Bargagli 2016*b*). Thus, mosses and lichens have been widely used as bioindicators to monitor atmospheric pollutants. Mercury (Hg) is a persistent pollutant that causes health and ecological concerns across the globe due to its gaseous elemental form (Hg^0) being transported long-distance in the air via atmospheric circulation (Schroeder and Munthe 1998; Agnan *et al.* 2016). Substantial numbers of studies have documented the use of mosses and lichens for monitoring atmospheric Hg depositions across the globe (Evans and Hutchinson 1996; Balarama Krishna *et al.* 2003; Bargagli *et al.* 2007; Kłos *et al.* 2012; Lodenius 2013; Bargagli 2016*a*, 2016*b*).

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Recently, mosses and lichens have increasingly been recognised to play an important role in global biogeochemical cycles. The moss and lichen covers can increase 10% of rainfall interception in forests (Porada *et al.* 2018), and can take up around 3.9 Pg of carbon per year (7% of net primary production), and 49 Tg of nitrogen per year (still with large uncertainties) on global land (Elbert *et al.* 2012; Porada *et al.* 2013; Davies-Barnard and Friedlingstein 2020). Given strong correlation between Hg and nutrient cycles in forests, we suggest that mosses and lichens not only monitor Hg pollution levels, but also play an important role in biogeochemical cycles of Hg.

Mosses and lichens both have a high cation exchange capacity, and earlier studies highlighted that mosses and lichens accumulated heavy metals via intracellular (i.e. reversibly absorbed on the cell surface and trapped as particulate matter and then transported into the cell) and extracellular processes (i.e. bound in exchangeable form or at chelating sites on the cell wall and the plasma membrane) during water and nutrients uptake (Bargagli 2016*b*; Stanković *et al.* 2018; Wang *et al.* 2019*a*). This means that uptake of atmospheric Hg^{2+} is likely a potential source for Hg accumulation in mosses and lichens. Several recent studies have revealed that Hg accumulation in moss and lichen is highly related to the level of atmospheric Hg^0, specifically with the evidence of Hg stable isotopes (Balarama Krishna *et al.* 2004; Enrico *et al.* 2016; Wang *et al.* 2020*b*; Monaci *et al.* 2022).

The Hg stable isotopes, which are quantified by mass dependent fractionation (MDF, reported as δ^{202}Hg), odd mass independent fractionation (odd-MIF, reported as Δ^{199}Hg and Δ^{201}Hg) and even mass independent fractionation (even-MIF, reported as Δ^{200}Hg), have been used as effective tools to trace Hg sources and processes in forest ecosystems. There are three typical endmembers for Hg sources in forests. One is the atmospheric Hg^0 deposition with negative odd-MIF and positive MDF, and slightly negative even-MIF (only around -0.05‰ in remote sites) signatures; another is the atmospheric Hg^{2+} deposition with both positive odd- and even-MIF signatures; the other is geogenic Hg input via rock weathering processes, with negative MDF and near zero odd- and even-MIF signatures (Demers *et al.* 2013; Fu *et al.* 2016, 2019*b*; Yu *et al.* 2016; Yuan *et al.* 2019; Kurz *et al.* 2020). Given few Hg biogeochemical processes induce Hg-MIF during the moss and lichen uptake of atmospheric Hg, the odd- and even-MIF signatures provide a new insight in identifying Hg sources in moss and lichen covers.

Different from most earlier studies that highlighted moss and lichen biomonitoring of atmospheric Hg pollution levels, in this study we hypothesised that uptake of atmospheric Hg by intensive moss and lichen covers in montane forests would largely increase the atmospheric depositions of Hg. Hence, we comprehensively determined the Hg concentration and isotopic compositions of mosses and lichens, analysed factors influencing Hg accumulation and estimated Hg sources and potential Hg deposition flux in a subtropical montane forest.

Experimental

Sites description

The study site was located at 2450–2650 m above sea level (asl) within Ailaoshan Station for Subtropical Forest Ecosystem Research Studies (ASSFERS) (101°01′E, 24°32′N), Southwest China. ASSFERS has a subtropical monsoon climate with an average annual temperature of 11.3°C and precipitation of 1800–2000 mm (Tan *et al.* 2011). ASSFERS belongs to the Indian monsoon and East Asian monsoon controlling zone, thus has a pronounced dry season (November to April) and a wet season (May to October) in each year (Song *et al.* 2015). The forest is mainly composed of *Lithocarpus xylocarpus*, *Castanopsis wattii*, *Lithocarpus chintungensis*, *Schima noronhae*, *Machilus viridis*, *Hartia sinensis* and *Manglietia insignis*, with a canopy height of 20–30 m and more than 85% canopy cover density (Liu *et al.* 2002).

Sample collection and pretreatment

Eighteen species of moss and lichen samples were collected at ASSFERS in September of 2016. For each species, we collected 4–5 replicates for data quality control. According to the epiphytic location, we divided moss samples into two groups that consisted of moss growing on the tree and on the ground. Similarly, we divided lichen samples into ground, rock and tree lichen samples. For the moss collection, we only sampled the green living part. The tree mosses and lichens were sampled from the 0–2 m height on the tree trunk. Once the sample was collected, it was packed into a zip-lock bag and taken back to the laboratory. At the laboratory, all samples were lightly washed with water three to five times to remove deposited dust and soil, given a final rinse with double distilled water (DDW) and subsequently placed in a 45°C oven to dry to a constant mass. Our earlier studies have well documented that oven-drying below 50°C will not lead to distinct Hg mass loss in vegetation (Wang *et al.* 2016; Li *et al.* 2022; Yuan *et al.* 2022*a*). After drying, the moss and lichen samples were ground to a fine powder by a precleaned grinder and sieved with a 100-mesh (150 μm) nylon screen for chemical analysis.

Hg concentration and isotope measurements

The protocol for Hg concentration measurement for vegetation has been described in detail in our previous work (Wang *et al.* 2016, 2017*a*). Briefly, the Hg concentrations of moss and lichen samples were measured by a DMA80 Hg analyser. The certified reference material (CRM) of BCR-482 (lichen, Hg = 480 ± 20 ng g^{-1}) was used for QA/QC (quality assurance/quality control) and measured every nine samples with an observed recovery of 95–105%.

Procedures for Hg isotope measurement of moss and lichen samples have been described previously (Wang *et al.* 2020*b*). Briefly, all samples were processed by a double-stage

tube furnace and trapping solutions (anti aqua regia, HNO_3/HCl = 2:1, v/v) for Hg preconcentration. The preconcentrated Hg solutions were diluted to 1 ng mL^{-1} before Hg isotope measurement on a Nu-Plasma II multicollector–inductively coupled plasma–mass spectrometer (MC-ICP-MS). The recoveries of preconcentration ranged from 98 ± 4% for the CRM of BCR-482 and 97 ± 6% for all samples. The Hg-MDF is reported in δ notation using the unit of permil (‰) referenced to the neighbouring NIST-3133 solution (Eqn 1):

$$\delta^{202}\text{Hg}\ (‰) = 1000 \times [(^{202}\text{Hg}/^{198}\text{Hg}_{\text{sample}}) / (^{202}\text{Hg}/^{198}\text{Hg}_{\text{NIST-3133}}) - 1] \quad (1)$$

xxx is 199, 200 and 201. MIF is reported as Δ^{xxx}Hg (Eqns 2–4) following the convention suggested by Blum and Bergquist (2007):

$$\Delta^{199}\text{Hg}\ (‰) = \delta^{199}\text{Hg} - 0.2520 \times \delta^{202}\text{Hg} \quad (2)$$

$$\Delta^{200}\text{Hg}\ (‰) = \delta^{200}\text{Hg} - 0.5024 \times \delta^{202}\text{Hg} \quad (3)$$

$$\Delta^{201}\text{Hg}\ (‰) = \delta^{201}\text{Hg} - 0.7520 \times \delta^{202}\text{Hg} \quad (4)$$

The Hg isotopic signatures for BCR-482 were measured as δ^{202}Hg = −1.67 ± 0.12‰, Δ^{199}Hg = −0.56 ± 0.08‰, Δ^{200}Hg = −0.01 ± 0.04‰ and Δ^{201}Hg = −0.58 ± 0.08‰ (mean ± 2 s.d., standard deviation, n = 6). The NIST-8610 was also analysed every 10 samples during the Hg isotope measurements, with isotopic signatures of δ^{202}Hg = −0.53 ± 0.08‰, Δ^{199}Hg = −0.00 ± 0.08‰ and Δ^{201}Hg = −0.03 ± 0.06‰ (mean ± 2 s.d., n = 12). All measured Hg isotopic signatures of CRM were consistent with standard values (Blum and Bergquist 2007; Estrade *et al.* 2010).

Statistical methods

Data were analysed using the statistical program R 4.10 with $P < 0.05$ as the level of significance. We used One-Way ANOVA and independent T-test to conduct the significant difference analysis when data were normally distributed. Otherwise, the Kruskal–Wallis test was applied. In addition, we estimated the Hg pool size of moss and lichen by Eqn 5:

$$\text{Hg}_{\text{Pool}} = C \times \text{Biomass} \quad (5)$$

where 'Hg_{Pool}' is the Hg pool of moss or lichen; 'C' is the Hg concentration of moss or lichen; 'Biomass' is the biomass of moss or lichen, which has been well documented in a previous study at ASSFERS (Ma 2009).

Results

Table 1 and Fig. 1 show the Hg concentration in samples of 10 species of moss and 8 species of lichen. The average of Hg concentration in moss was 110.0 ± 66.7 ng g^{-1} (n = 42). There was no significant difference ($P > 0.05$) in Hg concentration between tree mosses (111.2 ± 56.6 ng g^{-1}, n = 22) and ground mosses (107.8 ± 77.8 ng g^{-1}, n = 20). The Hg concentration of mosses showed a distinct species-specific difference. For example, the Hg concentration of *Polytrichum inflexum* (232.5 ± 46.7 ng g^{-1}, n = 4) was seven times higher than that of *Conocephalum conicum* (27.6 ± 1.3 ng g^{-1}, n = 4), although both moss species mainly grow on the ground. The average Hg concentration in lichen was 73.4 ± 47.7 ng g^{-1} (n = 32), and significantly lower than the value in moss ($P < 0.05$). The average Hg concentration of tree lichen (81.7 ± 49.2 ng g^{-1}, n = 25) was significantly greater than values of ground lichen (52.6 ± 32.6 ng g^{-1}, n = 4) and rock lichen (31.7 ± 16.9 ng g^{-1}, n = 3; $P < 0.05$). The Hg concentration distinctly varied among different species of lichen. The highest Hg concentration was found in *Lobaria retigera*, with a value of 179.0 ± 33.6 ng g^{-1} (n = 4).

Given variations of Hg concentration and epiphytic locations, we selected four species of tree moss, three species of ground moss, three species of tree lichen and two species of ground lichen to measure the Hg isotopic compositions. Tables 1, 2 and Fig. 2 show results of Hg isotopic compositions. The mean value of Hg isotopic compositions for tree-moss was δ^{202}Hg as −2.24 ± 0.05‰, Δ^{199}Hg as −0.32 ± 0.04‰, and Δ^{200}Hg as −0.02 ± 0.04‰ (n = 4). We observed similar Hg isotopic signatures for ground-moss (δ^{202}Hg = −2.16 ± 0.05‰, Δ^{199}Hg = −0.31 ± 0.04‰, Δ^{200}Hg = −0.03 ± 0.04‰, n = 3). The tree lichen had an average value of −1.67 ± 0.05‰ for δ^{202}Hg, 0.42 ± 0.04‰ for Δ^{199}Hg and −0.03 ± 0.04‰ for Δ^{200}Hg (n = 3). For the ground lichen, we observed −2.33 ± 0.05‰ of δ^{202}Hg, −0.21 ± 0.04‰ of Δ^{199}Hg and −0.02 ± 0.04‰ of Δ^{200}Hg (n = 2).

In this study, we mainly estimated the Hg pool sizes of tree mosses and lichens due to the much smaller biomass of mosses and lichens on the ground at ASSFERS (Ma 2009). Table 3 summarises the biomass and Hg pool size of mosses and lichens on trees. We found that the total Hg pool size for the living moss was 28.0 ± 16.5 μg m^{-2}, much higher than the Hg pool size in tree lichens (0.9 ± 1.0 μg m^{-2}). This was caused by the much-elevated moss biomass in contrast to the biomass of lichen (2.55 t ha^{-1} versus 0.12 t ha^{-1}). The tree moss Hg pool size was comparable to the Hg pool size in branch, and nearly accounted for more than 60% of Hg pool size in foliage and in wood and 11% of the total Hg pool size in tree biomass (Table 3).

Discussion

Hg^0 as the main sources in mosses and lichens

Earlier studies have well documented that without a root system, the Hg accumulated in moss and lichen was mainly

Table 1. Mercury concentrations and isotopic signatures in specific species of mosses and lichens.

Species	Mean[A]	s.d.	*N*	$\delta^{202}Hg$[B]	$\Delta^{199}Hg$[C]	$\Delta^{200}Hg$[C]	Location
Moss							
Sematophyllaceae	71.4	10.8	4	−2.20	−0.30	−0.05	Tree
Polytrichum inflexum	232.5	46.7	4	−2.55	−0.45	−0.06	Ground
Meteorium Dozy Molk	167.8	68.0	4				Tree
Plagiochilaceae	87.9	30.3	4	−2.31	−0.35	−0	Tree
Leucobryum juniperoideum	195.0		1				Tree
Leucobryum juniperoideum	149.4	16.4	3				Ground
Floribundaria floribunda	149.9	15.9	4	−2.48	−0.35	−0.02	Tree
Conocephalum conicum	27.6	15.9	4	−2.16	−0.21	0.00	Ground
Rhodobryum roseum	62.9	1.3	5				Ground
Polytrichum commune	88.2	4.8	4	−1.77	−0.27	−0.05	Ground
Herbertus sendtneri	68.8	6.5	5	−2.00	−0.31	−0.01	Tree
Lichen							
Lobaria retigera	179.0	33.6	4	−1.72	−0.46	−0.04	Tree
Ramalina dilacerata	36.0	3.6	4	−1.60	−0.55	−0.03	Tree
Cladonia rangiferina	52.6	28.2	4	−2.73	−0.35	0.01	Ground
Nostoc commune	18.5		1				Tree
Nostoc commune	31.7	13.8	3				Rock
Nostoc commune				−1.94	−0.08	−0.06	Ground
Sticta nylanderiana	69.5	14.8	4	−1.70	−0.28	−0.02	Tree
Cetrelia cetrarioides	80.4	4.6	4				Tree
Ramalina conduplicans	71.8	9.8	4				Tree
Usnea florida	69.5	9.9	5				Tree

[A]Mercury concentration of mosses and lichens (ng g^{-1}).
[B]Value of $\delta^{202}Hg$ (‰) in specific species of moss and lichen, s.d. = 0.05‰.
[C]Value of $\Delta^{199}Hg$ and $\Delta^{200}Hg$ in specific species of moss and lichen, s.d. = 0.04‰.

derived from atmospheric depositions (Calasans and Malm 1997; Bargagli 2016*b*; Wang *et al.* 2019*a*, 2020*b*). Atmospheric Hg depositions in forest mainly contain the atmospheric Hg^{2+} deposition via rainfall and particle, and atmospheric Hg^0 deposition via uptake by vegetation. Given no distinct Hg-MIF occurring during Hg deposition processes in forests (Wang *et al.* 2020*a*, 2020*b*) and largely different $\Delta^{199}Hg$ signatures between the endmember of atmospheric Hg^0 (negative) and Hg^{2+} (positive) signatures, we used the $\Delta^{199}Hg$ to build a two-endmember mixing model for estimation of Hg sources (Eqns 6, 7):

$$F_1 + F_2 = 1 \quad (6)$$

$$F_1 \times \Delta^{199}Hg_1 + F_2 \times \Delta^{199}Hg_2 = \Delta^{199}Hg_{moss/lichen} \quad (7)$$

where F_1 is the proportion of atmospheric Hg^0 input (%); F_2 is the proportion of atmospheric Hg^{2+} input (%); $\Delta^{199}Hg_1$ is the signature of atmospheric Hg^0 and $\Delta^{199}Hg_2$ is the signature of atmospheric Hg^{2+}. The $\Delta^{199}Hg$ signal for atmospheric Hg^0 was reported as -0.09 ± 0.08‰ ($n = 54$) by earlier studies (Yu *et al.* 2016; Fu *et al.* 2019*b*), and for atmospheric Hg^{2+} was 0.64 ± 0.29‰ ($n = 44$) in rainfall and particle-bound Hg at ASSFERS (Fu *et al.* 2019*a*; Li *et al.* 2019). The uncertainty of 0.04‰ caused by the bias during $\Delta^{199}Hg$ measurement was considered in our Hg isotopic mixing model. Our earlier assessments show that coupling the Hg isotope mixing model with Monte Carlo simulations effectively reduces the uncertainties of model results (Wang *et al.* 2020*a*, 2020*b*). These uncertainties were quantified by generating 1 million groups of MIF signatures randomly ranging from mean − s.d. to mean + s.d. to solve the Hg isotope mixing model.

The Hg isotopic mixing model showed that the atmospheric Hg^0 uptake dominated sources of Hg accumulation in mosses and lichens, with an average contribution of $89.2 \pm 22.8\%$ in mosses and $88.4 \pm 24.4\%$ in lichens (Fig. 3). This is consistent with earlier studies in montane

coniferous forests (Enrico *et al.* 2016; Wang *et al.* 2020*b*). There was no significant difference for the contribution of atmospheric Hg^0 sources between tree mosses (87.1 ± 26.3%) and ground mosses (90.1 ± 21.8%) ($P > 0.05$, Fig. 3). However, the atmospheric Hg^0 uptake contributed a lower ratio for tree lichens than ground lichens (61.3 ± 42.5% versus 93.6 ± 10.0%, $P < 0.05$, Fig. 3). Most earlier studies highlighted heavy metal uptake by moss and lichen via intracellular and extracellular processes along with water (Bargagli 2016*b*; Stanković *et al.* 2018; Wang *et al.* 2019*a*). However, this is not a case for Hg uptake since moss and lichen directly take up the vapour of Hg^0. A recent study revealed that Hg^0 oxidation in tree foliage could occur via a two-step single-electron transfer process, involving Hg^I and Hg^{II} formation mediated by non-enzymatic and enzymatic reactions (Liu *et al.* 2021*b*). The mechanism underlying the Hg^0 oxidation in the moss and lichen needs to be further studied.

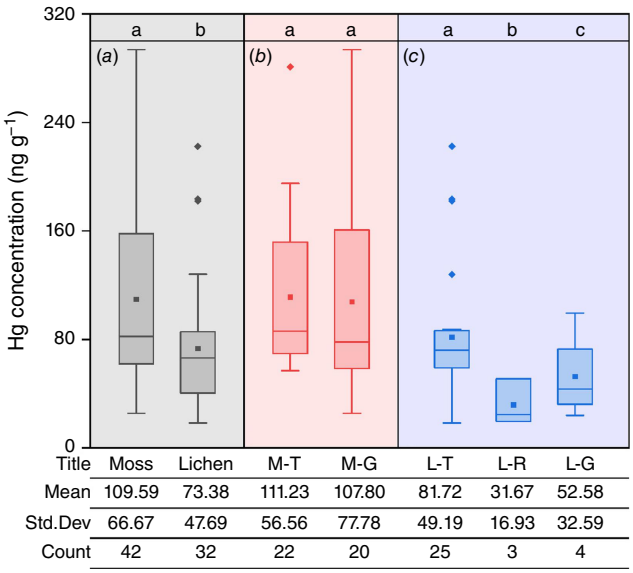

Fig. 1. Variation of mercury concentration in mosses and lichens. (*a*) Results for all moss and lichen samples. (*b*) Results for the moss samples growing on the tree (M-T) and ground (M-G). (*c*) Results for the lichen samples growing on the tree (L-T), rock (L-R) and ground (L-G). The lower-case letter represents the statistical difference at the 95% confidence level.

Morphological features and epiphytic locations influencing Hg accumulation

Earlier studies suggest that diffusion is an important pathway of atmospheric Hg uptake in mosses and lichens (Kłos *et al.* 2012; Lodenius 2013; Bargagli 2016*a*). Given strong relations between diffusion and morphological features (Bargagli 2016*b*; Stanković *et al.* 2018; Wang *et al.* 2019*a*), we suggest that morphological features would play an important role in controlling Hg concentrations in mosses and lichens. Our results show that the species of moss with the lower specific surface area has the lower Hg concentration. For example, the leafy-like mosses (e.g. *Conocephalum conicum, Rhodobryum roseum Limpr*, in Supplementary Fig. S1) have low Hg concentrations of 27.6–68.8 ng g^{-1}, in contrast to the Hg concentration of >100 ng g^{-1} in hairy-like mosses (e.g. *Polytrichum inflexum and Leucobryum juniperoideum*). Similarly, the lichen species *Lobaria retigera* has distinct dense rod-like or granular cleavage buds, which leads to a higher specific surface area and a greater Hg concentration than concentrations in other species of lichen ($P < 0.05$). Additionally, the higher Hg concentration in mosses than in lichens also can be partly attributed to the greater average specific surface area in mosses (Supplementary Figs S1, S2). Besides the

Table 2. Summary of Hg isotopic signatures for moss, lichen, stemflow, bark, foliage, litter and O layer soils.

Samples	δ^{202}Hg (‰)	s.d.	Δ^{199}Hg (‰)	s.d.	Δ^{200}Hg (‰)	s.d.	*N*	References
Moss	−2.21	0.05	−0.32	0.04	−0.03	0.04	7	This study
Lichen	−1.94	0.05	−0.34	0.04	−0.03	0.04	5	This study
M-T[A]	−2.24	0.05	−0.32	0.04	−0.02	0.04	4	This study
M-G[A]	−2.16	0.05	−0.31	0.04	−0.03	0.04	3	This study
L-T[A]	−1.67	0.05	−0.42	0.04	−0.03	0.04	3	This study
L-G[A]	−2.33	0.05	−0.21	0.04	−0.02	0.04	2	This study
Stemflow	−2.75	0.31	−0.28	0.23	−0.01	0.03	9	Li *et al.* (2019)
O layer	−2.18	0.31	−0.36	0.06	−0.01	0.03	21	Lu *et al.* (2021)
Litter	−2.71	0.29	−0.32	0.06	−0.03	0.03	24	Wang *et al.* (2019*b*)
Bark	−2.37	0.24	−0.45	0.06	−0.03	0.02	4	Liu *et al.* (2021*a*), Yuan *et al.* (2022*a*)
Foliage	−2.54	0.18	−0.29	0.05	−0.01	0.03	17	Liu *et al.* (2021*a*), Lu *et al.* (2021)

[A]M-T represents the moss on the tree, M-G is the moss on the ground, L-T is lichen on the tree and L-G is lichen on the ground.

morphological features, differences in gas exchange pathways and oxidation processes between mosses and lichens also contribute to their Hg concentration variations.

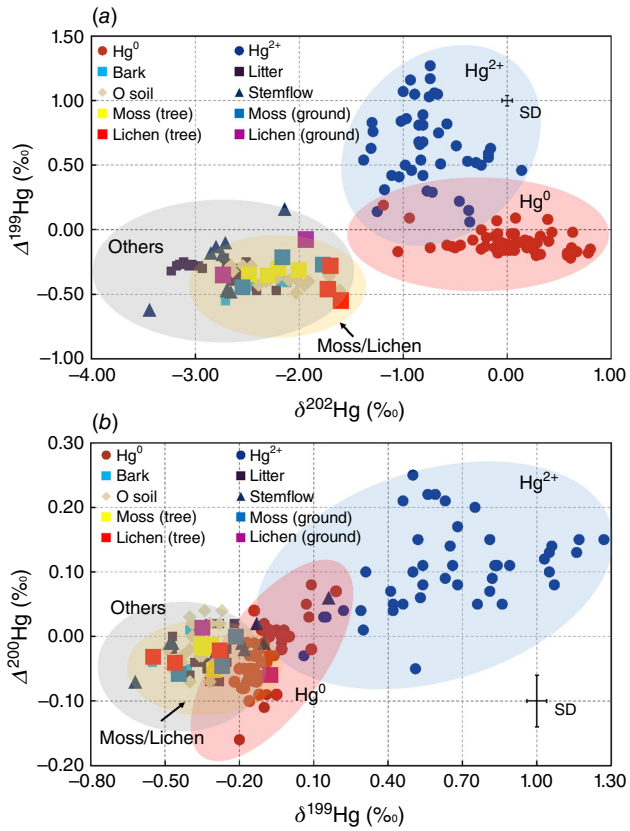

Fig. 2. Mercury isotopic signatures in atmospheric Hg^0, atmospheric Hg^{2+} (rainfall and PBM), bark, litter, O soil, stemflow, moss and lichen on trees and ground. (*a*) is for $\Delta^{199}Hg$ versus $\delta^{202}Hg$ and (*b*) is for $\Delta^{200}Hg$ versus $\Delta^{199}Hg$. The blue elliptic area in (*a*, *b*) represents the endmember of atmospheric Hg^{2+}, the red elliptic area means the endmember of atmospheric Hg^0 and the grey elliptic area refers to the Hg isotopic signatures for other samples (bark, litter, O soil, stemflow range). The Hg isotopic signatures of Hg^0, Hg^{2+}, bark, litter, O soil and stemflow have been documented in earlier studies (Yu et al. 2016; Fu *et al.* 2019*a*, 2019*b*; Li *et al.* 2019; Wang *et al.* 2019*b*; Liu *et al.* 2021*a*; Lu *et al.* 2021; Yuan *et al.* 2022*a*).

We found that tree lichens had significantly different Hg concentration and isotopic signatures in contrast to values in ground lichens, which suggests that the epiphytic locations could influence Hg uptake. The Hg isotopic modelling shows a higher atmospheric Hg^{2+} uptake by tree lichens (Fig. 3). The greater atmospheric Hg^{2+} input in the tree lichen is likely attributed to the elevated cloud water-induced Hg^{2+} input due to a higher frequency cloud water in montane forests (Luo *et al.* 2022). It is noted there are insignificant differences of Hg concentration and isotopic signatures between tree mosses and ground mosses. This is likely attributed to the high water holding capacity of mosses, which leads to the smaller difference of atmospheric Hg^{2+} contribution between tree mosses and ground mosses.

Distinct Hg pool size in tree mosses inducing an important Hg deposition

Given a 1–2 year lifespan and the Hg^0 contents of tree mosses, we estimated the tree moss induced Hg^0 flux using Eqn 8:

$$Hg_{flux} = (Hg_{Pool} \times f_{Hg^0})/T \quad (8)$$

where Hg_{Pool} is the Hg pool size in tree mosses, f_{Hg^0} is the Hg^0 contribution in tree mosses and T is the lifespan of tree moss. It is noted that the estimation of tree moss induced Hg^0 flux is associated with large uncertainties. One is that, given the large heterogeneities and substantial species of moss distribution, there are distinct uncertainties in moss biomass (Ma 2009). Additionally, the moss lifespan at our studied site has not been well documented, thus a rough estimation of a 1–2 year lifespan is based on our earlier observations in the montane forest (Wang *et al.* 2020*b*). Hence, we only estimated the potential range of this Hg^0 flux based on our current data and knowledge.

We could estimate a range of 13–26 $\mu g\, m^{-2}\, year^{-1}$ for moss induced atmospheric Hg^0 deposition in our montane forest. Earlier studies suggested that the Hg^0 uptake by the foliage dominating the atmospheric Hg^0 depositions in forests (Wang *et al.* 2016, 2017*b*, 2021; Xia *et al.* 2022).

Table 3. Mercury pool in biomass of forest at ASSFERS.

Samples	Biomass ($t\, ha^{-1}$)	Hg pool size ($\mu g\, m^{-2}$)	s.d.	Reference
Foliage	7.1	41	11	Liu *et al.* (2021*a*)
Branch	33	26	8.3	Liu *et al.* (2021*a*)
Bark	46	51	18	Liu *et al.* (2021*a*)
Wood	373	60	26	Liu *et al.* (2021*a*)
Root		215.3		Yuan *et al.* (2022*a*)
Moss[A]	2.6	28.0	16.5	This study
Lichen	0.1	0.9	1.0	This study

[A]Living part of the moss.

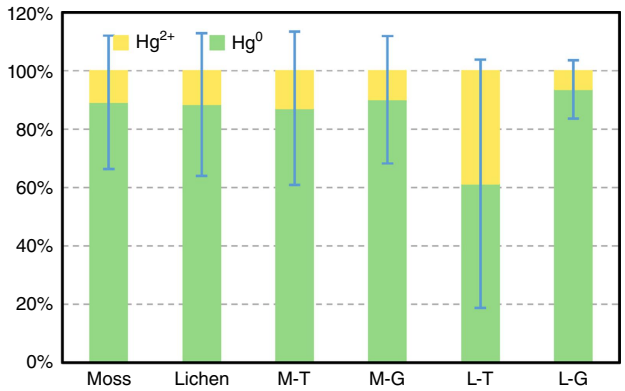

Fig. 3. The Hg isotopic mixing model estimated the Hg sources in mosses and lichens. M-T represents the moss on the tree, M-G is the moss on the ground, L-T is lichen on the tree and L-G is lichen on the ground. The error bars represent 1 standard deviation of the modelling results.

However, our estimate suggests that the distinct moss induced atmospheric Hg^0 deposition in montane forests is nearly comparable to 24.0 ± 21.6 μg m^{-2} $year^{-1}$ of litterfall Hg flux at ASSFERS (Wang *et al.* 2022; Yuan *et al.* 2022*b*). The comparable Hg-MIF signatures for lichens, mosses and organic soils (Fig. 2) further confirm that moss and lichen cover-induced atmospheric Hg^0 depositions are important Hg sources for forest soils.

In addition, we suggest that moss and lichen covers on the canopy would significantly influence stemflow (i.e. rainfall passing along the canopy and stem) Hg inputs. Earlier studies indicated that the stemflow would scrub previously deposited atmospheric Hg^{2+} on the canopy (Demers *et al.* 2007; Graydon *et al.* 2008; Blackwell *et al.* 2014; Blackwell and Driscoll 2015). Thus, these Hg inputs were mainly derived from atmospheric Hg^{2+} in earlier studies. However, we found that the Hg isotopic signatures in stemflow mostly overlap the signatures of tree moss and lichen covers and atmospheric Hg^0 (Fig. 2). This demonstrates the importance of atmospheric Hg^0 sources in stemflow Hg. Given the low water solubility of Hg^0, atmospheric Hg^0 is not the direct source of stemflow Hg. Thus, we suggest that the atmospheric Hg^0 uptake by these moss and lichen covers on the canopy, and the detritus of moss and lichen covers subsequent mixing into stemflow water, likely contribute to such a Hg^0 source.

Conclusions

In this study, we highlight that the enhanced Hg accumulation in mosses and lichens largely promotes the atmospheric Hg depositions in montane forests. The species, morphological characteristics and epiphytic state of mosses and lichens have a great impact on their Hg concentrations. Uptake of atmospheric Hg^0 contributes to 89.2 ± 22.8% Hg sources in mosses and 88.4 ± 24.4% in lichens. The tree moss cover-induced atmospheric Hg^0 deposition is comparable to litterfall Hg depositions. We suggest that moss and lichen cover-induced atmospheric Hg^0 deposition should be incorporated into the current forest Hg deposition mass budgets. Although large uncertainties exist because of limited data availability, our findings still highlight the need for future studies to better understand the Hg accumulation in moss covers, which will enable a more accurate quantification of the Hg^0 sink in montane forests.

Supplementary material

Morphological characteristics of mosses and lichens in Supplementary Figs S1, S2. Supplementary material is available online.

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