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Exchange of mercury between atmosphere and vegetation under contaminated conditions

M. Lodenius*, E. Tulisalo, A. Soltanpour-Gargari

Department of Limnology and Environmental Protection, University of Helsinki, P.O. Box 27, Helsinki FIN-00014, Finland

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Abstract

Adsorption and desorption of mercury was studied under laboratory conditions using moss (*Sphagnum girgensohnii*) and Rye grass (*Lolium perenne*) at different temperatures. Desorption was also studied in a transplantation experiment. The adsorption was rapid and strong for both plant species at different temperatures (+10 to +60 °C) and exposure times (1 h, 1 month) while the evaporation was negligible. Also the leaching of adsorbed mercury was of minor importance. The results emphasise the importance of vegetation in removal of mercury from the atmosphere. They also confirm the suitability of moss and grass for biomonitoring purposes. The high retention of mercury in moss even at +60 °C indicates the possibility of using higher temperatures in pretreatment of samples for mercury analyses. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Mercury; Vegetation; Adsorption; Desorption

1. Introduction

The dominant form of mercury in the atmosphere is gaseous elemental mercury (Hg^0) and there is a continuous exchange of mercury between atmosphere and vegetation. Mercury is transferred from the atmosphere to the vegetation by both wet and dry deposition. The deposition around a chlor-alkali plant as measured by the moss bag method was shown to be mainly in form of dry deposition (Lodenius, 1997). It is important to know the magnitude and velocity of the uptake processes at different environmental conditions.

In forested ecosystems throughfall and litterfall are primary deposition pathways. Conifer canopies accumulate more mercury from the atmosphere than deciduous forests as shown by higher deposition in throughfall and stemflow under conifers (Kolka et al., 1999). In a washing experiment the wash-off of dry deposition occurred rapidly, while foliar leaching occurred continuously during the washing experiment (up to 12 h; Rea et al., 2000). The annual throughfall deposition of mercury has been estimated to be greater ($10.5 \mu\text{g m}^{-2}$) than the precipitation mercury flux ($8.7 \mu\text{g m}^{-2}$) in a northern mixed-hardwood forest (Rea et al., 2001).

Experiments performed under controlled conditions show that also the transfer of mercury from vegetation to atmosphere may be considerable. The emission of mercury from vascular plants to

*Corresponding author.

E-mail address: martin.lodenius@helsinki.fi
(M. Lodenius).

the atmosphere was estimated to $10\text{--}90\text{ ng}^{-2}\text{ h}^{-1}$ in the light with much smaller emissions in the dark. Most of the mercury taken up by the roots of *Lepidium latifolium* during the growing season was emitted to the atmosphere (Todd et al., 1998a). The degassing rate from soil is strongly dependent on ambient temperature with both seasonal and daily variations (Ferrara et al., 1997). Measurements over forest areas in Tennessee and Sweden suggest that the mercury flux is dominated by emissions from plants and soil while dry deposition is less frequent. These fluxes are influenced by temperature, solar radiation and atmospheric turbulence (Lindberg et al., 1998). In an open gas exchange system, Hanson et al. (1995) showed that mercury was emitted from plant surfaces at low mercury concentrations in air ($0.5\text{--}1.5\text{ ng}^{-3}$). At intermediate concentrations ($9\text{--}20\text{ ng}^{-3}$) there was little exchange of mercury and at high air concentrations ($50\text{--}70\text{ ng}^{-3}$) mercury was deposited to the foliage. Thus the vegetation seems to be a dynamic exchange surface acting as a source at low air concentrations and as a sink at high concentrations.

The aim of this investigation was to study the capacity of two different plants to take up mercury from air and retain it in the tissues at different temperatures.

2. Material and methods

2.1. Moss experiments

Samples of moss (*Sphagnum girgensohnii*) were collected from an unpolluted area in southern Finland. The green parts of the moss material were cleaned but not washed. The sorption and desorption experiments were performed at different temperatures. Approximately 2.5 l of moss was placed as a 3-cm thick layer on a nylon net in a closed plastic chamber (volume 18.5 l; Fig. 1). A mercury droplet ($\approx 50\text{ mg}$) was applied on a petri dish to the floor of the chamber. A fan was used to enhance an even distribution of mercury in the air. An exposure time of 3 h at room temperature was chosen. This exposure gives a concentration of $0.5\text{--}1\text{ }\mu\text{g g}^{-1}$ dry wt. (dw) in the moss—a level that can be found in polluted environments (Lod-

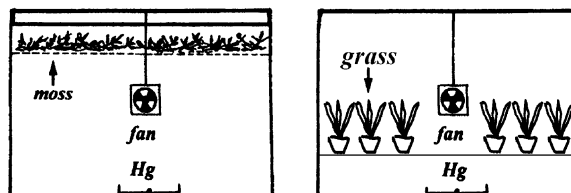


Fig. 1. Experimental design for the sorption experiments: moss (left) and grass (right).

enius and Tulisalo, 1984). After exposure homogeneity of the moss material was achieved by thorough mixing.

The sorption velocity in natural light at room temperature was measured for a period of 2 weeks (Experiment M1). The desorption by evaporation was measured in two experiments in the dark. The first one (M2) covered four temperatures ($+10$, $+22$, $+40$, $+60\text{ }^{\circ}\text{C}$) and 8 days. The second experiment (M3) covered three temperatures ($+10$, $+22$, $+40\text{ }^{\circ}\text{C}$) and 4 weeks. In the desorption experiments the moss was moistured daily by distilled water. In a field experiment (M4) we transplanted living moss (*Pleurozium schreberi*) from a polluted site near a chlor-alkali plant to an unpolluted site in southern Finland. In this area the mean monthly temperatures are $-3.7\text{ }^{\circ}\text{C}$ during the coldest months (December–March) and $+13.5\text{ }^{\circ}\text{C}$ during the warmest months (May–September). Green parts of the moss were collected ten times after transplantation from adjacent parts of the same stand. The mercury concentrations were monitored for a 2 year period (26 months).

Leaching of adsorbed mercury from the moss tissue was studied at room temperature ($22\text{ }^{\circ}\text{C}$; Experiment M5). Two parallel samples of dried moss (1.5 g) were placed into 200 ml of a solvent in 250 ml erlenmeyer beakers and shaken (200 rpm) in natural light for 10, 30, 60 and 120 min, respectively.

The solvents used were:

- distilled water (pH 7.9)
- acid (1 ml $\text{H}_2\text{SO}_4 + \text{HNO}_3$ 4:1/200 ml of water; pH 0.95)
- 0.05 mmol cysteine in water
- 1 mol cysteine in water.

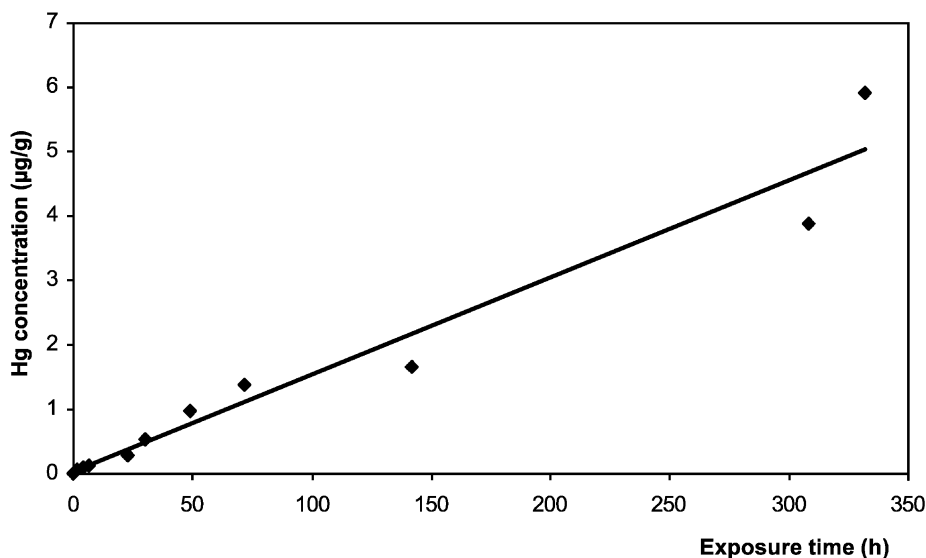


Fig. 2. Mercury concentrations in *Sphagnum* moss during 2 weeks (332 h) in an exposure chamber (Experiment M1).

After filtration (fast Whatman 41 filter) mercury contents were measured from the solutions.

2.2. Rye grass experiments

Rye grass (*Lolium multiflorum*) was grown in small porcelain pots until 10 cm high and exposed to mercury in an exposure chamber (Fig. 1). The soil surface was not isolated from the air. In the first experiment (G1) the grass was exposed for 2 weeks (336 h). Leaves and roots of grass and soil were analysed. In the second experiment (G2) the grass was exposed for 6 h and thereafter the concentrations were measured during a 16 days (384 h) period.

2.3. Chemical analysis

The samples were dried at +50 °C, homogenized and analysed in duplicate. The mercury concentrations were determined by cold vapour AAS (Bacharach MAS-50B) after digestion in strong acids ($\text{H}_2\text{SO}_4 + \text{HNO}_3$, 4:1). For a reference sample (Olive leaves BCR 62) we found $0.31 \pm 0.03 \mu\text{gHg g}^{-1} \text{ dw}$ ($N=4$) (certified 0.28 ± 0.02). Our determination limit was $0.01 \mu\text{g g}^{-1}$ for dry samples and $0.05 \mu\text{g l}^{-1}$ for water.

3. Results

Mercury was rapidly adsorbed from air into the moss tissue at room temperature. Significant amounts were sorbed during the first hours and the mosses seem to have a very good sorption capacity. During the 2 weeks experiment the increase in mercury concentration was nearly linear (M1; Fig. 2). No saturation could be observed during this period.

Mercury adsorbed by moss tissue was strongly retained and no significant changes in concentrations could be observed during the 8 days (M2; Fig. 3) or 4 weeks (M3; Fig. 4) experiments. The mercury concentrations were almost constant in both experiments at all temperatures from +10 to +60 °C. In the transplantation experiment (M4) the concentrations dropped steadily during the two monitored growing seasons (Fig. 5). Under winter time, no significant changes in mercury concentrations occurred. At the end of the second growing season the mercury level is near the background level and a weak increase can be seen after the second winter.

In the leaching experiment (M5) the concentrations were below or at the detection limit for distilled water and both concentrations of cysteine.

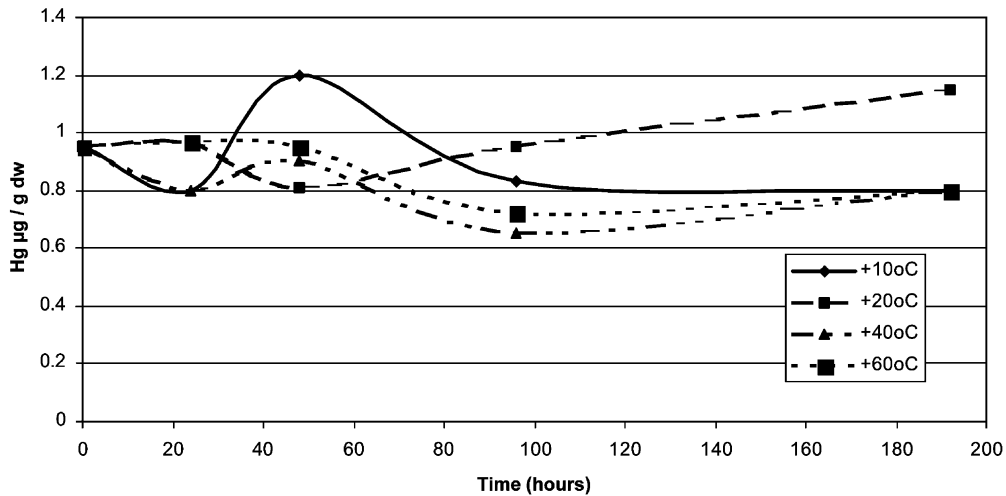


Fig. 3. Desorption of mercury from moss during 8 days (192 h) exposure in the dark (Experiment M2) at four temperatures.

For the acid solution a weak leaching could be detected and the amounts of mercury in water decreased slowly during the 2 h experiment. Only 3.3–5.5% of the mercury were leached out from the moss tissues (Fig. 6).

Mercury was taken up rapidly also in leaves of Rye grass and reached approximately the same concentrations as in *Sphagnum* moss (G1; Fig. 7). In the soil the concentration increased steadily but more slowly than in roots or leaves of grass. Also in Rye grass the absorbed mercury was retained

effectively during the 16 days experiment (G2; Fig. 8).

4. Discussion

The strong adsorption of mercury to vegetation was probably caused by the high rate of exposure. On the other hand, the desorption (evaporation/leaching) was weak even after a long period at low ambient mercury concentration. This would imply a stronger binding to plant tissue than in the

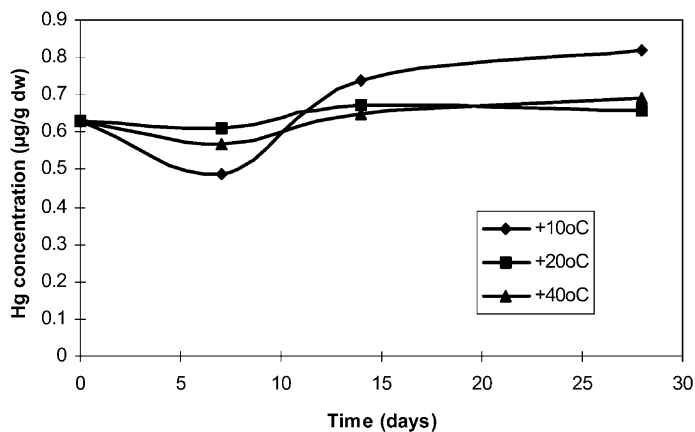


Fig. 4. Desorption of mercury from moss during a 4 weeks (720 h) exposure at three temperatures (Experiment M3).

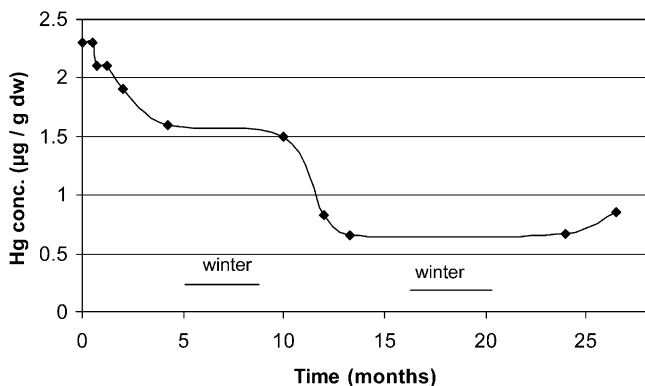


Fig. 5. Mercury concentrations in the moss *Pleurozium Schreberi* after transplantation (Experiment M4). The moss was transplanted from a polluted site near a chlor-alkali plant to an unpolluted site.

experiments by Hanson et al. (1995), who reported net losses at low ambient mercury concentrations. Also, Rea et al. (2000) showed that mercury originating from dry deposition at least in part could be removed by washing from leaves of live trees. As we chose dark conditions for our in vitro desorption experiments in order to ensure internal comparability, the influence of sunlight on the desorption should be investigated in more detail.

Moss species have in many reports (e.g. Kondoh et al., 1998) been considered as especially efficient

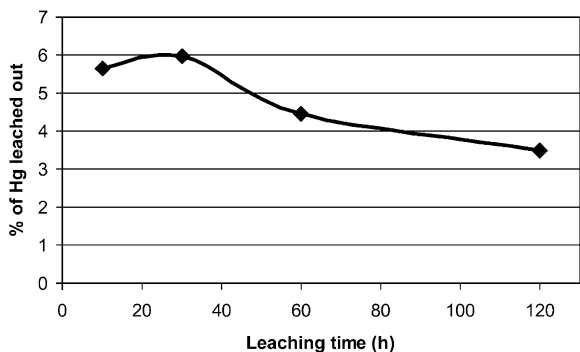


Fig. 6. Rate of mercury as % of total amount in moss leached out from 1.5 g (dw) of moss added to 200 ml of acid solution (H₂SO₄+HNO₃; pH 0.95). Mercury was analysed from four sequential samples (10, 30, 60 and 120 min, respectively; Experiment M5).

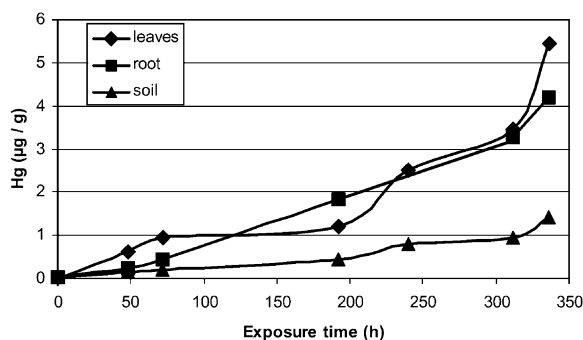


Fig. 7. Uptake of mercury in leaves and roots of Rye grass and in soil during a 2 weeks experiment (G1) in room temperature and sun light.

absorbers of heavy metals due to their complicated leaf structure. The high metal concentrations in moss and the use of them for biomonitoring purposes have also confirmed this view. Rye grass reached the same concentrations of mercury as moss although the background concentrations of moss and lichen species normally are much higher. This would imply an even higher uptake capacity by grass compared to moss. The decrease in mercury concentrations seen in the transplantation experiment is obviously due to both desorption and dilution due the growth of the moss. The concentrations did not decrease to the natural level approximately 0.1 µg g⁻¹ dw (Koski et al., 1988). Under natural conditions the concentrations are lower in the beginning of the growing season and

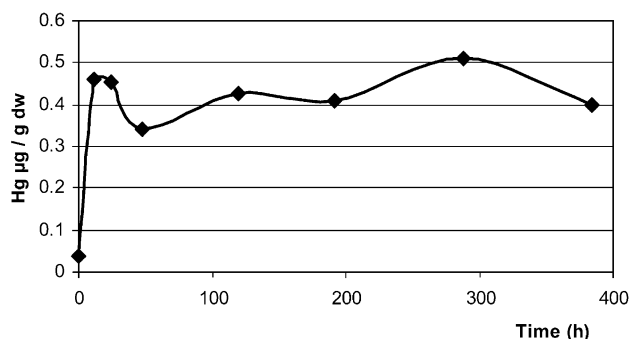


Fig. 8. Desorption of mercury in leaves of Rye grass during a 16 day (386 h) experiment (G2). Mercury exposure was carried out during the first 6 h only.

increase as a result of absorption of dry and wet deposition.

In contrast to several investigations (e.g. Ferrara et al., 1997; Lindberg et al., 1998; Todd et al., 1998b), we did not find any significant temperature effects which indicates a strong incorporation of the absorbed mercury into plant tissue. High temperatures are normally avoided in pretreatment and wet digestion of samples for mercury analyses. The strong sorption of mercury to moss even at +60 °C indicates broader possibilities to use normal analytical procedures (higher temperatures) for this kind of biological materials.

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