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The Science of the Total Environment 213 (1998) 53–56

**the Science of the  
Total Environment**  
An International Journal for Scientific Research  
into the Environment and its Relationship with Man

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# Dry and wet deposition of mercury near a chlor-alkali plant

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## Abstract

The dry and wet deposition near a Finnish chlor-alkali plant was estimated by using the moss-bag technique. The estimated net deposition was  $130 \text{ ng g}^{-1}$  per month or  $480 \mu\text{g m}^{-2}$  per year. Two-thirds of the deposition was dry and one-third wet. The results emphasize the importance of the direct uptake of atmospheric mercury by vegetation. © 1998 Elsevier Science B.V.

**Keywords:** Mercury; Deposition; Uptake; Moss; Vegetation

## 1. Introduction

More than 90% of mercury in the atmosphere is in the gas phase, mainly as  $\text{Hg}^0$  and the rate of particle bound mercury is small [approx. 2% (Brosset, 1987; Iverfeldt, 1991; Petersen et al., 1995)]. Mercury has a great evaporation rate even in a cool climate. Thus emissions to air may disperse over long distances. The oxidation to water soluble forms is slow and the half-life of elemental mercury is approx. 1 year (Brosset, 1987; Lindqvist et al., 1991). Mercury is emitted from a chlor-alkali plant as elemental mercury but little is known about the possible oxidation of chlorine compounds which may be present in this environment. Sorption and desorption are temperature dependent and differ for different mer-

cury species. Gaseous mercury ( $\text{Hg}^0$ ) may be removed from the atmosphere by wet or dry deposition.  $\text{Hg}^0$  may be oxidized by chemical oxidants to water soluble forms, e.g.  $\text{Hg}(\text{II})$ . Irreversible sorption of mercury by canopy surfaces may occur for both wet and dry deposition, but sorbed mercury may also be released by leaching or evaporation (Lindberg et al., 1994). Dissolved mercury species are obviously rapidly attached to vegetation surfaces or particles while the process and velocity of uptake of gaseous mercury (mainly  $\text{Hg}^0$ ) by vegetation is poorly known.

The sorption to and re-emission from vegetation can be assumed to depend on:

- Type and abundance of vegetation (different in summer and winter);
- Light and weather (stomata open/closed); and
- Air moisture and temperature.

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The aim of this study was to measure dry and wet deposition of mercury near an emitter of  $\text{Hg}^0$  by using the moss-bag technique and evaluate the importance of uptake processes.

## 2. Material and methods

Moss bags were placed near a chlor-alkali plant (Finnish Chemicals) in Kuusankoski, SE Finland, for the period 26 May–24 July 1995 (59 days). The moss-bag technique is based on the exceptionally effective ion-exchange of metals in the tissue of *Sphagnum* moss where metals are absorbed directly from the air (Lodenius, 1989; Crist et al., 1996). The moss was washed with 0.5 M HCl, rinsed with deionized  $\text{H}_2\text{O}$  and approx. 15 g (wet wt.) of moss tissue was placed in each nylon net ( $\phi$  5–7 cm). This procedure followed the Finnish standard method (Air protection, 1994) except that half of the moss bags were covered with plastic pots (Fig. 1) preventing these moss bags from getting wet deposition. The moss bags were placed 200 m northwest of the chlor-alkali plant. Seventeen normal and 17 covered moss bags were placed in trees at a height of 2.5–3.5 m. However, only 13 uncovered moss bags were found after the exposure.

The rainfall in the area was lower than normal, the total rainfall for June and July being 63.6 mm (average for the period 1961–1990 was 116 mm).

The moss material was dried at 45–50°C (Saiki and Fujiwara, 1985), homogenized and digested in strong acids ( $\text{H}_2\text{SO}_4 + \text{HNO}_3$ , 4:1). The mercury

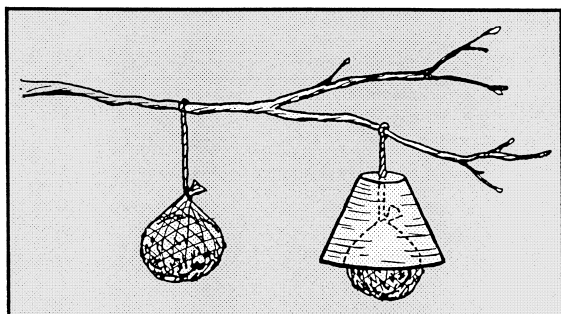


Fig. 1. Uncovered and covered moss bags.

concentrations were analyzed by cold vapour AAS (Bacharach MAS-50B).

## 3. Results

The accumulation was significantly higher in moss bags receiving both wet and dry deposition than in the covered moss bags (Table 1). The mean total (wet + dry) net accumulation of mercury was 130 ( $\pm 20$ ; S.D.) ng Hg per gram of moss per month. This can be estimated to correspond to a deposition of 480 ( $\pm 75$ )  $\mu\text{g m}^{-2}$  per year [surface occupied by moss 32  $\text{mg m}^{-2}$  (Lodenius and Tulisalo, 1984; Lodenius, 1995)]. Approximately two-thirds of the mercury deposition was dry and one-third wet (Fig. 2). The deposition measured now was bigger than that measured in 1994 (Lodenius, 1995).

## 4. Discussion

There is a continuous exchange of mercury between atmosphere and vegetation in both directions. Wet deposition is the most important form of removal of Hg from the atmosphere over water surfaces while both wet and dry processes are important over terrestrial ecosystems. Dry deposition includes absorption of gaseous and particle-bound mercury.

It is difficult to make reliable quantitative estimates of the deposition pathways of mercury. Different methods have been used: technical gauges, model calculations, throughfall and litterfall measurements and uptake in vascular plants and mosses (Table 2). There is an obvious need of more detailed information concerning the sorption process in vegetation. These could include

Table 1  
Estimated net deposition of mercury ( $\text{ng g}^{-1}$  per month)

|      | Total | Dry<br>( $n = 17$ ) | Wet<br>( $n = 13$ ) |
|------|-------|---------------------|---------------------|
| Mean | 126   | 84                  | 42                  |
| S.D. | 20    | 15                  | 26                  |

Wet deposition was calculated by subtracting dry deposition from total deposition.

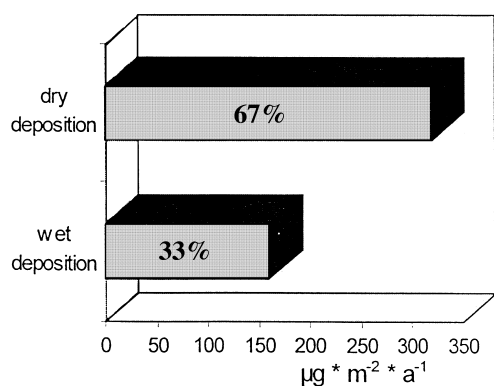


Fig. 2. Net dry and wet deposition as estimated by moss-bag measurements.

sorption and desorption of different mercury species at different temperatures and by different types of vegetation (trees, shrubs, grass, epiphytes).

In a spruce stand in southern Sweden the dry deposition of mercury has been estimated to be 50% of the wet deposition. The net uptake of mercury from soil by above-ground biomass was estimated to be near zero (Iverfeldt, 1991b;

Driscoll et al., 1994). Rea et al. (1996) found that the concentration in litterfall ( $53 \text{ ng g}^{-1}$ ) was significantly higher than in green foliage ( $34 \text{ ng g}^{-1}$ ) in a mixed hardwood forest indicating the importance of direct foliage uptake.

The emissions from chlor-alkali plants are assumed to be  $\text{Hg}^0$ , but little is known about the possible oxidation of elemental mercury or binding to particles in this environment with high temperature and presence of chlorine in the factory (Petersen et al., 1995). The sorption of  $\text{Hg}^0$  is obviously strongly dependent of the type of surface (vegetation). The uptake of mercury into moss tissue is much more efficient than in most vascular plants, for example. According to the moss bag results, dry deposition seems to be a more important pathway for the removal of mercury from the atmosphere into the vegetation than wet deposition (at least near a  $\text{Hg}^0$  emission source).

#### Acknowledgements

I am indebted to Mr Esa Tulisalo, B.Sc., for technical assistance.

Table 2  
Some estimates of net mercury deposition  $\mu\text{g m}^{-2}$  per year

| Type of study                              | Environment  | Hg deposition  | Reference                                   |
|--|--|--|---|
| Moss bag                                   | Chlor-alkali plant   | 200 320 (dry)<br>11 160 (wet)                            | Lodenius (1995),<br>this study              |
| Moss bag                                   | Chlor-alkali plant   | 1200 (dry + wet)   | Lodenius and Tulisalo (1984)                |
| Moss bag                                   | Background   | 8 (dry + wet)  | Lodenius and Tulisalo (1984)                |
| Throughfall                                | Background, pine canopy  | 0.9–26 (dry)   | Lindberg et al. (1995)                      |
| Throughfall, litterfall                    | Background, spruce canopy                                      | 4–7 (dry)<br>12 (wet)<br>40 (total flux to forest floor) | Iverfeldt (1991b)<br>Driscoll et al. (1994) |
| Model calculation                          | $2\text{--}6 \text{ ng m}^{-3} \text{ Hg}^0$ in air            | 0.5–180 (dry)  | Lindberg et al. (1995)                      |
| Gas exchange system:<br>oak, spruce, grass | Low air concentration<br>( $13\text{--}18 \text{ ng m}^{-3}$ ) | –48 (= net emission)<br>(dry)                            | Hanson et al. (1992)                        |
| Gas exchange system:<br>oak, spruce, grass | High air concentration<br>( $\sim 300 \text{ ng m}^{-3}$ )     | 1500 (dry)   | Hanson et al. (1992)                        |
| Throughfall                                | Mixed hardwood   | 11.7   | Rea et al. (1996)                           |
| Litterfall                                 | forest   | 13   |   |
| Precipitation                              |  | 7.9  |   |

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