How to measure dry deposition of mercury? - Some questions and critical remarks.

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Abstract: Dry deposition is an important pathway between air and terrestrial systems. The net deposition is affected by many factors including Hg concentration in air, temperature, light, and receiving landscape surfaces. The measurement of dry deposition using technical and biological methods is associated with many difficulties. The main problem is that the absorption process probably is different for different parts of a complex ecosystem including leaves, needles, bark, mushrooms, mosses, soil etc. The biological structure and physiology include different surfaces and cell structures and different physiological processes. Mercury is strongly bound to a plant material but the binding sites of mercury are not known: surface of the plants or inside the plant cells. For these reasons it would be very important to carry out a well designed comparison between data obtained by different techniques and propose the basis for standardized methodology to quantify dry deposition of mercury.

Key words: mercury, dry deposition, bio-monitoring, vegetation

INTRODUCTION

Dry deposition and re-emission are important pathway between air and terrestrial systems and these processes are affected by many factors. Dry deposition includes particulate deposition on soil, plants and other surfaces and uptake of gaseous mercury mainly by plants. Dry deposition has a very important influence on Hg fluxes. It can be seen as throughfall, litterfall and foliar leaching (REA ET AL., 2000, 2001). In one experiment twice as much Hg was deposited in a forested watershed compared to an open area. Conifer canopies were more efficient filters of airborne particulates than deciduous canopies (KOLKA ET AL., 1999). In a moss bag experiment near a chlor alkali plant two-thirds of the total monthly deposition (130 ng g^{-1}) was estimated to be dry deposition (LODENIUS, 1998) while e.g., IVERFELDT (1991) estimated wet deposition (12 µg m^{-2} a^{-1}) to dominate over the dry deposition (4-7 µg m^{-2} a^{-1}). In a northern mixed hardwood forest the annual throughfall was estimated to be greater (10.5 µg m^{-2}) than the precipitation flux (8.7 µg m^{-2}; REA ET AL., 2001). Depending on ambient concentrations, foliar surfaces in terrestrial forest landscapes may be a dynamic exchange surface that can function as a source or sink of mercury (HANSON ET AL., 1995).

There may also be considerable plant-to-atmosphere emissions which are greater in the light and at higher temperature (TODD ET AL., 1998a, 1998b). In a wetland in Florida LINDBERG ET AL. (2002) found that the predominant flux of Hg^0 in daytime was emission, greater in summer than in winter. Nighttime fluxes approached zero. As the Hg^0 flux correlated best with water vapour, the authors found it appropriate to define the Hg^0 flux as transpiration.

Another critical question is the temporal variation (diurnal, seasonal) which may be related to temperature and possibly other meteorological factors and to the occurrence of other chemical compounds, e.g., oxidants. The relation between dry and wet deposition of mercury is determined by meteorological factors but probably also by biological factors such as the occurrence of suitable biological structures. Estimation of total, dry and wet deposition under natural conditions is a difficult task and many previous attempts may have been based on too simplified calculations.

The objective of this paper is to outline experimental difficulties to accurately assess or monitor the amount of mercury deposited by the process of dry deposition and its importance for better understanding of mercury cycling.

FACTORS AFFECTING THE EXCHANGE OF MERCURY BETWEEN AIR AND VEGETATION

For dry deposition, one problem is to differentiate between: mercury(II) adsorbed or bound on dry particles and mercury(0) that can be adsorbed on the surface of biomonitors (and/or collectors) and/or oxidized and then bound on the surface. Although there are many attempts to determine the Hg species in air, a number of techniques are subjected to artefacts, mainly due to sampling procedures. E.g. collecting gaseous mercury in vessels of glass or teflon or by trapping on amalgam can not describe the uptake in plant tissues. Estimating dry deposition by using non-biological methods will not necessarily give accurate results. In order to have harmonized procedures that will produce comparable results it is necessary to accept a common protocol that represent real and undisturbed situation. The cost-effectiveness of methods proposed should be taken into consideration as well.

The dominant form of mercury in the atmosphere is Hg^0 which can be taken up by vegetation through stomata. We do not know if is it transformed to a water soluble form such as Hg^{2+} or attached directly to particles or to cell walls. AMADO FILHO ET AL. (2002) studied the moss *Tillandsia usneoides* in a contaminated environment using analytical scanning electron microscopy. They found no mercury in the mesophyll or vascular system cells and only small amounts in epidermal cells. Mercury was mostly absorbed by scales, stems and leaf surfaces. To some extent it was also attached to atmospheric particles deposited on the plant surfaces. In a laboratory experiment (LODENIUS ET AL., 2003) mercury was strongly attached to the tissues of both moss and grass with almost no leaching or evaporation in the temperature range +10 °C to +60 °C.

Absorption is most probably different for different parts of complex ecosystems in-

cluding leaves, needles, bark, mushrooms, mosses, soil etc. The biological structure and physiology include different surfaces and cell structures and different physiological processes. Certainly this biological absorption is different from deposition measured by technical collectors. Perhaps it is not possible to get a reliable estimate of dry deposition to a terrestrial ecosystem by using technical collectors. Mercury is strongly bound to plant material but we do not know the binding sites of mercury: surface of the plants or inside the plant cells. Nor do we know the biochemical binding mechanisms. For these reasons it would be very important to carry out a critical comparison between data obtained by different techniques. This comparison should include technical collectors and key components of terrestrial ecosystems. We also recommend that investigations should be carried out by using enriched stable isotope under experimental conditions as close to natural environment as possible. This may explain mechanisms of uptake and distribution of mercury in biomonitors.

CONCLUSIONS

Natural ecosystems are complex including many different species with different surfaces. Depending on factors such as temperature, light and ambient Hg concentrations the plants may take up or release mercury. Weather conditions greatly influences the routes for mercury: dry or wet deposition, absorption, leaching or evaporation. Consequently there are considerable temporal fluctuations in mercury fluxes. The binding of mercury to plant surfaces and transport processes of mercury within the plants are poorly known. Atmospheric mercury and dry deposition of mercury may be monitored using biological or technical methods giving results that, due to a complex biogeochemical behaviour of mercury, are not completely comparable. In routine monitoring of mercury or when interpreting results concerning concentrations or fluxes we should be aware of the factors influencing the results. It is recommended, therefore, that well structured studies are implemented in order to harmonize procedures for the determination of dry deposition of mercury.

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