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Determination of methylmercury fluxes across the air–water and air–soil interfaces by gas chromatography with electron capture detection

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Abstract A method for the determination of methylmercury (MeHg) fluxes across the air–water and air–soil interfaces was developed using an in situ chamber. The MeHg in the air coming out of the chamber was captured by a column containing sulfhydryl cotton fiber adsorbent. MeHg was then desorbed from the column by using 2 mol L⁻¹ HCl. The MeHg in the effluent was extracted with benzene, and determined by gas chromatography with electron capture detection. Finally, the MeHg flux was calculated using the chamber. The method was applied to simulated experiments, and the results showed that the MeHg fluxes in the air–water system were higher than those in the air–soil–water system. The method was also successfully applied to the field measurements of an environment polluted by a chemical factory, and the results showed that the MeHg fluxes across the air–soil and air–water interfaces were 0.21–3.09 and 0.14–0.79 ng m⁻² h⁻¹, respectively. The method will be a useful tool in the environmental study of MeHg.

Keywords Methylmercury · Flux · Gas chromatography · Air · Water · Soil

Introduction

Human activities, including combustion of fossil fuels, waste incineration, gold mining, and other applications

of mercury have significantly increased the release of mercury into the environment. Inorganic mercury can be converted into methylmercury (MeHg) under anaerobic conditions in biological systems, not only through microbial activity but also through chemical methylation in the absence of bacteria. MeHg is the most toxic among the mercury species because of its volatility and its ability to pass through biological membranes such as the blood/brain barrier and the placenta. It can cause irreversible central nervous system damage and fetal Minamata disease. MeHg is a global pollutant [1–4].

A number of methods have been proposed for the determination of MeHg, such as, fluorimetry [5], atomic absorption spectrometry [6, 7], atomic emission spectrometry [8], atomic fluorescence spectrometry [9], gas chromatography [10, 11], high-performance liquid chromatography [12, 13], ion chromatography [14], and capillary electrophoresis [15, 16]. The different methods have been used for the determination of MeHg in water [17–19], soil [20–22], and air [23, 24]. Recently, several authors have reviewed methods for the determination of MeHg in various samples, and their advantages and disadvantages have been pointed out [2, 25, 26]. However, little information is available on the determination of MeHg flux across the air–water or air–soil interface.

Measurement of MeHg flux is very important for several reasons. First, we need to know the magnitude and direction of the flux as well as the relative importance of the different source categories. Second, flux measurement or description of the key processes regulating the flux is used to drive atmospheric models. Third, flux measurement is used to validate the output of atmospheric models. The information on fluxes is needed at different spatial scales, and information on fluxes at lower scales is integrated to obtain information at a higher scale level. In this paper, a method for the determination of MeHg fluxes across the air–water and air–soil interfaces was developed using an in situ chamber by gas chromatography with electron capture detection (GC-ECD). The method was applied to simulated experiments and field measurements.

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Experimental

Apparatus

An HP 5890A gas chromatograph (Hewlett–Packard, USA) equipped with an electron capture detector and a HP 3396A integrator was used with a Supelco SPB–1701 fused silica capillary column (15 m×0.53-mm i.d., 1.00- μ m film thickness). An air-sampler (Laoshan Electrical Factory, Shandong, China) was used throughout the experiment. The box-shaped transparent chamber (80×20×20 cm) was constructed from organic glass, and its bottom-board could be opened.

Reagents

All reagents were of analytical reagent grade. MeHg chloride was purchased from Merck (Darmstadt, Germany), and the rest of reagents were obtained from BDH (Poole, UK). Doubly distilled water was used throughout. The stock solution at a concentration of $1 \times 10^2 \text{ mol L}^{-1}$ of MeHg chloride was prepared in a water/ethanol mixture (50:50, v/v) and stored in the dark at 4°C. Working standards were freshly prepared daily and handled in brown bottles that were washed before use with nitric acid and doubly distilled water. The sulfhydryl cotton fiber adsorbent was synthesized according to the procedure described in the literature [27, 28] and preserved on the brown dryer; 0.1 g of sulfhydryl cotton fiber adsorbent was placed into a column (sampling-tube), and wetted by diluted hydrochloric acid (pH = 3) prior to use.

Operating procedures

The bottom-board of the chamber was taken away. The chamber was then gently placed on the surface of soil or water. The air passing through two gas inlet ports entered the chamber. The MeHg in air coming out of the chamber was captured by two columns containing sulfhydryl cotton fiber adsorbent, which were connected to two gas outlet ports. The flow rate of air through the column was 1.0 L min^{-1} .

The MeHg was desorbed from the column containing sulfhydryl cotton fiber adsorbent by 5 mL of 2 mol L^{-1} HCl. MeHg in the effluent was then extracted twice with 0.5 mL of benzene. The extract was dried with anhydrous Na_2SO_4 , and analyzed by GC-ECD. The GC-ECD was carried out under the following conditions: injection port temperature 200°C, oven temperature 120°C, detector temperature 300°C, carrier gas N_2 at 5 mL min^{-1} , and make-up gas N_2 at 40 mL min^{-1} . Injection volume was $1 \mu\text{L}$, and quantification was based on peak heights using external standard method.

Results and discussion

Theory for the determination of methylmercury flux

The MeHg fluxes were assessed by using an in situ chamber, which isolated an area of soil (or water) surface and overlaying air (Fig. 1).

The amount of MeHg collected from the gas outlet of the flux chamber is defined as:

$$R_1 = R_e + R_c + R_f \quad (1)$$

where R_e is the amount of MeHg entering the flux chamber from the air out of the chamber, R_c is the amount of MeHg absorbed (or released) by the inner wall of the chamber, and R_f is the amount of MeHg released (or absorbed) from the soil (or water).

When the same (or another) flux chamber with the bottom-board was used, the amount of MeHg collected from the gas outlet of the flux chamber is defined as:

$$R_0 = R_e + R_c \quad (2)$$

From Eqs. 1 and 2, an equation, $R_f = R_1 - R_0$, was obtained. Thus, MeHg flux is defined as:

$$F_{\text{mh}} = R_f/S/T \quad (3)$$

where F_{mh} is MeHg flux, S is the area of soil (or water) covered by the chamber, and T is sampling time. If F_{mh} is positive, it means that MeHg is released from the soil (or water) to air; if F_{mh} is negative, then it means that soil (or water) absorbs the MeHg from the air.

Determination of methylmercury fluxes in the simulated experiments

In a flux chamber, 2 L of water and 2 mL of $1,000 \mu\text{g L}^{-1}$ MeHg chloride solution were added. At the same time, 2 L of water, 250 g of soil, and 2 mL of $1,000 \mu\text{g L}^{-1}$ MeHg chloride solution were added to another flux chamber. The flux chambers were put on the ground outdoors. Sunlight irradiated the flux chambers directly and the ambient temperature was about $25 \pm 2^\circ\text{C}$. The results of the simulated experiments are presented in Tables 1 and 2, respectively.

As can be seen in Tables 1 and 2, the MeHg fluxes decreased gradually. The reason was that the MeHg fluxes were correlated to the concentrations of MeHg in water and this would decrease because MeHg was emitted into the air from water. In addition, the MeHg fluxes in the water–air system were greater than those in

Fig. 1 Mechanism for the calculation of flux

Table 1 MeHg fluxes across the air–water interface

Time	Temperature (°C)	MeHg in air (ng m ⁻³)	Flux of MeHg (ng m ⁻² h ⁻¹)
10:30–12:30	32	411.8	154.4
12:30–14:30	37	177.6	66.59
14:30–16:30	37	87.75	32.91
16:30–18:30	36	67.42	25.28
18:30–20:30	34	33.54	12.58
20:30–22:30	31	29.96	11.23

Table 2 MeHg fluxes across the air–water–soil interface

Time	Temperature (°C)	MeHg in air (ng m ⁻³)	Flux of MeHg (ng m ⁻² h ⁻¹)
10:30–12:30	32	271.2	101.7
12:30–14:30	37	82.21	30.83
14:30–16:30	37	52.29	21.48
16:30–18:30	36	33.46	12.55
18:30–20:30	34	30.42	11.41
20:30–22:30	31	28.46	10.77

the water–soil–air system (Tables 1 and 2). This was because MeHg was adsorbed by soil, which would result in lower concentrations of MeHg in water in the water–soil–air system than in the water–air system.

The limit of detection was 2.5 µg L⁻¹, and the relative standard deviations were from 1.7 to 4.5%. The recoveries were in the range of 87–95%. In addition, gas chromatography with electron capture detection for the determination of MeHg has been validated by fluorimetric and spectrophotometric methods in previous reports [3, 5].

Determination of methylmercury fluxes in the field experiments

One sampling site for the air–soil system was near the entrance of a chemical factory, and another was located downwind, about 1 km away from the factory. The former site was covered with grass, whereas the latter is fertile. The air–water sampling site was located downwind, about 2 km away from the factory. The results of MeHg flux measurements are presented in Tables 3, 4, and 5. The MeHg fluxes across air–soil and air–water

Table 3 MeHg fluxes across the air–soil (covered with grass) interface

Time	Temperature (°C)	MeHg in air (ng m ⁻³)	Flux of MeHg (ng m ⁻² h ⁻¹)
9:05–10:35	31	36.78	0.33
10:35–12:05	37	41.50	0.21
12:05–13:35	39	42.78	2.08

Table 4 MeHg fluxes across air–soil interface

Time	Temperature (°C)	MeHg in air (ng m ⁻³)	Flux of MeHg (ng m ⁻² h ⁻¹)
7:50–10:20	29	24.67	3.09
10:20–12:50	35	26.10	1.11
12:50–15:20	38	25.70	0.53
15:20–17:50	37	26.23	0.43
17:50–20:20	36	26.63	0.31
20:20–22:50	32	25.27	1.45

Table 5 MeHg across the air–water interface

Time	Temperature (°C)	MeHg in air (ng m ⁻³)	Flux of MeHg (ng m ⁻² h ⁻¹)
8:10–12:10	30	15.42	0.14
12:10–16:10	38	17.96	0.41
16:10–20:10	36	19.33	0.79

interfaces were 0.21–3.09 and 0.14–0.79 ng m² h⁻¹, respectively.

Conclusions

A method for the determination of MeHg fluxes across air–water or air–soil interfaces was developed using an in situ chamber with sulfhydryl cotton fiber adsorbent by gas chromatography with electron capture detection. The method was successfully used for the determination of MeHg fluxes in simulated and real environments. This method will be a useful tool in the environmental study of MeHg.

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