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Vertical fluxes of volatile mercury over forest soil and lake surfaces in Sweden

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ABSTRACT

A flux chamber technique applied to volatile mercury species has been developed and evaluated. This technique can be used to measure the direction and magnitude of mercury transfer between the atmosphere and lake or soil surfaces. Measurements have been performed over four oligotrophic forest lakes in southwestern Sweden during 1988 and 1989. Net emission fluxes of mercury were measured from the lakes. The measured daytime fluxes during the warmer season (water temperatures 13–23°C) were within the range 3–20 ng h^{-1} m^{-2} (average 7.9 ng h^{-1} m^{-2}). The average night-time fluxes measured during the same season were 2 to 3 times smaller. Two sets of measurements, performed during the winter when water temperatures were ≤ 2°C, gave flux values close to zero. Flux measurements were also performed over soil in a coniferous forest. Compared to the situation for the forest lakes, the fluxes of mercury over forest soil are much lower in magnitude, with values ranging from approximately -2 to $+2$ ng h^{-1} m^{-2} during different seasons. Emission was observed with an average of 0.3 ng h^{-1} m^{-2} when soil temperature was about 10°C, while dry deposition was measured with an average of 0.9 ng h^{-1} m^{-2}, when soil temperature was <3°C.

1. Introduction

Being quite volatile, at least in its elemental and dimethylated forms, mercury (Hg) is widely dispersed in the atmosphere through emissions from anthropogenic sources and emissions or re-emissions from natural environmental surfaces such as water, soil and vegetation (Kothny, 1973; Seiler et al., 1980; Brosset, 1981; Siegel and Siegel, 1988; Schroeder et al., 1989). In the last decade, with continuing increases in fossil fuel combustion, waste incineration and industrial emissions, concern has again increased about the presence of Hg in the environment, due to its toxicity, its ecological transformation into potentially more hazardous compounds such as mono-methyl mercury, and its bioaccumulation in the food chain even in remote areas without any obvious sources nearby.

Estimates of the magnitude and direction of the transfer of pollutants between soil, water and air may be obtained by: (a) equilibrium calculations—using the Henry's law constant, which can obtained theoretically or preferably experimentally (Iverfeldt, 1984); (b) laboratory experiments—to supply data for (a), to verify the conclusions drawn from equilibrium calculations, and to simulate relevant environmental and chemical parameters under controlled conditions as close to those of the natural system as possible; (c) direct measurements in the field—the most straightforward approach.

Estimates of Hg flux from natural waters to the atmosphere, according to approach (a) or (b) have been published previously (Lerman, 1979; Kim and Fitzgerald, 1986). The flux chamber method, an example of approach (c), has been applied directly on-site for flux measurements of NO, NO_2, N_2O from soil (Slemr et al., 1984; Slemr and Seiler, 1984; Johansson and Granat, 1984; Johansson, 1984, 1987) and of volatile organic

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compounds, such as benzene, toluene, ethylbenzene, p-, m-, o-xylene and naphthalene, from a hazardous waste land treatment system (Dupont and Reineman, 1986), but our work represents the first application of this technology to the study of Hg fluxes in the Swedish environment.

In the present paper, results obtained from direct flux measurements of Hg over lake and soil surfaces are presented. The flux chamber technique used allows data to be obtained under dynamic environmental conditions. This attribute of the flux chamber technique is noteworthy, since natural systems are generally not static, and the kinetics of the chemical and physical changes are seldom known (Benes and Havlik, 1979; Schroeder, 1988). At present, chamber methods represent the only available technology for measuring the flux of Hg in the field. The use of micrometeorological methods, such as eddy flux or vertical concentration profile techniques, is not suitable for environmental trace contaminants (e.g., Hg), since selective, fast-response chemical sensors are required (Wesely et al., 1989). Besides, the field equipment needed for the chamber technique is simple, inexpensive, portable, and easy to set up and operate under field conditions. On the basis of our experience, the main problems encountered with the flux chamber technique were the difficulties in maintaining low and reproducible chamber blank values.

2. Experimental

2.1. Gold traps and DC plasma-AES analytical system

Vapor-phase Hg species occurring in the atmosphere can be pre-concentrated by collection on gold (wire, wool or a thin film coated on different kinds of inert support materials, such as quartz glass beads, silica sand, boron carbide, etc.) (Head and Nicholson, 1973; Fitzgerald and Gill, 1979; Mercer, 1979; Schroeder, 1982; Iverfeldt, 1984; Schroeder et al., 1985; Brosset, 1987).

In this investigation, airborne Hg was collected in gold traps that consist of a mixture of small pieces of solid gold and quartz glass in the approximate ratio of 1:1, contained in sampling tubes of quartz with a length of 10–12 cm, i.d. of 0.4 cm and o.d. of 0.5 cm. Newly prepared gold traps were soaked in conc. HNO_3 overnight and rinsed thoroughly with distilled and Milli-Q water. The traps were then heated for several minutes at about 600°C while purified N_2 gas flowed through them. Once the blank values were acceptable (the blank value of a gold trap is generally 2–3 pg of Hg), the traps were sealed with Parafilm® and stored in clean plastic bags.

Using a two-stage gold trap analysis technique, the Hg collected in the individual sampling traps was desorbed by heating and transferred to an analytical trap with purified helium as carrier gas. The analytical trap was then heated and the Hg thus released was analyzed by direct current plasma atomic emission spectroscopy (DC-AES). This instrumentation, together with its dimethyl mercury calibration system, has been described by Iverfeldt and Lindqvist (1982), and is similar to trace mercury analysis systems which have been used by others (Braman and Johnson, 1974; Bricker, 1980). The detection limit is about 2 pg Hg, which corresponds to a detection limit of ca. 0.05 ng m^{-3} for an air sample of 0.04 m^3. The amounts suitable for routine quantitative analysis of Hg are about 0.1–1.5 ng, i.e. if Hg concentrations are in the range of 2–30 ng m^{-3}, the sampling volume should be about 0.05 m^3.

2.2. Chamber technology and on-site set up

A stainless steel chamber with a removable bottom plate was constructed with the dimensions of $80 \times 20 \times 20$ cm. The construction material and physical size were chosen for their ease of handling during field work and cleaning in the laboratory. A detailed description of the chamber can be seen elsewhere (Xiao et al., 1988; Schroeder et al., 1989).

The sampling apparatus as used in the field measurements is presented in Fig. 1. Ambient air was drawn into the chamber through two inlet ports, while the traps for Hg collection were connected to the outlet ports. The collection efficiency for Hg on an individual gold trap was consistently >90% at a flow rate of 1 L min^{-1}. This, or a somewhat lower flow rate, was used for all sampling events. Three gold traps in sequence were always used during the field experiments. The first two gold traps are intended to collect vapor-phase Hg species in the air stream being sampled. The function of the third gold trap is to protect the back-up (i.e. the seond) sample trap against back-

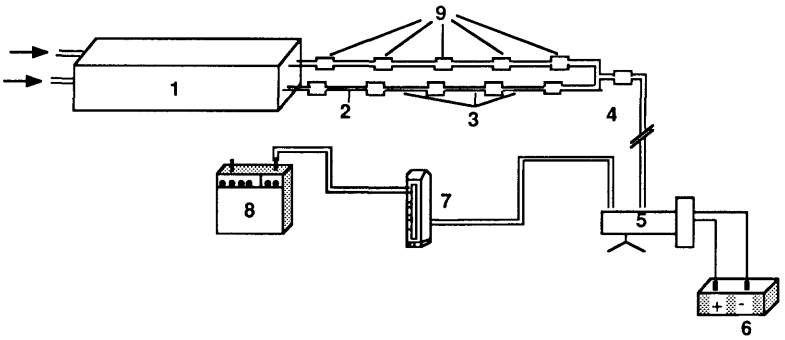

Fig. 1. On-site flux measurement apparatus, showing parallel sampling trains. 1. Stainless steel chamber with removable bottom plate. 2. Quartz wool trap for particulate mercury. 3. Gold traps (3 connected in series). 4. Three way connector. 5. Air sampling pump with 12 V motor. 6. 12V D.C. battery. 7. Rotameter for monitoring air sampling flow rate. 8. Gasmeter for determining total volume of air sampled. 9. Viton rubber tubing for connection of traps in sampling train.

diffusion of Hg coming from the other portions of the sampling system during those times when the sampling pump is not running. The gold traps were always placed behind one or two quartz wool traps, which collect particulate phase Hg associated with atmospheric aerosols.

With the flux chamber situated on top of a water or soil surface (cf. Fig. 2), the amount of Hg collected on the traps per unit time through the outlet ports of the chamber, R_0, is given by:

$$R_0 = R_i + R_c + R_s, \tag{1}$$

where, R_i is the rate at which gaseous Hg enters the chamber through the inlet ports, R_c is the rate at which Hg desorbs from the interior walls of the chamber, and R_s is the rate at which Hg is emitted from (or deposited to) the water/soil surface. Comments on relations between R_s and fluxes to and from uncovered (natural) surfaces will be given in Subsection 3.4.

R_0 was measured (with the bottom plate of the chamber removed) while the chamber either floated on the water surface with the aid of a styrofoam collar, or rested directly on the soil surface. In the latter case, care was taken to firmly press the bottom frame of the chamber into the soil to achieve as tight a seal as possible. To calculate R_i, the concentration of Hg in the air entering the chamber was determined experimentally in two separate sets of measurements spanning the same time period as the chamber blank determinations and the flux measurements. R_c, the chamber blank, was determined with the removable bottom plate attached to the chamber. R_s is the rate of release (or uptake) of Hg at the environmental surface being investigated, and is calculated by rearranging equation (1):

$$R_s = (R_0 - R_i) - R_c. \tag{2}$$

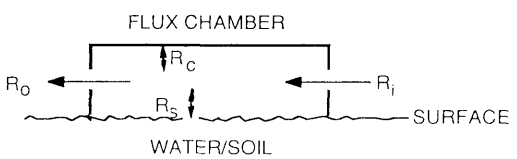

Fig. 2. Schematic diagram of the mass balance approach used when calculating mercury fluxes to and from water and soil surfaces.

The equations used to calculate the chamber blank value and the Hg flux from water and soil surfaces, along with a detailed example of calculations, can be found elsewhere (Xiao et al., 1988). It is important to note that R_s can assume either a positive value, corresponding to an emission of Hg, or a negative value, corresponding to a deposition of Hg.

Gold-coated diffusion denuder tubes (Munthe et al., 1990) were originally employed on the inlet side of the chamber during flux measurements. These are quartz glass tubes which have been coated on the inside with a thin film of gold and thus are capable of removing gas-phase Hg quantitatively from air. In this case, since the denuders remove the Hg from the incoming air streams, the

measurement procedures and calculations become simplified, and the independent measurement of the Hg concentration in ambient air could, in principle, be omitted. However, when gold-coated denuder tubes are used to remove Hg from the air entering the flux chamber through the inlet ports, a perfect seal around the bottom edges of the chamber is essential to prevent the infiltration of ambient air. A perfect seal is difficult to achieve when flux measurements are performed over soil, and unknown quantities of Hg will thus be introduced into the chamber during the measurement period. The denuders may also remove other chemical species normally present in ambient air, thereby possibly affecting the flux values. For example, ozone is known to be decomposed upon contact with a gold surface (Brosset, 1987). Thus, the use of denuders was discontinued after the preliminary series of field tests with the flux chamber had been completed.

In the early stages of this work, moisture was occasionally observed to have accumulated in the traps of the sampling train during some of the flux measurements. Temperature differences between air and water/soil were at times quite large, especially during night when the temperatures of the water or soil were higher than the surrounding air temperature. This temperature difference was sometimes more than 10°C, causing water vapor to condense on the interior walls of the chamber and in the gold traps as well. To prevent condensation of moisture in the traps during sampling, they were put in a thermostated box which was powered by a 12 V battery. The temperature was kept at 45–50°C. A similar procedure has been described earlier (Iverfeldt, 1984, 1988). The potential for moisture condensation on the inner surface of the flux chamber still exists and condensation of water vapor might conceivably have occurred in some of the measurements. Whether the presence of condensed water on the interior walls of the chamber would affect the field measurement data in any significant way is not known. However, given the low water solubilities of the two most likely Hg species (viz. Hg^0 and $(CH_3)_2Hg$), significant problems are not expected even if moisture condensation did occur on the chamber walls.

During the later stages of this work, a small electric fan powered by a 12 V battery was installed in the chamber to investigate the effects of stirring the air inside the chamber on the flux of Hg. To prevent possible contamination, the motor was situated outside and on top of the chamber. Investigations were performed by sampling the flux of mercury over soil and lake surfaces with and without the fan powered. No significant differences were observed.

Through examination of numerous experimental results contained in the project records, a relative standard deviation (RSD) of 5% was established for air concentration measurements of Hg. This RSD includes errors both from the analytical and the sampling steps involved in the overall measurement process. The 5% error was applied to the $(R_0 - R_i)$ item in equation (2) to get an error range. Chamber blank values were carefully measured four times when sampling was done during daytime: two times before and two times after each set of flux measurements. For the night time sampling, chamber blank values were measured two times: one time before and one time after the flux measurements. The arithmetic mean and the standard deviation of the chamber blank values, $R_c \pm \sigma$, were obtained from the chamber blank determinations carried out in the field. Subsequently, the range of uncertainty for a flux measurement was estimated by subtracting the lowest chamber blank value from the highest $(R_0 - R_i)$ value and the highest chamber blank value from the lowest $(R_0 - R_i)$ value. The measurement results with the highest uncertainties so calculated are presented in the Hg flux terms (ng h^{-1} m^{-2}) together with chamber blank values, in Tables 2, 3.

During the performance of this study at various locations, it was also found that Hg on aerosols generally contributed $\leqslant 5\%$ to the total gas-phase Hg. Since quartz wool filters were continuously used, the results presented in this paper are operationally defined as volatile vapor-phase Hg flux values.

3. Results and discussion

3.1. Description of sampling sites

Measurements of Hg fluxes were performed over four oligotrophic lakes in southwestern Sweden. These forest lakes do not receive any municipal or industrial wastewater discharges. For practical

reasons, most of the measurements were done close to the lakeshore. Site locations are indicated in Fig. 3, and some relevant data for these lakes and their fish population are listed in Table 1.

Mercury flux measurements over soil were conducted in a coniferous forest in the vicinity of Lake Gårdsjön. This lake, and its surrounding basin, continue to be used by various research groups for studying acid deposition and its effect on terrestrial plants and other receptors within the same catchment area. Much relevant information is thus available for this location (Andersson and Olssen, 1985; Hultberg and Grennfelt, 1986). To investigate the diurnal and seasonal variations, measurements were performed both during the day and at night as well as during the warmer and colder seasons of the year.

3.2. Flux of mercury from the surfaces of the four lakes

Table 2 summarizes all flux chamber measurements and air concentration determinations for Hg that were performed at the four forest lakes selected for this project. Each reported measurement value represents the arithmetic mean of 2 separate flux chamber determinations and duplicate determinations of atmospheric Hg concentrations. Also given are chamber blanks as well as the simultaneous water and air temperatures outside the chamber.

As depicted in Fig. 4, the entire series of Hg flux measurements performed during May 1988 over the 4 forest lakes exhibited a very consistent diurnal pattern, with Hg fluxes being clearly higher

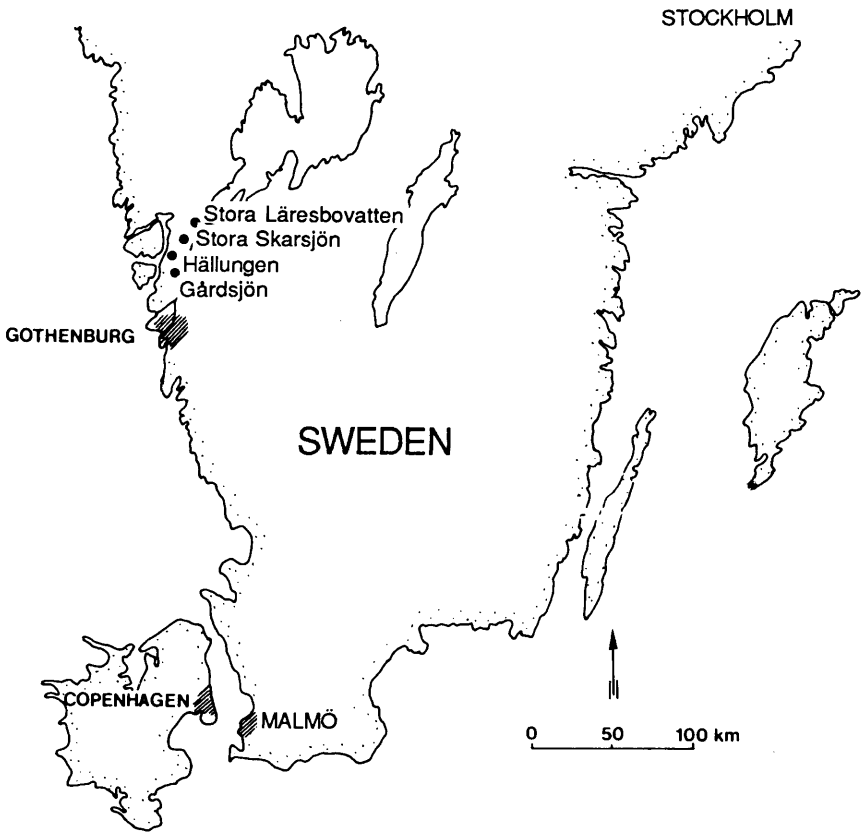

Fig. 3. Sampling locations for mercury flux measurements.

Table 1. *Mercury content in fish, color and pH of water of the four lakes chosen**

Lake	Average Hg concentration in fish (ppm)	Color** (mg Pt L^{-1})	pH
Stora Läresbovatten	1.14 (North Pike, 1 kg)	60–160	5.2–5.25
Stora Skarsjön	1.04 (North Pike, 1 kg)	20–32	6.3–6.6
Gårdsjön	0.52 (Perch, 0.4 kg)	12.6	4.7***
Hällungen	0.35 (North Pike, 1 kg)	9.0	6.6–6.9

* Data from H. Hultberg, (1988) Swedish Environmental Research Institute (IVL), Gothenburg, personal communication.

** A standard solution of 500 units is made by dissolving 500 mg platinum and 250 mg cobalt in 100 ml conc HCL and diluted to 1000 ml with distilled water.

*** Data from 1970; pH was 7.6 (after liming) in 1985.

during the daytime than at night. The same trend has previously been noticed by Fitzgerald and Gill (1979) at coastal sites and by Schroeder and Fanaki (1987, 1988) over inland water bodies. On the other hand, the Hg concentrations in ambient air, which were measured simultaneously with the fluxes, did not vary much between day and night, which is consistent with the isolated locations of the field sites.

To complement the results obtained with our flux chamber measurement system and to increase our confidence in the validity of the data generated with this technique, an additional experiment was done on 88-06-16 at Lake Hällungen. In this

Table 2. *Results of flux chamber measurements of mercury over the four lakes chosen*

Sampling site Lake	Sampling date	Hg flux (ng h^{-1} m^{-2})	Temp. water/air (°C)	Chamber blank (ng min^{-1}) $R_c \pm \sigma$	Average Hg conc in air (ng m^{-3})**
Gårdsjön	9 May 88(D)	8.3 ± 2.5*	15/17	0.011 ± 0.0049	2.33 ± 0.05
Gårdsjön	9 May 88(N)	2.5 ± 1.6	15/6.6	0.0087 ± 0.0035	2.39 ± 0.09
Gårdsjön	7 Jun. 88(D)	4.4 ± 1.1	19/19	0.0062 ± 0.0017	2.28 ± 0.05
Gårdsjön	12 Jan. 89(D)	0.19 ± 0.06	0.5/3	0.0003 ± 0.0002	4.16 ± 0.23
Gårdsjön	26 May 89(D)	10.4 ± 0.7	18/19	0.015 ± 0.0078	3.20 ± 0.07
Gårdsjön	5 Jun. 89(D)	8.9 ± 0.7	16/16	0.0034 ± 0.0005	2.81 ± 0.02
Läresbov.	16 May 88(D)	19.5 ± 2.5	23/24	0.016 ± 0.0033	2.24 ± 0.02
Läresbov.	16 May 88(N)	6.6 ± 1.3	19/11	0.0063 ± 0.0013	3.04 ± 0.55
Läresbov.	14 Jun. 88(D)	7.6 ± 0.9	22/18	0.0054 ± 0.0068	1.95 ± 0.01
Skarsjön	19 May 88(D)	6.4 ± 1.9	13/14	0.0066 ± 0.0034	1.59 ± 0.04
Skarsjön	19 May 88(N)	1.3 ± 0.4	12/0.4	0.0048 ± 0.00085	1.63 ± 0.62
Skarsjön	9 Jun. 88(D)	5.0 ± 0.8	18/20	0.0070 ± 0.00067	2.00
Hällungen	25 May 88(D)	3.4 ± 1.8	16/17	0.0084 ± 0.0034	2.58 ± 0.39
Hällungen	25 May 88(N)	1.6 ± 0.8	14/5	0.0036 ± 0.0019	2.46 ± 0.13
Hällungen	2 Jun. 88(D)	4.8 ± 0.9	15/11	0.0027 ± 0.0015	2.15 ± 0.06
Hällungen	16 Jun. 88(D)	8.0 ± 1.2	21/21	0.0090 ± 0.0016	2.78 ± 0.46
Hällungen	24 Sep. 88(D)	−0.5 ± 0.3	2/6	0.0044 ± 0.0022	3.52 ± 0.39

* This value represents the estimated maximum uncertainty (see text).

** Average of two separate determinations.

(D): day time measurement, chamber blanks were determined four times.

(N): night time measurement, chamber blanks were determined two times.

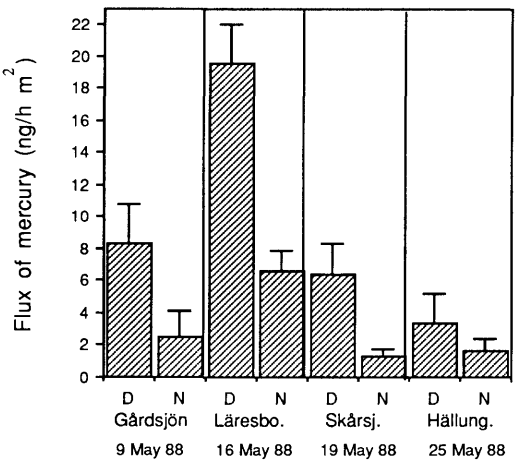

Fig. 4. Diurnal variation of mercury flux over the four lakes investigated in this study.

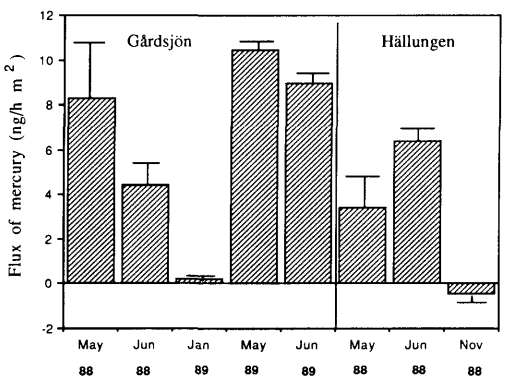

Fig. 5. Seasonal variations of the flux of mercury over Lake Gårdsjön and Lake Hällungen.

experiment, the concentration of Hg in the air was sampled simultaneously at two points: one location was ~30 cm over the water surface and the other was on land, about 4.5 m over the lake level and about 5–10 m away from the lake. Wind was blowing towards lake from land with a speed about 2–3 m s^{-1}. The concentration measured over land was used as a reference value, assuming it to be relatively unaffected by any emissions from the lake surface.

It was found that the Hg concentrations in the air were significantly different at the two sampling points. Near the water surface the concentration (average of 2 values) was 3.22 ± 0.08 ng m^{-3}, while at the height of 4.5 m the average concentration (for 2 values) of Hg in air was 2.32 ± 0.01 nh m^{-3}. These data indicate clearly that there existed an air concentration gradient, assumed to be caused by the emission of Hg from the water surface, which is consistent with the results obtained from the chamber measurements.

For the series of flux chamber measurements carried out over the surface of lakes Gårdsjön and Hällungen, a large seasonal variation was found (Fig. 5). The combined average value obtained from the wintertime measurements on these two lakes (-0.2 ng h^{-1} m^{-2}) was considerably lower than that from the summer measurements (7.9 ng h^{-1} m^{-2}) during May and June of 1988 and 1989.

The temperature dependence of Hg flux over lake surfaces was clearly shown by using the Arrhenius equation,

$$k = A\, e^{-E_a/RT},$$

where, k is the flux rate of Hg. The "activation energy" E_a was estimated to be 29.6 ± 1.0 Kcal mole^{-1} at water temperatures of 0.5–23°C (cf. Fig. 6). This value is higher than the "activation energy" of Hg release rate from soil with low organic content (12.8 ± 2.5 Kcal mole^{-1}, 5–70°C) and close to the value obtained for the Hg release rate from plants (28.0 ± 5.7 Kcal mole^{-1}, 10–21°C), both values having been obtained under controlled laboratory conditions (Siegel and Siegel, 1988).

The Hg volatilized from a lake to the surrounding air is probably in the form of Hg^0 and/or $(CH_3)_2Hg$. The volatile Hg species can be formed in sediments from Hg(II) species via biological or abiotic reduction processes (Spangler and Spigarelli, 1973; Steffan et al., 1988). Elemental Hg can also be formed in aqueous solution via the chemical reduction of mercuric ion in the presence of humic acid (Alberts et al., 1974). Even though Hg^0 dissolved in natural waters is unstable thermodynamically with respect to oxidation, the oxidation processes investigated so far seem to be relatively slow. Thus, the Hg^0 formed in the sediments and in the water could still pass unchanged through the oxidizing surface water layer to the atmosphere, as suggested by Lindqvist and Rodhe (1985).

Besides the aforementioned processes, another

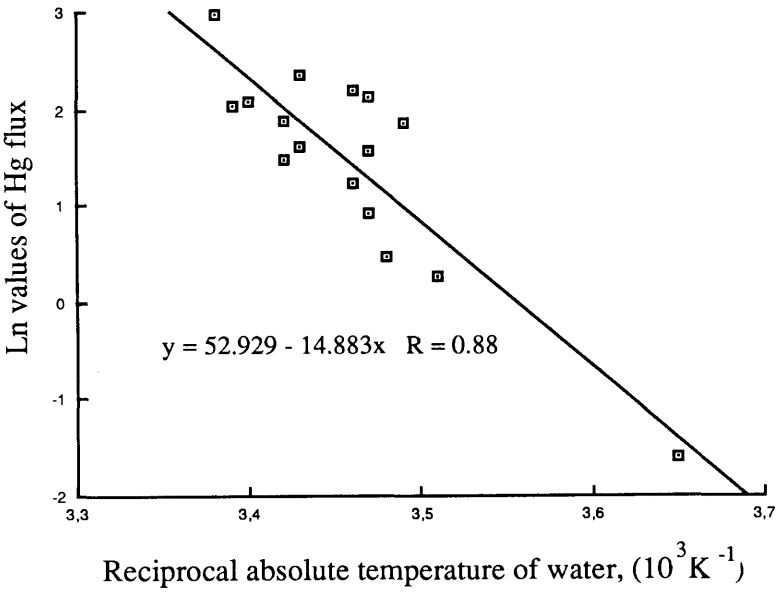

Fig. 6. Temperature dependence of mercury flux over lakes surfaces—the Arrhenius plot.

possible way of reducing oxidized forms of Hg to Hg^0 is through a sunlight-induced photochemical process. Iverfeldt (1984) observed a photochemically induced reduction when illuminating a dilute solution of divalent Hg with a xenon lamp in laboratory experiments. Brosset (1987) has also reported a sunlight-induced reduction of Hg in distilled-deionized water as well as in precipitation samples. Preliminary investigations of photolysis of diluted divalent Hg species in Milli-Q water recently carried out in this laboratory also support this argument.

The observed diurnal and seasonal variations of the Hg flux may be explained by the decreases in water/air temperature and intensity of solar radiation that occurs at night and during the winter. These factors are closely related to microbiological activity that may be responsible for the production of volatile Hg. The decrease in solar radiation intensity may also diminish the possibility and extent of photochemically induced reduction of the dissolved divalent Hg in the lake water.

Solar radiation can be absorbed by natural substances either in dissolved or particulate phases. Among such natural substances, the role of humic materials has been widely investigated, because they are among the most common and most strongly light absorbing constituents in natural waters (Power et al., 1987). The solar energy absorbed by fresh water humic substances can excite molecules that, in turn, are able to participate in different kinds of reactions with aquatic pollutants (Zepp et al., 1985; Cooper et al., 1988). These so-called photosensitized reactions may also be important in accelerating the sunlight-induced reduction of Hg. As can be seen from Tables 1 and 2, high flux values were obtained from lakes with high humic concentrations (as indicated by color).

3.3. Flux of Hg over soil

The results of all the flux measurements of Hg over soil in the coniferous forest adjacent to Lake Gårdsjön are listed in Table 3. The observed diurnal variations in the Hg fluxes at this location are illustrated in Fig. 7. The results of Hg flux measurements over soil are not so easy to interpret as those over lakes. Throughout the entire field measurement campaign, the Hg concentration in air was in the range 2.06–3.72 ng m^{-3}. The rates of Hg emissions from soil have been reported to be a function of temperature (Williston, 1986), time of the day, vegetation cover and Hg concentration in the soil itself (Kothny, 1973), both in the case of Hg-rich soils (Lindberg, 1987) and for red clay soil

Table 3. *Results of flux chamber measurements of mercury over soil in the coniferous forest near Lake Gårdsjön*

Sampling date	Hg flux (ng h^{-1} m^{-2})	Temperature soil/air (°C)	Chamber blank (ng min^{-1}) $R_c \pm \sigma$	Average Hg conc in air (ng m^{-3})
17 Dec. 87(D)	1.4 ± 0.2*	−5/−10	0.0036 ± 0.000071	2.06 ± 0.01**
9 Feb. 88(D)	-1.3 ± 0.2***	0.5/2.0	0.0022 ± 0.0002	2.84 ± 0.07**
11 Feb. 88(D)	-1.4 ± 0.6	3/2	0.0032 ± 0.0017	2.77
14 Apr. 88(D)	-2.0 ± 0.5	2/6	0.0099 ± 0.0012	3.01 ± 0.66**
14 Apr. 88(D)	-1.1 ± 0.4	2/3	0.010 ± 0.0012	2.67
15 Apr. 88(D)	-0.3 ± 0.2	3/11	0.0060 ± 0.0009	3.72 ± 0.21**
30 May 88(D)	2.5 ± 1.1	12/10	0.0042 ± 0.0024	2.39 ± 0.11**
30 May 88(N)	0.5 ± 0.5	10/8	0.0037 ± 0.0011	2.56 ± 0.15**
24 May 89(D)	-0.8 ± 0.7	13/20	0.011 ± 0.0012	2.61 ± 0.23**
24 May 89(N)	-1.0 ± 0.04	7/9	0.0080 ± 0.0001	2.38
12 Jun. 89(D)	0.14 ± 0.1	12/19	0.0042 ± 0.0008	2.79 ± 0.16**
12 Jun. 89(N)	0.17 ± 0.2	10/8–12	0.0022 ± 0.0004	2.52

* This value represents the estimated maximum uncertainty (see text).
** Average of two separate determinations.
*** The negative sign indicates a dry deposition flux.
(D): day time measurement, chamber blanks were determined four times.
(N): night time measurement, chamber blanks were determined two times.

with low organic content (Siegel and Siegel, 1979, 1988). In our study, the Hg fluxes between soil and air are quite low, often not significantly different from zero. If we define the results from the measurements conducted during May and June as the flux values of the warmer season (soil temperature about 10°C) and those obtained during December to April as the flux value of the colder season (daytime soil temperature <3°C), average values of 0.3 ± 0.4 and -0.9 ± 0.4 ng h^{-1} m^{-2} were obtained for the warm and cold seasons, respectively.

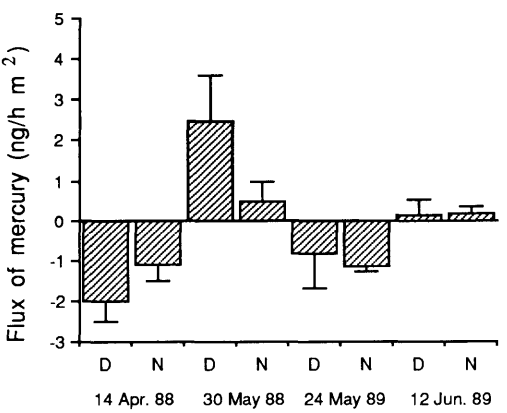

Fig. 7. Diurnal variations of the flux of mercury over forest soil at Lake Gårdsjön.

The diurnal variations of the flux of Hg over soil are quite irregular (Fig. 7). If biological and photochemical processes are important for the formation of volatile Hg species in soil, one would expect the flux of Hg to be dependent on temperature and intensity of solar radiation. Since the chamber, when placed over the soil, shuts out all light, the effect of solar radiation on the flux of Hg over soil could not be observed. The temperature varied little between day and night on those occasions when the diurnal variations were investigated. Thus, no firm conclusion can be drawn about the influence of solar radiation and temperature on the flux of Hg over soil. It is clear, however, that the net values of Hg flux measured over soil at the Lake Gårdsjön location are much lower than the values measured over the lake surfaces.

It should be pointed out that under forest trees, where flux measurements were performed, there was a lot of litter from the trees, covering the soil to a thickness of about 5 cm. Any Hg emanating from the soil underneath may be trapped by the litter either via the direct adsorption with the

large surfaces available or via the formation of complexes with humic materials formed by partial decay of organic content form the litter.

3.4. Evaluation of chamber technique

One of the problems with the flux chamber techniques arises from measurement uncertainties associated with chamber blanks. Since R_s is calculated as a difference between two measured terms, each with non-negligible error, the relative uncertainty attached to a derived Hg flux may be quite substantial. This becomes especially evident for those Hg flux values below 2 ng h^{-1} m^{-2}. The results of Hg flux measurements over soil surfaces are mostly within this range for the different seasons (both daytime and nighttime values).

It has been noticed on some occasions that chamber blank values measured after flux sampling were significantly higher than before flux sampling, both over lake and over soil. The increases found were outside the range of the normal variability of the chamber blank and were interpreted as an effect of interactions between the surface of the chamber and the Hg vapor present in the air inside it. For the lake measurements this effect can be explained by assuming that some of the Hg emitted from the lake surface was adsorbed on the surface on the chamber and later released when measuring the blank. The amount of Hg adsorbed in the chamber can be roughly estimated by calculating the difference between the blank values before and after the flux measurements. Assuming that this Hg originates from the lake surface, it can be converted to a flux value. For all the measurements, the result would translate into an increase of a few ng h^{-1} m^{-2} to the flux values reported in this paper.

For the flux sampling experiments, the opposite trend was found: for each duplicated sampling event (lasting about half an hour) the first flux value was always larger than the succeeding one. The difference was 30 to 50% for most of the measurements. This pattern may be the result of a decreased production rate. The surface layer is generally a more active region, especially if photochemical processes are occurring. When it is in place, the non-transparent chamber temporarily shields the surface, thus influencing (to an unknown extent) exchange of matter and energy (kinetic, thermal and radiative), which is likely to result in a reduction of biological and photochemical activity during the measurements. Also, the chamber modifies the normal interaction between wind and surface water, which would be expected to modify the exchange rate. All the results presented in Tables 2 and 3 are arithmetic averages of at least two sequential sampling events. If the first experimental values are indeed more representative of the true natural equilibrium state, the 30–50% difference should be taken into consideration, implying that the average values reported here are slightly too small.

It is interesting to note that the rate of dry deposition of gaseous mercury to the surface of soil and lake water can also be monitored by the chamber technique. This was observed with some of the soil (and one of the lake water) measurements during winter time, when temperatures of the soil (or water) were below 3°C, c.f. the negative values in Tables 2. 3.

To obtain more accurate data using a similar chamber technique, one of the solutions might be to construct a chamber with nickel or nickelplated materials to reduce the extent of the adsorption/desorption phenomenon experiences with Hg vapor on stainless steel (and most other) surfaces (Brosset, C. 1988, private communication). Since this material still does not allow sunlight to penetrate to the surface, biological/microbiological activity and photochemical processes could still be affected. Consequently, the best solution may be to build a transparent chamber with material that does not (or only weakly) absorb(s) Hg, e.g., Teflon film. However, even then, the chamber will influence the air flow. For characterizing Hg fluxes over soil, other types of soil (including open field sites) should be investigated.

4. Estimation of Hg budget for a forest ecosystem

To estimate the annual-average flux of Hg over lakes and the soil studied, we use the average value of all measurements conducted in May and June 1988 and 1989 as the "warmer" season's flux, and those conducted in November, January and April as "colder" season's flux. Further, we assume that day and night hours were equally long and assume a warmer season of 5 months (May to September), and a colder season of 7 months (October to April). Then the annual-average Hg flux values for

forest lake and soil were calculated to be 18.9 ± 5.2 and -3.8 ± 3.5 (in units of g km^{-2} yr^{-1}) respectively.

Using a thin-film gas-exchange model, Kim and Fitzgerald (1986) calculated an annual flux of mercury from the area of the equatorial Pacific ocean to the atmosphere. Their values were from 4.4 to 78.7 g km^{-2} yr^{-1}, with an average of 29 ± 19 g km^{-2} yr^{-1} ($n = 22$), which was quite close to our results measured from the lake surfaces. Recent calculations of elemental mercury fluxes from a seepage lake gave a considerably lower value of 0.5 ± 0.3 g km^{-2} yr^{-1} (Fitzgerald et al., 1991).

The actual Hg flux values over a one-year period are still very uncertain due to the limited amount of data. This estimate, therefore, should only be considered as preliminary, though the order of magnitude should be correct.

From the information available previously on the occurrence and cycling of Hg in the environment (Lindqvist et al., 1984, 1991), the Hg mass balance diagram (Fig. 8) was constructed for a typical oligotrophic forest lake and its surrounding draingage basin situated in the southern part of Sweden. For the purpose of this example and of calculation convenience, we assumed that the lake area is 1 km^2 and its drainage basin is 10 km^2. In this figure, total loads are the Hg amounts in the moss layer of the soil and in the lake water, respectively, assuming that the average Hg content is 2.5 mg m^{-2} in the humic layer of soil and 2 ng l^{-1} in the lake water, the total (dry + wet) deposition is about 20 g km^{-2} yr^{-1} and that the depth of the lake 2.5 m.

Only the flux values are derived directly from this investigation, as indicated by dotted arrows. In the soil case, the downward arrow represents dry deposition of mercury to the surface, which was measured by the chamber technique. The other results are taken from Lindqvist and Schroeder (1988) and Lindqvist et al. (1991). It should be noted that there is an appreciably higher rate of dry deposition on forest canopies (Lindqvist et al., 1991) than directly to soil, as reported here.

The main purpose of initiating this work was to provide this missing data, and thus make such budget estimates more realistic, both on a regional scale and for specific land and water (lake) ecosystem studies. The values presented here can be expected to vary from lake to lake, due to geographical location, the degree of acidification in the area, the humic layer thickness in the drainage basin, the humic substances, and Hg content in the lake, as well as other variables. If these values were representative for the whole of Sweden, the factor of re-emission from water surfaces would be quite close to the deposition rate estimated by Lindqvist and Schroeder (1988), while the factor of re-emission from soil would be rather small.

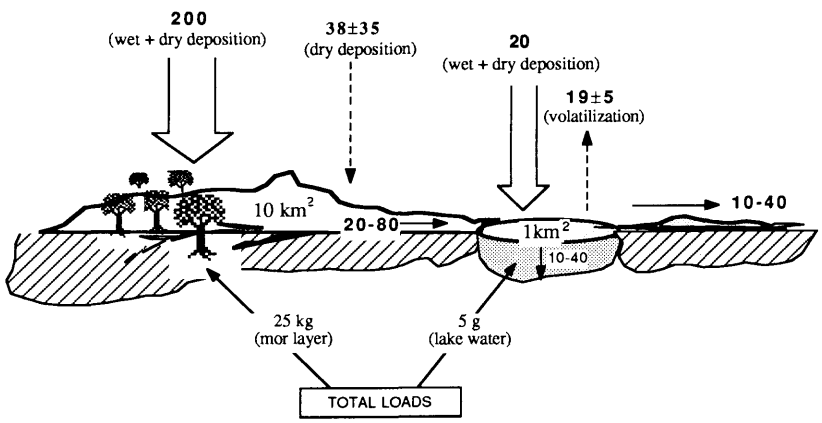

Fig. 8. Budget estimate of Hg for a typical Swedish oligotrophic forest lake and its drainage basin (g yr^{-1}).

5. Conclusions

Using a preconditioned stainless steel chamber, measurements of Hg fluxes over (lake) water and (forest) soil surfaces can be performed with reasonable reliability.

Significant diurnal and large seasonal variations in surface emission fluxes of vapor-phase Hg were found to occur and a pronounced temperature dependence of mercury fluxes was noticed from the waters of four Swedish forest lakes. Daytime flux values (average 9.4 ± 2.2 ng h^{-1} m^{-2}) were always larger than nighttime values (average 3.0 ± 1.0 ng h^{-1} m^{-2}) for the investigations conducted during May 1988. Emissions during the warmer seasons (7.9 ± 1.4 ng h^{-1} m^{-2}) were higher than during the colder seasons (-0.16 ± 0.2 ng h^{-1} m^{-2}) for the whole period of measurements.

The long time period of the field measurements over a coniferous forest soil surface (December 1987–June 1989) also allowed seasonal variations to be observed with an average emission value of 0.3 ± 0.4 ng h^{-1} m^{-2} for warmer seasons and an average dry deposition value of 0.9 ± 0.4 ng h^{-1} m^{-2} for colder seasons. The diurnal variations over soil were irregular.

The data presented, especially the flux values measured over forest lake and soil surfaces may be useful for estimating Hg budgets on local or regional scales.

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