Total gaseous mercury exchange between air and water at river and sea surfaces in Swedish coastal regions

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Abstract

This study includes five intensive field measurement campaigns. Four of the campaigns were performed over seawater surface during the summer and winter of 1997 and the summer of 1998 at Kristineberg Marine Research Station (KMRS). The fifth campaign was conducted over a river surface during the summer of 1999 at Knobesholm in southwestern Sweden. The major purpose of these campaigns was to determine emissions of mercury from natural waters in northern Europe. The influence of some physical parameters, i.e. temperature in water and air, relative humidity and solar radiation were also examined. Dynamic flux chamber technique coupled with automatic mercury vapour-phase analysers (Gardis 1A or Tekran 2357) was used. Both sites show net evasion during summer season, however, the surficial evasion rate of the river is more than one order of magnitude higher than that of the seawater. The high content of organic matter in the river in conjunction with strong insolation and subsequent water temperature variations may explain the high mercury evasion measured at the river site. An average evasion of $+11$ ng m^{-2} h^{-1} (varying from -2.5 to $+88.9$ ng m^{-2} h^{-1}) was obtained during the course of the river measurement. At the sea site, mercury evasion was found in the interval between -2.72 and $+8.84$ ng m^{-2} h^{-1} with an average evasion of $+0.61$ ng m^{-2} h^{-1}. Mercury evasion measured over both river and seawater surfaces exhibits a consistently diurnal pattern with maximum evasion during the daytime period and minimum evasion during the nighttime period. At the freshwater site, mercury evasion is strongly correlated with the intensity of net insolation, and negatively correlated with relative humidity. An exponential relationship between mercury evasion and water temperature was also observed at the freshwater measurement site. At the seawater site, a strong correlation between mercury evasion and intensity of UV$_A$ part of insolation was obtained. Insolation is speculated to play an important role in the formation of dissolved gaseous mercury in both river and seawater. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

A large amount of mercury, some 2000 t yr^{-1} (Mason et al., 1994), is introduced into the atmosphere by natural water systems. The total emissions of mercury are often simplified to three subcategories: natural-, anthropogenic- and reemission. The importance of natural emission and reemission to the biogeochemical cycling of Hg is not well known, but needs to be quantified more elaborately since reemission from the Northern Hemisphere seems to be dominated by the contribution from water systems. Calculations on the biogeochemical cycle of mercury show that evasion of mercury from the oceans exceeds those from soil and biota (Mason et al., 1994). The relative contribution of mercury emitted from freshwater compared with emissions from soils or other terrestrial sources are still unknown (Schroeder and Munthe, 1998). Natural water systems are often supersaturated with elemental mercury (Hg^0) (Schroeder and Munthe, 1998) that is the major component of dissolved gaseous mercury (DGM). There

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are several possible explanations to this. Oxidised mercury (HgII), which is the main form of mercury in deposition to water surfaces (Lindqvist et al., 1991), can be reduced both in biotic i.e. enzymatically catalysed by microorganisms (Mason et al., 1995) and abiotic processes (Allard and Arsenie, 1991; Xiao et al., 1994, 1995). Fractions of particles are transported to the bottom of the actual water system where its mercury content can be transformed into organic forms by microorganisms, i.e. being methylated, and available for bioaccumulation (Compesterau and Bartha, 1985). Moreover, elemental mercury can be formed from microbial degradation of methylmercury (Marvin-Dipasquale and Ormeland, 1998; Mason et al., 1995). Transportation of mercury from forest soils to waters and into aquatic organisms are closely related to the flow of organic matter. In both the terrestrial and the aquatic environment, Hg is strongly associated with humic substances. About 25% to 75% of the total load of Hg to lakes in southern and central Sweden originates from runoff transport of humic substances from the catchment area (Lindqvist et al., 1991). The influence of humic substances on the photoreduction of Hg(II) in fresh water was studied by Xiao et al. (1995) and in sea water by Costa and Liss (1999) and found to increase the production of Hg^0 in both cases. Super-saturation of elemental mercury will end up in evasion of this compound to the atmosphere. Such mercury evasion reduces the mercury burden in the water and may limit the methylmercury production and accumulation in fish.

Evasion of mercury from water systems to the atmosphere is important to study because they tend to proceed after the anthropogenic use of mercury is reduced, and gives information about the magnitude of the reemission (Mason et al., 1994). Hence there is a clear objective to increase the quantitative knowledge concerning air–sea exchange of mercury. One way of doing this is to calculate the flux i.e. the mercury evasion from a surface per sq. unit and time.

There are two general methods accessible for mercury evasion flux measurements, micrometeorological, (Lindberg et al., 1995a; Kim et al., 1995) and flux chamber techniques, especially the latter have been frequently (Kim and Lindberg, 1995; Capri and Lindberg, 1998; Poissant and Casimir, 1998; Ferrara and Mazzolai, 1998) used since the pioneering work by Xiao et al. (1991). Both methods show advantages and disadvantages. The chamber techniques are commonly used because of their low cost, simplicity of design and good detection limits (Chan et al., 1998). Disruptions of the local environment by covering the actual area with a chamber occur, affecting the influence of wind, concentration gradient, and relative humidity compared to the ambient conditions.

The micrometeorological techniques do not disrupt the environment and include wind as a parameter for flux measurements. One limitation of these techniques is the need for multiple samples to cover inhomogeneous situations. Comparisons between the micrometeorological technique and the flux chamber approach show that the chamber method measures consistently lower fluxes than the micrometeorological technique (Lindberg et al., 1995a, b; Gustin et al., 1999).

The major objective of this study was to investigate mercury emissions from two different water systems in Sweden, by using the dynamic flux chamber technique. The result was aimed at modelling studies in order to identify and quantify sources of atmospheric mercury in northern Europe. Since elemental mercury can volatilise from natural waters to the atmosphere, DGM was measured in this study. Influence of sunlight, temperature, relative humidity and seasons on mercury flux was studied. Four seawater campaigns, three during summer and one during winter, and one freshwater campaign during summer were carried out. The location of sites was chosen out of practical and logistical criteria as well as for serving as a representative for coastal seawater and river water.

2. Methodology

2.1. Site locations

The locations of sites are as indicated in Fig. 1. The measurements over fresh water were located at Knobesholm, 40 km east of the Swedish coastline, 120 km south of Göteborg. The experiment was performed on a small river, which is a runoff from the lake Borrsjön. The water depth in the river was 1–1.40 m, and the width approximately 25 m. The river and the lake are located in a remote forest area, creating a humic
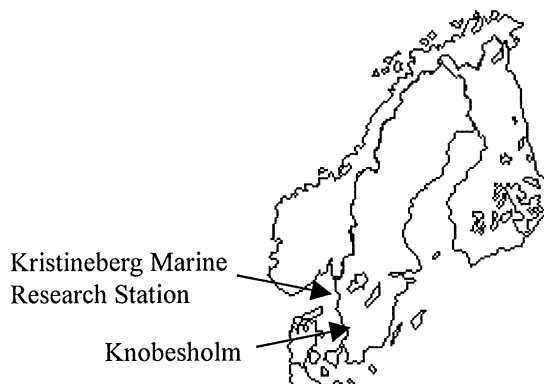

Fig. 1. Location of Hg evasion measurements in southwestern Sweden.

rich runoff from the catchment area. The shore along the river was covered with vegetation. Neither the lake nor the river receives industrial polluted water or municipal wastewater. The meteorological parameters, air temperatures inside and outside the flux chamber, water temperature, insolation and relative humidity were measured by a mini meteorological logger Skye Datahog 2 type SDL 5360. Sensors for temperature and insolation (a Kipp&Zonen Pyranometer Type CM3 designed to measure solar irradiance over the 305–2800 nm band) were connected to the logger and positioned in the very same place as the flux measurements were and, concurrently acquired with the flux measurements. The equipment for total gaseous mercury (TGM) analysis was placed sheltered in an abandoned laundry house, with low background mercury concentration (<6 ng m^{-3}), adjacent to the river. The water was analysed for several parameters such as pH, conductivity, total organic carbon (TOC), total mercury (Hg-tot) (Brosset, 1987), P and N. The chemical composition of the river water is specified in Table 1. The pH in the river water was 6.6 which is rather high for a natural fresh water in the specific area of Sweden. The total mercury concentration in the water was 2.36 ng dm^{-3}, $n = 4$,

which is typical for a natural fresh water in this area. (Lindqvist et al., 1991).

The seawater measurement site was located on the Swedish West Coast at the mouth of Fjord Gullmaren, 120 km north of Göteborg, in the open centre of a hexagonal shaped platform. The platform was placed 1 km off shore the Kristineberg marine research station (KMRS) and at a water depth of 9–10 m. The KMRS station is equipped with the standard meteorological instruments for air temperature, water temperature, wind speed, and intensity of UV$_A$ (320–400 nm) part of the insolation.

2.2. Mercury flux measurement technique

The dynamic flux chamber was made up of FEP Teflon after a prototype from Oak Ridge National Laboratories (ORNL) (Kim and Lindberg, 1995; Capri and Lindberg, 1998). This type of flux chamber permits measurement of gas flux from a small surface area and provides a sensitive means of measuring small fluxes. The rectangular, open-bottom chamber ($60 \times 20 \times 20$ cm) was supported by an external aluminum frame. One piece of polystyrene block wrapped with Teflon sheet was fastened on each side of the chamber to make it float on the water surface. Mercury flux from the water surface exposed in the chamber was calculated using Eq. (1)

$$F = \frac{(C_o - C_i)}{A} \times Q, \tag{1}$$

where F is the flux of total gaseous mercury in ng Hg m^{-2} h^{-1}; C_o and C_i are the concentration of TGM at the outlet and inlet in ng m^{-3}, respectively; A is the surface area of bottom of the chamber in m^2 (0.12 m^2); and Q is the flushing flow rate through the chamber in m^3 h^{-1} (~ 0.5 m^3 h^{-1}). The inlet was situated 20 cm above the water surface. The inlet and outlet mercury concentrations were monitored alternatively by using an automised set-up of magnetic switch valve interfaced with the mercury analyser (either Gardis or Tekran) at time intervals of 5–10 min (Fig. 2). The Teflon tubing

Table 1
Chemical composition of river water[a]

PH	6.6	SO_4^{2-} (mg dm^{-3})	5.8
Conductivity (mS cm^{-1})	7.99	Cl^- (mg dm^{-3})	11
Alkalinity (mequivalents dm^{-3})[b]	0.20	Ca^{2+} (mg dm^{-3})	5.9
Absorbance 420/5 (unfiltered)	0.245	Na^+ (mg dm^{-3})	6.9
Absorbance 420/5 (filtered)	0.197	K^+ (mg dm^{-3})	0.39
TOC (mg dm^{-3})	9.0	Mg^{2+} (mg dm^{-3})	1.6
Tot-P (µg dm^{-3})	1.00	Fe (mg dm^{-3})	1.12
Tot-N (µg dm^{-3})	386	Mn (µg dm^{-3})	57
		Hg-tot (ng dm^{-3})	2.35[c]

[a] The water analysis was conducted by Swedish University for Agricultural Science (SLU) in Ulltuna, except those for Hg-tot which were analysed by Swedish Environmental Research Institute (IVL) in Göteborg.
[b] Preferable notation, the number of moles of H$^+$ neutralised by the alkalinity in a litre of solution.
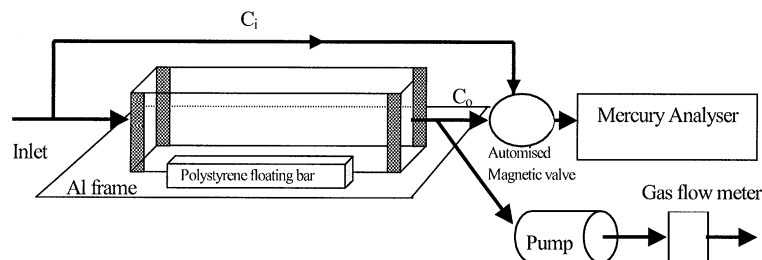[c] Average value out of four samples.

Fig. 2. Set-up of the dynamic flux chamber for measuring flux over water surfaces. C_i and C_o is the concentration of mercury in the inlet and outlet air, respectively.

both for the inlet and outlet measurements was slightly heated by heating bands to a temperature of 10°C above the ambient air temperature. Two heating fans, which were fastened at the corners of the aluminum frame, were very gently heating the flux chamber during the measurement campaigns to prevent water condensation on the inner wall of the flux chamber.

Before and after measurement campaigns, the chamber was extensively cleaned. First it was rinsed three times with diluted laboratory detergent, followed by a 10-fold rinse with Milli-Q water or tap water, and then kept outside in ambient air for some hours. Between the campaigns the chamber was stored in a well-ventilated house located in the sampling area. This practice eliminates the contamination of the chamber with, for example, laboratory air, which often contains higher mercury concentration than ambient air. The blank of the chamber was measured in the sunlight by sealing the chamber bottom to a large, clean piece of FEP Teflon. Negligible blanks were found which agrees well with the blank tests done by Capri and co-workers (Capri and Lindberg, 1998). The blank of the magnetic switch valves were tested by sucking ambient air directly into the mercury analyser or through the magnetic valves before the analyser; no difference in mercury concentrations were obtained.

2.3. Analytical techniques

TGM measurements. In the river water measurements the TGM concentration in the air was analysed with an automatic Mercury Vapour Analyser based on cold vapour atomic fluorescence spectroscopy (CVAFS) (Tekran 2537A). The working principle of the instrument has been described by Schroeder et al. (1995). The instrument was calibrated by routine automated additions of known concentrations of gaseous Hg^0 supplied by an internal permeation source, which was calibrated in the laboratory.

At the marine station, the TGM concentration was monitored with an automatic dual amalgamation and cold vapour atomic absorption spectrometry (Gardis 1A atmospheric mercury analyser Urba et al., 1995). The Gardis instrument was calibrated in the laboratory by injecting a known amount of mercury vapour. The detection limit of the instrument was 0.2 ng m^{-3}. The measurement results were recorded either by a chart recorder or a portable computer.

Both methods were recently intercompared at two field exercises, one at Mace Head, Ireland (Ebinghaus et al., 1999) and another at Sasetta, Italy (Munthe et al., 2001), and good agreement was reported for the TGM concentrations measured by these two instruments.

DGM measurements. In the riverwater campaign DGM samples were taken manually from a rubber boat with an acid washed 2 l Teflon beaker. The samples were then immediately transferred into a Teflon impinger. The Teflon impinger consisted of several Savillex cylindrical pieces with the inner diameter of 4.1 cm that were interconnected to make up a total length of 1.80 m and a volume of 2 dm^3. Mercury free argon gas was distributed from a glass frit positioned near the bottom of the impinger to sparge the water column of DGM, which was collected on a gold trap at the top outlet. By using this long and thin impinger, the contact time for the introduced gas bubbles with the water sample was extended in order to achieve an efficient removal of mercury. The flow rate of the argon gas was kept between 270 and 350 cm^3 min^{-1}. Each sample was purged for at least 90 min. The blank of this set-up was tested by purging MQ water and was found to be negligible.

During seawater campaigns, samples for dissolved gaseous mercury (DGM) were collected from the hexagonal platform at a depth of 20 cm by using an acid washed 2-dm Teflon beaker. All water samples were transferred into an extensively cleaned 500 ml borosilicate glass impinger immediately after collection, and purged with mercury free air for 30 min and the mercury evolved was collected on a gold trap. The flow rate of the mercury free air was 300 cm^3 min^{-1}. The gold traps were in all campaigns sealed and kept in plastic bags, transported to the laboratory and analysed with a Brooks Rand CVAFS-2 Mercury Analyser within 24 h.

Total mercury measurements. At the river water site, water samples for Hg-tot were taken and analysed by the Swedish Environmental Research Institute (IVL). These samples were obtained from the river directly, stored in ultra clean washed Teflon flasks kept dark and cold in double plastic zipbags and transported to the IVL lab where they were acidified with suprapur HCl from Merck. The samples were oxidised with BrCl. Excess of the oxidiser was reduced with aqueous hydroxylammonium chloride followed by the reduction of mercuric ions with the addition of acidified stannous chloride solution. Hg^0 formed in the samples was purged with mercury free nitrogen, collected on goldtraps and analysed by CVAFS.

3. Results and discussion

3.1. Measurements over river surface

The fresh water measurements were carried out in August 4–16, 1999. The average mercury flux over the river surface was +11.0 ng m^{-2} h^{-1}. This average flux is comparable with the average Hg flux (+11.2 ng m^{-2} h^{-1}) from lake Stora Läresbovatten in Sweden measured during summer by Xiao et al. (1991). The mercury fluxes measured over the river surface with the dynamic chamber as well as the TGM concentra-

Table 2
Statistical summary of the measurement results over the river surface

	Average	Median	S.D.	CV (%)	Min	Max	n
TGM[a] (ng m^{-3})	2.61	2.39	1.95	74.7	0.90	7.04	792
Evasion (ng m^{-2} h^{-1})	11.06	6.69	11.83	106.9	0.50	88.92	788
Deposition (ng m^{-2} h^{-1})	1.14	0.74	0.99	86.8	0.27	2.48	4

[a] TGM outside the chamber was measured in the air 20 cm above the water surface.

tions in the inlet air are summarised in Table 2. The relative difference between inlet and outlet TGM concentrations was typically $\sim$ 32% (median 34%), and $\sim$ 88% (median 75%), for a 24 h measurement period with an average Hg flux of $+3.9$ and $+10.8$ ng m^{-2} h^{-1}, respectively. The average inlet TGM concentration was 2.61 ng m^{-3} throughout the campaign, but at the beginning of the campaign inlet concentrations as high as 7 ng m^{-3} were observed which is rather high over open water. For all but four occasions that only occurred during night, evasion of mercury from the water surface was the sole exchange direction present. A clear diurnal pattern is shown in Fig. 3a. The mercury evasion peaked during the afternoon followed by reduced evasion during late afternoon and finally a minimum evasion at the beginning of sunrise, occasionally giving deposition during the night-time period. The mercury fluxes tracked the intensities of insolation very well with a linear correlation coefficient (r) of 0.6 ($n = 856$). The correlation between log flux and insolation gives a somewhat lower ($r = 0.4$) correlation coefficient implying a linear relationship. On August 11, a solar eclipse occurred at this location in northern Europe. The maximum coverage of the sun was 70% approximately during 1 h. The mercury fluxes observed during this event followed the insolation (Fig. 3b) while the temperature of water and air was almost constant. The connection between mercury flux and insolation can be assumed to be a consequence of photochemically produced DGM. Further, it is reasonable to assume that mercury evasion only occurs if the degree of saturation S is above unity,

$$S = H\text{DGM}/\text{TGM}, \tag{2}$$

where H is Henry's law constant corrected for temperature according to (Sanemasa, 1975),

$$H = \frac{M_\text{w}(10^{-1078/T+6.250})}{R\rho_\text{w}T} \tag{3}$$

where M_w is the molar weight of water 18.01×10^{-3} (kg mol^{-1}), R is the gas constant 8.2058×10^{-2} (atm dm^3 K^{-1} mol^{-1}), ρ_w is the density of water (kg dm^{-3}), and T is the temperature (K). Four DGM measurements were carried out on 16 August 1999. The average DGM concentration found was 0.56 ng dm^{-3}. At the present conditions, with TGM concentration of 2.6 ng m^{-3} and the river water temperature 20°C, the water is

saturated with DGM already at a concentration as low as 9.0 pg dm^{-3}. Obviously, the water was highly supersaturated in terms of DGM. In comparison, the mean total concentration of mercury was 2.35 ng dm^{-3}. The DGM concentration in the river water was significantly correlated ($r = 0.996, n = 4$) to the intensity of insolation (Fig. 4) implying photoreduction of oxidised mercury from the Hg-tot pool. According to our knowledge, there are limited data in the literature referring to the settings of our site, i.e. shallow fresh waters, high concentrations of TOC (Table 1), and with direct on-site analysis of DGM. Therefore, it cannot be judged if the DGM concentrations found in this study is representative of this special kind of water or not. In the work by Lindberg et al. (2000) rapid field analysis of DGM is pre-requested, due to the risk of significant losses of this fraction.

The mercury flux from the river was positively correlated with water and air temperature with an exponential relationship, and negatively linear correlated with relative humidity ($r = 0.7$) (Fig. 5a–c). The positively linear correlation between mercury flux and insolation and negatively linear correlation between mercury flux and relative humidity observed in this study were as well observed in Canada by Poissant and Casimir (1998). The strong correlation of Hg flux with water and air temperature obtained in this work was not found in their work.

The relation between mercury evasion and water temperature observed in our river measurements can be explained as follows. The flux can be expressed by the two-layer model (Liss and Slater, 1974) collaborated by Schroeder et al. (1992),

$$F = \frac{(\text{TGM} - H\text{DGM})}{((1/K_\text{a}) + (H/K_\text{w}))} \tag{4}$$

where K_a and K_w are overall air- and water-side mass transfer coefficients, respectively. If the water temperature is increased, assuming TGM, DGM, K_a and K_w being constant, the strong temperature behaviour of H will make the water more supersaturated and in turn, the mercury flux will increase. The temperature in the water showed a small diurnal variation, with the highest temperature in the late afternoon and the lowest at early mornings. The variation in temperature, was typically $\sim$ 4°C if the day had been sunny and $\sim$ 2°C during cloudy conditions. To test the influence of water temperature for the river measurements, fluxes were
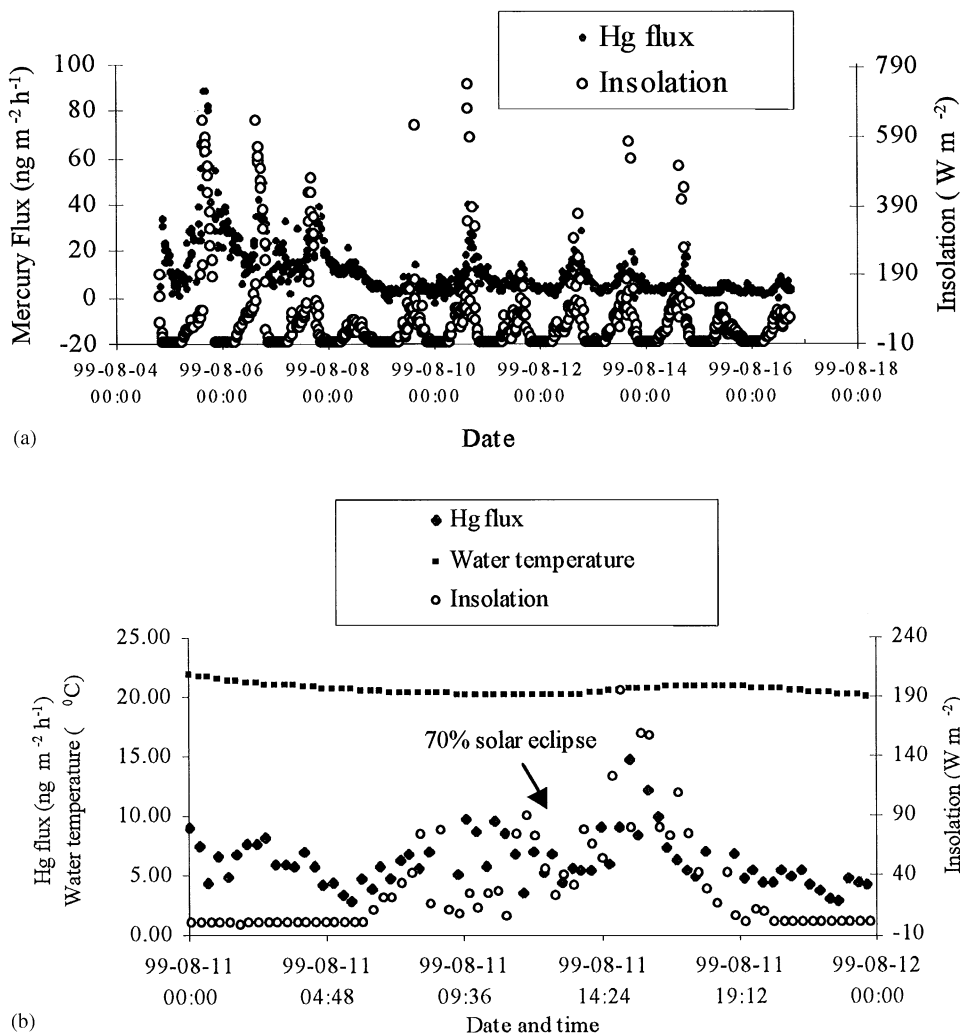
Fig. 3. Mercury evasion and insolation measured over the river surface on 4–16 August 1999 (Fig. 3a) and on the day (Fig. 3b) of the solar eclipse showing the effect of sunlight on mercury evasion and water temperature.
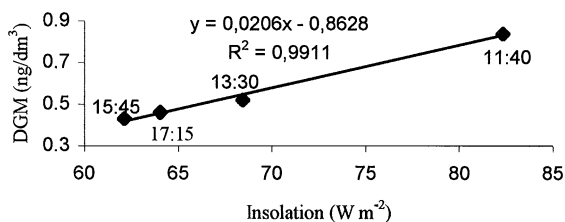

Fig. 4. DGM and insolation measured over the river surface on 99.08.16. The sampling times are shown in the diagram.

calculated at 17°C and 26°C, which correspond to the extreme water temperature range during the river measurements. The relative increase is 30%, showing a significant dependence of water temperature.

In our study, the air temperature gradient between the inside and outside of the chamber is significantly correlated with insolation ($r = 0.8$). During nighttime or cloudy weather conditions in general, there is only a slight difference ($<2°C$), but when exposed to direct sunshine, the gradient can be as high as 15°C. It has been suggested that during conditions where the air temperature is higher than the water temperature the vapour pressure of mercury in the gas phase above the water surface is significantly higher than what is calculated assuming equilibrium (Loux, 2000). At a temperature difference of 10°C, Loux estimates the vapour pressure of mercury to be more than 2 times higher above a water body at 20°C than that is calculated from Henry's law constant at the lower water temperature. This is really hard to believe and was also

$$y = -28{,}326x + 98{,}458$$
$$R^2 = 0{,}5989$$

(a)

$$y = -14{,}517x + 52{,}081$$
$$R^2 = 0{,}4393$$

(b)

$$y = -0{,}5164x + 53{,}998$$
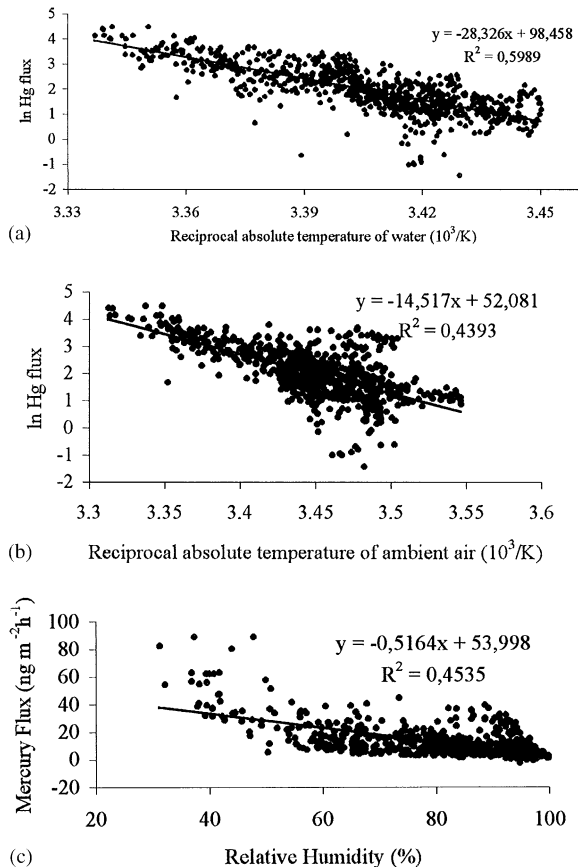$$R^2 = 0{,}4535$$

(c)

Fig. 5. Relationship between mercury evasion from the river surface vs. ambient air temperature (Fig. 5a), water temperature (Fig. 5b) and relative humidity in the ambient air (Fig. 5c).

not supported by any experimental evidence or theory. In the present work, fluxes were seen to correlate with insolation and water temperature. Both these effects can be understood as explained above. There is also a correlation with air temperature as is shown in Fig. 5b. Since an increase in air temperature in the chamber is likely to be a course of insolation such a correlation is reasonable, but should merely be considered as a side effect rather than something that promotes mercury flux. The negative linear correlation between mercury flux and relative humidity is also most likely a reflection of insolation.

3.2. Measurements over sea surface

Four flux measurement campaigns were carried out at KMRS from 23 June to 2 July 1997, 6–12 August 1997, 14–22 December 1997 and 17–23 June 1998, respectively. The first campaign comprised monitoring of air and water temperature, and UV_A intensity of insolation

from KMRS. During the second campaign, the meteorological instruments at KMRS were out of order. Under the third campaign, which was during winter, besides mercury evasion only water temperature was recorded. During the fourth campaign, only data for UV_A intensity of insolation and water temperature were available from KMRS. The observations covering the mercury measurements are summarised in Table 3. The average TGM concentration in the air, 20 cm above sea surface was 2.81 ng m^{-3} throughout the three summer campaigns. During all sampling campaigns, the water column was sampled for DGM during daytime. DGM concentrations in water varied from 0.04 to 0.1 ng dm^{-3}, which is close to what Iverfeldt (1984) obtained at the same site. It is obvious that during daytime seawater is in supersaturated in terms of DGM since saturation occurs at ~ 10 pg dm^{-3} under ambient conditions.

The measured mercury fluxes over seawater surface in all summer campaigns indicated evasion as well as dry deposition processes (Fig. 6a–c). The maximum evasion of mercury measured during the three summer campaigns was 8.8 ng m^{-2} h^{-1} whereas the maximum deposition was 2.7 ng m^{-2} h^{-1} (Table 3). As observed during the river measurement, evasion of mercury over seawater reached maximum values during midday and deposition occurred during nighttime. At the first and the fourth campaign, we also obtained data on UV_A intensity from the KMRS, and it is clear that the mercury evasion mimicked the UV_A intensities ($r = 0.63$ at the first campaign).

Fig. 7a and b shows the mercury evasion relationship with air and water temperature. From a statistical point of view, there is some degree of linear correlation between mercury evasion and air temperature ($r = 0.27$), at the $\alpha = 0.01$ level of significance (the critical values of r are ± 0.21 when $n = 152$) (Dixon and Massey Jr., 1969), but practically the correlation is very weak. This is also the case for the correlation between mercury evasion and water temperature. The average mercury flux of $+0.61$ ng m^{-2} h^{-1} obtained is similar to the literature values of mercury fluxes at coastal areas calculated by Costa and Liss (1999). Ferrara and Mazzolai (1998) used a similar approach to estimate summer fluxes over Mediterranean waters, which were found to be a magnitude higher compared to ours.

3.3. Mechanisms for DGM production and its correlation to mercury evasion

The role of abiotic photoreduction in forming elemental mercury in natural waters is very uncertain since, as mentioned in the introduction, there are several biotic ways possible. Because there is no time delay between changes in insolation or water temperature and flux in our studied water systems, biotic reduction is not

Table 3
Statistical summary of the measurement results over the sea surface. Fluxes are expressed in ng m^{-2} h^{-1}

Date		Average	Median	S.D.	CV (%)	Max	Min	n
All summer campaigns (Year.Month.Day)	TGM[a] (ng m^{-3})	2.81	2.75	0.69	24.6	5.36	1.62	827
97.06.23–97.07.02	Evasion	0.42	0.30	0.40	94.5	1.91	0	114
	Deposition	0.35	0.16	0.37	107.2	1.20	0.01	38
97.08.01–97.08.06	Evasion	1.00	0.77	0.82	82.5	3.97	0	249
	Deposition	0.36	0.26	0.25	69.2	1.03	0.06	44
97.12.14–97.12.22	Evasion	—	—	—	—	<1[b]	0[b]	—
	Deposition	—	—	—	—	<1[b]	0[b]	—
98.06.20–98.06.25	Evasion	1.01	0.46	1.33	131.9	8.84	0	179
	Deposition	0.57	0.24	0.67	117.3	2.72	0.02	55

[a] TGM concentrations in the air were measured at 20 cm above seawater.
[b] Range of TGM fluxes where the maximum values are set as upper limit.

considered as the driving force for the observed mercury evasion. Although the total mercury concentration in river water was not very high (about 2.3 ng dm^{-3}), the high concentration of organic matter (TOC concentration is up to 9.0 mg dm^{-3}) in the river may have facilitated an efficient photo chemical reduction process of Hg(II) (Xiao et al., 1995; Costa and Liss, 1999) forming DGM. Humic substances are polymacromolecules of high-molecular weight, with a carbon skeleton. They are identified as the source of organic matter capable of acting in a photosensitising manner in photochemical reactions (Spokes and Liss, 1995). The concentration of humic substances, both in forms of particles and dissolved fractions, plays an important role in complexing Hg(II) with its functional groups.

The reduction of cations in an aquatic environment by organic matter has been proposed to occur via two alternative routes (Costa(Ferreria da), 1997; Spokes and Liss, 1995 and references therein). These two pathways are covered by the Complex Formation Theory and the Reactive Intermediate Theory. In both cases, the reaction is thought to proceed via the same scheme. Absorption of a photon by an organic chromophore starts the process followed by the formation of an electronically excited state of corresponding species. In the complex formation theory the electron transfer causing the reduction of the cation may happen via ligand to metal charge transfer (LMCT) or by moving the electron to a less stable orbital from which it will be donated to the metal. Abiotic reduction of humic and fulvic mercury complexes by LMCT has been known for a long time (Costa, 1997 and references therein), and is probably one of the main paths for the mercury reduction in our fresh water system.

The DGM concentrations in the river water may also partly be explained by the content of particulate matter. As proposed by Nriagu (1994), photoreduction of mercury can most likely occur on particle surfaces. The electron donors are organic ligands that cover the particle surface and can serve as sacrificial reductants. In this case it is probable that the photoreduction of mercury is mediated by iron and manganese photoredox reactions. The concentrations of these metals in the river water are listed in Table 1. For the reactions to proceed, they must be linked to the oxidation of organic compounds (or other appropriate charge acceptors). This kind of photoreduction is presumably optimised by a moderate concentration of particles, since the process depends on both content of particle surfaces and light transmittance of the water. The difference in absorbance between filtered and unfiltered samples from the river (Table 1) shows that the concentration of particles is in agreement for quite clear water compared to other fresh water systems in Sweden (Wilander, 2000) thus providing good circumstances for light transmittance.

In the reactive intermediate theory photolytically produced reactants will reduce the cation. In a study by Pehkonen and Lin (1998) hydroperoxy radicals (HO$_2$), photolytically produced by oxalic acid in aerated aqueous solution, was found to reduce Hg(II) to Hg^0. The proposed mechanism in their work includes a two-electron transfer process performed in two steps. In the first rate-determining step Hg(II) is reduced to monovalent mercury (Hg(I)) by HO$_2$. The monovalent mercury is then proposed to react with HO$_2$ forming Hg^0. However, reduction via Hg(I) as an intermediate, is very unlikely because this species would immediately react with oxygen, which was present in the experiment, with subsequent oxidation to Hg(II) (Nazhat and Asmus, 1973; Pikaev et al., 1975) rather than react with HO$_2$. A comparison of lifetimes for Hg(I) due to some other possible reaction pathways is made by Gårdfeldt et al. (2001). It is clear from the comparison that in aerated solutions when the concentration of Hg(I) is low, the influence of dimerisation of Hg(I) (with rapid disproportion to Hg^0 and Hg(II)) can be precluded due to efficient oxidative scavenging by oxygen. This is also
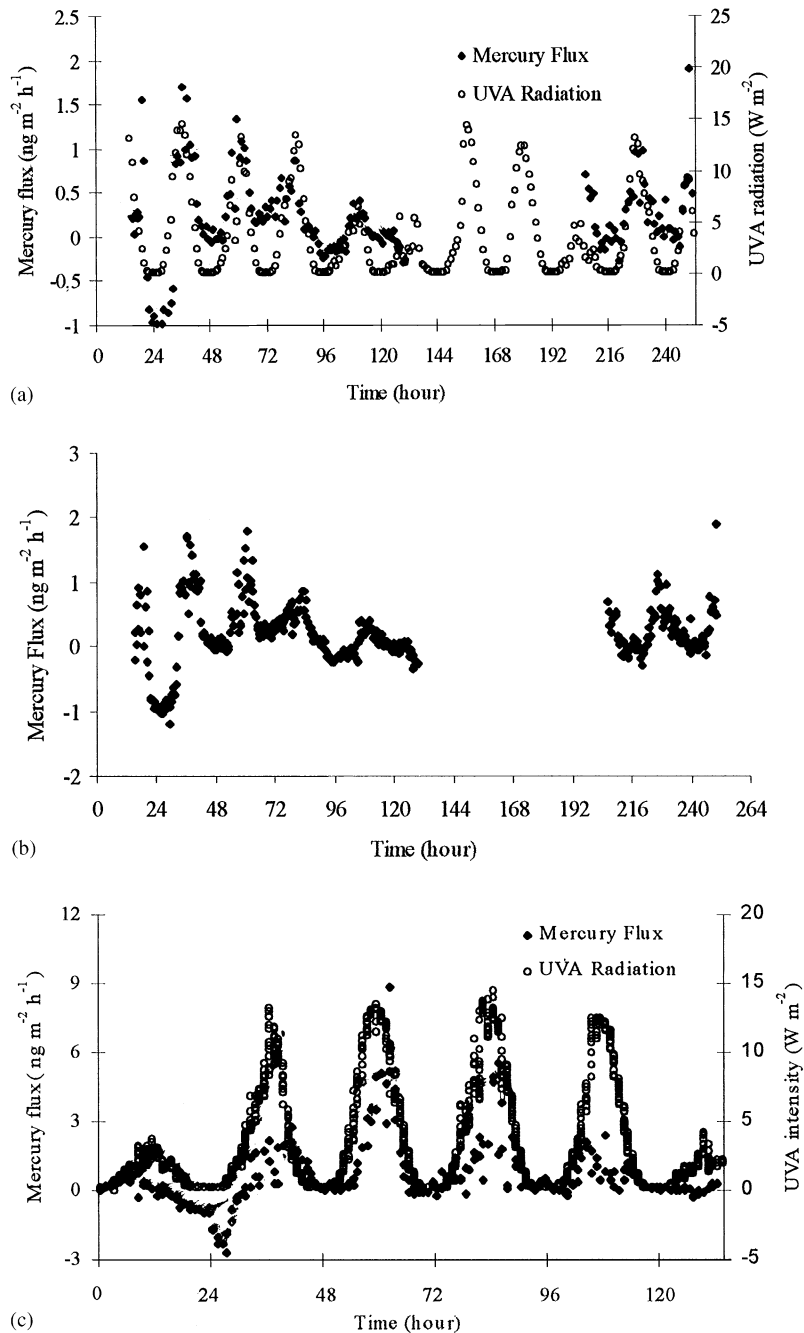
Fig. 6. Mercury evasional flux and UVA radiation measured over the sea surface from 23 June to 2 July 1997 (Fig. 6a), from 6 to 12 August 1997, and from 17 to 23 June 1998 (Fig. 6c).

true for oxygen saturated natural waters. Since the mechanism for the reduction of Hg(II) by HO_2 is not clear, the importance of this reaction in the river water is hard to estimate.

Photodegradation and oxidation by photolytically produced hydroxyl radicals, of methylmercury show

that Hg(II) is formed in both cases. This process has thus no direct influence of the DGM production or the flux of mercury, but may serve as a pool for reducible Hg(II) (Gårdfeldt et al., 2001).

In marine water, divalent mercury will form dissolved inorganic complexes, such as $HgCl_4^{2-}$, but also organic
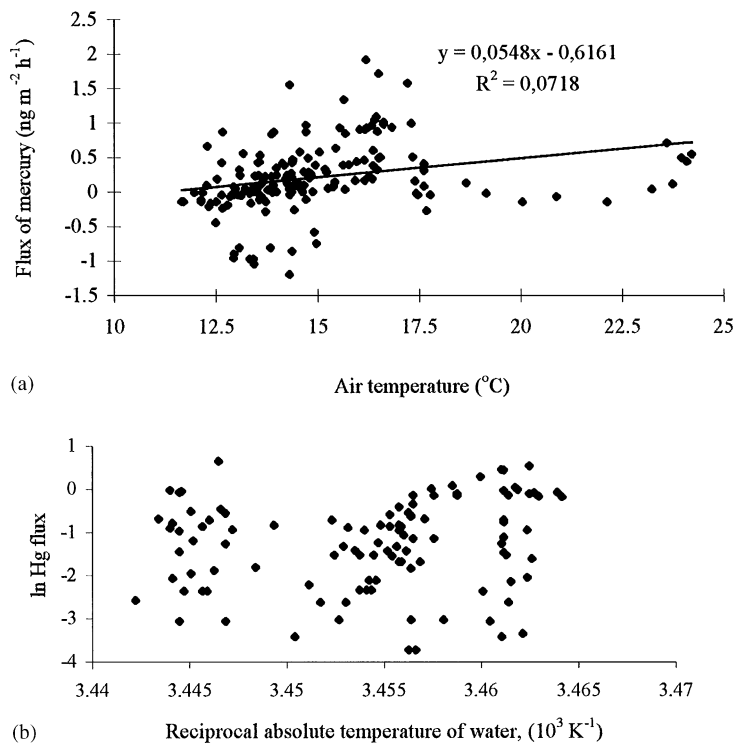
Fig. 7. Relationship between mercury evasion from the sea surface vs. ambient air temperature (Fig. 7a) and water temperature (Fig. 7b) from 23 June to 2 July 1997.

complexes with humic acids (Munthe, 1991; Costa and Liss, 1999). Reduction rates of Hg(II) in sea and fresh water were studied at different light intensities and disolved organic carbon (DOC) concentrations by Costa (1997). The result from that study shows that the reduction is dependent on light intensity and wavelength, DOC concentration, and is generally slower for seawater than for fresh water. This is in agreement with our results where the mercury evasion from the river is higher than that from the sea.

Laboratory studies show that mercury hydroxide complex can be photoreduced to form Hg^0, while the halide complex is found to be stable (Xiao et al., 1994). Horvath and Vogler (1993) also found this observation. Their study found that Hg(II) in chloride complexes was under certain circumstances reduced to Hg(I), but in the presence of oxygen this species is rapidly oxidised back to Hg(II). Experiments by Amyot et al. (1997) show that UV_A (320–400 nm), UV_B (280–320 nm) and visible light (400–700 nm) of solar radiation all contribute to the formation of DGM in seawater. It should be mentioned that sunlight might have two roles. Either enhancing the DGM production by photoreduction or it may gain oxidation of mercury by photolytically produced oxidising species (Lin and Pehkonen, 1999; Gårdfeldt et al., 2001) and thus controls the DGM level

in the water. In our study, the observed diurnal pattern of mercury flux over sea surface can be explained by net formation of DGM by solar radiation during daytime and dark oxidation of DGM to Hg(II) in the presence of chloride (Amyot et al., 1997).

The two major observations in this study are that river water shows much higher mercury evasion and DGM concentrations than the sea. Insertion of average values for DGM and TGM from the river measurements into the expression for estimating net flux by Eq. (4) gives support to our highest measured net evasion of mercury. K_a and K_w used in these calculations were similar to those reported by Schroeder et al. (1992), namely 9 and $0.09 \, m \, h^{-1}$, respectively. Since the photochemical mediated reduction of divalent mercury is likely to be important components of the evasion flux of mercury in aquatic systems, it would be interesting to perform online mercury speciation according to Lindberg et al. (2000).

4. Conclusions

● Both river and sea sites are net emission sources of Hg^0 to the atmosphere during summer; however, the

emission rate of the river is more than 10 times higher than that of the seawater.

- It is indicated by our measurement data that photo induced reduction processes play a crucial role in the formation of DGM in both river and sea-water systems in the study areas, even though we cannot exclude contributions from other processes. The high content of organic matter in the river in conjunction with strong insolation and high water temperature may explain the high DGM super-saturation and mercury evasion observed at the river site.
- Mercury fluxes measured over both the river and the seawater surface exhibit a consistently diurnal pattern during summer seasons, with maximum fluxes during the daytime period and minimum fluxes during the nighttime period.
- Due to a strong variation of the intensity of insolation at different seasons, it is important to conduct measurement campaigns in each season in order to more precisely estimate mercury flux from water surfaces.

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