

Air–sea exchange of volatile mercury in the North Atlantic Ocean

Maria E. Andersson^{a,*}, Jonas Sommar^b, Katarina Gårdfeldt^c, Sara Jutterström^a

^a Department of Chemistry, University of Gothenburg, Gothenburg, Sweden

^b State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, PR China

^c Department of Chemistry and Biological engineering, Chalmers University of Technology, Gothenburg, Sweden

ARTICLE INFO

Article history:

Received 11 December 2009

Received in revised form 25 October 2010

Accepted 21 January 2011

Available online 28 January 2011

Keywords:

Mercury

In situ measurements

Gas exchange

Flux

North Atlantic Ocean

DGHg

TGHg

Water measurements

Air measurements

ABSTRACT

Part of the Beringia 2005 expedition covered the North Atlantic Ocean. During this passage, dissolved gaseous mercury (DGHg) in seawater and atmospheric concentrations of total gaseous mercury (TGHg), carbon monoxide (CO), and ozone (O₃) were measured continuously at high resolution. In addition, meteorological parameters such as wind speed and water temperature were measured continuously by the ship's meteorological instrumentation. The DGHg concentration was measured using a continuous equilibrium system where the elemental mercury in the sea water was equilibrated with a stream of gas. The DGHg concentration was calculated using $DGHg = Hg_{eq}/k_H$, where Hg_{eq} is the concentration of elemental mercury in the equilibrated air and k_H is the dimensionless Henry's law constant. The degree of saturation was determined directly from the measurements $S = Hg_{eq}/TGHg$. The water sampled had an average DGHg concentration of 58 ± 10 fM and the average TGHg concentration was determined to 1.7 ± 0.1 ng m⁻³. The water sampled was under- and super-saturated with respect to elemental mercury covering a large range of saturation of 70 to 230% resulting in an average degree of saturation of $150 \pm 30\%$. Therefore, both evasion and deposition of elemental mercury were observed in the sampled water. In the light of the average flux, 2.1 ± 1.8 pmol m⁻² h⁻¹, it is concluded that mostly evasion occurred during the sampling period.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Mercury has a complex biogeochemical cycle where transport between different compartments and chemical transformations have to be taken into consideration. More than 25 years ago, Brosset (1981) presented a conceptual view of the mercury cycle based on early measurements of mercury pollution in Scandinavia. Since then, the cycle has been revised several times and a recent description was presented by Mason and Sheu (2002). Moreover, Strode et al. (2007) modelled the global mercury cycle taking into account the coupling between the ocean surface and the atmosphere.

Mercury is released to the atmosphere by several different processes. However, since the industrial revolution, the anthropogenic emissions of mercury increased drastically. Pacyna et al. (2001) concluded that the natural emissions were still greater than the anthropogenic, but that the latter category was increasing. In turn, Mason and Sheu (2002) considered the anthropogenic and natural emissions to have reached the same level. Evasion of volatile mercury from the oceanic surfaces into the atmosphere is driven by the aquatic mercury pools of natural and anthropogenic origin, i.e., natural evasion and re-emission respectively. The re-emission contributes to the mercury pool in the atmosphere to the same extent as the natural

and anthropogenic emission (Mason and Sheu, 2002). Moreover, Strode et al. (2007) considered 89% of the total oceanic evasion to be re-emission.

The greatest source of mercury to the oceans, 90%, is wet and dry deposition where the mercury is mostly in the oxidised form (Hg(II)) (Mason et al., 1994). The mercury deposited to the oceans follows different reaction pathways; it may react via biotic processes forming highly toxic organic mercury compounds, or by biotic and abiotic reduction processes forming dissolved gaseous mercury (DGHg) (Allard and Arsenie, 1991; Xiao et al., 1994, 1995; Mason et al., 1995; Costa and Liss, 1999; Amyot et al., 1997, 2004). Approximately 89% of the DGHg in the mixed layer of the ocean is considered to be produced via biotic and abiotic reduction processes (Strode et al., 2007). Due to effective reduction processes, many surface waters are supersaturated with respect to DGHg (Schroeder and Munthe, 1998; Fitzgerald et al., 2007). Therefore, a net flux of elemental mercury occurs to the atmosphere.

At coastal stations, a diurnal variation in the DGHg concentration has been observed where the DGHg concentration is closely related to solar radiation; consequently the maximum of DGHg is reached by midday (Amyot et al., 1994, 1997; Lanzilotta and Ferrara, 2001; Gårdfeldt et al., 2001). Moreover, in the Mediterranean Sea such diurnal patterns have been observed at off-shore sites during the summer and early spring (Andersson et al., 2007; Gårdfeldt et al., 2003). Fitzgerald et al. (2007) requests high resolution DGHg measurements in surface waters to detect the fast reactions involving

* Corresponding author.

E-mail address: maria.andersson@chem.gu.se (M.E. Andersson).

oxidation and reduction processes for mercury species to understand the cycling of Hg.

Different approaches have been used to estimate the air–sea exchange of elemental mercury between the ocean sea surface and the atmosphere. Two main approaches have been applied: flux chamber methods and estimation of flux using empirical relationships (Xiao et al., 1991; Kim and Lindberg, 1995; Capri and Lindberg, 1998; Poissant and Casimir, 1998; Ferrara and Mazzolai, 1998; Gärdfeldt et al., 2001, 2003; Ferrara et al., 2000, 2001; Amyot et al., 2004; Lindberg et al., 1995; Kim et al., 1995; Rolfhus and Fitzgerald, 2001; Poissant et al., 2000; Wängberg et al., 2001a, 2001b; Baeyens et al., 1991; Baeyens and Leermakers, 1998; Cossa et al., 1997; Andersson et al., 2007). Moreover, micro-meteorological techniques such as relaxed eddy accumulation (REA) have been used for mercury over soils (Olofsson et al., 2005; Bash and Miller, 2008) and may be available in the future for marine mercury measurements since it has been applied for other species (Zemmelink et al., 2004). The flux chamber methods have high temporal, but low spatial resolution. However, the measurements cannot be conducted during the movement of a ship or at high wind speeds. The calculation methods require input of various parameters, such as total gaseous mercury (TGHg) in air, DGHg in surface water, wind speed and water temperature. Moreover, if high time resolution continuous measurement may be applied, the accuracy of estimating the flux of mercury from the ocean surfaces will increase.

This work is part of a measurement series (Andersson et al., 2007, 2008a) that studies the variability of marine mercury evasion at different geographical sites and tests the hypothesis that evasion of Hg is restricted in colder environments, which contributes to the accumulation of Hg species in the Arctic. This paper focuses on mercury air–sea exchange in the North Atlantic Ocean during a transect as part of the Beringia 2005 expedition. This part is treated and presented separate from the rest of the expedition due to the differences between the areas sampled. Another goal was to provide information and measurements needed to improve the global mercury budget and cycle which lack measurements in large parts of the world's oceans and to provide information needed to estimate the global mercury cycle in a climate change scenario. Measurements of DGHg, TGHg, carbon monoxide (CO), ozone (O₃), temperature, and wind speed were carried out continuously in the North Atlantic from

north of Scotland to the west of Cape Farewell, Greenland. Using this data the air–sea exchange of mercury was estimated. The concentration and the calculated fluxes are discussed from the perspective of recent estimates of the global mercury cycle.

2. Experimental

From July 7 to 11, 2005, continuous measurements of DGHg, TGHg, CO, and O₃ were carried out along a transect across the North Atlantic Ocean onboard the Icebreaker Oden during the Beringia 2005 expedition (Fig. 1). The measurements started north of Scotland and were carried out until reaching the southern part of Greenland. The main feature of the large scale circulation of waters in the northern North Atlantic is the sub-polar gyre. Warm and saline waters are transported north via the North Atlantic Current (NAC) and are transformed by cooling and freshening into several varieties of SubPolar Mode Waters (SPMD) distributed over the area (e.g. McCartney and Talley, 1982; Read, 2001). One branch will continue north and enter the Nordic Seas and contribute to the Norwegian Atlantic Current, while other branches continue towards the west, circulating in the Irminger and Iceland Basins. East of Greenland the East Greenland Current brings cold, low-salinity waters originating from the Arctic Ocean and the Nordic Seas. Waters of polar origin mix with SPMD in the Labrador Sea and forms Subarctic Intermediate Water (SAIW) which then spreads northeast contributing to a large part of the mixing, spreading back into the Irminger Basin and dominates the interior (Fig. 1).

The IB Oden is 108 m long and 31 m wide and was rebuilt to meet scientific demands. It is equipped with meteorological and oceanographic instrumentations including winches and a CTD system. In this study, meteorological data was obtained from the ship's regular instrumentation. Wind speed was measured at the top of the ship, 30 m above sea level, and the water temperature was measured in the bow water inlet situated approximately 5 m below the sea surface, depending on the loading of the ship.

TGHg was sampled and analysed using a Tekran 2537A mercury vapour analyser (Schroeder et al., 1995). The instrument was placed on the fourth deck with an air inlet situated at the same deck 2 m above deck at a height of 20 m above the sea level. The tubing was heated to 45 °C due to the temperature differences between the outdoor and

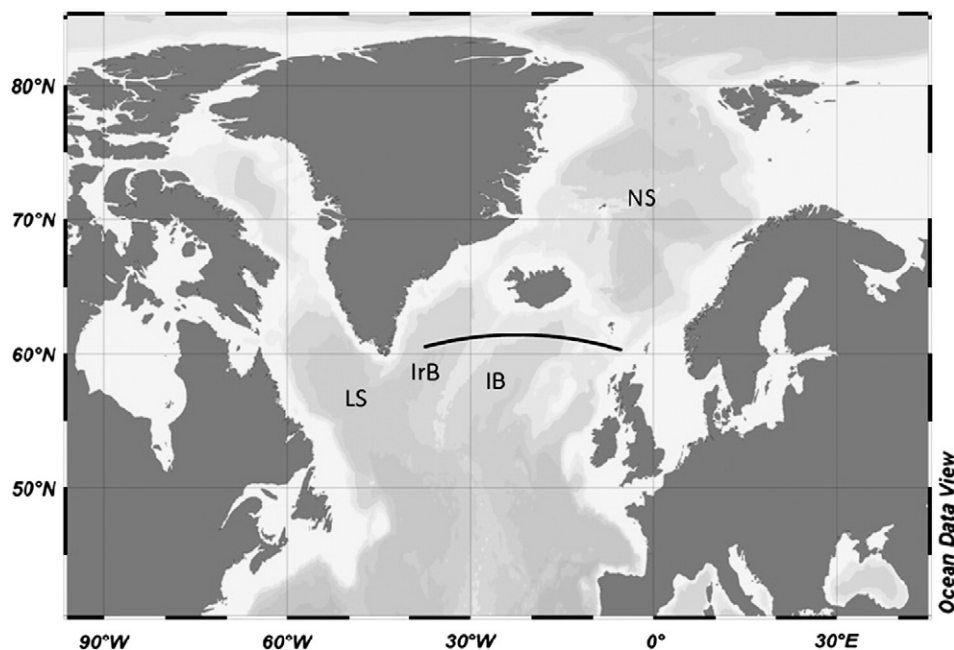


Fig. 1. The cruise track. (Program Schlitzer, R., 2009) and the different seas, i.e. IrB: Irminger Basin, IB: Iceland Basin, LS: Labrador Sea, NS: Nordic Seas.

indoor air. The sampling time and flow rate was 5 min and 1.5 L min⁻¹, respectively, which gave a detection limit of 0.1 ng m⁻³. To maintain high standard measurements the instrument was calibrated every two days using the internal calibration source and biweekly using gaseous elemental mercury injections.

The DGHg measurements were conducted with a continuous equilibrium system connected to the ship's bow water inlet (Andersson et al., 2008b). The system is based on equilibrium measurements; the incoming water was equilibrated with a stream of gas and then the equilibrated gas is measured by a Tekran 2537A and the DGHg can be calculated according to:

$$\text{DGHg} = \text{Hg}_{\text{eq}} / k_{\text{H}}$$

where Hg_{eq} is the Hg concentration in the out-going air and k_H is the dimensionless Henry's law constant for elemental mercury at the desired temperature and salinity (Andersson et al., 2008c). In addition, the degree of saturation S can be calculated directly from the measurements:

$$S = \text{Hg}_{\text{eq}} / \text{TGHg}$$

where TGHg is the concentration of mercury in ambient air and Hg_{eq} is the Hg concentration in the out-going air. In order to maintain high quality data the Tekran instrument was calibrated every week using the internal source and biweekly using injections of elemental mercury to the instrument. Along with that discrete samples were collected and compared to the semi-automatic system on a daily basis, a more detailed description of the system can be found in Andersson et al., 2008b.

Calculating the air–sea exchange from measured species is challenging. There are no models designed for mercury, instead the models used for CO₂ are used and recalculated to fit mercury. Recent reviews have suggested that the model developed by Nightingale et al. (2000) best represents the simulations made for mercury evasion (Qureshi et al., in review).

The model used requires measurements of DGHg, TGHg, water temperature T_w, and wind speed u₁₀ normalized to 10 m above sea level. The mercury air–sea exchange was calculated according to:

$$\text{Hg}_{\text{flux}} = k \times (\text{DGHg} - \text{TGHg} / k_{\text{H}})$$

where Hg_{flux} is the calculated air–sea exchange and k is the gas-transfer velocity, which is calculated according to the following equation:

$$k = \left(0.22 \times u_{10}^2 + 0.333 \times u_{10} \right) \times \left(\text{Sc}_{\text{Hg}} / 660 \right)$$

u₁₀ is the wind speed normalised to 10 m above sea surface according to:

$$u_{10} = (10.4u_z) / (\ln(z) + 8.1)$$

where z is the height where the wind speed was measured. The Schmidt number (Sc) is the ratio between the kinematic viscosity of the water and the aqueous diffusivity of mercury. The Wilke–Chang method described in Reid et al. (1987) was used to calculate the Sc_{Hg} and correction for sea-water was made (Wanninkhof, 1992 and references therein). The dependence of temperature and salinity of the viscosity and the diffusivity was calculated in each case.

The O₃ mixing ratios were measured using a O₃41M, Ansyco GmbH (Karlsruhe, Germany) analyser based on UV absorption (Jacobi and Schrems, 1999; Jacobi et al., 2006) with a time resolution of 10 min. Calibrations were carried out on a daily basis using an internal ozone generator. The detection limit was 1 ppbV at a sampling rate of 1 L min⁻¹.

CO mixing ratios were measured using an AL 5001, Aero-Laser GmbH (Garmisch-Partenkirchen, Germany) analyser based on a vacuum-UV resonance fluorescence technique (Gerbig et al., 1999) with a time resolution of 0.5 min. The instrument was calibrated daily using certified CO/synthetic air mixture. The detection limit was <1 ppbV.

The chlorophyll data used was not ship measurements, but instead remotely sensed surface ocean chlorophyll a (chl a). The data were obtained from the ocean color group at Goddard Space Flight Center (<http://oceandata.sci.gsfc.nasa.gov>). The product used was the Level-3 mapped 8-day from the MODIS Aqua satellite, with the resolution of 9 km.

3. Result and discussion

3.1. Measured species

A summary of the results can be seen in Table 1. Fig. 2 shows the concentrations of DGHg, TGHg, O₃ and CO measured. It has previously been reported that the volatile fraction of mercury, i.e., DGHg, in surface ocean waters generally consists exclusively of elemental mercury with a negligible fraction of other volatile mercury species such as dimethyl mercury. Therefore, the DGHg measured here consists entirely of Hg⁰ (Coquery and Cossa, 1995; Mason and Gill, 2005). The measured DGHg concentration varied between 28 and 89 fM with an average of 58 ± 10 fM in the water sampled. A slight decrease was observed eastward; however, this decrease cannot be considered statistically significant (*t*-test, 95% level of significance). However, the increase in DGHg concentration observed in the beginning of the transect can be related to higher chl a, Fig. 3. The peak observed in chl a coincides with the increase of DGHg in the surface waters. The variation seen has also been compared to salinity and water temperature, Fig. 4. It was observed that the salinity shows three different stages with higher salinity north of Scotland, decreasing in the open waters and then further decreasing when reaching the Icelandic ridge. This variation follows the changes in DGHg concentrations. The chl a can explain the increase in DGHg, but the salinity might also play an important role in the DGHg concentration observed. The more saline water originates from the Atlantic, which may contain more mercury, however, since there is a limited amount of data collected in the Atlantic Ocean, this statement needs further investigation. Since the waters in the North Atlantic were very close to saturation, Fig. 5, it can be speculated that the salinity along with temperature has a great influence on the measured DGHg concentration.

Only a few measurements campaigns for DGHg have been carried out in this area and adjacent regions. Mason et al. (1998) reported average DGHg concentrations from this area at 650 ± 390 fM, varying from 150 to 1500 fM, which are considerably higher than what was measured in this study. However, Mason et al. (1998) concluded that their concentrations represent a non-steady-state and the calculated air–sea exchange cannot be supported by atmospheric deposition or diffusion of Hg from deeper ocean layers. Table 2 shows a summary of DGHg observations from various oceanic waters. Large differences are observed in the published data, which means that more measurements are needed to be able to understand the complex process

Table 1
Summary of the results.

Parameter*	Average	Max.	Min.	Sd
DGM (fM)	58	89	28	10
TGM (ng m ⁻³)	1.7	2.2	1.2	0.1
Saturation (%)	150	230	70	30
Flux (pmol m ⁻² h ⁻¹)	2.1	12.6	-3.2	1.8

* Number of samples 559.

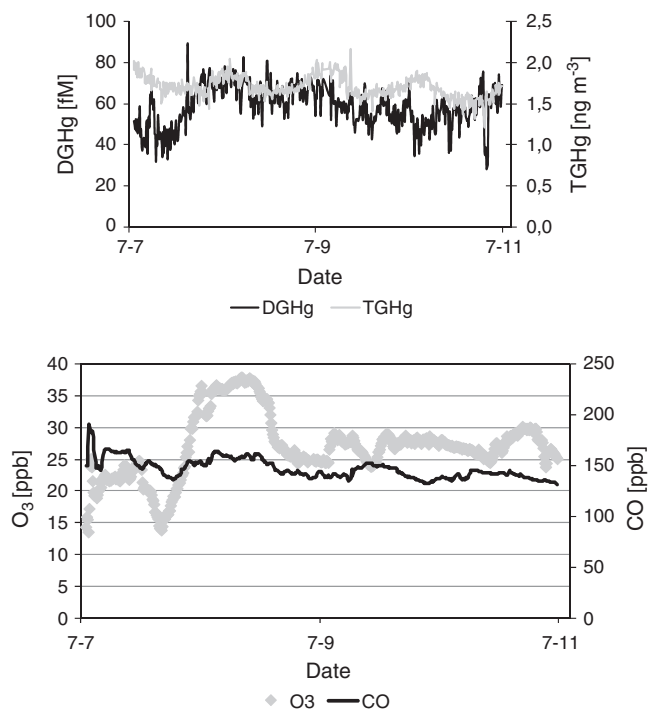


Fig. 2. Measured species along the cruise track.

involving DGHg in the world's oceans. The measurements conducted in adjacent regions to this study, i.e., the Mace Head station and in the North Sea, show concentrations in the same range as those presented here. However, it is important to consider these areas separately because chemical, physical, and biological processes may vary between sites. For measurements carried out at Mace Head, Ireland, the average DGHg concentration during a week in September 1999 was 107 fM (Gårdfeldt et al., 2003), slightly higher than the measurements presented here. The Mace Head is a coastal station situated southward from where the measurements presented here were carried out. This area might be influenced by higher biological activity and other physical processes since it is a coastal site. Studies carried out within the North Sea report average concentrations of 60 fM and 260 ± 110 fM (Baeyens and Leermakers, 1998; Coquery and Cossa, 1995, respectively). The result obtained by Baeyens and Leermakers (1998) was from one station, while the measurements by Coquery and Cossa (1995) were carried out at several stations within the North Sea. Andersson et al. (2008a) presented DGHg measurements from sub-Arctic and Arctic Ocean waters, covering a large concentration range from 25 fM to 670 fM with an average concentration of 220 ± 110 fM. However, the measurements were carried out during an extensive time period covering a large area.

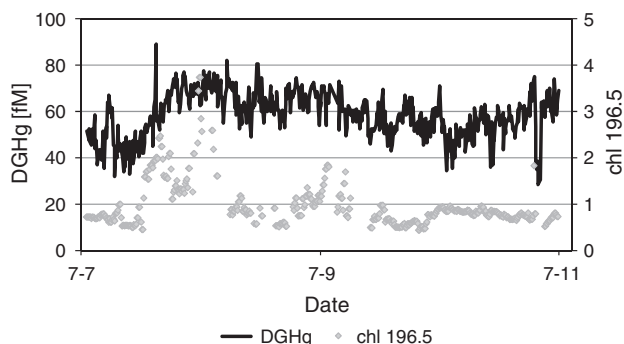


Fig. 3. DGHg concentration and chl along the cruise track.

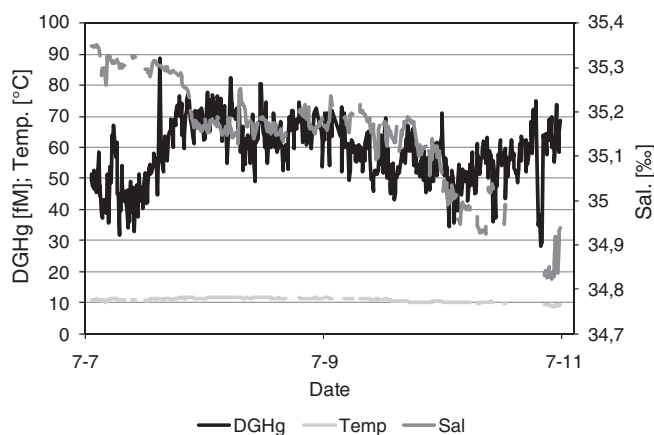


Fig. 4. DGHg, water temperature and salinity along the cruise track.

The atmospheric trace gas measurements were screened initially from events where the ship's exhaust influenced the measurements. This was achieved by using the O_3/CO ratio (Sommar et al., 2009). The TGHg concentrations measured in this study ranged from 1.2 to 2.2 ng m^{-3} with an average of $1.7 \pm 0.1 \text{ ng m}^{-3}$. The highest TGHg concentrations were observed each day in the early afternoon; this peak in TGHg coincides with the maximum solar radiations. This diurnal variation was observed along the whole transect. It should be noted that the mercury measured was both oxidized and elemental mercury, particulate mercury was not measured. There are several possible explanations for the diurnal variation; for example, higher evasions were observed at night (Section 3.2) and sea salt aerosols produced when the wind speed increased during the night, which might lead to oxidation of elemental mercury with subsequent deposition. All these explanations have been considered previously when observing diurnal variations in TGHg concentrations (Laurier et al., 2003; Kellerhals et al., 2003; Mao et al., 2008). In this data set it is hard to distinguish a specific parameter that explains the observed data. In Fig. 5 the evasion of mercury calculated along the transect is shown and during night-time the evasion of elemental mercury increases, which can help explain the increase of mercury. However the increase in TGHg is continuous even when the evasion decreases. It is therefore fair to assume that another process was involved which forms oxidized or elemental mercury, probably using photochemistry. The decrease during the afternoon can be related to oxidation processes. But there are no indications that the O_3 would be involved in this process, so other processes must be involved. Another likely explanation for the decrease during the afternoon would be that the mercury is attached to particles, for example sea salt particles, and deposited into the ocean. This deposition would not be seen in the DGHg measurements since the oxidized mercury is not detected. Of course, it should not be forgotten that boundary layer height and transport from adjacent areas would have an influence. The air measured during the measured period was of northern origin.

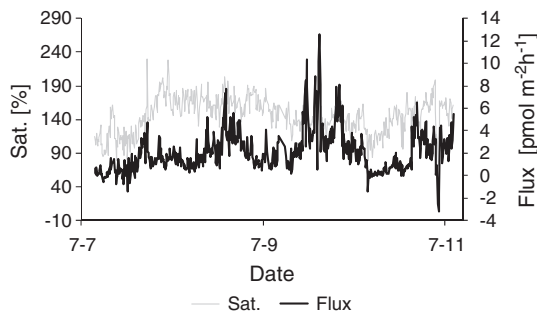


Fig. 5. Flux and degree of saturation along the cruise track.

Table 2

Comparison between some adjacent areas, and greater oceans.

Location	Longitudes*	Latitudes*	DGM	TGM	Flux	Water temp.	Ref.
			fM	ng m ⁻³	pmol m ⁻² day ⁻¹	K	
North Atlantic Ocean	5° E–40°W	60°N	58 ± 10	1.7 ± 0.1	50 ± 40	284	This work
North Atlantic Ocean	5°W–60°W	45°N–70°N	690 ± 390	2.1	–	–	Mason et al. (1998)
North Atlantic Ocean	5°W–60°W	45°N–70°N	–	–	200	–	Mason and Gill (2005)
Mace Head	10°W	59°N	107	1.6	320	289	Gårdfeldt et al. (2003)
Mace Head	10°W	59°N	–	1.75	–	–	Ebinghaus et al. (2002)
North Sea	8°E–2°E	50°N–56°N	60	1.2	59	–	Baeyens and Leermakers (1998)
North Sea	9°E–3°W	51°N–64°N	260 ± 110	1.9	110–224	–	Coquery and Cossa (1995)
North Hemisphere	–	–	–	0.44–15.95	–	–	Temme et al. (2003)
North Atlantic Ocean	–	54°N–85°N	–	1.53 ± 0.12	–	–	Aspmo et al. (2006)
Ny-Ålesund	11°5E	78°5 N	–	1.47	–	–	Berg et al. (2003)
Råö	11°6E	57°3 N	–	1.6	–	–	Wängberg et al. (2007)
South Atlantic Ocean	20°W–60°W	35°S–15°N	1200 ± 800	–	–	293	Mason and Sullivan (1999)
South Atlantic Ocean	20°W–60°W	35°S–15°N	–	1.54 ± 0.09	6000	293	Lamborg et al. (1999)
Equatorial Pacific	85°W–180°W	12°S–5°N	40–325	–	160–1440	–	Mason and Fitzgerald (1993)
Mediterranean Sea, summer	25°E–5°W	34°N–41°N	190	1.9	535	299	Andersson et al. (2007)
Mediterranean Sea, spring	18°E–11°E	25°N–40°N	120	1.6	180	288	Andersson et al. (2007)
Mediterranean Sea, autumn	19°E–12°E	37°N–46°N	190	1.6	590	293	Andersson et al. (2007)
East Mediterranean Sea	28°E–18°E	32°N–37°N	170	1.8	945	295	Gårdfeldt et al. (2003)
West Mediterranean Sea	6°E–9°E	38°N–41°N	75	1.8	300	297	Gårdfeldt et al. (2003)
Tyrrhenian Sea	8°E–13°E	38°N–42°N	95	1.73	500	297	Gårdfeldt et al. (2003)
Baltic Sea, summer	17°E–13°E	54°N–56°N	90	1.7	190	290	Wängberg et al. (2001a)
Baltic Sea, winter	19°E–15°E	54°N–56°N	90	1.39	100	276	Wängberg et al. (2001a)
Baltic Sea, winter	–	–	50–85	1–2	–25–25	–	Kuss and Schneider (2007)
Baltic Sea, spring	–	–	75–100	1–2	120–250	–	Kuss and Schneider (2007)
Baltic, Summer	–	–	95–160	1–2	370–750	–	Kuss and Schneider (2007)
Baltic, Autumn	–	–	55–70	1–2	100–250	–	Kuss and Schneider (2007)
Arctic	–	–	220 ± 110	–	0**	271	Andersson et al. (2008c)
Arctic	–	–	–	1.8	–	–	Sommar et al. (2009)

* If the exact coordinates are not given in the text approximation have been done from figures in each article.

** Ice covered areas.

The TGHg concentration measured is in the same range as previously measured at rural stations at mid-latitudes in the northern hemisphere. Ebinghaus et al. (2002) reported continuous TGHg measurements from the coastal rural station at Mace Head, Ireland, from 1995 to 2001 with an average concentration of 1.75 ng m⁻³. The concentration at this station remained constant during the period measured. Temme et al. (2003) presented ship-borne TGHg measurements from the northern hemisphere, observing a range in the measurements from 0.44 to 15.95 ng m⁻³. However, the high concentrations measured included contributions from local sources. The most recent measurement conducted for TGHg concentrations in the North Atlantic was presented by Aspmo et al. (2006) with an average of 1.53 ± 0.12 ng m⁻³ for open waters. TGHg data over the North Sea varied between 1.2 ng m⁻³ (Baeyens and Leermakers, 1998) and 1.9 ng m⁻³ (Coquery and Cossa, 1995). Mason et al. (1998) also conducted measurements of TGHg over the North Atlantic Ocean and the average concentration during that cruise was somewhat higher than in this work, namely 2.1 ng m⁻³. However, this might be explained by the observations made by Temme et al. (2003), where a comparison of data collected between 1977 and 2001 during different expeditions was presented. It was concluded that the values observed in 1990 were higher than those observed in 1977–1980 and 1996 and 2000. Long-term TGHg measurements also have been carried out at Ny-Ålesund, Svalbard, and Råö, Sweden, with annual average concentrations of 1.47 and 1.6 ng m⁻³ (Berg et al., 2003).

3.2. Estimation of mercury flux

As pointed out in the introduction, most natural waters are supersaturated with respect to DGHg (Schroeder and Munthe, 1998; Fitzgerald et al., 2007). In this study, both super-saturation and under-saturation (degree of saturation between 70% and 230%) were observed. However, most waters sampled were supersaturated,

resulting in an average degree of saturation of 150 ± 30%. This results in a net evasion of elemental Hg of 2.1 ± 1.8 pmol m⁻² h⁻¹, calculated according to Nightingale et al. (2000), from the area during the measured period, with a variation in the flux between –3.2 and 12.6 pmol m⁻² h⁻¹. Table 1 shows a summary of the average degree of saturation and the estimated air–sea exchange. Fig. 3 shows the degree of saturation as well as the flux estimation from the expedition. Since the air–sea exchange estimated shows positive and negative values, both deposition and evasion of elemental mercury occurred in the waters sampled. In order to relate this data to the global estimation, an approximate annual mercury flux from the area was calculated using the average annual wind speed, 9.5 m s⁻¹, and temperature, 281 K, obtained from the NOAA database. An annual average net evasion of 2.3 nmol m⁻² month⁻¹ was calculated. The net evasions presented in the literature differ substantially; data approximated for the North Atlantic Ocean were 60 nmol m⁻² month⁻¹ (Mason and Gill, 2005). For the North Sea the estimated net evasion was in the same range as the values obtained in this study, 1.7 to 6.7 nmol m⁻² month⁻¹ (Baeyens and Leermakers, 1998; Coquery and Cossa, 1995). Evasion from the Arctic Ocean observed by Andersson et al. (2008a) was considered limited by the sea ice cover.

The global mercury models in the literature describe the atmospheric transport and transformation of mercury (Bergan et al., 1999; Dastoor and Larocque, 2004; Seigneur et al., 2004; Ryaboshapko et al., 2007a, 2007b; Selin et al., 2007), but only a few of these models combine the atmospheric pool with the oceanic pool. The model by Strode et al. (2007) combines the atmosphere with the ocean mixed layer. The DGHg concentration by Strode et al. (2007) was presented as an average for the oceans but did not take into account any possible diurnal and spatial variations. The average concentration obtained (70 fM) is slightly higher than the concentrations obtained in this work, which was expected since the data set in this work was from a remote location in the North Atlantic Ocean and observed during a short period of time.

The TGHg concentration estimated from recent global models provides a concentration within the same range as presented here (1.5–1.7 ng m⁻³) (Seigneur et al., 2004; Selin et al., 2007).

In the global atmospheric models presented in literature, the evasion of mercury from the oceans is obtained from previous estimations of the global mercury cycle (e.g., Mason and Sheu, 2002; Mason et al., 1994). However, Strode et al. (2007) use their global model to determine the annual average flux from the ocean surface and found that the highest evasion was in the warmest waters with a decrease in evasion as the water temperature decreases. This is expected since the estimation of the air–sea exchange depends on the partitioning of mercury between the gaseous and aqueous phase according to the Henry's law constant (Andersson et al., 2008c). The data in Table 2 support the hypothesis that colder water has lower flux than warmer water, which may contribute to an accumulation of mercury in colder environments. In this study there was evidence of elemental mercury being deposited into the water surface layer due to under-saturation of the water sampled. That phenomenon also was suggested in the model by Strode et al. (2007). However, what will happen in a climate change scenario is under debate.

4. Conclusion

For the first time, both TGHg and DGHg were measured continuously with a high time resolution along a cruise track in the North Atlantic Ocean. The DGHg concentration measured during the expedition ranged from 29 to 90 fM, the average concentration was 58 ± 10 fM, and the TGHg concentration ranged from 1.2 to 2.2 ng m⁻³ with an average of 1.7 ± 0.1 ng m⁻³.

The average flux was calculated to 2.1 ± 1.8 pmol m⁻² h⁻¹. Depending on the degree of saturation and wind speed, both deposition (-3.2 pmol m⁻² h⁻¹) and evasion (12.6 pmol m⁻² h⁻¹) of elemental mercury occurred.

Acknowledgements

The Swedish Polar Secretariat is greatly appreciated for organising the BERINGIA 2005 expedition and the support before, during and after the expedition. We appreciated the onboard help and support by the captain and crew of IB Oden. PhD. Christian Temme thank you for lending us a Tekran 2537A!

References

Allard, B., Arsenie, I., 1991. Abiotic reduction of mercury by humic substances in aquatic systems—an important process for the mercury cycle. *Water, Air and Soil Pollution* 56, 457–464.

Amyot, M., Mielre, G., Lean, D.L., McQueen, D.J., 1994. Sunlight-induced formation of dissolved gaseous mercury in lake waters. *Environmental Science and Technology* 28, 2366–2371.

Amyot, M., Gill, G.A., Morel, F.M.M., 1997. Production and loss of dissolved gaseous mercury in coastal seawater. *Environmental Science and Technology* 31, 3606–3611.

Amyot, M., Southworth, G., Lindberg, S., Hintelmann, H., Lalonde, J., Ogrinc, N., Poulain, A., Sandilands, K., 2004. Formation and evasion of dissolved gaseous mercury in large enclosures amended with ²⁰⁰HgCl₂. *Atmospheric Environment* 38, 4279–4289.

Andersson, M.E., Gärdfeldt, K., Wängberg, I., Sprovieri, F., Pirrone, N., Lindqvist, O., 2007. Seasonal and daily variation of mercury evasion at coastal and off shore sites from the Mediterranean Sea. *Marine Chemistry* 104, 214–226.

Andersson, M.E., Sommar, J., Gärdfeldt, K., Lindqvist, O., 2008a. Accumulation of mercury in the Arctic Ocean. *Marine Chemistry* 110, 190–194.

Andersson, M.E., Gärdfeldt, K., Wängberg, I., 2008b. A description of an automatic continuous equilibrium system for measurement of dissolved gaseous mercury. *Analytical and Bioanalytical Chemistry* 391, 2277–2282.

Andersson, M.E., Gärdfeldt, K., Wängberg, I., Strömberg, D., 2008c. Determination of the Henry's law constant for elemental mercury. *Chemosphere* 73, 587–592.

Aspmo, K., Temme, C., Berg, T., Ferrari, C., Gauchard, P.-A., Fain, X., Wibetoe, G., 2006. Mercury in the atmosphere, snow and melt water ponds in the North Atlantic Ocean during Arctic summer. *Environmental Science and Technology* 40, 4083–4089.

Baeyens, W., Leermakers, M., 1998. Elemental mercury concentrations and formation rates in the Scheldt estuary and the North Sea. *Marine Chemistry* 60, 257–266.

Baeyens, W., Leermakers, M., Dedeurwaerder, H., Lansens, P., 1991. Modelization of the mercury fluxes at the air–sea interface. *Water, Air and Soil Pollution* 56, 731–744.

Bash, J.O., Miller, D.R., 2008. A relaxed eddy accumulation system for measuring surface fluxes of total gaseous mercury. *Journal of Atmospheric and Oceanic Technology* 25, 244–257.

Berg, T., Sekkesæter, S., Stinnes, E., Valdal, A.K., Wibetoe, G., 2003. Springtime mercury depletion of mercury in the European Arctic as observed at Svalbard. *Science of the Total Environment* 304, 43–51.

Bergan, T., Gallardo, L., Rodhe, H., 1999. Mercury in the global troposphere: a three-dimensional model study. *Atmospheric Environment* 33, 1575–1585.

Brosset, C., 1981. The mercury cycle. *Water, Air and Soil Pollution* 16, 253–255.

Capri, A., Lindberg, S., 1998. Application of a Teflon dynamic flux chamber for quantifying soil mercury fluxes: test and results over background soil. *Atmospheric Environment* 32, 873–882.

Coquery, M., Cossa, D., 1995. Mercury speciation in surface waters of the North Sea. *Netherlands Journal of Sea Research* 34, 245–257.

Cossa, D., Martin, J.-M., Takayanagi, K., Sanjuan, J., 1997. The distribution and cycling of mercury species in the western Mediterranean. *Deep-Sea Research II* 44 (3–4), 721–740.

Costa, M., Liss, P.S., 1999. Photoreduction of mercury in sea water and its possible implication for Hg⁰ air–sea fluxes. *Marine Chemistry* 68, 87–95.

Dastoor, A.P., Larocque, Y., 2004. Global circulation of atmospheric mercury: a modelling study. *Atmospheric Environment* 38, 147–161.

Ebinghaus, R., Kock, H.H., Coggins, A.M., Spain, T.G., Jennings, S.G., Temme, C., 2002. Long-term measurements of atmospheric mercury at Mace Head, Irish west coast, between 1995 and 2001. *Atmospheric Environment* 36, 5267–5276.

Ferrara, R., Mazzolai, B., 1998. A dynamic flux chamber to measure mercury emission from aquatic systems. *Science of the Total Environment* 215, 51–57.

Ferrara, R., Mazzolai, B., Lanzillotta, E., Nucaro, E., Pirrone, N., 2000. Temporal trends in gaseous mercury evasion from the Mediterranean seawaters. *Science of the Total Environment* 259, 183–190.

Ferrara, R., Lanzillotta, E., Ceccarini, C., 2001. Dissolved gaseous mercury concentration and mercury evasion flux from seawater in front of a chlor-alkali plant. *Environmental Technology* 22, 971–978.

Fitzgerald, W.F., Lamborg, C.H., Hammerschmidt, C.R., 2007. Marine biogeochemical cycling of mercury. *Chemical Reviews* 107, 641–662.

Gärdfeldt, K., Feng, X., Sommar, J., Lindqvist, O., 2001. Total gaseous exchange between air and water at river and sea surfaces in Swedish coastal regions. *Atmospheric Environment* 35, 3027–3038.

Gärdfeldt, K., Sommar, J., Ferrara, R., Ceccarini, C., Lanzillotta, E., Munthe, J., Wängberg, I., Lindqvist, O., Pirrone, N., Sprovieri, F., Pesenti, E., Strömberg, D., 2003. Evasion of mercury from coastal and open waters of the Atlantic Ocean and Mediterranean Sea. *Atmospheric Environment* 37 (Supplement 1), S73–S84.

Gerbig, C., Schmitgen, S., Kley, D., Volz-Thomas, A., Dewey, K., Haaks, D., 1999. An improved fast-response vacuum-UV resonance fluorescence CO instrument. *J. Geophys. Res.-Atmos.* 104, 1699–1704.

Jacobi, H.W., Schrems, O., 1999. Peroxyacetyl nitrate (PAN) distribution over the South Atlantic Ocean. *Phys. Chem.* 1, 5517–5521.

Jacobi, H.W., Kaleschke, L., Richter, A., Rozanov, A., Burrows, J.P., 2006. Observation of a fast ozone loss in the marginal ice zone of the Arctic Ocean. *J. Geophys. Res.-Atmos.* 111, D15309. doi:10.1029/2005jd006715.

Kellerhals, M., Beauchamp, S., Belzer, W., Blanchard, P., Froude, F., Harvey, B., McDonald, K., Pilote, M., Poissant, L., Puckett, K., Schroeder, B., Steffen, A., Tordin, R., 2003. Temporal and spatial variability of total gaseous mercury in Canada: results from the Canadian Atmospheric Mercury Measurement Network (CAMNet). *Atmospheric Environment* 37, 1003–1011.

Kim, K.H., Lindberg, S., 1995. Design and initial tests of dynamic enclosure chamber for measurements of vapour-phase mercury fluxes over soils. *Water, Air and Soil Pollution* 80, 1059–1068.

Kim, K.H., Lindberg, S.E., Meyers, T.P., 1995. Micrometeorological measurements of mercury vapour fluxes over background forest soils in eastern Tennessee. *Atmospheric Environment* 29, 267–282.

Kuss, J., Schneider, B., 2007. Variability of the gaseous elemental mercury sea–air flux of the Baltic Sea. *Environmental Science and Technology* 41, 8018–8023.

Lamborg, C.H., Rolhus, K.R., Fitzgerald, W.F., Kim, G., 1999. The atmospheric cycling and air–sea exchange of mercury species in the south and equatorial Atlantic Ocean. *Deep-Sea Research II* 46, 957–977.

Lanzillotta, E., Ferrara, R., 2001. Daily trend of dissolved gaseous mercury concentration in coastal seawater of the Mediterranean basin. *Chemosphere* 45, 935–940.

Laurier, F.J.G., Mason, R.P., Whalin, L., 2003. Reactive gaseous mercury formation in the North Pacific Ocean's marine boundary layer: a potential role of halogen chemistry. *Journal of Geophysical Research-Atmospheres* 108 art. no.-4529.

Lindberg, S.E., Kim, K.-H., Meyers, T.P., Owens, J.C., 1995. Micrometeorological gradient approach for quantifying air–surface exchange of mercury–vapour tests over contaminated soils. *Environmental Science and Technology* 29, 126–135.

Mao, H., Talbot, R.W., Sigler, J.M., Sive, B.C., Hegarty, J.D., 2008. Seasonal and diurnal variations of Hg⁰ over New England. *Atmospheric Chemistry and Physics* 8, 1403–1421.

Mason, R.P., Fitzgerald, W.F., 1993. The distribution and biogeochemical cycling of mercury in the equatorial Pacific Ocean. *Deep-Sea Research* 40, 1897–1924.

Mason, R.P., Gill, G.A., 2005. Mercury in the marine environment. In: Parsons, M.B., Percival, J.B. (Eds.), *Mineralogical Association of Canada Short Course 34, Mercury: Sources, Measurements, Cycles and Effects*, Halifax, Chapter 10, pp. 179–216.

- Mason, R.P., Sheu, G.-R., 2002. Role of the ocean in the global mercury cycle. *Global Biogeochemical Cycles* 16 (4), 40–1–40–14.
- Mason, R.P., Sullivan, K.A., 1999. The distribution and speciation of mercury in the South and equatorial Atlantic. *Deep-Sea Research II* 46, 937–956.
- Mason, R.P., Fitzgerald, W.F., Morel, F.M.M., 1994. The biogeochemical cycling of elemental mercury: anthropogenic influences. *Geochimica et Cosmochimica Acta* 58 (15), 3191–3198.
- Mason, R.P., Morel, F.M.M., Hemond, H.F., 1995. The role of micro organisms in elemental mercury formation in natural waters. *Water Air and Soil Pollution* 80, 775–787.
- Mason, R.P., Rolfhus, K.R., Fitzgerald, W.F., 1998. Mercury in the North Atlantic. *Marine Chemistry* 61, 37–53.
- McCartney, M.S., Talley, L.D., 1982. The Subpolar Mode Water of the North Atlantic. *J. Phys. Oceanogr.* 12, 1169–1188.
- Nightingale, P.D., Malin, G., Law, C.S., Watson, A.J., Liss, P.S., Liddicoat, M.I., Boutin, J., Upstill-Goddard, R.C., 2000. In situ evaluation of air–sea gas exchange parameterization using novel conservative and volatile tracers. *Global Biogeochemical Cycles* 14 (1), 373–387.
- Olofsson, M., Sommar, J., Ljungström, E., Andersson, M., Wängberg, I., 2005. Application of relaxed eddy accumulation technique to quantify Hg^0 fluxes over modified soil surfaces. *Water, Air, and Soil Pollution* 167, 331–352.
- Pacyna, E.G., Pacyna, J.M., Pirrone, N., 2001. European emissions of atmospheric mercury from anthropogenic sources in 1995. *Atmospheric Environment* 35, 2987–2996.
- Poissant, L., Casimir, A., 1998. Water–air and soil–air exchange rate of total gaseous mercury measured at background sites. *Atmospheric Environment* 32, 883–893.
- Poissant, L., Amyot, M., Pilote, M., Lean, D., 2000. Mercury water–air exchange over the Upper St. Lawrence River and Lake Ontario. *Environmental Science and Technology* 34, 3069–3078.
- Qureshi, A., MacLeod, M., Sunderland, E., Hungerbühler, K., in review. Exchange of elemental mercury between the oceans and the atmosphere, in: Liu, Guangliang, Cai, Yong, O'Driscoll, Nelson (Eds.), *Environmental Chemistry and Toxicology of Mercury*. John Wiley & Sons.
- Read, J.F., 2001. CONVEX-91: Water masses and circulation of the northeast Atlantic subpolar gyre. *Prog. Oceanogr.* 48, 461–510.
- Reid, R.C., Prausnitz, J.M., Poling, B.E., 1987. *The properties of gases and liquids*. McGraw-Hill, New York.
- Rolfhus, K.R., Fitzgerald, W.F., 2001. The evasion and spatial/temporal distribution of mercury species in Long Island Sound, CT-NY. *Geochimica et Cosmochimica Acta* 65 (3), 407–418.
- Ryaboshapko, A., Bullock, R.O., Christensen, J., Cohen, M., Dastoor, A., Ilyin, I., Petersen, G., Syrakov, D., Artz, R.S., Davignon, D., Draxler, R.R., Munthe, J., 2007a. Intercomparison study of atmospheric mercury models: 1. Comparison of models with short-term measurements. *Science of the Total Environment* 376, 228–240.
- Ryaboshapko, A., Bullock, R.O., Christensen, J., Cohen, M., Dastoor, A., Ilyin, I., Petersen, G., Syrakov, D., Travnikov, O., Artz, R.S., Davignon, D., Draxler, R.R., Munthe, J., Pacyna, J., 2007b. Intercomparison study of atmospheric mercury models: 2. Modelling results vs. long-term observations and comparison of country deposition budgets. *Science of the Total Environment* 377, 319–333.
- Schlitzer, R., 2009. Ocean Data View. <http://odv.awi.de>.
- Schroeder, W., Munthe, J., 1998. Atmospheric mercury—an overview. *Atmospheric Environment* 32 (5), 809–822.
- Schroeder, W., Keeler, G., Kock, H., Roussel, P., Sneebinger, D., Schaedlich, F., 1995. International field intercomparison of atmospheric mercury measurement methods. *Water, Air and Soil Pollution* 80, 611–620.
- Seigneur, C., Vijayaraghavan, K., Lohmar, K., Karamchandani, P., Scott, C., 2004. Global source attribution for mercury deposition in the United States. *Environmental Science and Technology* 38, 555–569.
- Selin, N.E., Jacob, D.J., Park, R.J., Yantosca, R.M., Strode, S., Jaegle, L., Jaffe, D., 2007. Chemical cycling and deposition of atmospheric mercury: global constraints from observations. *Journal of Geophysical Research* 112, D02308.
- Sommar, J., Andersson, M.E., Jacobi, H.-W., 2009. Circumpolar measurements of speciated mercury ozone and carbon monoxide in the boundary layer of the Arctic. *Atmospheric Chemistry and Physics Discussions* 9.
- Strode, S.A., Jaegle, L., Selin, N.E., Jacob, D.J., Park, R.J., Yantosca, R.M., Mason, R.P., Slemr, F., 2007. Air–sea exchange in the global mercury cycle. *Global Biogeochemical Cycles* 21 (GB1017).
- Temme, C., Slemr, F., Ebinghaus, R., Einax, J.W., 2003. Distribution of mercury over the Atlantic Ocean in 1996 and 1999–2001. *Atmospheric Environment* 37, 1889–1897.
- Wängberg, I., Schmolke, S., Schager, P., Munthe, J., Ebinghaus, R., Iverfeldt, Å., 2001a. Estimates of air–sea exchange of mercury in the Baltic Sea. *Atmospheric Environment* 35, 5477–5484.
- Wängberg, I., Munthe, J., Pirrone, N., Iverfeldt, Å., Bahlman, E., Costa, P., Ebinghaus, R., Feng, X., Ferrara, R., Gärdfeldt, K., Kock, H., Lanzilotta, E., Mamane, Y., Mas, F., Melamed, E., Osnat, Y., Prestbo, E., Sommar, J., Schmolke, S., Spain, G., Sprovieri, F., Tuncel, G., 2001b. Atmospheric mercury distribution in Northern Europe and in the Mediterranean region. *Atmospheric Environment* 35, 3019–3025.
- Wängberg, I., Munthe, J., Berg, T., Ebinghaus, R., Kock, H.H., Temme, C., Bieber, E., Spain, T.G., Stolk, A., 2007. Trends in air concentration and deposition of mercury in the coastal environment of the North Sea Area. *Atmospheric Environment* 41, 2612–2619.
- Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. *Journal of Geophysical Research* 97 (C5), 7373–7382.
- Xiao, Z., Munthe, J., Schroeder, W., Lindqvist, O., 1991. Vertical fluxes of volatile mercury over forest soil and lake surfaces in Sweden. *Tellus* 43B, 267–379.
- Xiao, Z.F., Munthe, J., Strömberg, D., Lindqvist, O., 1994. Photochemical behavior of inorganic compounds in aqueous solution. In: Watras, C., Huchabee, J. (Eds.), *Mercury pollution—integration and synthesis*. Lewis Publishers, Boca Raton, pp. 581–594.
- Xiao, Z.F., Strömberg, D., Lindqvist, O., 1995. Influence of humic substances on photolysis of divalent mercury in aqueous solution. *Water, Air, and Soil Pollution* 80, 789–798.
- Zemmelink, H.J., Gieskes, W.W.C., Klaassen, W., Beukema, W.J., de Groot, H.W., de Baar, H.J.W., Hints, E.J., McGillis, W.R., Dacey, J.W.H., 2004. Relaxed eddy accumulation measurements of the sea-to-air transfer of dimethylsulfide over the northeastern pacific. *Journal of Geophysical Research-Oceans* 109. doi:10.1029/2002jc001616.