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

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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 (O_3) 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 ± 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 occured during the sampling period.

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

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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; Gårdfeldt 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 (O_3), 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 O_3 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 SPDM 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

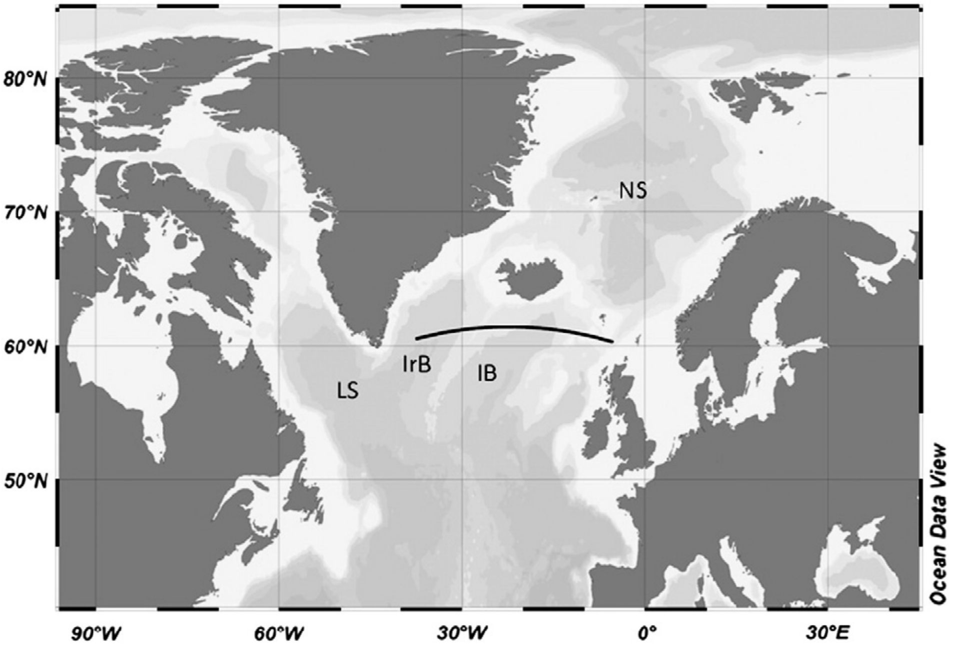

Fig. 1. The cruise track. (Program Schlitzer, R., 2009) and the different seas, i.e. IrB: Irminger Basin, IB; Iceland Basin, LS: Labrador Sea, NS: Nordic Seas.