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F. Sprovieri, N. Pirrone, R. Ebinghaus, H. Kock, A. Dommergue. A review of worldwide atmospheric mercury measurements. *Atmospheric Chemistry and Physics*, European Geosciences Union, 2010, 10 (17), pp.8245-8265. <10.5194/ACP-10-8245-2010>. <insu-00554374>

**HAL Id: insu-00554374**

**<https://hal-insu.archives-ouvertes.fr/insu-00554374>**

Submitted on 24 Feb 2012

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## A review of worldwide atmospheric mercury measurements

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Received: 15 December 2009 – Published in Atmos. Chem. Phys. Discuss.: 18 January 2010

Revised: 29 July 2010 – Accepted: 2 August 2010 – Published: 3 September 2010

**Abstract.** A large number of activities have been carried out to characterise the levels of mercury (Hg) species in ambient air and precipitation, in order to understand how they vary over time and how they depend on meteorological conditions. Following the discovery of atmospheric Hg depletion events (AMDEs) in Polar Regions, a significant research effort was made to assess the chemical-physical mechanisms behind the rapid conversion of atmospheric gaseous Hg ( $\text{Hg}^0$ ) into reactive and water-soluble forms which are potentially bioavailable. The understanding of the way in which Hg is released into the atmosphere, transformed, deposited and eventually incorporated into biota is of crucial importance not only for the polar regions but also for the marine environment in general. The oceans and seas are both sources and sinks of Hg and play a major role in the Hg cycle. In this work, the available Hg concentration datasets from a number of terrestrial sites (industrial, rural and remote) in both the Northern and Southern Hemispheres as well as over oceans and seas have been investigated. The higher Hg species concentration and variability observed in the Northern Hemisphere suggest that the majority of emissions and re-emissions occur there. The inter-hemispherical gradient with higher total gaseous mercury (TGM) concentrations in the Northern Hemisphere has remained nearly constant over the years for which data are available. The analysis of Hg concentration patterns indicates the differences in regional source/sink characteristics, with increasing variability toward areas strongly influenced by anthropogenic sources. The large increase in Hg emissions in rapidly developing countries (i.e., China, India) over the last decade, due primar-

ily to a sharp increase in energy production from coal combustion, are not currently reflected in the long-term measurements of TGM in ambient air and precipitation at continuous monitoring sites in either Northern Europe or North America. The discrepancy between observed gaseous Hg concentrations (steady or decreasing) and global Hg emission inventories (increasing) has not yet been explained, though the potential oxidation of the atmosphere during the last decade is increasing. Currently, however, a coordinated observational network for Hg does not exist.

### 1 Introduction

Mercury is emitted into the atmosphere from a variety of anthropogenic (i.e., power generation facilities, smelters, cement production, waste incineration and many others) (Pirrone et al., 1996, 1998, 2001) and natural sources (i.e., volcanoes, crustal degassing, oceans) in different chemical and physical forms (Pacyna et al., 2001; Carpi, 1997). In the troposphere, the most important species are gaseous elemental mercury ( $\text{Hg}^0$ ), divalent gaseous mercury ( $\text{Hg}^{\text{II}}$ ) which consists of various oxidised compounds and particle-bound Hg (Hg-p), that may include various Hg compounds. It should be noted that the information on the speciation/fractionation of Hg in different forms is largely operationally defined. Conversions between different Hg forms provide the basis for understanding the patterns from a local to a global scale. Mercury cycling between different environmental compartments depends on the rate of different chemical and physical mechanisms (i.e., dry deposition, wet scavenging) and meteorological conditions, as well as on the anthropogenic variables and forcing which affect its fate in the global environment.



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Experimental field data and model estimates indicate that anthropogenic Hg emissions are, at least, as great as those from natural sources contributing together to the global atmospheric pool. It was indeed observed from an analysis of lake sediments, ice cores and peat deposits from both hemispheres, a threefold increase of Hg deposition since pre-industrial times (Engstrom and Swain, 1997; Bindler et al., 2001; Biester et al., 2002; Lamborg et al., 2002; Lindberg et al., 2007 and references therein).

Recent studies have highlighted that in fast developing countries (i.e., China, India) mercury emissions are rapidly increasing in a dramatic fashion due primarily to a sharp increase in energy production from the combustion of coal (Pirrone et al., 2010). Recent estimates highlighted that Asian emissions are considered to be of global importance. However, potentially increased Asian emissions are neither reflected in both the long-term measurements of TGM and Hg in precipitation in Europe and North America. The reason for this is not yet clear, however, it was hypothesized that atmospheric Hg cycling is possibly faster than previously thought. Currently, it is extremely difficult to analyse the global long-term trends of mercury in the atmosphere due to the lack of a coordinated monitoring network scarce representation of measurements in the Southern Hemisphere. However, Ebinghaus et al. (1999) have shown that good agreement of the atmospheric Hg concentrations determined by different laboratories using different techniques makes a combination of datasets from different regions of the world feasible. Based on the existing data, there is a scientific consensus about the current global background concentration of airborne Hg which is considered to be in the range of 1.5 to 1.7 ng m<sup>-3</sup> in the Northern Hemisphere and 1.1 to 1.3 ng m<sup>-3</sup> in the Southern Hemisphere (Lindberg et al., 2007). The atmosphere provides the main environmental pathway for redistribution of Hg around the globe, therefore, quantifying the transfer of Hg from the air to the Earth's surface via wet and dry deposition is critically important.

A complementary approach to measurements at a few stationary sites for long periods consists of campaign measurements from moving platforms, such as ships or aircraft and non-permanent sampling sites distributed on a global scale. Occasional shipboard measurements on a large-scale geographical distribution should, thus, be a part of the global monitoring network for atmospheric Hg. With proper quality control to ensure comparability and a relatively low measurement uncertainty, the combination of intermittent shipboard and long-term ground measurements can provide information about the worldwide distribution and trend of atmospheric Hg. An effort attempted to reconstruct the worldwide trend of atmospheric Hg (TGM) concentrations from long-term measurements of known documented quality has been performed since 1977 by Slemr et al. (2003) through measurements carried out at 6 sites in the Northern Hemisphere, 2 sites in the Southern Hemisphere and multiple ship cruises over the Atlantic Ocean. The authors observed that

the TGM concentrations in the global atmosphere had been increasing since the first measurements in 1977 to a maximum in the late 1980s, after which Hg concentrations decreased to a minimum in 1996 and then remained nearly constant at a level of about 1.7 ng m<sup>-3</sup> in the Northern Hemisphere. In contrast, Lindberg et al. (2007) have pointed out a number of reasons to support the null hypothesis. In order to retrieve a history of atmospheric Hg<sup>0</sup> at middle and high northern latitudes, Hg<sup>0</sup> was measured in the interstitial air of firn (perennial snowpack) in the Greenland icecap. From this record, it has been shown that anthropogenic emissions caused a two-fold increase in boreal atmospheric Hg<sup>0</sup> concentrations before the 1970s, which possibly contributed to higher deposition rates of mercury both in industrialized and remote areas (Fain et al., 2008, 2009).

In contrast, TGM concentrations observed at remote locations in the Southern Hemisphere over the past 15–20 years show substantial changes (De Mora et al., 1993; Sprovieri and Pirrone, 2000; Sprovieri et al., 2002; Temme et al., 2003).

This paper provides an overview of atmospheric measurements performed at several terrestrial sites in the Northern (Europe, North America, Asia, Arctic) and Southern (South America, Africa, South Pole) Hemispheres and over the oceans and seas. The amount of data analysed for each continent/region is enormous; major findings of key studies/programmes carried out in all regions have been highlighted.

## 2 Results and discussion

### 2.1 Monitoring network needs and mercury measurements on a global scale

Mercury concentration measurements in ambient air of documented and accepted quality are available from the mid 1970s and the mid 1990s for the Northern and Southern Hemispheres, respectively. Long-term monitoring of atmospheric Hg with high time resolution began at Alert, Canada (January 1995) and Mace Head, Ireland (September 1995), and was followed by numerous other sites since then. In 1995, Fitzgerald's initiative for the installation of a global AMNET (Fitzgerald et al., 1995) has partly been accomplished on a regional scale within the Canadian Atmospheric Mercury Network (NADP/CAMNet) (established in 1996) which is part of the NADP/MDN. International programmes such as, the WMO-GAW, IGAC-IGBP and those in place in USA, Canadian and the UN-ECE's European Monitoring and Evaluation Programme (EMEP) have made substantial efforts to establish data centres and quality control programmes to enhance integration of air quality measurements from different national and regional networks, and to establish observational sites in under-sampled remote regions around the world. The value of long-term atmospheric Hg

monitoring and the need for additional sites is necessary to provide a dataset which can give new insights into Hg cycling on different temporal and spatial scales and, because “surprising discoveries”, such as the Atmospheric Mercury Depletion Events (AMDEs), may still be made. A coordinated observational network for mercury (Hg) is essential to the modelling community for model validation and to establish the source-receptor relationships within the Hg cycle. Existing measurement networks are not sufficient because of the lack of (a) observations of all forms of Hg in ambient air and in both wet and dry deposition; (b) co-located long-term measurements of Hg and other air pollutants; (c) representation of sites in the free-troposphere of both Southern and Northern Hemisphere; and (d) measurement sites that allow a careful investigation of inter-hemispheric transport and trends in background concentrations.

## 2.2 Mercury measurements in Europe

### Monitoring networks and trends

Continuous monitoring datasets exist for the time period 1998 to 2004 for two coastal background sites, Mace Head, on the West coast of Ireland and the Zingst peninsula on the southern shore of the Baltic Sea. Automated TGM measurements have been carried out and an evaluation of these two datasets has been published by Kock et al. (2005). Between 1998 and 2004 the annually averaged TGM concentrations measured at Mace Head ( $1.74 \text{ ng m}^{-3}$ ) and Zingst ( $1.64 \text{ ng m}^{-3}$ ) remained fairly stable. For both stations higher concentrations were detected during the winter months and lower concentrations during summer. Since Mace Head is located at the European inflow boundary and, therefore, considered to be less influenced by continental emissions, an unexpected West to East gradient was observed. No local anthropogenic Hg sources exist near the Mace Head station, thus, suggesting the important role of enhanced emissions from the sea. Extensive evaluation of Hg measurements in air and precipitation at EMEP or OSPAR stations, respectively, have been carried out by Wangberg et al. (2007). These data were obtained at coastal sites mainly around the North Sea and originate from Ireland, Netherlands, Germany, Norway and Sweden. The major finding was a reduction in deposition (10–30%) has occurred, probably due to emission decreases in Europe. No decreasing trend in TGM was observed during the 1995–2002 period. The authors suggest that a plausible explanation is that European TGM emission reductions may be compensated for by increasing emissions in other northern hemispheric regions. Table 1 shows the comparison between average Hg-species concentrations observed at 10 sites in Europe during the MOE-MAMCS and the next EU-MERCYMS projects (Pirrone et al., 2001, 2003; Wangberg et al., 2001; Munthe et al., 2003). TGM concentrations at Mace Head were higher than those observed at the two Swedish stations Rörvik and

Aspvreten and were more similar to that detected at Zingst on the German Baltic Sea coast. The results from Neuglobsow, Zingst, Rörvik and Aspvreten follow a slightly decreasing trend, which is in line with the location of the main European source areas. There are no local sources of Hg at Mace Head and slightly elevated concentrations are most likely caused by re-emissions from the sea surface (Pirrone et al., 2003; Munthe et al., 2003). Schmolke et al. (1999) found different TGM background concentrations in North-Central Europe and Southern Europe with median values in the range of 1.93, 1.78, 1.53 and  $1.54 \text{ ng m}^{-3}$  TGM were detected. The Total Particulate Mercury (TPM) distribution pattern in North-western Europe was measured during the MOE project, showing, as for the TGM, a south-to-north declining TPM gradient (Table 1). Since no direct emissions of particulate mercury were found, a possible explanation for the clear gradient is that TPM is formed after emissions and the measured fractions are actually secondary TPM (i.e., formed during transport). A plausible mechanism is adsorption of  $\text{Hg}^{\text{II}}$  on to existing particles which is an operationally defined gaseous Hg fraction present in ambient air.

A comparison of TGM, TPM and  $\text{Hg}^{\text{II}}$  measurements obtained during four synchronized seasonal field campaigns from 1998 to 1999 at 10 coastal sites in the Mediterranean Region (5 sites) and in North Europe (5 sites) during the MOE and MAMCS project showed that TGM was slightly higher in the Mediterranean, but also that TPM and  $\text{Hg}^{\text{II}}$  concentrations were significantly higher at Mediterranean sites compared to northern Europe, even though the density of industrial and urban centres is higher in northern compared to southern Europe (Pirrone et al., 2001, 2003; Sprovieri et al., 2003; Wangberg et al., 2001; Munthe et al., 2001). The most probable interpretation is that higher emission rates from the Mediterranean sea coupled with enhanced chemical and physical transformation processes occurring in the MBL lead to local production of RGM and TPM (Sprovieri et al., 2003; Hedgecock et al., 2003, 2005). Indeed, a few years later, photochemical processes in the MBL were found to enhance oxidation of  $\text{Hg}^0$  and this lead to increased concentrations of  $\text{Hg}^{\text{II}}$  and also of TPM via gas-particle partitioning (Wangberg et al., 2001; Hedgecock et al., 2003; Sprovieri et al., 2003; Pirrone et al., 2003). The enhanced re-emission fluxes of Hg from the sea surface are driven primarily by higher solar radiation, humidity and temperature in the Mediterranean basin, when compared to more northern seas. As in the Mediterranean MBL, high  $\text{Hg}^{\text{II}}$  concentrations have also been observed in the MBL of the North Atlantic (Bermuda) (Mason et al., 2001) and of the Pacific ocean (Laurier et al., 2003).

### 2.3 Over water Hg measurements and air/water exchange

The importance of Hg exchange processes between the atmosphere and surface waters has been highlighted in recent

**Table 1.** TGM, RGM and TPM average values observed at the selected coastal sites in the Mediterranean during the four seasonal campaigns of the MOE, MAMCS and MERCYMS projects. *D*: Day; *N*: Night.

Sampling Campaigns	Sites	Coordinates	Fall			Winter		
			TGM (ng m <sup>-3</sup> )	RGM (pg m <sup>-3</sup> )	TPM (pg m <sup>-3</sup> )	TGM (ng m <sup>-3</sup> )	RGM (pg m <sup>-3</sup> )	TPM (pg m <sup>-3</sup> )
<b>MOE</b>	Neuglobsow, Germany	53°8.6' N 13°02' E	2.22	–	98.83	2.14	19.86	21.00
	Zingst, Germany	54°26.2' N 12°43.5' E	1.60	–	70.93	1.67	37.48	21.65
	Rörvik, Sweden	57°24.8' N 11°56' E	2.69	15.30	18.58	1.40	19.19	4.78
	Aspvreten, Sweden	58°48' N 17°23' E	1.68	–	12.37	1.31	11.13	9.99
	Mace Head, Ireland	53°20' N 9°54' W	2.03	28.59	3.99	1.72	25.68	3.51
<b>MAMCS</b>	Mallorca, Spain	39°40' N 2°41' E	3.16	1.88	34.40	3.08	99.59	86.12
	Calabria, Italy	39°25' N 16°0.0' E	1.30	40.18	26.32	1.86	24.84	28.55
	Sicily, Italy	36°40' N 15°10' E	1.34	90.14	5.57	2.37	46.39	8.46
	Antalya, Turkey	36°28' N 30°20' E	1.68	–	14.66	8.71	10.44	14.39
	Haifa, Israel	32°40' N 34°56' E	1.83	–	115.39	0.90	36.14	27.30
<b>MERCYMS</b>	Cabo de Creus, Spain	42°19.2' N 3°18.9' E	1.60	2.20	9.60	1.50	0.24	9.10
	Thau Lagoon, France	43°25' N 3°35' E	1.60	8.60	3.00	2.90	41.90	82.00
	Piran Marine, Slovenia	45°32.9' N 13°33' E	–	4.50	–	0.80	1.00	18.70
	Calabria, Italy	39°25' N 16°0.0' E	1.30	1.60	1.00	1.90	4.20	6.10
	Haifa, Israel	32°40' N 34°56' E	<i>D</i> 1.19 <i>N</i> 0.78	33.00	89.00	<i>D</i> 0.80 <i>N</i> 0.50	2.20	3.90
Sampling Campaigns	Sites	Coordinates	Spring			Summer		
			TGM (ng m <sup>-3</sup> )	RGM (pg m <sup>-3</sup> )	TPM (pg m <sup>-3</sup> )	TGM (ng m <sup>-3</sup> )	RGM (pg m <sup>-3</sup> )	TPM (pg m <sup>-3</sup> )
<b>MOE</b>	Neuglobsow, Germany	53°8.6' N 13°02' E	1.98	27	46	1.58	28	31
	Zingst, Germany	54°26.2' N 12°43.5' E	1.47	55	24	1.69	9.1	22.5
	Rörvik, Sweden	57°24.8' N 11°56' E	1.54	18	8	1.39	17.4	7.61
	Aspvreten, Sweden	58°48' N 17°23' E	1.46	14	7	1.27	9.2	7.5
	Mace Head, Ireland	53°20' N 9°54' W	1.62	31	10	1.45	27.1	10.6
<b>MAMCS</b>	Mallorca, Spain	39°40' N 2°41' E	3.85	76.0	44	4.15	–	33.5
	Calabria, Italy	39°25' N 16°0.0' E	1.42	47	23	1.09	35.5	45.5
	Sicily, Italy	36°40' N 15°10' E	1.89	77.5	11	2.18	29.5	9.1
	Antalya, Turkey	36°28' N 30°20' E	1.34	21	25.2	–	–	65.2
	Haifa, Israel	32°40' N 34°56' E	1.45 35 98	–	–	4.1	–	–
<b>MERCYMS</b>	Cabo de Creus, Spain	42°19.2' N 3°18.9' E	1.60	2.2	9.6	2.10	1.2	11.2
	Thau Lagoon, France	43°25' N 3°35' E	1.60	8.6	3.0	3.30	191	662
	Piran Marine, Slovenia	45°32.9' N 13°33' E	–	4.5	–	4.00	15.4	9.4
	Calabria, Italy	39°25' N 16°0.0' E	1.30	1.6	1.0	1.60	–	–
	Haifa, Israel	32°40' N 34°56' E	<i>D</i> 1.19 <i>N</i> 0.78	33.0	89.0	<i>D</i> 1.24 <i>N</i> 1.21	8.3	23

studies related to the Mediterranean region; the lack of knowledge of the magnitude of these exchange mechanisms is one of the main factors affecting the overall uncertainty associated with the assessment of net fluxes of Hg between the atmospheric and marine environments in the Mediterranean region (Sprovieri et al., 2003; Hedgecock and Pirrone, 2004; Horvat et al., 2001, 2003; Gardfeldt et al., 2003; Kotnik et al., 2007; Sprovieri and Pirrone, 2008). The transformations of Hg and its compounds that take place in marine water are of crucial importance in understanding the way in which Hg is released into the atmosphere is eventually incorporated

into biota, thereby becoming a risk for human health and ecosystems. The major components of total mercury (Hg<sub>tot</sub>) in seawater are mercuric chloride complexes, mercuric ions associated with dissolved organic carbon (DOC) and suspended particles; most of the methylmercury is probably associated with DOC (Munthe, 1991; Horvat, 2001, 2003). Change from inorganic to methylated forms is the first step that occurs in Hg transformation in Hg bioaccumulation and although methylmercury represents only a very small amount of the Hg<sub>tot</sub> in aquatic ecosystems, it represents the dominant form in biota. Once methylmercury is formed, it enters

the food chain by rapid diffusion and tight binding to proteins. It attains its highest concentrations in the tissues of fish at the top of the aquatic food chain due to biomagnification through the trophic levels, thus, resulting in the exposure of fish-eating populations, often at levels exceeding what is regarded as safe (Horvat et al., 2001, 2003). Some forms of Hg can be reduced to Hg<sup>0</sup> both through biotic (Mason et al., 1995) and abiotic processes (Allard and Arsenie, 1991; Xiao et al., 1995; Costa and Liss, 1999) contributing to the super saturation of Dissolved Gaseous Mercury (DGM) found in natural waters and, thus, to the evasion of Hg to the atmosphere (Mason et al., 1995, 2001; Cossa et al., 1997; Schroeder and Munthe, 1998; Gardfeldt et al., 2003; Kotnik et al., 2007; Andersson et al., 2007). The efficiency of the evasion process depends upon the intensity of solar radiation and the temperature of both the air and the top-water micro-layer (Cossa et al., 1997; Andersson et al., 2007). The following section provides an overview of measurements, along with flux estimates, made for the Atlantic, Pacific, Arctic Oceans, and the Mediterranean, North and Baltic Seas. Most results show that the water is saturated in Hg<sup>0</sup>, thus, the resultant flux of Hg<sup>0</sup> is from the ocean to the atmosphere.

### 2.3.1 Mediterranean

In the framework of the MED-OCEANOR project (Pirrone et al., 2003; Sprovieri et al., 2003, 2008; Sprovieri et al., 2010) an in-depth investigation was carried out from 2000 to 2007 by several research groups to quantify and possibly explain spatial and temporal patterns of Hg-species concentrations in air, surface and deep water samples, and gaseous Hg exchange rates at the air-water interface over the Mediterranean Sea (Sprovieri et al., 2003; Sprovieri and Pirrone 2008; Gardfeldt et al., 2003; Horvat et al., 2003; Hedgecock et al., 2005; Pirrone et al., 2003; Kotnik et al., 2007). The sampling campaigns were performed during different seasons and covered both the western and eastern sectors of the Mediterranean basin. A statistical summary of the overwater Hg species observed during the Mediterranean cruises can be found in Table 2. Table 3 summarizes mercury evasion data observed from oceans and sea waters. The evasional flux observed by Ferrara et al. (2000) over the Tyrrhenian Sea during 1998 showed a typical daily trend, being highest at midday when the ambient temperature and solar radiation were at a maximum, and lowest, near to zero, during the night, suggesting that solar radiation is one of the major driving factors affecting the release of Hg<sup>0</sup> from surface waters. In addition, a seasonal trend was also observed, with minimum values during the winter period and maximum values during the summer, probably due to the higher water temperature that may have facilitated biotic and abiotic processes involving Hg in the water column. The average Hg evasion value for the Tyrrhenian Sea estimated by Ferrara et al. (2000), is consistent with a suggested gradient observed for the west to south-east transect. The average evasion estimated for the western Mediter-

anean Sea was lower than the eastern sector, probably due to the higher mean degree of Hg<sup>0</sup> saturation in the east compared to the west (Table 3). Past or present tectonic activity may contribute to the high DGM concentrations found in these areas, enhancing higher Hg evasions from the seawater (Horvat et al., 2003). The Hg<sup>0</sup> evasion reported by Gardfeldt et al. (2003) from the western Mediterranean and the Tyrrhenian Sea is of the same order of magnitude as that estimated by both Ferrara et al. (2000) and Cossa et al. (1997). DGM data combined with a gas-exchange model (Wanninkhof, 1992) suggested that about 66 tonnes of Hg<sup>0</sup> are released into the atmosphere from the Mediterranean Sea during the summer (Gardfeldt et al., 2003). This emission estimate is comparable with *t/y* of Hg emitted from stationary combustion facilities in Europe (Pirrone et al., 2010). The degree of saturation of top-waters observed by Andersson et al. (2007) in the Mediterranean sectors shows variations between seasons, explained by the differences in water temperatures. The total Hg<sup>0</sup> evasion from the Mediterranean Sea surface was calculated to be about 77 tons per year (Andersson et al., 2007). Assuming a worldwide Hg evasional flux from surface waters of 2600 *t/y* (Mason and Sheu, 2002; Pirrone et al., 2010), the Hg evasion from the Mediterranean Sea accounts for 3–4% of the overall Hg flux.

### 2.3.2 Atlantic Ocean

Table 2 shows a statistical summary of TGM measurements performed over the northern and southern Atlantic Ocean throughout several cruise campaigns by several research groups from 1977 to 2001 (Slemr and Langer, 1992; Lamborg et al., 1999; Mason et al., 2001; Temme et al., 2003; Laurier and Mason, 2007). The first measurements made on board of ships during north-south cruises over the Atlantic Ocean were made between 1977–1980 (Slemr et al., 1981, 1985) and repeated in 1990 and 1994 (Slemr and Langer, 1992; Slemr et al., 1995). In 1996, Lamborg et al. (1999) performed Hg measurements in the south and equatorial Atlantic Ocean from Montevideo, Uruguay to Barbados. The open-ocean samples recorded a distinctive inter-hemispheric gradient, which is consistent with a long-lived trace gas emitted to a greater extent in the Northern Hemisphere (Lamborg et al., 2002). In the Northern Hemisphere (NH), TGM mean values were almost always higher than those obtained in the Southern Hemisphere. All cruises show a pronounced concentration gradient between hemispheres. In addition, a rather homogeneous distribution of TGM in the Southern Hemisphere (SH) was observed during the previous cruises (Slemr et al., 1981, 1985, 1995; Slemr and Langer, 1992). When latitude is taken into account, the TGM concentrations measured on board ship are also comparable to measurements at remote coastal sites such as Mace Head (Ireland), Cape Point (South Africa) and Lista (Norway) (Ebinghaus et al., 2002; Baker et al., 2002). The agreement shows that a combination of long-term measurements at several sites

**Table 2.** Over waters TGM, Hg<sup>0</sup>, Hg<sup>II</sup> and Hg-p data observed in the Atlantic Ocean and Mediterranean sea during seasonal campaigns performed from 1977 to 2007.

Cruise	Range (ng m <sup>-3</sup> )	TGM Mean (ng m <sup>-3</sup> )	SD (ng m <sup>-3</sup> )	Range (ng m <sup>-3</sup> )	Hg <sup>0</sup> Mean (ng m <sup>-3</sup> )	SD (ng m <sup>-3</sup> )	Range (pg m <sup>-3</sup> )	Hg <sup>II</sup> Mean (pg m <sup>-3</sup> )	SD (pg m <sup>-3</sup> )	TGM (pg m <sup>-3</sup> )	Hg-p RGM (pg m <sup>-3</sup> )	TPM
Atlantic Northern Hemisphere <sup>a,b</sup>												
Oct 1977 <sup>c</sup>	1.0–3.6	1.8	0.4	–	–	–	–	–	–	–	–	–
Nov/Dec 1978	1.4–2.7	1.9	0.3	–	–	–	–	–	–	–	–	–
Jan/Feb 1979	1.6–3.1	2.2	0.4	–	–	–	–	–	–	–	–	–
Oct/Nov 1980	1.4–3.4	2.1	0.4	–	–	–	–	–	–	–	–	–
Oct/Nov 1990	1.4–3.4	2.3	0.4	–	–	–	–	–	–	–	–	–
Oct/Nov 1994	1.3–3.2	1.8	0.4	–	–	–	–	–	–	–	–	–
Oct/Nov 1996	0.4–16.0	2.1	1.0	–	–	–	–	–	–	–	–	–
Dec 1999/Jan 2000	1.4–3.7	2.0	0.3	–	–	–	–	–	–	–	–	–
Atlantic Southern Hemisphere <sup>a,d</sup>												
Oct 1977 <sup>c</sup>	0.8–1.7	1.2	0.3	–	–	–	–	–	–	–	–	–
Nov/Dec 1978	0.9–1.9	1.4	0.2	–	–	–	–	–	–	–	–	–
Jan/Feb 1979	1.1–2.1	1.3	0.2	–	–	–	–	–	–	–	–	–
Oct/Nov 1980	1.1–1.9	1.5	0.2	–	–	–	–	–	–	–	–	–
Oct/Nov 1990	0.9–2.4	1.5	0.3	–	–	–	–	–	–	–	–	–
Oct/Nov 1994	0.8–2.1	1.2	0.2	–	–	–	–	–	–	–	–	–
Oct/Nov 1996	1.0–2.3	1.4	0.1	–	–	–	–	–	–	–	–	–
Dec 1999/Jan 2000	0.5–1.8	1.3	0.1	–	–	–	–	–	–	–	–	–
Feb/Mar 2000	0.2–1.3	1.0	0.1	–	–	–	–	–	–	–	–	–
Jan/Feb 2001	0.8–1.4	1.1	0.1	–	–	–	–	–	–	–	–	–
Mediterranean Eastern sector <sup>e</sup>												
Jul/Aug 2000	0.2–9.5	1.9	0.5	–	–	–	1.1–8.6	3.8	2.0	1.9–16.4	7.3	4.5
Aug 2003	0.7–15.7	1.6	0.5	0.2–11.4	1.3	0.7	2.8–22.5	9.1	5.3	0.04–10.1	1.8	2.0
Mar/Apr 2004	1.0–2.0	1.6	0.2	1.1–1.9	1.6	0.1	0.6–9.7	3.9	2.5	1.9–5.7	3.6	1.1
Oct/Nov 2004	0.7–4.0	1.60	0.50	0.7–4.0	1.5	0.4	0.1–6.3	6.7	12.0	0.04–51	4.5	8.0
Jun 2005	–	–	–	0.1–5.4	2.00	0.70	0.8–40	8.2	8.1	0.04–9.1	2.9	2.0
Sep 2006	–	–	–	0.4–2.8	1.2	0.5	0.4–76	14.4	16.4	0.1–14.8	4.4	2.6
Mediterranean Western sector <sup>e</sup>												
Jul/Aug 2000	0.1–11.1	1.7	0.8	–	–	–	0.2–30.1	11.6	9.8	4.8–17	9.6	3.2
Aug 2003	0.1–32	2.2	1.5	0.8–2.8	1.2	0.2	1.0–13.1	6.3	4.4	0.3–7.1	1.4	1.7
Mar/Apr 2004	1.0–8.6	1.8	0.3	0.5–4.4	1.7	0.3	0.1–25.3	6.2	5.5	0.2–11.9	2.6	2.0
Jul 2007	–	–	–	0.2–116.9	2.20	4.00	0.1–97.8	8.2	10.4	0.4–77.5	11.2	10.1

<sup>a</sup> Measurements made during Walther Herwing cruises in 1977 and 1978, Meteor cruises in 1979 and 1980, and Polarstern cruises in 1990, 1994, 1996, and 1999–2001.

<sup>b</sup> Nord of ITCZ.

<sup>c</sup> Corrected for systematic error in the analytical method used during the Walther Herwing Cruise in 1977.

<sup>d</sup> South of ITCZ.

<sup>e</sup> Measurements made during Medeoceanor cruises from 2000 to 2007.

with snapshots of latitudinal distribution obtained by ship measurements is feasible and may provide information about the worldwide trends of atmospheric Hg. The gradient and higher variability observed in the Northern Hemisphere suggests that the majority of emissions and re-emissions are located in the Northern Hemisphere. The inter-hemispherical gradient with higher TGM concentrations in the Northern Hemisphere remained nearly constant over the years. Measurements of Hg-species over water have also been performed during the BATS cruises by Mason et al. (2001) and on a follow-up cruise in August 2003 (Laurier and Mason, 2007). Hg<sup>II</sup> measurements by Mason et al. (2001) represented the first reported measurements in the remote ocean MBL. Hg<sup>II</sup> showed a clear and consistent diurnal cycle with

maxima up to 27 pg m<sup>-3</sup> and minima often at the instrument detection limit, suggesting that Hg<sup>II</sup> formation is linked to photo-chemical processes. Similarly, a diurnal fluctuation in Hg<sup>II</sup> was found during a North Pacific cruise (Laurier et al., 2003), although concentrations were much higher, up to 100 pg m<sup>-3</sup>. For the subtropical North Pacific, the average Hg<sup>II</sup> concentration was 11.8 pg m<sup>-3</sup>, which was somewhat higher than that found in the North Atlantic, showing however, the same degree of variability. In the Atlantic Ocean, only few of these studies focused on measurements of DGM at offshore sites (Mason et al., 1998; Mason and Sullivan, 1999; Temme et al., 2005; Andersson 2008). Mason et al. (1998) carried out measurements in the North Atlantic Ocean, while Mason and Sullivan (1999) measured

**Table 3.** Mercury evasion from seawater surface of some aquatic environments.

Location	Flux <sup>a</sup> (ng m <sup>-2</sup> hr <sup>-1</sup> )	Method <sup>b</sup>	References
Open waters			
Baltic Sea autumn average	0.8–2.1	GEM	Kuss and Schneider (2007)
Baltic Sea winter average	0.8	GEM	Wangberg et al. (2001a)
Baltic Sea spring average	1.0–2.1	GEM	Kuss and Schneider (2007)
Baltic Sea spring average	1.6	GEM	Wangberg et al. (2001a)
Baltic Sea spring average	3.1–6.2	GEM	Kuss and Schneider (2007)
North Sea	1.6–2.5	GEM	Cossa et al. (1997)
North Sea	0.49–9.25	GEM	Baeyens and Leermakers (1998)
North Atlantic	15.9±10.8	GEM	Mason et al. (1998)
Equatorial and Southern Atlantic	80	GEM	Mason and Sullivan (1999)
The mid-Atlantic Bight adjacent the East Coast of North America	2.5	GEM	Mason et al. (2001)
Open waters, Mediterranean sites			
North West Mediterranean sites	1.2	GEM <sup>c</sup>	Cossa et al. (1997)
Western Mediterranean Sea	2.5	GEM	Gardfeldt et al. (2003)
Western Mediterranean Sea summer average	5.2	GEM	Andersson et al. (2007)
Tyrrhenian Sea	4.2	GEM	Gardfeldt et al. (2003)
Tyrrhenian Sea	1.8	FC	Ferrara et al. (2000)
Tyrrhenian Sea autumn average	3.2	GEM	Andersson et al. (2007)
Tyrrhenian Sea spring average	0.7	GEM	Andersson et al. (2007)
Tyrrhenian Sea summer average	4.1	GEM	Andersson et al. (2007)
Ionian Sea autumn average	3.8	GEM	Andersson et al. (2007)
Ionian Sea spring average	1.0	GEM	Andersson et al. (2007)
Ionian Sea summer average	2.8	GEM	Andersson et al. (2007)
Adriatic Sea autumn average	5.4	GEM	Andersson et al. (2007)
North Adriatic Sea autumn average	19.0	GEM	Andersson et al. (2007)
Strait of Sicily	2.3–40.5 <sup>d</sup>	GEM	Gardfeldt et al. (2003)
Strait of Sicily spring average	0.7	GEM	Andersson et al. (2007)
Strait of Sicily summer average	3.5	GEM	Andersson et al. (2007)
Strait of Messina summer average	12.4	GEM	Andersson et al. (2007)
Strait of Otranto autumn average	2.1	GEM	Andersson et al. (2007)
Strait of Otranto spring average	0.8	GEM	Andersson et al. (2007)
Strait of Otranto summer average	3.3	GEM	Andersson et al. (2007)
Eastern Mediterranean Sea	7.9	GEM	Gardfeldt et al. (2003)
Coastal waters			
Skagerack part the North Sea summer average	0.8	FC	Gardfeldt et al. (2001)
Atlantic water at the Irish west coast	2.7	GEM	Gardfeldt et al. (2003)
The Tyrrhenian Sea, polluted coastal zone	6.8	FC	Ferrara et al. (2000a)
Mediterranean Sea, near shore sites round Sardinia	3.8	FC	Gardfeldt et al. (2003)

<sup>a</sup> Average values from the corresponding sampling periods.

<sup>b</sup> GEM: Gas Exchange Models. FC: Flux Chamber.

<sup>c</sup> Not based on DGM measurements due to a high detection limit (26 pgL<sup>-1</sup>).

Literature data was to estimate Hg flux from the sea surface according to a global model, Cossa et al. (1997) and references therein.

<sup>d</sup> Range from the corresponding sampling period.

DGM in the equatorial and South Atlantic Ocean. The average concentration measured was 130±80 pg L<sup>-1</sup> and the flux estimated was 15.9±10.8 ng m<sup>-2</sup> h<sup>-1</sup> (Table 3). In 1996, higher DGM concentrations were measured by Mason and Sullivan (1999) in the equatorial and South At-

lantic Ocean than those in the North and consequently the estimated flux was higher (Table 3). It is suggested that the concentrations reflect a net accumulation of Hg<sup>0</sup> in the surface water. The flux was extrapolated to an annual flux of 700 ng m<sup>-2</sup> yr<sup>-1</sup>, a value that could not balance the



atmospheric input. Therefore, it was suggested that the DGM cycling in the surface waters was not in balance with the atmospheric input (Lamborg et al., 1999). Temme et al. (2005) measured DGM continuously in the North Atlantic Ocean in 2004, giving comparable DGM results reported in Andersson et al. (2008). An estimated flux, according to Nightingale et al. (2000), of  $750 \text{ ng m}^{-2} \text{ month}^{-1}$  has been estimated by Temme et al. (2005). Andersson (2008) continuously measured high resolution DGM concentrations in the North Atlantic in the summer of 2005 and the average flux was  $0.42 \pm 0.36 \text{ ng m}^{-2} \text{ h}^{-1}$ .

### 2.3.3 Pacific Ocean

Mercury measurements over the Pacific Ocean started in the early 1980s. There are insufficient data to extrapolate small variations in TGM concentrations over time for the North Pacific (Lamborg et al., 2002; Laurier and Mason, 2007) and to evaluate differences between seasons and latitude. More recent studies have included speciated measurements, particularly during a cruise between Japan and Hawaii in 2002 (Laurier et al., 2003). As for the Atlantic speciation data, there is clear evidence for a diurnal trend in  $\text{Hg}^{\text{II}}$  concentrations, especially in the latter part of the cruise where the ship was in a lower ozone region characterised by higher UV radiation and temperatures and lower wind speeds. In Laurier et al. (2003) all these factors have been considered as the main driver of enhanced photochemical production of  $\text{Hg}^{\text{II}}$  and increased atmospheric concentrations. Measurements of DGM in ocean waters were first made in the Equatorial Pacific Ocean (Kim and Fitzgerald, 1988; Fitzgerald, 1995). Across the equator, DGM varied from 10 to  $27 \text{ pg L}^{-1}$ , and waters were saturated relative to the atmosphere. In contrast, lower concentrations have been observed in the North Pacific. Measurements of DGM were also carried out in the equatorial Pacific Ocean during a cruise in 1990/91 (Mason et al., 1991; Mason and Fitzgerald, 1993). The estimated evasion rates ranged between 12 and  $230 \text{ ng m}^{-2} \text{ day}^{-1}$ , exceeding the rate of atmospheric deposition of  $16 \text{ ng m}^{-2} \text{ day}^{-1}$  for the region (Mason et al., 1994b), therefore, another source of inorganic Hg entering into the mixed layer is required to maintain mass balance. It has been suggested that equatorial upwelling of Hg into the thermocline provides this additional Hg source and this Hg is supplied to the equatorial thermocline by the southern circulation of Hg deposited at mid-latitudes (Mason and Fitzgerald, 1993; Mason et al., 1994b). From more recent DGM data, collected in May/June 2002 during a cruise in the North Pacific, the evasional flux estimated (based on the average wind speed, surface water temperatures and the gas exchange equation of Wanninkhof, 1992) is higher in the tropics and particularly during high wind speed events (Laurier et al., 2003).

### 2.3.4 Arctic Ocean

Measurements of DGM in Kongsfjorden in May 2002 show clear diurnal variation with concentrations up to  $70 \text{ pg L}^{-1}$  during daytime and  $12 \text{ pg L}^{-1}$  during the night time (Sommar et al., 2007). All waters were found to be saturated with respect to Hg with an evasion rate between 0.1 and  $7 \text{ ng m}^{-2} \text{ h}^{-1}$ ; the major findings were that the outgoing Hg flux was overestimated due to the fjord being partly ice covered, thus, hindering the wave field. St. Louis et al. (2007) carried out measurements of DGM at two ice-covered locations off of Ellesmere Island and found average concentrations of  $129 \pm 36 \text{ pg L}^{-1}$ , which corresponds to super-saturation conditions. The average flux calculated according to Wanninkhof and McGillis (1999) was  $5.4 \pm 1.2 \text{ ng m}^{-2} \text{ hr}^{-1}$  on average; higher fluxes would be expected during Hg depletion events and ice-breakup and melting in the Spring. Andersson et al. (2008) carried out continuous measurements of DGM along the west coast of Greenland, into the Canadian archipelago, along the Alaskan coast into Russia around the Wrangel Island and finally crossing the Arctic Ocean, from Barrow in Alaska across the North Pole to Spitsbergen. DGM concentration was in the range of  $5 \text{ pg L}^{-1}$  in the Canadian archipelago to  $134 \text{ pg L}^{-1}$  in the north of Alaska, with an overall average of  $45 \pm 22 \text{ pg L}^{-1}$ . Measurements were carried out in both ice-covered and non-ice-covered areas, and the DGM concentration increased up to 80% between non-ice-covered and ice-covered areas. During the transit through ice-covered areas, enhanced TGM concentrations were observed which were expected to be higher when the ship breaks the ice layer. An  $\text{Hg}^0$  evasion flux of  $98 \text{ ng m}^{-2} \text{ h}^{-1}$  was estimated. During summer 2005 (July–September), a cruise (the Beringia 2005 exp.) was performed over the Atlantic and Arctic Oceans from  $60^\circ$  to  $90^\circ$  N. The results reported by Sommar et al. (2010) have highlighted that higher TGM/ $\text{Hg}^0$  concentrations were observed during Arctic summer over the ice-capped sea. However, a rapid increase of TGM/ $\text{Hg}^0$  in air and surface water were observed when the Swedish icebreaker Oden went from the North Atlantic into the ice-covered waters of the Canadian Arctic archipelago. Higher  $\text{Hg}^0(\text{g})$  levels were, in fact, obtained along the sea-ice route ( $1.81 \pm 0.43 \text{ ng m}^{-3}$ ) compared to those observed in the MBL over ice-free oceanic waters ( $1.55 \pm 0.21 \text{ ng m}^{-3}$ ).

### 2.3.5 North Sea

Only a few studies to determine Hg speciation in the North Sea at offshore and coastal stations have been performed (Coquery and Cossa, 1995; Baeyens and Leermakers, 1998) (Table 3). These studies include DGM surface water measurement flux estimates. DGM concentrations observed at offshore sites by Coquery and Cossa (1995) ranged from the detection limit to  $70 \text{ pg L}^{-1}$ , however, the average DGM concentration for the entire study was  $52 \pm 22 \text{ pg L}^{-1}$ . Most

water samples were super-saturated with Hg giving a net evasion from the sea surface of  $0.9\text{--}1.8\text{ ng m}^{-2}\text{ h}^{-1}$ . The DGM concentration at the off-shore station was  $12\text{ pg L}^{-1}$  (Baeyens and Leermakers, 1998), which corresponds to an average net evasion of  $0.5\text{ ng m}^{-2}\text{ h}^{-1}$ , which was comparable to estimated deposition rates.

### 2.3.6 Baltic Sea

Six expeditions have been carried out in the Baltic Sea. Wangberg et al. (2001a) conducted two expeditions in summer 1997 and winter 1998 in the southern area. Higher flux ( $1.6\text{ ng m}^{-2}\text{ h}^{-1}$ ), calculated using the Wanninkhof (1992) model was estimated for the summer, whereas the winter estimate was much lower ( $0.8\text{ ng m}^{-2}\text{ h}^{-1}$ ) (Table 3). Kuss and Schneider (2007) carried out continuous measurements in the southern Baltic Sea during all seasons in 2006. The lowest DGM concentrations were measured during winter and autumn ( $10\text{--}17\text{ pg L}^{-1}$  and  $11\text{--}14\text{ pg L}^{-1}$ , respectively), whereas the highest concentrations were observed during summer (ranging between  $19\text{--}32\text{ pg L}^{-1}$ ) and spring (between  $15\text{--}20\text{ pg L}^{-1}$ ) (Table 3). Fluxes were calculated using the Weiss et al. (2007) model. The lowest flux was estimated to occur during the winter season (from  $-0.2$  to  $0.2\text{ ng m}^{-2}\text{ h}^{-1}$ ), whereas the highest was in the summer (between  $3.1$  and  $6.2\text{ ng m}^{-2}\text{ h}^{-1}$ ). During the spring and autumn expeditions, fluxes were ranging between  $1.0\text{--}2.1$  and  $0.8\text{--}2.1\text{ ng m}^{-2}\text{ h}^{-1}$ , respectively. On the basis of estimated flux evasion and deposition rates, mass balance was not achieved for the Baltic Sea suggesting that key sources, primary and secondary, have not been accounted for.

## 2.4 Mercury measurements in North America

Long-term monitoring of atmospheric Hg with high time resolution started at Alert, Canada in January 1995, which was the first milestone in the development and set up of the Canadian Atmospheric Mercury Network (CAMNet) (CAMNet, [www.msc.ec.gc.ca/arqp/camnet.e.cfm](http://www.msc.ec.gc.ca/arqp/camnet.e.cfm)) established in 1996. Wet deposition measured at the CAMNet sites are part of the Mercury Deposition Network (MDN, now AMNet), which includes sites in the United States and Canada (<http://nadp.sws.uiuc.edu/mdn/>). A statistically significant decreasing trend for TGM concentrations at several rural CAMNet sites was seen between 1995 and 2005 (Table 4). TGM concentrations at all the CAMNet sites were similar to or slightly lower than those observed at European background sites. Seasonal variations of TGM concentrations are observed for all sites. More recently, some sites within CAMNet have been measuring atmospheric Hg-species concentrations in addition to TGM. Table 5 presents an overview of Hg-species measurements performed in the USA since high-precision measurement techniques have been available (since the early 1990s). The spatial pattern of Hg concentrations observed in wet deposition samples at some MDN sites are not well correlated

with the spatial distribution of known Hg sources. In particular, there were low Hg concentrations in wet deposition samples collected close to coal-fired power plants in Pennsylvania and Ohio and high values at locations with fewer Hg sources (i.e., Florida). This confirms that removal processes are important in determining Hg deposition patterns (oxidation/scavenging) with changing meteorological conditions. The MDN is essential for understanding the spatial and temporal patterns of Hg in wet deposition, but without, at least, TGM and speciated Hg measurements in conjunction with precipitation measurements, little can be understood about the processes responsible for enhanced Hg deposition fluxes and temporal changes of Hg concentrations in wet deposition samples. The few studies that have both speciated Hg measurements in air and wet deposition samples suggest that Hg in deposition may vary by a factor of 2 between urban and rural sites, TGM by 50–75%, and PM may vary 5–10 fold between sites. More recently, some sites within CAMNet have been measuring atmospheric Hg-species concentrations in addition to TGM. Even though RGM and Hg-p constitute a relatively small portion of total Hg in air (0.2 to 1.4%), an evaluation of their concentrations in the atmosphere is essential to better understand the Hg cycle. Continuous measurements of RGM and p-Hg have been made in Quebec, Nova Scotia and Ontario. At St. Anicet near Montreal, Poissant et al. (2005) reported values of RGM and Hg-p ( $3\pm 11\text{ pg m}^{-3}$  and  $26\pm 54\text{ pg m}^{-3}$ , respectively) similar to those found by Han et al. (2004) at Point Petre (RGM:  $5\pm 5\text{ pg m}^{-3}$  and Hg-p:  $6\pm 7\text{ pg m}^{-3}$ ) and at Sterling on the south shore of Lake Ontario (RGM:  $6\pm 11\text{ pg m}^{-3}$ ). Additional continuous measurements of RGM and Hg-p are needed to fully assess the seasonality of these species. Since Canadian measurements began in 1995, Hg levels in the atmosphere have shown only a slight decline throughout most of Canada. The largest decreases in TGM were seen between 1996 and 2005 on the north shore of Lake Ontario, near Toronto and at St. Anicet, near Montréal, where levels were 13% lower. This is in good agreement with the overall trend in Hg-tot concentrations in precipitation observed within the comparable NADP-MDN sites, indicating that these changes are most likely driven by local or regional changes in Hg emissions. While SOPs are well established in wet deposition existing networks, SOPs to routinely measure dry deposition fluxes are still under development. Dry deposition measurement techniques have been developed (Keeler and Dvornich, 2005) for measuring the various forms of Hg in the atmosphere but their standardization is still not yet achieved.

## 2.5 Mercury measurements in South America and Mexico

Relatively few observations of atmospheric Hg have been performed in Central and South America, most of them have been carried out near to, or downwind of major emission sources (i.e., mining or industrial facilities, biomass fires).

**Table 4.** Statistical summary of TGM measurements at CAMNet sites. R-W means RURAL-WEST (RFL, EST, FCH, BRL); R-E:RURAL-EAST (KEI, STA); R-A: RURAL-AFFECTED (WBZ,PPT, EGB); R-C: RURAL-CENTRAL (BNT).

Station	N	Mean (ng m <sup>-3</sup> )	Median (ng m <sup>-3</sup> )	Min (ng m <sup>-3</sup> )	Max (ng m <sup>-3</sup> )	Lower quartile (ng m <sup>-3</sup> )	Upper quartile (ng m <sup>-3</sup> )	SD (ng m <sup>-3</sup> )
Alert	3603	1.55	1.58	0.03	3.12	1.45	1.73	0.37
Kejimkujik	3168	1.45	1.46	0.54	2.30	1.31	1.59	0.21
St. Andrews	2774	1.42	1.40	0.74	2.46	1.26	1.57	0.23
St. Anicet	3164	1.64	1.60	0.92	16.31	1.44	1.79	0.40
Point Petre	3275	1.78	1.73	0.80	4.26	1.55	1.93	0.34
Egbert	3207	1.67	1.66	0.95	6.90	1.50	1.80	0.27
Burnt Island	2680	1.58	1.58	0.99	2.48	1.43	1.72	0.21
Bratt's Lake	1424	1.53	1.52	0.79	2.68	1.38	1.64	0.24
Esther	878	1.65	1.65	1.19	2.14	1.54	1.75	0.15
Fort Chipewyan	305	1.36	1.35	0.95	1.77	1.28	1.47	0.15
Reifel Island	1642	1.67	1.67	0.91	2.92	1.56	1.79	0.19
Category (median of stations)								
R-W	2612	1.60	1.60	0.91	2.56	1.48	1.71	0.20
R-E	3263	1.43	1.43	0.88	2.09	1.31	1.56	0.19
R-A	3342	1.68	1.67	1.11	2.99	1.52	1.81	0.22
R-C	2680	1.58	1.58	0.99	2.48	1.43	1.72	0.21
ALL	3959	1.58	1.58	0.21	2.75	1.48	1.68	0.17

At present, there is no information in this region that can be used to establish long-term trends. All South American observations show Hg<sup>0</sup> concentrations substantially greater than the accepted global background level. TGM concentrations observed in rural areas of Brazil, near several tributaries of the Amazon river and urban areas (Rio de Janeiro, Manaus and Brasilia) were up to 10 ng m<sup>-3</sup>, whereas adjacent to mining areas concentrations were found to be up to 16 ng m<sup>-3</sup> (Hachiya et al., 1998). Higuera et al. (2005) observed very high TGM concentrations near historical mining regions along roads in the Coquimbo region of Northern Chile, reaching extremely high TGM values, up to 100 µg m<sup>-3</sup> at some gold recovery operations (milling and amalgamation). Fostier and Michelazzo (2006) performed TGM measurements at two sites in Sao Paulo State, Brazil, near an industrial area. An average TGM concentration of 7.0 ng m<sup>-3</sup> was observed at both sites. The enhancement in TGM, compared to the global background, was attributed to a wide array of industrial sources in the area. Higher TGM concentrations (mean 15.0 ng m<sup>-3</sup>) were also found by Amouroux et al. (1999) at several sites in French Guiana strongly influenced by mining activities along with illegal gold mining. Several high TGM concentrations (between 50 and 100 µg m<sup>-3</sup>) were observed by Garcia-Sanchez et al. (2006) in some gold processing shops within a highly polluted area due to past mining activities in the El Callao region of Venezuela.

Having the above in mind, it is clear that past and current gold mining activities in South America represent a large source of Hg entering into the atmosphere. Lacerda (1997) estimated 460 Mg yr<sup>-1</sup> released to the global environment of which 300 Mg yr<sup>-1</sup> is released to the atmosphere. While emissions of Hg from gold mining in South America are clearly a substantial source to the global atmosphere, there is a significant uncertainty in the current estimate.

In Mexico, TGM concentrations have been performed by De La Rosa et al. (2004) during short-term sampling campaigns at 4 sites in 2002 (two urban/industrial cities, Mexico City and Zacatecas, and two rural/remote sites, Puerto Angel and Huejutla). High variability in TGM levels were found between these sites suggesting a strong influence of local sources. In particular, at Zacatecas, though it is a smaller semi-urban centre compared to Mexico City, but with a history of gold and silver mining activities, the mean Hg values were very high at 71.7 ng m<sup>-3</sup>. At Mexico City, mean TGM values were found to be 34 ng m<sup>-3</sup>, whereas at the two rural/remote sites mean TGM concentrations were close to hemispheric background concentrations (1.46 and 1.32 ng m<sup>-3</sup>).

## 2.6 Mercury measurements at altitude (including aircraft)

In an effort to understand the relative importance of anthropogenic and natural emissions of airborne Hg, several studies have attempted to calculate Hg fluxes from source regions.

**Table 5.** Summary of Hg<sup>0</sup>, RGM and Hg-p measurements made at remote, rural and urban locations in the United States. NR: “not reported”.

Location	Duration of study	Hg <sup>0</sup> mean (ng m <sup>-3</sup> )	RGM mean (pg m <sup>-3</sup> )	Hg-p mean (pg m <sup>-3</sup> )	References
<b>Remote Sites</b>					
Mt. Bachelor, Storm Peak Lab., Colorado	1.5 yr, 4 mth 2 mth	1.4–1.8 1.6	39–60 20	4.4 9	Weiss-Penzias et al., 2007; Swartzendruber et al., 2006
Oregon Cheeka Peak, Washington	1 yr	1.45–1.55	0–2.7	0–2.9	Faïn et al., 2009a; Weiss-Penzias et al., 2003
Ship, between Bermuda and Barbados	2 mth	1.63±0.08	5.9	NR	Laurier and Mason, 2007
<b>Rural Sites</b>					
Chesapeake Bay Laboratory, Maryland	7 mth	1.7–1.8	6–13	NR	Laurier and Mason, 2007
Look Rock, Tennessee	2 mth	1.65	5	7	Valente et al., 2007
Salmon Creek Falls Reservoir, Idaho	1.25 yr	1.3–1.6	1–10	NR	Abbott et al., 2007
Great Mountain Forest, Connecticut	5 yr	1.4–1.6	NR	NR	Sigler and Lee, 2006
Cove Mountain, Tennessee	40 days	3.2	16.4	9.7	Gabriel et al., 2005
Dexter, Michigan	4 mth, 6 mth	1.49–1.51	2–3	12±5.2	Lynam and Keeler, 2005;
Potsdam, Stockton, and Sterling, New York	3 yr	1.84–2.59	NR	NR	Han et al., 2004
Pompano Beach, Florida	1 mth	1.6–2.0	1.6–4.9	3.5±2.8	Malcom et al., 2003
Stillpond, Maryland	1 yr	1.7±0.5	21±22	42±50	Sheu et al., 2002
Underhill, Vermont	1 yr	2	NR	NR	Burke et al., 1995
Walker Branch Watershed, Tennessee	6 studies over 3 yr	2.2	92±60	NR	Lindberg and Stratton, 1998
<b>Urban, Industrial, Mining, or Fire Sites</b>					
North-central Nevada	1 mth	2.5–3.0	7–13	9–13	Lyman et al., 2008
Detroit, Michigan	1 yr	2.2±1.3	17.7±28.9	20.8±30.0	Liu et al., 2007
Detroit, Michigan	2 mth	NR	NR	1–39	Lynam and Keeler, 2005
Desert Research Institute, Reno, Nevada	3 yr, 3 mth	2.1–2.5	37±28	7±9	Stamenkovic et al., 2007
Chicago, Illinois	15 mth	3.6±2.9	NR	70±67	Landis et al., 2002
Baltimore, Maryland	2 yr	4.4±2.7	89±150	74±197	Sheu et al., 2002
Athens, Georgia	5 days	3.9–8.7	9–129	NR	Landis et al., 2004
Tuscaloosa, Alabama	1 mth	4.05	16.4	16.4	Gabriel, et al., 2005
Earlham College, Richmond, Indiana	6 studies over 3 yr	4.1	104±57	NR	Lindberg and Stratton, 1998

This could be done additionally by correlating Hg enhancements in plumes to other tracers whose emissions are better known (i.e., CO). Most air quality monitoring networks rely entirely upon ground-based sites that sample within the boundary layer. Addressing global air quality problems such

as Hg contamination, however, requires observations made at higher altitudes in order to intercept intercontinental transport phenomena. Studies have shown that transport of pollution (including Hg) between Asia and the United States occurs primarily through the middle and upper troposphere,

and because of the highly episodic nature of this transport, there can be significant inhomogeneity in the air masses reaching the continental United States (Jaffe et al., 2005). Thus, sites that sample only air masses within the boundary layer would not allow a quantitative determination of long-range pollutant fluxes. Ebinghaus et al. (2007) observed enhanced CO and TGM on two CARIBIC (Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrumented Container) flights between São Paulo and Santiago de Chile in 2005. The measured TGM/CO ratio on these two flights, ( $1.2 \times 10^{-7}$  and  $2.4 \times 10^{-7}$  mole/mole, respectively) were similar to those found for biomass burning plumes. From these ratios, global emissions of TGM from biomass burning were estimated to be in the range of 210–750 Mg yr<sup>-1</sup>. While observations with aircraft provide detailed information about Hg in the upper troposphere/lower stratosphere (Banic et al., 2003; Ebinghaus et al., 2000; Friedli et al., 2004) and vertical profiles in the troposphere, they certainly do not provide long-term trends. Therefore, the use of intercontinental mountain-top monitoring sites, that are frequently in the free-troposphere (i.e., Mauna Loa, Hawaii) are essential in understanding the transport of Hg and other air pollutants (Weiss-Penzias et al., 2007). Currently, there are a number of high elevation sites including Mt. Bachelor in the western USA (Jaffe et al., 2003), Mauna Loa in Hawaii (Landis et al., 2005), Wank Mt. in Germany (Slemr et al., 2003), and the Lulin station in Taiwan (Sheu et al., 2007). In two recent studies, TGM and CO were measured in 22 pollution transport “events” at Mt. Bachelor (2800 m a.s.l.) between 2004 and 2005 (Weiss-Penzias et al., 2007). East Asian outflow events yielded a TGM/CO enhancement ratio of  $\sim 0.005$  ng m<sup>-3</sup> ppbv<sup>-1</sup>, whereas plumes from western USA anthropogenic sources and from biomass burning in the Pacific Northwest and Alaska gave a ratio of  $\sim 0.001$  ng m<sup>-3</sup> ppbv<sup>-1</sup>. Thus, the TGM/CO ratio is an important distinguishing feature to identify Asian long-range transport patterns. Scaling these ratios with estimated emissions of CO from China and global biomass burning, an emission of 620 Mg yr<sup>-1</sup> is calculated for total Hg emissions from Chinese anthropogenic sources and 670 Mg yr<sup>-1</sup> for global biomass burning. The Hg<sup>0</sup>/CO molar enhancement ratio was observed in pollution plumes at Cape Hedo Station, Okinawa, Japan and produced a value of  $6.2 \times 10^{-7}$  mol/mol ( $0.0056$  ng m<sup>-3</sup> ppbv<sup>-1</sup>) which is nearly twice the expected ratio based on emissions estimates from China (Jaffe et al., 2005). These plumes originated from the industrialized region of eastern China and produced a similar ratio to those observed at Mt. Bachelor, highlighting the discrepancy between the results observed and the recent Chinese emission inventories. These findings are probably due to large natural sources of Hg not accounted for and/or underestimated Hg emissions.

The first reported data on Hg-species performed at high altitude are from Mauna Loa, (Hawaii Monitoring Site, Landis et al., 2005) and Mt. Bachelor, (Oregon, USA, Swartzen-

druber et al., 2006). Both sites revealed elevated Hg<sup>II</sup> values in the free troposphere ( $\sim 350$  pg m<sup>-3</sup> at Mauna Loa and  $\sim 600$  pg m<sup>-3</sup> at Mt. Bachelor), reaching those of the most polluted urban environments. Several high Hg<sup>II</sup> events, generally accompanied by a decrease in Hg<sup>0</sup>, have been observed under meteorological conditions clearly marked by dry (free tropospheric) air at night (Swartzenruber et al., 2006). Swartzenruber et al. (2006) observed that the mean Hg<sup>II</sup> concentration at night was 60 pg m<sup>-3</sup>, whereas the daytime mean value was 39 pg m<sup>-3</sup> in contrast to other studies showing an Hg<sup>II</sup> maximum at solar noon. Hg-p concentrations were equivalent for day and night ( $\sim 4.4$  pg m<sup>-3</sup>). This implies that Hg<sup>II</sup> formed in situ was unable to condense to particles under these dry air conditions. Both these studies (Landis et al., 2005; Swartzenruber et al., 2006) found very similar observations pointing out that the high Hg<sup>II</sup> concentrations observed, first in Hawaii and later in Oregon were due to atmospheric oxidation and not related to pollution events. Similar results have been obtained in Colorado at a high altitude research station (Storm Peak Laboratory, 3220 m a.s.l.) by Fain et al. (2009a). They showed a very regular occurrence of high Hg<sup>II</sup> levels in dry tropospheric air that was not related to pollution events, but highlighted signs of atmospheric oxidation, likely in the free troposphere, and possibly over the Pacific Ocean. These observations provide evidence that the free tropospheric pool of Hg is enriched with Hg<sup>II</sup> compared to the boundary layer where high Hg<sup>II</sup> levels are mainly related to local and regional pollution.

## 2.7 Mercury measurements in Asia

Kim et al. (1996) reported TGM concentrations from 13 remote mountainous sampling stations in Korea, from 1987 to 1993. Table 6 reports a statistical summary of the mean concentrations of atmospheric Hg determined from a number of monitoring sites located in East Asian countries. Kim et al. (1996) observed that Hg levels and the wide spreading of the observed data suggests that Hg pollution in the Korean atmosphere may result in generally enhanced levels compared to other northern hemispheric regions. This finding is supported by Sohn et al. (1993) who reported rural concentrations in Korea to be between 1.0 to 7.0 ng m<sup>-3</sup> (mean 3.8 ng m<sup>-3</sup>) for the years 1988–1989. TGM monitoring data for the Korean GAW station (An-Myun Island) have been published by Nguyen et al. (2007). Measurements were routinely recorded between December 2004 and April 2006. The mean TGM concentration was  $4.61 \pm 2.21$  ng m<sup>-3</sup> with a range of 0.10–25.4 ng m<sup>-3</sup>. Analysis of the seasonal patterns indicated TGM concentration levels generally peaked in spring, while reaching a minimum in summer. Nguyen et al. (2007) concluded that Hg concentration levels at An-Myun Island over certain periods of time can be greatly affected by the combined effects of various local source processes and meteorological conditions favourable for major air mass transport phenomenon (i.e., Asian Dust storms).

**Table 6.** Statistical summary of the mean concentrations of atmospheric Hg determined from a number of monitoring sites located in the East Asian countries.

Countries	Sites	City/Province	Study period	Hg mean (ng m <sup>-3</sup> )	References
Korea					
1	Residential	Kwa Chun	99~00	5.25	Kim and Kim, 2001b
2	Han Nam	Seoul City	99~00	5.34	Kim and Kim, 2001b
3	13 Mountains	Nationwide, Korea	87~93	4.47	Kim and Kim, 1996
4	Yang Jae	Seoul City	99~00	5.26	Kim and Kim, 2001a
5	3 Terminals	Seoul City	Mar.98	6.54	Kim and Kim, 2001c
6	2 Mountains	Korea	97/98	7.03	Kim and Kim, 2001c
7	Hari	Kang Hwa Island	01/02	3.15	Kim et al., 2003
8	GAW Station	An-Myun Island	Dec.04/Apr.06	4.61	Nguyen et al., 2007
Japan					
9	Urban	Chiba and two others	91~96/94	31.6	Nakagawa and Hiromoto, 1997
10	Urban areas	Chiba and three others	91~96/95	10.3	Nakagawa and Hiromoto, 1997
11	Suburban	Kushiro and two others	91, 94, 95	5.73	Nakagawa and Hiromoto, 1997
12	Oceans	Japan sea/Pacific	91	3.4	Nakagawa and Hiromoto, 1997
13	Rural city	Hayama and two others	91~96, 95, 96	16.5	Nakagawa and Hiromoto, 1997
14	Farmland	Tukui and two others	95/93	42.4	Nakagawa and Hiromoto, 1997
15	Remote	Cape Hedo Station, Okinawa Island	2004	2.04	Jaffe et al., 2005
China					
16	Shijingshan	Beijing	Feb & Sep 98	6.75	Liu et al., 2002
17	Xuanwu	Beijing	Jan & Sep 98	16.7	Liu et al., 2002
18	Tiananmen Sq.	Beijing	Feb & Sep 98	10.5	Liu et al., 2002
19	Two rural sites	Beijing	Feb & Sep 98	3.75	Liu et al., 2002
20	Mountain sites	Guizhou	Unreported	3.35	Tan et al., 2000
21	Residential	Beijing	Jan & Feb 98	8.47	Liu et al., 2002
22	Urban	Guiyang	Nov 01/Nov 02	8.4	Feng et al., 2004
23	Urban	Guiyang	1996	11	Feng et al., 2003, 2004
24	Urban	Guiyang	1999	13	Feng et al., 2003, 2004
25	Moxi Base Station	Gongga Alpine Ecosys.	May 05/Jun 06	3.98	Fu et al., 2008
26	Mountain site	Changbai	May 05/Jun 06	3.58	Wan et al., 2009
27	Mt. Gongga	Sichuan	Apr 06/Jun 07	3.9	Fu et al., 2009
28	Mt. Leigong	South China	May 08/May 09	2.8	Fu et al., 2010

TGM concentrations were also carried out by Fu et al. (2008) at Moxi base station (102°07' E, 29°40' N, 1640 m a.s.l.) of the Gongga alpine ecosystem observation and experiment station of the Chinese academy of sciences (CAS) which belongs to the Chinese ecosystem research network (CERN). TGM concentrations ranged between 0.52 and 21.03 ng m<sup>-3</sup> from May 2005 to June 2006 with a geometric mean of 3.98 ng m<sup>-3</sup>. Seasonal TGM patterns correlated with meteorological parameters have highlighted that wind from the southeastern direction carried more Hg than other directions, suggesting that anthropogenic sources, in particular, local zinc smelting activities and fuel combustion, played a predominant role in the increase of TGM concentrations in this area. Similar TGM concentrations have been also recorded

by Wan et al. (2009a) during the same period at Changbai Mountain, a remote area in northeastern China. An annual arithmetic mean of 3.58±1.78 ng m<sup>-3</sup> was observed which is significantly higher than values obtained in remote areas of Europe and North America. Comparable results have also been observed from April 2006 to June 2007 in the Mt. Gongga area (Sichuan province, PR China) with an annual TGM geometric mean of 3.90±1.20 ng m<sup>-3</sup> (Fu et al., 2009). In order to highlight the spatial variation of TGM levels, Fu et al. (2009) reported geometric mean TGM concentrations, ranging from 1.60 to 20.1 ng m<sup>-3</sup>, using data collected during the warm season at 14 representative sampling sites. In this study, urbanized areas showed the highest TGM values (7.76±4.57 to 20.1±15.1 ng m<sup>-3</sup>), while TGM

concentrations for one town area were  $4.61 \pm 1.15 \text{ ng m}^{-3}$ , for four village areas the values ranged between  $3.26 \pm 0.63$  and  $8.45 \pm 3.06 \text{ ng m}^{-3}$  and for six remote regions between  $1.60 \pm 0.43$  and  $3.41 \pm 1.26 \text{ ng m}^{-3}$ . The authors suggested that industrial activities were an important source of atmospheric Hg and played an important role in the regional TGM distribution. Domestic coal and biomass combustion for residential heating were significant TGM sources in densely populated areas. High TGM concentrations compared to global background values were observed at the summit of Mt. Leigong in South China from May 2008 to May 2009 (Fu et al., 2010) with TGM concentrations averaging  $2.80 \pm 1.51 \text{ ng m}^{-3}$ , these values are, however, much lower than semi-rural and industrial/urban areas, indicating significant emissions of Hg in central, south and southwest China.

Urban data from Beijing, China, show a similar distribution between summer and winter. Liu et al. (2002) and Wang et al. (2007) report winter concentrations ranging between 8 and  $25 \text{ ng m}^{-3}$ , and lower values in the summer, between 5 and  $13 \text{ ng m}^{-3}$ , with autumn and spring concentrations in between. Feng et al. (2004) have reported TGM concentration data for Guiyang city in 2001 with a mean value of  $8.40 \text{ ng m}^{-3}$  on the basis of one year of observations (from November 2001 to November 2002). The average TGM concentration in ambient air observed in Guiyang in 1996 and 1999 was  $11 \text{ ng m}^{-3}$  and  $13 \text{ ng m}^{-3}$ , respectively (Feng et al., 2004). The authors concluded that TGM concentrations in Guiyang are significantly elevated compared to the continental global background values and that coal combustion from both industrial and domestic use is probably the primary atmospheric source. Similar data were obtained earlier (Feng et al., 2003) during 4 measurement campaigns in 2000 and 2001 in Guiyang. Significant Hg emissions from anthropogenic sources resulted in high levels of atmospheric Hg also in Guizhou (Feng et al., 2008). The annual Hg emission from anthropogenic sources in Guizhou, calculated by Feng et al. (2008) ranged between 22.6 and 55.5 t, which was about 6.3–10.3% of current total estimated Hg emissions in China. Hg-species as well as hazardous heavy metals in particles and in precipitation have been continuously measured from 2007 at Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS) located on the north end of the island of Okinawa, Japan. This monitoring station has been used for many years to study the outflow of pollution from China and East Asia (Jaffe et al., 2005). Monthly mean concentrations of  $\text{Hg}^0$  from October 2007 to January 2008 (UNEP/ABC (Atmospheric Brown Clouds) project) were approximately 1.3 to  $1.7 \text{ ng m}^{-3}$ , which were slightly lower than the spring observation in 2004 ( $2.04 \text{ ng m}^{-3}$ ) (Jaffe et al., 2005).

## 2.8 Mercury concentrations in Africa

Observations from Cape Point (South Africa) constitute the only long-term dataset of atmospheric TGM in the Southern Hemisphere. The monitoring of TGM was established at

the Cape Point Global Atmospheric Watch (GAW) station in September 1995. Baker et al. (2002) presented data of atmospheric Hg at Cape Point covering the period from the start of the measurements (September 1995) until June 1999. Atmospheric Hg concentrations were found to be fairly homogeneous over time ranging between  $1.2\text{--}1.4 \text{ ng m}^{-3}$ . Whilst no significant diurnal variation was detectable, a slight seasonal variation with a TGM minimum in March–May and maximum in June–August was observed. The existing Cape Point TGM database comprises both manual measurements with low temporal resolution as well as automated measurements with a resolution of 15 min. Good agreement exists between the manual analysis method and the automated measurements (Ebinghaus et al., 1999). The most prominent feature of the highly resolved TGM data is the frequent occurrence of events with almost complete mercury depletion which has so far not been observed at any other non-polar stations (Brunke et al., 2010). The Cape Point GAW station was found to constitute a suitable site for long-term monitoring of background TGM trends in the Southern Hemisphere (SH) (Baker et al., 2002).

## 2.9 Atmospheric mercury concentrations in Polar Regions

Polar Regions used to be considered pristine environments. Indeed, the Arctic is relatively far from industrial sites located in the Northern Hemisphere and is less populated than other parts of the world. In the Southern Hemisphere, Antarctica is even less populated and less impacted by anthropogenic activities, except on a local scale by the activities of few scientific stations. However, due to a combination of long-range transport associated with a specific climatology, the Arctic and, to a lesser extent Antarctica, are affected on a large scale by pollutants originating from the mid-latitudes of their respective hemispheres. The substantially different geographical distribution of landmasses around both poles influences the  $\text{Hg}^0$  annual mean concentration observed in the Arctic ( $\sim 1.6 \text{ ng m}^{-3}$ ) and Antarctica ( $\sim 1.0 \text{ ng m}^{-3}$ ). Research literature (Ebinghaus et al., 2002; Sprovieri et al., 2002, 2005a; Temme et al., 2003; Steffen et al., 2008; Domergue et al., 2010; Nguyen et al., 2009) provide a comprehensive assessment of the state of Hg science in the context of Atmospheric Mercury Depletion Events (AMDEs) in Polar Regions since 1995.

In the following sections we provide a short summary of the current understanding of Hg transport patterns of polar regions.

### 2.9.1 AMDEs in the Arctic

A surprising discovery that provided a great impetus for Arctic atmospheric chemistry research in several nations was the observation of an unusual phenomenon called Atmospheric Mercury Depletion Events (AMDEs) in the atmospheric

boundary layer of the Arctic and sub-arctic regions. First identified at Alert in the Canadian High Arctic (Schroeder et al., 1998), AMDEs occur during the 3-month period following polar sunrise. During these events,  $\text{Hg}^0$  may be converted to reactive and water-soluble forms,  $\text{Hg}^{\text{II}}$  and/or  $\text{Hg-p}$ , that deposit quickly into the snow/ice pack, thus, increasing the mercury deposition fluxes considerably. Springtime AMDEs have also been observed in Antarctica (Ebinghaus et al., 2002). AMDEs occur at the same time as tropospheric ozone depletion events (ODEs) suggesting that both species were removed by similar chemical mechanisms involving reactive halogen species (such as Br and BrO) across open waters and polynas. BrO is one of the species observed during ODEs and, therefore, often used as an indicator for such events. ODEs and AMDEs, were not observed by Sommar et al. (2010) during the Baring 2005 expedition and, therefore, do not appear to contribute to the removal of Hg and  $\text{O}_3$  during summer. This agrees well with the seasonal cycle of BrO in high latitudes derived from remote-sensing data (Hollwedel et al., 2004).

Several field experiments have been performed at different Arctic and sub-Arctic locations. A comprehensive review of measurements performed in the Arctic regions is reported in Steffen et al. (2008). The Arctic is currently undergoing rapid and dramatic changes including climate warming which is changing the timing and extent of sea ice and its coverage (Serreze et al., 2003) and it is affecting the seasons with winter coming later and spring melt coming earlier. Also, coal and fossil fuel combustion in Asia, a major global anthropogenic source of Hg, is expected to increase up to 350% between 1990 levels and 2020 (van Aardenne et al., 1999). The effects of these increasing emissions on AMDEs processes and the long-term deposition of Hg to the Polar Regions will only be discernible if long-term measurements are collected at numerous locations.

### 2.9.2 AMDEs in Antarctica

A comprehensive review of measurements in Antarctica is presented in a companion paper (Dommergue et al., 2010). The first extended baseline data for the concentration and speciation of atmospheric Hg in Antarctica were reported by De Mora et al. (1993). The measurements reported by Ebinghaus et al. (2002) comprise of the first annual time series of ground-level TGM concentrations in Antarctica to investigate the occurrence of possible AMDEs in south polar regions. The study also provides high-resolution data that can be compared with existing datasets of AMDEs in the Arctic, and reveals similarities. The TGM series measured at Neumayer showed several Hg depletion events during Antarctic springtime (between August and November 2000); TGM and  $\text{O}_3$  were strongly and positively correlated as seen in the Arctic boundary layer after polar sunrise. Simultaneous measurements of  $\text{Hg}^0$  and  $\text{Hg}^{\text{II}}$  were performed at Terra Nova Bay from November 2000 to January 2001. During the Arc-

tic summer, ODEs and MDEs were not observed throughout this period at Terra Nova Bay, however,  $\text{Hg}^{\text{II}}$  concentrations during the measurement period were surprisingly high and comparable with those at sites directly influenced by significant anthropogenic Hg sources. Recent studies performed in the Arctic (Lindberg et al., 2001) also report very high  $\text{Hg}^{\text{II}}$  concentrations between polar dawn and snowmelt, suggesting that there are specific mechanisms and/or characteristics of polar environments that at certain times, and apparently in the presence of surface snow, are extremely favourable to the production of  $\text{Hg}^{\text{II}}$ . Comparable  $\text{Hg}^{\text{II}}$  results have been reported by Temme et al. (2003) at Neumayer during Antarctic summertime suggesting that the snow-pack is directly involved in maintaining high  $\text{Hg}^{\text{II}}$  concentrations. Further studies are necessary to explain the reaction mechanism and the kinetics of the AMDEs and the  $\text{Hg}^{\text{II}}$  production in the Antarctic (Ebinghaus et al., 2002; Sprovieri et al., 2002; Temme et al., 2003). Long-term measurements of  $\text{Hg}^0$  and other atmospheric Hg species in the Polar Regions are very limited and need to be increased. These types of measurements can yield critical information for a better understanding of the processes involved in the Hg cycle in the polar atmosphere and the mechanisms characterising the deposition of this pollutant to this fragile environment.

### 3 Conclusions and research needs

In order to investigate both large-scale (spatial) and short/long-term (temporal) distribution characteristics of atmospheric Hg on a global scale, several Hg concentration datasets reported in peer-reviewed literature have been considered. The datasets cover terrestrial sites (industrial, rural and remote) in the Northern (Europe, North America, Asia, Arctic) and Southern (South America, Africa, Antarctica) Hemispheres as well as measurements performed over the oceans and seas. The higher spatiotemporal variability of Hg concentrations observed in the Northern Hemisphere confirms that the majority of emissions and re-emissions are located in the Northern Hemisphere. The inter-hemispherical gradient with higher TGM concentrations in the Northern Hemisphere has remained nearly constant over the years. The variation of Hg concentration shows increased amplitude in areas strongly influenced by anthropogenic sources. Concerning North-Central Europe, different background concentrations of TGM were detected from the most southern sampling site to the most northern site. Comparing data over different seasons, the patterns contrasted greatly between the Arctic and other areas in the Northern Hemisphere. It was found Hg concentrations generally peak during winter/spring in most areas due to direct or indirect influences of anthropogenic emissions. However, the Arctic region differs from this general pattern with lower values occurring in spring and higher values in summer. Concerning South Europe, TGM is slightly but significantly higher in the Mediterranean area



than in North Europe. One of the major findings was that TPM and Hg<sup>II</sup> concentrations were higher in the Mediterranean despite the higher density of industrial and urban centres in northern compared to southern Europe. The most probable interpretation is that higher emission rates from the Sea and/or more active photochemical processes in the MBL probably due to sunlight, temperature and the warmer climate in the Mediterranean basin result in a more rapid Hg cycling. High Hg<sup>II</sup> concentrations have also been observed in the MBL of the North Atlantic and the Pacific oceans. The importance of Hg exchange processes between the atmosphere and surface waters has been highlighted in recent studies related to the Mediterranean region; the lack of knowledge of the magnitude of these exchange mechanisms is one of the main factors affecting the overall uncertainty associated with the assessment of net fluxes of Hg between the atmospheric and marine environments. Most flux estimates over the Mediterranean, Atlantic, Pacific, Arctic oceans, North and Baltic Seas show that Hg concentrations appear to be saturated relative to the atmosphere, thus, the resultant flux of Hg<sup>0</sup> is from the ocean to the atmosphere. The open ocean atmospheric Hg measurements indicate a distinct inter-hemispheric gradient, which is consistent with a long-lived trace gas emitted to a greater extent in the Northern, rather than the Southern Hemisphere. The results of all cruises made over the Oceans highlighted that in the Northern Hemisphere TGM mean values are almost always higher than those obtained in the Southern Hemisphere, with a rather homogeneous distribution of TGM in the Southern Hemisphere. When latitude is taken into account, the TGM concentrations measured on board a ship are also comparable to measurements at remote coastal sites such as Mace Head (Ireland), Cape Point (South Africa), and Lista (Norway). TGM concentrations at all the North American sites (MDN) were similar to or slightly lower than those observed at European background sites, whereas all South American observations reported Hg<sup>0</sup> concentrations substantially greater than the accepted hemispheric background level, largely due to past and current gold mining activities. There are, however, uncertainties in the emission estimates for this region, and not enough information in either South or Central America to identify long-term trends. Long-term atmospheric Hg monitoring and additional ground-sites are important in order to provide datasets which can give new insights and information about the worldwide trends of atmospheric Hg.

A successful Hg monitoring network, would need to consist of a relatively small number of “intensive” sites, where the full range of measurements are made (i.e., Hg speciation in ambient air and dry deposition estimation, event-based wet deposition and fluxes, as well as ancillary parameters and detailed meteorology), and a larger number of “cluster” sites where only weekly wet deposition samples are collected. The cluster sites would allow for integration between the intensive sites, and examine the effects of local and regional conditions, while the intensive sites would provide the

detailed information needed to calibrate and test global and regional Hg models. Effective coordination among regional and national programmes with related observational needs can avoid redundant data collection efforts or data gaps that occur when individual programmes lack the resources to adequately support continued observational efforts. A monitoring Hg network on a global scale should leverage its efforts by collocating with other existing monitoring programmes such as the World Meteorological Organization’s Global Atmosphere Watch sites, US and Canadian Monitoring sites, and UN-ECE’s European Monitoring and Evaluation Programme (EMEP) sites. The principal goals of a global Hg monitoring network are (a) to study the temporal and spatial variability of atmospheric Hg species and atmospheric composition; (b) to provide long-term monitoring of changes in the physical and chemical state of Hg in the lower atmosphere and understand the causes of such changes; (c) to establish the links between changes in atmospheric Hg, tropospheric chemistry and climate; and (d) to support intensive field campaigns focusing on specific Hg processes occurring at various latitudes and seasons. The over-arching benefit of a coordinated Hg monitoring network would clearly be the production of high-quality measurement datasets on a global scale useful in developing and validating models on different spatial and temporal scales. It has become clear that while atmospheric Hg models have had some success in predicting the levels and trends in ambient Hg, the scarcity of global measurement data available for comparison make the exercise and results less significant. The models would benefit from measurements performed at ground-based sites distributed at different latitudes and altitudes as part of the coordinated network but would also benefit from closely linked intensive aircraft studies.

Taking into account the needs for model development, the Hg network would be characterised by (a) coordinated monitoring Hg wet deposition at global background sites far from anthropogenic sources, as well as sites strategically located in/downwind of various source areas; and (b) surface sites for continuous monitoring of Hg-species along with fundamental gas-phase species (i.e., CO, O<sub>3</sub>, particulate and NO<sub>x</sub>, SO<sub>x</sub>), including remote locations for tropospheric background conditions (i.e., Mt. Bachelor), sites suitable for measuring Asian outflow; locations where it will be possible to examine the reactions in the MBL and the reactions occurring in polar regions, where oxidation of Hg<sup>0</sup> is enhanced. In addition, aircraft-based studies are essential both to determine the vertical distribution of Hg and the correlations between Hg and other atmospheric species to evaluate the evolution of Hg<sup>0</sup>, Hg<sup>II</sup> and Hg in plumes downwind of major emission sources. Aircraft-based studies are also required to evaluate the effect of cloud processing on ambient Hg, as a basis for assessing the possible reduction of Hg<sup>II</sup> through aqueous reactions. It is clear that the development of a coordinated global Hg monitoring programme requires a high capacity for knowledge and technology transfer to support

national and international programmes and conventions (i.e., UNEP, UNECE-LRTAP, EU Mercury Strategy) in developing policy tools in order to identify regional Hg differences, temporal trends and for source attribution.

*Acknowledgements.* AD would like to acknowledge the Agence Nationale de la Recherche (ANR VMC, program VANISH).

Edited by: K.-H. Kim

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