1. Introduction

[2] The knowledge of the worldwide trend of atmospheric mercury concentrations during the last few decades would be valuable for at least two reasons. The trend might reveal the impact of the control measures [U.S. Environmental Protection Agency, 1997] on the global cycle of atmospheric mercury. The response of mercury concentrations to the control measures might also provide information about the poorly defined ratio of anthropogenic to natural emissions [Ebinghaus et al., 1999a]. Long-term monitoring by a network of stations was thus proposed [Fitzgerald, 1995]. In this paper we attempt the first reconstruction of the worldwide trend of total gaseous mercury (TGM) concentrations from the available long term measurements of known quality at 6 sites in the northern hemisphere (NH), 2 sites in the southern hemisphere (SH), and during 8 ship cruises over the Atlantic Ocean made intermittently since 1977.

2. Experimental

[3] The data used for the reconstruction of the TGM trend were collected at Rørvik, Wank, Lista, Mace Head, Ny Ålesund, Alert in the NH, Cape Point, Neumayer in the SH, and during 8 ship cruises over the Atlantic Ocean made since 1977 (RS Walther Herwig in 1977 and 1978, RS Meteor in 1979 and 1980, and RS Polarstern in 1990, 1994, 1996, and 1999/2000).

[4] Rørvik station (57°23′N, 11°55′E, 10 m a.s.l.) is located on the west coast of Onsala Peninsula near Gothenburg in Sweden. The measurements, using a manual sampling – gold amalgamation technique [Iverfeldt, 1991], started in 1980 and have been continued since. The samples were collected over a period of 6 h each and 4 to 151 samples were taken annually.

[5] The Wank site (47°31′N, 11°09′E, 1780 m a.s.l.) is located at the summit of the Wank mountain in southern Germany. The measurements using a manual sampling –
334 samples were taken annually each over a period of 2 h.

[6] The TGM measurements at Lista (58°06′N, 06°34′E, 10 m a.s.l.), the southernmost tip of Norway, started in 1992 and at Ny Ålesund (78°54′N, 11°53′E, 474 m a.s.l.) at Spitsbergen in 1994. The sampling and analyses were made in the same way as at Rörvik site [Iverfeldt, 1991]. 27–41 samples were taken annually at Lista and 17–350 at Ny Ålesund.

[7] Mace Head, on the west coast of Ireland (53°20′N, 09°54′W, 10 m a.s.l.) is operated as a World Meteorological Organization Global Atmosphere Watch (WMO-GAW) station. TGM has been measured since May 1996 using an automated mercury analyzer (Model 2537A, Tekran Inc., Toronto, Canada) [Ebinghaus et al., 2002b].

[8] The Alert Baseline Atmospheric Monitoring Observatory (82°28′N, 62°30′W) in Nunavut Territory, Canada, is also operated under the auspices of the WMO-GAW program. A Tekran mercury vapor analyzer has been operated at this site since January 1995 [Schroeder et al., 1998].

[9] The Cape Point station (34°21′S, 18°29′E) in South Africa is also a WMO-GAW station. The station is located at the southern tip of the Cape Peninsula on top of a peak 230 m a.s.l., ca 60 km south of Cape Town. TGM has been measured since September 1995 by the same techniques as used at Wank [Baker et al., 2002]. Apart from 1995, 37–173 samples, each taken over the period of 3 h, were analyzed annually.

[10] At Neumayer station in Antarctica, a Tekran analyzer has been operated from December 23, 2000, to February 5, 2001. The station is located at 70°39′S, 80°15′W, on the Ekströmisen, 8 km from Atka Bay [Ebinghaus et al., 2002a].

[11] Since 1977 TGM has been measured during 8 ship cruises mostly during the crossings of Atlantic Ocean from Germany to different ports in South America (Buenos Aires, Mar del Plata, Punta Quilla, Punta Arenas). Only the RS Meteor cruise in January/February 1979 and RS Polarstern cruise in December 1999/February 2000 went to Gulf of Guinea and to Cape Town, respectively. During 6 cruises until 1994, the measurement technique was the same as that used at the Wank. Usually about 100 samples, each over a period of 2–3 h, were taken in each hemisphere. The 1996 and 1999/2000 cruises were carried out using the automated Tekran analyzer [Temme et al., 2003]. With exception of the last cruise, the measurements were all made in the same season between October and December.

[12] The precision of individual measurements made by Tekran analyzer was ±0.05 with 30 min (1996 cruise) and ±0.1 ng/m³ with 15 min (all other measurements) sampling times. The precision of individual measurements was ±5.8% at Wank, Cape Point, and ship cruises, and ±2% at Rörvik, Lista, and Ny Ålesund. All techniques used here and the performance of the operating laboratories passed a test by an international field intercomparison at Mace Head in 1995 [Ebinghaus et al., 1999b]. The data presented here are thus of known and comparable quality.

3. Results and Discussion

[13] Figures 1a and 1b summarize the SH and NH data, respectively. Annual medians (cruise medians) are used to suppress the influence of occasional high TGM values due to episodes of local or regional pollution such as by biomass burning at Cape Point [Brunke et al., 2001] or low values due to polar springtime TGM depletion [Schroeder et al., 1998; Ebinghaus et al., 2002a]. All points are presented with 95% median confidence ranges [Sachs, 1978], the latter being sometimes smaller than the median symbols. The large confidence intervals of several annual medians at Rörvik are due to the limited number of measurements per year (e.g. 8 and 4 measurements in 1983 and 1992, respectively).

[14] Figure 1b shows a generally good agreement of ship measurements over the northern Atlantic Ocean with land-based measurements at Mace Head, Lista, Ny Ålesund, and Alert. TGM median values at the Wank site in southern Germany tend to be higher, most likely due to emissions in western and central Europe. Measurements at Rörvik in Sweden tend to provide higher TGM values in 1979–1980 and 1990 than onboard the ship are comparable in 1994, and tend to the lowest values in the NH thereafter. Taking into account the confidence ranges, the Rörvik data are still in reasonable agreement with measurements at Alert and Lista. All data suggest that the TGM concentrations in the NH had
been increasing since the first measurements in 1977 to a maximum in the 1980s, then decreased to a minimum in 1996 and have remained constant since that time at a level of about 1.7 ng/m³.  

[15] The period between 1980 and 1990 is covered only by the Rørvik data and by data reported by Fitzgerald [1995] for the North Pacific in 1980–1986. The latter data are generally lower than our North Atlantic measurements for 1990 [Slemr and Langer, 1992] but are comparable with those from 1977–1980 [Slemr et al., 1985]. Unfortunately, a rigorous quantitative comparison is not possible for several reasons: A) The comparability of the data has not been assured by an intercomparison. B) Many of the measurements were made near to equator and their ascension to NH is not possible without a meteorological analysis or additional air chemical data needed to assess the position of the ITCZ. C) The unknown sampling time of the data points reported by Fitzgerald [1995] preclude the consideration of the seasonality of TGM concentrations. But the broad agreement of our data measured over the Atlantic Ocean in 1977–1980 with data measured over the Pacific Ocean in 1980–1986 support our claim that the trend of the European and Atlantic data reported here is representative for the entire NH. This is to be expected on the basis of the rather long atmospheric mercury lifetime of about 1 yr [Slemr et al., 1985; Bergan et al., 1999].  

[16] The large confidence intervals of Rørvik annual medians prevent to get any information about the shape of the TGM time function between 1980 and 1990. Based on the significant increase of concentrations measured on the ship between the late 1980s and 1990 [Slemr and Langer, 1992] and a decrease between 1990 and 1996 well documented by the data presented here, the safe statement is that there must have been at least one maximum in the 1981–1990 period. When combined with the data of Fitzgerald [1995], our data here suggest that the TGM concentration in the NH is likely to have peaked in the second half of the 1980s.  

[17] The data for the SH shown in Figure 1a consist only of the ship, Cape Point, and Neumayer measurements. The TGM concentrations over the southern Atlantic Ocean are in reasonable agreement with those at Cape Point. TGM concentrations at the Neumayer station are slightly lower, suggesting a small negative southward gradient. Other available data are those reported by Fitzgerald [1995] for the southern Pacific Ocean in 1980–1986. As in the NH, his concentrations are lower than our data in 1990 but are comparable with our measurements made in 1977–1980.  

[18] TGM concentrations in the SH are about 1/3 lower than those in the NH. The ratio of medians in the NH to the SH derived from ship measurements varies around a mean value of 1.49 ± 0.11 (n = 8) suggesting that TGM in both hemispheres follows qualitatively the same trend. Most of the NH data after 1996 are within 0.6 ng/m³ compared to 0.3 ng/m³ in the SH. Higher concentrations and larger gradients in the NH are consistent with the TGM sources being located predominantly in the NH.  

[19] In summary, the direct observations of TGM in both hemispheres suggest that its concentration increased in the late 1970s to a maximum in 1980s (probably the second half of 1980s), then decreased to a minimum in mid 1990s and has remained nearly constant since. Trends of mercury deposition derived from sediment [Engstrom and Swain, 1997], ombrotropic peat bog [Benoit et al., 1994] and ice core analyses [Boutron et al., 1998] suggest similar temporal profiles but with an earlier onset of the decrease in 1970s, 1950–1980, and at about 1960, respectively. The sediment analyses by Engstrom and Swain [1997] show, however, that the onset of the deposition decrease depended on the location, with two of the three most remote locations in southeastern Alaska showing no decrease until 1990.  

[20] The observed temporal profile of the TGM concentrations is expected to result primarily from the temporal change of mercury emissions. Assuming the natural emissions and re-emissions of the mercury deposited since the begin of its anthropogenic use to be constant, the observed trend should result from the change in anthropogenic emissions. Estimates of global anthropogenic emissions by Nriagu and Pacyna [1988] and Pacyna and Pacyna [2002] amounted to 3560 (910–6200), 2140 (1270–2140), and 1900 t/yr at reference years 1979/1980, 1990, and 1995, respectively. In contrast to these inventories Pirrone et al. [1996] estimated the global anthropogenic emissions to increase by about 4%/yr from 1861 t/yr in 1983 to a peak of 2288 t/yr in 1989 and to decrease afterwards by about 1.3%/yr until 1992. This is qualitatively consistent with the observed trend. Quantitatively, however, both inventories estimate anthropogenic mercury emissions to decrease by only about 10% between 1990 and 1995.  

[21] In quantitative terms, the TGM concentrations over the northern Atlantic Ocean decreased from 2.31 ng/m³ in 1990 to about 1.88 ng/m³ in 1996 and 1999/2000, i.e. by 19% over the northern Atlantic Ocean on the basis of the 1990 data. This large decrease is also supported by the data from Wank and Lista. The corresponding decrease over the southern Atlantic Ocean was from 1.50 ng/m³ in 1990 to 1.31 ng/m³ in 1996 and 1999/2000, i.e. by 15%. Natural emissions and re-emissions are not well known but are with about 1600–3000 t/yr [Mason et al., 1994; Hudson et al., 1995] considered to be comparable with the anthropogenic ones. Assuming natural emissions and re-emissions to remain constant, the global decrease of the TGM concentrations of about 17% between 1990 and 1996 would imply a decrease of anthropogenic emissions by about 34% which is about 3–4 times larger than the 10% decrease suggested by estimates by Pacyna and Pacyna [2002] and Pirrone et al. [1996].  

[22] This already large discrepancy is further aggravated if speciation of the anthropogenic emissions is taken into account. According to Pacyna and Pacyna [2002] only 53% of the anthropogenic emissions consist of elemental mercury which enters the global cycle. The rest consists of bivalent and particulate mercury which is deposited within a relatively short distance to the sources. Recent laboratory investigations suggest the large scale photochemical reduction of bivalent to elemental mercury to be improbable [Garfeldt et al., 2002]. Consequently, assuming constant speciation between 1990 and 1996, the emissions of elemental mercury would have decreased only by about 120 t/yr between 1990 and 1996.  

[23] Based on simulations of a mercury cycle using a three-dimensional global model, Bergan et al. [1999] concluded, that the TGM concentration decrease observed during our ship cruises in the 1990–1996 period is not
consistent with the current emission estimates. They concluded that either the area of man-made to natural emissions (including re-emissions) has been underestimated or the natural emissions undergo large temporal variations. Since the TGM concentrations remained nearly constant since 1996, the underestimation of the area man-made to natural emissions seems to be the more likely explanation.

4. Conclusions

[24] TGM observations at 6 sites in the NH, 2 sites in the SH, and during 8 ship cruises over the Atlantic Ocean provide a consistent picture suggesting that the TGM concentration increased since the first measurements in 1977 to a maximum in 1980s (probably late 1980s) and then decreased to a plateau in 1996–2001. The observed worldwide concentration decrease in 1990–1996 period is much larger than predicted by the current inventories of anthropogenic and natural (including re-emission) emissions. The discrepancy suggests that either the temporal change of anthropogenic emissions is substantially larger than estimated or that the approximate ratio of man-made to natural emissions of about 1:1 is substantially underestimated. Credible future models of the global cycle of atmospheric mercury and emission estimates will thus have to reconcile not only the constraints imposed by the observed interhemispherical difference of the TGM concentrations and the prehistorical to present deposition ratios, but also the trends of the concentrations.

[25] Acknowledgments. Our thanks go to a multitude of people who helped to carry out the ship measurements at the RS \textit{Walther Herwig}, \textit{Meteor}, and \textit{Polarstern} and enabled to sustain the long-term TGM measurements at all sites mentioned here. This work was partly supported by the Deutsche Forschungsgemeinschaft. We also thank to two anonymous reviewers for constructive critical remarks.

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