Journal of Atmospheric Chemistry **3** (1985), 407–434. 0167–7764/85.15

Distribution, Speciation, and Budget of Atmospheric Mercury

F. SLEMR, G. SCHUSTER, and W. SEILER
Max Planck Institute for Chemistry, Saarstr. 23, 6500 Mainz, Federal Republic of Germany

(Received: 26 March 1985; in revised form: 22 November 1985)

Abstract. Total gaseous mercury (TGM) concentrations over the Atlantic Ocean and over Central Europe were measured repeatedly in the years 1978–1981. The latitudinal TGM distribution showed a pronounced and reproducible interhemispherical difference with higher TGM concentrations in the Northern Hemisphere. TGM was found to be vertically well mixed within the troposphere. The TGM concentration seems to increase with time at a rate of 10 ± 8%/yr in the Northern and 8 ± 3%/yr in the Southern Hemisphere. Measurements of mercury speciation showed that elemental mercury is the main TGM component contributing more than 92% and 83% of TGM in marine and continental air, respectively. The tropospheric mercury burden was calculated to be 6×10^9 g. The interhemispheric distribution and temporal and spatial variability of TGM imply a tropospheric residence time of TGM of about 1 yr. Sink strengths calculated independently from the measured mercury concentration on particles and in rainwater are consistent with the above figures.

Key words. Total gaseous mercury concentration, troposphere.

1. Introduction

Mercury pollution of the environment has led to severe poisoning in several countries. The most infamous epidemics occurred in Japan at Minamata and Niigata during the Fifties and Sixties (Takizawa, 1979). These incidents gave rise to the interest in the geochemical cycle of mercury, in its sources and sinks and its transport through the environment. It is now generally accepted that atmospheric transport is of major importance in the worldwide distribution of mercury in the environment and the qualitative aspects of the atmospheric Hg cycle seem to be well known (NAS, 1978a, b; Andren and Nriagu, 1979; Matheson, 1979; Kaiser and Tölg, 1980; Fitzgerald, 1976; Miller and Buchanan, 1979).

Mercury is emitted into the atmosphere by both anthropogenic activities and natural sources. Some of the important anthropogenic Hg sources are: discharges from production and consumption of mercury, e.g., from mercury cell chlor-alkali plants or discarded mercury amalgam batteries, smelting and mining of ores, burning of fossil fuels, and cement production (Watson, 1979). Weathering of rocks, degassing of soil, volcanic emissions (McNeal and Rose, 1974), and emissions from the oceans (Lantzy and Mackenzie, 1979) were identified as natural sources of atmospheric mercury. The removal of mercury from the atmosphere is assumed to be mainly due to dry deposition and wet deposition by rain and washout (Andren and Nriagu, 1979; Matheson, 1979).

Despite the consent about the qualitative features of the atmospheric Hg cycle, its quantitative assessment is subject to considerable discussion. Former estimates of the atmospheric mercury burden varied between 4 and 80 × 10^9 g Hg (Garrels *et al.*, 1975; Kothny, 1973; Thompson, 1971; Weiss *et al.*, 1971). More recent estimates tend towards lower numbers of between 0.8 and 5 × 10^9 g Hg (Andren and Nriagu, 1979; Lantzy and Mackenzie, 1979; Slemr *et al.*, 1981). Similar discrepancies are found for the estimates of a total mercury flux into the atmosphere which vary between 2.3 and 190 × 10^9 g Hg/yr (Andren and Nriagu, 1979; Garrels *et al.*, 1975; Jaworowski *et al.*, 1981; Kothny, 1973; Lantzy and Mackenzie, 1979; McNeal and Rose, 1974; Slemr *et al.*, 1981; Weiss *et al.*, 1971). The anthropogenic contribution is reported to account for 4 to 50% of the total mercury emissions (Andren and Nriagu, 1979; Garrels *et al.*, 1975; Kothny, 1973; Lantzy and Mackenzie, 1979; Lockeretz, 1974; McNeal and Rose, 1974; Weiss *et al.*, 1971). Finally, the reported residence times of Hg in the atmosphere differ by more than two orders of magnitude with a minimum value of 10 days and a maximum value of 5.7 yr (Andren and Nriagu, 1979; Garrels *et al.*, 1975; Kothny, 1973; Matsunaga and Goto, 1976; Miller and Buchanan, 1979; Slemr *et al.*, 1981; Weiss *et al.*, 1971). These large discrepancies are most likely due to a lack of sufficient Hg data and the analytical difficulties of measuring the different gaseous mercury species at sub ppt levels (Schroeder, 1982).

Recently, Slemr *et al.* (1981) reported measurements of the global distribution of mercury in the troposphere from which they calculated the atmospheric Hg burden to be about 5 × 10^9 g. Using the observed pronounced difference between the average mercury concentrations in the Northern and Southern Hemispheres, Slemr *et al.* estimated the atmospheric Hg residence time to be about 0.9 yr, indicating an annual source and sink strength of about 6 × 10^9 g Hg/yr. This value is one of the lowest so far reported in the literature and agrees well with the low Hg concentration in rainwater (Fogg and Fitzgerald, 1979; Matsunaga and Goto, 1976).

To improve the data base and support our recent conclusions, measurements of the total gaseous mercury (TGM) distribution in air of both hemispheres have been continued. In addition, techniques were developed to specify the individual mercury species, to allow measurement of the aerosol-bound mercury in air, and to measure the mercury concentration in rainwater. The results strongly support our recent conclusions of an average atmospheric residence time of one year and an annual source and sink strength of 6 × 10^9 g Hg/yr.

2. Experimental

2.1. *Sampling Sites and Procedures*

Mercury measurements were carried out during three ship cruises on the Atlantic Ocean, i.e., in November/December 1978 with the German RS *Walther Herwig* from Mar del Plata (38°S, 58°W) to Bremerhaven (54°N, 9°E); in January/February 1979 with the FS *Meteor* from Hamburg (54°N, 10°E) to Dakar (15°N, 18°W) and Freetown (8°N, 13°W);

and in October/November 1980 from Hamburg to Montevideo (35°S, 98°W). The itineraries of these three cruises are shown in Figure 1.

Gaseous mercury was sampled on the uppermost deck, about 15 m above sea level. Air was sucked into the collector through a glass tube of 2 m length (10 mm i.d.) stretched

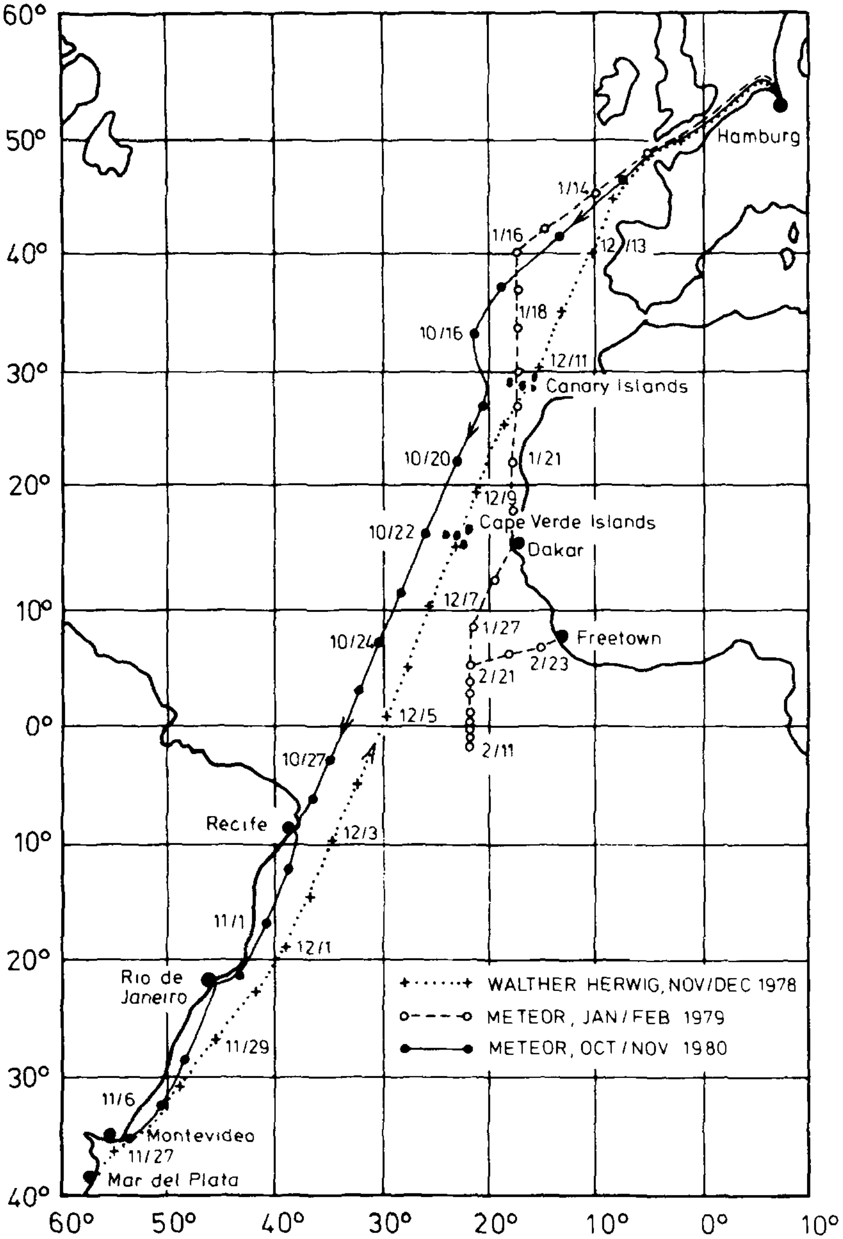

Fig. 1. Itinerary of the ship cruises in 1978, 1979, and 1980.

1.5 m ahead of the ship's railings. Between 8 and 12 samples (volume 200–400 l, sampling flow rate 10 l/min) were usually taken per day between 6 p.m. and midnight. In addition, replicate samples were repeatedly taken by means of a second sampling system installed on the same deck, either at the extreme left- or right-hand side. Results obtained from these two sampling systems were compared and used to assess the reproducibility of the method and to check the sampling system for contamination by the ship's body. The aerosol samples were collected with a filter system installed next to the sampling inlet for the gaseous mercury. The filter assembly was mounted 1.5 m in front of the railings and was directed towards the wind. Sample volumes varied between 6 and 23 m^3 and were taken within a sampling period of 20 h.

In this paper, only the results of measurements obtained at wind directions and speeds (relative to the ship's course) smaller than $\pm 70^\circ$ and larger than 6 knots respectively, were considered. Data obtained under these conditions were found to be free of contamination from the ship (Slemr *et al.*, 1981).

The technique developed for the determination of mercury specimens, i.e., dimethyl mercury (DMM), methyl mercury chloride (MMC), and particulate mercury, were tested at Deuselbach and Mainz prior to the ships' expeditions. These tests provided additional data on mercury concentration in continental air masses. Deuselbach is a regional background station of the German Environmental Protection Agency located about 100 km west of Mainz in a 'remote area' at an altitude of about 500 m above sea level. Both the gaseous and aerosol samples were taken at about 3.5 m above ground level. Air sampling in Mainz, a town on the periphery of the densely populated industrial Rhein-Main area, was performed on the roof of our institute building, about 15 m above the ground.

In addition, Hg measurements were performed in the free troposphere from 1975 to 1981 during several flights in an aircraft (type Hawker Siddeley 125) over Central Europe at altitudes of 1.8–12 km. The sampling technique and the procedure have already been described by Seiler *et al.* (1980). The first sample during each flight always tended to higher mercury mixing ratios. This is most likely due to memory effects of the stainless steel intake line and the high Hg mixing ratios observed during takeoff from the busy Cologne airport. These samples were not considered in later evaluation.

During the ship cruises in 1979 and 1980, rainwater samples were collected by means of glass funnels with 300 mm diameter openings connected to a 250 ml glass bottle. During the *Meteor* cruise in 1979, the funnel was brought to the uppermost deck shortly after the rainfall had started, rinsed three times with concentrated nitric acid (Baker, 66%, for mercury analysis) and then fixed about 50 cm in front of the ship's railing. The first 50 cm^3 of the rain water sample were discarded. The subsequent rainwater samples were brought to the laboratory immediately after sampling, for analysis and/or storage. After the rainfall had finished, the funnel was washed several times with concentrated nitric acid, sealed with Parafilm®, wrapped with aluminum foil, and then stored in the laboratory. Care was taken to keep the glass surface wet with concentrated nitric acid during the entire time of storage.

During the *Meteor* cruise in 1980, the funnel was permanently mounted about 50 cm in front of the front wall of the uppermost deck. The funnel remained dry during periods without rainfall and was covered with a polypropylene lid. Immediately after the beginning of the rainfall, the cover was removed and the funnel rinsed three times with concentrated nitric acid prior to sampling. In this case, the surface of the funnel was not permanently dampened with concentrated nitric acid so that mercury species diffusing through the lid were adsorbed on the funnel surface. Despite rinsing with concentrated nitric acid and discarding the first 50 cm^3 of the rainwater sample, the analysis of rainwater collected during the 1980 cruise always showed higher values than in 1979, which might be due to the different sampling procedure.

Rainwater samples from Mainz were collected by a collector consisting of two rectangular plates with a surface area of 1.5 x 0.75 m each. The plates were tilted in a V shape and mounted on top of a trailer. The rainwater sample was collected at the bottom edge of the V by a glass gutter and connected to a glass bottle by a 50 cm long glass tube. The glass plates were rinsed with concentrated nitric acid and kept together between the sampling periods. The gutter and the tube were also rinsed and stored, dampened with concentrated nitric acid.

2.2. *Determination of Total Gaseous Mercury (TGM)*

The method for the determination of TGM has already been described in detail by Slemr *et al.* (1979; 1981). In this method, air is passed through a collector filled with gold-coated quartz wool which accumulates the TGM quantitatively. After sampling, the collector is heated to about 700°C and the released mercury is determined either by atomic absorption (AAS) or by atomic emission (AES) spectroscopy at 253.7 nm. The latter detector is based on mercury excitation in a microwave argon plasma (Slemr *et al.*, 1978).

The TGM measuring system used prior to 1978 has been improved by two modifications. The first modification concerns the collector which is shown in Figure 2. This is distinguished from the older type (Slemr *et al.*, 1979) by a different geometry which improves the homogeneity of temperature distribution within the plug of gold-coated quartz wool during heating. This change results in a faster release of Hg and prevents the recollection of mercury vapor within the collector during heating and passing of the

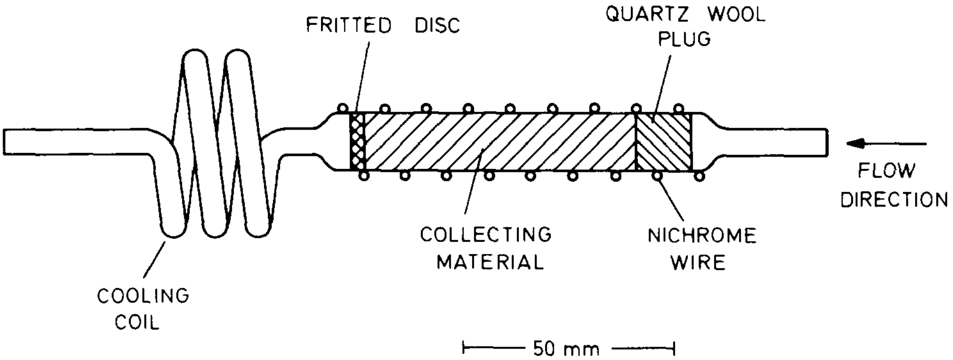

Fig. 2. Modified mercury collector.

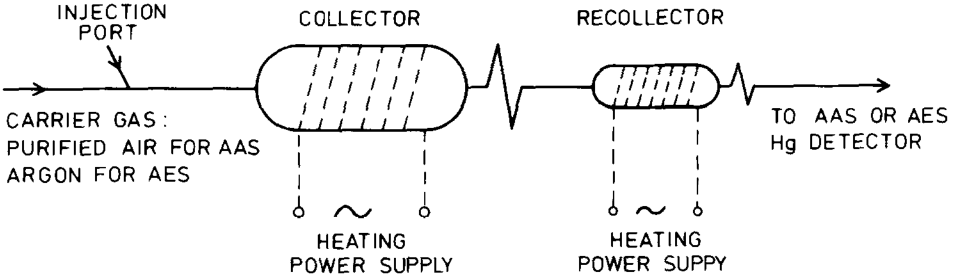

Fig. 3. Schematic diagram of the double amalgamation system for mercury analysis.

sample into the analytical detector. The collection efficiency of the modified collectors was 95 ± 1% for gold- and 94 ± 2% for silver-coated quartz wool at sampling rates $\leqslant$ 10 l (STP)/min.

The second modification concerns the AAS analytical device which has been changed into a double amalgamation, as system shown in Figure 3. In this system, the mercury accumulated on the sample (first) collector is released by heating under a steady flow of carrier gas and is recollected on a second collector which is directly connected to the optical cell of the AAS device. Possible contamination by adsorption and/or desorption of mercury in solenoid valves in the former AAS system (Slemr *et al.*, 1979) is thus avoided. Because of its small volume, the recollector reaches the releasing temperature of 700°C more rapidly, giving rise to sharp peaks which improve the precision of the TGM determination from ±14.5 to ±5.8%.

2.3. *Determination of Dimethyl Mercury (DMM) and Methyl Mercury Chloride (MMC) by Selective Collection*

The DMM determination is based on the different collection properties of gold and silver surfaces (Braman and Johnson, 1974). Whereas gold-coated quartz wool collectors adsorb DMM and all other mercury species quantitatively at sampling flow rates of up to 10 l/min, the DMM collection efficiency on silver-coated quartz wool collectors decreases rapidly with increasing sampling flow rates above 3 l/min, reaching values of only 4% at 10 l/min (Slemr *et al.*, 1978). Consequently, the difference in the Hg concentrations obtained by simultaneous measurements at flow rates of 10 l/min using silver- and gold-coated quartz collectors (differential method), must be due to the DMM content of the air. Similarly, the DMM content can be obtained from the analysis of a gold collector placed downstream from a silver collector (tandem method).

The detection limit of the differential method for DMM is given by the precision of the determination of the Hg content of the samplers, which is ±5.8% of the TGM concentration. The detection limit of DMM in the tandem method is limited by a variation of the collection efficiency of the silver and gold collector blanks and corresponds to about 2% of the TGM concentration during ship measurements.

Methyl mercury chloride was measured with a method developed by Braman and Johnson (1974). This is based on specific MMC absorption on NaOH-treated Chromosorb W. Air samples of up to 500 l were taken at a sampling flow rate of 2 l/min and analyzed by the AES detector. The MMC detection limit was 0.1 *ng* Hg/m^3, representing about a 5% TGM concentration. The reliability of this method is in doubt (W. H. Schroeder, personal communication). However, in two measurements in Deuselbach when the MMC concentration was high enough to be seen by the GC method described later, the method of selective collection and the GC method agreed to within 30%.

The described methods of selective collection for the determination of DMM and MMC are simple and, thus, suitable for routine measurements. However, they include the disadvantage of only determining classes of mercury compounds. In DMM and MMC measurements, probably other dialkyl mercury and alkyl mercury species, respectively, will also be codetermined. Thus, individual mercury compounds cannot be determined by these methods.

2.4. *Determination of DMM and MMC by Gas Chromatography (GC)*

For the determination of individual mercury compounds, a gas chromatographic method was developed. It is based on the collection of DMM and MMC on Chromosorb 106. The collected mercury species are then thermally desorbed and separated on a GC column before detection by AES. A similar method has recently been described by Ballantine and Zoller (1984).

Chromosorb 106 (1.2 g, 80/100 mesh) was packed into glass tubes (7.5 mm i.d., 100 mm long) and fixed between a fritted disc and a plug of glass wool. The tubes were preconditioned by flushing with nitrogen at 200°C for 48 h. Air samples of up to 100 and 700 l were taken for DMM and MMC, respectively, at flow rates of 0.5 l/min. Higher sample volumes were not taken because of the danger of a breakthrough of these species through the collector. The mercury species were desorbed at 170°C, recollected on the GC column kept at 50°C, and separated by a temperature programmed gas chromatography. Dimethyl mercury was determined by a GC equipped with a stainless steel column (l = 300 cm, i.d. = 3 mm) filled with Chromosorb 101 (80/100 mesh). Analysis of MMC was performed on a GC equipped with a glass column (l = 200 cm; i.d. = 3 mm) filled with 6% FFAP on Gas Chrom Q (80/100 mesh). The temperature program for both columns started at 50°C. After a period of 5 min, the column temperature was increased at a rate of 10°C/min up to a final temperature of 170°C which was held for 15 min. The AES detector was equipped with a Beenakker cavity (Beenakker, 1976) operated with helium as a carrier gas instead of argon which was used in the TGM determinations. The helium flow rate was 20 ml/min. The system was calibrated by injecting known amounts of DMM from a permeation tube or MMC in a benzene solution onto the collector. The detection limits of this method reflected the stability of the optical system under field conditions, and they varied between 0.03 and 0.13 ng Hg/m^3 for each species.

2.5. *Determination of Particulate Mercury*

Particulate mercury was determined using a pyrolysis technique. Aerosols were collected on a filter in a holder as shown in Figure 4. The glass fiber filter (Schleicher & Schüll, No. 8, 25 mm dia.) was located between a fritted disc and the inlet tube surrounded by a heating coil. Before sampling, the glass fiber filter was repeatedly baked out at 500°C for a period of 5 min. The released mercury was recollected on a gold-coated quartz collector and determined by AAS or AES. The efficiency of the Hg release and the blank value of this system was determined by repeated heating. Sample volumes varying between 6 and 23 m^3 yielded almost identical concentration values, indicating that the results are not affected by a possible Hg desorption from the aerosol on the filter.

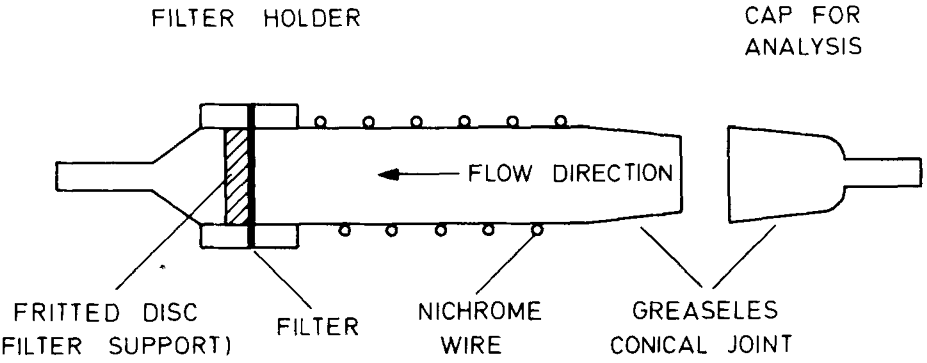

Fig. 4. Filter holder for the determination of particulate mercury.

The observation that the applied glass fiber filter adsorbed about 50% of the mercury (II) chloride (MC) from an MC-spiked ambient air stream is important for the interpretation of aerosol analysis. The filter did not adsorb Hg^0, DMM, and MMC when freshly cleaned by heating. After an exposure to 12 m^3 of urban air, the filter still did not adsorb Hg^0 and DMM but it adsorbed 40% of MMC in MMC-spiked ambient air in addition to 50% MC adsorption. The effect of MMC adsorption will probably be much lower in the remote areas where the aerosol content of the air is low. These observations clearly indicate that the Hg release obtained from this method is not exclusively due to particulate Hg, but also contains about 50% of gaseous MC and a small fraction of MMC if these species are present in the air. Conversely, the particulate Hg data can be used to estimate an upper limit for the MC concentration in the air.

2.6. *Determination of Mercury in Rain Water*

The Hg content of rain water was determined by the reduction-aeration method described by Kaiser *et al.* (1978). Rainwater samples were processed in two different ways: One aliquot of the sample was analysed immediately after the sampling, whereas the second was acidified and stored for 30–60 days. In order to avoid possible contamination, the samples were neither filtered nor oxidized. The results of the immediate analysis represent the amount of 'reactive' mercury (Baker, 1977), i.e., mercury species that are reduced to Hg^0 by $SnCl_2$. Those species are mainly Hg^{2+} and partly CH_3Hg^+. Analysis of acidified rainwater samples after a storage time of more than 30 days gives information on the total dissolved mercury content (Matsunaga *et al.*, 1979).

The rainwater samples were stored in sealed glass ampoules to avoid contamination or loss of volatile Hg species by diffusion through stoppers. The 250 ml Pyrex® ampoules were precleaned in the laboratory with acetone and concentrated nitric acid (Baker, 66%, for mercury analysis). The ampoules were then filled with 50 ml of concentrated nitric acid and sealed for transport. At the sampling site, nitric acid was discarded, and the ampoules were rinsed with about 50 ml of rain water. Only after this cleaning procedure were the ampoules filled with 100–150 ml of rain water, acidified with 10 ml of concentrated nitric acid, conserved with a preservation agent, and sealed for storage. To prevent mercury losses due to adsorption on the glass surface, 0.1 g of $K_2Cr_2O_7$ was added as a preservation agent to the rainwater samples taken in Germany (Christmann and Ingle, 1976; Matsunaga *et al.* 1979). Samples taken during the ships' expeditions were preserved in 100 ml of seawater with a known mercury content (Ambe and Suwabe, 1977). The results were corrected for the measured Hg content of additives.

3. Results

3.1. *Tropospheric TGM*

The latitudinal distributions of TGM over the Atlantic Ocean obtained during the expeditions in 1978, 1979, and 1980 are shown in Figures 5, 6, and 7, respectively. In these figures, each data point corresponds to the mercury concentration averaged over 1° latitude with the exception of the 1979 cruise where daily averages are plotted because of the lower number of individual measurements. The error bars represent the standard deviation of the averages. For comparison, all data including those obtained in 1977 (Slemr *et al.*, 1981) are plotted in Figure 8 relative to ITCZ. The location of the ITCZ varied between 5 and 12°N and was identified by a change of wind direction and by a change of simultaneously measured mixing ratios of CO and CH_4. The 1977 results were corrected for a systematic error of 13% due to the adsorption/desorption effects on solenoid valves used in the AAS analytical device until 1977. Table I summarizes the mean hemispheric Hg concentrations derived from the measured data.

The TGM concentrations show significant differences between the two hemispheres which were found during all cruises between 1977 and 1980. The lowest TGM concentrations were found in the Southern Hemisphere with values varying between about 1.1 and 1.6 ng Hg/m^3. The TGM values increase stepwise at the ITCZ and reach 1.6–2.2 ng Hg/m^3 at latitudes between ITCZ and 30°N. The highest TGM concentration was observed north of 30–40°N which is most likely due to the influence of continental air.

The TGM concentrations in both hemispheres are characterized by small coefficients

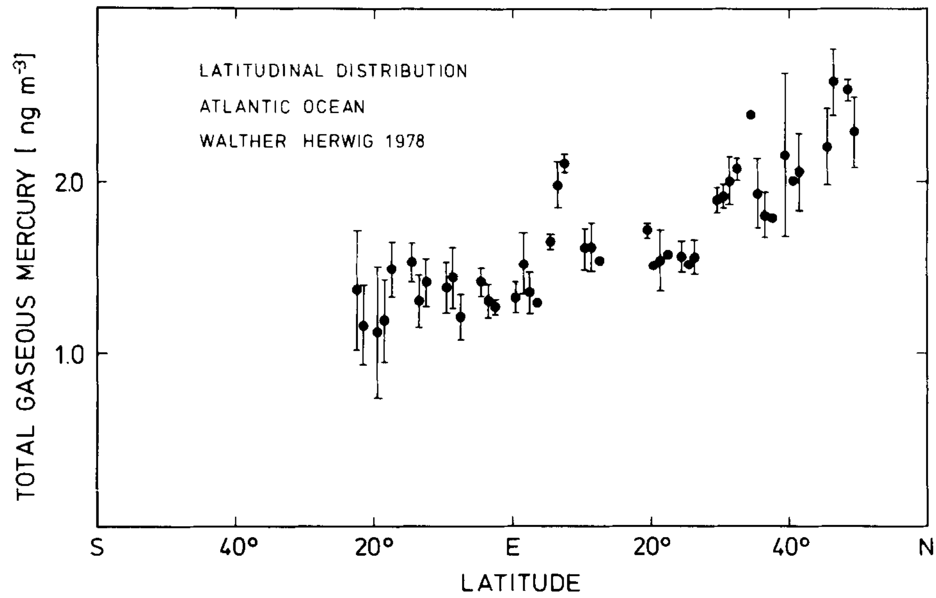

Fig. 5. Latitudinal distribution of total gaseous mercury (TGM) during the *Walther Herwig* cruise in 1978. Each data point represents the concentration average over 1° latitude and the error bars represent the standard deviation of the averages.

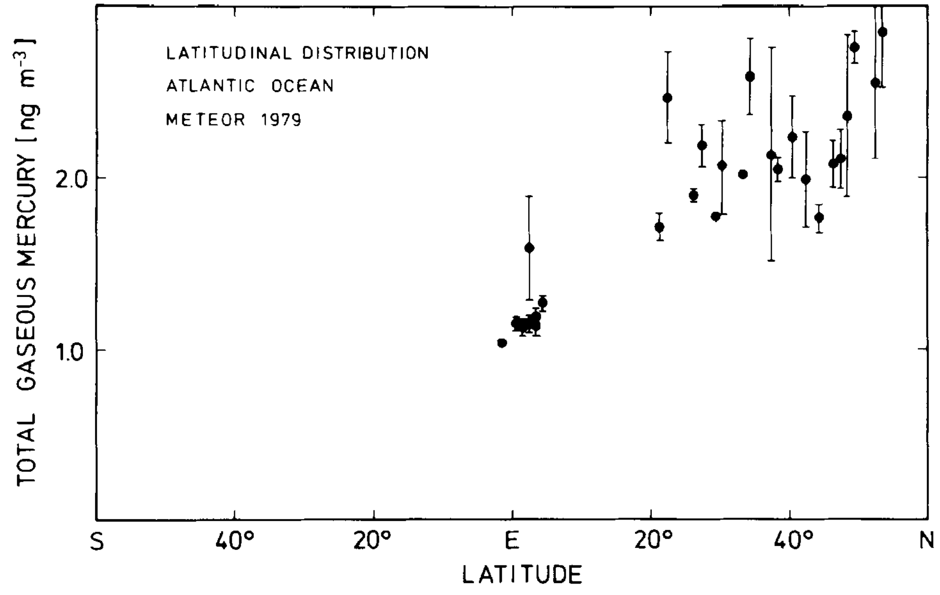

Fig. 6. Latitudinal distribution of TGM concentration during the *Meteor* cruise in 1979, Each data point and the error bars represent the daily concentration average and its standard deviation, respectively.

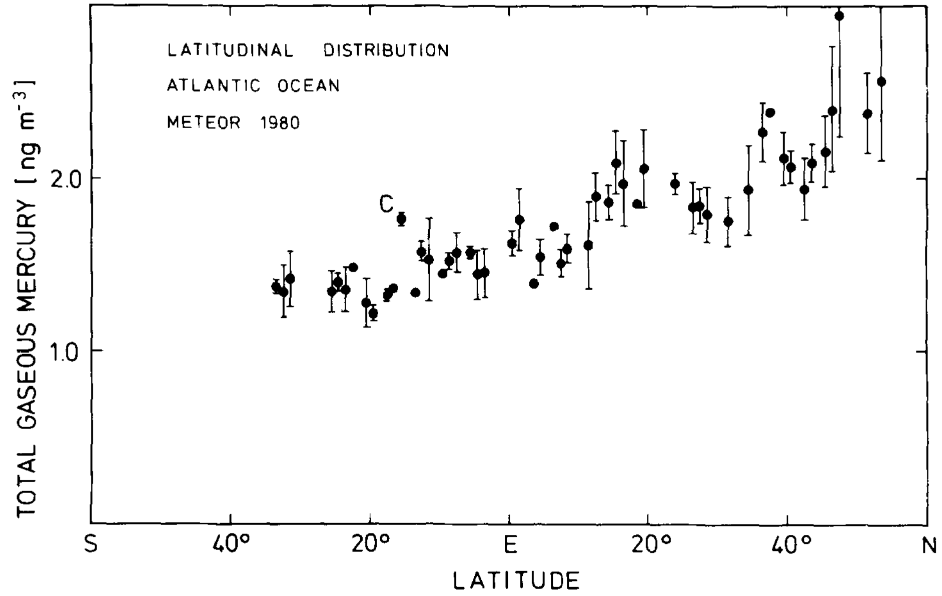

Fig. 7. Latitudinal distribution of TGM concentration during the *Meteor* cruise in 1980. Each data point represents the concentration average over 1° latitude. Point C shows measurements influenced by a plume of passing ship.

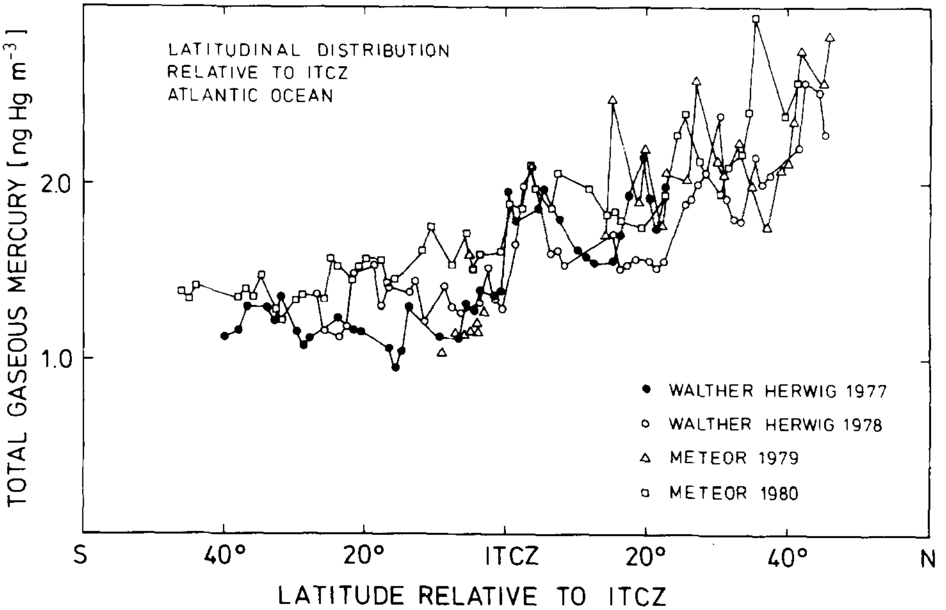

Fig. 8. Latitudinal distribution of TGM concentration relative to ITCZ during the cruises in 1978, 1979, 1980, and the *Walther Herwig* cruise in 1977 reported earlier (Slemr *et al.*, 1981).

Table I. Mean hemispherical TGM values

Cruise	Latitude	TGM concentration (ng Hg/m^3)			Number of samples	VK[a]
		range	mean	std.dev.		
Northern Hemispheric air[b]:						
Walther Herwig (1977)[c]	11–33°N	1.0–2.6	1.763	0.362	62	14.9
Walther Herwig (1978)	6–51°N	1.42–2.70	1.849	0.306	89	15.4
Meteor (1979)	21–53°N	1.63–3.06	2.169	0.382	52	16.6
Meteor (1980)	12–54°N	1.41–3.41	2.085	0.351	100	15.8
Northern Hemispheric air – all data			1.964	0.347	303	15.7
Southern Hemispheric air[d]:						
Walther Herwig (1977)	32°S–11°N	0.8–1.7	1.187	0.249	64	15.3
Walther Herwig (1978)	18°S–3°N	0.86–1.85	1.350	0.207	63	14.2
Meteor (1979)	2°S–4°N	1.07–2.09	1.259	0.216	37	16.2
Meteor (1980)	34°S–11°N	1.10–1.89	1.453	0.157	82	9.1
Southern Hemispheric air – all data			1.328	0.206	246	13.4

[a] Variation coefficient after correction for the reproducibility of the analytical method; i.e. $VK^2 = VK^2$ (measured) – VK^2 (analytical) with VK (analytical) of 14.5% during *Walther Herwig* 1977 and 5.8% afterwards.

[b] North of ITCZ.

[c] Corrected for systematic error of the analytical method used during *Walther Herwig* cruise in 1977, see text.

[d] South of ITCZ.

of variation with values ranging between 9 and 16% in the Southern Hemisphere and 15 and 17% in the Northern Hemisphere (Table I). These numbers are already corrected for the precision of the analytical method. The uniformity of the TGM concentration in the Northern and Southern Hemispheres is illustrated in Figure 9 showing the frequency distribution of the individual Hg values during all ship cruises. Using only values measured in the marine atmosphere, the most frequent TGM concentration in the Northern Hemisphere is 1.8–2.0 Hg/m^3 and in the Southern Hemisphere, 1.2–1.4 ng Hg/m^3.

Diurnal variations as reported by Seiler *et al.* (1980) and Fitzgerald *et al.* (1983) have not been observed during the individual cruises. Even though intensive mercury measurements were carried out for several days within the biologically active upwelling area near West Africa, the TGM concentrations varied within the range of analytical precision. Furthermore, the TGM concentration in this area did not differ significantly from that observed over other open ocean areas, indicating that the oceans are of minor importance as a source of atmospheric mercury.

The results of semicontinuous monitoring of the TGM concentration in the continental air carried out in September 1978 at Deuselbach are shown in Figure 10 together with the SO_2 concentrations measured by the German Federal Environment Agency. The TGM concentrations showed higher values from 4 to 6 September with daily averages of 3.2, 3.8 and 4.4 ng Hg/m^3. The concentrations decreased on 7 and 8 September to the mean

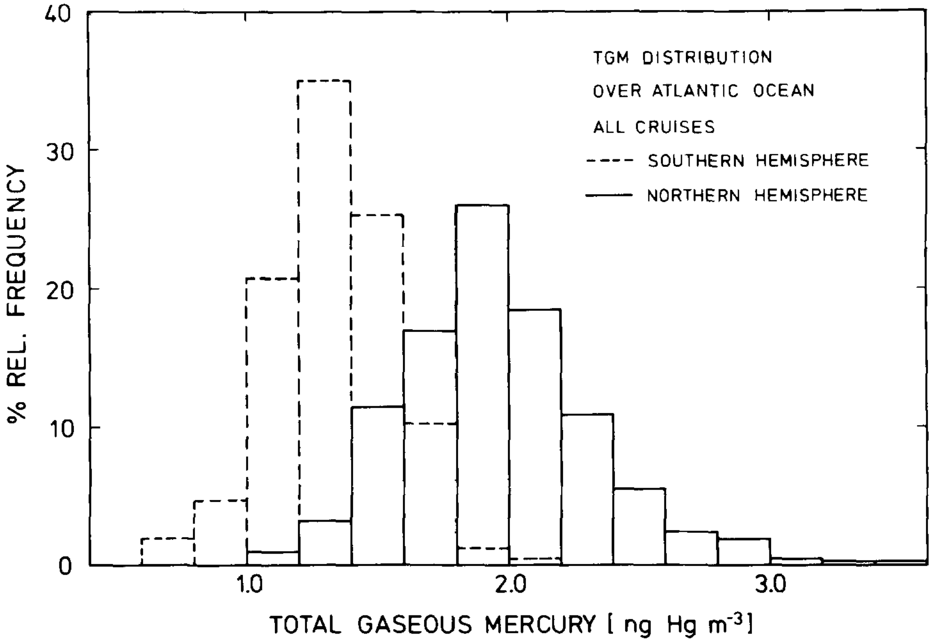

Fig. 9. Frequency distribution of the TGM concentration in the Northern and Southern Hemispheres.

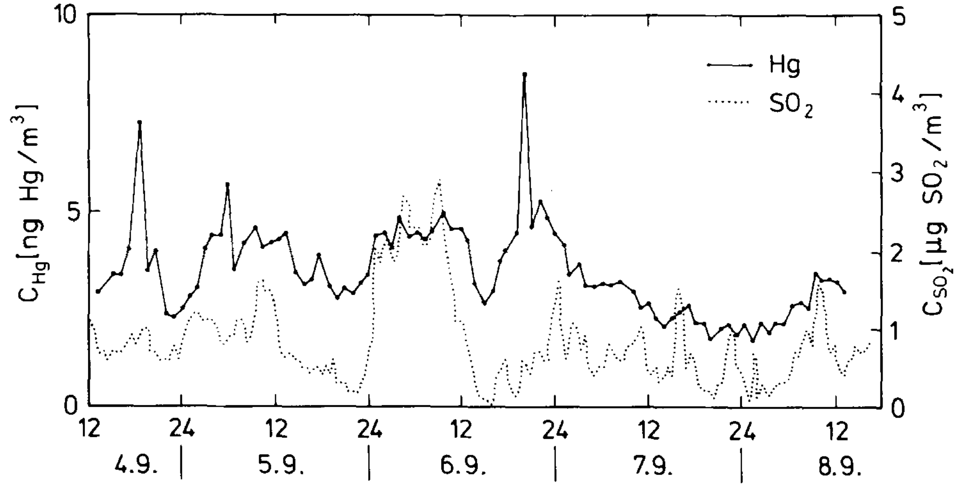

Fig. 10. Semicontinuous monitoring of TGM concentration and continuous monitoring of SO_2 concentration in Deuselbach in September 1978.

daily values of 2.8 and 2.6 ng Hg/m^3, respectively, which are typical for marine mid-latitudinal air masses in the Northern Hemisphere. Indeed, the trajectory analysis points to the Southwest of France as the origin of air masses on 7 and 8 September while from 4 to 6 September the air masses originated from a densely populated middle Europe.

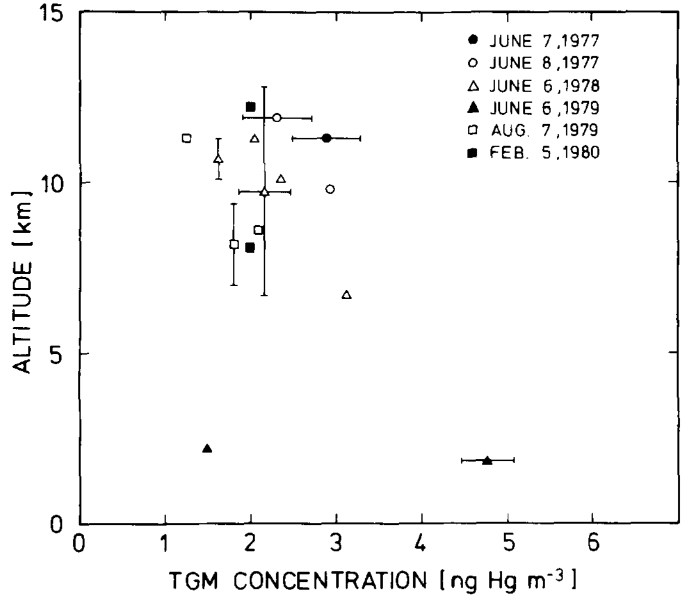

Fig. 11. Altitudinal distribution of TGM concentration over Southern France and North Sea.

The correlation of TGM with SO_2 concentrations was highly significant ($r = 0.4966$, $n = 93$), indicating that at least part of the TGM observed at Deuselbach is due to anthropogenic activities.

Monitoring of the TGM concentration in Mainz from 25 April to 7 May 1979, yielded mean daily values varying between 3.5 and 10.0 ng Hg/m^3 which exceeded those measured at Deuselbach by more than a factor of 2 and indicate the influence of local mercury sources. The highest TGM concentrations were found during stable weather conditions and, consequently, low air mass exchange when mercury could accumulate in the air. During periods with strong westerly winds, the TGM concentration was only slightly higher than the values observed over the Northern Atlantic.

The results of airplane measurements over Central Europe are summarized in Figure 11. Most of the data were obtained at altitudes between 6 and 12 km. The TGM concentrations range between 1.2 and 3.1 ng/m^3 with an average of 2.24 ± 0.51 ng Hg/m^3 ($n = 18$) which agrees reasonably well with the TGM concentrations observed in marine air masses at midlatitudes of the Northern Hemisphere, indicating that TGM is vertically well mixed in the troposphere. Differences in the TGM concentration between the troposphere and lower stratosphere were not found.

3.2. *Tropospheric DMM and MMC*

Dimethyl mercury was measured routinely during all ship cruises as well as at Deuselbach (September 1978) and in Mainz (March 1977 and May 1978) using the method of selective collection (tandem method). The GC method was applied during the 1978 cruise and

Table II. Speciation of atmospheric mercury

Mercury compound	Marine air masses	Rural site[a]	Urban site[b]
	(mean concentration in ng Hg m^{-3} (% of TGM))		
DMM	< 0.02[c] (< 2%)	< 0.05 (< 2%)	1.67 ± 1.16 (20%)
MMC	< 0.1[c] (< 5%)	0.41 ± 0.31 (14%)	1.47 ± 0.50 (15%)
Particulate mercury	N.H. 0.013 ± 0.018 (0.7%) S.H. 0.007 ± 0.004 (0.5%)	0.028 ± 0.010 (0.9%)	
TGM	N.H. 1.96 ± 0.35 S.H. 1.33 ± 0.21	3.45 ± 0.83	8.94 ± 4.16

[a] Deuselbach. [b] Mainz. [c] Median value.

during measurements at Deuselbach. The results are summarized in Table II. Dimethyl mercury was not detectable in 73% of the 253 measurements in marine air masses. When detectable, the most frequently encountered concentrations ranged between 0.02 and 0.12 ng Hg/m^3, which is less than 2% of the TGM. In Deuselbach, DMM was observed only in 34% of all measurements and the most frequently encountered values were below 0.2 ng Hg/m^3. The DMM concentrations were always lower than the detection limit of the GC method so that a comparison of the two sampling and analytical systems for measuring of DMM was not possible. High DMM concentrations were found only in strongly polluted air masses in Mainz. In this case, DMM concentrations were highly variable and ranged between 0.4 and 4.5 ng Hg/m^3 representing 4 to 47% of TGM. The high fraction of DMM relative to TGM in polluted air has already been reported by Slemr *et al.* (1981) and indicates the presence of strong local DMM sources. The low DMM concentrations in remote areas are supported by results of laboratory experiments by Niki *et al.* (1983) who determined high reaction rates of DMM with OH. With these rates, the lifetime of DMM in the troposphere is of the order of a day, which agrees with the spatial and temporal variation of DMM.

The results of MMC measurements are summarized in Table II. Thirty-eight measurements of MMC were made in marine air masses over the Atlantic Ocean in 1978, 1979, and 1980. Methyl mercury chloride concentrations above the detection limit of about 0.1 ng Hg/m^3 were observed only in 37% of all measurements. The most frequent values ranged between 0.1 and 0.2 ng Hg/m^3, representing less than 5% TGM. Higher values were observed at Deuselbach, with values ranging between 0.1 and 0.9 ng Hg/m^3. On the average, MMC in Deuselbach accounted for about 13% of the TGM concentration. The MMC concentrations in Mainz were still higher than in Deuselbach, but the fraction of MMC relative to TGM concentration was similar to that observed in Deuselbach (15%). Apparently, MMC is a general component of continental air masses contributing about 14% of the TGM.

3.3. *Particulate Mercury and Mercury Dissolved in Rain Water*

The results of the measuements of particulate bond mercury are summarized in Table II.

The mean concentrations of particulate bound mercury in marine atmosphere of the Northern and Southern Hemispheres were 0.013 ± 0.018 and 0.007 ± 0.004 ng Hg/m^3, respectively. The inter-hemispheric difference was not statistically significant. Substantially higher values of 0.028 ± 0.010 ng Hg/m^3 were observed in continental air masses in Deuselbach. The most frequently observed particulate bound mercury contributions to TGM were in the range between 0.0 and 0.2% in marine air masses and 0.9% in Deuselbach. Because of the adsorption of gaseous MC on the filter we also conclude that the concentration of gaseous MC cannot exceed values of about 0.4 and 2% of the TGM concentration in marine and continental air masses, respectively.

Results of rainwater analysis are listed in Table III. Direct analysis of rain water samples showed 'reactive mercury' concentrations of 3–14 ng Hg/l. An exception is the sample taken on 17 October 1980, which was almost certainly contaminated since the wind direction changed several times during the sampling and the wind speed relative to the ship was low. In general, the data obtained during the 1980 cruise are constantly higher by a factor of 4–5 than those from the 1979 cruise. Since both data sets were measured under clean marine conditions and, furthermore, the global mercury distribution in 1980 and 1979 did not differ significantly, we attribute the observed difference to the different sampling techniques. It is very likely that the high values found in 1980 are due to the adsorption of gaseous mercury on the wall of the collection system prior to rainfall with a subsequent incorporation of the adsorbed mercury into the rainwater during sampling.

The total dissolved mercury measured in the rainwater samples taken on 28 January

Table III. Mercury concentration in rainwater over the Atlantic Ocean and continental urban area

Location	Time	Mercury concentration	(ng (Hg/l)
Atlantic Ocean:		*direct analysis*	*stored samples*
6°N, 22°W	28.01.1979	4.3 ± 0.7 (2)	8.3 ± 3.6 (2)[a]
3°N, 22°W	08.02.1979	2.9	–
1°N, 22°W	16.02.1979	3.1	–
33°N, 22°W	17.10.1980	61.4[b]	–
12°N, 28°W	23.10.1980	13.2[d] ± 1.4 (2)	–
15°S, 36°W	01.11.1980	11.8[d]	–
29°S, 47°W	05.11.1980	14.3[d] ± 0.5 (2)	–
Continental urban area			
Mainz	10.06.1981	13.2 ± 3.5 (6)	55.4 ± 26.7 (8)[c]
Udenheim	01.07.1981	–	38.8 ± 11.0 (8)[c]
Udenheim	11.07.1981	–	25.4 ± 16.7 (6)[c]

[a] 160 ml sample acidified by 10 ml of concentrated HNO_3 and preserved with 50 ml of seawater with known mercury concentration, sealed in a glass ampoule, analysis after 6 months' storage.

[b] Changing wind directions, contaminated.

[c] Preserved by $K_2Cr_2O_7$ solution in HNO_3 and sealed in glass ampoules, analysis after 1 month's storage.

[d] Modified sampling technique, probably contaminated.

All given standard deviations result from the replicate analysis and represent the analytical precision.

1979, and 19 June 1981, range between 8 and 55 ng Hg/l and, thus, exceed the amount of 'reactive' mercury by a factor of 2–4. The difference between the 'reactive' and total mercury concentration was attributed by Fitzgerald (1976) to stable organo-mercury association. This assumption is in contrast to our experiments with MMC-spiked seawater which showed a 60% recovery of the MMC spike during the determination of 'reactive' mercury. On the other hand, Carr and Wilkniss (1973) and Andren and Harris (1975) reported strong association of Hg^{2+} with particles and organic matter, which would prevent Hg^{2+} from being determined as 'reactive' mercury.

4. Discussion

Measurements of mercury carried out in marine and continental air masses clearly demonstrate that gaseous mercury is a ubiquitous species within the Northern and Southern Hemispheres. The TGM seems to be uniformly distributed within the Southern Hemispheric troposphere over the Atlantic Ocean with average values of 1.33 ± 0.21 ng Hg/m^3. The concentrations of total gaseous mercury increase stepwise when passing the intertropical convergence zone from about 1.3 ng/m^3 south of the ITCZ to about 1.8 ng/m^3 north of the ITCZ and subsequently increase to higher TGM values when approaching higher latitudes. Average TGM concentrations of the Northern Hemisphere between the ITCZ and 50°N are 1.96 ± 0.34 ng/m^3 and, thus, exceed the corresponding Southern Hemispheric values by about 45%. An inter-hemispheric difference of TGM has also been found by Fitzgerald *et al.* (1983) over the Pacific Ocean with values of 1 ng/m^3 south and 1.5 ng/m^3 north of the ITCZ. The good agreement of these two data sets clearly demonstrates that the interhemispheric difference of TGM is a global phenomenon. According to Slemr *et al.* (1981), this difference implies a mean tropospheric residence time of TGM in the order of about one year. This relatively long residence time is in agreement with the small spatial and temporal variability of TGM in marine atmospheres of ±16% for the Northern Hemisphere and ±13% for the Southern Hemisphere over a period of 3 yr.

The TGM concentration seems to increase with time. This increase is illustrated by the frequency distributions of the TGM concentration in Figure 12 where within the period from 1977 to 1980 the most encountered values shift from 1.1 to 1.3 ng/m^3 in the Southern Hemisphere and from 1.8 to 1.9 ng/m^3 in the Northern Hemisphere. Taking the averages given in Table I and assuming a linear increase, the TGM average concentration is calculated to rise by 10 ± 8%/yr in the Northern and 8 ± 3%/yr in the Southern Hemisphere. The values agree well with the 6%/yr increase of the mean mercury deposition calculated from the mercury content of dated peat-bog samples in Denmark (Pheiffer Madsen, 1981) and with 5%/yr obtained from the analysis of dated soil strata in Germany (Kaiser *et al.*, 1978). From the mercury content of ice cores and the mercury cycle model by Lantzy and Mackenzie (1979), Millward (1982) derived rates of increase of 3.5 and 8.6%/yr for mercury emissions from continents to the atmosphere. However, in view of the limited time span of our measurements and of the standard deviation of the TGM concentration averages on the order of ± 15%, this agreement may be fortuitous and the

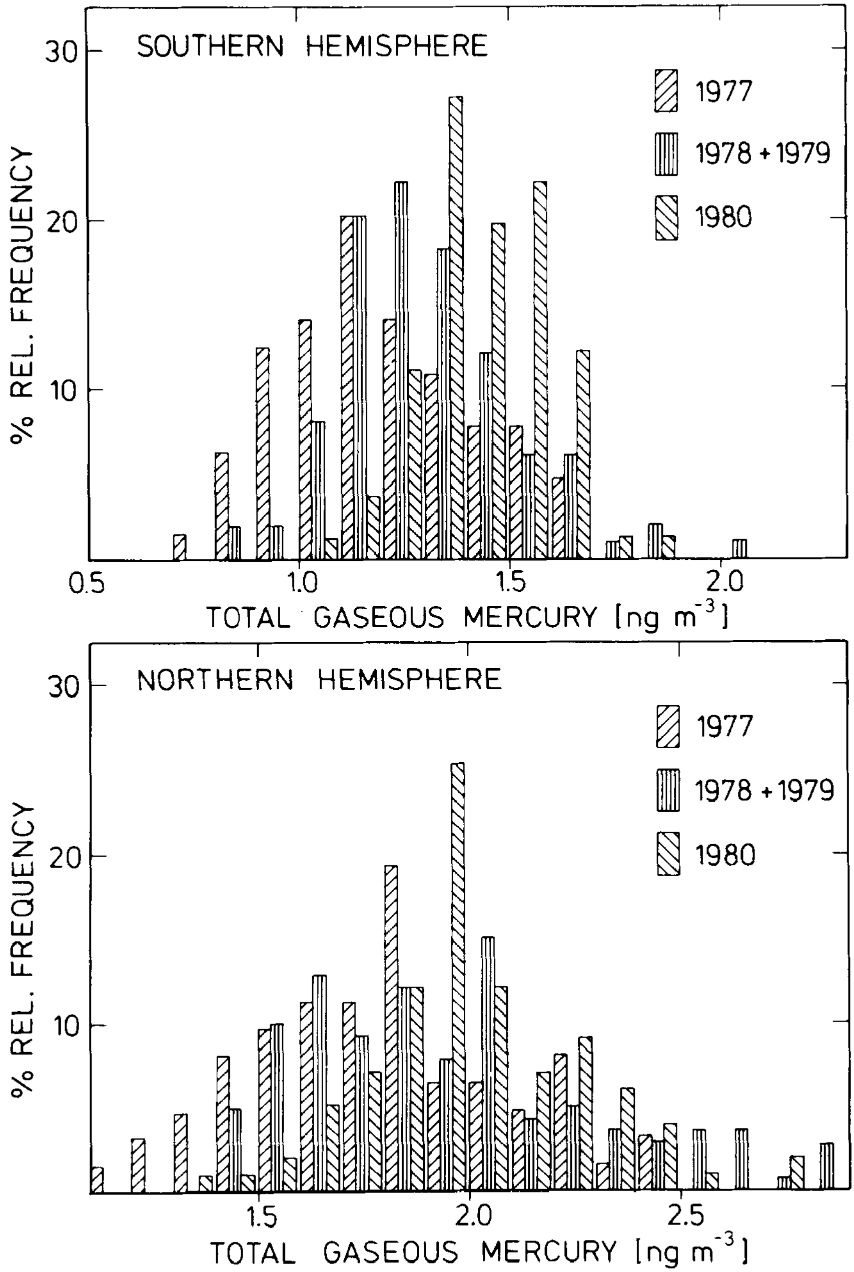

Fig. 12. Change of frequency distribution of TGM with time in the Southern and Northern Hemispheres.

increase of mercury burden needs corroboration by further measurements. Watson (1979) derived a 1.5%/yr increase of anthropogenic mercury emissions in the air from global mercury inventories, but Sheffield (1983) showed that such inventories are not very reliable, even on a national basis. Investigations of the long-term trend of mercury deposition by analysis of dated ice cores have, so far, been inconclusive (e.g., Applequist *et al.*, 1978; Weiss *et al.*, 1971; Weiss *et al.*, 1975; Wolff and Peel, 1985).

The TGM concentrations in continental air masses generally exceed those in marine atmospheres and, in addition, show higher temporal and spatial variability. The magnitude of TGM concentrations is dependent on the origin and history of the continental air mass showing maximum values in densely populated and industrial areas, e.g., in the Rhein-Main area of West Germany. High TGM concentrations were also observed over the southern Atlantic Ocean during advection of continental air from the South American continent (Slemr *et al.*, 1981) which is probably less polluted than the air over Western Germany. Similar to our observations, elevated TGM concentrations were also found by Thrane (1978), Fitzgerald and Gill (1979), Windom and Taylor (1979) and Schroeder (1981). The pronounced difference of TGM in continental and marine air masses clearly demonstrates that most of the tropospheric mercury is produced on the continents and that the oceans do not contribute significantly to the global mercury source strength. The high mercury concentrations in densely populated and industrialized areas as well as the positive correlation between SO_2 and TGM also indicate the existence of significant anthropogenic sources of gaseous mercury. Apparently, a significant fraction of the anthropogenically emitted mercury is emitted as organic mercury, most likely DMM. The occurrence of anthropogenic mercury sources has already been documented by others, e.g., Thrane (1978), Wroblewski *et al.* (1974), Lindberg (1980) and Kalb (1975).

The few measurements carried out in the free troposphere and lower stratosphere over southern France and the North Sea show values comparable to those observed in marine air masses at similar latitudes. This observation agrees well with former results reported by Seiler *et al.* (1980) and Schroeder (1981), indicating that TGM is vertically well mixed in the troposphere above the boundary layer. The elevated TGM value observed at an altitude of 1.8 km (see Figure 11) was obtained within the continental boundary layer and is comparable to the TGM values observed in Deuselbach. The uniform vertical distribution of TGM in the free troposphere, which was observed by us over Europe and South America and by Schroeder (1981) over Canada, disagrees with the results of Abramovskiy *et al.* (1975) who reported an exponential decrease of TGM concentrations with increasing altitude. At present, we cannot explain the difference between these sets of data. The low temporal variability of TGM concentrations observed over the Atlantic and Pacific Oceans, however, is in favor of a well mixed TGM concentration in the free troposphere. We, therefore, believe that the estimated residence time of about 10 days by Andren and Nriagu (1979) based on the exponential decrease of TGM in the troposphere does not reflect realistic conditions.

Concentrations of DMM in marine and rural continental air masses were generally lower than the detection limit of 0.02 ng Hg/m^3 and, thus, were lower than 1–2% of the observed TGM. Low DMM concentrations were also reported by Henriques and Isberg

(1975) as well as Johnson and Braman (1974). In contrast, high and variable DMM concentrations up to 2 ng Hg/m^3 were observed in the outskirts of Mainz (FRG) representing, on the average, 20% of the TGM. Much higher dialkyl mercury concentrations (>80 ng Hg/m^3) representing 47–99% of the observed TGM levels of 150–400 ng/m^3 were reported by Rawlings (1974) near a highway in Dallas. More recently, Fitzgerald *et al.* (1983) found DMM to represent 27–82% of TGM at levels of 2.9 ng/m^3 over Long Island Sound. The high concentrations of DMM and the high fraction of DMM relative to TGM in polluted atmospheres indicate that DMM has anthropogenic sources and that dialkyl mercury species represent a significant fraction of the anthropogenically emitted TGM. This conclusion is consistent with the observation of high DMM concentrations in samples contaminated by ship exhaust. Because of the strong spatial gradients and the high variability of DMM, the residence time of DMM in the lower troposphere must be relatively short. Comparison of DMM concentrations obtained in Mainz and Deuselbach (Table II) clearly demonstrate that DMM is rapidly removed from the troposphere. One sink mechanism for DMM is the reaction of DMM with OH radicals (Niki *et al.*, 1983). The reaction rate constant of 1.97×10^{-11} cm^3/molecule sec implies an average residence time for DMM in the troposphere on the order of less than 1 day, so that high DMM concentrations should only be expected near to the DMM sources. The reaction with OH is probably the only important removal process of DMM from the atmosphere. The high vapor pressure of DMM and its low solubility in water (Wasik *et al.*, 1976) makes removal by aerosol attachment followed by rain and washout unlikely (Junge, 1977). The final product of the DMM destruction is not known, but Niki *et al.* (1983) suggested CH_3HgOH to be a stable intermediate. The behaviour of this compound is probably very similar to MMC which is discussed next.

MMC concentrations of less than the detection limit of about 0.1 ng Hg/m^3 were found to be typical for marine air masses. In continental rural and urban air masses, MMC represented about 15% of TGM. Henriques and Isberg (1975) could not detect MMC over the Baltic Sea when applying a technique with a detection limit of about 5% of the TGM. Johnson and Braman (1974) reported the MMC concentrations in an urban area of Tampa, Florida, to be highly variable ranging from 0 to 93% of TGM. Nine of 11 measurements were below 10% of TGM and the highest MMC concentration was connected with TGM values over 10 ng Hg/m^3, indicating the presence of local MMC sources such as, e.g., the cooling channel of a power plant (Ballantine and Zoller, 1984) or a sewage treatment facility (Soldano *et al.*, 1975).

The fate of MMC in the troposphere is unknown. The more uniform distribution of MMC in continental air masses, however, indicates that MMC is removed more slowly than the shortlived DMM. One possible removal process is the reaction of MMC with OH radicals. The rate constant of this reaction has not yet been measured but it may be high enough to compete with other possible removal mechanisms, as is the case for the reaction between OH and DMM (Niki *et al.*, 1983) as well as OH and tetramethyl lead (Harrison and Laxen, 1978). The final product of this reaction will likely be either elemental mercury or HgO, which is expected to behave similarly to MC which is discussed later. Based on present data on MMC vapour pressure (Talmi and Mesmer, 1975) and the distribution coefficient between water and air (Talmi and Mesmer, 1975; Iverfeldt and Lindqvist, 1982) we assume that the attachment of MMC to aerosol as well as rain and washout may be other effective removal processes. The probability of this removal pathway of MMC and related compounds becomes evident from results by Niki *et al.* (1983) who observed a rapid loss of CH_3HgOH on the walls of the reactor.

The mean concentration of particulate mercury of 0.028, 0.013, and 0.007 ng Hg/m^3 observed in Deuselbach and over the northern and southern Atlantic Ocean, respectively, agree well with the figures of 0.035, 0.011, and 0.007 ng Hg/m^3 found by Millward and Griffin (1980) at higher and lower latitudes of the northern Atlantic, as well as over the southern Atlantic, respectively. Millward and Griffin found the inter-hemispherical difference to be statistically significant. Both data sets show that the gradient of particulate mercury approximately follows the gradient of the TGM values. The particulate mercury generally contributes less than 1% to the TGM. Fitzgerald and Gill (1979) observed particulate mercury to be 1% of the TGM in clean marine air at Pigeon Key, Florida, and about 3.6% in an urban area. Most recently, Fitzgerald *et al.* (1983) reported particulate mercury values of 0.0004 and 0.002 ng Hg/m^3 (0.03–0.11% of TGM) over Enewetak Atoll in the Pacific Ocean, 0.0007 ng Hg/m^3 (0.04% of TGM) over northwest Atlantic Ocean, and 0.020 ng Hg/m^3 (0.7% of TGM) in an urban area. In contrast, earlier data on particulate mercury reported by Matheson (1979), Rahn (1975), NAS (1978a), Peirson *et al.* (1973), and Dams and DeJonge (1976) show particulate mercury concentrations of around 0.1 ng/m^3 and more, which are most likely due to analytical difficulties in determining mercury concentrations in the order of 0.001 ng Hg/m^3.

According to our laboratory tests, about 50% of gaseous MC was adsorbed on the glass fiber filter used for the collection of particulate mercury. Since the analytical technique did not distinguish between adsorbed MC and particulate mercury, a systematic positive error of particulate mercury values due to MC adsorption is possible. Consequently, the values of 0.007 and 0.013 ng/m^3 for marine air masses and 0.028 ng/m^3 for continental air masses may represent upper limits of particulate mercury. On the other hand, these data also indicate that the maximum concentration of MC in marine and continental air masses may not be higher than 0.02–0.05 ng Hg/m^3 representing 1–2% of TGM. Johnson and Braman (1974) found the MC concentration to be highly variable ranging between 0 and 75% of the TGM concentration. High MC values were generally connected with high TGM values, indicating the influence of local sources. The fate of MC in the troposphere is unknown. Based on solubility data and the vapor pressure of MC (Phillips *et al.*, 1959; Kaiser and Tölg, 1980) it is likely that MC will be effectively removed by aerosol attachment and by rain and washout (Junge, 1977).

Summarizing the presently available data on mercury, we see that elemental mercury is generally the main component of TGM in the troposphere, contributing more than 92% of TGM in marine and 83% in continental air masses of remote areas. In the planetary boundary layers of densely populated areas, DMM and MMC may represent a substantial fraction of TGM, indicating that a significant fraction of the anthropogenic mercury is emitted as DMM and MMC. The predominance of elemental mercury on the global scale is in accordance with the short residence time of DMM, MMC and MC which we should expect because of the high reactivity of DMM with OH radicals and the low vapor pressure and high solubility of MMC and MC in water. Using the presently available data on reaction constants, vapor pressure, solubility, etc., the residence times of DMM and MC as well as MMC may be on the order of a few days and 2 months, respectively, which is much shorter than the residence time of elemental mercury (Slemr *et al.*, 1981). The removal mechanism of elemental mercury from the atmosphere is unknown but Hg^0 is oxidized probably by atmospheric ozone to HgO which, similarly to MC, is expected to be removed effectively by attachment to aerosol and by rain and washout. The reaction rate constant for $Hg^0 + O_3$ of 4.2×10^{-19} cm^3/molecule sec (Pjankov, 1949) implies under the assumption of mean tropospheric O_3 mixing ratio of 25 ppb, a tropospheric residence time of elemental mercury of 1 yr. This value is consistent with the observation of Hg^0 to be the dominant mercury species in the atmosphere and agrees excellently with TGM residence time derived later in this paper and that of Slemr *et al.* (1981).

Our analysis of rainwater samples has shown that mercury in rainwater must be present in different forms and that the 'reactive' mercury is about 20–50% of the total mercury concentration in rainwater. Since the total amount of 'reactive' mercury is dependent on the duration of sample storage (Matsunaga *et al.*, 1979), a comparison and assessment of the rainwater data compiled by Galloway *et al.* (1982) is difficult. In many cases the description of the analytical methods is not sufficient to decide whether the data refer to total mercury or 'reactive' mercury. Our average total mercury concentration of 25–55 ng/l found in rainwater in the urban area of Mainz/Udenheim agrees well with 23–75 ng/l measured by Rupert (1975) in the urban area of Göttingen, Germany, as well as with 60 ng/l measured by Schlesinger *et al.* (1974) in New Hampshire, and 65–123 ng/l found by Jonasson (1973) in the urban area of Ottawa. The average 'reactive' mercury concentration of 13 ng/l measured in Mainz is comparable to 7 ng/l reported by Bricker (1980) for Fort Pierce, Florida, and 10 ng/l measured by Fogg and Fitzgerald (1979) in Centreville, Mass., and Avery Point, Connecticut.

The 'reactive' mercury concentrations of 2.9–4.3 ng/l in rainwater over the equatorial Atlantic Ocean are higher than the value of 0.8 ng/l measured by Fogg and Fitzgerald (1979) at American Samoa, the 2 ng/l value reported by Fitzgerald *et al.* (1983) for the Marshall Islands, and also the values of 0.7–1.9 ng/l measured by Matsunaga and Goto (1976) in Hakodate City with wind blowing from the Pacific Ocean. The total mercury concentration of 8 ng/l found in marine air masses at 6°N agrees well with 11 ng/l found by Applequist *et al.* (1978) in the Greenland ice shield. The higher values of mercury concentrations in snow samples and ice cores reported by Herron *et al.* (1976), Carr and Wilkness (1973), Weiss *et al.* (1975), and by Jaworowski *et al.* (1981) may be influenced by mercury migration from the underlying soil (Jonasson, 1973) and by mercury enrichment in polar regions (Ottar, 1981). On the basis of available data we assume that the total mercury concentration of 25–60 and 8–11 ng/l may be representative of rainwater in continental and marine areas, respectively.

Assuming that the air of the Northern and Southern Hemispheres is vertically well mixed and applying the average mercury concentration of 1.96 and 1.33 ng Hg/m^3, respectively, the tropospheric mercury burden is calculated to be about 5.1×10^9 which agrees with 5×10^9 g published by Slemr *et al.* (1981). This figure does not consider the higher Hg concentrations over the continents which may add another 1×10^9 g. The latter figure is based on the assumption that the average Hg concentration in air over continents is 3–6 ng/m^3 and that the average thickness of the continental boundary layer is about 1 km. Both figures together result in a tropospheric mercury burden of about 6×10^9 g.

A very important parameter of the tropospheric mercury cycle is its residence time which can be estimated from the empirical relationship between the coefficient of variation and the residence time originally proposed by Junge (1974) and elaborated by Hamrud (1983). The coefficient of variation of all our TGM data is 24.3% and is given mainly by the inter-hemispheric difference. Application of the original relation by Junge (1974) gives a residence time of 0.6 yr which may be uncertain by a factor of 10 (Hamrud, 1983) since no assumptions concerning the source distribution were made. Assuming mercury to be mainly of anthropogenic origin and its sink to be uniformly distributed, the relation by Hamrud (1983) yields a residence time of 1.4 yr with an uncertainty of a factor of 3. A slightly lower value was obtained by Slemr *et al.* (1981) from a 1977 cruise on the Atlantic Ocean. Fitzgerald *et al.* (1983) calculated the residence time of 134–300 days from their data over the Pacific Ocean. If we subtract the standard deviation given by their analytical precision, this residence time may increase by 20–50% and thus agrees well with our estimate.

The average residence time of total gaseous mercury can also be calculated from the observed inter-hemispheric difference of the TGM concentrations. Using the procedure described by Slemr *et al.* (1981) and applying the average TGM concentration in marine atmosphere of 1.96 ng/m^3 in the Northern Hemisphere and 1.33 ng/m^3 in the Southern Hemisphere, the residence time is calculated to be 1.1 yr. This figure is based on the assumption that (a) 90% of the anthropogenic mercury emissions occurs in the Northern Hemisphere, (b) the anthropogenic emissions equal the natural mercury emissions and (c) the natural mercury emission is proportional to the continental surface area between 60°N and 60°S. The figures of 1.4 and 1.1 yr obtained from two independent calculations clearly indicate that the actual residence time may be in the order of 1 yr which is considerably higher than the estimates by Andren and Nriagu (1979), Garrels *et al.* (1975), and Kothny (1973) varying between 0.04 and 0.25 yr and lower than 5.7 yr as proposed by Matsunaga and Goto (1976).

With the knowledge of the tropospheric burden (M) and the tropospheric residence time (t) of TGM, the total flux of TGM (F) into the atmosphere can be calculated from the expression

$$F = \frac{M}{t} .$$

Assuming steady-state conditions, and applying the above figures for M and T, we obtain a total flux of TGM into the atmosphere of 6×10^9 g/yr. This emission rate is about one order of magnitude lower than estimates by Kothny (1973), Andren and Nriagu (1979), Garrels *et al.* (1975), Goldberg (1975), and Jaworowski *et al.* (1981) which appear to be largely overestimated.

Mercury is predominantly emitted into the atmosphere over the continents and is released to a large extent as DMM and/or MMC. This conclusion is consistent with the observation of strong gradients of TGM, DMM and MMC concentration between continental and marine air masses. Since the highest TGM concentrations were found in polluted air, we propose significant emissions of mercury are due to anthropogenic activities. Watson (1979) estimated the annual anthropogenic Hg emission rate to be about 2.5×10^9 g which would correspond to 40% of the total mercury flux into the atmosphere. The burning of fossil fuels is a major anthropogenic mercury source (Watson, 1979) and it can explain the annual variation of TGM concentration over Sweden reported by Brosset (1982) with maximum in winter and minimum in summer. The amplitude of this annual variation indicates that anthropogenic mercury emissions can represent more than 50% of all emissions in industrialized regions.

The flux of mercury into the atmosphere must be balanced by corresponding sink mechanisms acting in the troposphere. The mercury sink by rain and washout can be estimated from the rainwater data. Assuming the rainwater mercury concentration of 25–60 ng/l to be representative for the continental areas of Northern Hemisphere and 8–11 ng/l for all other regions, and using the precipitation distribution given by Baumgartner and Reichel (1975), the annual mercury flux accounts for $5\text{–}8 \times 10^9$ g Hg/yr which agrees reasonably well with the emission figures. A flux of $4\text{–}5 \times 10^9$ g Hg/yr is obtained if we use the observed particulate mercury concentrations of 0.007–0.013 ng Hg/m^3 for marine atmospheres, 0.03 ng/m^3 for rural continental areas and 0.1 ng Hg/m^3 for polluted continental areas and apply an average residence time of tropospheric aerosols of 5 days (Prospero *et al.*, 1983). This flux does not include the direct wet and dry deposition of gaseous mercury species and, therefore, is in good agreement with the flux estimate based on the rain water data.

Both independent estimates of the mercury flux from the atmosphere are centered around 6×10^9 g/yr and, thus, agree well with the flux implied by the atmospheric mercury burden and the tropospheric residence time of mercury evidenced by its variability and its concentration difference between Southern and Northern Hemisphere. This agreement is especially notable since the estimates based on rainwater and particulate mercury data likely encompass the final products of the chemical oxidation of DMM, MMC, and MC. Consequently, the sum of global fluxes of DMM, MMC, and other mercury species exceeding about 6×10^9 g Hg/yr are improbable.

Acknowledgements

We are indebted to the Federal Ministry of Agriculture for the permission to take part in the Atlantic cruise of the FFS *Walther Herwig*. We thank the crews of the FFS *Walther Herwig* and of the FS *Meteor* for their support of our measurements. We are also grateful to K.-J. Rumpel from the German Environment Protection Agency for providing the

SO_2 data and for support of our measurements in Deuselbach. Valuable comments on the manuscript by W. H. Schroeder are gratefully acknowledged as well as the correction of the manuscript by P. Haug. This work was performed as a part of the program of Sonderforschungsbereich 73, receiving partial funds through the Deutsche Forschungsgemeinschaft.

References

Abramovskiy, B. P., Anokhin, Y. A., Ionov, V. A., Nazarov, E. M., and Ostromogilskiy, A. K., 1975, Global balance and maximum permissible mercury emissions into the atmosphere, in *Second Joint U.S./U.S.S.R. Symp. Comprehensive Analysis of the Environment Proc.*, Honolulu, U.S. Environ. Prot. Agency 600/9-76-024.

Ambe, M. and Suwabe, K., 1977, The preparation of standard solutions of mercury at the ppb level, *Anal. Chim. Acta* **92**, 55–60.

Andren, A. W. and Nriagu, J. O., 1979, The global cycle of mercury, in J. O. Nriagu (ed.), *The Biogeochemistry of Mercury in the Environment*, Elsevier/North-Holland Biomedical Press, Amsterdam, pp. 1–21.

Andren, A. W. and Harris, R. C., 1975, Observations on the association between mercury and organic matter dissolved in natural waters, *Geochim. Cosmochim. Acta* **39**, 1253–1257.

Appelquist, H., Jensen, K. O., Sevel, T., and Hammer, C., 1978, Mercury in the Greenland ice sheet, *Nature* **273**, 657–659.

Baker, C. W., 1977, Mercury in surface waters of seas around the United Kingdom, *Nature* **270**, 230–232.

Ballantine, D. S. Jr. and Zoller, W. H., 1984, Collection and determination of volatile organic mercury compounds in the atmosphere by gas chromatography with microwave plasma detection, *Anal. Chem.* **56**, 1288–1293.

Baumgartner, A. and Reichel, E., 1975, *The World Water Balance*, Elsevier, New York, 1975.

Beenakker, C. I. M., 1976, A cavity for microwave induced plasmas operated in helium and argon at atmospheric pressure, *Spectrochim. Acta* **31B**, 483–486.

Braman, R. S. and Johnson, D. L., 1974, Selective absorption tubes and emission technique for determination of ambient forms of mercury in air, *Environ. Sci. Technol.* **8**, 996–1003.

Bricker, J. L., 1980, Atomic emission spectrometer determination of mercury in natural waters at the part-per-trillion level, *Anal. Chem.* **52**, 492–496.

Brosset, C., 1982, Total airborne mercury and its possible origin, *Water Air Soil Pollut.* **17**, 37–52.

Carr, R. A. and Wilkness, P. E., 1973, Mercury in the Greenland ice sheet: Further data, *Science* **181**, 843–844.

Carr, R. A. and Wilkness, P. E., 1973, Mercury: Short-term storage of natural waters, *Environ. Sci. Technol.* 7, 62–63.

Christmann, D. R. and Ingle, J. D. Jr., 1976, Problems with sub-ppb mercury determinations: Preservation of standards and prevention of water mist interferences, *Anal. Chim. Acta* **86**, 53–62.

Dams, R and DeJonge, J., 1976, Chemical composition of Swiss aerosols from the Jungfraujoch, *Atmos. Environ.* **10**, 1079–1084.

Fitzgerald, W. F., 1976, Mercury studies of seawater and rain: Geochemical flux implications, in H. L. Windom and R. A. Duce (eds.), *Marine Pollutant Transfer*, Lexington Books, Lexington, Mass., pp. 121–134.

Fitzgerald, W. F. and Gill, G. A., 1979, Subnanogram determination of mercury by two-stage-gold amalgamation and gas phase detection applied to atmospheric analysis, *Anal. Chem.* **51**, 1714–1720.

Fitzgerald, W. F., 1979, Distribution of mercury in natural waters in J. O. Nriagu (ed.), *The Biogeochemistry of Mercury in the Environment*, Elsevier/North-Holland Biomedical Press, Amsterdam, pp. 161–173.

Fitzgerald, W. F., Gill, G. A., and Hewitt, A. D., 1983, Air-sea exchange of mercury, in Wong *et al.* (eds.) *Trace Metals in Sea Water*, Plenum, pp. 297–315.

Fogg, T. R. and Fitzgerald, W. F., 1979, Mercury in southern New England coastal rains, *J. Geophys. Res.* **84**, 6987–6989.

Galloway, J. N., Thornton, J. D., Norton, S. A., Volchok, H. L., and McLean, R. A. N., 1982, Trace metals in atmospheric deposition: A review and assessment, *Atmos. Environ.* **16**, 1677–1700.

Garrels, R. M., Mackenzie, F. T., and Hunt, C., 1975, *Chemical Cycles and the Global Environment Assessing Human Influences*, William Kaufman, Los Altos, Calif.

Goldberg, E. D., 1975, Atmospheric transport of mercury from continents to the oceans, in *Proceedings of a Workshop on the Tropospheric Transport of Pollutants to the Ocean*, Natl. Res. Council, Miami, 1975.

Hamrud, M., 1983, Residence time and spatial variability for gases in the atmosphere, *Tellus* **35B**, 295–303.

Harrison, R. M. and Laxen, D. P. H., 1978, Sink processes for tetraalkyllead compounds in the atmosphere, *Environ. Sci. Technol.* **12**, 1384–1392.

Henriques, A., and Isberg, J., 1975, A new method for collection and separation of metallic mercury and organo-mercury compounds in air, *Chem. Scripta* **8**, 173–176.

Herron, M. M., Langway, C. C., Weiss, M. V., Huxey, P., Kerr, R., and Gragin, J., 1976, Vanadium and other elements in Greenland ice cores, CRREL Report, 76–24.

Iverfeldt, A., and Lindqvist, O., 1982, Distribution equilibrium of methyl mercury chloride between water and air, *Atmos. Environ.* **16**, 2917–2925.

Jaworowski, Z., Bysiek, M., and Kownacka, L., 1981, Flow of metals into the global atmosphere, *Geochim. Cosmochim. Acta* **45**, 2185–2199.

Johnson, D. L. and Braman, R. S., 1974, Distribution of atmospheric mercury species near ground, *Environ. Sci. Technol.* **8**, 1003–1009.

Jonasson, I. R., 1973, Migration of trace metals in snow, *Nature* **241**, 447–448.

Junge, C. E., 1974, Residence time and variability of tropospheric trace gases, *Tellus* **26**, 477–488.

Junge, C. E., 1977, Basic considerations about trace constituents in the atmosphere as related to the fate of global pollutants, in I. H. Suffet (ed.), *Fate of Pollutants in the Air and Water Environments*, Part 1, Vol. 8, John Wiley, New York, pp. 7–23.

Kaiser, G., and Tölg, G., 1980, in O. Hutzinger (ed.), *The Handbook of Environmental Chemistry*, Vol. 3, Part A, Springer Verlag, Berlin, pp. 1–58.

Kaiser, G., Götz, D., Tölg, G., Knapp, G., Maichin, B., and Spitzy, H., 1978, Untersuchung von systematischen Fehlern bei der Bestimmung von Hg-Gesamtgehalten im Bereich 10^{-5}% in anorganischen und organischen Matrices mit zwei unabhängigen Verbundverfahren, *Z. Anal. Chem.* **291**, 278–291.

Kaiser, G., Tölg, G., and Schlichting, E., 1978, Natürliche und anthropogene Quecksilberanreicherung in Filderlehm-Böden, in *Sonderreihe Umwelttagung*, Univ. Hohenheim.

Kalb, G. W., 1975, Total mercury mass balance at a coal-fired power plant, in S. P. Babu (ed.), *Trace Elements in Fuel*, Adv. Chem. Ser. No. 141, ACS, Washington, D. C.

Kothny, E. L., 1973, The three-phase equilibrium of mercury in nature, in E. L. Kothny (ed.), *Trace Elements in the Environment*, Adv. Chem. Ser. No. 123, Am. Chem. Soc., Washington, D.C., pp. 48–80.

Lantzy, R. J. and Mackenzie, F. T., 1979, Atmospheric trace metals: Global cycles and assessment of man's impact, *Geochim. Cosmochim. Acta* **43**, 511–525.

Lindberg, S. E., 1980, Mercury partitioning in a power plant plume and its influence on atmospheric removal mechanisms, *Atmos. Environ.* **14**, 227–231.

Lockeretz, W., 1974, Deposition of air-borne mercury near point sources, *Water, Air, Soil Pollut.* **3**, 179–193.

Matheson, D. H., 1979, Mercury in the atmosphere and in precipitation, in J. O. Nriagu (ed.), *The Biogeochemistry of Mercury in the Environment*, Elsevier/North-Holland Biochemical Press, Amsterdam, pp. 114–129.

Matsunaga, K. and Goto, T., 1976, Mercury in the air and precipitation, *Geochem. J.* **10**, 107–109.

Matsunaga, K., Konishi, S., and Nishimura, M., 1979, Possible errors caused prior to measurement of mercury in natural waters with special reference to seawater, *Environ. Sci. Technol.* **13**, 63–65.

McNeal, J. M. and Rose, A. W., 1974, The geochemistry of mercury in sedimentary rocks and soils in Pennsylvania, *Geochim. Cosmochim. Acta.* **38**, 1759–1784.

Miller, D. R. and Buchanan, J. M., 1979, Atmospheric transport of mercury: Exposure commitment and uncertainty calculations, Monitoring and Assessment Research Centre Report, No. 14, University of London.

Millward, G. E. and Griffin, J. M., 1980, Concentrations of particulate mercury in the Atlantic marine atmosphere, *Sci. Total Environ.* **16**, 239–248.

Millward, G. E., Nonsteady state simulations of the global mercury cycle, *J. Geophys. Res.* 87, 8891–8897.

National Academy of Sciences, 1978a, *Tropospheric Transport of Pollutants and Other Substances to the Ocean*, Report Nat. Acad. Sci., Washington, D.C.

National Academy of Sciences, 1978b, *An Assessment of Mercury in the Environment*, Report Nat. Acad. Sci., Washington, D.C.

Niki, H., Maker, P. D., Savage, C. M., Breitenbach, L. P., 1983, A long-path Fourier transform infrared study of the kinetics and mechanism for the OH-radical initiated oxidation of dimethylmercury, *J. Phys. Chem.* 87, 4978–4981.

Ottar, B., 1981, The transfer of airborne pollutants to the Arctic region, *Atmos. Environ.* **15**, 1439–1445.

Pheiffer Madsen, P., 1981, Peat bog records of atmospheric mercury deposition, *Nature* **293**, 127–130.

Phillips, G. F., Dixon, B. E., and Lidzey, R. G., 1959, The volatility of organo-mercury compounds, *J. Sci. Food Agric.* **10**, 604–610.

Pjankov, V. A., 1949, Kinetics of the reaction of mercury vapour with ozone, *Zhur. Obshestven. Khim.* 19, 224–229.

Prospero, J. M., Charlson, R. J., Mohnen, V., Jaenicke, R., Delany, A. C., Moyers, J., Zoller, W., Rahn, K., 1983, The atmospheric aerosol system: an overview, *Rev. Geophys. Space Phys.* 21, 1607–1629.

Rahn, K. A., 1975, Chemical composition of the atmospheric aerosol: A compilation, *Extern* **4**, 286–313.

Rawlings, G. D., 1974, Identification and measurement of the major chemical forms of mercury in urban atmospheres, Dissertation, Texas A & M University.

Ruppert, H., 1975, Geochemical investigations on atmospheric precipitation in a medium-sized city (Göttingen, F.R.G.), *Water, Air, Soil Pollut.* 4, 447–460.

Schlesinger, W. H., Reiners, W. A., and Knopman, D. S., 1974, Heavy metal concentrations and deposition in bulk precipitation in montane ecosystems of New Hampshire, U.S.A., *Environ. Pollut.* 6, 39–47.

Schroeder, W. H., 1981, Recent developments in the measurement of atmospheric mercury, *Canad. Res.* 14, 33–41.

Schroeder, W. H., 1982, Sampling and analysis of mercury and its compounds in the atmosphere, *Environ. Sci. Technol.* 16, 394A–400A.

Seiler, W., Eberling, C., and Slemr, F., 1980, Global distribution of gaseous mercury in the troposphere, *Pageoph* **118**, 964–974.

Sheffield, A., 1983, National inventory of sources and emissions of mercury (1978), Environment Canada, Report EPS-3-AP-81-1.

Slemr, F., Seiler, W., and Schuster, G., 1978, Quecksilber in der Troposphäre, *Ber. Bunsenges. Phys. Chem.* 82, 1142–1146.

Slemr, F., Seiler, W., Eberling, C., and Roggendorf, P., 1979, The determination of total gaseous mercury in air at background levels, *Anal. Chim. Acta* **110**, 35–47.

Slemr, F., Seiler, W., and Schuster, G., 1981, Latitudinal distribution of mercury over the Atlantic Ocean, *J. Geophys. Res.* **86**, 1159–1166.

Soldano, B. A., Bien, P., and Kwan, P., 1975, Air-borne organo-mercury and elemental mercury emissions with emphasis on central sewage facilities, *Atmos. Environ.* 9, 941–944.

Takizawa, Y., 1979, Epidemiology of mercury poisoning, in J. O. Nriagu (ed.), *The Biogeochemistry of Mercury in the Environment*, Elsevier/North-Holland Biomedical Press, Amsterdam.

Talmi, Y. and Mesmer, R. E., 1975, Studies on vaporization and halogen decomposition of methyl mercury compounds using GC with a microwave detector, *Water Res.* 9, 547–552.

Thompson, J. E., 1971, Air-borne mercury, in 'Hazards of Mercury', *Environ. Res.* 4, 1–69.

Thrane, K. E., 1978, Background levels in air of lead, cadmium, mercury, and some other chlorinated hydrocarbons measured in South Norway, *Atmos. Environ.* **12**, 1155–1161.

Wasik, S. P., Brown, R. L., Minor, J. I. Jr., 1976, Partition coefficients and solubility measurements of dimethylmercury in fresh and sea water over a temperature range 0–25°C, *J. Environ. Sci. Health* **A11**, 99–105.

Watson, W. D. Jr., 1979, Economic considerations in controlling mercury pollution, in *The Biogeochemistry of Mercury in the Environment*, Elsevier/North-Holland Biomedical Press, Amsterdam, pp. 41–77.

Weiss, H. V., Koide, M., and Goldberg, E. D., 1971, Mercury in a Greenland ice sheet: Evidence of recent input by man, *Science* **174**, 692–694.

Weiss, H. V., Bertine, K., Koide, M., and Goldberg, E. D., 1975, The chemical composition of a Greenland glacier, *Geochim. Cosmochim. Acta* **39**, 1–10.

Williston, S. H., 1968, Mercury in the atmosphere, *J. Geophys. Res.* **73**, 7051–7055.

Windom, H. L. and Taylor, F. E., 1979, The flux of mercury in the South Atlantic Bight, Deep-Sea Res. **26A**, 283–292.

Wolff, E. W. and Peel, D. A., 1985, The record of global pollution in polar snow and ice, *Nature* **313**, 535–540.

Wroblewski, S. C., Spittler, T. J., and Harrison, P. R., 1974, Mercury concentration in the atmosphere of Chicago, *J. Air Pollut. Control. Assoc.* **24**, 778–781.