

Antarctic Springtime Depletion of Atmospheric Mercury

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Unlike other heavy metals that are inherently associated with atmospheric aerosols, mercury in ambient air exists predominantly in the gaseous elemental form. Because of its prolonged atmospheric residence time, elemental mercury vapor is distributed on a global scale. Recently, Canadian researchers have discovered that total gaseous mercury levels in the lower tropospheric boundary layer in the Canadian Arctic are often significantly depleted during the months after polar sunrise. A possible explanation may involve oxidation of elemental mercury, followed by adsorption and deposition of the oxidized form, leading to an increased input of atmospheric mercury into the Arctic ecosystem. Here we present the first continuous high-time-resolution measurements of total gaseous mercury in the Antarctic covering a 12-month period between January 2000 and January 2001 at the German Antarctic research station Neumayer (70°39' S, 8°15' W). We report that mercury depletion events also occur in the Antarctic after polar sunrise and compare our measurements with a data set from Alert, Nunavut, Canada. We also present indications that BrO radicals and ozone play a key role in the boundary-layer chemistry during springtime mercury depletion events in the Antarctic troposphere.

Introduction

Mercury as a Global Pollutant. Long-range atmospheric transport of mercury, its transformation to more toxic

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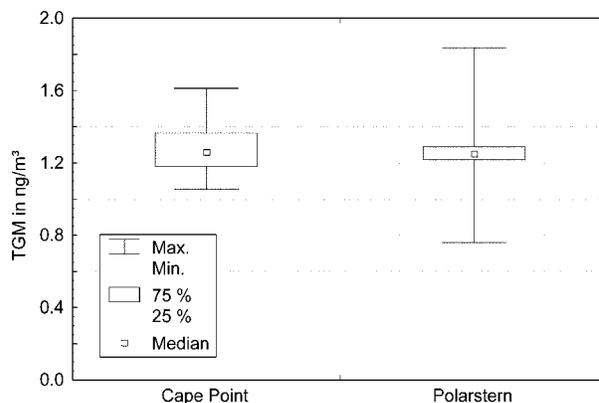


FIGURE 1. Whisker and box plot representation of the background concentrations of total gaseous mercury measured with two different methods in the Southern Hemisphere in the time period between December 1999 and January 2000. An automatic Tekran analyzer was running on board the German RV *Polarstern* on the way from Germany to Antarctica, and all TGM concentrations south of the ITCZ (inter-tropical convergence zone) were plotted. A different method with manual sampling of mercury on gold- or silver-coated quartz wool was used at the Global Atmosphere Watch (GAW) station at Cape Point, South Africa.

methylmercury compounds, and the substantial bioaccumulation mainly in the aquatic food chain have motivated intensive research on mercury as a pollutant of global concern. A low aqueous solubility and chemical reactivity of elemental mercury (Hg^0), which is by far the dominating component of total gaseous mercury (1, 2), are the major reasons for its long atmospheric residence time. This long lifetime permits long-range atmospheric transport of mercury to regions far from centers of anthropogenic activity, for example, the Atlantic and Pacific Oceans and the Arctic (3–8). The background concentration of total gaseous mercury (TGM) is generally around 1.7 and 1.3 ng m^{-3} in the lower troposphere of the Northern and Southern Hemispheres, respectively (4).

Atmospheric Cycling of Mercury in Polar Regions.

Recently, highly time-resolved TGM measurements in the Arctic have shown that lower tropospheric TGM levels are at times significantly depleted, while mercury concentrations in snow are concurrently increased during the first three months after polar sunrise (9–11). A possible explanation may involve chemical or photochemical oxidation of Hg^0 to Hg^{2+} [resulting either in particle-associated mercury (PM) and/or reactive gaseous mercury (RGM) species (12)] and significantly enhanced deposition fluxes of mercury leading to unequivocally increased input of atmospheric mercury into the Arctic ecosystem (9). The Arctic TGM depletion phenomenon is strongly correlated with ground-level ozone depletion episodes (9). These tropospheric ozone loss events in the Arctic are associated with enhanced bromine monoxide concentrations in the free troposphere (13). It is hypothesized that Br atoms and/or BrO radicals are involved in a chemical reaction that destroys ozone (14). The following depletion of atmospheric boundary-layer mercury (at times up to an altitude of ≈ 1 km) is due to a reaction between gaseous elemental mercury and BrO free radicals (15, 16).

Recent studies have reported short-term boundary-layer ozone depletion events for the Antarctic (17). At Neumayer [relative to the beginning of spring in both hemispheres (see Table 3)], the ozone depletion events occur 1–2 months earlier than in the Arctic, are less frequent, and are of shorter

TABLE 1. Comparison of Mean TGM Concentrations Measured from Manual Injections of Mercury-Saturated Air with the Calculated Theoretical Value of the Reference Material (Pure Elemental Mercury)

date	instrument	<i>n</i>	calcd theor value (ng m ⁻³)	measd mean concn with 95% conf. limit (ng m ⁻³)	<i>t</i> -test value	95% <i>t</i> -distrib value (two-sided)
02/12/99 (GKSS)	Tekran 2537A (082) direct injection	7	28.554	29.456 ± 1.455	1.52	2.45
14/02/00 (Neumayer)	Tekran 2537A (082) inj in heated sample line	3	11.330	11.354 ± 0.451	0.23	4.30
18/07/01 (GKSS)	Tekran 2537A (082) direct injection	10	17.568	17.557 ± 0.372	0.07	2.26
19/07/01 (GKSS)	Tekran 2537A (083) direct injection	10	17.568	17.359 ± 0.391	1.27	2.26

TABLE 2. Statistical Data from Background Concentrations of Total Gaseous Mercury Measured with Two Different Methods in the Southern Hemisphere in the Time Period between December 1999 and January 2000

site	<i>n</i>	median	min.	max.	range	lower quartile	upper quartile	interquartile range
Cape Point station (34° S, 18° E)	59	1.261	1.054	1.612	0.558	1.178	1.367	0.188
Polarstern (2–70° S)	1612	1.251	0.758	1.835	1.077	1.216	1.290	0.075

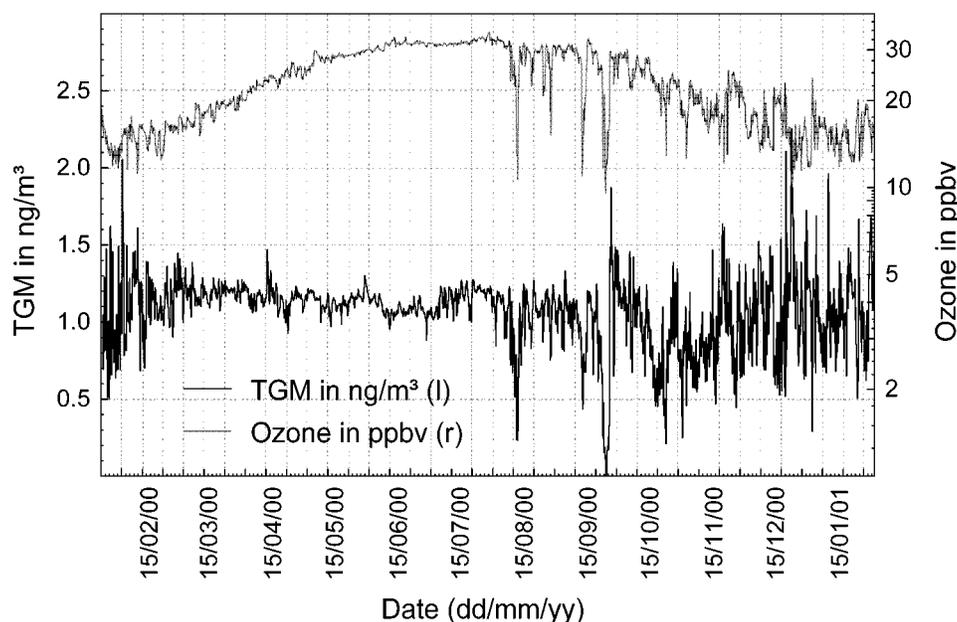


FIGURE 2. Annual time series of 1-h averaged TGM and surface-level ozone concentrations at Neumayer, January 2000–January 2001. The TGM concentrations were obtained from two separate Tekran analyzers, and mean values were used if both analyzers were operating in parallel. Ozone concentrations are mixing ratios by volume (1 ppbv = one part per billion by volume).

duration (18). Strong and sudden increases in the tropospheric BrO mixing ratio during spring were also found for the Antarctic using differential optical absorption spectrometry (DOAS) measurements (19) and observations from satellite instruments (13, 20). Friess (21) documented that the numerous strong and sudden enhancements of BrO detected during August and September 1999 and 2000 at Neumayer are caused by BrO located in the lower troposphere, released by well-known autocatalytic processes on acidified sea-salt surfaces. The strong depletion of near-surface ozone is caused by catalytic cycles involving bromine (21).

The measurements reported here comprise the first annual time series of ground-level TGM concentrations in the Antarctic to investigate the occurrence of possible mercury depletion events (MDEs) in south polar regions. This study also provides high-resolution data of total gaseous mercury concentrations in the Antarctic that can be com-

pared with existing data sets of MDEs in the Arctic to reveal similarities and differences in the temporal and quantitative sequence of MDEs after polar sunrise.

Experimental Section

Sampling Location. In the period from January 2000 to January 2001, highly time-resolved measurements of TGM were carried out at the German Antarctic research station Neumayer, operated throughout the year by the Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany. The site is located at 70°39' S, 8°15' W on the Ekströmmisen, about 8 km from Atka Bay. At Neumayer, the maximum solar incidence angle is 42.8°. The sun stays permanently above the horizon from November 19 to January 24 and permanently below the horizon from May 19 to July 27. The analyzers were installed at the Neumayer Air Chemistry Observatory (ACO), which is approximately 1.6 km south of the main site. The new observatory (since January

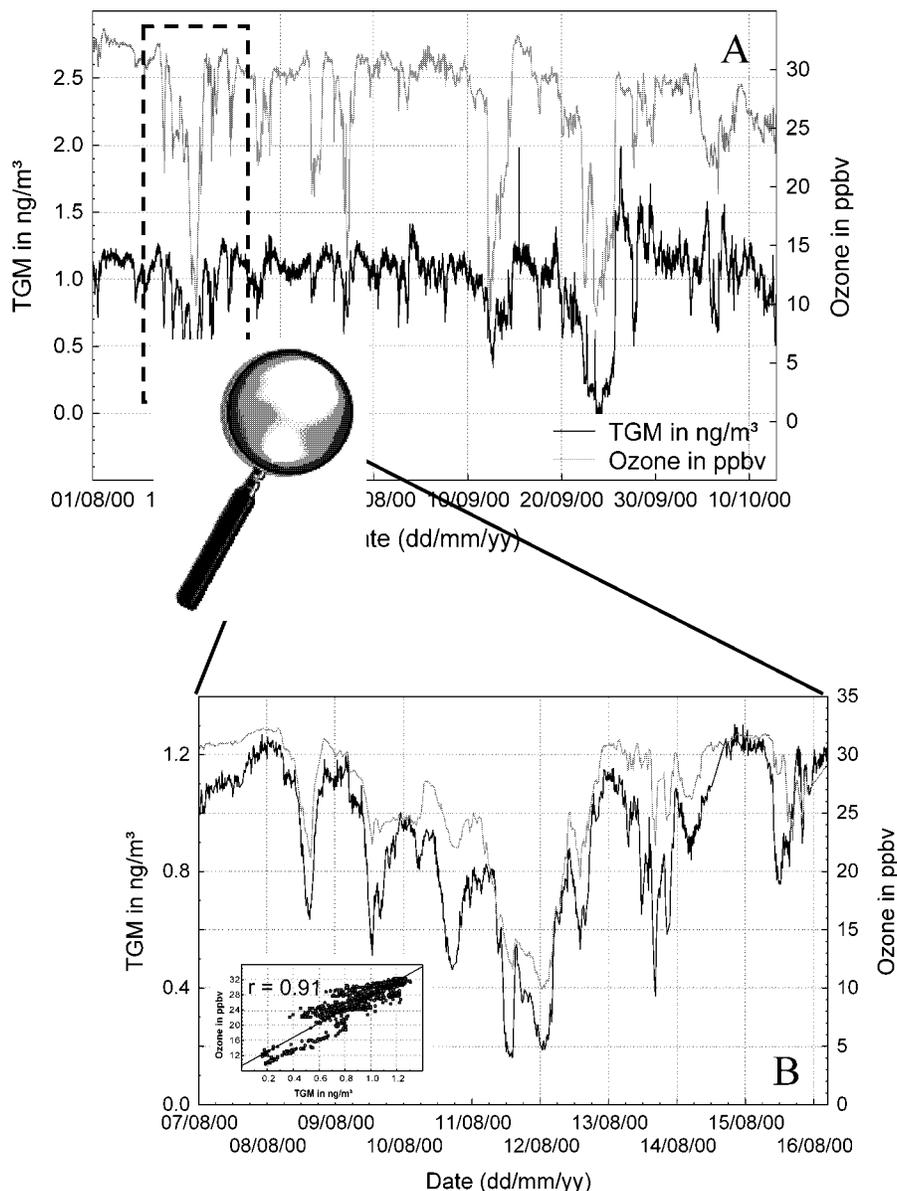


FIGURE 3. Ozone and TGM concentrations during the MDEs from August to October 2000 (A) and for the first event at the beginning of August 2000 (B). TGM concentrations are mean values from two separate analyzers in the highest time resolution (15 min). Ozone concentrations are 15-min averaged surface-level ozone concentrations. Both analyzers (ozone and TGM) were running at the Neumayer Air Chemistry Observatory and were measuring concentrations in the planetary boundary layer. The scatter plot of the depletion events from the 7th to the 16th of August 2000 reveals a high correlation coefficient of $r = 0.91$ between ozone and TGM concentrations.

1995) was designed as a container building placed on a platform some meters above the snow. It is used as a large clean air laboratory to study one of the undisturbed parts of the earth's atmosphere. Local pollution by vehicles and the base itself can be a potential problem for many measurements concerning the background status of the Antarctic troposphere. But because the prevailing wind direction is from the east and the northern wind direction is very rare, contamination from the base can be excluded most of the time. Nevertheless, supplementary control of the contamination situation is done (wind direction, wind speed, condensation nuclei, snow drift, PAH concentration).

Instruments. Two Tekran gas-phase mercury vapor analyzers (model 2537A) were installed at Neumayer Station in January 2000. The setup, accuracy, and precision of this instrument has been assessed during field intercomparisons at an urban/industrial site (6) and at a remote marine background location (22). The Tekran analyzers were operated with a 15-min integrated sampling frequency. The

sample inlet with a drift protection (no filter) was located 6 m above the snow surface on top of the ACO. The air was sampled at a flow rate of 1.0 L min^{-1} through a heated sample line about 10 m in length. Each Tekran analyzer has its own Teflon tube running through the same heated sample line and ending up with a $0.45\text{-}\mu\text{m}$ PTFE filter in front of the inlet of the analyzer. The analyzers were calibrated every 25 h with an internal automatic permeation source injection. Additional manual injections through the heated Teflon line were also carried out to ensure the reproducibility of the sampling line (see Quality Control paragraph). The detection limit for TGM in this operation mode is better than 0.1 ng m^{-3} .

BrO total density values were generated at the University of Bremen using the DOAS algorithm on operational GOME (Global Ozone Monitoring Experiment) level-1 data as described in ref 23. Both stratospheric and tropospheric BrO contribute to the observed columns. As the spatial and temporal variability of stratospheric BrO is small, all the

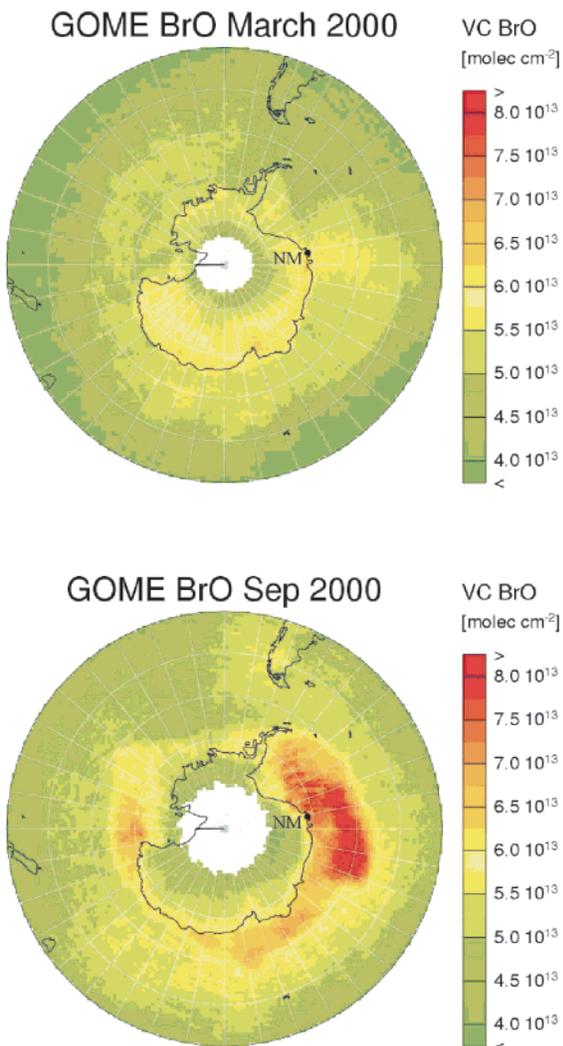


FIGURE 4. GOME (Global Ozone Monitoring Experiment) observations of the BrO vertical column density over the Antarctic from March and September 2000 (NM = Neumayer Station at 70°39' S, 8°15' W). The areas where elevated tropospheric BrO concentrations build up and decay are clearly visible around the Antarctic continent (no satellite data are available for the white areas on the map).

enhanced BrO values above the Antarctic ice sheet are attributed to large tropospheric concentrations of BrO. Furthermore, under both clear and cloudy sky conditions, BrO densities have been observed within the range of typical stratospheric values, whereas significantly enhanced BrO densities were only detected under clear sky conditions when the spectrometers aboard the satellite were able to measure deep down into the troposphere. Ozone mixing ratios were measured continuously by means of an Ansyco ozone analyzer (model O341M) based on UV absorption with a detection limit of 1 ppbv.

Quality Control. To ensure the repeatability of the measurements, the following sampling protocol was used at Neumayer: For quality assurance, two analyzers were operated in parallel for 1 week. When the correspondence of the two Tekran analyzers had been tested and quantified, one analyzer started measuring TGM for the next 3 weeks, and the other one was turned off. The next comparison followed after 3 weeks as described above. After polar sunrise in August 2000, both analyzers were operating in parallel during the time interval between Antarctic springtime and the end of the measurement period. Beside the calibrations,

automated standard additions had been carried out every 8.75 h over the entire measurement period to check the sensitivity of the signal and therefore the stability of the detector response and the internal permeation source. The accuracy of the measurements was verified by manual injections of a known volume of air from a saturated mercury vapor atmosphere at a known temperature. This procedure was applied before, during, and after the analyzers were running in the chemical observatory at Neumayer between January 2000 and January 2001 (Table 1).

In each case, the critical values obtained from a *t*-table at *P* = 95% and the particular degrees of freedom are bigger than the calculated mean from the measured TGM concentrations. There are no significant differences between the theoretical and the measured values.

The results in Table 1 confirm the accuracy of this method. To demonstrate the trueness of the results, further comparative measurements of TGM with two different methods were carried out before the instruments had been set up at Neumayer. One of the Tekran analyzer was operated on board the German RV *Polarstern* on the way from Germany to the Antarctic between December 1999 and January 2000 to investigate and understand the mercury distribution on a global scale with the background of an inter-hemispheric gradient (F. Slemr, personal communication).

These *Polarstern* TGM measurement results can be compared with TGM data obtained at the same time with a different method at the Global Atmosphere Watch (GAW) station at Cape Point, South Africa, operated by the South African Weather Bureau and the Fraunhofer Institute for Atmospheric Environmental Research, Germany. It is one of the most important measurement sites in the Southern Hemisphere to get information about background concentrations of environmentally important trace gases. Previous studies (4, 24) have shown that total gaseous mercury background concentrations over the Atlantic Ocean in the Southern Hemisphere are very homogeneous and are about 25% lower than the Northern Hemispherical TGM background concentrations.

At this station, total gaseous mercury was collected manually on gold- or silver-coated quartz wool and analyzed by atomic fluorescence spectroscopy. This technique was also validated by an international intercomparison conducted at Mace Head, Ireland, in 1995 (22).

The results are shown in Figure 1 and Table 2. A robust statistic with a median instead of a mean value is used because the analytical data are contaminated by outliers and conform only broadly to a normal distribution. It can be shown that the results obtained on similar air masses with both methods are in good agreement; therefore, it can be considered that the results from each method are true. This intercomparison also reconfirms the homogeneous distribution of atmospheric mercury in the Southern Hemisphere far away from centers of anthropogenic emissions.

Results and Discussion

First Annual Time Series of TGM in Antarctica. The results of TGM measurements and ground-level ozone concentrations for the time period January 2000 to January 2001 are presented in Figure 2. The arithmetic mean of all TGM measurements between January 2000 and January 2001 was $1.063 \pm 0.235 \text{ ng m}^{-3}$ whereby the complete data set conform only broadly to a normal distribution. The TGM data can briefly be characterized for three different time periods:

(i) Between January and February 2000 and December 2000–February 2001, TGM concentrations were highly variable ($1.043 \pm 0.284 \text{ ng m}^{-3}$). During this time period, TGM and ozone concentrations are frequently negatively correlated. High concentration peaks of more than 2.0 ng

First: 15 min TGM / lag: 15 min ozone

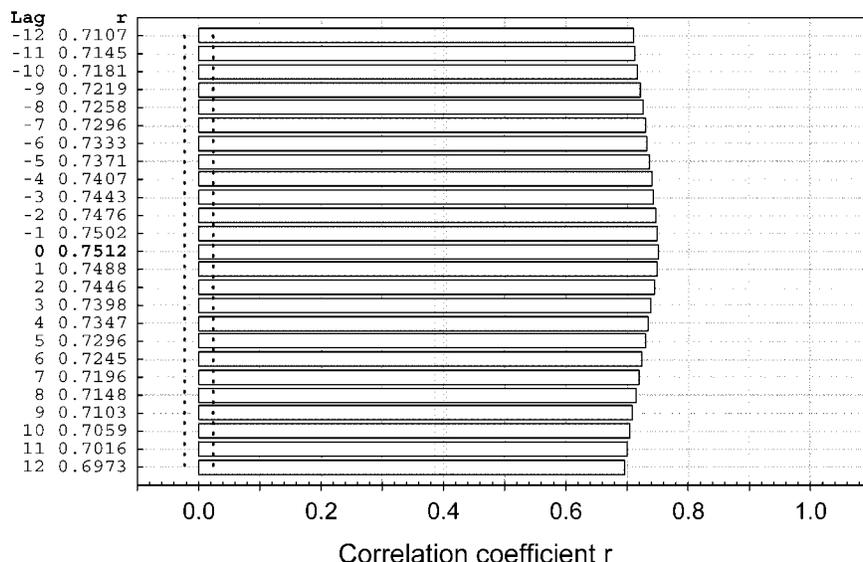


FIGURE 5. Cross-correlation function of TGM (mean values from two separate analyzers in the highest time resolution [15 min]) and 15-min averaged ground-level ozone concentrations during the mercury depletion events (MDEs) from August to October 2000. The highest correlation coefficient ($r = 0.75$) is found at a lag-time of zero.

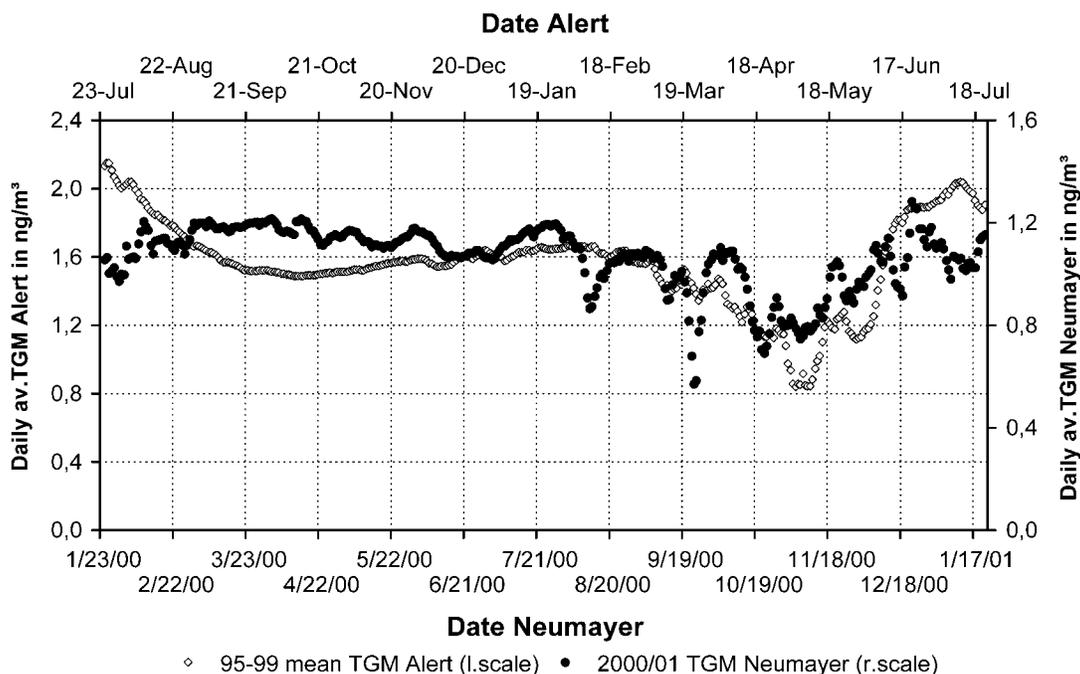


FIGURE 6. Comparison of the annual time series of total gaseous mercury concentrations in the Antarctic (Neumayer) and Arctic (Alert). (◇) mean of daily averages from 1995 to 1999 TGM concentrations at Alert, (●) daily averages of TGM concentrations at Neumayer (2000/2001). All data are exponentially smoothed with $\alpha = 0.2$. The Alert time scale is shifted by 182 days as compared to the Neumayer time scale (Table 3).

m^{-3} can be related to anthropogenic activities near the ACO during summer campaigns.

(ii) Between March and July 2000, the TGM concentrations remained at a fairly constant level of $1.146 \pm 0.075 \text{ ng m}^{-3}$ while ozone concentrations constantly increased. This background level of TGM is in good agreement with the average background concentrations in the Southern Hemisphere, presented in Figure 1 and Table 2.

(iii) Between August and November 2000, several simultaneous depletion events of surface-level TGM and ozone were detected with minimum daily average TGM concentrations of about 0.1 ng m^{-3} . The arithmetic mean during MDEs

was calculated with $0.958 \pm 0.278 \text{ ng m}^{-3}$. In the following, we want to focus on this third period where MDEs occur concurrently with ozone depletions in the troposphere during Antarctic springtime.

Correlation Analysis. The correlation analysis of the complete TGM and ozone data set from January 2000 to January 2001 yields a very low correlation coefficient of $r = 0.09$; hence, no linear relationship among these two variables is evident. But the TGM concentration pattern between August and October 2000 shows a strong positive correlation with ozone (Figure 3A). Statistical analysis of these time series has revealed a highly significant correlation coefficient of r

TABLE 3. Climatological Seasons and Their Corresponding Julian Days for the Antarctic and the Arctic

season	Julian day	
	Antarctic	Arctic
spring	244–334	60–151
summer	335–59	152–243
autumn	60–151	244–334
winter	152–243	335–59

= 0.75 (see maximum at lag = 0 in Figure 5) for the complete springtime events between ozone and TGM, which is complementary to the data reported for the Canadian Arctic (9). Single depletion events of a few days (Figure 3B) even show a stronger correlation between TGM and surface-level ozone ($r = 0.91$).

BrO Radicals. It could also be shown that MDEs coincide with enhanced occurrence of BrO radicals in the Antarctic atmosphere during springtime as measured from the satellite-based GOME instrument (Figure 4). The GOME satellite pictures show clouds of enhanced BrO on the sea ice around the Antarctic continent after polar sunrise (September). Air masses at ground coming from the sea ice surface, accompanied by BrO enhancements, could be a necessary prerequisite for the MDEs at Neumayer. Possible sources and precursors of BrO at this region have been investigated by Friess (21).

Timing of Atmospheric Reaction during MDEs. The maximum in the cross-correlation function of ozone and TGM in the highest time resolution during the depletion events between August and October 2000 occurs at a lag of zero (Figure 5). Thus, it appears that the suggested reaction involving ozone, Br atoms, and/or the resulting BrO radicals along with vapor-phase elemental mercury (i) must be a very fast (photochemically induced/mediated) reaction that is completed on-site in less than 15 min within the sampled air-mass or (ii) has already occurred before the depleted air parcels are advected to the measurement location.

Comparison with the Arctic. Figure 6 shows the first comparison of total gaseous mercury concentrations in the two polar regions. The daily average concentrations of TGM at Neumayer 2000/2001 with MDEs during Antarctic springtime (August–November) are compared with the mean daily average concentrations of the 1995–1999 TGM concentrations measured at Alert, Nunavut, Canada (82°28' N, 62°30' W), showing the Arctic MDEs between March and June. Note that the Alert time scale is shifted by 182 days as compared to the Neumayer time scale (Table 3).

At Neumayer, the first MDEs occur about 1–2 months earlier than in the Arctic at Alert. We suggest that the relatively earlier beginning of mercury depletion events after polar sunrise in the Antarctic is due to the following reasons:

(i) The different latitudinal positions of the two sampling sites. Neumayer is located at 70° S, and the sun comes up for the first time on July 27 each year, whereas Alert has a position of 82° N, and polar sunrise takes place by about March 1. Therefore a time difference in the beginning of MDEs of about 35 days could be related to the relatively different beginning of local sunrise.

(ii) Most of the sea ice where enhanced BrO concentrations are found (Figure 4) is located north of Neumayer station at lower latitudes and can cover the ocean up to 55° S at the end of the Antarctic winter. The Arctic sea ice is found north of Alert at higher latitudes and around the North Pole. Therefore, the sea ice as a possible place where the photochemical reaction of ozone and Br atoms and/or the following reaction of BrO radicals and vapor-phase elemental mercury can take place is exposed much earlier to the sun in the Antarctic than in the Arctic during the springtime.

The annual time series measured at the Neumayer station gives clear evidence that MDEs do also occur in the Antarctic. Furthermore, it is evident that MDEs coincide with ozone depletion events in the lower troposphere and that the hypothesis is supported that free BrO radicals are involved.

MDEs can be expected to result in an increased input of atmospheric mercury in the comparatively short springtime period in polar regions when the ecosystem is initiating the highest biological activity, and they are therefore an important feature in the global cycle of this pollutant. Further studies are necessary to explain the reaction mechanism and the kinetics of the MDEs identified during our measurements in the Antarctic. It is also important to combine these results with trajectory calculations in combination with sea ice maps in order to investigate the origin of the depleted air masses and the actual places of the chemical reaction involving ozone, reactive bromine species, and elemental mercury, respectively.

Acknowledgments

We thank G. König-Langlo and R. Weller of the Alfred Wegener Institute for their assistance in providing the meteorological and supplementary chemical data for the Neumayer Station. Special thanks go to F. Slemr from the Fraunhofer Institute for Atmospheric Environmental Research and E.-G. Brunke from the South African Weather Bureau for their cooperation in carrying out the intercomparison of background concentrations in the Southern Hemisphere in order to investigate the accuracy of our instruments. We also thank W. Winkler from Seefelder Messtechnik GmbH and F. Schaedlich from Tekran Inc. for the support of analytical equipment. Calibrated GOME level-1 data were provided by the ESA through DFD/DLR Oberpfaffenhofen, Germany. All meteorological data for the German Neumayer Station can be obtained from <http://www.awi-bremerhaven.de>. Further information about atmospheric mercury in polar regions is also available from Environment Canada (<http://www.ec.gc.ca>). Satellite data of ozone and BrO can be requested from <http://www.iup.physik.uni-bremen.de>.

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Received for review September 20, 2001. Revised manuscript received November 27, 2001. Accepted December 20, 2001.

ES015710Z