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Atmospheric mercury observations from Antarctica: seasonal variation and source and sink region calculations

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Abstract. Long term atmospheric mercury measurements in the Southern Hemisphere are scarce and in Antarctica completely absent. Recent studies have shown that the Antarctic continent plays an important role in the global mercury cycle. Therefore, long term measurements of gaseous elemental mercury (GEM) were initiated at the Norwegian Antarctic Research Station, Troll (TRS) in order to improve our understanding of atmospheric transport, transformation and removal processes of GEM. GEM measurements started in February 2007 and are still ongoing, and this paper presents results from the first four years. The mean annual GEM concentration of $0.93 \pm 0.19\,\mathrm{ng\,m^{-3}}$ is in good agreement with other recent southern-hemispheric measurements. Measurements of GEM were combined with the output of the Lagrangian particle dispersion model FLEXPART, for a statistical analysis of GEM source and sink regions. It was found that the ocean is a source of GEM to TRS year round, especially in summer and fall. On time scales of up to 20 days, there is little direct transport of GEM to TRS from Southern Hemisphere continents, but sources there are important for determining the overall GEM load in the Southern Hemisphere and for the mean GEM concentration at TRS. Further, the sea ice and marginal ice zones are GEM sinks in spring as also seen in the Arctic, but the Antarctic oceanic sink seems weaker. Contrary to the Arctic, a strong summer time GEM sink was found, when air originates from the Antarctic plateau, which shows that the summertime removal mechanism of GEM is completely different and is caused by other chemical processes than the springtime atmospheric mercury depletion events. The results were corroborated by an analysis of ozone source and sink regions.

1 Introduction

Antarctica is the most remote of all continents and is usually perceived as an isolated and hostile place and a symbol of the last great wilderness untouched by human disturbance. However, like other remote regions on Earth, it is not escaping the impact of local pollutant emissions due to increasing human presence and pollution imported from other continents (Priddle, 2002; Bargagli, 2005; Bergstrom et al., 2006; Stohl and Sodemann, 2010). Mercury behaves exceptionally for a metal in the environment; it has a very complex biogeochemical cycle and exists in a variety of forms in the atmosphere, such as gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM) and particulate bound mercury (PBM). The discovery of a unique scavenging process called atmospheric mercury depletion events (AMDEs), where the concentration of atmospheric mercury drops precipitously within hours (Schroeder et al., 1998), resulted in intensified research on atmospheric mercury. Mercury is now being monitored at many sites, although mainly in the Northern Hemisphere. Measurements in the Southern Hemisphere are generally scarce and particularly in the Antarctic regions mainly sporadic measurements have been made. Efforts have been initiated to study AMDEs at coastal sites (Ebinghaus et al., 2002; Temme et al., 2003a; Sprovieri et al., 2002; Brooks et al., 2008a) and more recently the Antarctic plateau has become a new focus of attention (Brooks et al., 2008b). These efforts show us that we currently underestimate the role of this continent in the global mercury cycle (Dommergue et al., 2010). Intensive measurement campaigns with extensive measurement programs provide large amounts of information that

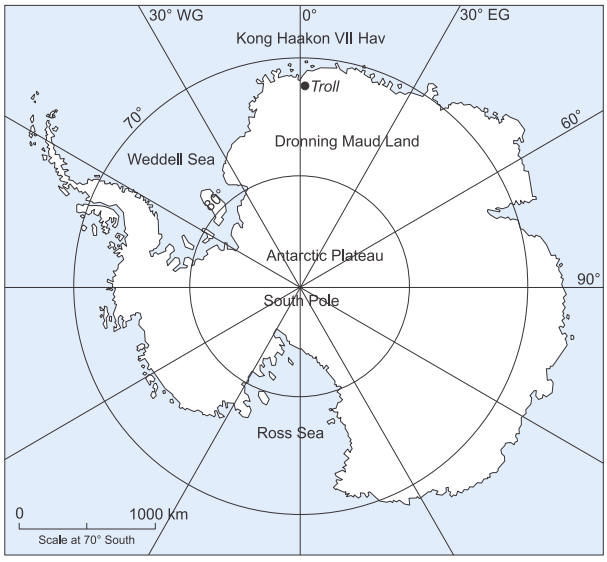

Fig. 1. Map of Antarctica indicating the location of TRS and other geographical areas referred to in the text.

apply to a short time period, however, care should be taken when extrapolating to annual budgets and large geographical areas. Long term monitoring can provide valuable information on seasonal and annual variation as well as long term concentration trends, and hence the global mercury cycle. Combining such large data sets with corresponding atmospheric transport model output allows a statistical analysis of the sources and sinks of mercury in large regions around the measurement site (Hirdman et al., 2009) by investigating the origin of high and, respectively, low measured mercury concentrations.

To extend the global mercury database and improve the current understanding of the atmospheric transport, transformation and removal processes of GEM over Antarctica, long-term monitoring of GEM at the Norwegian research station Troll was started in 2007. The data from Troll is to our knowledge the longest times series of GEM from the Antarctic continent and measurements are still ongoing. In this study we present seasonal and annual GEM concentration variations and present a statistical analysis of the source- and sink regions for GEM observed at Troll.

2 Methods

2.1 Site description

The Norwegian Antarctic Troll Research Station (TRS) is located in Queen Maud Land at 72°01′ S, 2°32′ E at an elevation of 1275 m and approximately 220 km from the Antarctic coast (Fig. 1). TRS is situated on snow-free bedrock and accessible by air-transport during Antarctic summer, facilitated by a blue-ice airfield on the glacier 7 km north of the main station. After TRS was turned from a summer into an all-year station in 2005, the *Norwegian Institute for Air Research* (NILU) deployed a container-housed atmospheric observatory in February 2007. TRS is one of the few stations located on the slope of the Antarctic ice sheet (and the only one manned year-round). It is exposed to a varying influence from both the Antarctic plateau and the Southern Ocean, while the environment at other long-term activity stations either is of coastal or high-elevation continental nature. A detailed description of TRS can be found in Hansen et al. (2009) along with meteorological conditions, instrument set-up and some first results.

2.2 Experimental

Measurements of GEM were initiated in February 2007. A Tekran gas phase analyser (Model 2537A, Tekran Inc) was installed to collect and determine GEM concentrations in air. The instrument was programmed to sample air at a flow rate of 1.5 lpm with a 5 min time resolution. For data analysis, 1 h averages were used, unless otherwise stated. Auto calibrations were performed every 25 h using the instrument's internal calibration source. The internal calibration source was checked against manual injections using a Tekran mercury vapour primary calibration unit (Model 2505, Tekran Inc) once per year. Injections were performed on mercury free air generated by a Tekran zero air generator (Model 1100, Tekran Inc). The accuracy as determined by the internal calibration source verification was better than 2 %. The sample inlet is located approximately 6 m above surface. The sample stream is filtered at the inlet using a 2µm Teflon filter. Due to the extremely cold and dry Antarctic air, no heated sample line was used and no soda lime was applied. The quality assurance and control protocol applied on all data left a data coverage of more than 94 % during the entire sampling period. More details on quality control can be found in Berg et al. (2003) and Aspmo et al. (2005). Additionally, atmospheric in situ concentrations of ozone were recorded by UV absorption spectrometry (API 400). Ozone (O_3) concentrations were measured with 1-min time resolution, and 1 h averages were used for data analysis, unless otherwise stated. More details on O_3 measurements can be found in Hansen et al. (2009). For the analysis of source regions, GEM and O_3 data were averaged to 3 h to fit with the time resolution of our transport model output.

2.3 Source and sink region analysis

To identify sources and sinks of measured GEM and O_3, 3-hourly backward simulations from TRS with the Lagrangian particle dispersion model FLEXPART (Stohl et al., 1998, 2005) were used. FLEXPART was driven with 3-hourly operational meteorological data from the European Centre for Medium-Range Weather Forecasts with $1° \times 1°$ resolution.

During every 3-h interval, 60 000 particles were released at the measurement point and followed backward for 20 days to calculate emission sensitivity (S) on a $1^\circ \times 1^\circ$ grid, under the assumption that removal processes can be neglected. S (in units of s m^{-3}) in a particular grid cell is proportional to the particle residence time in that cell and measures the simulated concentration at the receptor that a source of unit strength (1 kg s^{-1}) in the cell would produce. The S distribution in a 100 m layer adjacent to the surface (so-called footprint layer) was used as input to the statistical analysis of surface sources and sinks. A statistical method described in detail in Hirdman et al. (2009, 2010) was used to identify possible source and sink regions of GEM. The method is similar to older methods based on trajectory calculations (Ashbaugh, 1983; Ashbaugh et al., 1985) but takes advantage of the superior quality of Lagrangian particle dispersion model output compared to simple trajectories, which ignore turbulence and convection. Every one of M measurements were related to a modelled footprint S field, and the average footprint S_T was calculated as

$$S_T(i,j) = \frac{1}{M}\sum_{m=1}^{M} S(i,j,m) \quad (1)$$

where i, j are grid indices of S. Then, the subset of the data with the highest 10 % (or, respectively, lowest 10 %) of measured GEM concentrations was selected to calculate

$$S_P(i,j) = \frac{1}{L}\sum_{l=1}^{L} S(i,j,l) \quad (2)$$

where the suffix P indicates the percentile (10 % or 90 %). Calculations of the 10th and 90th percentiles for GEM and O_3 concentrations were made for each month separately and for each year with available measurements. Thereafter, the results for the months in each predefined season were combined together over the whole time period (2007–2010). The ratio

$$R_P(i,j) = \frac{L}{M}\frac{S_P(i,j)}{S_T(i,j)} \quad (3)$$

can then be used for identifying grid cells that are likely sources (or sinks) of GEM. If air mass transport patterns were the same for the data subset and for the full data set, one would expect $R_p(i,j) = 0.1$ for all i,j. Information on sources and sinks of GEM are contained in the deviations from this expected value. For the top decile of the data, for instance, $R_{90}(i,j) > 0.1$ means that high measured GEM concentrations are associated preferentially with high S values in grid cell (i,j), indicating a likely source, whereas $R_{90}(i,j) < 0.1$ indicates a possible sink or at least the absence of a source. Conversely, when using the lowest decile of the data, $R_{10}(i,j) > 0.1$ indicates a likely sink in grid cell (i,j), and $R_{10}(i,j) < 0.1$ a source or at least the absence of a sink.

Not all features of R_P are statistically significant. Therefore, calculation of R_P was limited to grid cells where $S_T > 5 \times 10^{-9}$ s m^{-3} and a bootstrap resampling analysis was employed to ensure statistical significance. For more details on the method, see Hirdman et al. (2009, 2010).

3 Results and discussion

3.1 Mercury concentrations at TRS compared to Zeppelin (Spitsbergen, Arctic) and measurements in the Southern Hemisphere

The arithmetic mean GEM concentration during more than four years of continuous measurements at TRS was 0.93 ± 0.19 ng m^{-3}, whereas the median concentration was 0.97 ng m^{-3}. This is, to the best of the authors' knowledge, the longest time series of GEM from the Antarctic continent and the only annual time series covering more than a year. The mean GEM concentration observed at TRS is in good agreement with other recent observations from high latitudes in the Southern Hemisphere (Ebinghaus et al., 2002; Xia et a., 2010; Temme et al., 2003b). Figure 2a shows a box and whisker plot comparing NILUs Antarctic GEM measurements at TRS and Arctic GEM measurements obtained at Zeppelin station, Spitsbergen (78°54′ N, 11°52′ E). As shown in Fig. 2a, the annual concentration variability is rather similar at the two locations, whereas the distribution is shifted towards lower concentrations at TRS. The GEM concentrations observed at TRS are only about two-thirds of the GEM concentrations at Zeppelin (1.57 ng m^{-3}, annual average 2007–2010). The mean concentration at Zeppelin falls within the range of what is being considered the northern-hemispheric background concentration, 1.5–1.7 ng m^{-3} (Slemr et al., 2003). GEM concentrations observed in the Southern Hemisphere are lower because most of the mercury emission sources are located in the Northern Hemisphere (Pacyna et al., 2006) and in the atmosphere the lifetime of GEM (Schroeder and Munthe, 1995) is not long enough for homogeneous mixing on a global scale. At Cape Point, South Africa, Slemr et al. (2008) observed a small significant decrease in atmospheric mercury concentrations from 1.29 ng m^{-3} in 1996 to 1.19 ng m^{-3} in 2004. This decline in concentration has continued and Brunke et al. (2010) reported GEM concentrations from Cape Point from 2007 and 2008 to be 0.94 ± 0.16 ng m^{-3}. Slemr et al. (2003) suggested a small negative concentration gradient of GEM towards high southerly latitudes, as the median GEM concentration observed at the German Antarctic research station Neumayer in 2000 and 2001 was 1.10 ng m^{-3} (Ebinghaus, 2002). However, this southward decreasing concentration gradient is not apparent in the data presented here as the concentrations at Cape Point and TRS are practically equal. Our time series is not long enough for trend analysis, but the data presented here does not show any change in

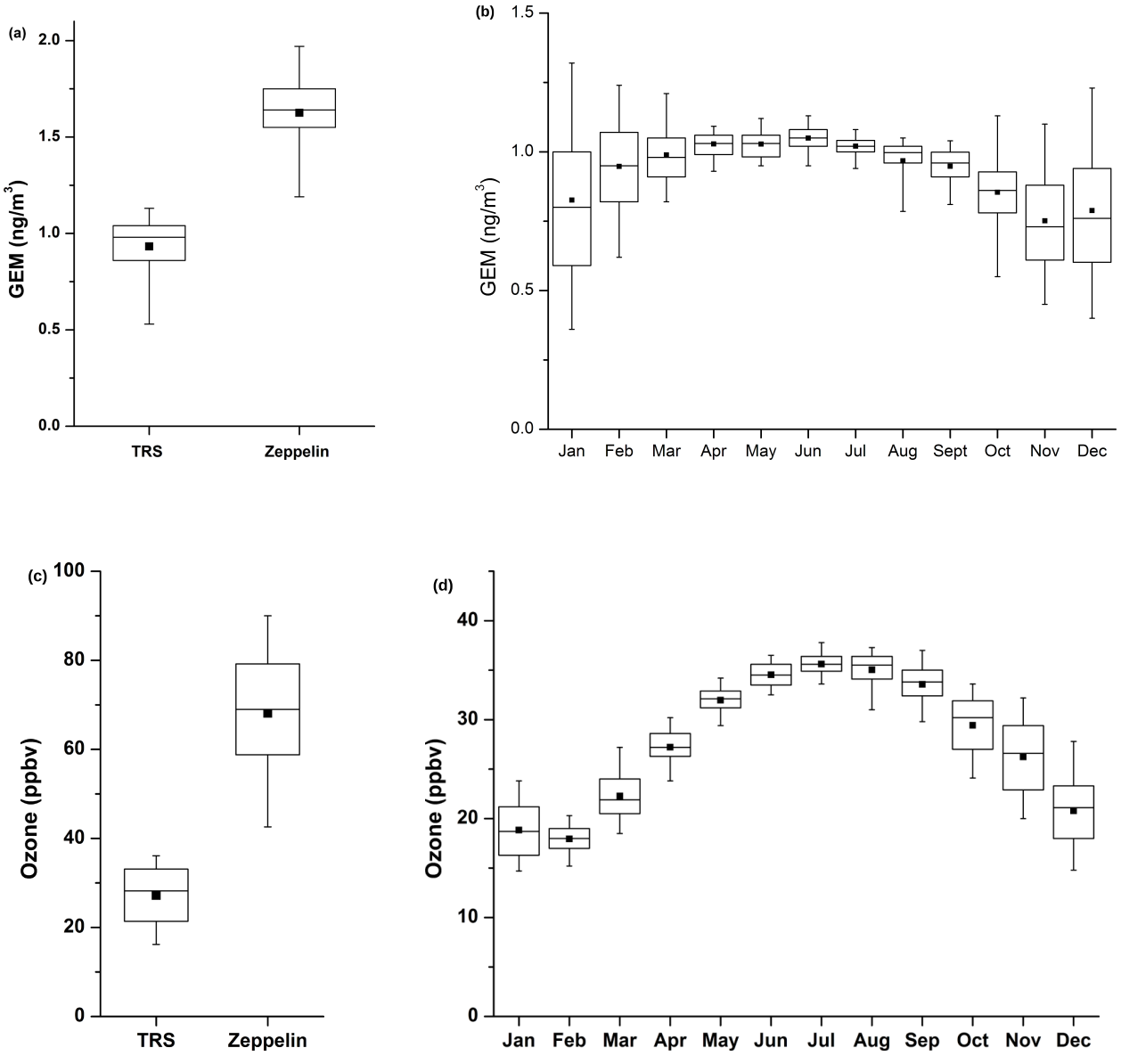

Fig. 2. **(a)** Box and whisker plot presenting the concentration distribution of GEM measurements at TRS (Antarctic) and Zeppelin (Arctic). **(b)** Box and whisker plot presenting the monthly GEM concentration distribution from all the data collected at TRS. The middle line in the box shows the median concentration, the box indicates the range between the 25th and the 75th percentile. Whiskers above and below the box indicate the 90th and 10th percentile respectively. The filled square shows the arithmetic mean. **(c)** and **(d)** is the same as **(a)** and **(b)** but for O_3.

annual mean or median GEM concentration from February 2007 to June 2011. As argued by Cole et al. (2011) the Polar Regions are different, compared to temperate latitudes, with respect to how they respond to mercury emissions reductions.

3.2 Seasonal variation in mercury concentrations at TRS

Figure 2b shows through monthly box plots of all data collected the seasonal variation of measured GEM concentrations. The median GEM concentration shows a maximum in winter and a minimum in summer, contrary to observations from Cape Point for which Slemr et al. (2008) and Brunke et al. (2010) hypothesized that the seasonality predominantly was driven by mercury emissions. At TRS the winter maximum is most likely caused by the lack of photochemical oxidation processes during the polar night (from May to July). For the convenience of the reader, box plots for O_3, similar to the GEM box plots, are also shown in Fig. 2.

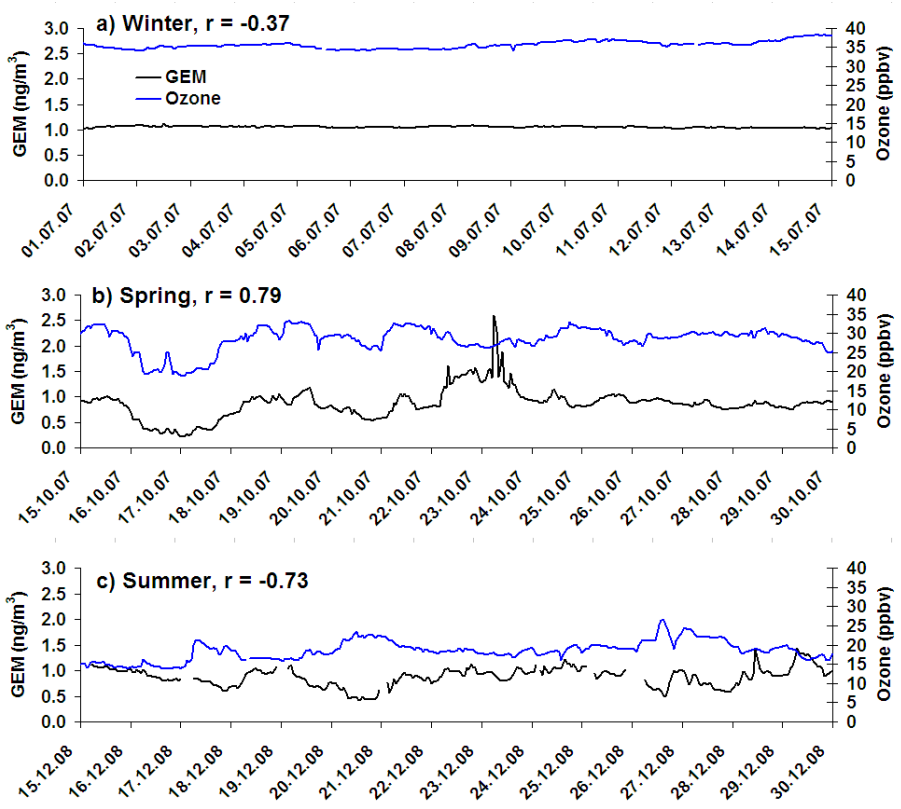

Fig. 3. Time series of GEM and Ozone concentrations from TRS representing the seasons**(a)** winter,**(b)** spring and**(c)** summer. The correlation coefficient, *r*, for GEM and Ozone is also indicated.

From late fall through winter (April–July), GEM concentrations remain at a virtually constant level of $1.00 \pm 0.07\,\mathrm{ng\,m^{-3}}$ (Fig. 3a), and the median concentration equals the mean. In spring and summer (August–February) GEM concentrations are highly variable ranging from 0.02 to $3.04\,\mathrm{ng\,m^{-3}}$ and with mean concentration of $0.86 \pm 0.24\,\mathrm{ng\,m^{-3}}$. The high variability suggests that exchange processes at the surface (sources and/or sinks) must be more active at high southern latitudes in spring and summer than during winter. In spring (August, September and October), the median concentration is higher than the mean concentration, indicating that the springtime mean is influenced by episodic low concentrations caused by AMDEs as also observed by Ebinghaus et al. (2002). In summer (November, December and January), the median concentration is lower compared to the mean indicating that the mean is influenced by episodic high concentrations. These observations are in good agreement with measurements performed at the German Antarctic research station Neumayer in 2000 and 2001 (Ebinghaus et al., 2002).

Diurnal variation in the GEM concentrations was not observed at any time of the year at TRS. A possible reason for this is the absence of sources or sinks for GEM with a diurnal cycle in the vicinity of this site. The ground surrounding TRS is mainly snow free bedrock year round, a type of surface that does not lead to substantial deposition followed by solar radiation induced re-emission. Additionally, the sample inlet is located 6 m above ground, perhaps too high to observe minor diurnal variations that may be present closer to the surface.

3.3 AMDEs at TRS

From the end of August until the end of October, AMDEs were observed at TRS in strong positive correlation with O_3 (correlation coefficients *r* up to 0.79) (Fig. 3b). AMDEs are often operationally defined as GEM concentrations below $1.0\,\mathrm{ng\,m^{-3}}$ for AMDEs observed in the Arctic. Using the same relative decrease in GEM concentrations for the Antarctic, AMDEs at TRS would occur at GEM concentrations below $0.6\,\mathrm{ng\,m^{-3}}$. This occurs in 5 % of the springtime observations as in contrast to 21 % of the observations at Zeppelin in the Arctic (Berg et al., 2011). As seen in the Fig. 4, periodic GEM concentrations below $0.6\,\mathrm{ng\,m^{-3}}$ also occur after the end of October, however these GEM depletions are not caused by AMDE chemistry as GEM is anti-correlated with O_3 in these cases (Fig. 3c), as also discussed in Temme et al., 2003a (see also following discussion).

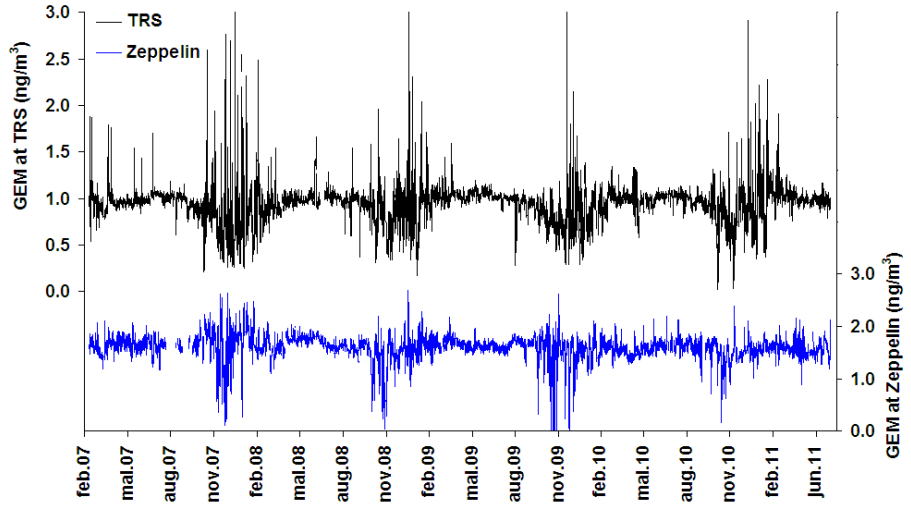

Fig. 4. Comparison of the time series of GEM concentrations from TRS in the Antarctic and Zeppelin in the Arctic. The time series from Zeppelin is shifted 182 days forward as compared to the TRS time series such that the seasons coincide.

3.4 Statistical analysis of source and sink regions

Figure 5 shows R_P fields for both the highest and lowest 10 % of all GEM data divided into the different seasons; winter, spring, summer and fall. Winter is represented as the months May–July, spring is represented by September–October, summer is represented by November–January and fall is represented by February. March, April and August data are not included in the analysis, because these months turned out to be transition periods not falling clearly into one of the above defined seasons. The R_{90} plots, representing the highest 10 % of all GEM measurements show that the open ocean is to a varying degree a source region of GEM to TRS all year round (Fig. 5, upper panels). Especially in summer and fall, the open ocean is a strong source of GEM (Fig. 5c–d). The highest R_{90} values are found over the high-latitude seas surrounding Antarctica. This is similar to the Arctic situation, where Hirdman et al. (2009) also found the Arctic Ocean to be a source of GEM in summer, after being a strong sink in spring. They suggested that some of the mercury lost in spring from the Arctic atmosphere during AMDEs could be re-emitted in summer. In the Antarctic case, the spring-time oceanic sink appears weaker (Fig. 5f), as the R_{10} values do not exceed 0.25 as compared to 0.5 in the Arctic case (Hirdman et al., 2009, Fig. 1e). This may in part be caused by the location of TRS not being exposed directly to depletion events but rather to transport of mercury-depleted air, as can also be seen by the lower frequency of AMDEs at TRS compared to Zeppelin (see above). However, the strong oceanic emissions in summer (Fig. 5c) may be a result of spring-time deposited mercury or evasion resulting from a sea ice free ocean.

The figure also shows that emissions of mercury from the Southern Hemisphere continents do not contribute significantly to direct transport of GEM to TRS. South Africa, one of the largest emitters of mercury globally (Pacyna et al., 2010), does not appear as an identifiable source region for GEM at TRS. Meridional transport from South Africa to Antarctica typically takes more than 20–30 days, especially in summer (Stohl and Sodemann, 2010) and does not occur frequently enough on the 20 day timescale of the FLEXPART calculations to be represented in the statistics. Even when extending the calculations to 30 days we did not register a clear signal because on this time scale the sampled air masses are a mixture of air originating from many different regions at the same time and do not cause clear concentration variability at the measurement station. In addition, on these timescales modeled transport also becomes very uncertain. Correspondingly, the other continents do not appear directly as source regions for GEM at TRS in our analysis. However, these emissions are certainly important for determining the overall GEM loading in the Southern Hemisphere atmosphere and, thus, also for the mean concentrations measured at TRS. Indeed, especially for spring (Fig. 5b) the analysis provides a hint that transport from lower-latitude regions (including the tip of South America) is frequently associated with the highest GEM concentrations, suggesting mid-latitude sources of the observed high GEM concentrations, although the particular source regions could not be resolved.

Considering the R_{10} plots, representing the lowest 10 % of all GEM measurements, for winter (Fig. 5e), the R_{10} values are almost everywhere below 0.15 and mostly below 0.1. This indicates that air masses associated with low GEM concentrations avoid surface contact and therefore often descend from above the boundary layer. In spring (Fig. 5f),

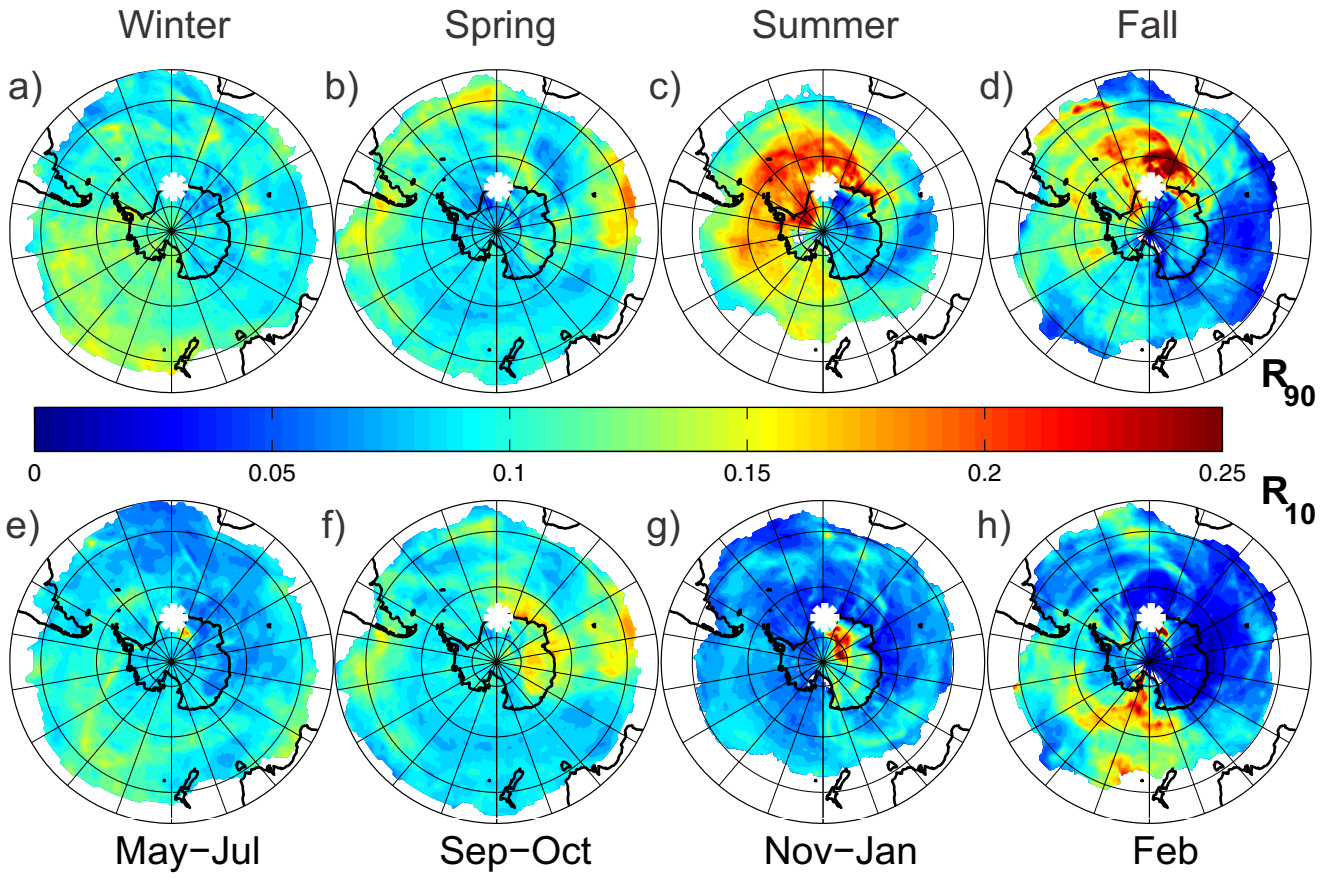

Fig. 5. Fields of R_{90} (top four panels) and R_{10} (bottom four panels) for GEM measurements at TRS from 2007 through June 2010. The location of TRS is marked with a white asterisk. Areas where S_T is below the threshold are plotted white.

however, the highest R_{10} values are found in conjunction with sea ice and marginal ice zones, indicating removal at the surface. This is the area where AMDEs are known to occur (Kaleschke et al., 2004; Simpson et al., 2007; Steffen et al., 2008). Additionally, high R_{10} values are found over the Antarctic plateau where there are no emission sources. In summer (Fig. 5g) on the other hand, when the sea ice extent is at an absolute minimum, no surface removal is observed in this area, and the highest R_{10} values are found exclusively over the Antarctic plateau. In fall (Fig. 5h), the area with high R_{10} values over the plateau is small, but the Ross Sea appears as an additional sink.

In spring, O_3 and GEM chemistry is closely tied together both in the Arctic and Antarctic atmosphere (Schroeder et al., 1998; Ebinghaus et al., 2002). To support the validity of the interpretation of the GEM plots, the statistical analysis was repeated for O_3. The R_{10} plots for O_3 (Fig 6 lower panels) shows that air masses over the Antarctic continent and the seas surrounding it containing low concentrations of O_3 have above average surface contact ($R_{10} > 0.1$), thus O_3 is destroyed at the surface. In spring (Fig. 6f), low O_3 concentrations mainly originate from sea ice dense areas surrounding Queen Maud Land as also seen for GEM (Fig. 5f), though the extent of low GEM values is smaller than for O_3. The R_{90} plots for O_3 (Fig. 6a–d) show that air masses containing high concentrations of O_3 have in general little surface contact. This probably indicates descent from the stratosphere into the free troposphere followed by mixing into the boundary layer over Antarctica. Only air masses originating from low-latitudes (north of 30° S) are associated with high O_3 concentrations, probably indicating transport of photochemically formed O_3 from lower latitudes even though the actual continental source regions cannot be resolved. The R_{90} summer and fall plots (Fig. 6c–d) shows O_3 rich air originating from the Antarctic Plateau. This is exactly the same area from where air low in GEM comes from.

In contrast to the Arctic where the periodic low concentration GEM episodes end with the onset of snowmelt (Lindberg et al., 2002), episodic low GEM concentrations are observed at TRS throughout the summer (see Fig. 4). Sprovieri et al. (2003) and Brooks et al. (2008a) argue that halogen chemistry causes the summertime depletion of GEM such as during the springtime AMDEs. Contrary to that, Sprovieri et al. (2003) who carried out Hg species measurements at

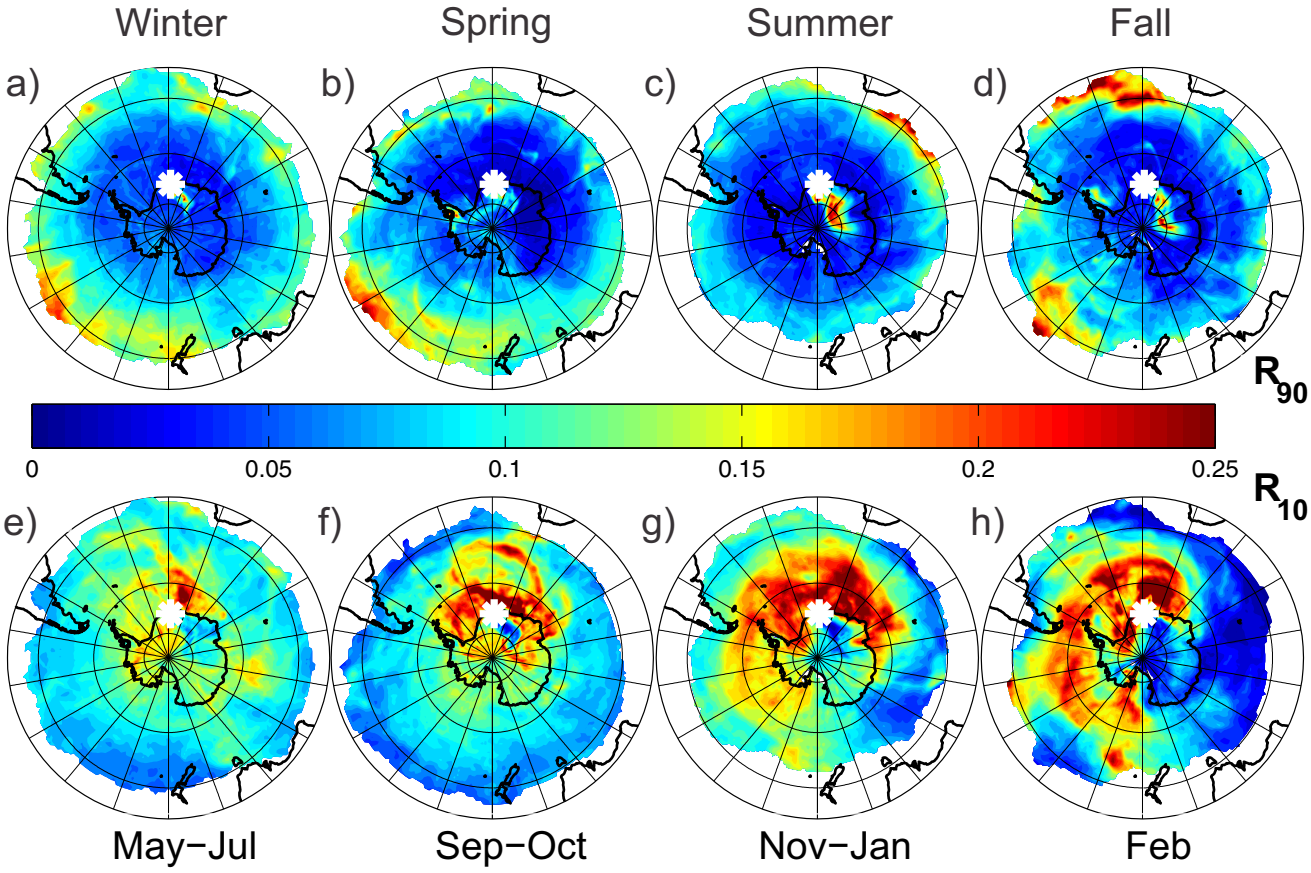

Fig. 6. Fields of R_{90} (top four panels) and R_{10} (bottom four panels) for ozone measurements at TRS from 2007 through June 2010. The location of TRS is marked with a white asterisk. Areas where S_T is below the threshold are plotted white.

the Italian Antarctic research base, Terra Nova Bay, close to the Ross Sea, put forward a hypothesis that the summer time low level GEM and the coinciding high level GOM could be due to purely meteorological factors rather than atmospheric chemistry processes, such as stratification of the planetary boundary layer. The height of the atmospheric mixed layer changes over time, which also leads to changes of its chemical composition. This is particularly valid for species emitted from the ground or sea surface, the dilution of which depends on the mixed layer height. However, our plots and data show that the summertime low GEM concentrations are not caused by either of the two explanations; it must be a different mechanism than AMDEs because transport from remaining sea ice regions (e.g., in the Weddell Sea) is not associated with low GEM concentrations at TRS in summer and fall (Fig. 5g–h) and it cannot be stratification of the planetary boundary layer as a pure meteorological phenomenon because GEM and O_3 are anti-correlated. As proposed by Temme et al. (2003a), AMDEs in Antarctica end abruptly in the beginning of November and another oxidation mechanism takes over. They suggested that GEM oxidation had already occurred before air parcels were advected to their measurement location. The Antarctic plateau mixed-layer represents a highly oxidizing environment during summer resulting from low temperatures typically not exceeding $-25\,^{\circ}\mathrm{C}$ leading to frequent cases of strong near surface temperature inversions in combination with continuous sunlight giving rise to non-stop photochemical reactions both within the snowpack and the atmospheric boundary layer (Crawford et al., 2001; Davis et al., 2008). These conditions result in an efficient release of NO_x from the snowpack to the atmosphere, leading to extremely high NO mixing ratios. NO rapidly converts abundant HO_2 into OH, enhancing the OH concentration and O_3 production. Summertime OH concentrations over the Antarctic Plateau ($\sim 10^6\,\mathrm{cm}^{-3}$) are considerably higher than coastal OH concentrations ($\sim 10^5\,\mathrm{cm}^{-3}$) (Bloss et al., 2007) in part due to the low mixing layer at the South Pole but also the effect of snowpack emissions of NO_x (Davis et al., 2004). Temme et al. (2003a) proposed OH, HO_2, and $O(^1D)$ as possible GEM oxidants, whereas Holmes et al. (2010) argued that OH is an ineffective Hg^0 oxidant over Antarctica and Br is effective. In the model by Holmes et al. (2010), Br radicals over Antarctica originate from photolysis of halocarbons emitted from the ocean, and

due to the cold and dry Antarctic air they have a lifetime of weeks or longer, whereby they efficiently oxidize Hg^0 leading to high concentrations of GOM. The high concentrations of GOM observed at the coastal sites by Temme et al. (2003a) and Sprovieri et al. (2003) were likely transported from the Antarctic Plateau to the measurement location. This would be consistent with our finding that in summer the lowest GEM concentrations are associated with transport from the Plateau (Fig. 5g), suggesting an oxidative sink there.

Figure 6c–d shows that the same transport pathway from the Antarctic Plateau, which causes low GEM concentrations at TRS, is associated with the highest O_3 concentrations at TRS in summer and fall. This shows clearly that the mechanism removing the GEM must be different from the AMDE chemistry. Air over Antarctica is generally subsiding, which brings Hg depleted air down to the surface. Since O_3 increases with altitude due to stratospheric influence, subsidence also brings high O_3 concentrations, and consequently increased O_3 and depleted Hg concentrations will be observed at TRS when free-tropospheric air reaches the surface over the Antarctic Plateau and is subsequently being transported to TRS.

4 Conclusions

More than four years of atmospheric mercury measurements from the Antarctic Research Station Troll are presented in this paper. The mean concentration of GEM was $0.93 \pm 0.19\,\mathrm{ng\,m^{-3}}$, which is in good agreement with recent GEM measurements at other high latitude sites in the Southern Hemisphere. Significant long-term decreases in GEM concentrations are observed at many monitoring sites both in the Northern hemisphere and at Cape Point, South Africa due to reduced reemissions from a legacy of historical anthropogenic mercury pollution, as discussed in Slemr et al. (2011). However, no such change in the annual mean or median concentration could be detected in the rather short time series from TRS.

A seasonal concentration variation was observed at TRS, with a maximum in winter and minimum in summer. The wintertime maximum is caused by absent photochemical removal processes, which allows for a build-up of atmospheric mercury. Spring and summer show highly variable GEM concentrations indicating extremely active surface exchange processes at this time of the year. No diurnal variation was observed throughout the year, which is likely caused by the nature of the surrounding surfaces being not ideal for deposition followed by radiation induced re-emission. AMDEs were observed every spring in strong correlation with O_3; however the depletions seem weaker when compared to the Arctic as seen in both the oceanic springtime sink and the AMDE occurrence frequency.

Statistical analysis of source and sink regions show that the ocean is a source of mercury to TRS all year round, and especially in summer and fall. This is likely caused by oceanic emission of springtime deposited GEM or evasion resulting from a sea ice free ocean. None of the Southern Hemispheric continents are a direct source of mercury to TRS, but they do contribute significantly to the overall mercury loading in the Southern Hemisphere atmosphere. Sinks for GEM in winter are lacking indicating that air masses containing low GEM concentrations avoid surface contact and often descend from above the boundary layer. In spring, removal of GEM is observed at the surface in conjunction with sea ice and marginal ice zones, caused by AMDEs. In summer, no oceanic sink is observed, however the interior of the Antarctic plateau appears as a strong sink, indicating that the frequent low GEM concentration episodes observed during summer are caused by a different mechanism than AMDEs.

A statistical analysis of O_3 showed that the Antarctic continent and the surrounding seas are a sink, thus O_3 is destroyed at the surface. In spring this sink is mainly located within sea ice dense areas surrounding Queen Maud Land, the same area as where the springtime GEM sink is found. In summer on the other hand the situation is different; the oceanic O_3 sink is maintained, but the GEM sink region is found over the Antarctic plateau where air rich in O_3 is coming from. The Antarctic Plateau is a highly oxidizing environment in summer; these conditions result in an efficient oxidation of GEM by Br radicals. The results show that the same transport pathway from the Antarctic plateau causing low GEM concentrations at TRS is associated with the highest O_3 concentrations at TRS in summer and fall, and the high O_3 concentrations observed at TRS is most likely caused by subsiding air over the Antarctic plateau with stratospheric influence. With our methods we cannot conclude which of the mechanisms are most important, however it is likely a combination of both. Ultimately, this suggests that the elevated summertime concentration of oxidized mercury species observed by others at coastal locations may result from different chemical processes than those causing AMDEs.

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