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Total gaseous mercury concentrations at the Cape Point GAW station and their seasonality

F. Slemr¹, E.-G. Brunke², C. Labuschagne², R. Ebinghaus³

¹Max Planck Institute for Chemistry, Atmospheric Chemistry Division, P.O. Box 3060, D-55020 Mainz, Germany

²South African Weather Service, P.O. Box 320, Stellenbosch 7599, South Africa

³GKSS-Research Centre, Institute for Coastal Research (GKSS), Max-Planck-Straße 1, D-21502 Geesthacht, Germany

Abstract

Total gaseous mercury (TGM) has been measured at the WMO Global Atmosphere Watch (GAW) station at Cape Point, South Africa, since September 1995. Annual medians suggest a small but significant decrease of TGM concentrations from 1.29 ng m⁻³ in 1996 to 1.19 ng m⁻³ in 2004. Background TGM concentrations at Cape Point show a pronounced seasonal variation with a maximum in January and February and a minimum in July, August and September. This seasonal variation is opposite in phase to that of CO at Cape Point, whereas at Mace Head in the northern hemisphere the seasonal variations of TGM and CO are in phase. This behavior is in approximate agreement with the seasonal variation of major mercury sources in both hemispheres, suggesting lesser influence of the seasonality of sinks. The different seasonal variations of TGM concentrations in the northern and southern hemispheres may pose an important constraint on the global models of atmospheric mercury.
Mercury, in contrast to other metals, is volatile and its vapor can be transported in air over large distances because of its low reactivity and solubility. After oxidation to less volatile and more soluble compounds it is deposited (e.g. Slemr et al, 1985; Lin et al., 2006). Part of the deposited mercury compounds is then converted to more toxic methyl mercury which bioaccumulates in the aquatic food chain. The high concentration of methyl mercury in the predatory fish pose a serious risk for people and animals which depend on a fish diet (e.g. Mergler et al., 2007; Scheuhammer et al., 2007). Consequently, the research on atmospheric mercury has intensified during the last decade (Lindberg et al., 2007).

Despite of the substantial progress, the understanding of the global atmospheric cycle is still incomplete (e.g. Lin et al., 2006). Natural and anthropogenic mercury emissions are not well known (e.g. Lindberg et al., 2007). The major knowledge gap, however, concerns the mechanism of the oxidation of highly volatile and almost insoluble gaseous elemental mercury (GEM) into less volatile and more soluble oxidized mercury species and their incorporation into particles (Lin et al., 2006). As the oxidized mercury species are readily removed from the atmosphere by dry and wet deposition (Lin et al., 2006), the rate of the GEM oxidation controls the removal of mercury from the atmosphere. Three major oxidation mechanisms by reactions with O₃, OH (Lin et al, 2006), and Br/BrO (Holmes et al., 2006) have been proposed but their relative importance is still unclear (Lin et al., 2006).

Long term monitoring of mercury can provide valuable constraints on emissions and on the oxidation mechanism of atmospheric mercury. Mercury is now being monitored at many sites in the northern hemisphere (NH) but, to the best of our knowledge, only two longer term
systematic measurements have been reported from the southern hemisphere (SH) so far. Ebinghaus et al. (2002a) measured total gaseous mercury (TGM) at the German Antarctic research station from January 2000 to January 2001. Baker et al. (2002) reported first results of the long term monitoring of TGM at the Cape Point observatory in South Africa covering a period from September 1995 to June 1999. The latter measurements have been continued and here we present the trend and seasonal variation derived from measurements covering almost a 10 year period since September 1995 until the December 2004.

**Experimental**

The Cape Point station (34°21’S, 18°29’E) is operated as one of the World Meteorological Organisation (WMO) Global Atmospheric Watch (GAW) baseline monitoring sites. The station is located at the southern tip of the Cape Peninsula within the Cape Point National Park on top of a peak 230 m above sea level and about 60 km south of Cape Town. The station has been in operation since the end of the 1970s. It receives clean marine air masses for most of the time and has, therefore, been used to study the trends and seasonal variations of CO₂, CO, CH₄, N₂O, O₃ and halocarbons at midlatitudes of the SH (e.g. Brunke et al, 1990; Oltmans et al, 1998).

As the primary objective of the TGM monitoring at Cape Point was to determine trends and seasonal variations, only 8 samples were typically taken every other week using a programmable sequential sampler providing about 200 samples per year. The sampling and analysis are described in detail by Baker et al. (2002). The technique measures the total gaseous mercury (TGM) under most conditions and was in excellent agreement with other TGM techniques during the intercomparison at Mace Head (Ebinghaus et al., 1999).
Results and discussion

TGM measurements at Cape Point are summarized in Table 1. During three years the measurements cover only a part of the year: September to December in 1995, January to March in 1997, and May, July, August and September in 1998. Because of the seasonal variation discussed later they cannot be regarded as representative for the whole year. The remaining medians for 1996 and 1999 - 2004 suggest a small but significant decreasing trend of TGM concentrations of $0.015 \pm 0.004$ ng m$^{-3}$ year$^{-1}$ ($R^2 = 0.740$, $n = 7$). Annual medians were used because they are less sensitive to extreme values than averages.

Fig. 1 shows the annual TGM medians for Cape Point together with the TGM medians at the Neumayer station, Antarctica (Ebinghaus et al., 2002a) and southern hemispheric TGM measurements during ship cruises on the Atlantic Ocean in 1994, 1996, and 1999 – 2001 (Temme et al., 2003b). An exact comparison of all these measurements is not possible because of their different spatial and temporal coverage. However, the ship measurements in 1996 and 2000 agree approximately with those from Cape Point while the data from the 1994 are lower for unknown reasons. The TGM concentrations at the Neumayer station in Antarctica tend to be somewhat lower - possibly because of the mercury depletion events.

The seasonal variation of TGM and CO concentrations at Cape Point is shown in Fig. 2. For comparison, seasonal variation of TGM and CO concentrations at Mace Head at the west coast of Ireland in the NH is also shown. Mace Head is one of the ALE/GAGE/AGAGE stations used to study trends and seasonal variations of halocarbons, CO$_2$, CO, CH$_4$, H$_2$, O$_3$ (Simmonds et al., 2005), and mercury (Ebinghaus et al., 2002b). Only baseline data were taken to eliminate the influence of nearby sources. At Cape Point TGM measurements in air with $^{222}$Rn concentrations of less than 600 mBq m$^{-3}$ were considered to be of baseline quality
in contrast to continental air masses, which exceed 1200 mBq m\(^{-3}\) (Brunke et al., 2004). Without \(^{222}\)Rn data, the baseline periods at Mace Head were identified by the NAME Lagrangian dispersion model (Manning et al., 2003). To eliminate the year to year variation of background TGM, the monthly means of TGM concentrations were normalized to annual medians. The TGM points in Fig. 2 then represent an average of relative monthly means over the period from March 1999 to December 2004, for which the \(^{222}\)Rn measurements were available, and the uncertainty bars represent their standard deviation. The TGM points and their uncertainty bars for Mace Head were derived in the same way as those for Cape Point. The absolute monthly means of TGM concentrations can be calculated by using the average annual median TGM concentrations over the period 1999 – 2004 of 1.203 ± 0.038 ng m\(^{-3}\) at Cape Point and 1.724 ± 0.060 ng m\(^{-3}\) at Mace Head, respectively. The CO data points and their uncertainty bars represent the baseline monthly averages of CO concentrations with their corresponding standard deviations.

To the best of our knowledge, the seasonal variation of TGM concentration in Fig. 2 is the first one derived from a long term monitoring in the SH. It shows maximum TGM concentrations in January and February (austral summer) and a minimum during austral winter. Although measurements by Ebinghaus et al. (2002a) and Temme et al. (2003a) in the Antarctic cover a whole year, the seasonal variation of their measurements is obscured by the frequent mercury depletion events starting in July and ending in February. A preliminary analysis of Cape Point data from September 1995 to June 1999 suggested a TGM minimum in March – May and a maximum in June – August (Baker et al., 2002), but no attempt was made to filter out the baseline data.

In spite of the occasionally large uncertainty bars for the monthly mean TGM concentrations, Fig. 2 shows that the seasonal variation of TGM relative to that of CO is opposite in phase in
the SH and in phase in the NH. The amplitude of the seasonal variations of 0.134 at Cape Point appears to be somewhat larger than those for Mace Head (0.097), although this difference may not be significant in view of the large uncertainties of the monthly means. The amplitude of the CO concentrations at Cape Point is 32.2 ppb in absolute and 0.49 in relative terms, at Mace Head 69.4 ppb and 0.58, respectively. The inverse average ratio of relative TGM (0.116) to CO (0.54) amplitudes of 4.7 suggest a correspondingly longer lifetime of TGM relative to that of CO, i.e. about 0.83 yr if the lifetime of CO of 0.18 yr is assumed (Warneck, 1988).

The seasonal variation of CO concentrations is driven mainly by the seasonal variation of its major sink due to the reaction with OH. The major source of OH radicals is photolysis of O$_3$ leading partly to O($^1$D) atoms and their subsequent reaction with H$_2$O. The seasonalities of solar irradiation (i.e. wavelength < 310 nm) and of water vapor concentrations lead to a pronounced seasonal variation of OH with a maximum concentration in summer and a minimum one in winter (Spivakovsky et al., 2000). The CO concentration follows the inverse pattern with a delay of about 2 months. The similar seasonal behavior of TGM and CO in the NH was sometimes taken as a sign in favor of OH driven oxidation for TGM (Bergan and Rodhe, 2001). The opposite behavior in the SH, however, suggests that this may be incorrect.

We hypothesize that the seasonal variation of TGM in the SH might be driven predominantly by its emissions. A summary of the currently available information about the seasonality of mercury emissions is shown in Fig. 3. The seasonality and magnitude of oceanic mercury emissions were taken from the results of model by Strode et al. (2006). The emissions from biomass burning were calculated using the seasonal variation of CO emissions given by Duncan et al. (2003) and Hg/CO emission ratios of 1.89 and 1.36 $\times 10^{-7}$ mol/mol in the southern and northern hemispheres, respectively (Ebinghaus et al., 2007). The anthropogenic
mercury emissions for 2000 (Wilson et al., 2006) were allocated to the hemispheres and to combustion and other sources. For the combustion sources the hemispheric seasonal variations given by Rotty (1987) were used to calculate their monthly contributions. The interhemispheric flux was calculated using the seasonal cycle of the interhemispheric exchange time derived by Levin and Hessheimer (1996) from $^{85}$Kr measurements and the seasonally variable north-south TGM gradient. Because of the higher TGM concentrations in the NH the flux is always negative from the NH perspective and positive for the SH. The total emissions, including the north to south transport, vary from 152 t/yr in May to 296 t/yr in December in the SH, and from 105 t/yr in December to 234 t/yr in May in the NH.

The emissions considered in Fig. 3 yield a total of 4562 t/yr, representing 69% of the total emissions estimated by Mason and Sheu (2002). The remaining 1605 t/yr are broadly ascribed to land emissions (Mason and Sheu, 2002) including volcanic emissions of 110 – 700 t/yr (Nriagu and Becker, 2003; Pyle and Mather, 2003), primary emissions from mercury deposits of about 500 t/yr (Lindquist et al., 1991), and reemissions of previously deposited mercury. The latter two are known to vary with temperature, solar radiation, and precipitation (Gustin et al., 1997) leading to a seasonal variation with maximum emissions in summer and a minimum in winter. As the contributions of volcanic emissions, primary emissions, and reemissions are not well known, the seasonality of the land emissions cannot be estimated. But it will be in phase with the emissions in the SH and thus increase the seasonal amplitude of the overall emissions there. In the NH, it will be out of phase with the emissions and will thus reduce the amplitude of the emission seasonality.

In summary, the seasonality of TGM emissions in Fig. 3 is in reasonable agreement with the baseline TGM observations at Cape Point and Mace Head suggesting a lesser influence of the sink seasonality. Of the three potential sinks due to reactions with OH, O$_3$, and Br (Lin et al,
2006; Holmes et al., 2006) the most pronounced seasonality can be expected for OH. The resemblance of the TGM seasonality to the seasonality of the sources is thus more consistent with O3 and Br oxidation of elemental mercury than with oxidation by OH.

Conclusion

The measurements of total gaseous mercury (TGM) made at the WMO Global Atmosphere Watch (GAW) station at Cape Point, South Africa, since September 1995 suggest a small but significant decrease of annual median TGM concentrations from 1.29 ng m$^{-3}$ in 1996 to 1.19 ng m$^{-3}$ in 2004.

Baseline TGM concentrations at Cape Point show a pronounced seasonal variation with a maximum in austral summer and a minimum in austral winter. This seasonal variation is opposite in phase to that of CO at Cape Point, whereas in the NH at Mace Head the seasonal variations of TGM and CO are in phase. This behavior seems to be dominated by the seasonal variation of major mercury sources in both hemispheres, suggesting lesser influence of the sink seasonality. We are aware, that this explanation is speculative in view of the combined uncertainties of the emission estimates. But, if the seasonality observed at Cape Point is confirmed at other sites in the SH, the different seasonalities in the northern and southern hemispheres of TGM concentrations may pose an important constraint on the global models of atmospheric mercury.

Acknowledgments

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has provided the baseline intervals for Mace Head observations. The measurements were established with the financial help of the Deutsche Forschungsgemeinschaft.

References


**Figure Labels**

Figure 1: TGM concentrations measured at Cape Point, Neumayer station (Antarctica) and onboard ships over the Atlantic Ocean in the southern hemisphere. The concentrations are given in ng/m3 (STP, i.e. 273.2 K, 1013 mbar). The points and bars represent the annual medians (cruise medians for ship cruises) and their 95% confidence intervals.
Figure 2: Seasonal variation of TGM (relative monthly averages and their standard deviation, see text) and CO (absolute monthly averages and their standard deviations) at Cape Point and Mace Head. Only baseline data are considered in this diagram, see text.

Figure 3: Seasonal variation of the emissions from oceans, biomass burning, anthropogenic activities, and of the interhemispheric flux. Details of calculations are given in the text.

Tables

Table 1: Summary of the TGM measurements at Cape Point.

<table>
<thead>
<tr>
<th>Year</th>
<th>Range [ng m⁻³]</th>
<th>Average ± Standard deviation [ng m⁻³]</th>
<th>Median [ng m⁻³]</th>
<th>95% confidence interval of median [ng m⁻³]</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1995</td>
<td>1.23 – 3.16</td>
<td>1.518 ± 0.372</td>
<td>1.42</td>
<td>1.34 - 1.54</td>
<td>26</td>
</tr>
<tr>
<td>1996</td>
<td>0.93 – 1.88</td>
<td>1.297 ± 0.136</td>
<td>1.29</td>
<td>1.26 – 1.31</td>
<td>212</td>
</tr>
<tr>
<td>1997</td>
<td>0.73 – 1.60</td>
<td>1.182 ± 0.174</td>
<td>1.17</td>
<td>1.11 – 1.22</td>
<td>50</td>
</tr>
<tr>
<td>1998</td>
<td>0.95 – 1.82</td>
<td>1.308 ± 0.167</td>
<td>1.28</td>
<td>1.24 – 1.37</td>
<td>38</td>
</tr>
<tr>
<td>1999</td>
<td>0.78 – 1.61</td>
<td>1.244 ± 0.139</td>
<td>1.25</td>
<td>1.23 – 1.27</td>
<td>163</td>
</tr>
<tr>
<td>2000</td>
<td>0.49 – 2.18</td>
<td>1.227 ± 0.174</td>
<td>1.21</td>
<td>1.18 – 1.22</td>
<td>173</td>
</tr>
<tr>
<td>2001</td>
<td>0.84 – 6.78</td>
<td>1.452 ± 0.817</td>
<td>1.24</td>
<td>1.21 – 1.28</td>
<td>152</td>
</tr>
<tr>
<td>2002</td>
<td>0.92 – 1.64</td>
<td>1.200 ± 0.132</td>
<td>1.18</td>
<td>1.14 – 1.20</td>
<td>143</td>
</tr>
<tr>
<td>2003</td>
<td>0.93 – 1.60</td>
<td>1.176 ± 0.110</td>
<td>1.15</td>
<td>1.14 – 1.18</td>
<td>125</td>
</tr>
<tr>
<td>2004</td>
<td>0.78 – 2.37</td>
<td>1.261 ± 0.247</td>
<td>1.19</td>
<td>1.17 – 1.22</td>
<td>155</td>
</tr>
</tbody>
</table>
Figures

Fig. 1:
Fig. 2: