

Gaseous elemental mercury depletion events observed at Cape Point during 2007–2008

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Abstract. Gaseous mercury in the marine boundary layer has been measured with a 15 min temporal resolution at the Global Atmosphere Watch station Cape Point since March 2007. The most prominent features of the data until July 2008 are the frequent occurrences of pollution (PEs) and depletion events (DEs). Both types of events originate mostly within a short transport distance (up to about 100 km), which are embedded in air masses ranging from marine background to continental. The Hg/CO emission ratios observed during the PEs are within the range reported for biomass burning and industrial/urban emissions. The depletion of gaseous mercury during the DEs is in many cases almost complete and suggests an atmospheric residence time of elemental mercury as short as a few dozens of hours, which is in contrast to the commonly used estimate of approximately 1 year. The DEs observed at Cape Point are not accompanied by simultaneous depletion of ozone which distinguishes them from the halogen driven atmospheric mercury depletion events (AMDEs) observed in Polar Regions. Nonetheless, DEs similar to those observed at Cape Point have also been observed at other places in the marine boundary layer. Additional measurements of mercury speciation and of possible mercury oxidants are hence called for to reveal the chemical mechanism of the newly observed DEs and to assess its importance on larger scales.

1 Introduction

Mercury (Hg), a prominent global environmental pollutant, having both anthropogenic and natural sources of comparable magnitude (Nriagu, 1989; Mason and Sheu, 2002) has evoked worldwide concern among the research community (Pirrone and Mason, 2009 and references therein). It has thus remained high on the priority lists of a large number of international agreements and conventions. The globally averaged atmospheric residence time (ignoring localized influences) of gaseous elemental mercury (GEM) approximates about one year (Slemr et al., 1985; Lindqvist and Rodhe, 1985; Schroeder and Munthe, 1998; Bergan and Rodhe, 2001). More recently, studies by Weiss-Penzias et al. (2003) and Hedgecock et al. (2005) alluded to shorter lifetimes (ca. 0.5–6 months) in marine boundary layer environments. As such, GEM can be distributed via long-range atmospheric transport over inter-hemispheric distances.

The existing Cape Point atmospheric gaseous mercury data base comprises both manual measurements with low temporal resolution (initiated in September 1995; Baker et al., 2002) as well as automated measurements with a resolution of 15 min (since March 2007). Good agreement exists between the long-term TGM monitoring results obtained via a manual analysis method and those for the automated system (Ebinghaus et al., 1999). This first time series (2007–2008) of temporary highly resolved data provides information on a new type of depletion event (DEs), not previously recognized to this magnitude and extent, and also to a lesser degree, on pollution events (PEs). The DEs we report here are not accompanied by a simultaneous depletion of ozone. This is in stark contrast to the atmospheric mercury depletion



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events (AMDEs), which have so far only been observed in the Polar Regions (Schroeder et al., 1998; Ebinghaus et al., 2002) and which are chemically driven by a combination of solar radiation, halogens (predominantly bromine) and the sea-ice interface (Steffen et al., 2008).

To the best of our knowledge the Cape Point observations constitute the only long-term data set of atmospheric Total Gaseous Mercury (TGM) in the Southern Hemisphere (SH).

2 Station information and measuring technique

The Cape Point station (34°21' S, 18°29' E) is managed by the South African Weather Service. It is part of the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) network and as such of major importance to the international community for atmospheric and climate change research. The laboratory constitutes a good platform for the continuous measurement of atmospheric parameters as well as field campaigns. The geographic location of the station is shown in Fig. 1.

Cape Point is about 60 km south of Cape Town, and located on top of a coastal cliff 230 m above sea level at the southern-most tip of the Cape Peninsula. Due to its unique location, a sector exceeding 300° is surrounded by the ocean and the rest by sparsely vegetated, rocky terrain. The plant growth in the nature reserve itself belongs to the Cape floral kingdom, which comprises a large variety of heath, *Erica*, *Protea*, *Gladiolus* and other shrubs endemic to the region (Cowling et al., 1992, 1996). The site experiences moderate temperatures, dry summers with occasional biomass burning episodes in the surrounding area and increased precipitation during austral winter.

The dominant wind direction is from the south-eastern sector which is representative of clean maritime air from the Southern Ocean (Brunke et al., 2004). Trace gas measurements performed under these conditions are used to assess long-term trends (Brunke et al., 1990) within the mid-latitudes of the Southern Hemisphere (SH). Cape Point is, however, occasionally also subjected to air from the northern to north-eastern sector (mainly during the austral winter), which is influenced by anthropogenic emissions from the greater Cape Town area and/or by other continental sources.

Within the framework of the WMO-GAW program, continuous trace gas measurements (for example: CO₂, CH₄, CO and O₃) have been made at Cape Point in excess of 20 years now. In addition to these environmentally important trace gases, meteorological parameters as well as ²²²Rn (Whittlestone et al., 1992) are also being monitored. The ²²²Rn program started in 1999 and essentially serves to classify air masses into maritime, continental or mixed (Brunke et al., 2004). Ten-day isentropic back trajectories from NOAA ESRL (<http://www.esrl.noaa.gov/gmd>) have been utilized to identify the origin of the air associated with the PEs and DEs. In 2005 a measurement program for aerosol opti-

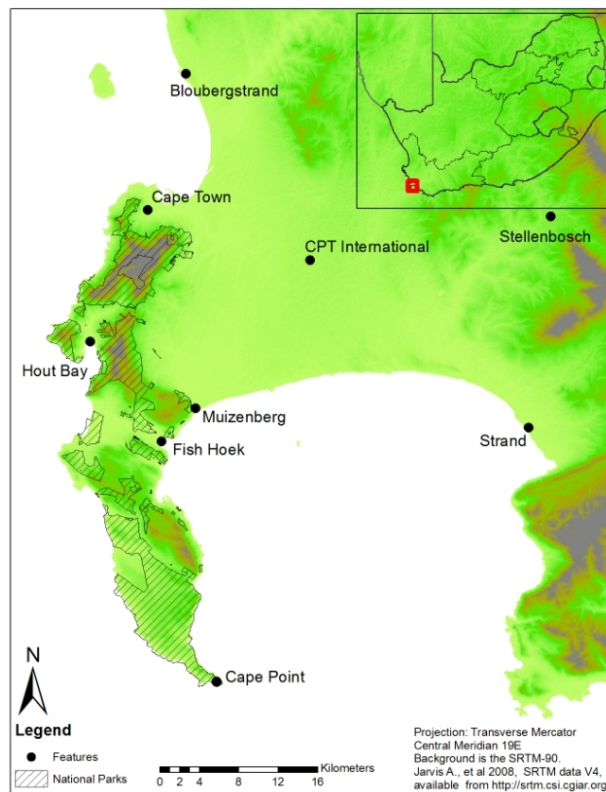


Fig. 1. Map of the Cape Peninsula with the location of the GAW station at Cape Point.

cal properties was started in close co-operation with NOAA-ESRL (<http://www.esrl.noaa.gov/gmd/aero>). Light scattering at three wavelengths is being measured for the PM₁ and PM₁₀ size fractions, using integrating nephelometry. The measurement of condensation nuclei (CN) concentrations via condensation particle counter started only in February 2008. The uncertainties (expressed as percentage variations at currently observed background levels) for CO₂, CH₄, CO and O₃ amount to 0.01, 0.2, 4.0, and 4.0, respectively. Analytical details of the atmospheric parameters measured have been summarized under www.empa.ch/gaw/gawsis and have also been described in previous publications (Brunke et al., 1990; Scheel et al., 1990; WMO report no. 161, 2005). Factors affecting the sensitivity and accuracy of the Cape Point ²²²Rn detector have been discussed by Brunke et al. (2002) and by references therein.

Gaseous mercury concentrations have been measured since September 1995 (Baker et al., 2002). The current instrument in use since March 2007 is a Tekran 2537A vapour-phase mercury analyzer manufactured by Tekran Inc., Toronto, Canada. It is capable of measuring low level mercury concentrations typically observed at background locations (Ebinghaus et al., 1999; Munthe et al., 2001). The analyzer was set up in an air-conditioned laboratory and

programmed to sample air at a flow rate of 1 litre min^{-1} for 15-min sampling intervals. The TGM detection limit in this operating mode is about 0.05 ng m^{-3} . The span of the analyzer is checked by an internal permeation source once every 25 h. The air sample intake was attached to a 30-m aluminium sampling mast at a height of approximately 5 m above rocky ground and about 235 m above sea level. A 45-mm diameter Teflon filter (pore size $0.2 \mu\text{m}$) upstream of the instrument protects the analyzer against contamination by particulate matter. The filter was replaced every other week. The 15-min TGM data have been converted to 30-min averages for comparison to other trace gas and meteorological data being measured simultaneously at Cape Point.

Scientific consensus exists that AMDEs are periods during which rapid atmospheric oxidation reactions reduce the concentration of gaseous elemental mercury (Hg^0) (sometimes to concentrations below 0.1 ng m^{-3}) (Steffen et al., 2008), while producing oxidized gaseous (frequently referred to as reactive gaseous mercury, RGM) and particulate Hg, which leads to elevated deposition (Lindberg et al., 2007). In recent years, controversial discussions about the chemical composition of gaseous mercury at high altitudes of RGM and/or TPM (i.e. as a consequence of depletion events) have led to different interpretations of the mercury species measured with a Tekran 2537A analyzer (Temme et al., 2003). Because operationally defined RGM has been shown to adsorb on a large variety of materials, the major question is whether, at high RGM levels, the gaseous divalent inorganic mercury species could pass through the sampling line and the particulate filter upstream of a Tekran 2537A to add up with elemental mercury yielding total gaseous mercury (TGM). Under very dry and cold conditions in the Antarctic lower troposphere Temme et al. (2003) demonstrated that RGM passes the sampling lines and the filter. However, under the prevailing atmospheric conditions at Cape Point (higher temperature and air humidity, in addition to hygroscopic sea salt aerosols) we assume that the RGM fraction will not reach the Au traps and that the measured atmospheric mercury concentration thus represents exclusively Gaseous Elemental Mercury (GEM). Thus, in contrast to our previous papers (Brunke et al., 2001; Baker et al., 2002; Slemr et al., 2008), we refer in this paper to these measurements as GEM species.

The unique characteristic of the many DEs at Cape Point raises the question whether these observations are not perhaps due to analytical artefacts? Deactivation of the gold traps used to enrich mercury from the ambient air has been frequently observed by other Tekran operators. As shown in the discussion accompanying of this paper, the calibrations with the internal permeation source which coincide with DEs were comparable with the calibrations outside of the DEs thereby excluding any possible gold trap deactivation. However, this finding still permits the possibility of temporary artefacts existing within the sampling line. Such artefacts in sampling lines are usually irreversible and, to the best of our knowledge, no reversible artefact of this type has been re-

ported so far. A standard addition test at the inlet during a DE would definitively resolve this issue, but due to logistical and instrumental constraints it has not been carried out yet. Neither has it been performed as part of most AMDE studies. In summary, we can rule out artefacts due to a temporary deactivation of the gold traps, but we cannot altogether exclude a small but improbable likelihood of temporary artefacts in the inlet tubing.

3 Results and discussion

During the 14-month period under discussion here (March 2007 till June 2008), the mean Cape Point GEM concentration (20248 data points) amounted to $0.944 \pm 0.160 \text{ ng m}^{-3}$ with a maximum of 5.44 and a minimum below the detection limit of about 0.05 ng m^{-3} . Figure 2a and b shows an extract of this time series (March 2007 till December 2007) as well as GEM concentrations from Mace Head (Kock et al., 2005) in the Northern Hemisphere (NH) for comparison.

As can be seen, the Cape Point GEM levels (SH) are about 0.6 times lower than those for the NH (Slemr et al., 2008). Beside this inter-hemispheric difference, both data sets display occasional pollution events (PEs). However, the major difference between the two data sets are the numerous depletion events (DEs), which have been observed at Cape Point, but so far not at Mace Head. In order to make unbiased comparisons between the various depletion and pollution events throughout the measuring period, the effect of seasonality has to be taken into account. This was done by applying an eleven day moving percentile to the 30-min data. Upper and lower cutoff limits (equating to 0.18 ng m^{-3} above and below the moving percentile) have been selected by visual inspection and applied to the data. In this way values that lie above and below these thresholds have been identified and extracted as DEs and PEs respectively for further study.

In the next two sections we will first describe three examples of depletion events and one example of a pollution event. The following section discusses the statistics of occurrence of these events and their relations to other parameters measured at Cape Point. In the last section the Cape Point GEM seasonal variations will be compared to those from earlier observations.

3.1 Depletion events (DEs)

During a typical depletion event the mercury concentration decreases from average background levels of about 1 ng m^{-3} to $<0.20 \text{ ng m}^{-3}$, often within about 1–3 h. These events have been observed under continental, marine as well as mixed air conditions, which were assigned relative to their respective ^{222}Rn levels (Brunke et al., 2004). Examples for all three conditions are shown below.

Figure 3 shows a DE observed on 3 April 2007, at ^{222}Rn levels (2nd panel from the bottom) ranging between 2000

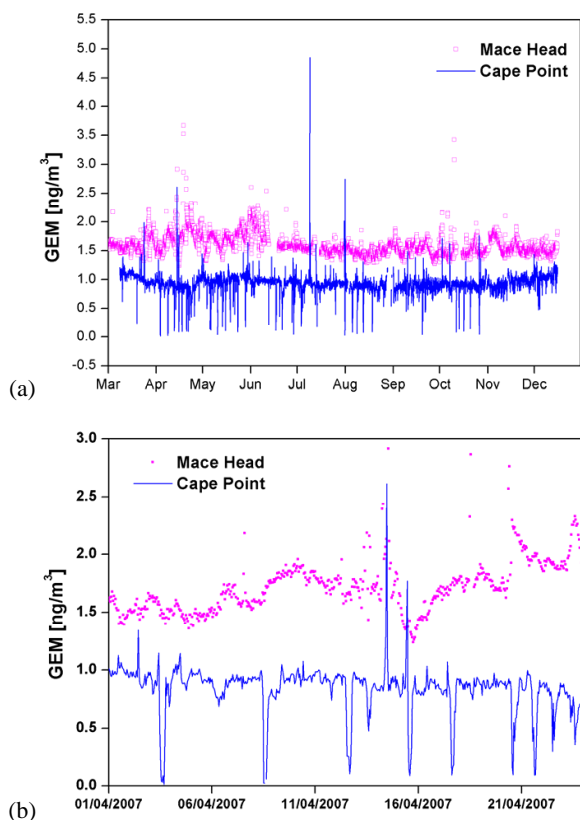


Fig. 2. (a) GEM time series for two sites: Mace Head (source: Kock et al., 2005), representing the Northern Hemisphere and Cape Point, the Southern Hemisphere (March 2007–December 2007). (b) Zoomed-in section for April 2007 highlighting DEs at Cape Point.

and 3800 mBq m^{-3} . These ^{222}Rn levels are typically indicative of air mass strongly influenced by continental sources. This was clearly supported by air mass back trajectories, which originated from the Gauteng-Swaziland region with a low travelling height of about 1000 m during the last 24 h prior to reaching Cape Point. The GEM concentration shown in the lowermost panel starts to decrease at 10:30, drops to almost zero levels between 13:00 and 16:00, and reaches the pre-event value again at 17:30. During this event, the CO mole fractions varied between 100–200 ppb, which is about 2–4 times higher than the normal background. Surface O_3 concentrations (2nd panel from the bottom) increased during the event, reaching a maximum of 100 ppb at 15:00 and then subsequently decreased. A second ozone peak at 20:00–21:30 was not accompanied by any GEM change. The start of the DE at 10:30 coincided with the decrease of the wind velocity (shown in uppermost panel) to below 4 m s^{-1} and the DE ended at 17:00 when the wind velocity and direction started to increase and change, respectively. Wind direction, albeit uncertain at low wind velocities due to the complex local topography, points to the north during this event. Observed aerosol backscattering for particles smaller than 1 and

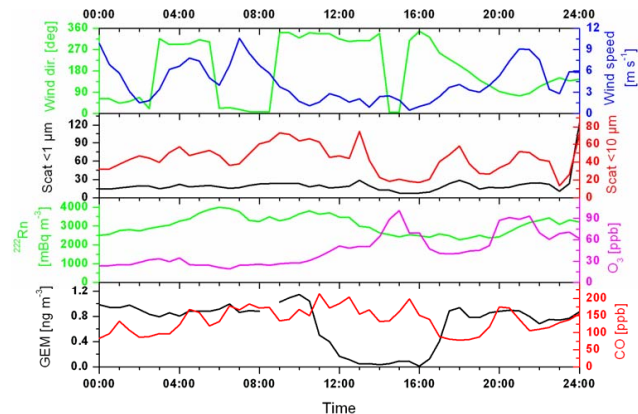


Fig. 3. GEM depletion event (DE) on 3 April 2007.

$10 \mu\text{m}$ (shown in 2nd panel from the top) is variable without any apparent correlation with the GEM concentration.

Figure 4 shows another significant DE on the 12 April 2007. This specific event lasted almost 8 hours and reached a minimum GEM concentration of 0.1 ng m^{-3} under clean maritime conditions. It was characterized by winds changing direction from 82° to 198° at low wind velocities (ranging between 1.5 – 5 m s^{-1}). The start of this event, at about 11:30, roughly coincided with a decrease of the wind velocity from about 6.5 m s^{-1} to below 4 m s^{-1} , and its end at about 19:00 was related to a change in wind direction. While no ^{222}Rn data was available during the duration of this specific DE, the concentration between midnight and 09:00 (prior to the event) varied around the 300 mBq m^{-3} level. Both CO and O_3 showed undisturbed mole fractions of 45 and 24 ppb, respectively, corresponding to typical background levels for that time of the year. These indications of the air mass being unaffected by local sources are also supported by the two daily back trajectories which have their origin in the SW Atlantic. Another significant aspect might be the travelling height of the air parcel at about 3000 m, 24 h prior to reaching the station in combination with changing relative humidity: 80% before and after the event, but decreasing to 55% during the event (not shown in Fig. 4). Aerosol backscattering for both the 1 and $10 \mu\text{m}$ fraction (2nd panel from top) suggest an increase in aerosol concentration during the DE, roughly inversely correlated with the GEM concentration. Although the trajectory and lower humidity values both point to a possible injection of upper tropospheric air, the observed CO mole fraction is not below background, which would be expected in that case and O_3 not above (for this specific time of the year). This suggests that the DE was not caused by subsiding air. It is worth to note that the common feature of this DE and the DE in Fig. 3 is the low wind velocity.

DEs have also been seen in air masses of mixed origin as exemplified by two events on 19 September 2007 (data not shown here). NOAA-ESRL back trajectories show that the air mass under investigation at Cape Point on this and on the

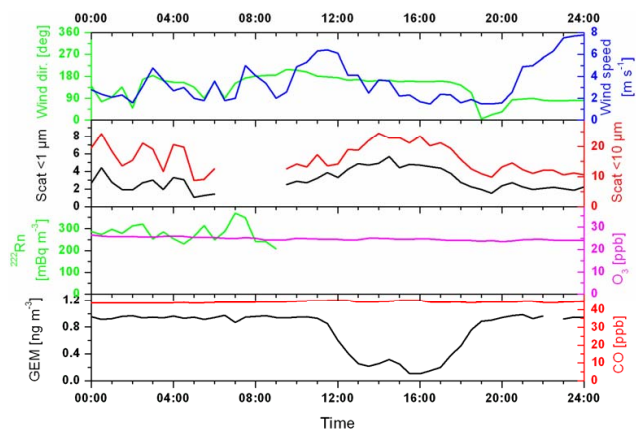


Fig. 4. GEM depletion event (DE) on 12 April 2007.

previous day originated from the SW and W Atlantic. However, on 18 September the air trajectory also moved across the SW tip of the Cape Province for several hours prior to arriving at Cape Point. This caused some continental air to be entrained. The first event occurred on September 19 at 17:30–21:00 and the second started on 19 September at about 23:00 and ended on 20 September at 03:30. The wind velocity during the first event varied between 3 and 6.5 m s^{-1} and during the second one between 4 and 7 m s^{-1} . The beginning and the end of the first event seem to have coincided with a change of the wind direction, but no such coincidence was observed during the second event. The first event was accompanied by a slight increase of CO and O₃ mole fractions from 75 to 105 and from 35 to 46 ppb, respectively. During the second event the CO mole fraction peaked at approximately twice its background level (142 ppb), whilst O₃ peaked at 48 ppb (1.5 times the background). The end of the second event coincided with a drop of O₃ mole fraction from about 40 to 26 ppb. The ²²²Rn concentration was about 880 mBq m^{-3} during the first event and 400 mBq m^{-3} during the second. No obvious correlation was observed between the GEM concentration and aerosol measurements. What makes this DE unusual is its occurrence during the night with no UV irradiation as a driving force. The wind direction fluctuated from 203° to 286° with the velocity ranging between 3 and 7 m s^{-1} . We think that these and a few other night-time DEs have originated during the day under similar conditions (although not clearly understood yet) and that these GEM-depleted air masses were transported to the station during the night.

3.2 Pollution events (PEs)

As would be expected from localities that are occasionally impacted upon by air masses that have recently been in contact with anthropogenic sources or even biomass burning emissions (Brunke et al., 2001; Obrist et al., 2008) instances of GEM pollution events (PEs) have been observed at Cape

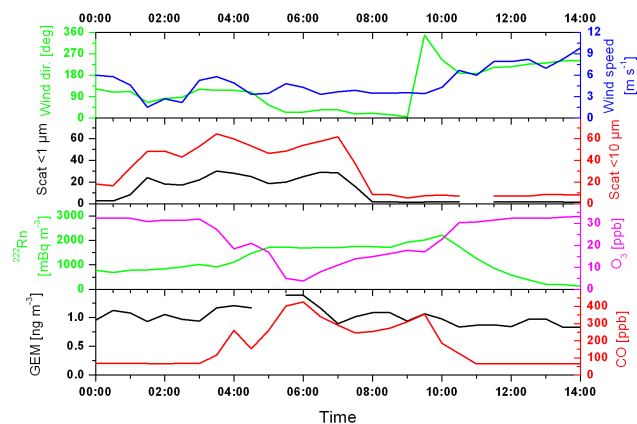


Fig. 5. GEM pollution event (PE) on 15 September 2007.

Point. One such example is the PE, which took place on the 15 September 2007 between 02:30 and 10:30 (Fig. 5). It was characterized by a maximum GEM level of 1.4 ng m^{-3} (1.5 times its background), and ²²²Rn, CO and O₃ levels of 1514 mBq m^{-3} , 420 ppb (7 times background) and 4 ppb (i.e. only 12.5% of the normal level), respectively. Aerosol backscattering of the 1 and 10 μm particle fractions showed elevated levels between 01:00 and 08:00, which preceded the CO and GEM maxima and ended before these two parameters returned to “normal”. Note that GEM is roughly positively correlated with CO which in turn is tightly negatively correlated with O₃. The correlation with ²²²Rn is only weak and a correlation with aerosol light scattering is virtually nonexistent. The negative correlation of CO with O₃ suggests titrations of O₃ by NO emitted together with CO in the area north of Cape Point. Although the trajectories indicate that the air was derived from the SW Atlantic, there was a measure of low level (<1000 m) re-circulation in the vicinity of the SW Cape. We believe that this episode is a typical reflection of a nocturnal inversion breakup situation accompanied by corresponding airflow towards the south.

After having described a few specific DE and PE case histories, the focus will now be on the overall behaviour of these events in relation to other parameters and an assessment of the characteristic patterns of their occurrence. All events will be scrutinized in terms of their relationship to CO and O₃ as well as wind direction and their influence on the diurnal cycle.

3.3 Other features characterising PEs and DEs

Correlation coefficients (r) between GEM and CO as well as GEM and O₃ have been determined for both PEs as well as DEs and plotted against ²²²Rn (not shown here) in an attempt to better understand the origin and mechanism of these events. The plots with ²²²Rn have confirmed that both event types are not preferentially restricted to one specific air mass regime, but are embedded in clean maritime as well as in

continental air having ^{222}Rn levels ranging from <150 (marine) up to 4000 mBq m^{-3} (continental).

No significant correlation between GEM and CO was observed during the DEs (GEM concentrations ranged from 0.1 to 0.85 ng m^{-3}). CO mole fractions fluctuated between 45 and 200 ppb for the whole range of GEM values with a few occasional outliers. A plot of CO vs. GEM for the observed PEs reveals two populations suggesting two different sources. The first population displays PEs up to 2.1 ng m^{-3} accompanied by CO mole fractions reaching levels of up to 800 ppb CO. The second group of PEs shows GEM concentrations up to 5.4 ng m^{-3} , but lower CO levels fluctuating between 50 and 300 ppb . High CO peak mole fractions at relatively low peak GEM concentrations are characteristic for biomass burning plumes, whereas high peak GEM concentrations at relatively low peak CO levels are usually encountered in plumes from urban/industrial regions (Weiss-Penzias et al., 2007).

GEM/CO emission ratios have been determined for 34 PEs from correlations of GEM with CO in an attempt to constrain their origin. The emission ratios were calculated as slopes of straight lines obtained by orthogonal (major axis) fitting (York, 1966; Cantrell, 2008). The measurement uncertainties are estimated to be 50 pg m^{-3} for GEM and 1 ppb for CO (range: 20 to 80 ppb). 80% of the correlations were significant at the 99% and higher confidence level and the rest at a level exceeding 95% . With the exception of an episode observed on 23 March 2007, the GEM/CO ratios vary between 0.3 and $5 \text{ pg m}^{-3} \text{ ppb}^{-1}$ and agree well with values reported in the literature ranging from about $1.5 \text{ pg m}^{-3} \text{ ppb}$ for biomass burning to about $7 \text{ pg m}^{-3} \text{ ppb}$ for Asian and European outflow (Slemr et al., 2009, and references therein).

GEM vs. O_3 for DEs show both positive and negative correlations with no preferred tendency. In contrast to the DEs, the PEs do reveal a preference for GEM vs. O_3 to be negatively correlated, especially for continental air (r ranging from $+0.5$ to -0.9). This suggests that GEM pollution more often occurs in stagnant urban air masses, where a build-up of GEM from anthropogenic sources is likely. Such conditions typically prevail during a nocturnal winter inversion and subsequent breakup (Banta et al., 1998) where O_3 has been titrated down to low levels by locally emitted NO (Sillman, 1999). Peak GEM values (PEs) are believed to reflect known anthropogenic sources such as coal burning and waste incineration (Pacyna et al., 2001; UNEP, 2002). Since South Africa's coal driven power stations in the Gauteng and Mpumalanga region constitute a strong Hg source (Dabrowski et al., 2008) long-range transport from up country is also likely to show up as PEs at Cape Point – an aspect, which requires further investigation.

The relationship between DEs and aerosol parameters was investigated for several reasons. As in the case of Arctic and Antarctic mercury depletion, the chemical species responsible for the depletion are released from the sea and might thus be connected with enhanced sea salt particle concentrations.

For the marine boundary layer in temperate regions Holmes et al. (2009) have shown that 80 to 95% of ionic Hg(II) should be present in sea-salt aerosols rather than gas-phase, and that deposition of sea-salt aerosols is the major pathway delivering Hg(II) to the ocean. Mechanisms involving heterogeneous-type reactions would need enhanced aerosol concentrations. Furthermore, photochemical reactions responsible for the DEs might also produce small particles. We observed a significant negative correlation of GEM with PM_{10} and PM_{10} scattering, (such as shown in Fig. 4), during several events, especially when the DE was embedded in very clean air. In more polluted air masses no significant relationship was detected. No apparent correlation of CN with GEM concentrations was observed during the few DEs observed since the start of the CN measurements in February 2008.

In order to better understand and elucidate the origin of DEs and PEs, their relationships to wind direction and velocity were also assessed. Wind data (30-min average values) associated with the duration of both pollution and depletion events were extracted and combined into two separate data sub-sets, respectively. The wind data for these two sub-sets were allocated to 12 sectors subtending angles of 30° each. The frequency of these wind data points (for velocities $>5 \text{ m s}^{-1}$) within each sector in the form of angular frequency distributions (wind roses) is shown in Fig. 6. Although there is no major difference in the overall result between data for all winds and data associated with wind velocities $>5 \text{ m s}^{-1}$, we have excluded the low velocity winds ($<5 \text{ m s}^{-1}$), because wind directions at these lower speeds are unreliable, especially due to the complex local topography. Nonetheless, it is important to note that this filter removes wind data for about half of the DEs which have associated wind velocities below 5 m s^{-1} .

Despite eliminating wind data from about 50% of the DEs, the depletion events occur essentially at all wind directions. The apparent preference for the E-SE and SW-N sectors with a lesser preference for the S and NE quadrants is not very pronounced and may disappear if the data below 5 m s^{-1} were included. Furthermore, DEs occur almost exclusively at wind velocities $<10 \text{ m s}^{-1}$. In contrast, the wind rose for the PEs shows that these originate primarily from the N sector, although a small E-SE component also exists.

Pollution events (PEs) as well as DEs may influence the shape and the amplitude of the GEM diurnal cycles. Figure 7 thus shows a composite hourly percentage frequency of occurrence of PEs and DEs. The PEs tend to occur mainly between $08:00$ and $13:00$, although a substantial proportion also takes place during the night and, less frequently, during the rest of the day. The DEs take place predominantly between $12:00$ and $19:00$ with only a few events at other day-times. The coincidence of the hours of maximum occurrence of DEs with those of maximum solar radiation, suggests that photochemical processes are probably involved in the mechanisms responsible for the DEs.

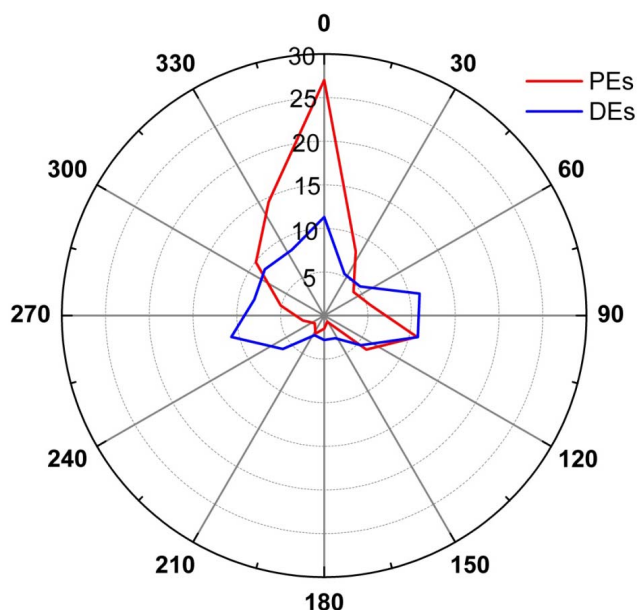


Fig. 6. Angular frequency distribution for pollution and depletion events (PEs and DEs) at wind velocities $> 5 \text{ m s}^{-1}$.

We propose that the primary occurrence of PEs during morning to noon hours reflects the breakup of nocturnal urban air inversions. These air parcels are often loaded with an anthropogenic components and capable of travelling under favourable air flow conditions from the north towards Cape Point. DEs, which are more a noon to afternoon phenomenon, suggest photochemistry as one of the important driving components for possible chemical reactions involved in GEM oxidation. The low wind velocities and undefined wind direction suggest that DEs are a local phenomenon.

3.4 Seasonal variations

While the current data set is rather short (1.2 years), it suggests that there is no pronounced seasonal preference for the occurrences of DEs and PEs (Fig. 8). The monthly DE frequency in the year 2007 was substantially higher than in comparable months of 2008. For instance, only one PE/month was registered for January and February 2008, whilst March and April had none. For May 2008, eight PEs have been noted. From April to September 2007 DEs exceeded 8 events/month, while from January 2008 to June 2008 the frequency of DEs amounted on average to only two per month.

Although the occurrence of DEs and PEs exerts a substantial influence on the shape of the diurnal variation, they have little influence on the overall annual cycle, because of their short duration. The composite seasonal cycle of GEM (March 2007 till June 2008) is shown in Fig. 9 as a box and whisker plot. It is similar to that presented by Slemr et al. (2008), which was derived from low temporally resolved

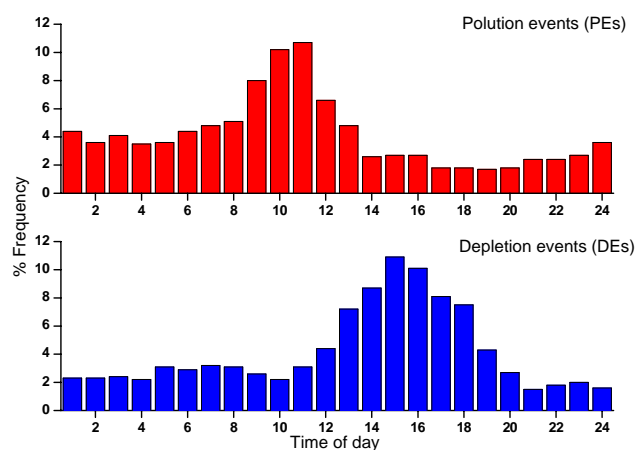


Fig. 7. Composite percentage frequency occurrence of pollution and depletion events (PEs and DEs) for the 2007/08 sampling season, as a function of time of day.

GEM measurements at Cape Point made between 1995 and 2006. Figure 9 shows that GEM concentration maxima occur during austral summer and the minima during winter. This behaviour is opposite in phase to that of carbon monoxide (CO) observed at Cape Point. With some outliers (e.g. January and April) the annual maximum and minimum (median values) have been observed in December and August respectively, giving rise to an average peak-to-peak value of 0.546 ng m^{-3} .

Monthly outliers suggest that the source-sink processes controlling the annual cycle are somewhat variable and less stable than the annually repetitive OH driver, which is believed to be the dominant mechanism for the GEM cycle in the NH (Slemr et al., 2008). Moreover, oceanic Hg sources may also be of greater quantitative significance in the SH than in the NH (Slemr et al., 2008).

4 Conclusions and summary

The most prominent feature of the highly resolved Cape Point GEM data (15-min averages) is the frequent occurrence of events with almost complete mercury depletion, which have only in a few instances been observed at other non-polar localities. These DEs mostly appear in the afternoon between 13:00 and 18:00 and normally last about 5 h. Furthermore, they occur only at wind velocities below 10 m s^{-1} and predominantly less than 5 m s^{-1} without any directional preference, which at such low wind speeds is uncertain at Cape Point due to its complex topography. Their start and end times frequently coincide with changes in wind velocity and/or wind direction and in several cases also with changes in CO and O_3 mole fractions which suggest a changing air mass. The DEs encountered at Cape Point are embedded in all types of air masses ranging from background marine air

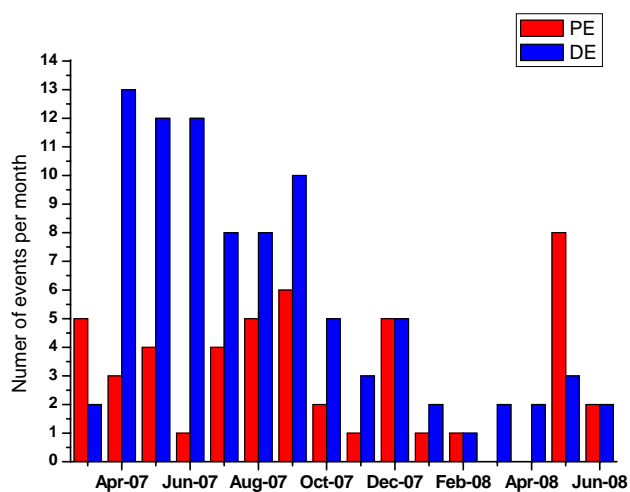


Fig. 8. Monthly frequency of DEs and PEs over the measuring period (March 2007–June 2008).

to polluted continental. No systematic correlation has yet been detected between the GEM concentrations during the DEs and other trace gases (CO , CO_2 , and O_3) measured at Cape Point. The search for a relationship between the GEM concentrations and aerosol parameters has so far been inconclusive: negative correlations were observed between GEM concentration and PM_{10} and $\text{PM}_{2.5}$ scattering (i.e. slightly enhanced aerosol concentrations during DEs) in a few cases but not in most.

All these features together are largely consistent with a scenario of fast photochemical conversion of elemental mercury to RGM or PM which are not measured by our instrument. The short duration of the DEs and the low wind velocity suggest that the area affected by these reactions is rather small, i.e. with a radius of about 100 km around the Cape Point station. The DEs occur only at low wind velocities when a sufficient concentration of the unknown oxidants builds up from the emissions within the area. The DEs occurred at all seasons but for hitherto unknown reasons substantially less frequently in 2008 than in comparable months of 2007. No similar DEs have been detected so far during the long-term mercury monitoring at Mace Head, a site at the western coast of Ireland which in many respects resembles Cape Point. Similar but much shallower DEs (up to a maximum depletion of about 30%) have been observed at Cheeka Peak Observatory near the Pacific coast in Washington State (Weiss-Penzias et al., 2003). But these events were almost always connected to increased O_3 and CO mole fractions suggesting a rapid photo-oxidation of elemental mercury in polluted air. No such systematic coincidence was observed at Cape Point. A slight depletion of elementary mercury during the daytime is predicted by photochemical models within the marine boundary layer of the mid-latitudes (Hedgecock and Pirrone, 2001 and 2005) but the extent of the predicted

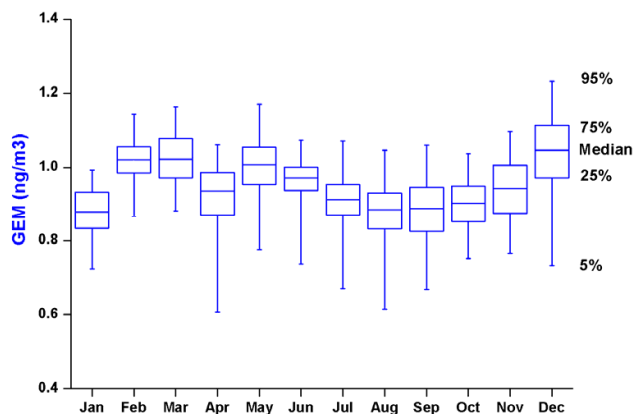


Fig. 9. Box and whisker plot showing composite seasonal Cape Point GEM cycle (March 2007–June 2008).

depletion is only a small fraction of the depletions observed at Cape Point.

An alternative scenario of DEs, driven entirely by meteorological processes, like convection and advection (or both) is not consistent with the majority of the Cape Point observations. RGM was observed to constitute a substantial part of TGM in air originating from the middle and upper troposphere, but only a small fraction in the continental boundary layer (Swartzendruber et al., 2006). Although Cape Point is located within a subsidence band of the southern Hadley cell, the pattern of occurrence of DEs is not consistent with the possibility of occasional exchange between boundary layer and upper tropospheric air. Such changes of air masses should be accompanied by concurrent lower ^{222}Rn and GEM levels. Only one of some 60 DEs shows the expected low ^{222}Rn concentrations. Even then the start and the end of that particular DE do not adequately match the temporal drop and increase of ^{222}Rn concentrations. The RGM concentrations observed by Swartzendruber et al. (2006) at Mount Bachelor Observatory never exceeded 25% of TGM, whereas the mercury depletion observed at Cape Point is frequently almost complete. An occasional exchange of marine and continental boundary layer air is expected to be connected with the same variations of ^{222}Rn concentrations as mentioned above and can thus be ruled out by the same arguments.

The frequent events with almost complete depletion of mercury at Cape Point are, at first sight, similar to atmospheric mercury depletion events (AMDEs) seen in the Polar Regions (Steffen et al., 2008). However, these were observed exclusively in spring and early summer and were attributed to bromine chemistry initiated by the release of bromine compounds from ice or sea water and driven by solar radiation (Lindberg et al., 2002; Calvert and Lindberg, 2003; Steffen et al., 2008). In contrast, the DEs at Cape Point do not fit the pattern of polar AMDEs in several important aspects. Opposite to polar AMDEs which are invariably connected to concurrent ozone depletion (Lindberg et al., 2002; Steffen et al.,

2008), no such depletion has yet been observed during the DEs at Cape Point. Opposite to polar AMDEs which occur exclusively during the spring and early summer, Fig. 8 shows that the DEs at Cape Point occur during all seasons albeit with different and currently not well characterised monthly frequencies. The polar AMDEs also tend to last longer – up to several days – which are consistent with large areas of high BrO concentrations observed by satellites over the Polar Regions (Steffen et al., 2008).

DEs which closely resemble those described by us here for Cape Point have already been reported by Temme et al. (2003). The measurements shown by Temme et al. (2003) in Fig. 6 of their paper have demonstrated that real chemical transformation of elemental mercury during DEs, although unexplained, has – indeed – taken place. For instance on 1 and 2 January 2000, TGM and Hg^0 concentrations measured at Neumayer, Antarctica, have decreased by about 80% and on January 3 by about 50%. In both cases, the depletion was accompanied by a simultaneous increase of RGM and ozone concentrations. The latter observation clearly distinguishes this type of DE from the well documented AMDEs (Schroeder et al., 1998; Ebinghaus et al., 2002). The increase of RGM concentration also documents that a chemical transformation of Hg^0 must have taken place, even if the RGM increase represents merely a fraction of the Hg^0 that had disappeared. Furthermore, these events are characterized by changes in meteorological parameters such as declining wind speeds towards the end of the episode as well as by their short duration periods (less than a day). All this points to a local or regional phenomenon at most. The DEs also tend to be related to solar radiation. An increase of CN concentration during the DE on 1 and 2 January is similar to the observation of slightly increased scattering during some of the Cape Point DEs. Consequently, we believe that the DEs observed at Cape Point are of the same or of a very similar type as those described by Temme et al. (2003).

In addition to the DEs observed at Cape Point and Neumayer stations, we believe that such events have also been observed sporadically during cruises of the RV Polarstern over the southern and northern Atlantic Oceans in 2008 and 2009 (Joachim Kuss, unpublished results). So far all these measurements including those at Neumayer and Cape Point have only been made in the marine boundary layer. The DEs reported by Weiss-Penzias et al. (2003) for Cheeka Peak Observatory might also be similar to those observed at Cape Point coinciding with the plumes of polluted air. However, the Cape Point observations show that polluted air is not a necessary precondition for DEs.

From a chemical perspective the most important difference between the Cape Point type DEs and the AMDEs, is the absence of ozone depletion during DEs at Cape Point. The absence of the concurrent ozone depletion essentially precludes the possibility of Br and BrO reactions which were found to be responsible for polar GEM depletion (Calvert and Lindberg, 2003; Steffen et al., 2008) and of iodine reactions

(Calvert and Lindberg, 2003; Carpenter, 2003). Model simulations of the homogeneous halogen-ozone-mercury reactions by Calvert and Lindberg (2003) suggest smaller ozone depletion accompanied by smaller mercury depletion when BrCl and Cl_2 are the major reagents. But the almost complete depletion of mercury frequently observed at Cape Point would require much higher BrCl and Cl_2 concentrations, which in turn would significantly reduce ozone concentrations. Consequently, halogen photochemistry of AMDEs does not fit our observations even if the large uncertainties of many kinetic parameters are taken into account (Lin et al., 2006; Seigneur and Lohman, 2008).

Weiss-Penzias et al. (2003) made a rough estimate of the lifetime of elemental mercury in pollution plumes from their transport time to Cheeka Peak Observatory and found that it could be as short as 56 h. The DEs at Cape Point suggest a comparable or even a shorter lifetime. The gas phase reaction with ozone is too slow at ozone mole fractions observed at Cape Point even at the highest rate constant reported (Lin et al., 2006), and the reactions with OH and H_2O_2 are too slow at their concentrations expected in the MBL. But the vegetation of the Cape Peninsula might emit volatile organic compounds that in combination with marine chlorine emissions might enhance the reactivity without O_3 destruction (Chang et al., 2002; Tanaka et al., 2003) and reduce the lifetime of elemental mercury. But this explanation does not fit the observations by Temme et al. (2003) and neither those of Joachim Kuss (unpublished results), the latter with DEs far from any vegetated coast. In summary, the chemical mechanism of the Cape Point type DE remains unexplained and additional measurements are required to elucidate it. Such work would entail speciation of mercury and the determination of halogens, halocarbons, other volatile organic compounds and nitrogen oxides. Highly resolved mercury monitoring at other similar sites in the SH is also called for to further substantiate the occurrence of these Cape Point type DEs elsewhere and thus affirm its importance to the global atmospheric mercury cycle.

The short duration of almost all pollution episodes (PEs) and their coincidence with ozone depletion as well as the prevailing northerly wind direction suggest transport from a nearby region north of Cape Point, i.e. from the greater Cape Town metropolitan area and perhaps even from the rural areas further north. The ozone depletion is in this case caused by a “titration” reaction with NO emitted by the burning of fossil fuels and biomass and by the transport time which is too short to replenish ozone by photochemical reactions. The Hg/CO emission ratios are variable ranging from low values typical for biomass burning to high values observed for emissions from urban/industrial areas. Only very few events associated with long-range transport were observed.

Because of their short duration, the DEs and PEs do not substantially influence the seasonal variation of the GEM concentration at Cape Point. The GEM concentrations peak in austral summer and early fall (December–March) and

reach their minimum at the end of austral winter and early spring, i.e. during July–October. This seasonal variation is thus comparable to that derived by Slemr et al. (2008) from long-term GEM measurements at Cape Point at low temporal resolution of about 200 samples per year. The difference to a typical seasonal variation of TGM concentration in the NH was attributed by Slemr et al. (2008) to the predominance of seasonal variations of oceanic emissions, the emissions from biomass burning, and to the seasonal variation of the north-south transport.

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