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**Total gaseous
mercury depletion
events observed at
Cape Point**

E.-G. Brunke et al.

Total gaseous mercury depletion events observed at Cape Point during 2007–2008

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Received: 18 March 2009 – Accepted: 23 April 2009 – Published: 5 October 2009

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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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 almost quantitative in many cases and suggests a lifetime 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 characteristics of the DE occurrence at Cape Point is neither similar to the halogen driven atmospheric mercury depletion events (AMDEs) observed in Polar Regions nor to the DEs reported for plumes of urban air. Additional measurements are necessary to reveal the chemical mechanism of the observed DEs and to assess its importance on larger scales.

1 Introduction

Mercury (Hg), a prominent global environmental pollutant, with anthropogenic and natural sources of comparable magnitude (Nriagu, 1989; Mason and Sheu, 2002) has evoked world-wide concern among the research community. It has thus remained high on the priority lists of a large number of international agreements and conventions. Mercury, having a fairly long atmospheric residence time (about 1 year) (Slemr et al., 1985; Lindqvist and Rodhe, 1985), can be distributed via long-range atmospheric transport along inter-hemispheric distances. The existing Cape Point atmospheric Total Gaseous Mercury (TGM) data base comprises both manual measurements with low temporal resolution (initiated in 1995; Baker et al., 2002) as well as automated

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measurements with a resolution of 15 min (present program 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 high resolution data provides new information on previously undetected depletion events (DEs) and also to a lesser extent, on pollution events (PEs). DEs have so far only been observed in the Polar Regions (Schroeder et al., 1998; Ebinghaus, 2002) and are hence of special interest for further investigation. Although Poissant and Pilote (2003) have reported AMDEs for Kuujuaupik/Whapmagoostui (a site along Hudson Bay coast – situated to the south of the Arctic Polar Circle), the climatology is quasi-polar and includes the occurrence of sea ice.

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 to the south of Cape Town, and located on top of a 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 and 1996). The site experiences moderate temperatures, dry summers with occasional biomass

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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). Use has also been made of 10-day isentropic back trajectories from NOAA ESRL (<http://www.esrl.noaa.gov/gmd>) in an attempt to identify the origin of the air associated with the PEs and DEs. In 2005 a measurement program for aerosol optical properties was started in close cooperation 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, 0.09, 0.28, and 0.9, 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 161, 2005). Factors affecting the sensitivity and accuracy of the Cape Point ²²²Rn detector have been discussed by Brunke et al. (2002) and references therein.

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The current instrument in use at Cape Point to measure gaseous mercury concentrations 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 and 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 μm) 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 ease of comparison to other trace gas and meteorological data being measured simultaneously at Cape Point.

Scientific consensus exists that Atmospheric Mercury Depletion Events (AMDEs) are periods during which rapid atmospheric oxidation reactions reduce the concentration of gaseous elemental mercury (Hg⁰) (sometimes to concentrations below 0.1 ng m⁻³), 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 TGM at high levels of RGM and/or TPM (i.e. as a consequence of depletion events) have led to different interpretations of the parameter TGM 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 level, 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 Hg(0) yielding TGM. This (i.e. Hg(0)+RGM=TGM) has been demonstrated by Temme et al. (2003) under very dry and cold conditions in the Antarctic lower troposphere. However, under the prevailing atmospheric conditions at Cape Point (higher temperature, high humidity,

and 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 [Hg^0].

3 Results and discussion

5 During the 14-month period under discussion here (March 2007 till June 2008), the mean Cape Point TGM concentration (20 248 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 TGM concentrations from Mace Head (Kock et al., 2005)
10 in the Northern Hemisphere (NH) for comparison.

As can be seen, the Cape Point TGM levels (SH) are about 0.6 times lower than those for the NH (Slemr et al., 2008). Besides this inter-hemispheric difference, both data sets display occasional pollution events (PEs). However, the major difference
15 observed at Cape Point, but so far not at Mace Head and any other non-polar site in the NH. 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
20 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
25 occurrence of these events and their relations to other parameters measured at Cape Point. In the last section the Cape Point TGM seasonal variations will be compared to those from earlier observations.

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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 given below:

Figure 3 shows a DE observed on 3 April 2007, at ^{222}Rn levels (2nd panel from the bottom) ranging between 2000 and 3800 mBq m^{-3} . These ^{222}Rn levels are typically indicative of air 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 TGM 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 TGM 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, points to the north during this event. Observed aerosol backscattering for particles smaller than 1 and $10 \mu\text{m}$ (shown in 2nd panel from the top) is variable without any apparent correlation with the TGM concentration.

Figure 4 shows another significant DE on the 12 April 2007. This specific event lasted almost 8 hours and reached a minimum 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 $5\text{--}1.5 \text{ m s}^{-1}$). The start of this event, at about 11:30,

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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 of wind direction. Although 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 is 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 TGM 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 e.g. two events in September 2007 (data not shown here). The first event occurred on 19 September 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 O_3 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 O_3 peaked at 48 ppb (1.5 times the background). The end of the second event coincided with a drop of O_3 mole frac-

tion from about 40 to 26 ppb. The ^{222}Rn 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 TGM 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 several other DEs have originated during the day under similar conditions (although not clearly understood yet) and that these TGM-deprived 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 (Obrist et al., 2008; Brunke et al., 2001) instances of TGM pollution events (PEs) have been observed at Cape 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 TGM level of 1.4 ng m^{-3} (1.5 times its background), and ^{222}Rn , CO and O_3 levels of 1514 mBq m^{-3} , 420 ppb (7 times background) and 4 ppb (8 times below the normal level), respectively. Aerosol backscattering of the 1 and $10 \mu\text{m}$ particle fractions showed elevated levels between 01:00 and 08:00, which preceded the CO and TGM highs and ended before these two parameters returned to “normal”. Note that TGM is roughly positively correlated with CO which in turn is tightly negatively correlated with O_3 . The correlation with ^{222}Rn is only weak and a correlation with aerosol is virtually nonexistent. The negative correlation of CO with O_3 suggests titrations of O_3 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 appropriate airflow towards the south.

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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 TGM and CO as well as TGM 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 ²²²Rn levels ranging from <150 (marine) up to 4000 mBq m⁻³ (continental).

No significant correlation between TGM and CO was observed during the DEs (TGM 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 TGM values with a few occasional outliers. A plot of CO vs. TGM 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 TGM 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 TGM concentrations are characteristic for biomass burning plumes, whereas high peak TGM concentrations at relatively low peak CO levels are usually encountered in plumes from urban/industrial regions (Weiss-Penzias et al., 2007).

TGM/CO emission ratios have been determined for 34 PEs from correlations of TGM 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 have been set at 50 pg m⁻³ for TGM and 1 ppb for CO. 80% of the correlations were significant at the 99% and higher confidence level

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and the rest at a level exceeding 95%. With the exception of an episode observed on March 23, 2007, the TGM/CO ratios vary between 0.3 and 5 pg m^{-3} ppb and agree well with values reported in the literature ranging from about 1.5 pg m^{-3} ppb for biomass burning to about 7 pg m^{-3} ppb for Asian and European outflow (Slemr et al., 2009 and references therein).

TGM 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 TGM vs. O_3 to be negatively correlated, especially for continental air (r ranging from -0.4 to -1.0). This suggests that TGM pollution more often occurs in stagnant urban air masses, where a build-up of TGM 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 NO (Sillman, 1999). Peak TGM 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 gold mining and coal combustion region in Gauteng and Mpumalanga constitutes 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.

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 TGM with PM_1 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

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was detected. No apparent correlation of CN with TGM 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 wind roses is shown in Fig. 6. Wind data with velocities $<5 \text{ m s}^{-1}$ have been excluded, because of the unreliability of directions at such low velocities. 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 during winds with 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 TGM 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 daytimes. 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.

We propose that the primary occurrence of PEs during morning to noon hours re-

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flects the breakup of nocturnal urban air inversions. These air parcels are often loaded with an anthropogenic component 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 TGM destruction. 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/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 TGM (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 temporal resolution TGM measurements at Cape Point made between 1995 and 2006. Figure 9 shows that TGM 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 TGM cycle in the NH (Slemr et al.,

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2008). Moreover, oceanic Hg sources may also be of greater quantitative significance in the SH than in the NH (Slemr et al., 2008).

4 Summary and conclusions

The most prominent feature of the highly resolved Cape Point TGM data (15 min averages) is the frequent occurrence of events with almost complete mercury depletion which have so far not been observed at any other non-polar station. 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 below 5 m s^{-1} without any directional preference, which at such low wind velocities is uncertain anyway. Their start and end times frequently coincide with changes of wind velocity and/or wind direction and in several cases also with changes in CO and O₃ mole fractions which suggest a changing air mass. The DEs are embedded in all types of air masses encountered at Cape Point ranging from background marine air to polluted continental. So far, no systematic correlation has been detected between the TGM concentrations during the DEs and other trace gases (CO, CO₂, and O₃) measured at Cape Point. Furthermore, the search for a relationship between the TGM concentrations and aerosol parameters has so far been inconclusive: negative correlations were observed between TGM concentration and PM₁ and PM₁₀ 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

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detected so far during the long-term mercury monitoring at Mace Head, a site at the western coast of Ireland which in many respects is similar to 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 O₃ 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 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 part 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 ²²²Rn and TGM levels. Only one of some 60 DEs shows the expected low ²²²Rn concentrations. Even then the start and the end of that particular DE do not adequately match the temporal drop and increase of ²²²Rn 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 quantitative. An occasional exchange of marine and continental boundary layer air are expected to be connected with the same variations of ²²²Rn 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

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similar to atmospheric mercury depletion events (AMDEs) seen in the Polar Regions (Steffen et al., 2008). 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). 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 so far 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).

From a chemical point of view the most important of these differences is the absence of ozone depletion during the DEs observed 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 TGM 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 Cl₂ are the major reagents. But the almost complete mercury depletion observed frequently at Cape Point would require much higher BrCl and Cl₂ concentrations, which in turn would significantly reduce ozone concentrations. Consequently, halogen photochemistry of AMDEs does not fit the 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 the 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

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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 H₂O₂ 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 O₃ destruction (Chang et al., 2002; Tanaka et al., 2003) and reduce the lifetime of elemental mercury. In summary, the chemical mechanism of the DEs at Cape Point remains unexplained and additional measurements are required to elucidate it, such as the speciation of mercury at Cape Point and the determination of the 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 prove or disprove the singularity of the DE occurrence at Cape Point and thus their importance for the global atmospheric cycle of mercury.

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 TGM concentration at Cape Point. The TGM 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 TGM measurements at Cape Point with 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.

5 *Acknowledgements.* The assistance rendered by Bhawoodien Parker and Thumeka Mkololo in maintaining the Tekran TGM analyser in good working order at Cape Point is being greatly appreciated. Furthermore, we are grateful towards Danie van der Spuy for having assisted in the data preparation process and to Thumeka Mkololo for having partaken in some of the data evaluation. We would also like to acknowledge EPA, Ireland for having made Mace Head
10 TGM data available for comparison purposes and thank NOAA ESRL GMD for their trajectory calculations.

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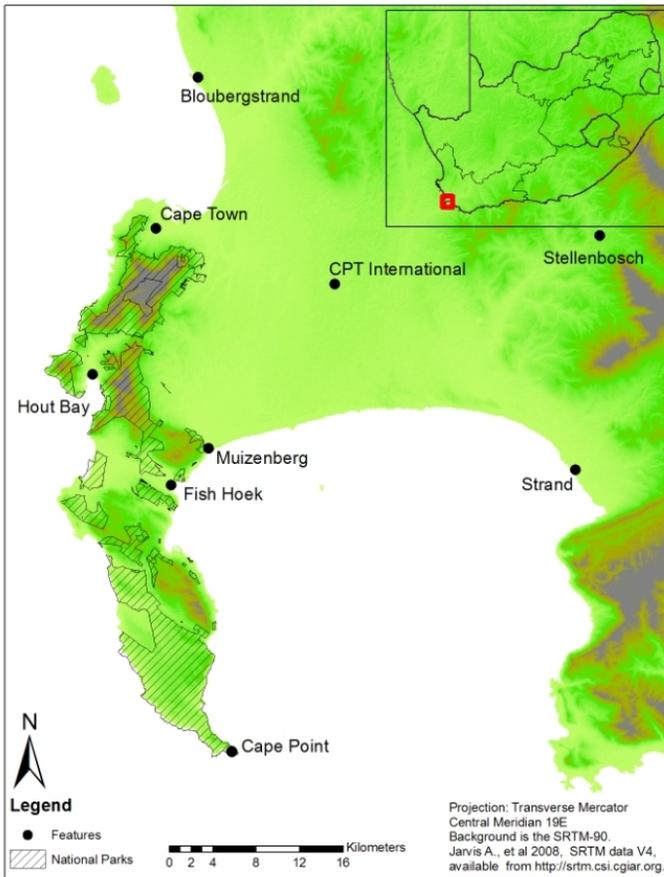


Fig. 1. Map of the Cape Peninsula with the location of the GAW station at Cape Point.

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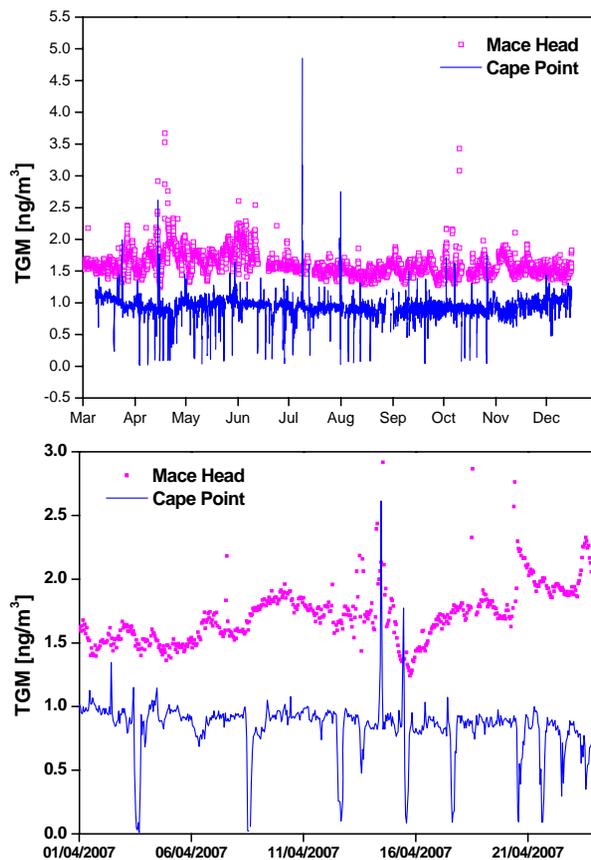


Fig. 2. (a) TGM time series for two sites: Mace Head (source: Kock et al., 2005), representing the Northern Hemisphere and Cape Point, the Southern Hemisphere (March 2007–December 2007). (b) Zoomed-in section for April 2007 highlighting DEs at Cape Point.

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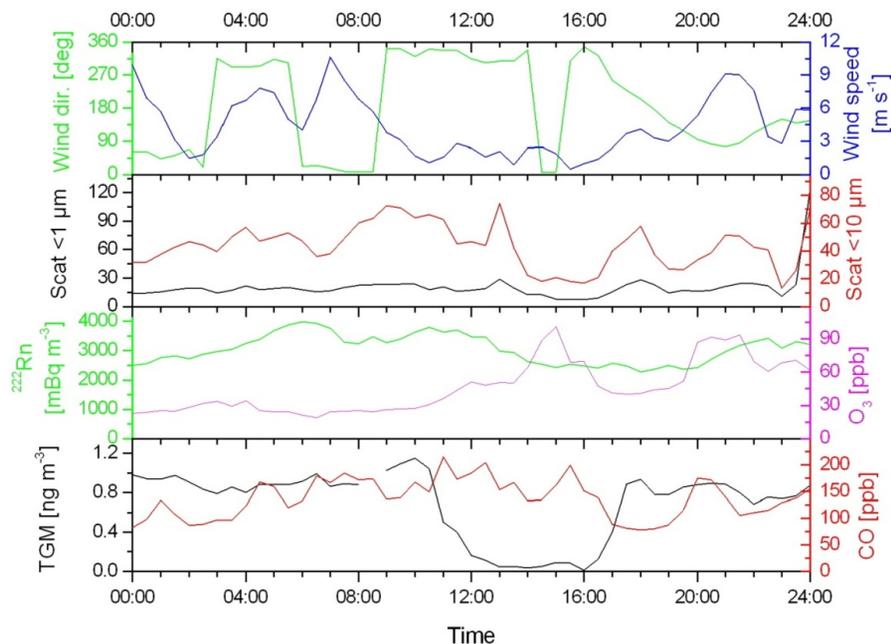


Fig. 3. TGM depletion event (DE) on 3 April 2007.

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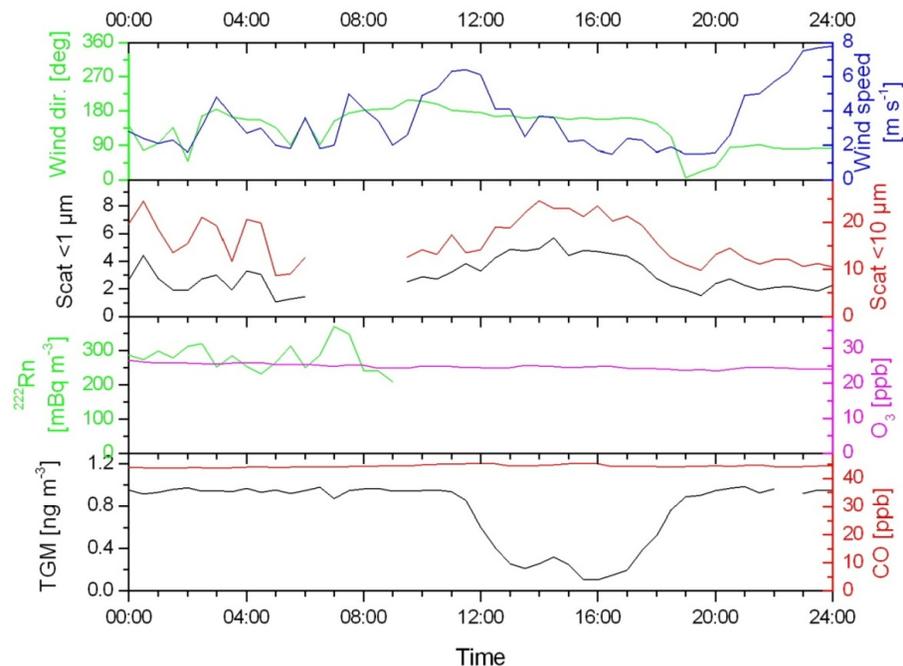
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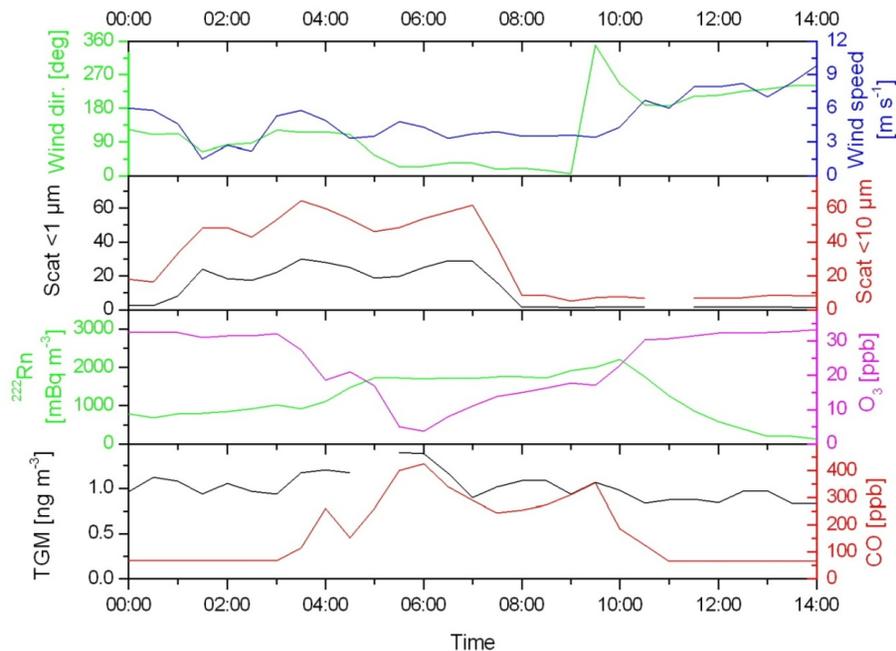
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**Fig. 4.** TGM depletion event (DE) on 12 April 2007.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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

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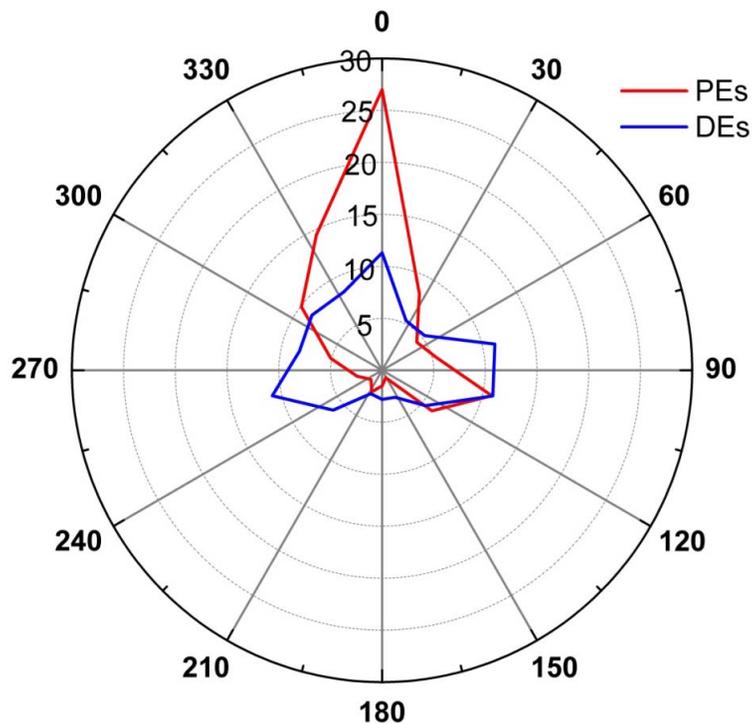


Fig. 6. Wind (velocities $>5 \text{ m s}^{-1}$) frequency distributions for pollution and depletion events (PEs and DEs).

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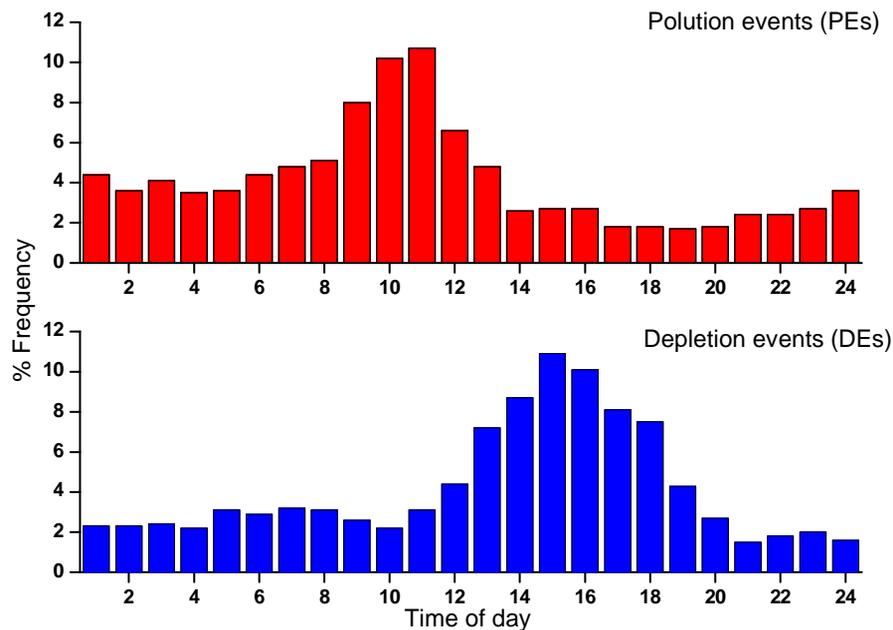


Fig. 7. Composite percentage frequency occurrence of pollution and depletion events (PEs and DEs) for the 2007/2008 sampling season, as a function of time of day.

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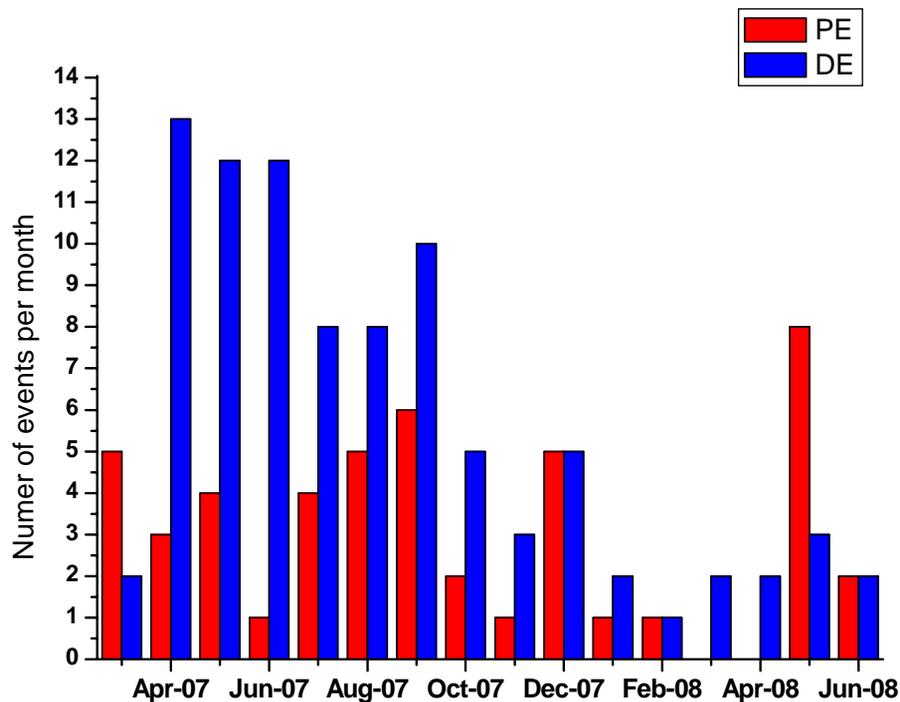


Fig. 8. Monthly frequency of TGM DEs and PEs over the measuring period (March 2007–June 2008).

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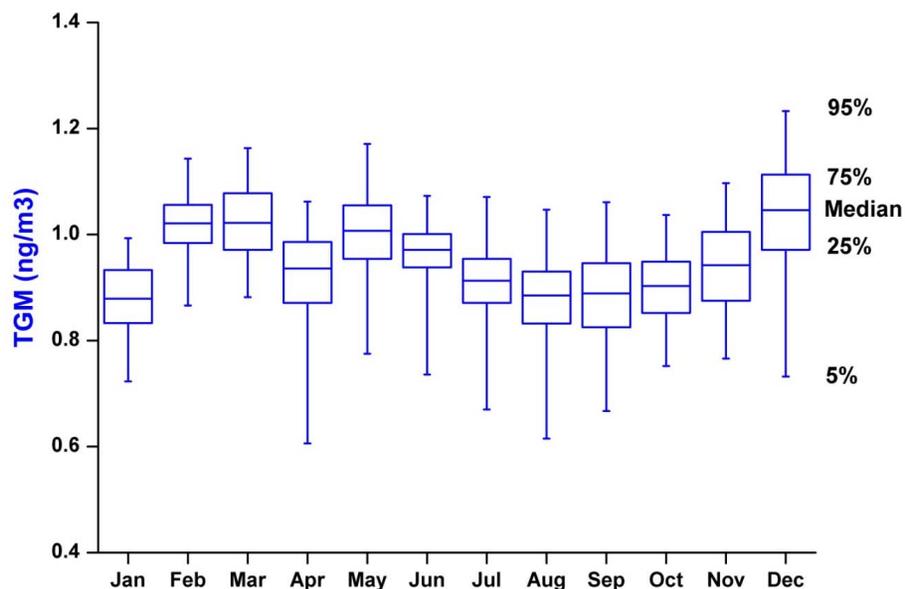


Fig. 9. Box and whisker plot showing composite seasonal Cape Point TGM cycle (March 2007–June 2008).

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