Brunke, E.-G.; Walters, C.; Mkololo, T.; Martin, L.; Labuschagne, C.; Silwana, B.; Slemr, F.; Weigelt, A.; Ebinghaus, R.; Somerset, V.:

Mercury in the atmosphere and in rainwater at Cape Point, South Africa

In: Atmospheric Environment (2015) Elsevier

DOI: 10.1016/j.atmosenv.2015.10.059

Mercury measurements (2007-2013) made in the atmosphere and in rainwater at Cape Point, South Africa

Ernst-Günther Brunke[1], Chavon Walters[2], Thumeka Mkololo[1], Lynwill Martin[1], Casper Labuschagne[1], Bongiwe Silwana[2], Franz Slemr[3], Andreas Weigelt[4], Ralf Ebinghaus[4], and Vernon Somerset[2¥]

[1]South African Weather Service c/o CSIR, P.O. Box 320, Stellenbosch 7599, South Africa
[2]Natural Resources and the Environment (NRE), Council for Scientific and Industrial Research (CSIR), Stellenbosch, 7600, South Africa.
[3]Max-Planck-Institut für Chemie, Hahn-Meitner-Weg 1, 55128 Mainz, Germany
[4]Helmholtz-Zentrum Geesthacht (HZG), Institute of Coastal Research, Max-Planck-Strasse 1, D-21502 Geesthacht, Germany,

Abstract

Mercury measurements were concurrently made in air (Gaseous Elemental Mercury, i.e. GEM) as well as in precipitation samples (Total mercury, i.e. TotHg) over a seven year period (2007-2013) at Cape Point, South Africa, during the rainy seasons (May – October). Eighty-five rain events, almost exclusively associated with cold fronts, have been identified of which 75% reached the Cape Point observatory directly across the Atlantic Ocean from the south, while 19% moved in to the measuring site via the Cape Town metropolitan region. In statistic terms the GEM, TotHg, CO and ^{222}Rn levels within the urban-marine events do not differ from those seen in the marine rain episodes. Over the 2007 – 2013 period, the May till Oct averages for GEM ranged from 0.913 ng m^{-3} to 1.108 ng m^{-3}, while TotHg concentrations ranged from 0.03 to 52.5 ng L^{-1} (overall average: 9.91 ng L^{-1}). A positive correlation (R^2 = 0.49, n=7) has been found between the average annual (May till October) GEM concentrations in air and TotHg concentration in rainwater suggesting a close relationship between the two species. The wetter years are normally associated with higher GEM and TotHg levels. Both GEM and TotHg annual means correlate positively with total annual (May till October) rain depths. If one or two outlier years are removed from the data set the R^2 values for the averages from the remaining years increases to 0.97 (n=5) and 0.89 (n=5) for GEM and TotHg, respectively. The relationship between annual mean GEM and annual precipitation depth also holds for the period 1996-2004 (R^2 = 0.6, n=8) when GEM was measured manually (low resolution data). A positive correlation was also seen between annual average GEM concentrations and the El Niño Southern Oscillation (ENSO) Index (SOI), for the 1996-2004 period (R^2 = 0.7, n=8). For the 2007-2013 periods this relationship was also positive but less pronounced. The relationship between annual precipitation depth and annual SOI suggests that the inter-annual variations of GEM (Hg^0) concentration might be caused by large-scale meteorological processes including variations in sea surface temperatures which could affect air-sea flux processes as well as changes in long-range transport and precipitation patterns.

Keywords: Gaseous Elemental Mercury; Atmospheric; Total mercury; Rainwater; Cape Point

1. Introduction

Mercury (Hg) is regarded as a highly toxic heavy metal and is also considered a global pollutant due to its long range transport and its bio-accumulation in the aquatic nutrition chain. Mercury is discharged into the atmosphere through both natural and anthropogenic sources. Atmospheric Hg consists mostly of gaseous elemental mercury (GEM), with small fractions of

¥ Vernon Somerset; Tel.: +27.21.8882631; Fax: +27.86.6631789; Email: vsomerset@csir.co.za; vsomerset@gmail.com

gaseous oxidized mercury (GOM) and particle bound mercury (PBM) which together usually represent less than 3% of total atmospheric mercury (Schroeder and Munthe, 1998; Lindberg et al., 2007, Sprovieri et al., 2010). Because of its high vapour pressure and low solubility, GEM has to be oxidized to RGM to be removed from the atmosphere. In contrast to GEM, RGM and PM are readily removed from the atmosphere by rain and washout as well as by dry deposition (Lindberg et al., 2007). Wet and dry deposition thus represents an important source of mercury to terrestrial and aquatic systems (Mason and Sullivan, 1998; Prestbo and Gay, 2009) and as such is often used to assess the adverse effects of Hg (Fitzgerald et al., 1998; Kotnik et al., 2002). Long-term measurements of rainwater Hg have been reported by several authors worldwide, but most of the present monitoring sites are located in the Northern Hemisphere (NH) (Mason et al., 2000; Laurier and Mason, 2007; Dutt et al., 2009; Prestbo and Gay, 2009; Gratz et al., 2009; Caffrey et al., 2010; Lombard et al., 2011). Only a few measurement of Hg in rainwater have been reported in the Southern Hemisphere (SH) so far (Lamborg et al., 1999; Mirlean et al., 2005; Dutt et al., 2009, Gichuki and Mason, 2013).

In Southern Africa, limited work has been conducted to understand the factors that influence the atmospheric wet and dry deposition of Hg (Gichuki and Mason 2013; Masekoameng et al., 2010). In the study conducted by Williams et al. (2011) mercury was measured in the water management area and reported values ranged between 1.51-2.00 ng/L and 20.01-50.00 ng/g for TotHg in water and sediment samples, respectively. Similarly, for Southern America and Australia, limited work has been conducted to characterise Hg in precipitation, although a few studies have reported TotHg concentrations in wet deposition and watershed studies (Mirlean et al., 2005; Biester et al., 2002; Dutt et al., 2009; Lamborg et al., 1999).

GEM has been measured at Cape Point, South Africa, between 1995 and 2004 and since 2007 until present. Different aspects of these measurements have been reported in the literature such as the GEM seasonality (Slemr et al., 2008), long-term trends (Slemr et al., 2011), occasional depletion events (Brunke et al., 2010), and the use of the data for the estimation of anthropogenic emissions and terrestrial fluxes in southern Africa (Brunke et al., 2012; Slemr et al., 2013). Measurements of TotHg in rainwater have been made since June 2007 and the first results for the period from 2007 until December 2009 were already reported by Gichuki and Mason (2013). They presented a seasonal analysis of TotHg concentrations in wet deposition samples. The results of their study have also shown that both marine and continental air masses classified via ^{222}Rn and CO (Brunke et al., 2012) could influence the measured TotHg concentrations in wet deposition at Cape Point. They emphasized the need for more accurate long-term TotHg measurements in order to improve our understanding of the chemical and atmospheric processes driving deposition at Cape Point and its links between GEM measured at the same site.

The data presented in this study provides a summary of Cape Point GEM and TotHg concentrations measured until the end of 2013, their inter-annual variations, their relationship among themselves and with meteorological parameters such as annual precipitation depth and El Niño Southern Oscillation (ENSO). The findings from the analysis of this extended data set reveal new insights into the relation between GEM, TotHg, and meteorological parameters.

2. Study Site and Methods

2.1. Geographic Location and Climate

The Cape Point Global Atmosphere Watch (GAW) station (34° 21´S, 18° 29´E) is managed by the South African Weather Service (SAWS) and is one of more than 30 GAW baseline stations of the World Meteorological Organisation (WMO). The laboratory is located about 60 km to the

south of the greater Cape Town area (Fig. 1). It is situated within a National Park at the southern tip of the Cape Peninsula on top of a cliff (230 m a.s.l.). The station has been in operation since 1978 and its current continuous measuring program includes Hg (GEM), CO, ^{222}Rn, surface O_3, CH_4, N_2O, CO_2, halocarbon species (e.g. CFC-11 and 12), aerosol optical density and optical properties, as well as solar and meteorological parameters (http://gaw.empa.ch/gawsis).

Cape Point experiences a Mediterranean-type climate that is characterized by rather dry summers comprising moderate temperatures. The austral autumn to spring season (May till October) normally experience increased precipitation due to the passage of cold fronts moving from West to East. Furthermore, the prevailing wind direction at Cape Point during austral summer is mainly from the southeast to the southwest, while during winter the air is more strongly advected to the station from the north to northwestern quadrant (Rautenbach and Smith 2001; Brunke et al., 2004). As such Cape Point generally receives clean marine air from the Southern Atlantic, especially during the summer months. However, at times (mainly during the winter period) continental and polluted air masses are observed at the site more frequently. The polluted events provide interesting data, but can easily be filtered out using ^{222}Rn as an effective tracer for maritime air (Brunke et al., 2004). This procedure is applied routinely for the purposes of detecting long-term trends for trace gases, such as CO_2, CH_4, CO and others under background conditions.

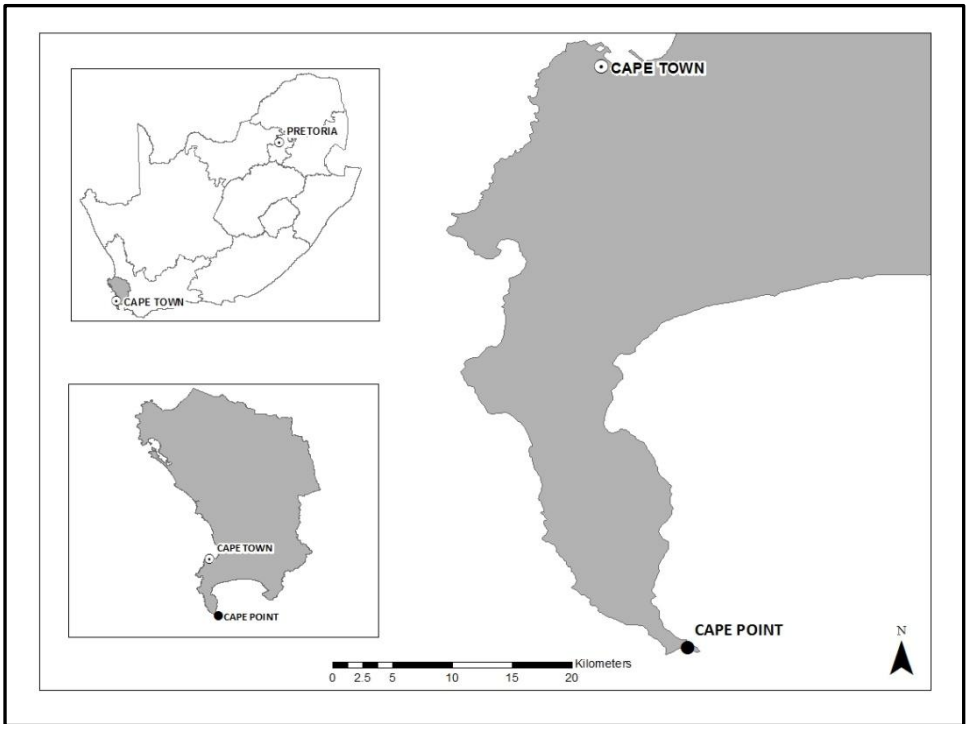


Fig. 1: Map showing the location of Cape Town, Pretoria and Cape Point at the southern end of the Cape Peninsula with Cape Town 60 km to the north.

The main source of Hg in the South African environment is from anthropogenic emissions mostly due to burning low grade coal at coal-fired power stations, the main source of energy production in South Africa (Dabrowski et al., 2008; Masekoameng et al., 2010; Williams et al., 2010). Other anthropogenic sources that may also play a role are from waste incineration, biomass burning, cement production and artisanal gold mining (Gichuki and Mason, 2013; Dabrowski et al., 2008). Although the greater Cape Town area emits mercury (e.g. from diesel

driven vehicles and waste incineration), the major anthropogenic Hg sources are located 1500 – 2000 km to the north-west of Cape Point in the Gauteng and Mpumalanga provinces where former mine dumps from gold mining (Dabrowski et al., 2008) and large coal-burning power stations are located. Although Cape Point is subjected mainly to the advection of marine air, continental air also reaches the station, especially during the winter months thereby bringing with it traces of local and regional pollution (Brunke et al., 2004). However, the major source region affecting Cape Point GEM levels is thought to be located in the Southern Ocean as is indicated by back trajectory studies (Brunke et al., 2004).

2.2. Measurements and Analysis

2.2.1. Atmospheric mercury sampling

GEM has been measured at Cape Point by a manual amalgamation technique (Slemr et al., 2008) since September 1995 until December 2004 and by a Tekran 2537A instrument (Tekran Inc., Toronto, Canada; Steffen and Schroeder, 1999) since March 2007. The manual technique provided about 200 GEM concentrations per year, each averaged over a 3 h sampling time. In this paper we use primarily the latter data with a resolution of 15 min. The start of the highly resolved GEM measurements in 2007 roughly coincides with the commencement of the CSIR's Hg precipitation project (Gichuki and Mason, 2013). The air measurements were made in compliance with the standard operating procedures of the GMOS (Global Mercury Observation System, www.gmos.eu) project.

3.2.2. Rainfall collection and analysis

Weekly precipitation samples were collected as a continuation of the project started by Gichuki and Mason (2013) in June 2007 almost exclusively during the rainy season which at Cape Point lasts from May till October. The sample equipment cleaning protocol and sample collection generally consisted of standard protocols for TotHg in acid-cleaned Teflon® bottles (US EPA, 1996; Williams et al., 2011). Rainwater samples were collected using a homemade glass funnel connected to a 500 mL Teflon® bottle (Gichuki and Mason, 2013). After each weekly sample the Teflon® sampling bottle was disconnected from the rain funnel and the sample was preserved by spiking it with 0.5% (v/v) trace metal grade hydrochloric acid solution, followed by sample refrigeration during storage.

The analytical protocol for the rain sample comprised the digestion with bromine chloride (BrCl) and reduction with hydroxylamine hydrochloride ($NH_2OH.HCl$) and stannous chloride ($SnCl_2.2H_2O$). The released elemental Hg vapour was trapped by amalgamation on a gold surface and was detected after thermo-desorption by cold vapour atomic fluorescence spectrometry (CVAFS). Rainwater volumes were recorded for each sampling events. Data are presented as volume-weighted mean (VWM) Hg concentrations (ng/L) for each weekly sample (Williams et al., 2011; Gichuki and Mason, 2013).

3.2.3. Atmospheric gases and precipitation data organisation

The sampler was exposed for one week at a time, i.e. from one Monday till the next and thus collected some mercury by dry deposition, which - according to Gichuki and Mason (2013) - is negligible. Over the seven year period, 138 weekly samples were collected, of which 12 samples were dry (no rain water at all) leaving a total of 126 wet samples. Of these weekly samples a few constituted more than one event, while a few others were too small to be analysed.

In our approach to identify meaningful rainfall events (ranging from hours to a few days) we used 30 min average rainfall data obtained from the SAWS automatic rain gauge. If rain was collected continuously over a period of three hours or more and exceeded a total rain depth of 6 mm, it was classified as a rain event. A precipitation gap exceeding five hours or more was arbitrarily chosen to separate different rain events from one another. The half-hourly precipitation maximum of an event was selected to represent the temporal apex for that episode. In accordance, the respective GEM, CO and ^{222}Rn median - in addition to the total rain depth (total volume water collected) - were determined for the duration of each respective event and assigned to the time stamp of that rain maximum. In total, 85 rain events out of the 126 wet weekly samples have been identified to meet these criteria. Notwithstanding, the somewhat subjective approach in identifying the start and end times of each rainfall episode, we are confident that this method is more accurate than simply working with the composite weekly samples and assigning supplementary data to them.

Whilst low ^{222}Rn concentration is an excellent tracer for marine air (Brunke et al., 2004), elevated CO levels represent a good indicator of anthropogenic activities (Scheel et al., 1998). Since CO has a strong annual cycle (Seiler et al., 1984), the data have been de-seasonalised so that CO concentrations investigated here can be related to any marine and urban-continental signatures unaffected by CO's seasonality. An arbitrary offset was applied to the de-seasonalised CO time series so that minimum levels approximated 27 ppb. All values exceeding 27 ppb are hence due to urban-continental signatures.

3. Results and Discussion

3.1. Backward trajectories for rain events

Ten-day isentropic back trajectories (NOAA Hysplit Model; http://www.arl.noaa.gov/HYSPLIT.php.) with 4-hourly resolution and a 500m arrival altitude were generated for the 85 rain events identified during 2007 - 2013. The time of the highest rain intensity (apex) observed at the station during a rain episode was selected as the arrival time of the respective air mass trajectory for that event.

It was found that almost all cold fronts which led to rain events were associated with trajectories originating from the Atlantic Ocean. There were no rain events of continental origin. Of the rain events identified, 75% correspond to air masses which reached Cape Point directly from within the southern quadrant (140° to 280°) without moving over land first. About 19% of all trajectories made a small bypass over the Cape Town metropolitan area before reaching the GAW station. The 7th of August 2013 represents an example of the former, while the 29th of May 2013 is an example of the latter trajectory type (Fig. 2). The remaining trajectories (6%) made diversions over the southern tip of Africa (Agulhas) before reaching Cape Point (not shown here), thereby possibly entraining some continental air.

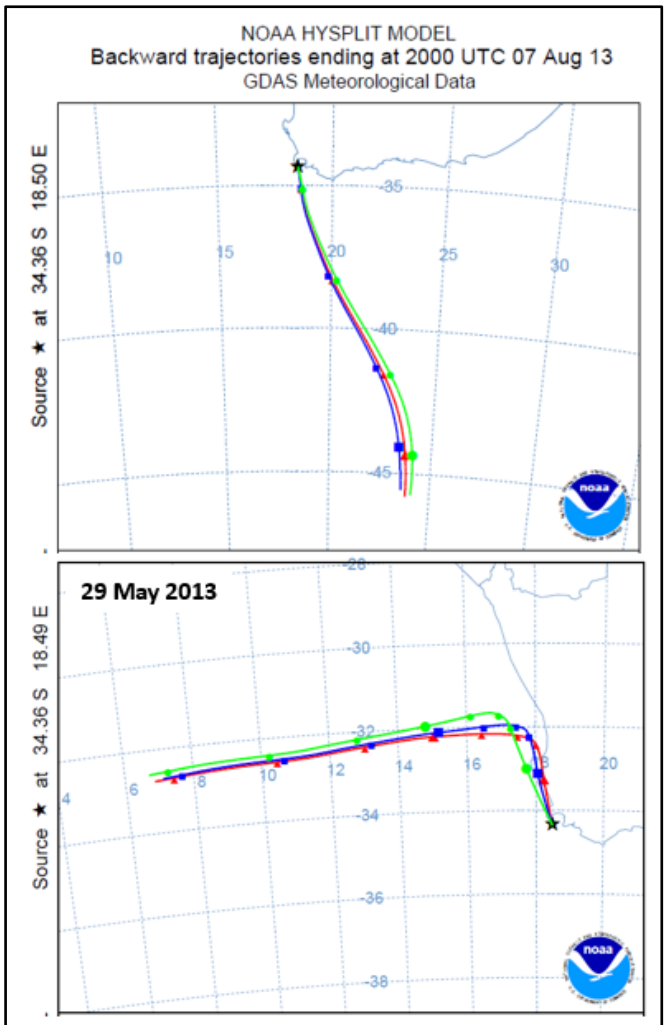


Fig. 2. Backward trajectories associated with cold fronts reaching Cape Point directly from the Southern Ocean (top) or transgressing over Cape Town first (bottom).

3.2. Air quality associated with rain events

^{222}Rn concentrations and de-seasonalised CO data measured during these rain events have been summarized in the histograms shown in Fig. 3. Approximately 64% of the ^{222}Rn concentrations fall below 250 mBq m^{-3}, which is considered to represent essentially marine air (Brunke et al., 2004). Likewise, 85% of the de-seasonalised CO data fall within the range between 27 to 37 ppb. The small variability of only 10 ppb shows that the influence of urban-continental air was small. As substantiated by the trajectories, we conclude that rain events are generally associated with clean marine air masses. Even if a cold front sweeps over Cape Town first, the altitude of the clouds and their limited temporal exposure to anthropogenic sources essentially precludes the uptake of pollutants in most cases.

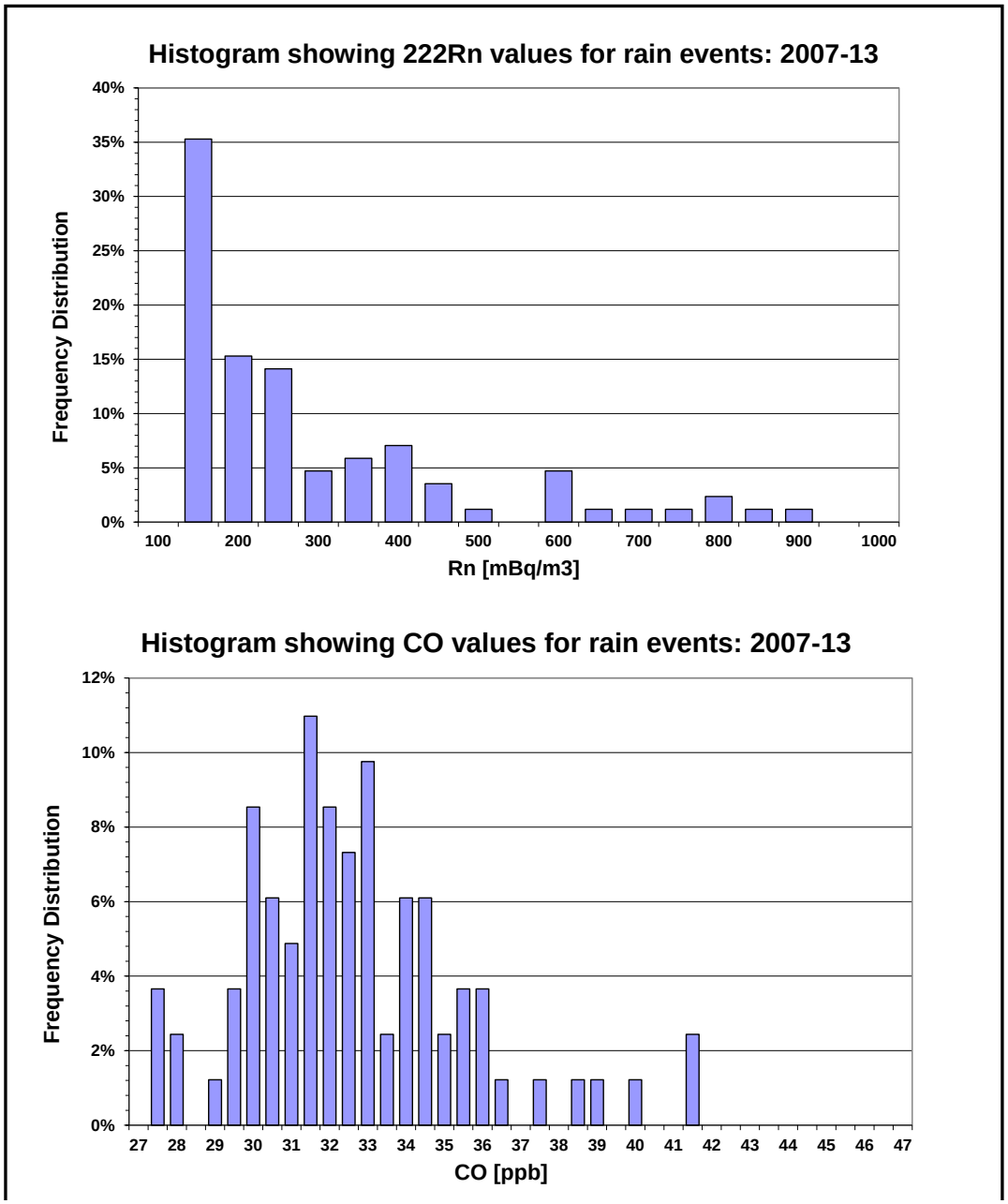


Fig. 3. Histograms for ^{222}Rn (top) and CO (bottom) for the 85 rain events.

A few exceptions do, however, exist where elevated values for CO and ^{222}Rn have been observed. To illustrate the above, we present here a few individual examples of both marine and marine-urban frontal rain episodes.

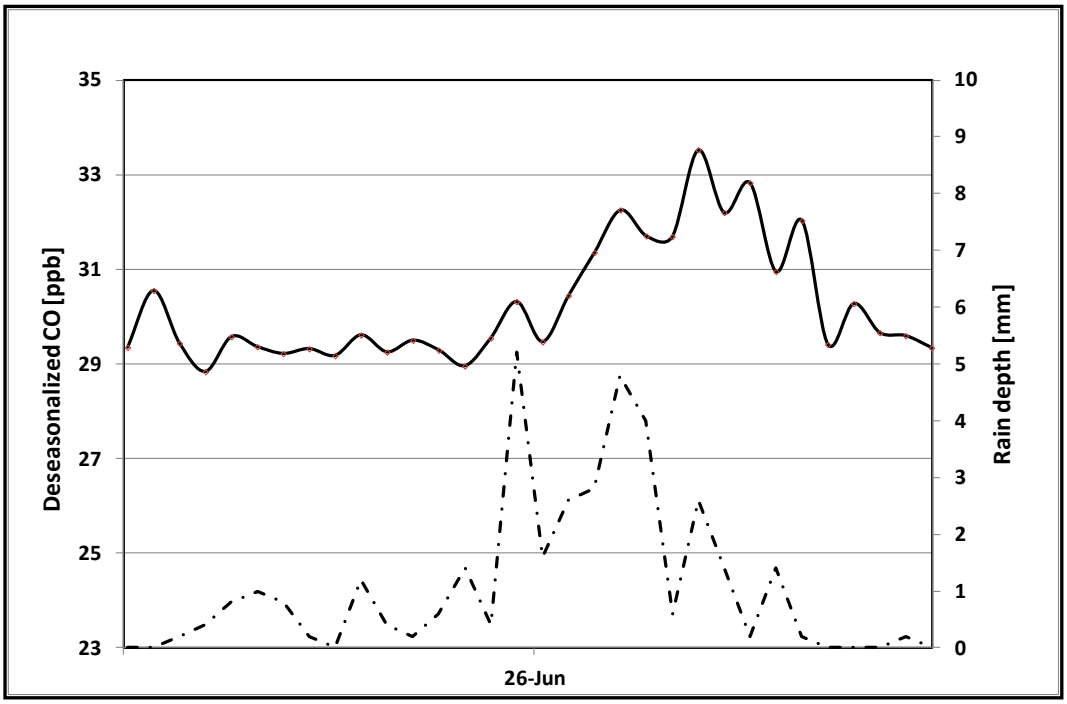


Fig. 4. De-seasonalised CO (solid line) and rain depth (dotted line) for 25th and 26th of June 2007 revealing minimal anthropogenic influences.

On the 25th and 26th of June 2007 the rain event (Fig. 4) was accompanied by relatively low CO levels, which varied from 29 to 34 ppb (2 to 7 ppb above the 27 ppb CO offset) indicating only a negligible contribution from urban sources. A few instances have been observed where CO mixing ratios reached levels in the vicinity of 400 ppb (e.g. on August 1, 2009, or June, 30, 2010). However, these constitute exceptions rather than the rule and might also have been affected by the difficulty in clearly defining the temporal extent of the rain event in question, as mentioned above. In most cases the CO mole fractions varied only slightly during rain episodes – as was seen for 1st July 2010 or 22nd September 2012 – when the CO variability was within 1 ppb.

Table 1: Summary statistics for GEM, TotHg, CO and ^{222}Rn (2007-2013) for marine and urban rain events. Marine rain events are defined by back trajectories directly from the southern Atlantic Ocean whereas the urban events encompass the back trajectories which crossed the greater Cape Town area.

	47 marine rain events		20 urban rain events	
Species	Average	Std dev	Average	Std dev
GEM [ng m^{-3}]	1.018	0.040	1.003	0.053
TotHg [ng L^{-1}]	8.6	8.1	10.3	11.6
CO [ppb]	32.1	1.6	35.8	5.4
^{222}Rn [mBq m^{-3}]	201	74	287	188

Table 1 shows a summary of GEM, TotHg, CO, and ^{222}Rn concentrations measured during the rain events with back trajectories from the southern Atlantic Ocean (marine) and with back

trajectories which crossed the urban region of Cape Town (urban). From the 85 events 47 trajectories were typical marine and 20 typical urban. Events associated with trajectories of a mixed nature were rejected in order to obtain a clear distinction between the two types.
Despite the significantly larger concentrations of CO (significant at > 99.9% level) and ^{222}Rn (significant at > 99% level) during the urban type rain events, there is neither a noteworthy difference in GEM nor in TotHg concentrations. In the case of TotHg its large standard deviation may prevent the detection of any possible difference. However, since no difference was found in the much less variable GEM concentrations, we conclude that the short transport of urban air masses over the Cape Town area neither influences GEM or TotHg concentrations. Consequently, we do not differentiate between marine and urban rain events in the following analysis.

3.3. Relationship between GEM and TotHg

In Figure 5 we compare GEM concentration in air with Hg found in rain samples (TotHg) during the rainy season: averages for May till October for each year. The TotHg values in Figure 5 have been converted to annual Volume Weighted Means (VWM) as described by Prestbo and Gay (2009). Figure 5, shows a positive correlation (R^2 = 0.49; n=7) between annual mean GEM concentrations and TotHg concentrations over the seven year period despite large inter-annual variations for both. The years, 2010 and 2011 were characterized by relatively low GEM values (0.970 and 0.962 ng m^{-3} respectively) as well as correspondingly low TotHg (VWM) levels (1.6 and 2.1 ng L^{-1} respectively). In contrast, the years 2008 and 2012 both showed rather higher Hg values for both GEM and TotHg. For GEM: 1.026 and 1.092 ng m^{-3} and for TotHg: 24.3 and 14.6 ng L^{-1}, respectively.

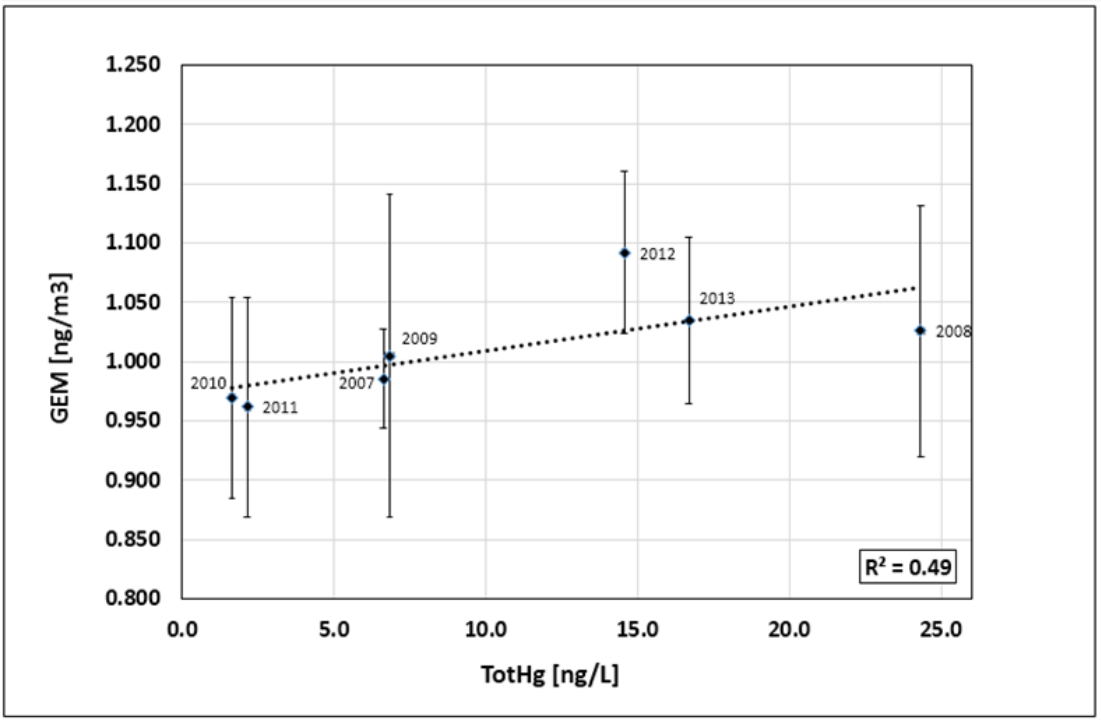


Fig. 5. Correlation plot of annual average GEM concentrations [ng m^{-3}] vs. annual average TotHg (VWM) [ng L^{-1}] over the seven year period (2007-2013). Error bars represent standard deviations and linear regression: GEM = 0.0037*TotHg + 0.972.

Positive correlations between total gaseous mercury (TGM) in air measured at Canadian Atmospheric Mercury Measurement Network (CAMNet) sites and TotHg in precipitation at nearby US Mercury Deposition Network (MDN) sites have been reported by Cole et al. (2014). Since GOM and PBM together represented mostly about 1% of TGM (Cole et al., 2014), the correlation also applies to GEM vs. TotHg. Both TGM and TotHg concentrations decreased with a comparable rate between 1998 and 2011, despite steady or increasing global mercury emissions (Wilson et al., 2010; Streets et al., 2011). This discrepancy was resolved by Soerensen et al. (2012) who attributed the decreasing trend to declining mercury emissions from the North Atlantic due to the reduction of mercury levels in surface sea water. The positive correlation of TotHg vs. GEM is thus an indication that both are a function of mercury emissions. The application of this conclusion to the Cape Point measurements raises the question as to the origin of the inter-annual variations observed for GEM and TotHg?

Figure 6 shows a positive correlation of both annual average GEM concentrations and annual average TotHg with annual precipitation (volume of collected rain sample). As can be seen, the May – October periods for 2007, 2010 and 2011 constitute drier years, with the annual precipitation ranging between 52 and 134 mm, while 2009 and 2013 comprise wetter years with annual precipitation of 275 and 476 mm, respectively. The years, 2008, 2012 and 2013 are characterised by higher standard deviations than the other years. Although the correlation factors (R^2) for all years are relatively small, comprising 0.23 and 0.27 for GEM and TotHg respectively, much higher R^2 values (0.97 for GEM (n=5) and 0.89 for TotHg (n=5)) are obtained (graph not shown here), if the extreme two years (2008 and 2012) are removed from the data set. The relative differences between GEM and TotHg are variable (Fig. 6) and cannot be ascribed to any identifiable process yet. Although the drier years such as 2010 and 2011 are characterized by larger differences and the wetter years e.g. 2013 by smaller differences, this pattern is not consistent. The years 2008 and 2012, for instance, were characterized by rather smaller differences between GEM and TotHg and were not very wet either (197 mm rain depth).

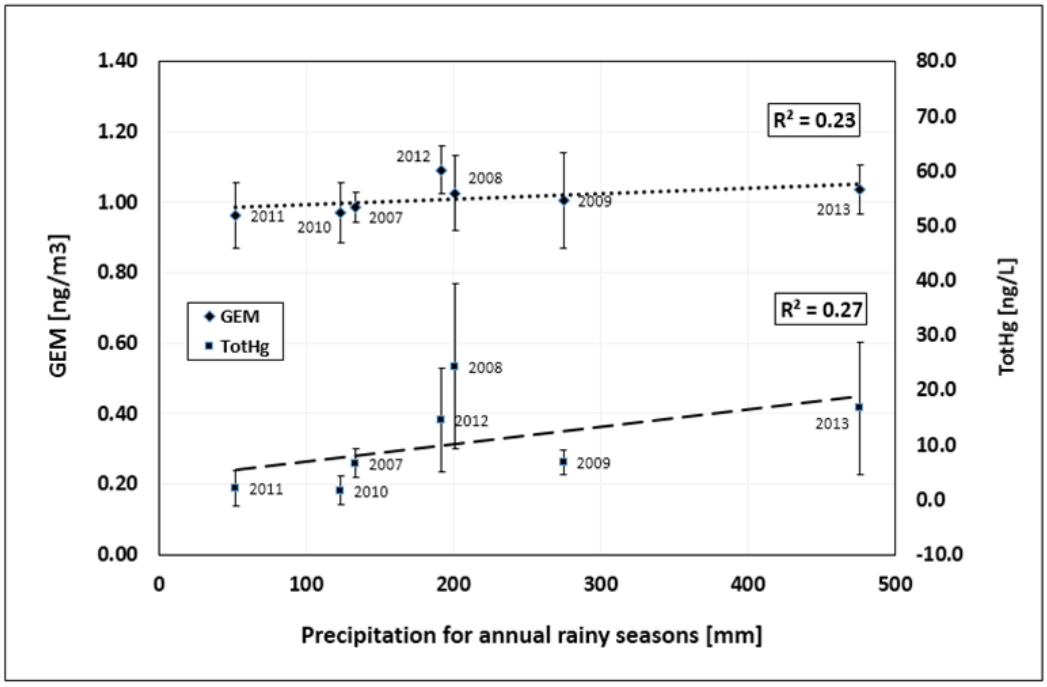


Fig. 6. Comparison of GEM concentrations [ng m^{-3}] (dotted line) and TotHg [ng L^{-1}] (dashed line) vs. annual rain depth [mm] over seven years (2007-2013). Error bars represent standard deviations. Linear regressions: GEM = 0.0002*Rain depth+0.978 and TotHg = 0.0316*Rain depth + 3.831.

The positive relationship between annual average GEM concentrations (May till October) and the corresponding annual precipitation at Cape Point was also found for the manual measurements made during 1996 - 2004 (Slemr et al., 2008). TotHg was not measured during this period. GEM average concentrations over the rainy season (May - October) vs. annual precipitation over this period shows a positive correlation (R^2 = 0.2; n=8). As for the high resolution data, if one or two outliers (in this case only 1998) are removed from the data set, the R^2 value increases to 0.6 (n=7; with significance > 95% confidence level; graph not shown here). The positive correlation of both GEM data sets (1996 – 2004 and 2007 - 2013) with annual precipitation lead us to suggest that the inter-annual GEM and TotHg variations in the southern hemisphere might be controlled by large-scale meteorological processes.

3.4. Influence of El Niño Southern Oscillation (ENSO)

Annual rainfall in Namibia and South Africa is dependent on ENSO cycles with El Niño years being drier and La Niña years being wetter (Preston-White and Tyson, 1988; Rautenbach and Smith, 2001). Consequently, good correlations between GEM and annual precipitation for the years 1996-2004 (low resolution GEM data) and 2007-2013 (high resolution GEM data) as well as between annual average TotHg concentrations and annual precipitation during the 2007-2013 period suggest that both GEM and TotHg also fall under the influence of the ENSO cycles. To investigate this dependence we use the Southern Oscillation Index (SOI; http://www.bom.gov.au/climate/current/soi2.shtml), which is based on the observed sea level pressure difference between Tahiti and Darwin, Australia. Annual average GEM concentrations correlate positively with SOI both in the 1996-2004 (shown in Fig. 7) as well as for the 2007-2013 periods (not shown). Fig. 7 shows a positive correlation (R^2 = 0.7; n=8, significant at > 99% confidence level) between GEM and the SOI for the low resolution data (1996-2004). The annual average GEM concentration for 1997 was not considered because data from May until October are missing. For the high resolution data (2007-2013), the R^2 value amounts to 0.4 (n=6, 2007 removed as outlier) and is significant at > 90% confidence level.

TotHg (2007-2013) and rainfall (both 1996-2004 and 2007-2013 periods) were also searched for correlations with SOI. This was again done for the rainy season: May till October. However, no significant correlations have been found.

However, the positive relationship between GEM and the SOI is compelling (Fig. 7). It suggests either a direct influence of meteorology on GEM concentrations or an indirect one through meteorological influences on mercury emissions. A direct influence might be through sea surface temperatures which naturally have a bearing on rainfall, especially in southern Africa (Preston-White and Tyson, 1988), and/or long-range transport processes (Pirrone and Mason, 2009) – also from the NH - might be controlling inter-annual variations of atmospheric Hg levels in SH mid-latitudes. Variable wind strengths could possibly also affect the Hg ocean to atmosphere flux rates (Xu et al., 2012).

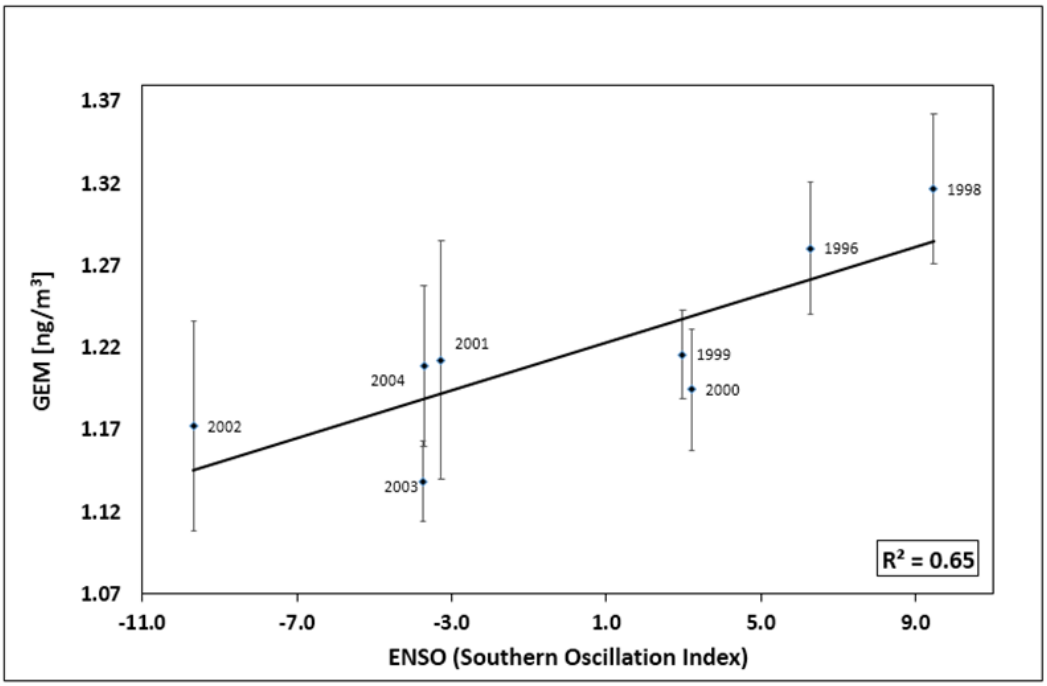


Fig. 7. Relationship between GEM averages (May till Oct) and Southern Oscillation Index (SOI, http://www.bom.gov.au/climate/current/soi2.shtml): 1996-2004. The error bars represent GEM standard deviations. Linear regression: GEM = 0.007*SOI + 1.216.

The correlations between GEM and TotHg observed here and in Canada and the northeastern US suggest that both are linked to hemispheric emissions (Slemr et al., 2011; Cole et al., 2014) in the first place. Meteorological processes can influence the mercury emissions directly, e.g. by periodical changes of surface ocean temperatures during ENSO events, or indirectly via extended droughts leading to increased biomass burning. We note that oceanic emissions may represent 45% of all mercury emissions and emissions from biomass burning with a contribution of ~4% are not negligible either (Holmes et al., 2010). Meteorological processes can also influence the oxidation of GEM to species prone to rain and washout. Gratz et al. (2009) pointed out that the uptake of Hg by rainwater is a function of the effective conversion of GEM to GOM which comprises fine particle bound mercury (PBM) as well as divalent reactive gaseous mercury (RGM). However, changing oxidation rates would influence TotHg concentrations to a substantially larger degree than those of GEM and would, at constant emissions, lead to an anti-correlation between GEM and TotHg concentrations. We thus conclude that the meteorological influence on emissions is the major reason for the positive GEM vs. TotHg and GEM vs. SOI correlations.

4. Conclusions

The rain episodes at Cape Point (2007-2013) are almost exclusively linked to cold fronts from the Atlantic Ocean. 75% of all air mass trajectories coupled to these rain events reach the Cape Point GAW station directly from the southern ocean, while 19% arrive there with a short bypass over the Cape Town metropolitan area. Merely 6% approach Cape Point along the sea from the East via the Cape Agulhas sub-continental region. The atmospheric levels of CO and ^{222}Rn in the identified 85 rain events are largely characteristic of maritime conditions. Although rain fronts which passed over the Cape Town region before arriving at Cape Point sometimes

have slightly elevated CO and ^{222}Rn levels, no significant local anthropogenic influences were detected in GEM and TotHg concentrations observed at Cape Point.

The average GEM levels for the wet season (May till October) over the 2007-2013 period show a positive correlation (R^2 = 0.49; n=7) with TotHg. Furthermore, the time series (2007-2013) for both GEM and TotHg in the rain events (plotted as a function of rain depth) displays similar, relative inter-annual concentration variations over the measuring period. This confirms the close coupling which exists for Hg within these two different media. If the years 2008 and 2012 (rain depth about 200 mm) are removed from the data series, the R^2 values improve significantly, i.e. to 0.97 for GEM and 0.89 for TotHg (VWM), respectively. Other processes might - indeed - have affected these two years which were negligible or absent in the other five years. A significant correlation has also been found between GEM and SOI during the 1996-2004 period.

These correlations suggest that the inter-annual variations of GEM and TotHg concentrations are primarily influenced by large scale meteorology. Meteorological influences on mercury sinks e.g. through an increased oxidation rate or enhanced precipitation would, at constant emissions, lead to an anti-correlation between GEM and TotHg. The observed positive correlation between GEM and TotHg thus implies that meteorological factors comprise the dominating process controlling mercury sources. Mercury emissions might - for instance - be influenced by changing sea surface temperatures or by large scale droughts leading to increased biomass burning (Monks et al., 2012). These examples are consistent with the observed GEM vs. SOI correlation.

Acknowledgements

The GEM measurements made at Cape Point have been supported by the South African Weather Service and have also received financial support from the Global Mercury Observing System (GMOS), a European Community funded FP7 project (ENV.2010.4.1.3-2). Furthermore, the collection and analysis of the precipitation samples have been financially supported by the Council for Scientific and Industrial Research (CSIR) and the National Research Foundation (NRF) of South Africa. We are also grateful to NOAA for their trajectory Hysplit model. We would also like to thank Robert Mason and Susan Gichuki from the University of Connecticut (USA) for their assistance with the rain sampler provision and set-up. We are grateful to Danie van der Spuy for the general maintenance of the Tekran analyser at Cape Point.

References

Biester, H., Kilian, R., Franzen, C., Woda, C., Mangini, A., Scholer, H.F. 2002 Elevated mercury accumulation in a peat bog of the Magellanic Moorlands, Chile (53ºS) - an anthropogenic signal from the Southern Hemisphere. Earth and Planetary Science Letters 201, 609-620.

Brunke, E.-G., Labuschagne, C., Parker, B., Scheel, H.E., Whittlestone, S. 2004. Baseline air mass selection at Cape Point, South Africa: Application of ^{222}Rn and other filter criteria to CO_2. Atmospheric Environment 38, 5693-5702.

Brunke, E-G., Labuschagne, C., Ebinghaus, R., Kock, H. and Slemr, F. 2010. Gaseous elemental mercury depletion events observed at Cape Point during 2007-2008. Atmospheric Chemistry and Physics 10, 1121-1131.

Brunke, E.-G., Ebinghaus, R., Kock, H.H., Labuschagne, C., Slemr, F. 2012. Emissions of mercury in southern Africa derived from long-term observations at Cape Point, South Africa. Atmospheric Chemistry and Physics 12, 7465-7474.

Caffrey, J.M., Landing, W.M., Nolek, S.D., Gosnell, K.J., Bagui, S.S., Bagui, S.C. 2010. Atmospheric deposition of mercury and major ions to the Pensacola (Florida) watershed: spatial, seasonal, and inter-annual variability. Atmospheric Chemistry and Physics 10, 5425–5434.

Cole, A.S., Steffen, A., Eckley, C.S., Narayan, J., Pilote, M., Tordon, R., Graydon, J.A., Louis, V.L.St., Xu, X., Branfireun, B.A. 2014. A survey of mercury in air and precipitation across Canada: Patterns and trends. Atmosphere 5, 635-668.

Dabrowski, J.M., Ashton, P.J., Murray, K., Leaner, J.J., Mason, R.P. 2008. Anthropogenic mercury emissions in South Africa: Coal combustion in power plants. Atmospheric Environment 42, 6620–6626.

Dutt, U., Nelson, P.F., Morrison, A.L., Strezov, V. 2009. Mercury wet deposition and coal-fired power station contributions: An Australian study. Fuel Processing Technology 90, 1354–1359.

Fitzgerald, W.F., Engstrom, D.R., Mason, R.P., Nater, E.A. 1998. The case for atmospheric mercury contamination in remote areas. Environmental Science & Technology 32, 1–7.

Gichuki, S.W., Mason, R.P. 2013. Mercury and metals in South African precipitation. Atmospheric Environment 79, 286-298.

Gratz, L. E., Keeler, G.J., Miller, E.K. 2009. Long-term relationships between mercury wet deposition and meteorology. Atmospheric Environment 43, 6218–6229.

Holmes, C.D., Jacob, D.J., Corbitt, E.S., Mao, J., Yang, X., Talbot, R., Slemr, F. 2010. Global atmospheric model for mercury including oxidation by bromine atoms. Atmospheric Chemistry and Physics 10, 12037-12057.

Kotnik, J., Horvat, M., Jereb, V. 2002. Modelling of mercury geochemical cycle in Lake Velenje, Slovenia. Environmental Modelling & Software 17, 593–611.

Lamborg, C.H., Rolfhus, K.R., Fitzgerald, W.F., Kim, G. 1999. The atmospheric cycling and air-sea exchange of mercury species in the South and equatorial Atlantic Ocean. Deep-Sea Research II 46, 957-977.

Laurier, F., Mason, R. 2007. Mercury concentration and speciation in the coastal and open ocean boundary layer. Journal of Geophysical Research 112, D06302, doi:10.1029/2006JD007320.

Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X., Fitzgerald, W., Pirrone, N., Prestbo, E., Seigneur, C. 2007. A synthesis in progress and uncertainties in attribution of sources of mercury in deposition. Ambio 36(1), 19-32.

Lombard, M.A.S., Bryce, J.G., Mao, H. Talbot, R. 2011. Mercury deposition in Southern New Hampshire, 2006–2009. Atmospheric Chemistry and Physics 11, 7657–7668.

519 Masekoameng, K.E., Leaner, J., Dabrowski, J. 2010. Trends in anthropogenic mercury
520 emissions estimated for South Africa during 2000 – 2006. Atmospheric Environment 44, 3007-
521 3014.
522
523 Mason, R.P., Sullivan, K.A. 1998. Mercury and methyl mercury transport through an urban
524 watershed. Water Research 32, 321–330.
525
526 Mason, R.P., Laporte, J.M, Andres, S. 2000. Factors controlling the bioaccumulation of
527 mercury, methylmercury, arsenic, selenium and cadmium by freshwater invertebrates and fish.
528 Archives of Environmental Contamination and Toxicology 38, 283 – 297.
529
530 Mirlean, N., Larned, S.T., Nikora, V., Kutter, V.T. 2005. Mercury in lakes and lake fishes on a
531 conservation-industry gradient in Brazil. Chemosphere 60, 226–236.
532
533 Monks, S.A., Arnold, S.R., Chipperfield, M.P. 2012. Evidence for El Niño–Southern Oscillation
534 (ENSO) influence on Arctic CO interannual variability through biomass burning emissions.
535 Geophysical Research Letters 39, L14804, doi:10.1029/2012GL052512.
536
537 Pirrone, N., Mason, R. 2009. Mercury Fate and Transport in the Global Atmosphere: Emissions,
538 Measurements and Models, Springer, New York USA, 2009.
539
540 Prestbo, E.M., Gay, D.A. 2009. Wet deposition of mercury in the U.S. and Canada, 1996–2005:
541 Results and analysis of the NADP mercury deposition network (MDN). Atmospheric
542 Environment 43, 4223–4233.
543
544 Preston-Whyte, R.A., Tyson, P.D. 1988. The Atmosphere and Weather of Southern Africa.
545 University of the Witwatersrand, Johannesburg, Oxford University Press, Cape Town, 375 pp.
546
547 Rautenbach, C. J. de W., Smith, I.N. 2001. Teleconnections between global sea-surface
548 temperatures and the interannual variablility of observed and model simulated rainfall over
549 southern Africa. Journal of Hydrology 254, 1-15.
550
551 Scheel, H.E., Brunke, E-G., Sladkovic, R., Seiler, W. 1998. In situ CO concentrations at the sites
552 Zugspitze (47 °N, 11 °E) and Cape Point (34 °S, 18 °E) in April and October 1994. Journal of
553 Geophysical Research 103, D15, 19295-19304.
554
555 Schroeder, W. H., Munthe, J. 1998. Atmospheric mercury - an overview. Atmospheric
556 Environment 32, 809-822.
557
558 Seiler, W., Giehl, H., Halliday, E.C., Brunke E-G. 1984. The seasonality of carbon monoxide
559 abundance in the Southern Hemisphere. Tellus 36B, 4, 219-231.
560
561 Slemr, F., Brunke, E.-G., Labuschagne, C., Ebinghaus, R. 2008. Total gaseous mercury
562 concentrations at the Cape Point GAW station and their seasonality, Geophys. Res. Lett., 35,
563 L11807, doi:10.1029/2008GL033741.
564
565 Slemr, F., Brunke, E.-G., Ebinghaus, R., Kuss, J. 2011. Worldwide trend of atmospheric
566 mercury since 1995. Atmospheric Chemistry and Physics 11, 4779-4787.
567

Slemr, F., Brunke, E.-G., Whittelstone, S., Zahorowski, W., Ebinghaus, R., Kock, H.H., Labuschagne, C. 2013. ^{222}Rn-calibrated mercury fluxes from terrestrial surface of southern Africa. Atmospheric Chemistry and Physics 13, 6421-6428.

Soerensen, A.L., Jacob, D.J., Streets, D.G., Witt, M.L.I., Ebinghaus, R., Mason, R.P., Andersson, M., Sunderland, E.M. 2012. Multi-decadal decline of mercury in the North Atlantic atmosphere explained by changing subsurface seawater concentrations. Geophysical Research Letters 39, L21810, doi:10.1029/2012GL053736.

Sprovieri, F., Pirrone, N., Ebinghaus, R., Kock, H., Dommergue, A. 2010. A review of worldwide atmospheric mercury measurements. Atmospheric Chemistry and Physics 10, 8245-8265.

Steffen, A., Schroeder, W. 1999. Standard operation procedures manual for total gaseous mercury measurements, Canadian Mercury Measurement Network (CAMNet), Version 4.0.

Streets, D.G., Devane, M.K., Lu, Z., Bond, T.C., Sunderland, E.M., Jacob, D.J. 2011. All-time releases of mercury to the atmosphere from human activities. Environmental Science & Technology 45, 10485-10491.

US EPA (United States Environmental Protection Agency). 1996. Method 1669: sampling ambient water for trace metals at EPA water quality criteria levels. EPA publication no.: 821-R-96-008. Washington DC, USA.

Williams, C.R., Leaner, J.J., Nel, J.M., Somerset, V.S. 2010. Mercury concentrations in water resources potentially impacted by coal-fired power stations and artisanal gold mining in Mpumalanga, South Africa. Journal of Environmental Science & Health A45, 1363–1373.

Williams, C.R., Leaner, J.J., Somerset, V.S., Nel, J.M. 2011. Mercury concentrations at a historically mercury-contaminated site in KwaZulu-Natal (South Africa). Environmental Science and Pollution Research 18, 1079–1089.

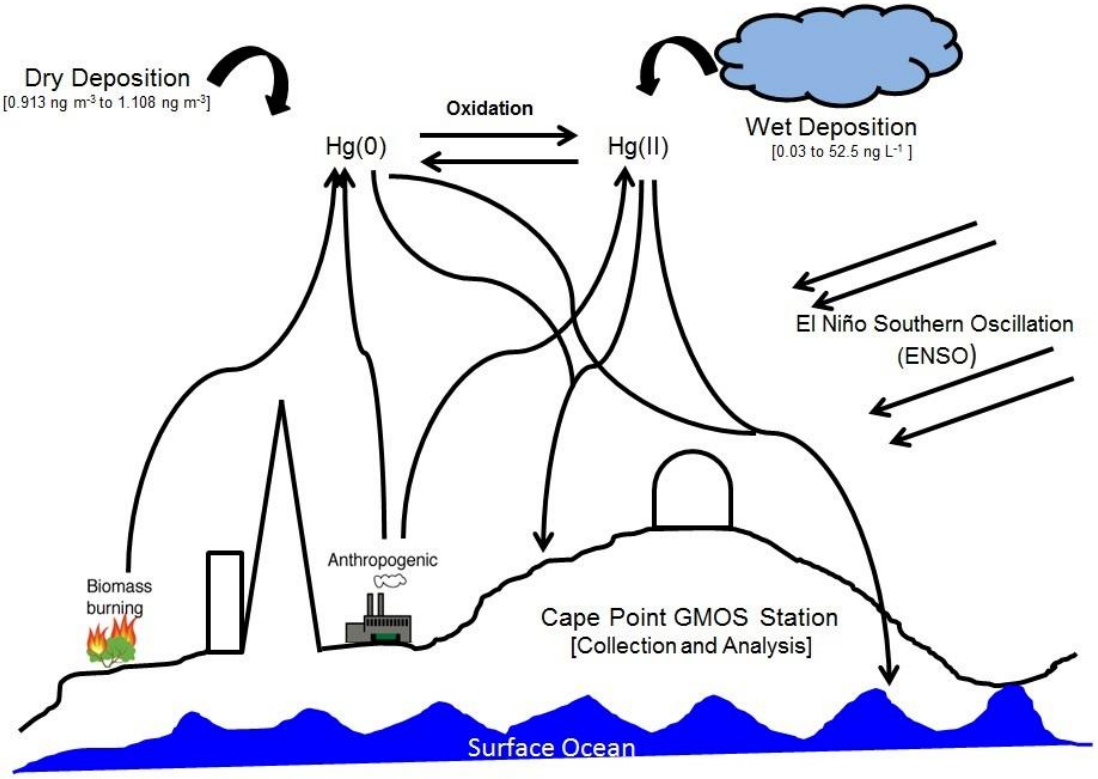
Wilson, S., Munthe, J., Sundseth, K., Kindbom, K., Maxson, P., Pacyna, J., Steenhuisen, F. 2010. Updating historical global inventories of anthropogenic mercury emissions to air. AMAP Tech. Rep. 3, 14 pp., Arctic Monitoring and Assessment Programme, Oslo.

Xu, L.Q., Liu, R.H., Wang, J.Y., Tan, A.K., Yu, P. 2012. Mercury emission flux in the Jiaozhou Bay measured by flux chamber. Procedia Environmental Sciences 13, 1500-1506.

Mercury measurements (2007-2013) made in the atmosphere and in rainwater at Cape Point, South Africa

Ernst-Günther Brunke[1], Chavon Walters[2], Thumeka Mkololo[1], Lynwill Martin[1], Casper Labuschagne[1], Bongiwe Silwana[2], Franz Slemr[3], Andreas Weigelt[4], Ralf Ebinghaus[4], and Vernon Somerset[2¥]

[1]South African Weather Service c/o CSIR, P.O. Box 320, Stellenbosch 7599, South Africa
[2]Natural Resources and the Environment (NRE), Council for Scientific and Industrial Research (CSIR), Stellenbosch, 7600, South Africa.
[3]Max-Planck-Institut für Chemie, Hahn-Meitner-Weg 1, 55128 Mainz, Germany
[4]Helmholtz-Zentrum Geesthacht (HZG), Institute of Coastal Research, Max-Planck-Strasse 1, D-21502 Geesthacht, Germany,



¥ Vernon Somerset; Tel.: +27.21.8882631; Fax: +27.86.6631789; Email: vsomerset@csir.co.za; vsomerset@gmail.com

Mercury measurements (2007-2013) made in the atmosphere and in rainwater at Cape Point, South Africa

Ernst-Günther Brunke[1], Chavon Walters[2], Thumeka Mkololo[1], Lynwill Martin[1], Casper Labuschagne[1], Bongiwe Silwana[2], Franz Slemr[3], Andreas Weigelt[4], Ralf Ebinghaus[4], and Vernon Somerset[2¥]

[1]South African Weather Service c/o CSIR, P.O. Box 320, Stellenbosch 7599, South Africa
[2]Natural Resources and the Environment (NRE), Council for Scientific and Industrial Research (CSIR), Stellenbosch, 7600, South Africa.
[3]Max-Planck-Institut für Chemie, Hahn-Meitner-Weg 1, 55128 Mainz, Germany
[4]Helmholtz-Zentrum Geesthacht (HZG), Institute of Coastal Research, Max-Planck-Strasse 1, D-21502 Geesthacht, Germany,

Highlights

- Extended summary provided of GEM and THg measured at Cape Point, South Africa.
- Positive correlation observed between GEM and TotHg concentrations.
- Meteorological factors such as the El Niño Southern Oscillation (ENSO) contributed.
- Mercury emissions are influenced by increased biomass burning in drier seasons.
- Data presented provides novel information on atmospheric behaviour of mercury.

¥ Vernon Somerset; Tel.: +27.21.8882631; Fax: +27.86.6631789; Email: vsomerset@csir.co.za; vsomerset@gmail.com