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^{222}Rn-calibrated mercury fluxes from terrestrial surface of southern Africa

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Abstract. Gaseous elemental mercury (GEM) and ^{222}Rn, a radioactive gas of primarily terrestrial origin with a half-life of 3.8 days, have been measured simultaneously at Cape Point, South Africa, since March 2007. Between March 2007 and December 2011, altogether 191 events with high ^{222}Rn concentrations were identified. GEM correlated with ^{222}Rn in 94 of the events and was constant during almost all the remaining events without significant correlation. The average GEM / ^{222}Rn flux ratio of all events including the non-significant ones was -0.0001 with a standard error of ± 0.0030 pg mBq^{-1}. Weighted with the event duration, the average GEM / ^{222}Rn flux ratio was -0.0048 ± 0.0011 pg mBq^{-1}. With an emission rate of 1.1 ^{222}Rn atoms cm^{-2} s^{-1} and a correction for the transport time, this flux ratio corresponds to a radon-calibrated flux of about -0.54 ng GEM m^{-2} h^{-1} with a standard error of ± 0.13 ng GEM m^{-2} h^{-1} ($n = 191$). With wet deposition, which is not included in this estimate, the terrestrial surface of southern Africa seems to be a net mercury sink of about -1.55 ng m^{-2} h^{-1}. The additional contribution of an unknown but presumably significant deposition of reactive gaseous mercury would further increase this sink.

1 Introduction

Mercury poses a serious environmental issue because of its transformation to methyl mercury, which is a potent toxin to humans and animals (Mergler et al., 2007; Scheuhammer et al., 2007). Of primary concern are thus the emissions of mercury, which due to the long atmospheric residence time of elemental mercury (Lindberg et al., 2007) can be distributed all over the world. According to the current emission inventories and models, anthropogenic emissions represent the largest mercury source with 2880 t yr^{-1}, followed by 2680 t yr^{-1} from the oceans and 1850 t yr^{-1} from the terrestrial surfaces (Mason, 2009; Pirrone et al., 2010). Whereas anthropogenic emissions are believed to be known with an uncertainty of ± 30 %, the uncertainties of the emissions from oceans and terrestrial surfaces are considered to be ± 50 % and more (Lin et al., 2006; Lindberg et al, 2007).

The uncertainties related to emissions from terrestrial surfaces originate mostly from the poor knowledge of the emission mechanisms, the worldwide up-scaling of a small number of field measurements made in a few geographic regions, and the measurement challenges (Lindberg et al., 2007; Gustin et al., 2008; Mason, 2009; Smith-Downey et al., 2010). Mercury emission from terrestrial surfaces is dependent on meteorological conditions, type of soil and vegetation, and historical atmospheric deposition (Zhang and Lindberg, 1999; Gustin et al., 2000, 2008; Gustin, 2003; Song and Van Heyst, 2005; Bash, 2010; Smith-Downey et al., 2010). The influence of these parameters has been studied in the laboratory and in the field, but the underlying mechanisms are still not well understood (Mason, 2009). The flux can be bi-directional depending on the mercury concentration in ambient air: deposition at higher concentrations and emission at lower concentrations with a cross-over point termed "compensation point" (e.g. Hanson et al., 1995; Lindberg et al., 1998; Zhang et al., 2009). An intercomparison of field

flux measurement techniques revealed substantial disparities between the chamber and the micrometeorological methods (Gustin and Lindberg, 2000). In addition to all these challenges, field flux measurements have so far been carried out almost exclusively in temperate regions of North America and Europe. Their up-scaling to other regions in the Northern and Southern Hemisphere is thus necessarily fraught with large additional uncertainties.

^{222}Rn is a radioactive gas of predominantly terrestrial origin with a half-life of 3.8 days. Its emission rate from soil is relatively evenly distributed (Zhang et al., 2011 and references therein) making ^{222}Rn a good tracer for studies of emissions from terrestrial surfaces (Zahorowski et al., 2004). According to Jacob et al. (1997), the assumption of a uniform ^{222}Rn emission rate of 1 atom cm^{-2} s^{-1} is accurate to roughly 25 % globally, or by a factor of 2 regionally. ^{222}Rn has been successfully used to derive regional emissions of CO_2, CH_4, and N_2O (e.g. Gaudry et al., 1990; Wilson et al., 1997; Zahorowski et al., 2004; Hirsch, 2007). To the best of our knowledge, its only application to mercury flux estimations has been reported by Obrist et al. (2006). They found good agreement between fluxes estimated from the accumulation of Hg and ^{222}Rn in the stable nocturnal boundary layer and those measured by the modified Bowen ratio micrometeorological technique. The major advantage of the Hg/^{222}Rn method is its capability to estimate regional fluxes and by this its capability to avoid shortcomings related to up-scaling of point measurements in the field (Wilson et al., 1997; Obrist et al., 2006). In this paper we use concurrent measurements of gaseous elemental mercury and ^{222}Rn at Cape Point, South Africa, to derive the regional mercury flux from southern Africa.

2 Experimental

The Cape Point station (34°21′ S, 18°29′ E) is part of the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) network. 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 southernmost tip of the Cape Peninsula. The site is located in a nature reserve and 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). The site is occasionally also subjected to air from the northern to north-eastern sector (mainly during austral winter), which is influenced by anthropogenic emissions from the greater Cape Town area and/or by other continental sources (both local and regional).

Within the framework of the WMO-GAW programme, continuous trace gas measurements of CO_2, CH_4, CO and O_3 have been made at Cape Point for more than 30 yr now (Scheel et al., 1990). The ^{222}Rn measuring programme started in 1999 and serves mostly to classify air masses into maritime, continental or mixed (Brunke et al., 2004). Gaseous mercury concentrations had been measured intermittently (about 200 samples per year) since September 1995 until December 2004 (Slemr et al., 2008) and have been continuously with a resolution of 15 min since March 2007 (Brunke et al., 2010). Only the high-resolution data until the end of 2011 were used in this work.

Continuous measurements of gaseous mercury are made using a Tekran 2537A vapour-phase mercury analyser (Tekran Inc., Toronto, Canada). The Tekran 2537A is capable of measuring low-level mercury concentrations typically observed at background locations (Ebinghaus et al., 1999; Munthe et al., 2001). The analyzer is operated in an air-conditioned laboratory and run with a sampling air flow rate of 1 L min^{-1} at 15 min sampling intervals. The span of the analyzer is checked by an internal permeation source once every 25 h. The permeation rate of the internal permeation source was determined by repeated injections of mercury saturated vapour from a primary mercury source (Tekran Model 2505) and was found to be stable within 2 % over the period of the measurements. The air sample intake was attached to a 30 m high aluminium sampling mast at a height of approximately 5 m above the rocky surface and about 235 m above sea level. A Teflon filter (pore size 0.2 µm; ID = 45 mm) upstream of the instrument protects the analyzer against contamination by particulate matter. The filter was replaced once every two weeks. The 15 min TGM data have been converted to 30 min averages so that comparisons with ^{222}Rn, other trace gas and meteorological data being measured simultaneously at Cape Point could be made. Under the prevailing atmospheric conditions at Cape Point (higher temperature and air humidity, in addition to hygroscopic sea salt aerosols), we assume that reactive gaseous mercury (RGM) will be adsorbed by the inlet tubing and the aerosol filter and that the measured atmospheric mercury concentration thus represents exclusively gaseous elemental mercury (GEM) (Brunke et al., 2010). All GEM concentrations are given in ng m^{-3} (STP, i.e. at 273.2 K and 1013 hPa). The precision of the 30 min GEM measurements was ~ 0.035 ng m^{-3} and their overall uncertainty including the uncertainty of the permeation rate and the sampling flow calibrations ~ 5 %.

Since 1999 a ^{222}Rn detector designed by the Australian Nuclear Science & Technology Organisation (ANSTO) and manufactured by AGH Industries (Riverwood, Australia) has been installed at Cape Point. The so-called two-filter instrument is described in detail by Whittlestone and Zahorowski (1998) and Brunke et al. (2002) and was run with 30 min resolution. Briefly, radon and thoron decay products are removed from the air by the first filter. Decay products newly formed under controlled conditions in the instrument delay tank are then retained by a second filter. Their alpha radiation is determined by a zinc sulfide scintillator. The

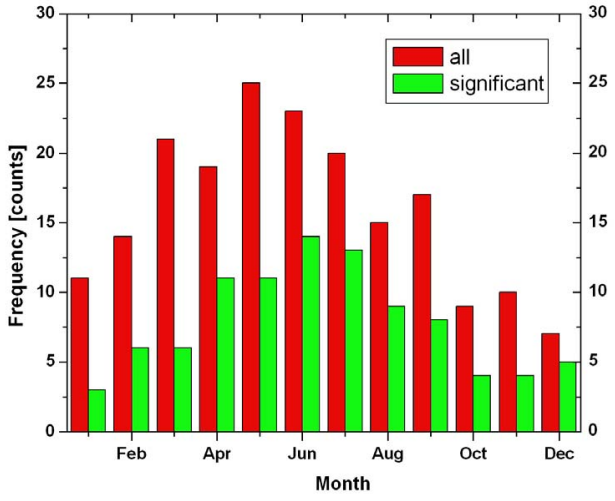

Fig. 1. Monthly frequency of events with ^{222}Rn concentrations $> 1000\,\mathrm{mBq\,m^{-3}}$ ("all") and those with significant GEM vs. ^{222}Rn correlations ("significant").

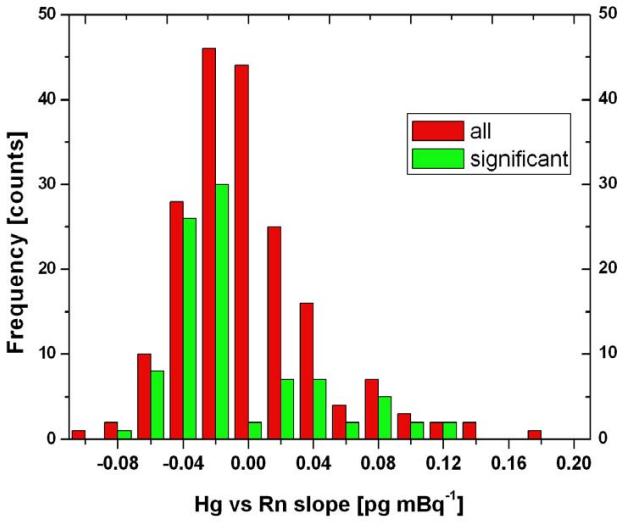

Fig. 2. Frequency distribution of all Hg/^{222}Rn slopes and only of those which are significant.

detection limit of the instrument at Cape Point is quoted to be $33\,\mathrm{mBq\,m^{-3}}$ (Brunke et al., 2002).

Hg vs. ^{222}Rn was correlated using orthogonal regression (Cantrell, 2008), which takes the uncertainties of both correlated parameters into account. Factors affecting the sensitivity and accuracy of the Cape Point ^{222}Rn detector have been discussed by Brunke et al. (2002) and by references therein. For the correlations here, the GEM and ^{222}Rn uncertainties were set to $0.05\,\mathrm{ng\,m^{-3}}$ and $50\,\mathrm{mBq\,m^{-3}}$, respectively. As ^{222}Rn is always emitted, the positive slope sign stands for mercury emissions and the negative one for mercury deposition. The mean values throughout the paper are given with the standard errors of the mean instead of the more common standard deviations of individual measurements.

The regions of origin for the pollution events were interpreted using ten-day isentropic back trajectories from NOAA ESRL (Earth System Research Laboratory of National Oceanic and Atmospheric Administration, http://www.esrl.noaa.gov/gmd) and seven-day back trajectories calculated by NILU (Norwegian Institute for Air Research) using the FLEXTRA model (http://www.nilu.no/projects/ccc/trajectories/).

3 Results and discussion

Altogether 191 events with ^{222}Rn concentrations above $1000\,\mathrm{mBq\,m^{-3}}$, which lasted usually for more than a day, have been identified between March 2007 and December 2011. Their seasonal occurrence frequency is shown in Fig. 1. Most of them occur in the months March–September, in agreement with the seasonal variation of wind direction at Cape Point (Brunke et al., 2004). The events can extend up to 7 days, but most of them last 2–4 days. Their duration is thus substantially longer than that of the depletion events or the typical pollution plumes observed at Cape Point, which generally last only several hours (Brunke et al., 2010, 2012). Using time series and scatter plots, this difference allows us to discriminate against the depletion events, the anthropogenic emissions and emission from biomass burning. Fifty-six events with enhanced ^{222}Rn concentrations coincided with such depletion and pollution events. These short depletion and pollution events were eliminated for the subsequent analysis of the relationship between Hg and ^{222}Rn in the ^{222}Rn events.

Figure 2 shows the frequency distribution of the GEM / ^{222}Rn slopes from the correlations. In 94 events the correlations were meaningful at least at the 95 % significance level. The insignificant correlations for the remaining events may either imply that there is no relation whatsoever or that the GEM concentration remains constant during the ^{222}Rn event. Figure 2 shows that the latter is the case, i.e. that the largest difference between the frequency of all and significant GEM / ^{222}Rn slopes is in the bin with the central value of $0.00\,\mathrm{pg\,mBq^{-1}}$ (-0.01 to $+0.01\,\mathrm{pg\,mBq^{-1}}$), followed by the bins with the central values -0.02, $+0.02$, and $+0.04\,\mathrm{pg\,mBq^{-1}}$. In the remaining bins almost all correlations are significant. Thus the 97 events with insignificant GEM vs. ^{222}Rn correlations and a slope close to zero still provide meaningful information about the net GEM flux between the surface and the atmosphere, and we have included them in subsequent analyses. The average GEM / ^{222}Rn slope of all 191 events is $-0.0001 \pm 0.0030\,\mathrm{pg\,mBq^{-1}}$, which is statistically indistinguishable from the average of $-0.0057 \pm 0.0051\,\mathrm{pg\ mBq^{-1}}$ for 94 events with significant correlations. Both averages cannot be statistically distinguished from zero flux.

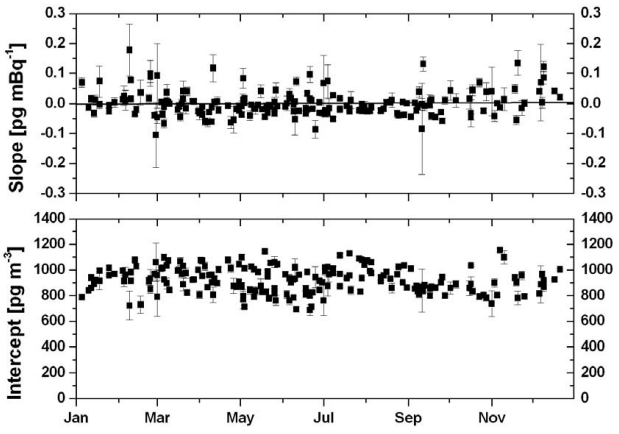

Fig. 3. Seasonal variation of the GEM / ^{222}Rn slopes (upper panel) and the intercepts (bottom panel).

Figure 3 shows the slopes and the intercepts of all GEM vs. ^{222}Rn correlations in the upper and lower panel, respectively. The intercepts represent the background mercury concentrations at Cape Point. They vary between 0.69 and 1.15 ng m^{-3} and average 0.92 $\pm$0.01 ng m^{-3} for all correlations and 0.93 ± 0.01 ng m^{-3} for the significant ones. The intercepts do not show any apparent seasonal variation. The slopes vary between -0.105 and $+0.178$ pg mBq^{-1}, and they also do not show any pronounced dependency on season. A plot of the slopes against the intercepts (not shown) also does not reveal any dependence of the flux on background GEM concentration. However, the average of slopes for the austral autumn–winter months (April to September) is negative and with -0.0091 ± 0.0032 pg mBq^{-1} ($n = 72$) significantly lower (at > 99.9 % confidence level) than the positive average for the spring–summer period (October to March) of $+0.0150 \pm 0.0056$ pg mBq^{-1} ($n = 119$). This is consistent with the expected temperature dependence of fluxes, but the stimulation of the flux by seasonally variable precipitation in the interior of southern Africa with its maximum in the summer months may also contribute.

Two backward trajectories for the ^{222}Rn events are shown in Fig. 4: one for 12:00 UTC of 10 February 2008 (left panel), and the other for 12:00 UTC of 30 March 2007 (right panel). Both look similar and are typical for most of the ^{222}Rn events presented here. They encompass usually South Africa and the neighbouring countries of Namibia, Botswana, Zimbabwe, and Mozambique. The GEM / ^{222}Rn flux ratio was $+0.077 \pm 0.008$ pg mBq^{-1} for the event on 10 February 2008. However, the event on 30 March 2007 (the lowest of all events with significant correlations) had a flux ratio of merely -0.026 ± 0.005 pg mBq^{-1}. This and the trajectory analysis of other events could not reveal any systematic dependence of the terrestrial flux ratios on backward trajectories.

Precipitation is known to stimulate the emission of mercury from soils, especially in arid regions (e.g. Song and Van Heyst, 2005; Cobbett et al., 2007; Xin et al., 2007). Therefore, the occurrence of precipitation along the backward trajectories was investigated for 7 of the events with the highest emission and 5 events associated with the highest deposition. The events with the highest emission were more frequently connected to intermediate rain over southern Africa (4 events) than those with highest deposition (1 event), suggesting indeed some degree of stimulation of mercury emissions by precipitation.

The terrestrial surface of southern Africa is presumed to emit about 1.1 ^{222}Rn atoms cm^{-2} s^{-1} corresponding to 23.1 mBq m^{-2} s^{-1} (Zhang et al., 2011). With this emission rate, the radon-calibrated GEM flux of southern Africa varied between -8.7 and $+14.8$ ng m^{-2} h^{-1}. The un-weighted average GEM / ^{222}Rn flux ratio of all events of -0.0001 ± 0.0030 pg mBq^{-1} corresponds to a flux of -0.01 ± 0.25 ng m^{-2} h^{-1}. The event duration weighted average GEM / ^{222}Rn flux ratio of all events was -0.0048 ± 0.0011 pg mBq^{-1} corresponding to the GEM flux of -0.40 $\pm$0.09 ng m^{-2} h^{-1}. ^{222}Rn decay has not been considered in these estimates. Assuming an average transport time of 2 days (corresponding to a transport distance of $\sim$ 1000 km), the absolute flux value would increase by about 36 % to -0.01 ± 0.34 ng m^{-2} h^{-1} for an un-weighted mean and -0.54 ± 0.13 ng m^{-2} h^{-1} if weighted with event durations.

To the best of our knowledge, we are not aware of any long-term measurements of mercury species over southern Africa. The reactive gaseous mercury (RGM) concentration in the marine boundary layer around southern Africa is smaller than 7 pg m^{-3} (Soerensen et al., 2010a) representing less than 1 % of the GEM concentration. Because of much lower halogen concentrations in the continental boundary layer, even lower RGM concentrations can be expected over southern Africa. Assuming that the concentration of particulate mercury is within the same range (Slemr et al., 1985), the contribution of RGM and particulate mercury dry deposition could still be significant because of their much higher deposition velocities (Selin et al., 2007). In fact, modelled dry deposition of RGM for southern Africa is comparable to that for GEM, each ranging from about 1 to 5 ng m^{-2} h^{-1} (Smith-Downey et al., 2010). The occurrence of GEM depletion events at Cape Point was reported by Brunke et al. (2010), but their mechanism remains obscure. With some 50 events per year lasting on average $\sim$ 5 h, they are unlikely to contribute substantially to the mercury flux even if all GEM were converted to RGM and/or to particulate mercury and deposited.

The terrestrial surface of southern Africa might be quite unique due to its arid characteristics and as a result of its location in the Southern Hemisphere. Our unweighted average flux of -0.01 ± 0.34 ng m^{-2} h^{-1} is smaller than 0.4 ± 0.5 ng m^{-2} h^{-1} measured over a period of 1 yr on the forest floor in Standing Stone State Forest in

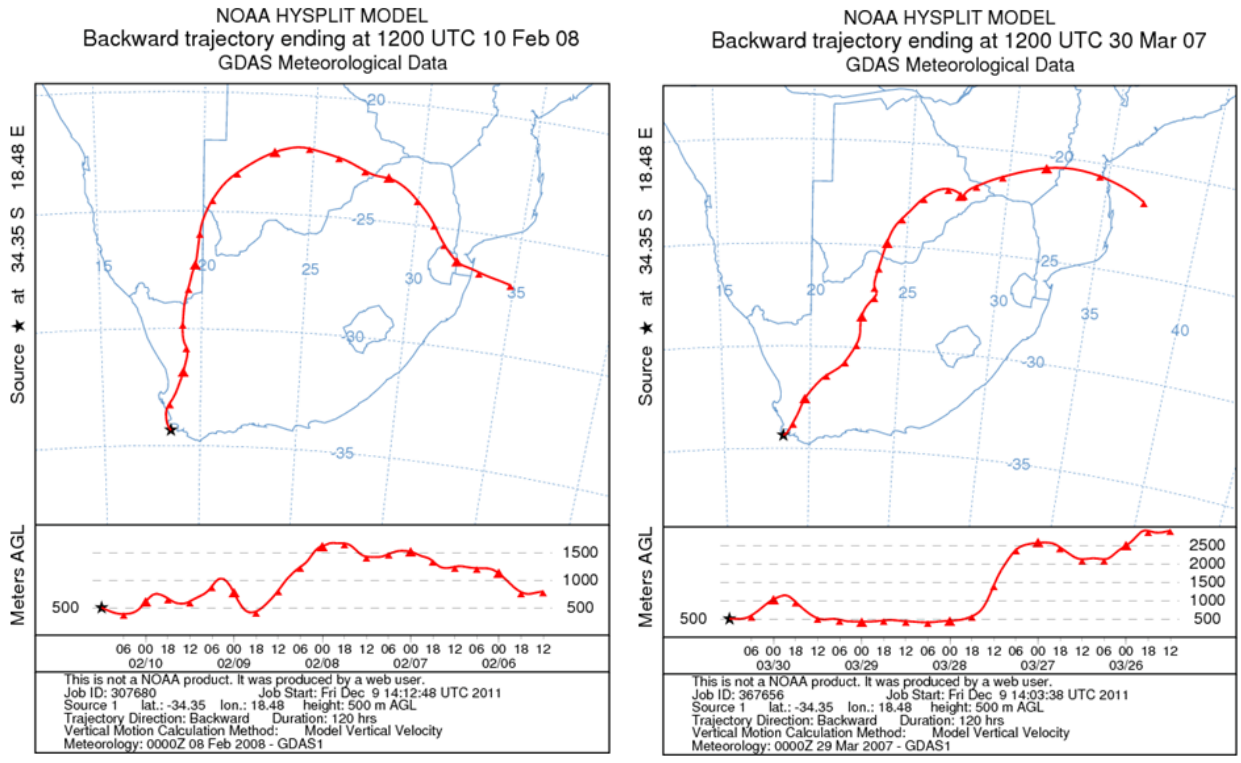

Fig. 4. Backward trajectory for 12:00 of 10 February 2008 (left panel), and 12:00 of 30 March 2007 (right panel). The GEM / ^{222}Rn flux ratio was $+0.077 \pm 0.008$ pg mBq^{-1} for the event on 10 February 2008, and -0.026 ± 0.005 pg mBq^{-1} for the event on 30 March 2007.

Tennessee (Kuiken et al., 2008a) but within the uncertainty of 0.2 ± 0.9 ng m^{-2} h^{-1}, measured at six forested sites in different states of the eastern USA (Kuiken et al., 2008b). Substantially larger average net emissions of 1.71 (estimate from 1.14 to 4.55) and 1.60 (estimate from 0.86 to 3.20) ng m^{-2} h^{-1} can be derived from Table 7.5 of the compilation by Mason (2009) for deserts/metalliferrous zones and savannah regions, respectively, in tropical/subtropical regions.

The radon-calibrated GEM fluxes derived by us do not include mercury wet deposition. Precipitation measurements at Cape Point and Pretoria in 2007–2009 yield an average wet deposition of -1.01 and -2.32 ng m^{-2} h^{-1}, respectively (Gichuki and Mason, 2013). The GEOS model by Selin et al. (2008) predicts a wet deposition flux of about -0.34 to -0.11 ng m^{-2} h^{-1} for pre-industrial times in southern Africa and an enrichment factor of ~ 4 due to anthropogenic activities yielding a current deposition of about -1.37 to -0.46 ng m^{-2} h^{-1}. A soil model by Smith-Downey et al. (2010) predicts a wet deposition rate ranging from ~ -0.5 ng m^{-2} h^{-1} in the vicinity of Cape Point to -4.6 ng m^{-2} h^{-1} in the industrial region around Johannesburg. An improved GEOS model by Soerensen et al. (2010b) predicts a wet deposition flux of -1.10 ng m^{-2} h^{-1} for Cape Point. Thus the wet deposition predicted by models is in reasonable agreement with the measurements of Gichuki and Mason (2013). Assuming an average wet deposition flux of -1.01 ng m^{-2} h^{-1} to be representative of southern Africa and the event duration weighted dry GEM flux of -0.54 ± 0.13 ng m^{-2} h^{-1} from this work, the net deposition over southern Africa would be about -1.55 ng m^{-2} h^{-1}. Additional unknown deposition of RGM and particulate mercury would further increase the net deposition. The terrestrial surface of southern Africa thus seems to be a net sink for atmospheric mercury. The GEOS model by Selin et al. (2008) predicts soils to be a net mercury sink of some -0.61 ng m^{-2} h^{-1}, if re-emission by biomass burning is excluded and the flux to all terrestrial surfaces is considered to be the same. The exclusion of biomass burning is justified, since we excluded the short pollution events from our radon-calibrated fluxes. The model-predicted net deposition rate is thus smaller than our radon-calibrated fluxes. Speciated mercury measurements and more data on wet deposition in southern Africa would further constrain the uncertainty of the net mercury deposition in this area.

4 Conclusions

Radon-calibrated fluxes of mercury over the terrestrial surface of southern Africa were derived from concurrent measurements of GEM and ^{222}Rn at Cape Point between March

2007 and December 2011. The average dry GEM flux over this period was $-0.01 \pm 0.34\,\mathrm{ng\,m^{-2}\,h^{-1}}$, and the average weighted by event duration was $-0.54 \pm 0.13\,\mathrm{ng\,m^{-2}\,h^{-1}}$ (standard error with $n = 191$, both after correction for ^{222}Rn decay). No pronounced seasonal flux variation was observed, but the average flux for spring–summer months (October–March) is positive and significantly different from the negative flux during the autumn–winter months (April–September). This seasonal variation is consistent with the expectation of higher fluxes at higher surface temperatures. But stimulation of mercury emissions by precipitation in combination with the summer maximum of precipitation in the interior of southern Africa may also have contributed. The fluxes derived here tend to be smaller than fluxes measured at mid-latitudes of the Northern Hemisphere and the emissions predicted by the models. By including wet mercury deposition ($-1.01\,\mathrm{ng\,m^{-2}\,h^{-1}}$), but discounting the RGM dry deposition, the terrestrial surface of southern Africa thus represents a significant net sink for atmospheric mercury of $-1.55\,\mathrm{ng\,m^{-2}\,h^{-1}}$. This net sink is larger than the net mercury flux of $-0.61\,\mathrm{ng\,m^{-2}\,h^{-1}}$ predicted by the GEOS model (Selin et al., 2008). An addition of the unknown RGM dry deposition would further increase this difference.

We believe, however, that the fluxes determined here should be viewed with caution. The uncertainty of wet deposition fluxes over southern Africa is still too large due to the lack of measurements. Furthermore, information about RGM fluxes is missing altogether. The extrapolation of our results to other areas is also not possible. Mercury emissions from soils are dependent on soil humidity (Song and Van Heyst, 2005) and can be expected to be smaller in arid southern Africa than elsewhere. Being located in the Southern Hemisphere, southern Africa has also received less historical mercury deposition than comparable regions in the Northern Hemisphere, probably leading to smaller emissions or even a net deposition of mercury imported from the Northern Hemisphere. Consequently, the determination of radon-calibrated mercury fluxes in other regions would be highly desirable.

We are well aware that our approach is simplified and the issues such as flux calculations, event duration weighting, and the correction for ^{222}Rn decay could probably be much better addressed by inverse modelling. We hope that this work will stimulate the interest of modellers.

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