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^{222}Rn calibrated mercury fluxes from terrestrial surfaces of southern Africa derived from observations at Cape Point, South 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 2009 altogether 59 events with high ^{222}Rn concentrations were identified. GEM correlated with ^{222}Rn in 41 of the events and was constant during the remaining events without significant correlation. The average GEM/^{222}Rn emission ratio of all events was -0.0047 ± 0.0054 pg mBq^{-1}, with ± 0.0054 being the standard error of the average. With an emission rate of 1.1 ^{222}Rn atoms cm^{-2} s^{-1} and a correction for the transport duration, this emission ratio corresponds to a radon calibrated flux of about -0.53 ± 0.62 ng m^{-2} h^{-1} which is statistically not distinguishable from zero. With wet deposition, which is not included in this estimate, the terrestrial surface of southern Africa appears to be a net mercury sink.

Key words: Heavy metals, mercury, emission, deposition, flux, terrestrial surface

Introduction

Mercury emissions from terrestrial surfaces represent with 1850 t yr^{-1} the third largest source of mercury after anthropogenic and ocean emissions of 2880 and 2680 t yr^{-1}, respectively (Pirrone et al., 2010). However, they have an uncertainty of about ±50% (Lindberg et al., 2007). This uncertainty originates from the inadequate knowledge of the emission mechanisms, the worldwide scaling of a small number of field measurements made in a few geographical regions, and the measurement challenges (Lindberg et al., 2007; Gustin et al., 2008; Mason, 2009).

^{222}Rn is a radioactive gas of predominantly terrestrial origin with a half-time of 3.8 days (in the following denoted simply as Rn). Its emission rate from soil is relatively evenly distributed making Rn a good tracer for studies of emissions from terrestrial surfaces (Zahorowski et al., 2004). The major advantage of the Rn related methods is their capability to estimate regional fluxes. In this work we use concurrent measurements of GEM and Rn made at Cape Point, South Africa, to estimate the regional mercury flux from southern Africa.

Materials and Methods

The Cape Point station is part of the World Meteorological Organization´s (WMO) Global Atmosphere Watch (GAW) network. It is located about 60 km south of Cape Town on top of a coastal cliff 230 m above sea level at the southern-most tip of the Cape Peninsula. The dominant wind direction is from the south-eastern sector which is representative of clean maritime air. Occasionally, the site is also subjected to air from the northern to north-eastern sector which is influenced by anthropogenic emissions from the greater Cape Town area and by other continental sources.

Since 1999 a two-filter instrument for the measurement of Rn (Brunke et al., 2002) and since March 2007 a Tekran 2537A analyser for the continuous measurement of mercury are operated at Cape Point. Under the prevailing conditions of higher temperature, humid air and sea salt aerosols we presume that reactive gaseous mercury (RGM) will not pass through the inlet tubing. Consequently, only GEM is being measured. GEM vs. Rn was correlated using orthonormal regression (Cantrell, 2008) which takes the uncertainties of both correlated parameters into account. The uncertainties of GEM and Rn measurenments were set to 0.05 ng m^{-3} and

50 mBq m^{-3}, respectively. The geographical origin of the Rn events was interpreted using ten-day isentropic back trajectories from NOAA ESRL and seven-day back trajectories calculated by NILU using the FLEXTRA model.

Results and Discussion

Altogether 59 events with Rn concentrations above 1000 mBq m^{-3} have been identified between March 2007 and December 2009 and most of them occur in April to October, in agreement with the climatology of Cape Point. 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 and pollution events which generally last only a few hours (Brunke et al., 2010). This difference enables us to discriminate against the depletion and pollution events. Twenty-six events with high Rn concentrations coincided with depletion and pollution events which were eliminated from the data.

Fig. 1 shows the frequency distribution of the GEM/Rn slopes from the correlations. In 41 events the correlation was significant at least at the 95% significance level. Fig. 1 shows that the slopes for the remaining events are centered around zero, i.e. in the bin with a central value of 0 pg mBq^{-1}, followed by the bins with the central values -0.02, +0.02, and +0.04 pg mBq^{-1}. Thus we consider the slopes of the 18 events with insignificant GEM vs. Rn correlations representative for very small fluxes between the terrestrial surface and atmosphere and we include them in the subsequent analysis. The average GEM/Rn slope of all events is -0.0047 ±0.0418 pg mBq^{-1} (n=59), which is statistically not different from zero.

Backward trajectories and a transport model (Whittlestone et al., 2009) show that the fetch for the Rn events encompasses South Africa and the neighboring countries of Namibia, Botswana, Zimbabwe, Mozambique, Lesotho and Swaziland. The terrestrial surface of southern Africa is presumed to emit about 1.1 Rn atoms cm^{-2} s^{-1} corresponding to 23.1 mBq m^{-2} s^{-1}. With this emission rate the radon calibrated GEM flux of southern Africa varied between -5.2 and + 10.9 ng m^{-2} h^{-1}, with negative values meaning deposition. The average GEM flux and its standard error (standard deviation/$\sqrt{n}$) was -0.39 ± 0.45 ng m^{-2} h^{-1}, and was statistically not different from zero. After correction for Rn decay during an average transport time of 2 days, the GEM flux was -0.53 ± 0.62 ng m^{-2} h^{-1}.

The flux estimated above does not include the deposition of RGM and particulate mercury (PM) which were emitted as such since only GEM was measured. But it will include the oxidation of GEM during the transport from the source regions of the event and the deposition of its products RGM and possibly PM. The deposition of RGM and PM from GEM oxidation may constitute a small part of the deposition of these species near RGM and PM sources but it may be dominating far away from them. The estimated flux also does not include wet mercury deposition. RGM and PM from GEM oxidation may also contribute to it. A comparison with models without resolving the contributions of the individual processes is thus difficult. We would only like to note that the addition of dry deposition of RGM and PM originating from RGM and PM emissions and the wet mercury deposition will result in a negative net mercury flux, i.e. the terrestrial surface of southern Africa appears to be a net mercury sink.

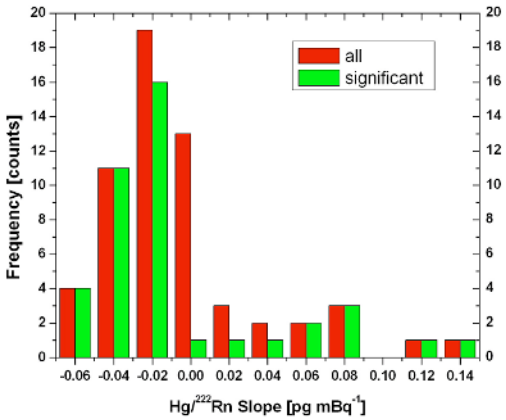

Fig. 1 Frequency distribution of GEM/Rn slopes.

Conclusion

The radon calibrated GEM flux is slightly negative albeit not statistically different from zero. With dry deposition fluxes of RGM and PM which were emitted as such and the wet mercury deposition the terrestrial surfaces of southern Africa appear to be a net sink of atmospheric mercury. We believe, however, that this result should not be generalized. Mercury emissions from soils are dependent on soil humidity and can be expected to be smaller in arid southern Africa than elsewhere. Being located in southern hemisphere, southern Africa has also received less historical mercury deposition than comparable regions in the northern hemisphere, possibly leading to smaller emissions or even a net deposition of mercury imported from the northern hemisphere.

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