Final Draft
of the original manuscript:

Ebinghaus, R.; Slemr, F.; Brenninkmeijer, C.A.M.; Velthoven, P.van; Zahn, A.;
Hermann, M.; O'Sullivan, D.A.; Oram, D.E.:

**Emissions of gaseous mercury from biomass burning in South
America in 2005 observed during CARIBIC flights**

In: Geophysical Research Letters (2007) AGU

DOI: 10.1029/2006GL028866

Emissions of gaseous mercury from biomass burning in South America in 2005 observed during the CARIBIC flights

R. Ebinghaus¹, F. Slemr², C.A.M. Brenninkmeijer², P. van Velthoven³, A. Zahn⁴, M. Hermann⁵

¹GKSS-Research Centre, Institute for Coastal Research, Max-Planck-Straße 1, D-21502 Geesthacht, Germany

²Max-Planck-Institut für Chemie (MPI), Joh.-J.-Becherweg 27, D-55128 Mainz, Germany

³Royal Netherlands Meteorological Institute (KNMI), P.O. Box 201, NL-3730 AE De Bilt, Netherlands

⁴Institut für Meteorologie und Klimaforschung (IMK), Forschungszentrum Karlsruhe, Weberstrasse 5, D-76133 Karlsruhe, Germany

⁵Leibniz-Institut für Troposphärenforschung, Permoserstrasse 15, D-04318 Leipzig, Germany

Abstract

Plumes of biomass burning effluents were observed during CARIBIC flights between São Paulo and Santiago de Chile on August 31 and October 5, 2005, as well as during the last part of the flight from Frankfurt to São Paulo on October 4, 2005. Total gaseous mercury (TGM) correlated with CO on August 31 and October 4 yielding a TGM/CO emission ratio of $(1.17 \pm 0.15) \times 10^{-7}$ and $(2.39 \pm 0.99) \times 10^{-7}$ mol/mol, respectively. No significant TGM/CO correlation was observed on October 5 probably because of variable background concentrations of both gases. The TGM/CO emission ratios observed here over South America fall within a rather narrow range of $(0.67 - 2.39) \times 10^{-7}$ mol/mol reported hitherto for sites as geographically different as South Africa, Canada, and the U.S.A. This narrow range suggests that the TGM emissions from biomass burning represent 3 - 11% of all mercury emissions. TGM emissions from biomass burning are larger than anthropogenic emissions in the southern hemisphere during the burning season in August - October.

Introduction

Mercury is emitted into the atmosphere from a number of natural as well as anthropogenic sources. Long-range atmospheric transport, the transformation to highly toxic methylmercury and subsequent bioaccumulation in the aquatic foodchain are considered to result in human exposure of hazardous levels in sea food even in ecosystems remote from local sources (NRC, 2000).

Worldwide mercury emissions by anthropogenic activities such as fossil fuel combustion, metal and cement production, waste incineration, are presumed to be 2235 t/yr in 1995 (Pacyna and Pacyna, 2002) and 2190 t/yr in 2000 (Pacyna et al., 2006), representing about one third of total mercury emissions of about 6600 t/yr (Mason and Sheu, 2002, and citations therein). Half of the remaining emissions is attributed to natural emissions from land and oceans and the other half to reemission of anthropogenically derived mercury (Mason and Sheu, 2002). However, emissions of mercury from biomass burning, an important source of many other pollutants (e.g. Andreae and Merlet, 2001) are not mentioned in the studies.

In this paper we report observations of mercury emissions from large scale biomass burning in South America. The biomass burning plumes were observed during regular CARIBIC (Civil Aircraft for *Regular Investigation of the Atmosphere Based on an Instrumented Container*) flights to South America in 2005.

Substantial emissions of mercury from burning have been reported only recently. Brunke et al. (2001) observed an Hg/CO emission ratio of 2.1×10^{-7} mol/mol during a fire of mixed vegetation (fynbos shrub, pine, rooikrans) at Cape Point in South Africa. Friedli et al. (2001; 2003a; 2003b) reported Hg/CO emission ratios of 0.67×10^{-7} mol/mol for a forest wildfire in Washington (USA) and 2.04×10^{-7} mol/mol for a fire burning black spruce in a boreal forest in Quebec (Canada). Hg/CO emission ratios of 1.46×10^{-7} and 1.57×10^{-7} mol/mol for biomass burning in Pacific Northwest and Alaska, respectively, were derived recently from observations at Mt Bachelor observatory (Weiss-Penzias et al., 2006). With a total CO emission of 437 Tg/yr from biomass burning (Duncan et al., 2003), these emission ratios suggest mercury emissions ranging from 209 to 656 T/yr, a substantial part of the total emissions mentioned above.

Results reported here and the corresponding Hg/CO emission ratios are comparable with those mentioned above and underline the global importance of mercury emissions from biomass burning.

Experimental

The new CARIBIC container (Brenninkmeijer et al., 2006) holds automated analyzers for total gaseous mercury (TGM), CO, O₃, NO, NO_y, CO₂, O₂, total and gaseous H₂O, oxygenated volatile organic compounds, fine aerosol particles (three counters for particles with diameters >4 nm, >12nm, and >18nm), larger particles (>150nm, optical particle counter), and for halogen oxides (DOAS). In addition, whole air and aerosol samples are taken during the flight and analysed for greenhouse gases, hydrocarbons, halocarbons, and elemental composition of aerosols, respectively. The TGM instrument is a Tekran[®] instrument based on enrichment of mercury, after passing through a 0.2 µm PTFE filter, on a gold collector followed by detection by atomic fluorescence upon its thermal desorption from the gold substrate. The instrument was modified for automatic operation at air pressures down to 200 hPa. During the flights reported here it was operated with 15 min long sampling intervals with a measurement uncertainty of about 0.05 ng/m³. The TGM concentration is given in ng/m³(STP, i.e. standard pressure of 1013.13 hPa and a standard temperature of 273.14 K). CO was measured by a fast VUV fluorescence detector with a time resolution of 1 s and a measurement uncertainty of about 1 ppb. For details of the instruments and inlet system see Brenninkmeijer et al. (2006). For correlations with TGM the CO data were averaged over the sampling interval of the TGM instrument.

The CARIBIC container is operated monthly onboard a Lufthansa Airbus 340-600 during long-distance flights to South America or Southeast Asia. The flights reported here were all made on the route Frankfurt - São Paulo - Santiago de Chile and back.

Results and discussion

Figure 1 gives an overview of the flight of October 4-5, 2005, from Frankfurt to São Paulo. With the exception of about an hour at the beginning and at about October 5, 1:00 UTC most of the flight took place in the upper troposphere at an altitude of about 11 km. The pronounced minimum in O₃ concentrations on October 5 at about 4:50 UTC coincided with

the crossing of the ITCZ at a latitude of about 6°N, as was found from analysis of satellite observations of clouds and of meteorological analysis of data provided by ECMWF. Apart from the lower concentrations in the stratosphere, TGM concentration shows a pronounced latitudinal gradient with lower concentrations in the southern hemisphere as reported earlier (Slemr et al., 1985). Superposed on this general gradient are local TGM maxima on October 5 at about 4:00 (10°N), 6:30 (8°S), and 8:30 (18°S). All three TGM maxima are accompanied by maxima of NO_y but only the last two by pronounced CO maxima. 8 day backward trajectories based on ECMWF analysis data (Scheele et al., 1996) for the first maximum suggest significant mercury emissions from the region of West Africa. Lack of enhanced concentrations of tracers for biomass burning, such as CO, CH₃CN, CH₃Cl, and CH₃Br in this plume preclude emissions from this source. In contrast, the two plumes before landing at São Paulo bear all characteristic features of biomass burning: enhanced concentrations of CH₃CN, CH₃Cl, CH₃Br in addition to those of NO_y, CO, and aerosols. Higher concentrations of O₃ and of large aerosols (>150nm) together with a lack of smaller particles in the plume at 6:30 UTC and the opposite characteristics of the plume at 8:30 UTC suggest that the latter is a fresh plume and the former one that already has been photochemically processed. The backward trajectories for the two maximum TGM measurements at 6:30 UTC originate near the surface over Central Brasil, south of the Amazon river (southern Pará and Mato Grosso) about 6 days before. The backward trajectories for the two maximum TGM concentrations at 8:30 UTC point to a source region further north. Some of the trajectories for these maxima show a different behaviour with a long range high altitude transport (above 250 hPa) of air from above the Pacific Ocean. Convection of polluted air polluted to the flight level from a region of south-west Brazil (Mato Grosso do Sul) is suggested by satellite pictures showing a pronounced cloud band in this region. Satellite pictures (AQUA/MODIS, TERRA/MODIS, GOES-12) report numerous fires on October 4 in Brazil and Paraguay with highest density in Bahia, Goiás, Tocantins, Minas Gerais, Mato Grosso, and Pará.

Pronounced biomass burning plumes were also observed during the short flights from São Paulo to Santiago de Chile and back on August 31 and October 5, 2005 (not shown). All four 3 h flights are very similar with a tropospheric section for about 1 h after the take off or before landing at São Paulo and a stratospheric one for the rest of the flight (with exception of the descent to Santiago). The tropospheric section is characterised by very high CO concentrations of up to 480 ppb on August 31 and 350 ppb on October 5. The data on concentrations of O₃, NO_y, aerosols, CH₃CN, and halocarbons, although not as complete as those shown above for the flight on October 4, all indicate plumes of biomass burning with some photochemical processing between the two extremes observed on October 4. All backward trajectories for the tropospheric part of the two flights on August 31 indicate a high altitude long range transport (above 300 hPa) from above southern Pacific Ocean. The observed pollution must then be brought to the flight level by deep convection, most probably in a cloud band extending from states Paraná and São Paulo in Brazil to northern Bolivia as shown by satellite pictures and ECMWF analyses. On August 31 the strongest fire activity observed by satellites was located in Pará, Mato Grosso, Amazonas, and Rondonia, but substantial activity was also detected in Tocantins, Minas Gerais, São Paulo, as well as in Peru and Paraguay.

On October 5 all backward trajectories for the tropospheric part of the flight show a slow transport from northern South America of air masses originating near the surface in a large region encompassing the Amazon basin, Peru, Ecuador, Colombia and Venezuela. A cloud band with the same position as on August 31 suggests additional convection of polluted air in the states of Paraná and São Paulo. In summary, the observed air pollution on August 31 was injected by a deep convection of polluted air masses from southern Brazil into homogeneous

southern hemispheric background air masses whereas on October 5 into air masses which were already preloaded by emissions from a large part of northern South America. These air masses were transported southward and upward by the South American low level jet (Marengo et al. 2004) and by convection triggered by this jet, likely through interaction with the upper level jet.

Correlation of TGM with CO have been used to derive information about the TGM/CO emission ratio of biomass burning (Andreae and Merlet, 2001; Brunke et al., 2001; Friedli et al., 2003a and 2003b, Weiss-Penzias et al., 2006). We use orthogonal regression (York, 1966) with TGM and CO uncertainties set to 0.05 ng/m^3 and 1 ppb, respectively. Significant correlations of Hg with CO were observed on August 31 (flights 123 and 124, significance level 99.9%) and for the fresh plume on October 4 (flight 126, 95%), but not for the plume observed on October 5 (flights 127 and 128). The above meteorological analysis suggests that the lack of correlation on October 5 was most probably due to inhomogeneous background both of TGM and CO.

The TGM/CO emission ratios are summarized in Table 1 together with other ratios reported so far biomass burning in the literature. Despite of very different regions (boreal and tropical forests) and types of vegetations (fynbos shrubs, pines, tropical vegetation) they all fit a rather narrow range of $(0.67 - 2.39) \times 10^{-7} \text{ mol/mol}$. A total average emission of 437 Tg CO/yr from biomass burning over the years 1996 - 2000 (Duncan et al., 2003) then implies an average total TGM emission of 209 - 746 t/yr, representing 3 - 11% of total mercury emissions. Based on the geographical distribution of the CO emissions (Duncan et al., 2003), almost all of the mercury will be emitted in the tropics ($30^\circ\text{N} - 30^\circ\text{S}$). Emission of TGM from biomass burning will vary strongly from year to year, and may reach as much as 257 - 917 t/yr in years with anomalously high biomass burning such as 1997/1998 (Langenfelds et al., 2002). As for other gases, the interannual variation of TGM concentrations caused by interannual variation of biomass burning of this magnitude should be revealed by long term high precision monitoring of TGM. Fig. 2 shows also that the emission of mercury from biomass burning is strongly dependent on the season. Based on CO emission of 188 Tg/yr (Duncan et al., 2003) about 90 - 321 t/yr of TGM will be emitted in the southern hemisphere between June and November. During these months the emission from biomass burning is comparable to or even surpass total anthropogenic mercury emissions in the southern hemisphere (Wilson et al., 2006).

Conclusion

Plumes of biomass burning with enhanced TGM concentrations were observed over South America during the CARIBIC flights on August 31, October 4 and October 5, 2005. TGM/CO emission ratio of $(1.17 \pm 0.15) \times 10^{-7}$ and $(2.39 \pm 0.99) \times 10^{-7} \text{ mol/mol}$ was derived from the observations on August 31 and October 4, respectively. These are the first TGM/CO emission ratios reported for tropics where 90% of all CO from biomass burning is emitted (Duncan et al., 2003). The TGM/CO emission ratio observed in the tropics fall in a rather narrow range of emissions ratios determined elsewhere lending confidence in estimates of worldwide TGM emissions from biomass burning. With 3 - 11% of all mercury emissions, biomass burning represents one of the major mercury sources which has to be included in global and regional models of atmospheric mercury.

Acknowledgments

We are especially indebted to Lufthansa for their technical and organisational support of the CARIBIC project. We thank also all 11 CARIBIC partners who contribute to the operation of

the instrumented container and, specifically to Hans Kock and Jan Boedewadt who modified and operate the mercury analyser. Satellite fire observations were provided by the Global Fire Monitoring Center (GFMC). We also acknowledge funding from DG XII of the Commission of the European Communities and the German Bundesministerium für Bildung und Forschung.

References

Andreae, M.O., P. Merlet, Emissions of trace gases and aerosols from biomass burning, *Global Biogeochem. Cycles* 15, 955-966, 2001.

Brenninkmeijer, C.A.M., et al., Civil aircraft for the regular investigation of the atmosphere based on an instrumented container: the new CARIBIC system, paper in preparation, 2006.

Brunke, E.-G., C. Labuschagne, F. Slemr, Gaseous mercury emissions from a fire in the Cape Peninsula, South Africa, during January 2000, *Geophys. Res. Lett.* 28, 1483-1486, 2001.

Duncan, B.N., R.V. Martin, A.C. Staudt, R. Yevich, J.A. Logan, Interannual and seasonal variability of biomass burning emissions constrained by satellite observations, *J. Geophys. Res.* 108, doi:10.1029/2002JD002378, 2003.

Friedli, H.R., L.F. Radke, J.Y. Lu, Mercury in smoke from biomass fires, *Geophys. Res. Lett.* 28, 3223-3226, 2001.

Friedli, H.R., L.F. Radke, J.Y. Lu, C.M. Banic, W.R. Leitch, J.I. MacPherson, Mercury emissions from burning of biomass from temperate North American forests: laboratory and airborne measurements, *Atmos. Environ.* 37, 253-267, 2003a.

Friedli, H.R., L.F. Radke, R. Prescott, P.V. Hobbs, P. Sinha, Mercury emissions from the August 2001 wildfires in Washington State and an agricultural waste fire in Oregon and atmospheric mercury budget estimates, *Global Biogeochem. Cycles* 17, 1039, doi:10.1029/2002GB001972, 2003b.

Langenfelds, R.L., R.J. Francey, B.C. Pak, L.P. Steele, J. Lloyd, C.M. Trudinger, C.E. Allison, Interannual growth rate variations of atmospheric CO₂ and its $\delta^{13}\text{C}$, H₂, CH₄, and CO between 1992 and 1999 linked to biomass burning, *Global Biogeochem. Cycles* 16, doi:10.1029/2001GB001466, 2002.

Lindqvist, O., K. Johansson, M. Aastrup, A. Andersson, L. Bringmark, G. Hovsenius, L. Håkanson, Å. Iverfeldt, M. Meili, B. Timm, Mercury in the Swedish environment - recent research on causes, consequences and corrective methods, *Water Air Soil Pollut.* 55, 1-261, 1991.

Marengo, J.A., R.S. Wagner, C. Saulo and M. Nicolini, Climatology of the Low-Level Jet East of the Andes as Derived from the NCEP-NCAR Reanalyses: Characteristics and Temporal Variability, *J. Climate* 17, 12, 2261-2280, 2004.

Mason, R.P., G.-R. Sheu, Role of the ocean in the global mercury cycle, *Global Biogeochem. Cycles* 16, doi:10.1029/2001GB001440, 2002.

National Research Council, *Toxicological Effects of Methylmercury*, National Academy Press, Washington, DC, 2000.

Pacyna, E.G., J.M. Pacyna, Global emissions of mercury from anthropogenic sources in 1995, *Water Air Soil Pollut.* 137, 149-165, 2002.

Pacyna, E.G., J.M. Pacyna, F. Steenhuisen, S. Wilson, Global anthropogenic mercury emission inventory for 2000, *Atmos. Environ.* 40, 4048-4063, 2006.

Scheele, M., P. Siegmund en P. van Velthoven, Sensitivity of trajectories to data resolution and its dependence on the starting point: in or outside a tropopause fold, *Meteorol. Appl.* 3, 267-273, 1996.

Slemr, F., G. Schuster, W. Seiler, Distribution, speciation, and budget of atmospheric mercury, *J. Atmos. Chem.* 3, 407-434, 1985.

Weiss-Penzias, P. et al, ???

Wilson, S.J., F. Steenhuisen, J.M. Pacyna, E.G. Pacyna, Mapping the spatial distribution of global anthropogenic mercury emission inventories, *Atmos. Environ.* 40, 4621-4632, 2006.

York, D., Least-squares fitting of a straight line, *Can J. Physics* 44, 1079-1086, 1966.

Tables

Region	Hg/CO emission ratio [mol/mol]	Reference
South America, Aug. 31, 2005, flights #123 + 124	$(1.17 \pm 0.15) \times 10^{-7}$, $R^2=0.9243$, n=7, 99.9%	This work
South America, Oct. 5, 2005, flight #126	$(2.39 \pm 0.99) \times 10^{-7}$, $R^2=0.5396$, n=7, 95%	This work
Cape Point, South Africa	$(2.10 \pm 0.21) \times 10^{-7}$	Brunke et al. (2001)
Quebec, Canada	2.04×10^{-7}	Friedli et al. (2003a)
State Washington, U.S.A.	$(0.67 \pm 0.04) \times 10^{-7}$	Friedli et al. (2003b)
Pacific Northwest, U.S.A.	$(1.46 \pm 0.90) \times 10^{-7}$	Weiss-Penzias et al. (2006)
Alaska, U.S.A.	$(1.57 \pm 0.67) \times 10^{-7}$	Weiss-Penzias et al. (2006)

Figures

Fig. 1: CARIBIC flight on October 4, 2005, from Frankfurt to Sao Paulo.

Fig. 2: Seasonal variation of mercury emissions in the northern and southern hemispheres. Emissions from oceans and their seasonality are taken from Strode et al. (2006), anthropogenic emissions are distributed geographically according to Wilson et al. (2006) and are assumed to be independent of season. The emissions from biomass burning were calculated using the seasonal variation of CO emissions given by Duncan et al. (2003) and Hg/CO emission ratios of 1.89 and 1.36×10^{-7} mol/mol in the southern and northern hemisphere, respectively.