Distribution of Gaseous Elemental Mercury in the Upper Troposphere and Lower Stratosphere

F. Slemr[1], R. Ebinghaus[2], H.H. Kock[2], C.A.M. Brenninkmeijer[1], T. Schuck[1], A. Zahn[3], P. van Velthoven[4], M. Hermann[5], B. Martinsson[6]

[1]Max Planck Institute for Chemistry, Mainz, Germany; [2]GKSS Geesthacht, Germany; [3]Forschungszentrum Karlsruhe, Germany; [4]KNMI, de Bilt, the Netherlands; [5]Leibniz Institute for Tropospheric Research, Leipzig, Germany; [6]Department of nuclear Physics, University of Lund, Sweden

Introduction

Gaseous elemental mercury (GEM) has been measured since May 2005 using a long-range passenger aircraft Airbus 340-600 of Lufthansa German Airlines equipped with the new **CARIBIC** (**C**ivil **A**ircraft for **R**egular **I**nvestigation of the Atmosphere **B**ased on an **I**nstrument **C**ontainer, **http://www.caribic-atmospheric.com**) container and inlet system. The most prominent features of the unique data set are (1) frequent observations of emission plumes, (2) the seasonality of the GEM concentrations in the upper tropophere (UT), and (3) the decrease of GEM concentration in the lower stratosphere (LS).

Experimental

The new CARIBIC onboard Airbus 340-600 consists of a newly designed inlet and a newly constructed container with a total of 15 instruments. GEM, O_3, CO, CO_2, H_2O (vapour and total), NO, NOy, O_2, selected oxygenated compounds (PTR-MS), aerosol particles (>4nm, >12nm, >18 nm), particle size distribution (>150nm), and bromine oxides and some other compounds (MAX-DOAS) are measured continuously. 28 whole air samples per flight are taken and analysed for greenhouse gases, hydrocarbons, and halocarbons. 18 aerosol samples pro flight are collected and analysed for elemental composition and particle morphology. Because of the time needed for the analyses of the samples the CARIBIC flights are currently made with a frequency of one flight sequence (4 single flights) per month (details see in the CARIBIC homepage).

GEM is measured by a Tekran instrument based on enrichment of mercury on a gold wire and detection after thermodesorption at 700°C by an atomic fluorescence detector. Aerosols are filtered out by 0.2 µm PTFE filter and reactive gaseous mercury is lost in the inlet and tubing upstream of the instrument. The instrument was modified for an unattended operation at 200 - 300 hPa (stronger pump, hardware and software for the storage of the data and the communication with the computer controlling the entire instrumentation and is now operated with a 5 min resolution has a precision of about 0.05 ng/m^3. For correlations, with other measurements, all parameters were integrated over the sampling time of the TGM measurement.

We report here on data set obtained since May 2005 up to March 2007 consisting of 7 flights on the route Frankfurt - São Paulo - Santiago de Chile and 12 flights on the route Frankfurt - Guangzhou – Manila. Fig. 1 shows a typical flight overview.

Acknowledgments

We thank all CARIBIC partners (see homepage) for their efforts to create and operate this unique observation platform and to the agencies and companies who funded these efforts (EU, BMBF, Deutsche Lufthansa).

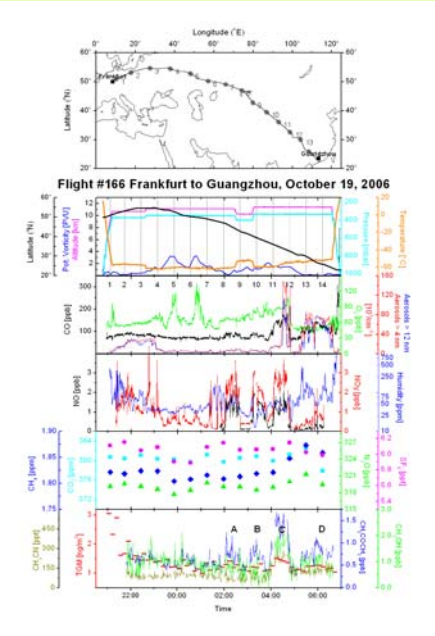

Fig. 1: An overview of the measurements during the flight # 166. The observed emission plumes are marked A, B, C, and D.

Date	Latitude [°N]	Longitude [°E]	Hg/CO slope [pg m^{-3} ppb^{-1}]
July 6, 2006	25.1-31.1	100.3-108.2	6.52 ± 0.62
August 1, 2006	23.9-30.6	102.4-112.8	7.31 ± 1.13
September 8, 2006	15.3-22.7	113.6-120.5	9.40 ± 1.92
October 20, 2006, plume C	30.4-38.1	89.5-103.3	3.90 ± 0.86
October 20, 2006, plume D	23.4-31.0	100.2-112.0	6.93 ± 1.74

Table 1: Hg/CO emission ratio observed during the flights Frankfurt – Guangzhou – Manila.

Results

Fig. 1 shows an overview of selected data from the flight # 166. Stratospheric air was sampled at about 23:55 and 0:50 as indicated by high concentrations of PV, O_3, NOy, and by low values of H_2O and mercury. Four plumes of air polluted by mercury emissions are marked by A, B, C, D. Of these the plume C is accompanied by high concentrations of CH_3CN suggesting an influence of biomass burning.

Plumes

The emission ratios derived from the plumes observations during the China flights are summarised in Table 1. Those from plumes of biomass burning observed over South America have already been published (Ebinghaus et al., Geophys. Res. Lett. *34*, L08813, doi:10.1029/2006GL028866, 2007). With the exception of the plume C, all plumes originated in China and are characterised by Hg/CO emission ratio of about 7 pg m^{-3} ppb^{-1} which is typical for plumes from this region (Weiss-Penzias et al., Atmos. Environ. 41, 4366, 2007). The plume C with Hg/CO emission ratio of 3.9 pg m^{-3} ppb^{-1} originates from northern India. Its low emission ratio suggest a mixture of of emissions from biomass burning and other anthorpogenic sources.

Distribution in the upper troposphere

The first insight into the GEM distribution in the upper troposphere is shown in Figures 2 and 3. During most of the China flights, GEM was found to correlate well with CO. Hg/CO slope was found to vary strongly with season from about 3.5 pg m^{-3} ppb^{-1} in winter to about 13 pg m^{-3} ppb^{-1} in early autumn. The minimum value corresponds roughly to the range of biomass burning and anthropogenic Hg/CO emission ratios and the seasonal variation may result mainly from the different lifetime of CO and GEM.

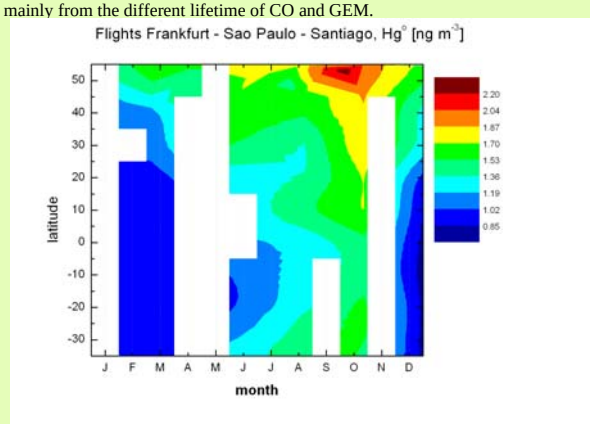

Fig. 2: Time-latitude distribution of GEM in the upper troposphere. Elevated GEM concentrations in the southern hemisphere in August and October are due to biomass burning.

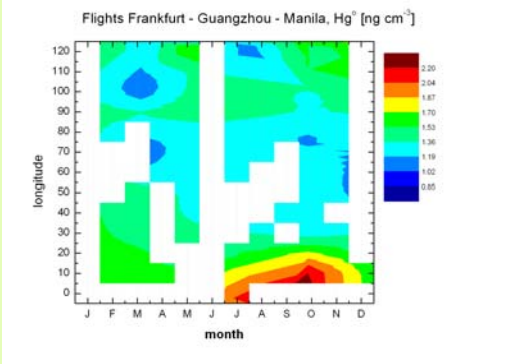

Fig. 3: Time-longitude distribution of GEM concentrations during the China flights. Concentrations at a longitude > 110°E are higher for most of the year than those corresponding to a latitude of 20-25°N indicating the influence of anthropogenic emissions.

Stratosphere

In the stratosphere GEM concentrations always decreased with the increasing O_3 concentrations and PV. The lowest measured GEM concentration was 0.25 ng m^{-3} during the flight # 146 on April 29, 2006. The best correlations were found with CO with a seasonably invariable slope of about 10 pg m^{-3} ppb^{-1}. A correlation of GEM with SF_6 combined with the average increase of SF_6 of 0.230 ppt yr^{-1} (Stiller et al., Atmos. Chem. Phys. 8, 677, 2008) suggest a GEM destruction rate of about 0.44 ng m^{-3} yr^{-1}. The Hg measurements on aerosol samples taken during the flights have not been successful so far, but measurements with aerosol spectrometer (Murphy et al., Environ. Sci. Technol. 40, 3163, 2006) suggest conversion to oxidised form carried by the particles.

Conclusions

GEM measurements with a new CARIBIC system have provided the first insight into the large-scale GEM distribution in the upper troposphere and its seasonal variation. Plumes of mercury emissions from different sources are frequently observed in the upper troposphere. They can be classified according to the Hg/CO emission ratio. GEM concentrations in the stratosphere decrease with increasing O_3 and PV. As mercury as an element cannot be removed from the stratosphere rapidly, the observations suggest a transformation to reactive gaseous mercury or mercury compounds carried by particles. Complementary findings of high mercury concentrations on stratospheric aerosols by others suggest the latter to be dominating.