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European emissions of mercury derived from long-term observations at Mace Head, on the western Irish coast

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Abstract

Many emission inventories for mercury have been compiled but rarely constrained using observations of ambient air concentrations with a known quality. In this paper, we derive Hg/CO, Hg/halocarbon, and Hg/CH_4 emission ratios from pollution episodes observed during the long-term mercury monitoring at the Mace Head Atmospheric Research Station in Ireland. The average Hg/CO emission ratio from 15 pollution episodes with air originating from the European continent observed between 1996 and 2003 was $0.0050 \pm 0.0021\,\mathrm{ng\,m^{-3}\,ppbv^{-1}}$, i.e. $(5.5 \pm 2.3) \times 10^{-7}$ mol/mol, which is almost identical to the ratio reported recently for the continental plumes of eastern Asia. Mercury correlated also with $CFCl_3$ (CFC-11), CF_2Cl_2 (CFC-12), CH_3CCl_3, CCl_4, CCl_2FCF_2Cl (CFC-113), $CHCl_3$, N_2O, and CH_4 during the pollution episodes. The mercury emissions calculated from the emission ratios and the European emissions of the above gases are in reasonable agreement with the estimated anthropogenic total mercury emissions of 250 t/yr in 1995. However, the measurements encompass almost exclusively elemental mercury whose anthropogenic emissions are estimated to be only $152\,\mathrm{t\,yr^{-1}}$. Several hypotheses are proposed to explain this discrepancy, such as natural sources, underestimation of the emissions of elementary mercury, and erroneous speciation of anthropogenic emissions.

Keywords: Mercury; Emission; CO; Halocarbons; Inventory

1. Introduction

Emissions of mercury into the atmosphere are of concern because of its medium- and long-range transport, deposition, biomethylation, bioaccumulation of methyl mercury compounds in the aquatic nutritional chain and its strong neurotoxic properties (Lindqvist, 1991; US EPA, 1997). Consequently, many researchers have tried to estimate the natural and anthropogenic emissions of mercury and to establish spatially and temporally resolved emission inventories (e.g., Nriagu and Pacyna, 1988; Nriagu, 1989; Pirrone et al., 1996, 1998; Pacyna and Pacyna, 2002; Pacyna et al., 2003; Pyle and Mather, 2003). However, these estimates are uncertain because emission data for many sources, e.g. waste incineration (Pacyna et al., 2006), and/or source areas are not well known (Lin et al., 2006). The emission estimates are further complicated by the

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large-scale air/surface exchange processes (e.g., Lindberg et al., 1998) and the large uncertainties in speciation of anthropogenically and naturally emitted mercury (e.g., Carpi, 1997; Lindberg et al., 2005; Lin et al., 2006). In addition, the emission estimates have so far mostly ignored the recently reported substantial emissions from biomass burning (Brunke et al., 2001; Friedli et al., 2001, 2003).

In view of these difficulties and the difficulties connected with representativeness of measurements of air/surface fluxes (Lindberg et al., 1998) it is surprising that only a few trials have been made so far to confront the emission estimates, with constraints derived from increasing amount of high-quality observations. Slemr et al. (2003) found a qualitative agreement of the concentration trends observed at eight sites in the Northern and Southern Hemispheres as well as from ships with a maximum of estimated mercury emissions in the 1980s and decreasing emissions afterwards. However, the observed decrease in the 1990–95 period is contrary to the increase of worldwide antropogenic emissions in the same time from 1881 to 2235 t yr^{-1} (Pacyna et al., 2006). On a smaller spatial and temporal scale, correlations of concentrations of two substances measured in the lee of investigated areas are frequently used to calculate emission ratios (e.g., Hansen et al., 1989; Brunke et al., 2001; Slemr et al., 2002; Palmer et al., 2003; Jaffe et al., 2005), which can then be compared with the emission ratios derived from emission inventories (Slemr et al., 2002). Lee et al. (2001) calculated a Hg/CO_2 emission ratio for the northeastern United States in winter from long-term monitoring of Hg and CO_2 at a site in Connecticut and used it to calculate anthropogenic emissions of elemental mercury which they found substantially larger than the emissions based on model studies. Only recently, Jaffe et al. (2005) and Weiss-Penzias et al. (2006) calculated Hg/CO emission ratios of eastern Asia outflow from long-term monitoring of Hg and CO at sites in Japan and at the west coast of the US and they found them twice as large as the emission ratios calculated from the current inventories for anthropogenically emitted Hg and CO in eastern Asia.

In this paper we estimate emission ratios of Hg to CO, six halocarbons, N_2O, and CH_4 for selected pollution episodes, with air masses passing over Europe from the long-term monitoring of these species at Mace Head on the western coast of Ireland. We use essentially the same methodology as Jaffe et al. (2005) but extend it to other substances monitored at Mace Head. From emission ratios derived from correlations and calculated emissions of CO, $CFCl_3$ (CFC-11), CF_2Cl_2 (CFC-12), CH_3CCl_3, CCl_4, CCl_2FCF_2Cl (CFC-113), $CHCl_3$, N_2O, and CH_4 we estimate the mercury emission and compare it with the published mercury inventory.

2. Experimental

Mace Head is located in County Galway near Carna on the west coast of Ireland at 53°20′N, 9°54′W. The station is part of the ALE/GAGE/AGAGE global network designed to monitor trends of greenhouse gases and halocarbons (Prinn et al., 2000). The station and the mercury measurements are described in detail by Ebinghaus et al. (2002). Briefly, total gaseous mercury (TGM) was measured by an automatic dual channel, single amalgamation cold vapour atomic fluorescence analyser (Model 2537A, Tekran, Inc., Toronto, Canada). The air sample was passed through a 0.2 μm PTFE filter upstream of the instrument. Speciation measurements during an international intercomparison at Mace Head in September 1995 indicated that only about 3% of the gaseous mercury was in the reactive inorganic form (Ebinghaus et al., 1999). Particulate mercury representing about 2% of total mercury is filtered out (Ebinghaus et al., 1999). The instrument was run with 10 min sampling time in 1996 and 1997 and with 15 min afterwards.

Carbon monoxide was recorded every 40 min using a hot mercuric oxide reduction gas detector (Derwent et al., 2001). $CFCl_3$ (CFC-11), CF_2Cl_2 (CFC-12), CH_3CCl_3, CCl_4, CCl_2FCF_2Cl (CFC-113), $CHCl_3$, N_2O, and CH_4 were measured every 40 min by a custom-designed automated gas chromatograph system installed at each AGAGE station and described in detail by Prinn et al. (2000) and O'Doherty et al. (2001). CO data were available until the end of 2003, the data for other trace gases only until the end of 1999. The mercury data with higher temporal resolution were averaged to fit the temporal resolution of other trace gases.

The pollution episodes were selected manually by looking for the coincidence of enhanced TGM and CO daily mean concentrations over a period of at least 3 days. Twelve episodes with TGM concentrations enhanced by at least 0.5 ng/m^3 and flow from different parts of Europe were found in the 1996–2003 period. Detailed analyses of the 5-day backward trajectories revealed that three of the