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European and Mediterranean mercury modelling: Local and long-range contributions to the deposition flux

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HIGHLIGHTS

- Gas phase conversion of Hg^0 to Hg^{II} by O_3/OH is not very consistent with observations.
- A Br/BrO oxidation mechanism compared best with observed Hg precipitation fluxes.
- Local emissions contribute most to the overall Hg deposition flux in the summer.
- Long-range transport of Hg contributes most to winter Hg deposition.

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ABSTRACT

Mercury (Hg) is a global pollutant that is known to have adverse effects on human health, and most human exposure to toxic methylmercury is through fish consumption. Soluble Hg compounds in the marine environment can be methylated in the water column and enter the base of the food chain. Atmospheric deposition is the most important pathway by which Hg enters marine ecosystems. The atmospheric chemistry of Hg has been simulated over Europe and the Mediterranean for the year 2009, using the WRF/Chem model and employing two different gas phase Hg oxidation mechanisms. The contributions to the marine deposition flux from dry deposition, synoptic scale wet deposition and convective wet deposition have been determined. The Hg deposition fluxes resulting from trans-continental transport and local/regional emission sources has been determined using both Br/BrO and O_3/OH atmospheric oxidation mechanisms. The two mechanisms give significantly different annual deposition fluxes (129 Mg and 266 Mg respectively) over the modelling domain. Dry deposition is more significant using the O_3/OH mechanism, while proportionally convective wet deposition is enhanced using the Br/BrO mechanism. The simulations using the Br/BrO oxidation compared best with observed Hg fluxes in precipitation. Local/regional Hg emissions have the most impact within the model domain during the summer. A comparison of simulations using the 2005 and 2010 AMAP/UNEP Hg emission inventories show that although there is a decrease of 33% in anthropogenic emissions between the two reference years, the total simulated deposition in the regions diminishes by only 12%. Simulations using the 2010 inventory reproduce observations somewhat better than those using the 2005 inventory for 2009.

1. Introduction

Mercury (Hg) is a global pollutant, and the subject of the recent Minamata convention (http://www.mercuryconvention.org/) which aims to protect the environment and human health from the deleterious effects of Hg exposure (Selin, 2014). As was the case in Minamata (see the Minamata mercury events timeline in UNEP (2013a, b)) most human exposure to methylmercury is through the consumption of contaminated sea food (Chen et al., 2008; Oken et al., 2012). Methylmercury bioaccumulates through the food web

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and therefore is found in high concentrations in long-lived piscivorous fish.

Recent research suggests that inorganic Hg compounds can be methylated in the water column (see Sunderland et al. (2009); Mason et al. (2012); Blum et al. (2013); Lamborg et al. (2014); Žagar et al. (2014)). The main input of inorganic Hg (as Hg^{II} compounds) to marine ecosystems occurs via deposition from the atmosphere, through both dry and wet deposition processes. A number of global, regional and box models to study the Hg cycle in the atmosphere have been developed over the last 20 years. Recently with the advent of ever more powerful computers, the possibilities for modelling atmospheric, oceanic, terrestrial and riverine Hg have multiplied. A recent review by Ariya et al. (2015) gives a very thorough summary of recent modelling progress, and the stumbling blocks that still exist. Using the WRF/Chem-Hg model simulations of the atmospheric Hg cycle over Europe and the Mediterranean for the year 2009 have been performed using the most recent AMAP/UNEP anthropogenic emission inventory (2010) (AMAP/UNEP, 2013). The results are compared to those obtained using the 2005 emission inventory (AMAP/UNEP, 2008), to see how the differences in the inventories – total emissions, speciation and emission height – impact on the simulated Hg deposition fields. The results have been analysed in order to evaluate the contribution to total Hg deposition fluxes from dry, synoptic and convective wet deposition. The Mediterranean troposphere is influenced by emissions originating within Europe, North America and even Asia (Lelieveld et al., 2002), and therefore model runs to distinguish the local, versus long-range transport, contributions to the deposition fields were performed. The results using the 2005 and 2010 emission inventories were compared to see how much the reduction of local anthropogenic emissions was reflected in the proportion of Hg deposition from local versus long-range transport. Due to the continuing debate over the precise atmospheric Hg oxidation mechanism (Hynes et al., 2009; Subir et al., 2011, 2012; Weiss-Penzias et al., 2014), simulations using a Br/BrO based Hg oxidation mechanism as well as O_3/OH were performed.

2. Model description

Gas phase chemistry of Hg and a parametrised representation of atmospheric Hg aqueous chemistry have been added to the RADM2 chemical mechanism in WRF/Chem (version 3.4) using KPP (Sandu and Sander, 2006) and the WKC coupler (Salzmann and Lawrence, 2006). Anthropogenic and natural Hg emissions have also been included and dry and wet deposition processes for Hg have been implemented (see the SI and Gencarelli et al. (2014) for further details).

2.1. Model domain

A coarse domain covering Europe and the Mediterranean, including parts of North Africa and the Middle East (81 by 81 km) and 28 sigma vertical levels from the surface to 50 hPa was used. Within this a nested domain (27 by 27 km) covering all of the Mediterranean and a large part of Europe was used, Fig. 1. Meteorological input was from the Global Forecast System (GFS, 1 ° by 1 °) at six hourly intervals, and nudging applied for temperature, wind and moisture parameters. Chemical initial and boundary conditions (IC/BC) were taken from the global Hg model ECHMERIT (Jung et al., 2009; De Simone et al., 2014). Further details of the model, and the various physics options employed can be found in Gencarelli et al. (2014) and references therein.

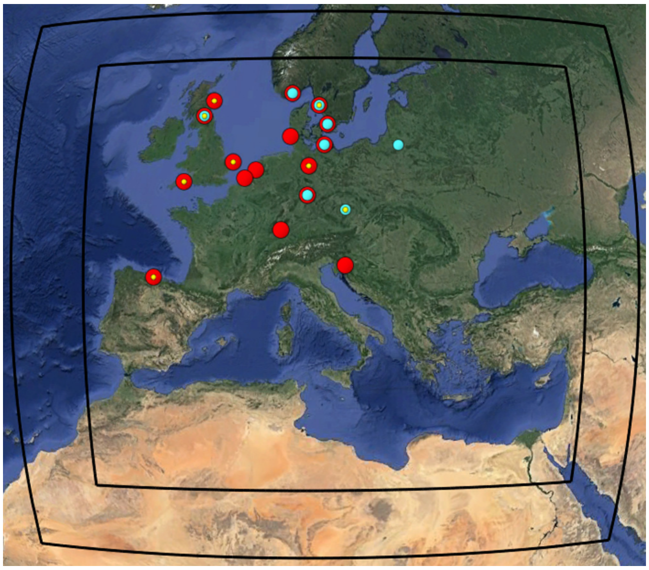

Fig. 1. Model domains and location to the EMEP measurement stations used for measurement comparisons (white triangles, map pointers, black dots for wet deposition, TGM and PBM respectively in B/W, red points for wet deposition, cyan for TGM and yellow for PBM) displayed in Google™ Earth. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Emissions

2.2.1. Anthropogenic emissions

Some recent modelling studies have made use of modified anthropogenic emission inventories, either in terms of emission totals or in terms of the emission speciation (see for example Selin et al. (2008); Amos et al. (2012); Kos et al. (2013); Horowitz et al. (2014)). However, these studies mostly consider the problem of Hg speciation in coal fired power plants as specified in the U.S. National Emissions Inventory. The speciation of Hg in the AMAP/UNEP emissions inventory has been questioned (Bieser et al., 2014), however this study referred to the 2005 inventory and not the most recent 2010 inventory. The AMAP/UNEP 2010 inventory (AMAP/UNEP, 2013) is a significant improvement over the 2005 version (AMAP/UNEP, 2008) and has been used here. However a year long simulation using the 2005 inventory was also performed in order to assess how significant the changes in emissions and deposition are over the modelling domain, and particularly in terms of deposition to the Mediterranean. The differences in the two inventories (for the fine modelling domain used in this study can be found in Table A.1). For non-mercury anthropogenic emissions the RETRO (http://www.retro.enes.org/) and EDGAR v4 (http://www.edgar.jrc.ec.europa.eu/) databases were used.

The WRF/Chem emission preprocessor package (Freitas et al., 2011) was used to prepare all the anthropogenic emission input files.

2.2.2. Natural emissions

Hg emissions from biomass burning are included making use of the Hg/CO enhancement ratio (Friedli et al., 2009; De Simone et al., 2015), the FINNv1 emissions inventory (Wiedinmyer et al., 2011) and the built in plume rise module (Grell et al., 2011). Evasion of Hg^0 from the sea surface (based on Wanninkhof (1992) parametrisation), has also been included for all the marine regions in the modelling domain, (see Gencarelli et al. (2014) for details). Biogenic emissions of non-Hg species are calculated on-line with the Guenther scheme (Guenther et al., 1993, 1994), using the option