

IMPACT OF MARINE MERCURY CYCLING ON COASTAL ATMOSPHERIC MERCURY CONCENTRATIONS IN THE NORTH- AND BALTIC SEA REGION

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Keywords: mercury;modelling;oceanair-sea exchange

Introduction

Mercury is a toxic substance that poses a severe risk to human life and ecosystems. Because of its global nature, monitoring and reduction of mercury pollution has been a focus of several international conventions, such as the UN-ECE Convention on Long-Range Transport of Atmospheric Pollution (LRTAP), the UNEP global mercury partnership (UNEP, 2013a), and the Minamata Convention on mercury (UNEP, 2013b).

In the environment, mercury is constantly exchanged between ocean, atmosphere, lithosphere, and biosphere. Therefore, in order to understand the global fate of mercury, it is important to take into account all environmental compartments. Here we aim to study the role of the ocean and the atmosphere-ocean interactions in the regional system of North and Baltic Sea using a coupled ocean-atmosphere modelling system. The mercury flux from the Baltic has been estimated in the past based on a limited amount of observations. We compare modeled air-sea fluxes and their spatial and temporal variability with observations and investigate the influence of the North and Baltic Sea on regional atmospheric mercury transport.

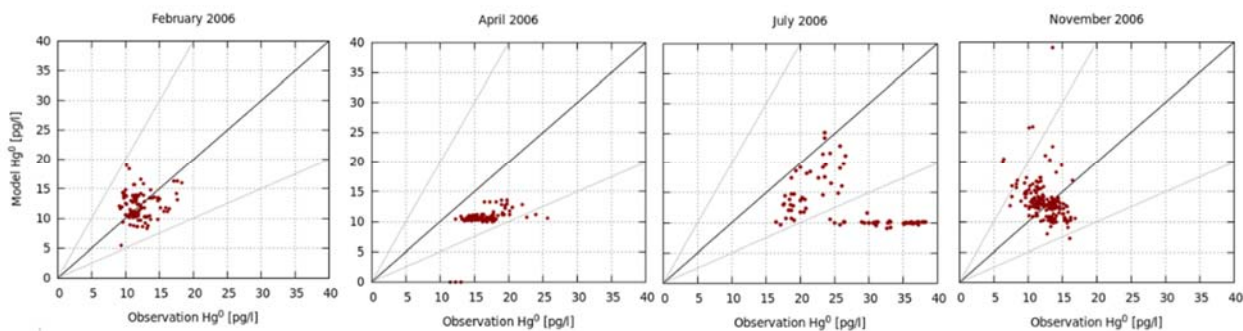
Methods

For this study we coupled the Eulerian regional atmospheric chemistry transport model (CTM) CMAQ (Byun & Schere, 2006). CMAQ is run on a 24x24 km² domain covering the whole North- and Baltic Sea region which is nested into a 72x72 km² domain covering the whole of Europe. We coupled the CMAQ model to the ocean coupled hydrodynamic biogeochemical model ECOSMO (Schrum et al., 2006; Daewel & Schrum, 2013). We expanded ECOSMO with a model for marine mercury cycling, resolving transport, sedimentation and resuspension, partitioning, and chemical speciation of mercury to determine the mercury flux between the two compartments in the North and Baltic Sea region (Bieser and Schrum, 2016). The combined model system, further referred to as MECOSMO-CMAQ, was run on a 10x10 km² grid for 15 years (1993 to 2008) using a 15 year spin up time for the ocean model. Initial conditions for mercury concentrations in the ocean were interpolated from observations.

To implement mercury chemistry in the ECOSMO framework we introduced the species elemental mercury, inorganic oxidized mercury, and methylated mercury into the model. While elemental mercury (Hg⁰) is always treated as dissolved in the aqueous phase, oxidized mercury Hg^{II} is either dissolved or associated to particles. Moreover, for particulate bound mercury we distinguish between three kinds of particles: phytoplankton, zooplankton, and inanimate particulate organic carbon. Concerning methylated mercury we distinguish dissolved mono-methylmercury, particulate bound mono-methylmercury and dissolved gaseous di-methylmercury.

Results and Discussion

Only a small fraction of mercury in the ocean exists as elemental Hg^0 . In order to model the air-sea exchange of mercury the model needs to be capable to reproduce dissolved elemental mercury concentrations in the surface water. For the model evaluation we compared modelled surface Hg^0 concentrations to observations from six cruises in the Baltic Sea. This includes two cruises in July 1997 and March 1998 (Wängberg et al., 2001) and four cruises in 2006 (Kuss and Schneider, 2007). For the evaluation we used daily model output for the nearest model grid cell. As depicted in figure 1, most model values are within a factor of 2 of the observations. The only exception being Hg^0 peaks observed in the



Bornholm and Gotland Sea during July 2006, which the model cannot reproduce. This could be due to increased biologically induced reduction of Hg^{2+} in this region. Currently, we perform model sensitivity runs to further investigate this interesting feature.

Figure 1. Comparison of observed (Kuss and Schneider, 2007) and modelled Hg^0 concentrations in the Baltic.

The evaluation of modelled air-sea fluxes is difficult because there are no direct measurements available. Observation based fluxes are calculated based on measurements of DEM and TGM using different parametrizations for wind speed dependent exchange velocity and Henry's Law constant. Kuss and Schneider (2007) estimated the annual mercury evasion from the central Baltic for 2006 to be in the range of 2700 kg/a – 5900 kg/a. For this region, which excludes the Gulfs of Bothnia, Finland, and Riga the model calculates a flux of 3600 kg/a for 2006. In order to calculate the net Hg budget we also take into account wet deposition of 3400 kg/a and the annual riverine Hg inflow of 1400 kg/a (HELCOM, 2011). This leads to an accumulation of Hg in the Baltic Sea in the range of 1200 kg/a. The modelled inter-annual variability of the net air-sea exchange is around 25%. However, for a reliable estimation of the Baltic Hg budget more information on the riverine inflow (amount and temporal variability) is needed.

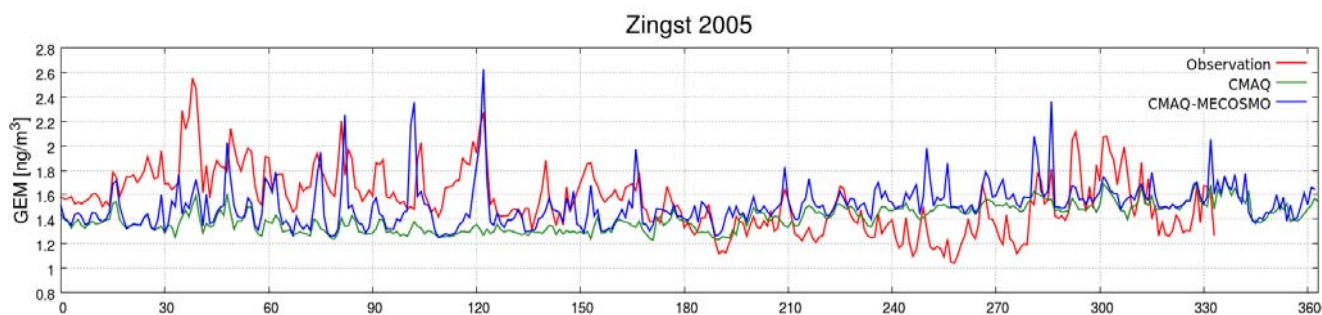


Figure 2. Observed and modelled Hg^0 concentrations (with and without ocean coupling) at the EMEP station Zingst.

Finally, we investigated the feedback of the oceanic Hg evasion on the atmosphere. A comparison to data from 5 EMEP stations indicates that the air-sea flux influences GEM concentrations on a regional scale during spring, summer, and autumn. On seasonal average GEM concentrations were increased between 1% (winter) and 5% (summer) in the Baltic Sea region through coupling to the ocean model. At coastal stations downwind of the Baltic Sea, the coupled ocean-atmosphere model was better at reproducing peak

Hg⁰ concentrations (Fig. 2). Because around 50% of the mercury deposition over land is due to dry deposition of GEM, this will also influence the total mercury deposition over land.

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