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Modelling of the atmospheric dispersion of mercury emitted from the power sector in Poland

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HIGHLIGHTS

- Applicability of the new chemical model of mercury was demonstrated.
- Hg reactions with bromine compounds have significant impact on modelling results.
- The contribution of polish sources in monthly Hg deposition varies from 10 to 22%.
- In some areas power sector is responsible for more than 50% of total wet deposition.

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ABSTRACT

Poland belongs to the group of EU countries with the highest levels of mercury emissions, with a large portion of these emissions being related to coal combustion. This paper presents a modelling analysis of the impact that the Polish power sector has on the atmospheric concentrations of mercury. A detailed mercury emission inventory is used to analyse the concentration and deposition of mercury. For this study, a chemical scheme devoted to mercury transformations in the atmosphere was implemented into the Polyphemus air quality system. The system was then used to perform simulations for 2008 in two domains i.e. over Europe and over Poland. The impact of various parameters on concentration and wet scavenging of mercury has been analysed. The results of the mercury ambient concentrations and depositions, are presented. Additionally, the contribution of natural and anthropogenic sources to mercury deposition in Poland is shown. The performed works showed that the national sources have low impact to overall deposition, however local contribution in wet deposition of big emitters may reach 50%. Sensitive analysis showed a significant impact of reaction with bromine compound and scavenging coefficient on modelled results of mercury concentration and deposition.

1. Introduction

The pathway of mercury dispersion in the atmosphere is complex (Subir et al., 2011). Elemental gaseous mercury –GEM (Hg^0), can be considered as a global pollutant due to its long lifetime in the atmosphere (~1 year). Reactive gaseous -RGM (Hg^{II} and Hg^{I}) and particulate forms of mercury (Hg_P) are deposited more quickly by wet and dry deposition processes. It should be noticed, that after mercury moves through the water chain it can be transformed by aquatic microorganisms into methyl-mercury (MeHg), which is much more toxic than the other forms. Subsequently, MeHg is bioaccumulated in living organisms e.g. fish and enters the human food chain (Munthe et al., 2007). This could lead to neurotoxic impacts on people. Evidence of the negative effects of mercury on human health and the environment has led to intergovernmental preparation of a global legally binding instrument on mercury, completed successfully in 2014 (UNEP, 2014)

The monitoring of mercury concentration and deposition over Europe is currently insufficient to provide accurate data on mercury concentrations and depositions. In some parts of Europe there is a lack of sampling stations and thus such areas are not covered by monitoring at all. Therefore, it appears necessary to complement the results of measurements by the modelling methods, keeping in mind the remaining uncertainties of mercury (Subir et al., 2011). One of the key issues in reactive dispersion modelling of mercury is the chemistry model that represents the reactions and mass

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exchange between the gaseous, aqueous and particulate phases. During the last few decades several chemical schemes have been implemented in different Chemistry Transport Models (CTM) developed to represent the atmospheric dispersion of mercury. Some intercomparison works were performed over Europe (Ryaboshapko et al., 2007a), (Ryaboshapko et al., 2007b). These works were taken into account in the implementation of a chemistry scheme devoted to mercury into the framework of the Polyphemus air quality modelling system (Mallet et al., 2007). Some additional refinements have been proposed recently to improve the modelling of mercury fate and transport in the atmosphere, which were incorporated into the analysis. The system was then used to perform simulations for 2008 in two domains i.e. over Europe and Poland with nesting approach to generate the boundary concentration. In Section 2, the mercury dispersion model used for this study is outlined. In Section 3, the configuration of simulations performed for 2008 is described. The results are analysed in Section 4. In that section the impact of the total emissions from Poland, as well as the emissions from the Polish power sector on deposition in Poland is assessed.

2. Modelling of atmospheric mercury

2.1. Implemented chemical scheme

Many numerical mercury models of Eulerian (ADOM, CAMx, CMAQ-Hg, CMAQ ver. 4.7.1, CTM-Hg, MSCE-HM, MSCE-HM-Hem, GEOS-Chem, ECHMERIT, MOZART, DEHM, GLEMOS, ADOM) and Lagrangian (HYSPLIT, RCTM-Hg) types have been developed to evaluate the atmospheric dispersion of mercury on regional, continental and global scales (Ryaboshapko et al., 2007a). These models consider the main chemical reactions and transformation of mercury in the gaseous and aqueous phases. However, some significant differences can be found, not only in the value of the kinetic rates of the chemical transformations, but also in chemical reactions taken into account. The review of chemicals schemes of mercury implemented in various models, showed some differences compared to our model. For instance oxidation reaction of elemental gaseous mercury with hypobromite radical is only included in GLEMOS, CTM-Hg models (Jonson et al., 2010), (Seigneur et al., 2009). The chemical scheme used for our study takes into account the reactions and transitions of mercury in the gaseous, aqueous and particulate phases presented in Fig. 1. This scheme is an upgraded version of the chemical model previously introduced in (Roustan et al., 2005). The main developments in this model are related to the reactions and transformations of mercury with bromine.

In this model the particulate mercury is distributed among 10 different size sections (between 0.01 and 10 μm with the following threshold limits: 0.01–0.02 – 0.0398–0.0794 – 0.1585–0.3162 – 0.6310–1.2589 – 2.5119–5.0119–10). All the equilibrium constants and chemical rates used to quantify the physicochemical processes considered in the chemical scheme are presented in Table 1. The values of parameters were determined based on literature review (relevant references are provided in the last column of Table 1).

Due to the lack of values of Henry constants for HgBrOH and HgBr the same values as for $HgBr_2$ were assumed. As presented in Fig. 1 the following compounds: HgBrOH and $HgBr_2$ are directly derived from HgBr. Therefore, with this assumption the total amount of mercury transformed from the gaseous to the aqueous phase will be equal irrespectively of whether the three compounds of mercury with bromine ($HgBr_2$, HgBrOH and HgBr) or only one compound i.e. $HgBr_2$ are considered. The mechanism proposed by (Bullock and Brehme, 2002) was adopted to model the sorption and desorption of dissolved [Hg^{2+}] on the particulate matter (black carbon is the primary sorbent) in the aqueous phase. The sorption coefficient of 680 [$dm^3_{water}.g^{-3}_{PBC}$] and time constant for the sorption equilibrium of 3600 s was adopted from work of (Seigneur et al., 1998) and (Bullock and Brehme, 2002), respectively.

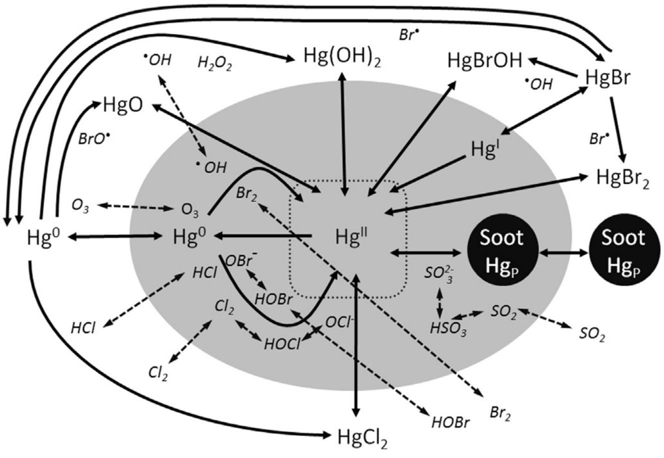

Fig. 1. The implemented chemical model for mercury. In this picture the gaseous and aqueous phases are marked by white and grey, respectively. The line arrows show possible transformations of mercury. The dashed arrows show additional species used in the model which react with mercury.

The concentration of SO_2, H_2O_2, O_3, $HO_2^{\cdot}$, $OH^{\cdot}$ and black carbon (soot) in aerosols were generated in each cell with a time step 3 h by simulation run for 2008 with the use of the Polyphemus/Polair air quality model. The evaluation of Polyphemus concentration results over Europe for pollutants such as PM, SO_2 and O_3 were presented in the work of (Mallet et al., 2007), (Lecœur and Seigneur, 2013).

The concentrations of other compounds which react with mercury were assumed to be as presented in Table 2.

It should be noticed that the concentration of those species have a significant influence on mercury reactions in the atmosphere. On the other hand, the mercury concentration does not have a big impact on the concentration of those species. One should bear in mind that the concentration of those species can vary significantly (in particular over Poland due to large big emissions of pollutants) and the chosen values represent only estimates. That it is certainly a simplification and the impact of these assumptions should be examined in future work.

2.2. Deposition

For both: gaseous and particulate compounds the dry deposition is represented using the parametric model of vertical eddy fluxes in the atmosphere from (Louis, 1979) for the part of the mass transfer dominated by turbulence. The dry deposition parameterization is completed for gaseous species based on the model presented in (Zhang et al., 2003) with parameters for mercury included in (Zhang et al., 2009). The dry deposition velocities for particulate species were generated based on (Zhang et al., 2001). The use of different sized sections to represent the population of particles leads to different dry deposition velocities for each size section.

The wet deposition is split between in-cloud (rainout) and below cloud (washout) scavenging. The in-cloud scavenging was calculated for elemental mercury (Hg^0_{aq}), reactive mercury (Hg^{II}_{aq}) and particulate (Hg_P) species following the parameterization of (Maryon et al., 1996). The cloud presence diagnosis is simply based on a threshold (0.05 g.m^{-3}) of the liquid water content. The below-cloud scavenging for gaseous mercury compounds (Hg^0, HgO,