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Atmospheric
Chemistry
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Discussions

Interactive comment on “Simulation of atmospheric mercury depletion events (AMDEs) during polar springtime using the MECCA box model” *by* Z.-Q. Xie et al.

Z.-Q. Xie et al.

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Thanks Ian Hedgecock for the very detailed comments on our ACPD paper! It is very helpful for us to prepare this final version. Most of questions have been addressed. Below is a point by point answer to Ians’ comments.

Specific Comments: 1. AMDEs are recorded in a fixed geographical position and do not always present the same characteristics. Some are associated with elevated levels of RGM (Reactive Gaseous Mercury, that is gas phase Hg(II) compounds), others with high concentrations of Hg associated with particulates. In many cases the concentration of Hg in snow is found to increase during AMDEs, but this is not always the case. It has been suggested that this variability in AMDE characteristics could be attributed to the relative contributions at the measurement site, of locally occurring atmospheric chemistry and of transport of air already depleted in Hg to the site. The recent review of AMDEs by Steffen et al., (A synthesis of atmospheric mercury depletion event chemistry linking atmosphere, snow and water. Atmos. Chem. Phys., 8, 1445-1482, 2008) contains a discussion of this aspect of AMDEs. It would be useful then if the authors use of the box model is to represent locally occurring chemistry or perhaps the chemistry occurring within an airmass which is being transported, this would determine which field study results the model results might be compared to.

You are right. We have specified better what our model study refers to. As you have already guessed, we can only model locally occurring chemistry with MECCA. MECCA has a very detailed chemistry but basically no meteorology. Advection of an air mass already depleted in Hg cannot be modeled with MECCA.

2. In fact the authors do not actually compare the modelled concentrations of RGM, or Hg associated with particulate matter to any of the numerous field experiments whose results are available in the literature. There was an intensive study at Ny-Alesund in 2003 and a number of papers concerning Hg in the atmosphere, snow pack and aerosols can be found in issue 39 of volume 39 (2005) of Atmospheric Environment. Section 4.2.2, Mercury speciation and AMDEs, of Steffen at al, ACPD 8, S6173-8211;S6175,2008, contains a number of references which would be useful too.

We already have compared our model results to observations from Barrow. We thank Ian Hedgecock for making us aware of further field data for comparison. Compared to the field measurements at Ny-Alesund during an AMDE, our model results show higher RGM. A potential explanation for this discrepancy is now discussed in the text.

3. In section 3.1 the authors comment on the maxima of $HgCl_2$ and $HgBr_2$ concentrations but do not compare this with any of the many RGM measurements, rather they compare it to measurements of Hg in snow during an made, concluding that the model predictions are consistent with observations. This is would clearly not be the case

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for those AMDEs where very little if any change in Hg concentration is snow is seen. (See discussion in Steffen et al., 2008). The authors then state that the model does not include deposition without making clear why, this could perhaps have provided a method to compare the model to Hg concentrations in snow, which would have been useful. However perhaps the deposition of Hg occurring due to aerosol loss might be compared to the increases in Hg concentration in surface snow? I realize there is a difficulty here due to re-emission of Hg after AMDEs (Hedgecock and Pirrone, 2008).

We have switched off dry deposition in the model because under the conditions of our model calculations, there is enough aerosol surface available so that uptake of RGM to aerosols dominates over dry deposition.

4. Just a quick observation regarding table 1. There were a number of model studies including halogens (admittedly only Cl) in the 90's as well which are not included here, two of spring immediately to mind, (A Chemical Kinetic Mechanism for Atmospheric Inorganic Mercury Christian Seigneur, Jacek Wrobel, Elpida Constantinou, Environ. Sci. Technol.; 1994; 28(9); 1589-1597. DOI: 10.1021/es00058a009 and Modelling the atmospheric mercury cycle-chemistry in fog droplets, Karin Pleuel, John Munthe, Atmospheric Environment, 29, 1995, 1441-1457, both of which were important to the beginnings of atmospheric Hg modelling). Perhaps the authors should specify that they are listing only the more recent. Hedgecock and Pirrone 2001, 2004 and Hedgecock et al., 2003 should probably be included in this list as well. There are a number of studies from Daniel Jacob's group at Harvard which are not included, one which specifically comes to mind on the subject of Br is: Holmes, C. D., D. J. Jacob, and X. Yang, 2006, Global lifetime of elemental mercury against oxidation by atomic bromine in the free troposphere, Geophys. Res. Lett. 33, L20808, doi:10.1029/ 2006GL027176

Thanks for the suggestions! We have added the related studies to Table 1.

5. Also on the subject of Table 1, the authors state in the last line of the introduction (and again at the end of section 3.1;To the best of our knowledge, the work presented

here is the first model study of AMDEs including bromine chemistry with a fully coupled gas/aqueous chemistry mechanism. Actually just a few weeks before the authors submitted our group published the following article; Chasing quicksilver northward: mercury chemistry in the Arctic troposphere, I. M. Hedgecock, N. Pirrone, F. Sprovieri , Environ. Chem. 2008, 5, 131. doi:10.1071/EN08001 A slightly different approach to model AMDEs was used. By using the observed O3 concentration decrease to constrain the Br emissions in the model, we used a box model very similar to that used here to see if measured rate constants for the Hg + Br reaction can reproduce the observed decrease (rate and extent) of Hg, the measured concentrations of RGM and Hg associated with particulates and to estimate the deposition of Hg resulting from an observed made. (Our model, AMCOTS was originally based on MOCCA, a predecessor to MECCA, kindly given to us by Rolf Sander).

Thanks for making us aware of your new paper! It is very interesting to see that your study also finds that the measured rate coefficients for Hg with halogens cannot fully explain the rate of GEM depletion.

6. The authors have used a chemical mechanism which includes reactions which have been studied experimentally, some which have been studied theoretically and some which are hypothetical, and this is not immediately clear to the reader. Note d to table 1 in Calvert and Lindberg (2004) states, "Value assumed here by analogy with the theoretical estimates of HgBr recombination rates with Br, OH, and I at 273 K and one atmosphere pressure (Goodsite et al., 2004)", this note applies to the reactions below: HgBr+X -> BrHgX X=BrO, Cl, ClO, I, OI, OH, HgBr. HgCl+X ->HgXCl X=Br, BrO, Cl, ClO, I, IO, OH. HgI+X -> HgIX X=Br, BrO, Cl, ClO, I, IO, OH. HgOH+X -> HOHgX X=Br, BrO, Cl, ClO, I, IO, OH. These are reactions, with the exception of those in note d of Calvert and Lindberg, which have never been studied either theoretically or experimentally. I think it is important that the reader is aware of this.

In our Table 2, we already explain in the footnote that the last four rate coefficients are estimates. We agree that it is a good idea to add a note about the origin of k(HgBr+Br).

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7. Regarding the aerosol in the model, is the liquid water content used for the sea salt aerosol from the literature? And also why was the sulphate aerosol not included?As I recall in the article by Sander et al., (Modeling the chemistry of ozone, halogen compounds, and hydrocarbons in the arctic troposphere during spring. Tellus, 49B, 522-532,1997), the sea salt aerosol was not included but the sulphate aerosol was.

As mentioned at the beginning of the "Results and discussion" section, the conditions of the model run are similar to those in Sander et al. (2006). In that study, a LWC of 5E-10 m3/m3 was necessary to produce a realistic bromine explosion. And actually, the chemistry on background sulphate aerosol WAS switched on in the model runs. However, we forgot to mention this in the model description.

8. However by far the most important point I would like to make is the following: Previous modelling studies have shown that in sea salt aerosol particles the complexes HgCl3-, HgCl4–, HgBr3- and HgBr4– are important 'reservoirs' of Hg. It appears that these have not been included in the aqueous phase equilibria regarding Hg complexes. This omission necessarily affects the results from the modelling studies as without them the concentration of neutral HgCl2 and HgBr2 are higher than otherwise and being neutral species they may pass from the aqueous to the gas phase to maintain their gas/aqueous phase equilibria, as discussed in Hedgecock et al., 2001.

We have added these aqueous phase equilibria and run the model again. All of the figures were updated accordingly. The level of HgCl2 decrease due to high levels of chlorine, while HgBr2 have some slightly changed. Although both HgCl2 and HgBr2 have changed to some degree, it does not has a significant effect on the main conclusions.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 13197, 2008.

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