

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

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Comment on [Simulation of atmospheric mercury depletion events \(AMDEs\) during polar springtime using the MECCA box model](#); by Z.-Q. Xie, R. Sander, U. Pöschl, and F. Slemr

AMDEs are potentially an important pathway by which Hg is introduced into Arctic ecosystems, however these events are not fully understood and studies which can increase our knowledge of the mechanisms by which they occur are necessary. This article uses a box model to study the atmospheric chemistry involved in AMDEs, and provides further evidence that the reaction between Hg and Br is very important in the

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atmosphere, and in certain circumstances, such as those when AMDEs occur it is the most important atmospheric reaction involving elemental Hg.

To my mind however there are a number of points in the article which the authors should at least be aware of, and if they so wish amend in their final revised version. There are also two concerns which are I think are of particular importance to the validity of this study which are at the end of this comment.

The first concerns AMDEs themselves. 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.

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 et al, *ACPD* 8, S6173&#8211;S6175, 2008, contains a number of references which would be useful too.

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In section 3.1 the authors comment on the maxima of HgCl<sub>2</sub> and HgBr<sub>2</sub> 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 AMDE, concluding that the model predictions are consistent with observations. This would clearly not be the case for those AMDEs where very little if any change in Hg concentration in 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 realise there is a difficulty here due to re-emission of Hg after AMDEs (Hedgecock and Pirrone, 2008).

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 which 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 Pleueel, 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

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

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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 O<sub>3</sub> 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).

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:  $\text{HgBr} + \text{X} \rightarrow \text{BrHgX}$  X=BrO, Cl, ClO, I, OI, OH, HgBr.  $\text{HgCl} + \text{X} \rightarrow \text{HgXCl}$  X=Br, BrO, Cl, ClO, I, IO, OH.  $\text{HgI} + \text{X} \rightarrow \text{HgIX}$  X=Br, BrO, Cl, ClO, I, IO, OH.  $\text{HgOH} + \text{X} \rightarrow \text{HOHgX}$  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.

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.

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  $\text{HgCl}_3^-$ ,  $\text{HgCl}_4^{2-}$ ,  $\text{HgBr}_3^-$  and  $\text{HgBr}_4^{2-}$  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  $\text{HgCl}_2$  and  $\text{HgBr}_2$  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.

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