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Atmospheric
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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.

Anonymous Referee #1

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This work addresses an interesting problem, which is the fast depletion of atmospheric mercury during spring in Arctic and Antarctic regions. The authors used an existing box model of atmospheric chemistry, added a set of chemical reactions to simulate the chemistry of mercury species and attempted to reproduce observed ambient concentrations during polar mercury depletion events, in particular the synchronicity of the mercury and ozone depletion. They also varied some uncertain parameters (e.g., some reaction kinetics) to constrain their model based on the observations. Previous work by others has addressed the selection of chemical kinetics of mercury reactions to obtain simulations that were compatible with observations of mercury concentrations. Most of this previous work has focused on the global cycling of mercury (e.g., Seigneur

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et al., J. Geophys. Res., 111, D22306, doi:10.1029/2005JD006780, 2006; Selin et al., J. Geophys. Res., 112, D02308, doi:10.1029/2006JD007450, 2007). The current work is, therefore, potentially very interesting because it tries to constrain the mercury chemistry using observations that are spatially and temporally limited. However, some revisions are warranted to correct an error and to reconcile some assumptions with results obtained by other researchers who have investigated the atmospheric chemistry of mercury.

The authors selected the kinetics of Pal and Ariya (Phys. Chem. Chem. Phys., 6, 572-579, 2004) for the oxidation of mercury by ozone in the gas phase (line 25, p. 13201). This kinetics is not used in global and regional models of atmospheric mercury because it oxidizes Hg(0) too quickly and leads to Hg(0) concentrations that are too low compared to observations (Seigneur et al., 2006; Selin et al., 2007). Although it is unlikely that the kinetics of this reaction has a significant effect on the main conclusions, the authors need to reconcile their work with those earlier results. Note that Seigneur et al. (2006) did not rule out the fast kinetics of Pal and Ariya (2004) entirely and considered that it may apply for limited sets of conditions where heterogeneous processes could be important (and MDE could represent such a scenario)

The statement that the oxidation of Hg(0) is faster in the aqueous phase than in the gas phase is incorrect (lines 17-18, p. 13202). It is true that the aqueous-phase oxidation of Hg(0) by ozone and OH radicals is fast; however, one must take into account the atmospheric liquid water content and the aqueous concentrations of the oxidants and elemental mercury when comparing the aqueous-phase kinetics with that of the gas-phase. For a liquid water content of 0.1 g/m3, the mass of Hg(0) present in the liquid phase is less than one millionth of the mass presnt in the gas phase. Therefore, the aqueous-phase reactions only affect a very small fraction of Hg(0) and, as a result, the atmospheric half-life of Hg(0) is significantly longer for the aqueous-phase chemistry than for the gas-phase chemistry. Thus, the atmospheric oxidation of Hg(0) by ozone and OH is governed by gas-phase chemistry.

The work by Gardfeldt and Johnson (J. Phys. Chem., 107, 4478-4482) on the reduction of Hg(II) by HO2 in the aqueous phase should be mentioned and its implications should be discussed.

The authors conclude that the lower bounds of the kinetics for the oxidation of Hg(0) by Br and BrO lead to better agreement with the observations of Hg(0) during polar mercury depletion events. Some more discussion of this result is warranted. For example, Skov et al. (2004) derived empirical estimates of the first-order oxidation of Hg(0) during depletion events at Station Nord (using the depletion of ozone as a means to estimate the Br concentrations) and obtained values in the range of 0.8 x 10-12 to 1.2 x 10-12 molec-1 cm3 s-1 for the effective rate of the Hg(0) + Br reaction. One could assume that the results of any modeling study depend on the assumptions made for the choice of initial conditions and parameter values. Some further discussion on the robustness of the conclusions obtained in this work would be useful.

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

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