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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical transformations of Hg° during Arctic mercury depletion events sampled from the NASA DC-8" *by* S. Y. Kim et al.

Anonymous Referee #1

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This manuscript aims to understand the chemical mechanisms driving the occurrence of MDE in the Arctic spring using an extensive dataset from measurements using the NASA DC-8 aircraft and box model results. In summary, I consider the observational results to be a particular strength of the manuscript, providing exellent (spatial) information on the occurrence of MDEs in the polar atmosphere. However, analyses, comparisons, and discussions of observed spatial patterns seem insufficient and are in need of improvements. Figures are too many, they are currently not well edited, and they focus on individual MDEs while summary figures showing general patterns (or highlighting differences) are missing. My main criticism on the manuscript refers to the modeling component: in my view, there is a lack of comparison of model results

with observational results, and the model component is almost fully detached from observations. The use of box model simulations may not be the best analysis tool for the observations: box models mainly reproduce temporal patters of individual air masses, while aircraft observations have strong spatial characteristics. A more suitable modeling analysis may hence include a model with vertical and/or areal outputs which might allow much better comparison of observations. Finally, the discussion and conclusions of the study re-iterates many previously reported results from observational and modeling studies, and does not seem to focus enough on specific novelties (e.g., vertical and areal aspects and implications, effects of pollution) gained from this aircraft campaign.

Observational data: Experimental observations are sound and very comprehensive, showing detailed spatial patterns of MDE along with a suite of other chemicals. I see particular strength of the manuscript in reported spatial patterns, probably one of the most comprehensive data sets on springtime MDEs. However, I was surprised about a shortage of more detailed discussion of observations, and few novel conclusions in regards to the occurrence MDEs were drawn beyond what is already known. The authors describe 8 selected, individual MDEs events, associated ozone and Br2 levels and concentrations of other chemicals and pollutants, and origin of observed air masses through back-trajectory analyses. No summary or systematic comparisons of these cases are made in order to elucidate common (or different) patterns causing these MDE. Main conclusion points in regards to the 8 events were that “MDEs were found only near the surface over the ocean” (in section 3), that “Hg0. . ..is characterized by a precipitous fall from >100ppqv to the LOD” (section 3), and that “air masses inside the MDEs transported at low level over the ocean, and thus a distinguishable chemical feature of the a is that it is likely halogen rich”. It seems that the authors could develop much more comprehensive analyses of observed MDE, their occurrence, and clearly discuss the implications of these observations.

The figures presented in this manuscript are not presented and edited well. For example, Figure 3 shows 16 figure panels of individual MDEs events, and comparisons

ACPD

10, C3063–C3067, 2010

among these figures are difficult. Hg0 is shown on an axis ranging from 0 to 2000 ppqv, although Hg0 levels only range from pre-MDE levels of 100 to 250 ppqv to <50 during MDE – given that Hg0 is the most important observation, this should be presented in a more readable way. Legends and figure axes are marked inconsistently (e.g., no subscript fonts for O3, Br2, Soluble_Bromine, ALTP and GPS_Altitude [Altitude in m??], x-axis are poorly readable with time marked in seconds). The same problem refers to 60 figure panels (!) relating to modeling results (Figure 6), where legends and titles are not well marked and some lines cover others (e.g., use dashed lines). What I miss is a clear focus on the truly important results and "summary" figures that show general patterns (e.g., scatter plots of (all?) Hg0 against Br2 levels, etc.) rather then presenting each case on an individual basis.

On page 10080, line 4-10: the authors state that 14 MDE were observed with Hg0 mixing rations depleted below 50 ppqv. However, the discussion of MDE events as well as box model analyses only focus on 8 cases that "exhibited generally distinct features of MDEs, i.e., the concurrence of high Br2, low O3, and low Hg0 mixing rations". This selection seems highly subjective and causes bias since the authors only consider cases with high bromine levels– what about the other cases? It seems to me that there is as much to learn from the cases where high Br2 and low O3 are not present? In the abstract, the authors state that "MDEs occurred near he surface and always over the Arctic Ocean accompanied by concurrent ozone (O3) depletions, enhancement in Br2 mixing rations. . ..". This seems incorrect because the authors only selected the cases where they observed O3 depletions and Br2 increases in the first place. . ..what about the other 6 cases where this was not the case?

Modeling data: I consider he box modeling component a particular weakness of the study, or maybe more specifically the lack of comparing model results with observed data. For example, the authors describe in detail modeled lifetimes of Hg0 for various box model simulations, including (i) base case simulations (section 4.1), (ii) influence of rate constants (section 4.2); (iii) influence of halogen concentrations (section 4.3)

ACPD

10, C3063–C3067, 2010

and (iv) influence of photolysis rate constants. However, it is not mentioned how these calculated lifetimes compare to observational results, so what is the purpose of these sensitivity analyses? I suggest that modeling results are directly compared to observations, e.g., in common figures showing both observations and model results. A similar problem relates to the model results showing the different products of Hg oxidation (e.g., HgO, HgCl, HgBr, Hg Br2, etc) and how the composition of oxidized Hg changes as rate constants and photolysis constants change– while this seems interesting, it is not entirely clear what the value of these results are and no clear discussions and conclusions are made in regards to these results.

Possibly, there is an inherent problem of the chosen modeling approach which impedes good comparisons of aircraft observations to model results. Flight observations represent a spatial approach (e.g., airplane descends from higher altitude air masses into the boundary layer, stays within the boundary layer for some distance, and then climbs out of the area of MDEs). On the other hand, the box model approach lacks a spatial component but rather focuses on temporal patterns of a given air mass (e.g., provide lifetimes of Hg0 against oxidation, degree of Hg0 depletion, etc.). The two data sets, hence, may be difficult (or impossible) to compare in detail and I wonder if other model approaches (i.e., such as vertical models or spatial models showing geographical distribution of MDEs) would be more suited to support and analyze the results of the aircraft campaign? In addition, the current modeling results seems to mainly re-iterate well-known characteristics of polar MDEs, e.g., the authors state that "the results suggest a close relation between O3 and Hg0", that simulations suggest "negligible effect of Hg0 reaction with BrO on the occurrence of MDEs", and that "emissions of halogen compounds is imperative to the occurrence of MDEs and ODEs in the Arctic springtime". These results are not particularly novel. Interesting novel aspects, however, include effects of NOx regimes and photolysis rate constants, and it might be worthwile to focus model analysis more on these aspects.

I have a few other, more minor issues/questions in regards to the modeling component:

ACPD

10, C3063–C3067, 2010

Interactive Comment

Description of sensitivity experiments using various rate constants and photolysis constants is somewhat confusing, with some information given in the method description, some in tables, and some in supplementary information. I suggest to make a clear table with all sensitivity analyses runs, clearly name each simulation run and have consistent names/description of these in the text, in the methods section, and in the figure legends. It is unclear to me why the authors only consider gas-phase reactions – shouldn't they add all known reactions with Hg0 in order to assess likely mechanisms for MDE are in the Arctic environment? Also, I was surprised that sea-salt aerosol uptake and deposition isn't included in the models given that in the marine boundary layer this is the main removal pathway for oxidized Hg?

Others: The final abstract in regards to climate change seems speculative, is not supported by measurements nor by the model runs, and in my view should be deleted.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 10077, 2010.