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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Air-snowpack exchange of bromine, ozone and mercury in the springtime Arctic simulated by the 1-D model PHANTAS – Part 1: In-snow bromine activation and its impact on ozone" *by* K. Toyota et al.

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Reply to Referee #1 (Hans-Werner Jacobi)

We thank all the referees for providing useful comments and strong support to our manuscript. Here we reply to the referee Hans-Werner Jacobi by answering each specific comment.

Comment #1
Page 20345, line 22ff: The destruction of ozone can occur during one day as observed by Jacobi et al. (2010).

Reply:
In the introduction section of the revised manuscript, we will refer to this observational inference as a possible lower limit of the timescale.

Comment #2
Introduction, last paragraph: The authors decided to publish their study in two parts, which is probably reasonable taking into the account the length of a merged manuscript and the somewhat different audiences regarding ODEs and MDEs. Nevertheless, I believe that the authors can better describe the two parts. I think they should explain that they used the same model set-up with the same equations and mechanisms. These mechanisms included halogen, ozone, and mercury chemistry. The manuscript here forms part I and describes the model set-up in detail and the results regarding halogen and ozone chemistry. Part II then presents the results for mercury. I recommend that this information should be given here. I also would not call part II a "companion paper". This sounds to me like an additional study and not like part II of the same study.

Reply:
In revised manuscripts for the Part 1 & 2 papers, we will stop using the phrase "companion paper" and will simply call them "Part 1" and "Part 2" when referring to one of the papers from another. Also, in the introduction section, we will give an explicit description of the fact that the same model runs are re-used for the discussion of ozone/bromine chemistry and mercury chemistry in Part 1 and Part 2, respectively.

Comment #3
Page 20348, line 15ff and chapter 2.6: What is the basis for the assumption of an interconnected liquid phase that enables vertical transport in the snow? In chapter 2.6 the authors refer to Huthwelker et al., 2006; Domine et al., 2008; Gladich et al.,

2011. However in Domine et al., 2008 such a liquid network is not mentioned. I am not convinced that the other references can justify such an assumption.

Reply:
Surface disorder is certainly present on “pure” ice at 253 K assumed in our model runs. And, the thickness of the surface disorder is likely to increase by the presence of ionic impurities in the ice and by exposure of some gaseous contaminants to the ice surface, as supported by experimental and theoretical studies (e.g., Elbaum et al., 1993; Wettlaufer, 1999; Döpenschmidt and Butt, 2000; Bluhm et al., 2002; McNeill et al., 2006). Water molecules and dissolved ions in the surface disorder are certainly more mobile than those “locked” inside the solid matrix, as also supported by experimental and theoretical/numerical studies (e.g., Furukawa and Nada, 1997; Carignano et al., 2007; Gladich et al., 2011). Since snowpack consists of snow grains quite often if not always sintered or in contact with neighboring grains, it seems reasonable to assume that the surface of the snow grains is largely connected throughout the snowpack in a topological sense. Thus, if dissolved impurities are located in the liquid-like layer (LLL) uniformly on each snow grain as presumed in our study, they should be subject to diffusion throughout the layers of snowpack at the rates on the same order as estimated for water molecules and ions in the surface-disorder layer of a single ice grain. In the revised manuscript, we will replace our rationale for assuming diffusivity along the hypothetical LLL network with the statement provided above.

We came to recognize, however, that representing this hypothetical diffusivity by the self-diffusivity of water molecules in bulk super-cooled water (as was done in our model runs) is not necessarily appropriate, especially because the thickness of the LLL was only 0.556 nm for the brine volume fraction (1.11×10^{-5}) prescribed based on the concentrations of impurities (mainly Na^+ & Cl^-) and the specific surface area (SSA) of snow grains. Lateral diffusivity of ions in such a shallow LLL is most likely smaller than that in bulk super-cooled water at the same temperature, perhaps by an order of magnitude (Carignano et al., 2007). Therefore, we will replace model runs discussed in our

Part 1 & 2 papers with newly conducted ones in which the LLL diffusivity is reduced by a factor of 10. We have confirmed that delays in the simulated timescale of ODEs are often not negligible but generally minor (less than 1 day). This update will not modify our discussion in the Part 1 paper except for minor changes in stated numbers. Discussion in the Part 2 paper on the behavior of deposited Hg in the snowpack needs somewhat major changes, though.

We also admit that, while writing up the ACPD version of our Part 1 & 2 papers, we were not fully aware of experimental evidence somewhat contradictory to our assumption, viz. the inhomogeneity of impurity distributions in and on natural and artificial ice. Two review papers (Bartels-Rausch et al., 2012; Domine et al., 2013) that came across recently to our attention gave comprehensive accounts of knowns and unknowns in regard to where impurities are located in natural snow grains, and hence will be cited in the revised manuscript to indicate a potential limitation of our model.

Comment #4
Chapter 2.10, 3. Paragraph: More recent observations of the chemical composition of the seasonal snowpack in the Arctic can be found in Jacobi et al. (J. Geophys. Res., 117, D00R13, doi:10.1029/2011JD016654, 2013)

Reply:
We will revise the paragraph by referring to this paper by Jacobi et al. as suggested here by the referee Jacobi, along with another set of comprehensive observations by Krnavek et al. (2012) as suggested by Referee #2, from the viewpoint of representativeness of our scenario chosen for snow chemistry. We thank the referees for updating us with the latest field studies, but we could not manage, within a given time frame of manuscript revision, to investigate what changes the model will or will not simulate by using those concentrations of snowpack composition different than our choice. This is a possible subject of follow-up studies.

Comment #5

Chapter 2.10, 4. Paragraph: The calculation of the pH of the LLL in the model is certainly a very crucial point and needs to be discussed. However, I am surprised to see that the authors begin the discussion with the precipitation of mirabilite as a major source of uncertainty, while later stating that some model runs showed no large impact. I actually would not expect no impact from the formation of mirabilite. Other factors (some are also mentioned by the authors) are probably more important like the aerosol deposition, the behavior of HCl and other volatile acids, the volume of the LLL fraction and the inclusion of all impurities in the LLL, the parameterization of the LLL as ideal solution and so on. Unfortunately, no field observations of the pH of the surface layer of the snow grains exist and the simulated values cannot be compared. Nevertheless, I recommend re-writing this paragraph to discuss the major uncertainties regarding the simulation of the pH.

Reply:
Yes, it indeed seems inappropriate that we started our discussion from the issue of mirabilite precipitation missing in our model, since it was rather irrelevant to the pH of the LLL anyway. The paragraph will be rewritten as suggested. Moreover, this entire paragraph will be moved to Results and Discussion and then expanded by adding new graphs (adapted from those currently included in the supplement) to discuss changes in the simulated pH of the LLL and its impact on simulated bromine activation in sensitivity runs.

Comment #6
Figures: In the current size, the colored contour plots in the printed version are almost useless because it is impossible to distinguish the details described in the text (which seems in fact to be a general feature of ACP articles). These details are only visible in the electronic version after enlarging the figure by a factor of 3 or 4. I recommend using larger contour plots in the printed version.

Reply:
This problem became evident after the manuscript had been typeset for ACPD, although we anticipated that it would be solved at least partially when the same figure is to be typeset for ACP. Nonetheless, in order to address concerns of the referee, we have adjusted Figure 6 to ensure the visibility of details when printed: (1) by changing the length/height aspect ratio of each plate, and (2) by enlarging the vertical scale of y-axis on the snowpack side.

Finally, editorial issues noted by the referee have been handled as suggested. One of his comments calls for some explanation, which we provide here.

Comment #7 (editorial suggestion)
Page 20363, line 5 (and throughout the manuscript): What are "in-snow emissions"?

Reply:
By "in-snow emissions", we meant the emissions of gaseous species into the snowpack interstitial air as a result of unknown chemistry in and/or on the snow grains. Their emission rates were adjusted empirically. In this study, we adopted this approach for HCHO and CH_3CHO, because simulating condensed-phase organic chemistry on snow grains was beyond our scope. In the revised manuscript, we will use the phrase "empirical in-snow emissions" every time we refer to the in-snow emissions of HCHO and CH_3CHO.

References

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 20341, 2013.