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Discussions
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Interactive comment on "Air-snowpack exchange of bromine, ozone and mercury in the springtime Arctic simulated by the 1-D model PHANTAS – Part 2: Mercury and its speciation" *by* K. Toyota et al.

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Reply to Referee #2

We thank Referee #2 for providing useful comments. Here we reply to the referee by answering each specific comment.

Reply to major comments

Major Comment #1
Some details of the model are unclear. Likely these are explained in the companion paper, but this needs to made clear in this manuscript. Some questions I had were: What is the specific surface area of the snow? What solute concentration is used in the model? These parameters will determine the liquid volume of the snowpack, and its thickness at snow grain surfaces, since the method of Cho et al. is used to determine LLL liquid volume in this model.

Reply:
These questions by the referee are mostly answered in the Part 1 paper for SSA (= 217 cm^2/g of ice), snow solute concentrations (Cl^- = 70 μmol/L etc.) and resultant liquid volume fraction (= 1.11 x 10^{-5}), whereas the inferred thickness of the LLL (= 0.556 nm) is not. In the revised manuscript, we will help readers look up model details in the Part 1 paper by pointing relevant sections and tables as much as possible. At the same time, specific details/numbers asked by the referee will be given in the Part 2 paper as well.

Major Comment #2
I am unclear as to why the authors choose to model the LLL as being interconnected between snow grains. They cite some previous studies as suggesting this, but I am not convinced that this is supported. For example, Rosenthal et al. (one of the papers cited by the authors) say that they saw impurity networks along grain boundaries only on snow that had been stored for 8 months and sublimated under high vacuum. In fresh snow and snow stored for two months, no such networks were observed. Recently, Domine et al. (2012) also reported seeing networks of impurities at grain boundaries only after significant sublimation of snow samples.

Reply:
In our model, the LLL was assumed to cover the surface of each snow grain uniformly.

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Since neighboring snow grains are often in contact with or oven sintered each other, it seemed reasonable to assume that such a topological connection would result in the LLL network across the snowpack layers. However, as criticized here by the referee, we now feel that citation to Rosenthal et al. does not really support our assumption of LLL network in the way we conceived. And, if indeed dissolved impurities are located mainly in pockets inside the grains and in veins along grain boundaries and grooves as persuaded by Domine et al. (2013), they would hardly be transferred over distance greater than the size of each grain in the snowpack (unless compressed like ice cores in which the veins are more likely connected through the triple junctions of grains).

In the revised manuscript, we will adjust concerning statement to rationalize our assumption of the LLL network simply on the basis of somewhat arguable existence of uniform coverage of the LLL around snow grains. We will also indicate some reservations by referring to Domine et al. (2013). Of course, some studies support our network assumption, e.g., a molecular dynamics simulation on the mobility of dissolved ions in the surface-disorder layer of ice (Carignano et al., 2007), unless for thermodynamic reasons curvature at the grooves of sintered grains preferentially traps ions migrating from the surrounding flat surface.

By the way, 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. Please refer to our response to comment #3 from the referee Jacobi who reviewed the Part 1 paper. 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. On the other hand, discussion in the Part 2 paper on the behavior of deposited Hg in the snowpack needs a somewhat major revision; the previously stated length scale of “a few centimeter” for a notable signal from the vertical migration of deposited mercury in the top snowpack on 8-day timescale is now 1 cm.

Major Comment #3

The authors use Henry's law to determine partitioning of mercury compounds between the atmosphere and the snowpack. I am curious as to whether Henry's law is a good way to model this. To my knowledge, the uptake of most species to ice occurs via adsorption (and is almost exclusively a surface process). Since Henry's law deals with bulk partitioning, it may not be an appropriate way to model partitioning between the atmosphere and snow surfaces.

Reply:
Actually, we did not intend to rule out the sorption mechanism on ice surface (including burial uptake via co-adsorption with water vapor) but rather to indicate that brine (Cl^- and Br^-) chemistry in salty snowpack could provide an alternative explanation for observed phenomena on air-snow Hg partitioning such as the fast dry deposition of gaseous oxidized mercury (GOM) on the snow surface (Skov et al., 2006). To our knowledge, however, the adsorption of GOM on ice surface has not been investigated via laboratory experiments. Observed high concentrations of mercury in surface hoar on the snowpack and diamond dust in the springtime Arctic certainly imply the efficient uptake of GOM via surface adsorption (Douglass et al., 2005, 2008). At this point, however, it is a qualitative speculation on the basis of experimentally confirmed data for the adsorption of non-mercury species on the ice surface (Abbatt et al., 2003) and for the adsorption of GOM on solid substrates other than ice at higher temperatures of our present interest (e.g., Rutter and Schauer, 2007). Hence we would have been required to estimate (or speculate) the adsorption isotherm for GOM on ice to study its impact in the context of polar snowpack by incorporating the process in our model. On the other hand, the unimportance of gaseous elemental mercury (GEM) uptake on ice and snow in the atmospheric environment has been indicated from the experimental determination of adsorption isotherm on ice itself (Bartels-Rausch et al., 2008). In the revised manuscript, we will stress these points.

Major Comment #4
Have the authors done sensitivity runs to determine how variations in LLL thickness

will affect mercury partitioning between air and snow, and on how this these variations will affect its ultimate fate? This might justify the authorsæěů decision not to account for effects of temperature and impurity concentrations on LLL thickness.

Reply:
In order to provide some answers to this question by the referee, we have performed sensitivity runs in which the LLL volume on ice is simply scaled up or down by a factor of 5 from that calculated by the Cho et al. equation at 253 K. We have also performed another sensitivity run in which temperature is raised to 268 K for calculating all the physical and chemical processes, which increased the LLL volume on ice from that calculated by the Cho et al. equation approximately by a factor of 5. Analysis of apparent dry deposition velocities of GOM on the snow surface from these runs will be used to discuss the points raised here by the referee.

Reply to minor comments

Minor comment #1
What volume does the SIA comprise in the model? What is the surface area to volume ratio of the SIA in the model? This is important to know since the model predicts different SIA and ambient gas-phase concentrations of several species, presumably due at least in part to the high surface area to volume of the SIA.

Reply:
Answers to these questions can be derived from information of snowpack microphysics provided in the Part 1 paper (page 20348, last paragraph–please note a typographic error in the diameter of snow grains; 0.3 mm, instead of 0.3 μm, was a correct value used in the model). The volume fraction of SIA is dictated by porosity, which is 0.663 in our model snowpack. By rearranging the unit of specific surface area (SSA = 217 cm^2 per gram of ice), the surface area to volume ratio of the SIA is calculated to be 101 cm^2

per cm^3 of SIA volume. In the revised manuscript, we will refer to this number in Part 1 & 2 papers.

Minor comment #2
This model assumes that all solutes are excluded to the ice surface to form a liquid solution that is in contact with the atmosphere due to the interconnection of the LLL assumed in this model. However, not all solutes will be expelled to the surfaces of snow grains. A large fraction will be excluded into regions within the grains such as veins and pockets. The liquid solution in these regions will not come in contact with the atmosphere. Therefore this model may significantly overestimate the amount of "liquid" (or LLL) that will participate in multiphase chemistry. Finally, Domine et al. 2013 point out that even in fairly salty snow, there will not be enough liquid formed to wet snow surfaces. I do not expect models to present entirely physical descriptions of snow surfaces, but I think this issue should be acknowledged in the manuscript.

Reply:
Yes, veins and pockets at grain boundaries and/or within grains are indeed isolated from rapid multiphase reactions of our interest. In the Part 1 paper (Page 20353, Lines 14-18), we pointed out this problem although we now feel that our wording was not sophisticated enough (and hence will be revised with citation to Domine et al., 2013). We will touch on this limitation of our model framework in the Part 2 paper as well.

Minor comment #3
The authors state the following: "In this work, the e-folding depth for the attenuation is assumed to be 7.5 cm (King and Simpson, 2001; Peterson et al., 2002; Qiu et al., 2002; Simpson et al., 2002). We thus neglect the possibility of enhanced actinic fluxes that can occur near the top of the snowpack under certain conditions (Abbatt et al., 2012)." I do not see an issue with ignore potential actinic flux enhancements at snowpack surfaces, but I donæĕůt think the above discussion provides a justification for it. I recommend either removing these statements and simply stating that enhanced actinic fluxes were not considered, or providing a more relevant justification.

Reply:
In the revised manuscript, we will drop the second sentence (referring to the possibility of enhanced actinic fluxes) quoted here by the referee.

Minor comment #4
page 6 line 3: "...but the share of Br-atoms against that of BrO-radicals is uncertain owing to error bars associated with the unknown surface and third-body effects." Are the authors talking about the relative concentrations of Br and BrO? This should be more clearly worded.

Reply:
We wanted to indicate uncertainty in rate constants for Hg oxidation involving Br and BrO in the environmental conditions rather than uncertainty in the concentrations of Br and BrO. We will revise the sentence.

References

Abbatt (2003), Chem. Rev., 103, 4783-4800.
Bartels-Rausch et al. (2008), Environ. Res. Lett., 3, 045009, doi:10.1088/1748-9326/3/4/045009, 2008.
Carignano et al. (2007), Chem. Phys. Lett., 436, 99-103.
Domine et al. (2013), J. Phys. Chem. A, 117, 4733-4749.
Douglas et al. (2005), Geophys. Res. Lett., 32, L04502, doi:10.1029/2004GL022132.
Douglas et al. (2008), Environ. Sci. Technol., 42, 1542-1551.
Rutter and Schauer (2007), Atmos. Environ., 41, 8647-8657.
Skov et al. (2006), Atmos. Environ., 40, 5542-5463.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 22151, 2013.

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