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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Modeling chemistry in and above snow at Summit, Greenland – Part 1: Model description and results" *by* J. L. Thomas et al.

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Overview.

This manuscript describes modeling of (photo)chemistry in the snowpack at Summit, Greenland during a three-day period in June. The authors use a modified version of the MISTRA model, with a snowpack added to previously described boundary layer chemistry. While there are some portions of the modeling that could be improved, overall this is the most chemically sophisticated model of the snowpack that I have seen. Even better, the results are extremely interesting and give us a detailed mechanistic look at oxidant, nitrogen, and halogen cycling in a coupled snowpack-boundary layer system.

Major Comments.

1. Section 2.2. (a) The 1 mm snow grain radius is on the large end of values, at least for surface snow at Summit. Is the QLL-to-air mass transport (and, therefore, snow-to-air flux) in the model very sensitive to grain radius? (b) There is good evidence that the "liquid layer" (as termed in the manuscript) is not a true liquid water solution. Thus it is typically called a "quasi-liquid layer (QLL)" or "liquid-like layer (LLL)". While the authors may treat it as a (concentrated) aqueous solution in the model, I encourage them to refer to it as a QLL or LLL when discussing it. (c) The QLL (or LLL) thickness seems arbitrary. How did the authors decide on 10 nm? Does the thickness vary with temperature and, therefore, depth in the snowpack? (d) As the authors point out later, a more physically realistic method to determine the QLL volume would be to use the freezing-point depression model (e.g., as described by Cho et al. (2002)), which determines the QLL volume based on temperature and total solute concentration. Otherwise, the model is missing the impact of temperature (and depth) on QLL concentrations. See comment 3 below for more discussion of this issue. (e) In natural (and laboratory) snow/ice grains, some of the QLL is present at the air-ice interface, but some is present internally within snow crystals (e.g., at grain boundaries). In the model, all of the QLL is present at the surface. Broadly speaking, how might putting some of the QLL internally affect the results?

2. Chemical reactions. (a) There are two significant halogen reactions that I don't see in the Supplemental Material: Cl + Cl- = Cl2-, and Br + Br- = Br2-. These would seem to be important since OH-initiated chemistry in the QLL is significant. Were these reactions included in the model (but inadvertently omitted from the list of reactions)? If they were not included, I fear that halogen radical chemistry in the model is significantly incomplete and urge the authors to do a sensitivity run to see if including the reactions alters the results. (b) While not necessarily needed for this study, for future work I encourage the authors to add the mixed halide radical reactions that form BrCl- (e.g., Br + Cl- = BrCl-), as well as the various sinks of BrCl-. These are compiled in Anastasio

and Matthew (ACP, 6, 2439, 2006). (c) R1. The authors didn't include the channel of nitrate photolysis that makes nitrite and O(3P) (Dubowski et al., J. Phys. Chem. A, 106, 6967,2002). Based on past work (e.g., Jones et al., ACP, 8, 3789, 2008), photolysis of the resulting nitrite can be a large source of NO. This omission should be addressed. (d) R4. Given the high HOx levels in snow, I would think that HO2 + NO = OH + NO2 is the dominant pathway converting NO to NO2. Is this not true? This idea should be addressed.

3. Section 2.4. (a) The treatment of the QLL is the major weakness of the manuscript, but some variation on this weakness shared by most (all?) current models of snow chemistry. Since the thicknesses of the QLL and the ice grain radii are somewhat arbitrary, the associated value of phi(max) is similarly somewhat arbitrary. In contrast, the value of phi(max) can be calculated as a function of temperature and total solute concentration based on freezing point depression (FPD) (e.g., Cho et al., 2002). The authors should calculate the expected value of phi(max) based on FPD and compare this value to theirs in the text; the total solute level for the FPD calculations should be determined for all measured ions (e.g., including sulfate, ammonium, oxalate, estimated DOC, etc.) and not just those included in the modeling. Assuming temperature varies significantly with depth, it would interesting to see how the current model and FPD values of phi(max) compare both at the surface (e.g., at midday) and at some depth. (b) p. 30938, lines 9-10. Perhaps phi in the environment is "...determined by how ions segregate...", but in the model phi is essentially a fitted parameter (at least for nitrate and protons). This should be made clear. (c) p. 30938, line 11: "...numerous studies have shown enhancement of ions on ice surfaces..." line 20: "...chloride is concentrated at the surface..." This wording should be corrected: most (all?) of these studies have shown that ions are enhanced in liquid-like layers, but not necessarily that these layers are at the surface. e.g., the work of Cho et al. (2002) used NMR, which interrogates the entire sample volume, not just the surface. (d) Based on the data in Table 2, the QLL is initially pH $\sim$ 2. Since this is such an important chemical parameter, the actual value should be included in the text or table. Is pH fixed or allowed to vary?

4. Section 3.2. NOx. (a) Do the authors have evidence to support their statement that it is reasonable for only 6% of total nitrate to be present in the QLL (and thus available for photochemistry)? Jacobi and coworkers estimated that the value at Summit is between 80 - 100% (Atm Env, 38, 1687, 2004). Similarly, relatively crude calculations show that having approximately 50 - 100% of nitrate available for photochemistry gives good agreement with previously measured NOx fluxes (Chu and Anastasio, J. Phys. Chem. A, 107, 9594, 2003). Granted, the modeling in the current work is much more sophisticated, but the 6% value is by far the lowest I recall seeing. (b) Detlev Helmig has some great in-snow NO and NO2 data at Summit that show the same depth and time-dependence as your Figures. 4 and 5. He also has in-snow O3 data. I don't believe the data have been published yet, but it is something to keep in mind for your future work, as they would make for excellent comparisons.

5. Section 3.3. BrO. (a) p. 30947. The relative contributions from H2O2 and NO3- towards OH are interesting and are similar to a past field study (Anastasio et al., Atm Env, 41, 5110, 2007). However, in this past field work all of the snowgrain H2O2 and NO3- was assumed to be available for photochemistry, in contrast to the current work. How does the QLL flux of OH in the current work compare to that measured in the field? (b) p. 30949. The role of aerosol Br is interesting. Considering a column extending from the photic zone of the snowpack to the top of the atmospheric boundary layer, what fraction of Br at midday is present in/on the snow grains, in the firn air, in aerosol particles, and in the gas-phase of the BL?

6. Section 3.4. O3. While the ozone levels in the snow are not as "depleted" as one sees in Arctic ODEs, the levels are certainly lower than in the BL. I encourage the authors to point out this latter point; by what percent are O3 levels reduced at 0.5 m compared to at the surface?

7. Table 2 (a) Were the measured concentrations of Br-, Cl-, and NO3- for surface snow? Were measurements also made as a function of depth in the snowpack? If so, were these used in the model or were the concentrations assumed constant with

depth? If the latter, nitrate concentrations are likely overestimated at lower depths, since this would be applying the summer values (which tend to be highest) to spring and winter layers in the snowpack. This might be part of the reason why the "QLL nitrate" ends up being quite low (i.e., 6% of total nitrate).

Minor Comments.

1. There are a number of run-on sentences that need to be trimmed or broken into two sentences. In several cases a comma is used when a period or semicolon is needed. (a) p. 30929, lines 6-8; (b) p. 30931, lines 15 – 18; (c) p. 30932, lines 22 – 24; (d) p. 30937, lines 18-19; (e) p. 30949, line 22; (f) p. 30950, lines 6-8.

2. There are a few other sentences that are awkwardly written or that contain typographic errors: (a) p. 30931, lines 26 – 27: the references should be separated from the rest of sentence, e.g., using dashes, commas, or parentheses; (b) p. 30933, line 12: "he temperature"; (c) p. 30949, lines 6-8: the sentence needs to be fixed; (d) p. 30950, line 8: noun-verb disagreement "sensitivity do".

3. Section 2.2.1. It is not clear how tightly the parameters in equation 3 were constrained by measured surface temperatures. Were in-snow temperatures measured? If so, were these measurements used in the model?

4. p. 30947, lines 2-3. (a) For the halide sensitivity runs, condition (2) is neutral pH – is this pH 5.6 (i.e., in equilibrium with atmospheric CO2) or pH 7? (b) What is the pH for the other test runs?

5. p. 30947, lines 5-6. Can the authors discern from their results of this third condition (k(OH + Br-) = 0) that OH + Cl- is an important pathway, that other oxidants with bromide are important, or that some other mechanism is significant for Br2 release?

6. Fig. 9. Since the BL and firn air O3 values are similar, I suggest using the same color scale for ozone concentration in both panels A and B. This would make for easier air-snow comparisons.

Overall Assessment.

While there are a few issues that need to be addressed, I am very supportive of this manuscript and look forward to reading the final version.

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