

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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The authors thank C. Anastasio for his perspective and comments as well as his careful reading of the manuscript. It is clear that his suggestions and comments have improved the study and the authors appreciate his suggestions. We have taken most of the suggestions and provide the specific details relating to each individual comment below.

COMMENT: 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

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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.

RESPONSE: None

Major Comments.

COMMENT: 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?

RESPONSE: The 1 mm snow surface grain radius is consistent with observations from a prior campaign at Summit 2003-2004. While the snow grain size data is not specifically included, a summary of the campaign and findings can be found in Dibb, J. E., et al. (Atmos. Env. 2007, doi:10.1016/j.atmosenv.2006.12.006). We have completed a sensitivity run with a snow grain radius of 0.5 mm for the purposes of comparison. We have found that the model is sensitive to the choice of snow grain radius and with a decreased snow grain size, both the predicted NO and BrO are higher than in the base case model run. For a constant volume of snow decreasing the radius results in increased number of snow grains, which increases the total volume of the liquid layer. For a factor of two decrease in the radius, the BrO increases by a factor of 4 and the NO increases by a factor of 1.5. We believe the dependence on snow grain size is very interesting as the reviewer pointed out and we hope to study this more in the future.

COMMENT: (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.

RESPONSE: We were sensitive as to what we should call the "liquid layer" because we are treating this as an aqueous layer and not a "quasi-liquid layer" in that we are using

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mostly aqueous phase rate constants. As noted by Rolf Sander in his review of A. Saiz-Lopez and C. S. Boxe's paper from 2008 (Interactive Comment, ACPD, 8, S602-S603, 2008) "if the layer was really a QLL, then it would be quite uncertain if aqueous-phase rate coefficients could be used for the chemistry at all". We agree with this perspective and believe when using aqueous rate constants and quantities we should not use the term QLL. We believe the terms liquid layer or liquid-like layer are a more accurate description of our model approach, we have updated the manuscript to refer to our layer as a liquid-like layer (LLL) as suggested.

COMMENT: (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?

RESPONSE: We believe the properties of the LLL are not currently well known (see the more in depth response to H.-W. Jacobi's comment on this point). We took the value from the compilation of Rosenberg (Physics Today, 58, 50, 2005) with data for the thickness of the liquid layer on the surface of pure ice. There is a wide range of measurements for the thickness of the liquid layer on the surface pure ice over the temperature range relevant to our model. In addition, some of the measurements show significant temperature dependence of the liquid layer over this temperature range and some do not. Given that measurements for pure ice range from 1 nm to ~30 nm over the temperature range of interest, we picked a thickness that is the mid range of these measurements (the atomic-force microscopy experiments in Figure 4 of Rosenberg, Physics Today, 58, 50, 2005, data courtesy of Hans-Jurgen Butt). This measurement does not show significant temperature dependence over the temperature range of interest, as a result we did not include temperature dependence of the liquid layer thickness.

A more recent study Křepelová et al. (PCCP, 12, 8870, 2010) used XPS and NEXAFS to study the liquid layer of ice upon exposure to HNO₃. As noted in our response to H.-W. Jacobi, a nanometer thick liquid like layer was not observed in this study, which further complicates even our basic understanding of the liquid like layer on the surface

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upon exposure to HNO₃.

Given the available information regarding the liquid layer thickness for pure water ice, we believe it is not possible at this time to include a meaningful description of the liquid layer as a function of temperature for water ice containing ions.

We have added the following sentences in the paper to clarify this point: We took the LLL thickness from the compilation of Rosenberg (2005) that includes data for the thickness of the liquid layer on the surface of pure ice. There is a wide range of measurements in temperature range relevant to our model. Given that measurements for pure ice range from 1 nm to ~30 nm, we chose a thickness in the mid range of these measurements. There is also evidence that the liquid layer thickness varies with temperature and ion content. However, there is no clear parameterization of how thickness varies and we have not included temperature or ion content dependence in the current model version.

COMMENT: (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.

RESPONSE: We believe it is interesting to implement the model of the liquid layer thickness as described in by Cho et al. (J. Phys. Chem. B 106, 11226, 2002) for the purposes of a sensitivity study in the future. However, (as noted in our response to H.-W. Jacobi) it's not completely clear that the QLL present internally within the ice matrix (studied by Cho and co-workers) and the liquid layer at the ice-air surface of a snow grain have the same properties. It has been shown at the surface of liquids and thin water films the presence of the liquid-vapor interface significantly alters the structure compared to a bulk solution with the same composition (see for example the recent paper by Richards et al., J. Phys. Chem. A, 2011, doi:10.1021/jp109560j) and the

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same may be true for the ion-ice-water-air system. Therefore, we don't believe it's possible to conclude that the model of Cho et al. should be used as the only reasonable description of the surface liquid layer.

COMMENT: (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?

RESPONSE: One could look at our results as only taking into consideration the LLL present at the surface of snow grains (the part in direct contact with the interstitial air). If the LLL is located within the snow crystals (not in contact with air) then it is unlikely that the species produced via photochemistry would be transported to the interstitial air. In our model these species would be considered in the bulk ice, or non-reactive species.

If the LLL is present at grain boundaries that are directly in contact with the interstitial air, with a different geometry than a spherical snow grain, the main impact would be in the treatment of mass transfer. One would need to define the most likely geometry and then derive a Schwartz-like expression for the mass transfer rate. It is likely that if the LLL is present at grain boundaries the surface area would be lower than for a spherical snow grain and the corresponding mass transfer rate would be slower, reducing the flux out of the snow grain of NO₂ and other species produced in the LLL.

COMMENT: 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.

RESPONSE: These reactions are treated as fast equilibrium reactions in the model

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and were included in the base case model run. The equilibrium processes (mostly acid-base chemistry) were not included in the original electronic supplement and have been added as an additional table (Table 4) in the electronic supplement.

COMMENT: (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).

RESPONSE: We appreciate the comment and will look into this in the future.

COMMENT: (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.

RESPONSE: We have included this channel, but this reaction was only included in the electronic supplement (Aqueous phase reaction number: hv10). We have added this channel to the main manuscript to clarify it has been included in the model.

COMMENT: (d) R4. Given the high HO_x 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.

RESPONSE: The dominant pathway is the reaction of NO with O₃ in our model run. This reaction is typically at least four times faster than the reaction of NO with HO₂ for the conditions in our model. One can calculate the rate constants at 250 K for the HO₂ + NO and NO + O₃ reactions to find that the HO₂/O₃ ratio needs to be above 8 × 10⁻⁴ for the HO₂ channel to dominate. In our model the HO₂/O₃ ratio is never above 4 × 10⁻⁴ in the region where photochemistry occurs, therefore the ozone channel is faster than the HO₂ channel. We have added a few words to the manuscript to address this point.

COMMENT: 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

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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 be 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.

RESPONSE: We do not consider that the model discussed above is necessarily the only reasonable description of the liquid layer. However, we agree it's worthwhile to compare our value with the value suggested from freezing point depression. The experiments described by Cho et al. studied the liquid brine layer concentrations for bulk NaCl solutions that ranged from 1×10^{-3} - 0.5 M (for comparison the total measured ion composition in melted surface snow grains at Summit measured by liquid chromatography was on average 5×10^{-6} M in 2008). The quasi-brine layer present in the ice (for relatively concentrated solutions) was well described by freezing point depression. In the temperature range of our model, this would result in total ion concentrations in the liquid layer larger than 5 M (assuming a density of the liquid layer of 1 g/mL). In order for us to have a liquid layer that contained 5 M total solute concentration within the limitation of the total amount of ions measured in melted surface snow, we would need to use either a significantly different structure of the liquid layer or a much thinner liquid layer. Also, it's not immediately clear that aqueous rate constants would apply for such concentrated brine layers that are up to 14 M in their total ion concentration at 250 K.

We believe that a concentrated brine layer and the liquid layer at the surface of ice are fundamentally different. The brine layer forms primarily because ions lower the

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freezing point and the solution can remain liquid far below the freezing point of pure water. At the surface, however, the liquid layer forms due to anisotropy present at the interface as the ordered structure of the ice lattice transitions to the relative vacuum of the gas phase. At the surface there is a disordered, liquid-like layer, in which "liquid-like" chemistry can occur. Of course, at the surface of a snow grain, there is only one liquid layer and it contains a combination of the properties of both types of liquid layer. However, we don't believe the liquid layer in which we are interested has been completely characterized by the measurements presented in Cho et al. (2002). We have added a short discussion of all of these issues to the manuscript as requested.

COMMENT: (b) p. 30938, lines 9-10. Perhaps ϕ in the environment is "...determined by how ions segregate...", but in the model ϕ is essentially a fitted parameter (at least for nitrate and protons). This should be made clear.

RESPONSE: We have clarified this in the manuscript.

COMMENT (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.

RESPONSE: This has been reworded.

COMMENT: (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?

RESPONSE: The pH is not fixed and is calculated from the H^+ concentration that varies due to the reactions that form H^+ and the acid-base equilibrium reactions involving H^+ . We have added the initial pH to the text.

COMMENT: 4. Section 3.2. NO_x. (a) Do the authors have evidence to support their

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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 NO_x 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.

RESPONSE: Given that H.-W. Jacobi commented the amount of nitrate in the liquid layer is most likely lower than our chosen initialization, it shows that there remains significant uncertainty in how to determine a reasonable initial nitrate concentration in the liquid layer. We have updated the manuscript by taking out the statement that 6% is reasonable and added a discussion of the range of reasonable estimates.

COMMENT: (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.

RESPONSE: We completely agree and hope to compare with this data in the future.

COMMENT: 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?

RESPONSE: The past measurements based on all of the snowgrain H₂O₂ and NO₃⁻ being in the liquid layer suggested that H₂O₂ produces approximately 100 times more OH than NO₃⁻. In the present study we predict that less of the OH is produced from H₂O₂ and than in the study of Anastasio et al. (Atm Env, 41, 5110, 2007). Without measurements of H₂O₂ in either the gas phase or the snow grains in 2008 it's difficult

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to say exactly how these numbers compare.

COMMENT: (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?

RESPONSE: The majority of the bromine is present in the snow pack as bromide (>99%). There is only a small amount of bromide present in aerosols because there is a very small total number concentration of aerosols at Summit. The remainder of the total bromine is approximately equally distributed between the atmospheric boundary layer and the top 30 cm of the snow pack.

COMMENT: 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?

RESPONSE: We agree and have added some wording to the text to clarify this point.

COMMENT: 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).

RESPONSE: The measurement were made for surface snow, we also have depth profiles for nitrate for pits dug during the summer 2008 campaign. For one of the three pits, the nitrate concentration decreased with depth within the first 20 cm below the snow surface. For the other two pits the nitrate concentration stayed relatively constant until well below the region influenced by photochemistry. We have completed a sensitivity run in which we initialize the nitrate at the surface with the same concentration as the

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base run and linearly decreased the concentration between 0 cm and 25 cm until it reaches 25% the surface concentration. Below this we used a constant concentration equal to 25% of the surface concentration. This decreased mid-day NO by 25% at 1.5 meters above the snow surface. This alone cannot explain why the LLL nitrate is less than 100% of the total nitrate in the liquid layer. More importantly, this resulted in a 50% reduction in BrO predicted at 1.5 meters above the snow surface, leading to poor agreement with the measured BrO mixing ratios. Given the uncertainty in the nitrate concentration in the liquid layer discussed above, we have chosen to use the initialization that results in best agreement with both the measured NO and BrO mixing ratios.

Minor Comments.

COMMENT: 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.

RESPONSE: We have updated the paper according to these suggestions.

COMMENT: 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”.

RESPONSE: We have updated the paper as suggested.

COMMENT: 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?

RESPONSE: We did not measure either surface or in-snow temperatures, however Detlev Helmig was measuring in-snow temperatures during the GSHOX campaign (a

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personal communication with him was referenced in the manuscript). We used his measurements to decide both the surface temperature amplitude and minimum and we compared with his in-snow data to ensure the calculated temperature fluctuation in the firn was reasonable.

COMMENT: 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?

RESPONSE: For the halide sensitivity runs the pH was initialized equal to the base case run. Neutral pH is initially pH 7, which quickly equilibrates with the atmospheric CO₂ to pH ~5.6.

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

RESPONSE: It is very difficult to make this type of conclusion because the system is very complex. However, we can say that the OH + Br⁻ reaction is important initially and that other oxidants contribute to Br₂ release.

COMMENT: 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.

RESPONSE: This has been updated so the panels A and B have the same color scale.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 30927, 2010.

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