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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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The authors thank H.W. Jacobi for his careful reading of the manuscript and his suggestions for improving this study. We have taken most of the suggestions and provide the specific details relating to each individual comment below.

COMMENT: The authors describe the application of the 1D chemistry model MISTRA to conditions at Summit, Greenland. To consider the snowpack, the model was extended beyond the atmospheric boundary layer to include further layers with snow and the specific chemical reactions occurring in the snowpack. While MISTRA includes a comprehensive chemical scheme including gas and aqueous phase reactions and

phase transfer in the snowpack, the representation of the physico-chemical conditions in the snow (e.g. heat transport and radiative transfer in the snow, liquid fraction of the snow. . .) remains simple. The authors are able to reproduce certain observations (NO, BrO, O3) made during a 3-day period in summer 2008 at Summit, which is characterized by consistent meteorological conditions and minor impact from long-range transport. However, the agreement namely for the NO concentrations are enforced by an arbitrary chosen fraction of nitrate present in the liquid fraction of the snow, which is used to represent the reaction volume for the chemical reactions in the snow. Nevertheless, the study represents an important step forward with respect to the modeling of photo-chemical processes in the snow and their impact on the composition of the atmospheric boundary layer over snow-covered regions and towards fully coupled snow chemistry and physics modeling. Therefore, the manuscript covers important topics for Atmospheric Chemistry and Physics warranting publication after considering the comments listed below.
RESPONSE: None

COMMENT: Chapter 2.2.2 describes the parameterizations used for the gas transport in the firn and the exchange with the atmosphere. The effect of wind pumping is related to the square of the horizontal wind speed. As far as I understand a constant wind speed of 3 m/s is used throughout the modeling period.
RESPONSE: This is correct, in the model run we approximated the impact of transport due to wind speed as the average of the observed wind speed. The referee has brought up an important point that we have investigated further (see below).

COMMENT: I believe that this approach is simplifying too much the transport processes, especially since the authors later conclude that the stability of the boundary layer and its impact on the vertical transport in the gas phase is a dominating factor for the simulated concentrations. Shouldn't this also have an impact on the vertical transport between the snow and the atmosphere and within the firn? What is the range and variability of the observed wind speeds? Would it be possible to use observed wind

speeds instead of an average value? What would be the impact?
RESPONSE: We have added a plot of the observed 2 m and 10 m wind speeds (Figure 1) and results from a run with the hourly averaged measured wind speed (Figures 2 and 3) to the electronic supplement. For the run using the hourly averaged surface wind speeds the predicted atmospheric mixing ratios are very similar to the base case run (with constant wind speed). One can understand why this is the case by comparing the modeled vertical turbulent exchange coefficient at mid-day in the atmosphere ($\sim$0.1 m^2 s^{-1}) to the calculated vertical wind pumping speed at the surface (U_{firn}=1.9×10^{-2} m s^{-1}), which we approximate as the wind pumping speed multiplied by the grid spacing to get an effective surface diffusion constant due to wind pumping (D_{eff}=Δz U_{firn}=2.2×10^{-4} m^2 s^{-1}). We have good indication that the modeled exchange rates in the atmosphere are reasonable because we have compared with the measured boundary layer profiles during this focus period. The diffusion constant for gases contributes less at the surface. For example, the NO diffusion constant at the surface is 6.0×10^{-6} m^2 s^{-1} and varies slightly with temperature. The atmospheric concentrations in the model are to a large degree dominated by the depth of the boundary layer, which shows a strong diurnal variation.

COMMENT: The impact should also depend on the ratio between the two processes wind pumping and molecular diffusion. I also recommend to show a plot of the relative contributions of these two processes as a function of time and depth in the supplement.
RESPONSE: At the surface it's clear that wind pumping is more important than diffusion (as discussed above). However, in the snow pack both are much slower than exchange in the atmosphere at mid-day when boundary layer venting occurs. Below the surface, for example at a depth of 2 cm, diffusion is the dominant process determining transport of gases. We have added a plot of the relative contribution of wind pumping and diffusion at the surface and a depth of 2 cm to the effective diffusion constant in the electronic supplement (Figure 4). We have also added the predicted BrO mixing ratio at a depth of 2 cm using constant and measured 10 m wind speeds (also shown in the electronic supplement, Figure 4). At the surface wind pumping dominates

and below 2 cm diffusion is the dominant transport process in the model.

COMMENT: In the simulations, all chemical processes in the snow occur in a liquid fraction. Therefore, concentrations of the reactive species in this liquid fraction are important. In contrast, concentrations of these species are available from melted snow samples indicating only bulk snow concentrations. To derive concentrations in the liquid fraction, the knowledge of the partitioning between the liquid fraction and the remaining solid part is crucial. Unfortunately, the partitioning has never been directly measured on a scale of a snow grain and only some indirect estimates for some reactive species are available. However, the partitioning of nitrate is a crucial point in the simulations. The authors decided to use the partitioning for nitrate to adjust their simulations to agree with the observed atmospheric NO concentrations. While this a possible approach, the manuscript would in my opinion be much stronger if the authors would have applied their modeling framework for other compounds present in the gas phase and in the snow also to HNO3/nitrate and then present discrepancies between simulations and observations. For H2O2 and HCHO, the authors used atmospheric concentrations and Henry's law to calculated initial concentrations of both species in the liquid fraction (Tab. 2). They could have used the same approach for HNO3 to determine initial nitrate concentrations. Overall, the application of Henry's law may remain questionable for the uptake in the liquid fraction of the snow, but in my opinion such an approach would be more consistent. With 10 pptV of HNO3, T=255 K, and the data given in the supplement for the HNO3 equilibrium I derive an HNO3 concentration in the liquid fraction on the order of 2.3E-4 M, which will almost completely dissociate into nitrate. There is some confusion regarding the values for this equilibrium and the references given (see minor comment below). In any case, the equilibrium concentration is considerably lower then the initial nitrate concentration used in the simulation of Csnow * phi=3.5E-6 M * 2.5E3=8.8E-3 M. By the way, the values used from Lelieveld and Crutzen for the HNO3 equilibrium used in the simulations are at the low end of what can be found in the literature. Almost any other set of values reported in the compilation by Sander would make the difference between the equilibrium and the used initial nitrate concentration smaller.

RESPONSE: We have completed two sensitivity runs and added the results to the electronic supplement for the purposes of addressing this comment, the first run uses an initial nitrate and H^+ concentration in the liquid layer equal to 2.3×10^{-4} M as suggested by the reviewer. The results show the predicted BrO and NO mixing ratios do not represent the observations (Figures 5 and 6, electronic supplement). We have also taken the reviewer's suggestion and completed a second sensitivity run with a higher value for the Henry's law constant for HNO_3 (using 2.6×10^6 and 8700 for kH and -deltaH/R respectively (Chameides 1984)) and then initialized the H^+ and nitrate according to the Henry's law equilibrium concentration of HNO_3. (1.17×10^{-3} M) This sensitivity run produces significantly lower BrO and NO mixing ratios than measured in 2008 (Figures 7 and 8, electronic supplement). There are significant uncertainties in the model, including applicability of Henry's law constants to the liquid layer as well as the applicability of aqueous phase rate constants to the liquid layer. A detailed sensitivity study of Henry's law constants is beyond the scope of the current study, although it should be investigated further in the future. We hope that our model study adds to the motivation for further laboratory and field studies that will eventually lead to an improved understanding of chemistry in the liquid layer.

COMMENT: Maybe the difference between equilibrium and initial concentration also contributes to the simulated release of HNO3 from the snowpack (bottom, page 30944), although a deposition has previously been observed at Summit as reported in the same paragraph?

RESPONSE: We included a discussion of gas phase HNO_3 vertical gradients because this is the one model output that does not agree well with what is currently in the literature. However, given the agreement with a number of other prior and current measurements, we believe that this is a point that should be noted and investigated further in the future. There are many possible explanations as to why the model and measurements from 2000 disagree, however this does not invalidate the value of the current study but simply points out an area for future work. Furthermore, it is important to point out for the 2000 study different meteorological conditions, atmospheric mixing ratios, as well as different measurements make it difficult to directly compare model results with the measurement from different year. We added the HNO$_3$ discussion in the paper for completeness because we believe HNO$_3$ deposition to the snow surface is an issue that should be addressed in the future.

COMMENT: In the model, many N-containing compounds (NOx, N2O5, HNO3, BrNO3,...) are produced in the upper layers of the snow and part of the them are released to the atmosphere. What are the calculated changes in the total budget of nitrogen in the snow? Since in the simulations the snowpack even releases HNO3, the snow is probably constantly losing N. I recommend to calculate and present the simulated flux of total-N between the snow and the atmosphere. Maybe this could even be done as a function of depth to show which snow layers gain and loose N in the simulations? There are differences in the diurnal cycles of NO and BrO at 1.5m for the three simulated days and smaller trends in the peak values of NO2, BrO in the firn, and O3 in the firn and at 1.5m. What is causing these differences since the major physical parameters remain unchanged (except the temperature)? Can this be related to a depletion of N in the snow?
RESPONSE: We have added a plot of the nitrate concentration as a function of time in the snow liquid layer and in the atmospheric aerosol (electronic supplement, Figure 9). The reviewer is right, the snow is losing nitrogen, however only a few percent of the total available in the liquid layer at the beginning of the run. Considering the limitations of the model (it does not include input of HNO$_3$ from outside sources, e.g. from transport) we believe the results presented are consistent with what is known. It should be noted that the amount of nitrate loss would not be detected by liquid ion chromatography of melted surface snow samples conducted by Jack Dibb's group during this study. We believe a comprehensive analysis of the nitrogen budget is best left for the follow on paper which will include a more detailed analysis of both the nitrogen and halogen budgets in the snowpack.

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Interactive Discussion

Discussion Paper

COMMENT: In many instances (volume of the liquid fraction; nitrate partitioning; surface reactions related to BrNO3 and N2O5; HONO, H2O2, and HOx chemistry) the authors refer to sensitivity studies that will be presented in an accompanying paper supposed to be submitted as part 2 to the same special issue. I agree that all this material should not be presented in a single paper, but needs to be cut into two parts. Nevertheless, since these issues touch upon many critical points in part 1 it would make sense to have this paper available during the review of this manuscript. The results of the sensitivity studies could strongly support (or contradict. . .) the choices made for the simulation presented in part 1. Maybe the further review of part 1 should be delayed until the appearance of part 2 in ACPD?
RESPONSE: We have added some of the suggested sensitivity studies (above) to the supplemental material. For a complete set of sensitivity runs, we believe another (separate) publication is needed. We believe this paper stands on its own scientifically and should be published without delay. The second paper is currently being written and will be available for review by the scientific community in the near future.

Minor comments:

COMMENT: Tab. 2: The values for the liquid layer are confusing. In my opinion, only the numbers for HCHO and H2O2 in column 4 are the correct values for the liquid layer. In contrast, the values for the ions are the bulk snow concentrations reported by Dibb et al. (or deduced). Therefore, they do not represent the liquid layer concentrations. I recommend to use two different columns for liquid layer and bulk snow concentrations and to give all numbers.
RESPONSE: We have updated the table according to the reviewers comment.

COMMENT: Supplement, values for Henry's law: In the manuscript the authors use the compilation by Sander as reference, while in the supplement the authors refer to the specific publications. This should be made consistent and I prefer to stick to the specific publication because of the considerable scatter for many values in the compilation by Sander.

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Interactive Discussion

Discussion Paper

RESPONSE: We have updated the table in the paper to reflect the original references.

COMMENT: However, the given values for HNO3 do not agree with the values in the cited reference by Lelieveld and Crutzen (1.7E5 and 8694 for kH and -deltaH/R instead of 2.1E5 and 8700). Which values have been used in the simulations?
RESPONSE: The incorrect reference was listed in the table. The value used in the model is from Brimblecombe and Clegg (1989). The value used is consistent with the original paper, but is slightly different from the value listed in the compilation of Sander. We have updated the reference in the electronic supplement to reflect the correct original reference. For clarity we have also updated the table to contain the same notation as the compilation by Sander, separating K_A from the Henry's law constant.

COMMENT: Page 30934, line 16f: Please give the used values for Tamp and tmin. Is the same cycle used for all three days?
RESPONSE: We have added the value of T_{amp} and t_{min} used in the model run to the paper, the same values were used for all three days of the model run, which we believe is reasonable based on discussions with Detlev Helmig as cited in the personal communication in the paper.

COMMENT: Page 30941, line 21:. . . the initial nitrate concentration in the liquid layer is the only adjustable parameter used. . .: In a strict sense this is correct, because only the nitrate concentration was adjusted. But this was done only after certain physical parameters for the snow (e.g. the liquid fraction) were selected. The authors are right that these parameters have not been adjusted here, but they are of course adjustable and different numbers could have been selected. I recommend to reword this phrase.
RESPONSE: We have reworded this phrase to read: The initial nitrate concentration is an adjustable parameter that was used to model NO photochemistry.

COMMENT: Page 30941, line 23:. . . the derived value is reasonable. . .: On what information is this statement based? See comment above. According to Henry's law the nitrate concentration should be significantly lower. The authors may want to compare

the derived partitioning to measured values of the HNO3 solubility in ice (Thibert, E., and F. Dominé, J. Phys. Chem. B 102, 4432-4439, 1998) and to distribution coefficients of some nitrate salts in the ice-water system (e.g. Gross, G.W., Can. J. Phys. 81 (1/2), 439-450, 2003).
RESPONSE: There are a number of studies looking at the HNO_3-ice-water-air systems. However, there isn't conclusive evidence that directly relates the concentration of nitrate and liquid layer thickness to a given gas phase HNO_3 concentration. We have perhaps overstated our confidence in the value we used and this phrase has been reworded.

There are several issues that make it difficult to correctly estimate the amount of nitrate in the liquid layer including the dynamic nature of snow that can allow for partial thawing and refreezing which may contribute to ion mobility between the ice lattice and the liquid layer, which could either decrease or increase the nitrate liquid layer concentration.

We believe the amount of nitrate in the liquid layer is reasonable because this number is consistent with the trend for the air-water interface, in which nitrate is suggested to be less concentrated than either chloride or bromide. We understand, however, that this may not apply for ice where HNO_3 is less soluble than HCl as shown by Thibert and F. Dominé (J. Phys. Chem. B 102, 4432-4439, 1998).

There are several methods that have been used to study the HNO_3-ice-water-air system in the lab. The first is to prepare a model ice surface and expose it to a known amount of HNO_3 and assume the loss of HNO_3 is due to uptake to the liquid layer or to the underlying ice. However, these techniques do not allow for true knowledge of the composition of the liquid layer. The second method used is to set up a system where the ice surface itself can be studied as has recently been done using XPS and NEXAFS by K?epelová et al. (Phys. Chem. Chem. Phys., 12, 8870, 2010). They note "at the microsopic level, the interaction of HNO_3 with ice has not yet been resolved. Moreover, direct spectroscopy studies of trace gas ice interactions under atmospherically relevant conditions and in the thermodynamic ice stability regime are scarce at present." This study does make some progress towards understanding the liquid layer structure for the HNO_3-ice-water-air system because it probes directly the surface of the ice and the associated liquid layer upon exposure to gas phase HNO_3. This study showed that for conditions of low nitrate coverage 20% of water molecules involved in nitrate hydration and 80% remaining clean ice. However a nanometer thick liquid like layer was not observed, which further complicates even our basic understanding of the liquid like layer containing HNO_3 at the surface of ice.

Another way to understand the HNO_3-ice-water-air system is to study a different system that has some of the properties of the system. For example, a study completed by Cho et al. (J. Phys. Chem. B 106, 11226, 2002) suggests the liquid like phase of dilute NaCl aqueous solutions is well described by freezing point depression. This study most likely didn't probe the liquid layer present at the ice-air interface, but instead probed the NaCl present in as a quasi-brine layer internally within the ice. It's not completely clear that this study well represents the liquid-like layer of interest because of the absence of a probe specific to the ice-air interface. We are, however, interested in investigating this model of the liquid layer for the purposes of sensitivity runs in future work.

Given the number of studies with different information about this system, we believe the best evidence we have is that the amount of nitrate in the liquid layer results in correct prediction of the observed NO. We have removed the phrase "the derived value is reasonable" in order to let the reader decide for themselves if the value we have used is reasonable or not.

COMMENT: Page 30944, line 8:. . . with larger errors. . .: The larger ranges of the NOx gradients during the night shown by Honrath et al. are due to a higher variability and not to larger errors.
RESPONSE: We have removed this phase.

COMMENT: Page 30944, first paragraph: The authors compare here absolute values of simulated and previously measured (1999 and 2000) NOx gradients. However, the

average NOx concentrations in 1999 and 2000 were between 33 and 40 pptV, while the simulated values in 2008 are probably higher (based on Fig. 5 and 6C). Therefore, it would be better to compare only the diurnal cycles and not the absolute gradients.
RESPONSE: We have removed the reference to the absolute values and have limited the discussion to the sign and diurnal variation of the vertical gradient.

COMMENT: Fig. 4, 5, 6, 7, 9B: Three different depth ranges are used in these plots. They would be easier to compare if they are all cut off at 1 m depth. In general, the contour plots should be larger to make the structure more visible.
RESPONSE: The depth of these plots was originally chosen so that variations in each chemical species could be seen as a function of depth. We have updated the plots so they all have a constant depth of 1 meter. We have also increased the size of the plots and have asked the editors to do the same in the final published version.

COMMENT: Fig. 8: The simulated BrO mixing ratios correspond to which day?
RESPONSE: The model run starts with 10 June 2008 at 0:00 local time and continues for three days until 13 June 2008, the measurements that are used are from this three day period. We have updated the time and date on the plots so this is clear.

Editorial comments: COMMENT Page 30934, line 12: To calculate the temperature...
REPONSE: This correction has been made.

COMMENT: Page 30941, line 1:... as a result from...
RESPONSE: We believe the original text is correct.

COMMENT: Page 30944, line 21: According to Honrath et al. the lower inlet for the HNO3 measurements was at 2 cm.
RESPONSE: We have updated the manuscript to reflect the correct inlet height.

COMMENT: Page 30944, line 25f:... a small flux of HNO3... (max of ∼1.5 ppt)... (max of ∼0.25 ppt): The sentence refers to fluxes, while the units correspond to gradients. Make this consistent.

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Interactive Discussion

Discussion Paper

RESPONSE: We have updated the sentence to read: a small gradient of HNO_3

COMMENT: Page 30945, line 18: ratio instead of ratios.
RESPONSE: We have updated this sentence to read: most likely due to the low initial gas phase reactive bromine mixing ratio in the interstitial air and atmosphere

COMMENT: Page 30948, line 4:. . . 15-75 %
RESPONSE: We have updated the manuscript to reflect this change.

COMMENT: Page 30951, line 17:. . . show that the atmospheric. . .
RESPONSE: We have updated the manuscript to reflect this change.

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