**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

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

H.-W. Jacobi (Referee)

jacobi@lgge.obs.ujf-grenoble.fr

Received and published: 2 February 2011

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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. The comments include two major issues concerning the treatment of HNO3/nitrate in the snow and the vertical transport in the snowpack and between the snow and the atmosphere, which in my opinion need to be addressed before publication.

Major comments:

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. As a result the transport due to the wind pumping also remains constant throughout the calculations. I believe that this approach is simplifying to 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? 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

Interactive Comment

supplement.

In the simulations, all chemical processes in the snow occur in a liquid fraction. There-
fore, concentrations of the reactive species in this liquid fraction are important. In
contrast, concentrations of these species are available from melted snow samples in-
dicating 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 ap-
plied their modeling framework for other compounds present in the gas phase and in
the snow also to HNO_3/nitrate and then present discrepancies between simulations
and observations. For H_2O_2 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 HNO_3 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 HNO_3, T = 255 K, and the data given in the sup-
plement for the HNO_3 equilibrium I derive an HNO_3 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 HNO_3 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 con-

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

centration smaller. 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?

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?

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?

Minor comments:

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.

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. 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?

Page 30934, line 16f: Please give the used values for Tamp and tmin. Is the same cycle used for all three days?

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.

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).

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.

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.

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.

Fig. 8: The simulated BrO mixing ratios correspond to which day?

Editorial comments:

Page 30934, line 12: To calculate the temperature . . .

Page 30941, line 1: . . . as a result from . . .

Page 30944, line 21: According to Honrath et al. the lower inlet for the HNO3 measurements was at 2 cm.

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.

Page 30945, line 18: ratio instead of ratios.

Page 30948, line 4: . . . 15-75 %

Page 30951, line 17: . . . show that the atmospheric . . .

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper